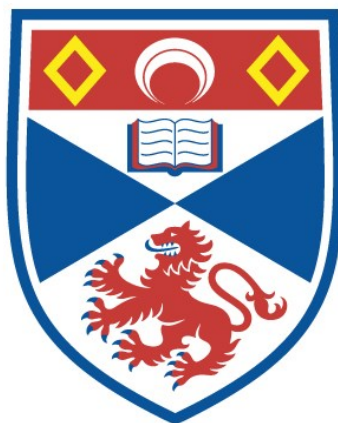# PREPARATION, STRUCTURE AND REACTIVITY OF SOME NEW TYPES OF STABILISED PHOSPHORUS YLIDES

Nazira Karodia

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

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PREPARATION, STRUCTURE AND REACTIVITY OF SOME NEW TYPES OF STABILISED PHOSPHORUS YLIDES

by

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Thesis presented for the degree of

DOCTOR OF PHILOSOPHY

University of St Andrews

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DEDICATION

To my family

DECLARATION

I, Nazira Karodia, hereby certify that this thesis is a record of my own work, has been composed by myself and that it has not has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

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ABSTRACT

Sixteen examples of the previously unknown β,γ,β'-trioxo phosphorus ylides have been prepared and fully characterised. Upon flash vacuum pyrolysis (FVP) these undergo clean loss of Ph_3PO selectively across the central position to afford diacylalkynes in most cases. The pyrolysis results are discussed in the light of the fully assigned ^{13}C NMR spectra presented and in particular the values of $^2J_{P-C(C=O)}$.

Six examples of the higher homologues, the $\beta,\gamma,\beta',\gamma'$-tetraoxo ylides have also been prepared and are found, quite unexpectedly, to give poor results upon FVP but to undergo moderately successful Ph_3PO extrusion to afford trioxoalkynes using conventional pyrolysis. The known β,γ-dioxophosphonium salts required as precursors to these have been characterised by NMR for the first time and are shown to exist predominantly as mixtures of E and Z enol forms in solution.

By reaction with oxalyl chloride, a range of higher polyoxo bis ylides has been obtained, including three examples of hexaoxo bis ylides which are remarkable in containing an acyclic series of eight contiguous C=X centres. The ^{13}C NMR spectra for the oxalyl bis ylides are interesting due to the pattern of coupling observed to both phosphorus atoms. These compounds do not in general give any useful results from FVP presumably due to the thermal instability of the expected products.

The reactivity of dioxo, trioxo, tetraoxo and oxalyl bis ylides towards a variety of oxidants has been examined and has given promising preliminary results for the formation of vicinal polycarbonyl compounds. Vicinal triones and tetraones are readily obtained and some evidence for a pentaone was obtained in one case. All the products readily form the molecular hydrates with geminal diol structures and these have been characterised spectroscopically. Reaction of the various ylide types with NO_2 has been examined and a range of

different processes is observed including formation of nitriles accompanied in one case by ring nitration of a phenyl group.

A total of twenty five β-aminoacyl ylides derived from N-alkoxycarbonyl protected amino acids have been prepared using a carbodiimide coupling method and have been fully characterised. Upon FVP at 600 °C these readily lose Ph_3PO to afford protected acetylenic amino acid derivatives and twelve examples of these valuable chiral compounds have been obtained in moderate yield. By standard reactions these products have been transformed into simple chiral analogues of the important neurotransmitter GABA in four cases. Removal of the N -protecting group in the amino acid derived ylides results in a change in pyrolysis behaviour: ethanol is eliminated rather than Ph_3PO to give novel cyclic stabilised ylides related in structure to the tetramic acids.

Finally, samples of one trioxo ylide, one tetraoxo ylide, one tetraoxo bis ylide and one hexaoxo bis ylide have been sent for solid state structure determination by X-ray methods. The results obtained provide ready confirmation of the important contribution of phosphonium enolate forms to the structures of these but give surprising results as regards the conformational preference for *syn* and *anti* alignments of the adjacent C=X units along the chain.

CONTENTS

$$\underset{\underset{\displaystyle Ph_3P}{\|}}{\overset{\displaystyle R^1}{\diagdown}}\!\!\!\overset{O}{\underset{O}{C}}\!-\!\overset{O}{\underset{O}{C}}\!-\!\overset{O}{C}\!-\!\overset{O}{C}\!-\!R^2$$

2. Oxidation of Ylides with Oxone

$$Ph_3P = \underset{\underset{O}{\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{|}}}}{}$$

I   Reactions of Phosphorus Ylides with NO_2

1.   Oxidation Reactions

$$Ph_3P = \underset{\underset{O}{\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{|}}}}{}$$

5.   Reactions of Acetylenic Amino Acid Esters
a.   Hydrobromination:

Preparation of GABA Analogues

6.   Preparation of Mosher Acid Derivatives

DISCUSSION

APPENDIX

REFERENCES

INTRODUCTION

Historical Background

Though Michaelis and Gimborn prepared the first ever ylide,[1] they failed to understand its structure which as we now know consists of a carbanion attached to a heteroatom registering a high positive charge **1**. After these early pioneering chemists the field of ylides was relatively under-researched except for the work of Staudinger and his group in the 1920's.[2] The discovery of the Wittig reaction[3] in 1953 generated new interest in the area, resulting in a lively study of phosphorus ylides in particular and organophosphorus compounds in general.[4, 5]

A   Structure and Reactivity of β-Oxo Ylides

The first stable ylide isolated was initially assigned the structure **2** which contains a pentacoordinate phosphorus atom.[1] However Ramirez and his co-workers[6] demonstrated that the structure was that of an ylide **3** and not the cyclic compound. Thereafter the central issue in the debate about structure concerned the nature of the bonding between phosphorus and the ylidic carbanion.

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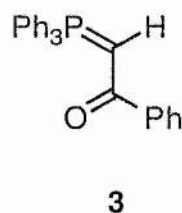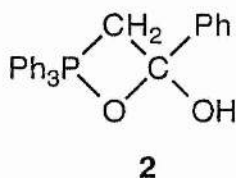
In the case of β-oxo ylides, the ylide carbanion can interact with the adjacent oxo group to give a stable enolate form and the three resonance structures **4a–c** can be considered.

4 a   **4 b**   **4 c**
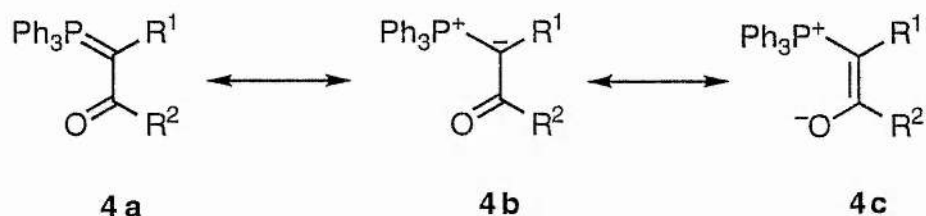
Support for the contribution from these different forms is provided by the spectroscopic characteristics, including a broad band at 300-400 nm in the UV spectrum,[7] ascribed to $\pi-\pi^*$ transition of the C=P bond and a band between 1200-1220 cm^{-1} in the IR spectrum,[8] assigned to the C=P stretching vibration. The decrease in the double bond character of the carbonyl group associated with **4c** is indicated by the lower than normal carbonyl stretching frequency. For example the oxo ylide **3** displays a carbonyl absorption at 1529 cm^{-1} which compares with a value of 1667 cm^{-1} for the conjugate oxo phosphonium salt. For the ethoxycarbonyl ylide **4** (R^1= H, R^2 = OEt) and the conjugate phosphonium salt, the carbonyl absorptions are observed at 1620 cm^{-1} and 1720-1740 cm^{-1} respectively. This is consistent with experimental observations on alkylation and acylation of β-oxo ylides. Whereas keto ylides undergo *O*-alkylation/acylation, ester ylides provide *C*- substituted products. It may be concluded that keto ylides have more enolic character, as indicated in **4c**, than do ester ylides.

^{1}H NMR studies on ylides in solution have shown that protons attached to the ylide carbon are less shielded in β-oxo stabilised ylides compared to non-stabilised ylides,[9] and this reflects the removal of charge density at the carbon in the former. The phosphorus chemical shift values of stabilised ylides are usually lower, relative to the corresponding phosphonium salt.[10] In some

2

cases ^{13}C-^{31}P coupling constants have provided valuable information on the ylide structure.[11]

E–Z isomerisation in β-oxo phosphorus ylides arising from hindered rotation about the C=C double bond, as in structure **4c**, has been examined using variable temperature NMR experiments.[12] *E–Z* isomers are detected in ester ylides as shown, whereas one form, in which P and O are *Z* to one another as in **4a**, predominates in keto ylides.

X-ray studies on the β-oxo phosphorus ylides demonstrate the degree of conjugation between the P=C double bond and the carbonyl group and give a measure of the relative significance of the dominant resonance structures **4a–c**. Early X-ray diffraction characterisation of the α-halo ylides[13] **5** indicated that the P–C and C(2)–O bonds were longer than the isolated, non conjugated analogues and the C(1)–C(2) bonds were shorter. This implied delocalisation involving the resonance structure as in **4c**. Furthermore the dihedral angle between P–C(1) and C(2)–O was found to be small, suggesting double bond character as in **4c**. Recent work[14,15] on X-ray crystal structure determinations on stabilised ylides such as **6** provides further support for the relevance of these canonical forms and shows in particular that in the crystal the keto carbonyl is *syn* to the ylide bond while the ester carbonyl is *anti* to it.
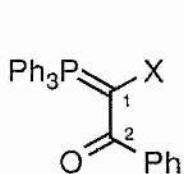
5

X = Cl, Br

6
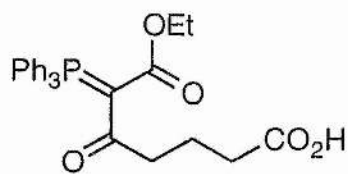
B   Synthesis of β-Oxo Ylides

A wide range of ylides containing different functional groups has been prepared and employed in synthesis. However only the preparation of β-oxo triphenylphosphonium ylides will be discussed in detail.

1. Synthesis of Ylides in General

The commonest route to phosphorus ylides in general is the "salt method" and this involves two stages. Triphenylphosphine is reacted with the halide **7** to form the precursor phosphonium salt **8**. While the choice of halide, solvent and reaction temperature may affect the yields obtained, there is no major problem associated with this step.

$$XCHR^1R^2 \xrightarrow{Ph_3P} \left[Ph_3P^+CHR^1R^2\right]X^- \underset{H^+}{\overset{B^-}{\rightleftharpoons}} Ph_3P=CR^1R^2 + BH + X^-$$
$$\quad\; \mathbf{7} \qquad\qquad\qquad \mathbf{8} \qquad\qquad\qquad\qquad \mathbf{9}$$
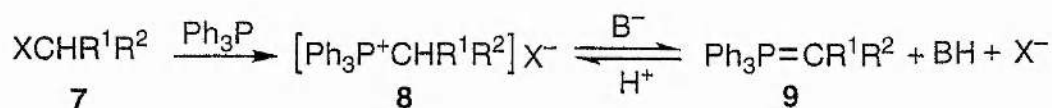
The removal of an α-proton from the corresponding phosphonium salt **8** with a base provides the ylide **9**. The choice of base is crucial in that it must not react with other functional groups on the ylide.

The properties of the ylide **9** are almost entirely dependent on the reactivity, or basicity, of the ylidic carbanion which is controlled by the nature of the substituents R^1 and R^2. In addition the groups on the phosphorus affect the ability of the atom to "carry" the partial positive charge, but the overall effect is inductive and not conjugative.[16] It is notable that trialkylphosphonium ylides are more basic than the triphenyl analogues.

The ylide is more stable and less reactive when R^1 and/or R^2 are more effective at delocalising the partial negative charge of the carbanion, or when one substituent can conjugate with the P=C π bond. This effect is illustrated by ylides **3** and **10**. Whereas ylide **3** is stable in air and is prepared with aqueous

base, **10** is only stable in a moisture free environment and is generated with alkyl lithium or metal amide bases.

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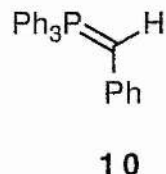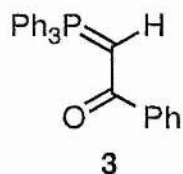
β-oxo ylides may be prepared directly from α-halo compounds. but this method is only useful for the synthesis of monosubstituted alkoxycarbonyl and acyl(methylene) triphenylphosphoranes. Since this is not a successful technique for more exotic ylides,[17] other methods have been developed.

More complex ylides may be obtained from simple ylides, providing that they contain a proton on the ylidic carbon. A discussion of the acylation of simple ylides now follows.

2. Acylation by Acid Chlorides

Usually β-oxo ylides are synthesised by the acylation of a precursor ylide **11** to form the phosphonium salt **12**. This is followed by proton abstraction to afford the functionalised ylide. The conversion of the salt **12** to the ylide **13** may be achieved by any base stronger than **13**, including a second equivalent of **11** in a trans-ylidation process.[18] Since the deprotonation occurs more readily than the acylation, this means that if **11** is reacted with a one equivalent of an acid chloride, the products will be **13** (0.5 equiv.) and the conjugate phosphonium salt of **11** (0.5 equiv.). In order to obtain **13**, a 2:1 ratio of **11** and acid chloride is required.

5
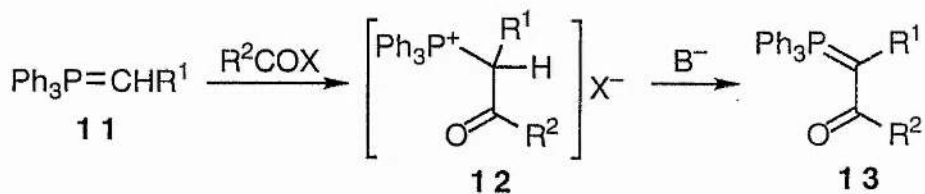
This technique for the acylation by acid chlorides is powerful and reliable unless the acid chloride possesses an acidic proton which the ylide **11** can abstract giving ketene derived products. Except for this limitation, the choice of R[2] is wide and includes examples such as alkyl,[19] aryl,[19] perfluoroalkyl,[20] haloalkyl[21] and alkoxy.[22]

β-Oxo ylides have the potential not only for *C*-acylation (at the ylidic carbon) but also for *O*-acylation (at the β-carbonyl) depending on the reaction conditions used. Ester stabilised ylides are usually acylated on the ylidic carbon,[23] but recent literature[24] has shown that *O*-acylation can occur at low temperatures. Ethyl 2-(triphenylphosphoranylidene)propionate **14** was reacted with the acid chloride at −10 °C to afford the enol-ester-ether **15**. Rearrangement to the usual product occured upon warming. Structural confirmation of **15** was obtained from spectroscopic and X-ray crystallographic data.
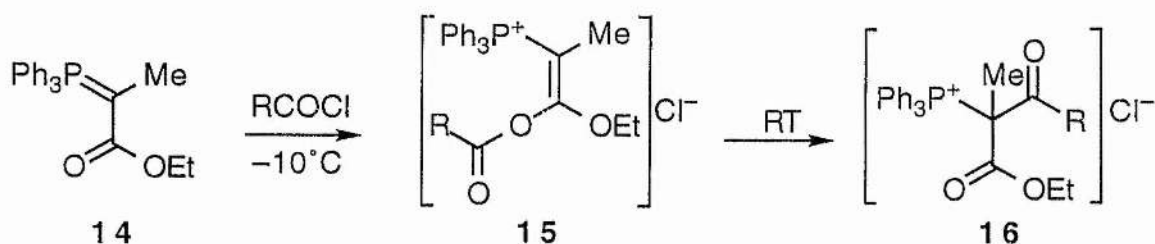
Ketone stabilised ylides react differently with acid chlorides in that *O*-acylation dominates.[6, 25] In one case the unusual *O*-acylated product **18** was

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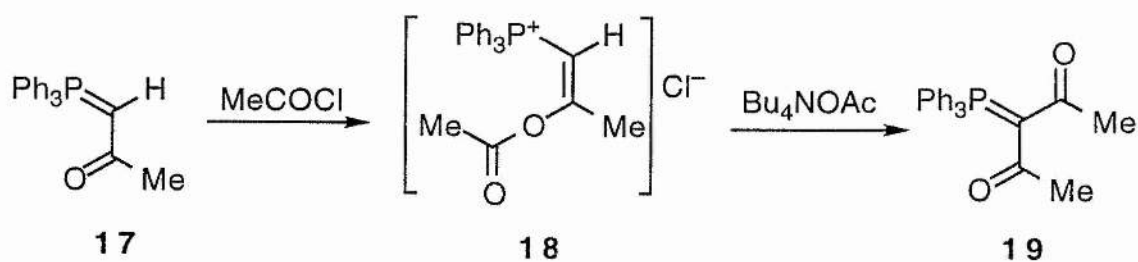
isolated and further reaction in the presence of tetrabutylammonium acetate afforded the *C*-acylated product **19**.[26]

New methods have been employed to counteract the loss of half an equivalent of starting ylide due to trans-ylidation. Competitive ketene formation is another disadvantage encountered during trans-ylidation.[27] An efficient and popular alternative is to perform the experiment in the presence of one equivalent of triethylamine.[28] The use of the proton scavenger, *N,O*-bis-(trimethylsilyl)acetamide (BSA),[29a] and sodium bis(trimethylsilyl)amide[29] also eliminate the need for the second equivalent of ylide. Other acylating reagents which also involve trans-ylidation, but regenerate the second equivalent of ylide, have proved successful and are described in later sections.

3. Acylation by Anhydrides

Most acid anhydrides are effective in acylating phosphonium ylides. Ester stabilised ylides such as **20** have been reacted with a number of acyclic anhydrides to produce the phosphonium salts **21**. The latter are transformed into the required acylated ylide **22** and carboxylic acid upon heating.[26]
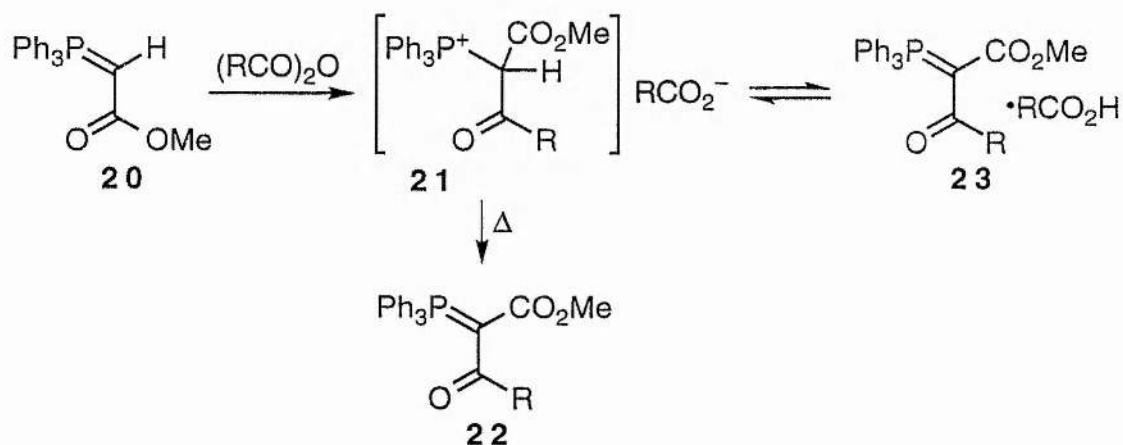
Further and more recent information on the structure and bonding in the salt has emerged.[30] The stabilised ylide **20** was reacted with acetic anhydride (R = Me) at low temperature and the product analysed. The crystal

structure showed that the salt actually exists as the free ylide together with one molecule of acetic acid as indicated in **23**.

This method of acylation has been effective and a number of groups have used acid anhydrides in the synthesis of oxo ylides for further elaboration.[21,31]

In contrast, the reaction with cyclic anhydrides **24** is not consistent.[32] This is due to lactone formation **25** resulting from an internal Wittig reaction with one of the carbonyl groups. Dialkenation products are also possible.[33]
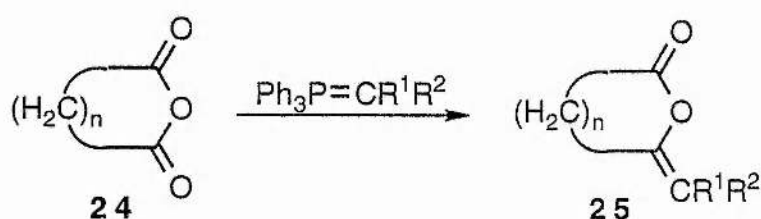
4. Acylation by esters

While acid halides have been predominantly used as acylating agents in the preparation of oxo ylides, some esters are known to perform the same function.[34] Esters can react with ylides in the two ways outlined in the scheme below. The initial attack of the ylide carbanion on the ester carbonyl produces intermediate **26**. If this intermediate is uncomplexed, the Wittig product **27** is favoured; and when **26** is complexed by a metal the Wittig reaction is retarded and the formation of the acyl ylide **13** is favoured.
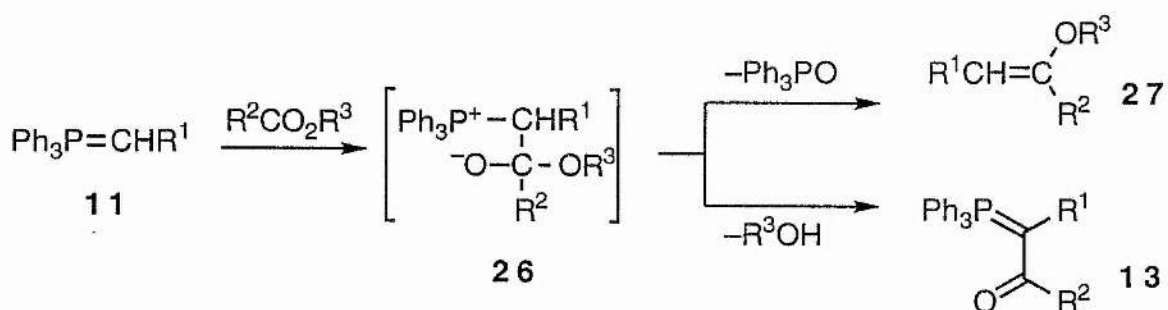
Both pathways result in synthetically useful compounds and the

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conditions governing both reactions are well understood.[34] Some special esters such as formates and oxalates undergo exclusive Wittig reaction.[35]

A new general route to β-oxo ylides involves the use of trimethylsilyl esters of acids together with the silyl ylide **28**.[29, 36] This technique was used to prepare a large variety of ylides **29** some of which are described in greater detail later.
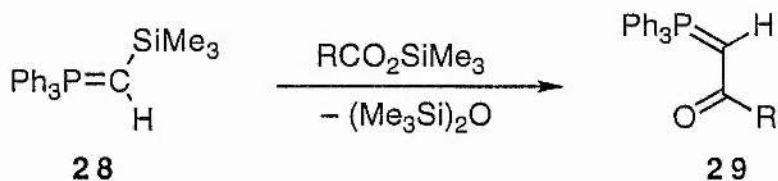
5. Acylation by Lactones

Early workers showed that the enol γ-lactones **30** react at the carbonyl function to form an acyl ylide which undergoes an intramolecular Wittig reaction.[37] The overall result is substitution of the oxygen of **30** by the ylide alkyl group to afford **32**. This reaction has proved useful in the preparation of steroids.
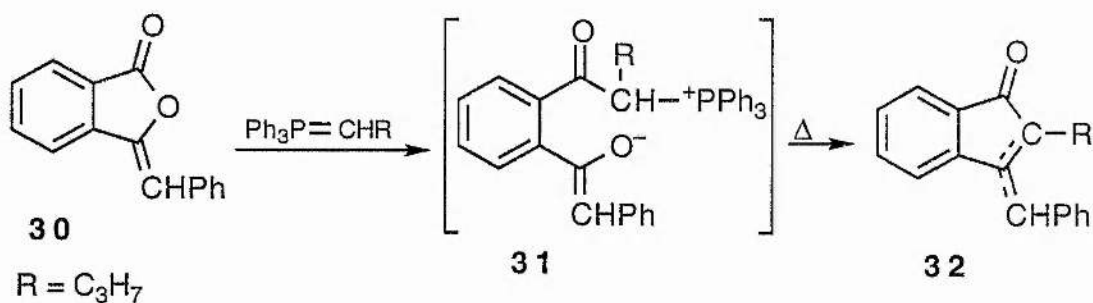
In addition there have been reports of ring opening of β-lactones to produce δ-hydroxy acyl ylides.[38] At variance with other accounts, attack of the ylidic carbanion at the methylene position of β-propiolactone and butyrolactone has been reported.[39] It appears that the reaction of lactones with ylides is not fully understood.

6. Acylation by Thioesters

In the pursuit of other acylating compounds it was discovered that the reaction of ylides with thioesters was an efficient route to β-oxo ylides.[19] The success of this method relies on the greater basicity of the thiolate anion formed in the first step, and thus the abstraction of the α-proton from the salt **33** occurs readily to yield the ylide and the volatile thiol. This method has been successfully exploited for the preparation of a range of acyl ylides.
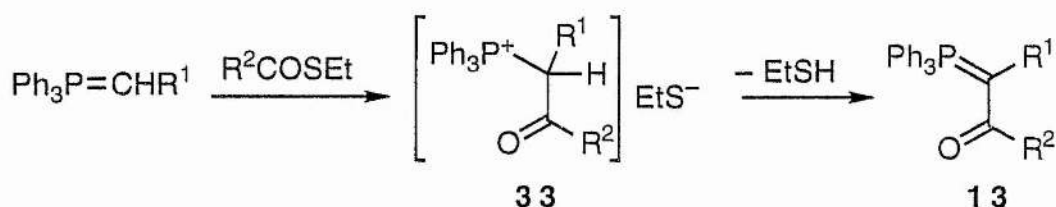
7. Acylation by Amides

Generally amides have not been found to be good acylating agents. However early work documents the use of acyl imidazoles as an alternative to trans-ylidation.[40] N-Formyl imidazole **34** was reacted with the non-stabilised phosphorane to afford imidazole **35** and (formylmethylene)triphenyl phosphorane **36**. Potentially, any N-acyl imidazole could be used.[41] The mechanism involves attack on the carbonyl followed by expulsion of the imidazole anion. The latter successfully removes the proton from the corresponding phosphonium salt to provide the acylated products.
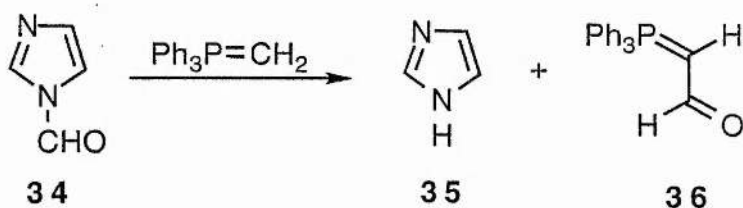
Chloromethylenedimethylammonium chloride[42] and more recently tetramethylformamidinium chloride[43] were used as masked amides for effecting similar formylation reactions of ylides.

8. Acylation by Carboxylic Acids

It has recently emerged that free carboxylic acids, in some instances, may be used directly as acylating agents.[44] Bis-(trimethylsilyl) methylenetriphenylphosphorane **37**, prepared from the monosilyl ylide **28** and trimethylsilyl bromide or iodide, reacts with carboxylic acids to provide acyl ylides and hexamethyldisiloxane.
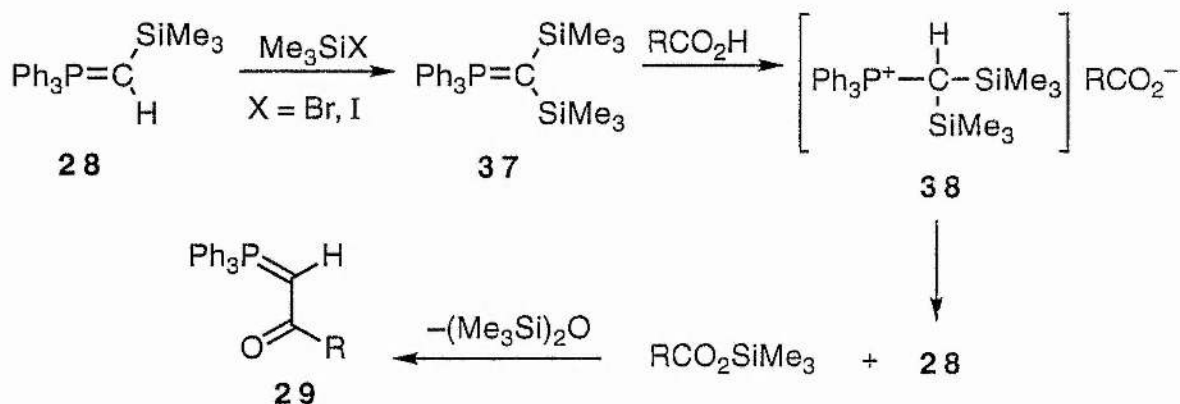
The mechanism proposed initially involves the formation of the phosphonium salt **38** resulting from protonation of the ylide. The intermediate then decomposes into the silylester and the monosilyl ylide **28**. Acylation is accompanied by production of the disiloxane which may be easily removed. The utility of the method was exemplified by the preparation of a
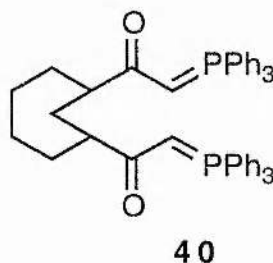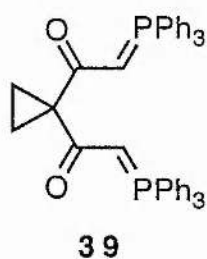
variety of different types of ylides. The attractive bis-ylides **39** and **40** are representatives.

A novel route to β-keto ylides involves the use of acids together with a peptide coupling reagent.[45] This is described in greater detail later.

C   Pyrolysis of β-Oxo Ylides as a Route to Alkynes

β-Oxo ylides are particularly susceptible to thermal decomposition and are known to undergo extrusion of triphenylphosphine oxide. This method, which may be regarded as a type of intramolecular Wittig reaction, is an attractive and successful route to acetylenic compounds.

In the first documented example in 1959, α-benzoylbenzylidene triphenylphosphorane **13a** was heated at 300 °C for 30 minutes. The products, diphenylacetylene and phosphine oxide, were obtained in quantitative yield. However, no alkynes were formed from **13b,c** when the substituent on the ylidic carbon was H.[46]
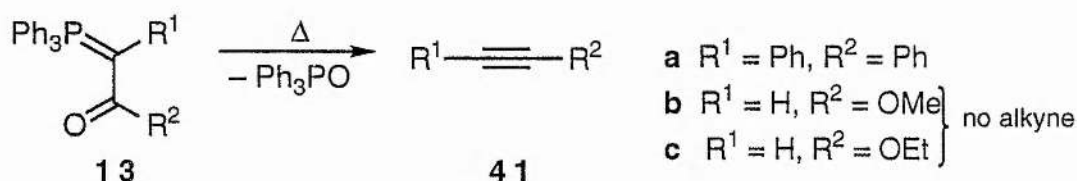
This conversion was later successfully extended to ylides bearing ester (R^1 = CO_2Et) and nitrile (R^1 = CN) substituents.[25] Märkl[47] noted that this was a sound and general route to acetylenic esters (R^1 = CO_2Me). The thermolysis of several methoxycarbonyl ylides **42** at 220–260 °C under vacuum lead to the formation of the acetylenic esters **43** in 65–80% yield and hydrolysis of the esters provided the acetylenic acids **44**.
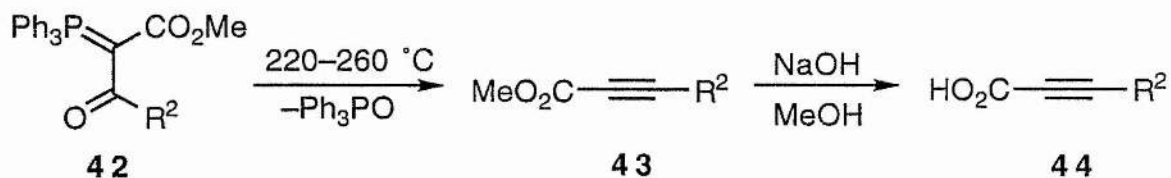
Dialkynes have also been prepared by pyrolysis. The original investigation was limited to alkynoyl ylides **45** with R^1 a stabilising group.

Although the yields were moderate, the pyrolysis as a technique was successful.[28]

R^3 = Ph; R^1 = CN, CO_2Et, Ph
R^3 = Bu^n; R^1 = CN, CO_2Et, Ph
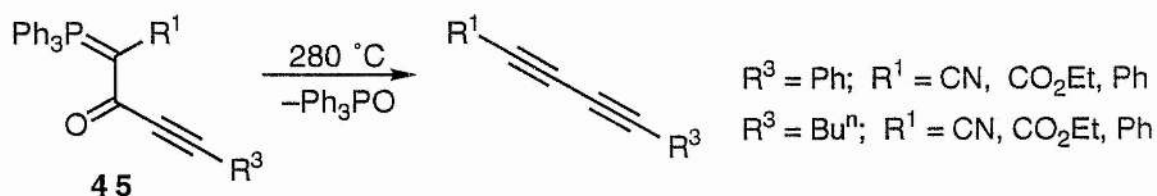
It was also observed that pyrolysis of the bis-ylide **46** did not give the dialkyne nor Ph_3PO. Instead triphenylphosphine was eliminated to leave an intractable tarry residue.[28]
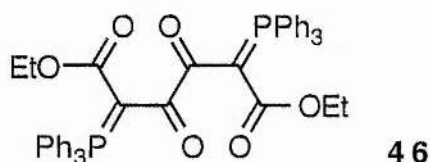
Conventional pyrolysis has been used to gain access to a range of compounds including acetylenic diacids,[48] diarylalkynes,[49] acetylenic ketones,[26] perfluorinated acetylenic nitriles,[50] perfluoroalkynylphosphonates,[51] aryloxy perfluoroalkynes,[52] aryl-trifluoromethyl alkynes,[53] acetylenic thioesters,[54] thioalkynes,[55] arylselenoalkynes[56] and α-haloalkynes.[57]

From the examples cited it is apparent that the success of the traditional pyrolysis is dependent on the R^1 substituent in structure **13** either being electron withdrawing, such as COR, CO_2R, CN, SR, SeAr, OAr, CHO, $PO(OPh)_2$, or capable of stabilising the phosphonium ylide. Another disadvantage of conventional pyrolysis is the sustained exposure of the compounds to excessively high temperatures which results in low yields or tarry residues. Side reactions are encouraged under these condition, including partial extrusion of phosphine and isomerisation of the alkynes to allenes.

The development and successful application of flash vacuum pyrolysis (FVP) has overcome these limitations. Flash vacuum pyrolysis, in contrast to traditional pyrolysis, employs a flow system and a combination of high

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temperatures and low pressures which ensures a relatively brief "hot zone" contact time for the substrate. The technique is therefore mild and is ideal for promoting extrusion and elimination reactions. Typical common fragments which may be expelled include carbon monoxide, carbon dioxide, ethylene, sulphur dioxide, sulphur monoxide, acetone, hydrogen chloride, and most significantly for this work, triphenylphosphine oxide from the substrate to yield the desired product. A comprehensive review of the scope of the pyrolysis technique is available.[58]

The extrusion of Ph_3PO from β-oxo alkylidenetriphenylphosphoranes using FVP as a general route to alkynes was first reported from this laboratory in 1985.[59] Pyrolysis of acylated ylides **13** with R^1 an alkyl group or H, resulted in a clean conversion to the desired alkynes. Several examples of terminal alkynes (R^1 = H) which were previously not available by pyrolysis, were obtained in good yields. An additional advantage lay in the collection of the products in the pyrolysis trap, naturally separated from phosphine oxide because of their higher volatility.

The experiments were performed at 750 °C at a pressure of 10^{-2} torr. Although the temperature is high, the contact time in the "hot zone" is sufficiently short to ensure mild pyrolysis conditions with no major side products. In particular the absence of the isomeric allenes, reported from traditional pyrolysis, was pleasing.

R^1 = H, Me, Pr^n

R^2 = Me, Et, Pr^n, Pr^i, Ph, Bu^n, Bu^t, c-Bu, $Pent^n$, c-Hex, CH=CHMe
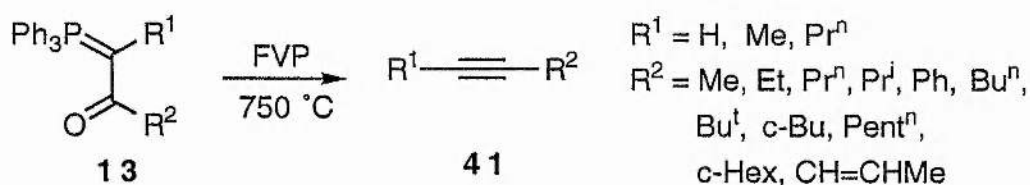
A further fragmentation process was only observed in one case **47**, where R^2 = cyclobutyl. It was surmised that the ring strain was relieved by extrusion of ethene, resulting in the formation of a vinyl alkyne **49** in good yield. A

reduction of the temperature ensured an increase in the proportion of the cyclobutyl alkyne **48**.
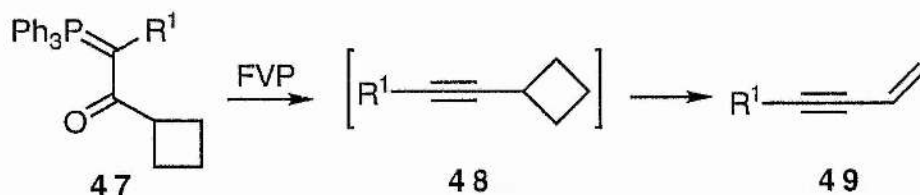
Temperature dependent secondary fragmentation processes were also observed when α-acyl-α-ethoxycarbonyl ylides were pyrolysed.[60] FVP of ylides **50** at 500 °C gave the expected acetylenic esters **51** in excellent yields. More significantly FVP of the same ylides at 750 °C is accompanied by the unexpected loss of the ethoxycarbonyl group to yield the terminal alkynes **52**. The ethoxycarbonyl group fragments partly into ethene and CO_2 and partly into acetaldehyde and CO.
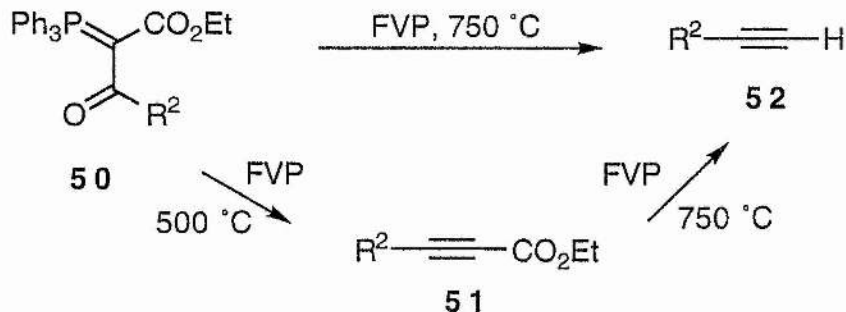
A further report from this laboratory described the extension of this reaction to give diacetylenic esters and terminal 1,3-diynes.[61] The FVP of a variety of alkynoyl ylides at 500 °C provided diacetylenic esters **54** in improved yields. For direct comparison, **53** (R^3= Ph) was pyrolysed and the corresponding diyne **54** was obtained in 53% yield compared, to 16% obtained by conventional pyrolysis.
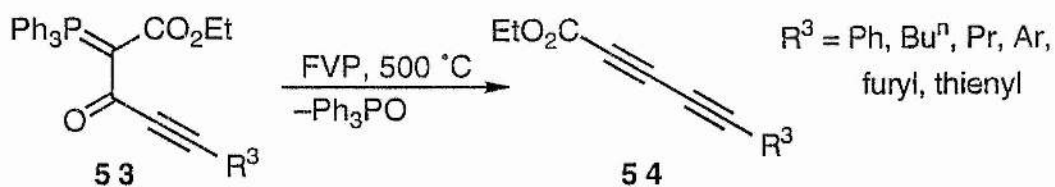
As expected, FVP of the same ylides at 750 °C led to the formation of terminal 1,3-diynes. This paper goes on to describe the novel stepwise construction of one example of a triacetylenic ester. Hydrolysis and chlorination of the diacetylenic ester **54** obtained in the first pyrolysis yields the diacetylenic chloride **55**. Subsequent acylation with the starting ylide and pyrolysis provided the triacetylenic ester **56** in 30% yield.
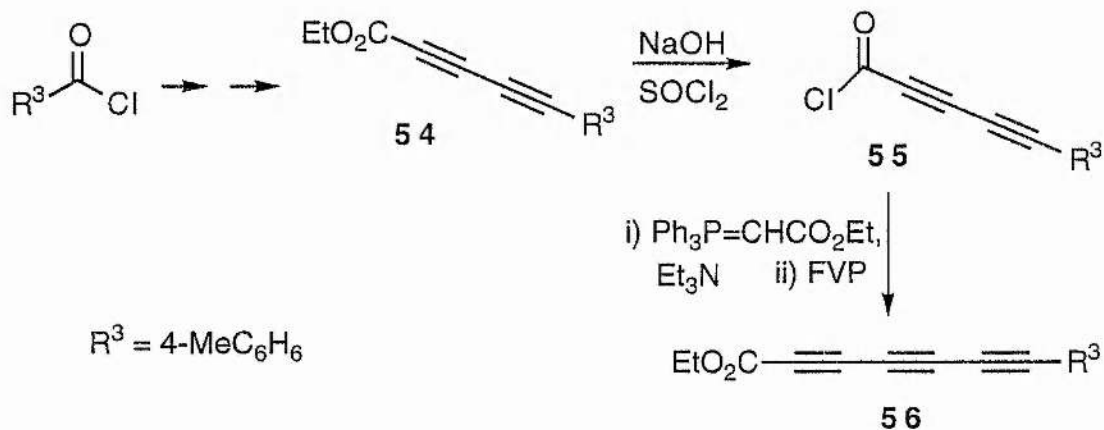
An additional advantage of the method is that other unsymmetrical diynes may be prepared by simply using ylides with different substituents. Unsymmetrical diynes are of interest in non-linear optics as potential second harmonic generators.

Early literature shows a few examples of the conventional thermal conversion of β-oxo-γ,δ-unsaturated ylides into enynes.[25, 47] Note that ylides bearing alkyl substituents at the ylidic carbon did not give the enynes. However successful results have been obtained by the use of FVP.[62] A range of substituted cinnamoyl ylides **57** (R[1] = H, alkyl, aryl) were pyrolysed under

16

FVP conditions at 500 °C to yield the *E* isomer **58** as the major product, whereas FVP at 700 °C led to a mixture of *E* and *Z* isomers.
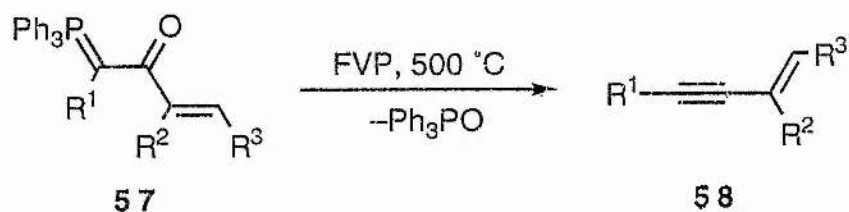
The oxo ylides **59** possessing *o*-methoxybenzoyl or *o*-(methylsulphanyl) benzoyl groups undergo interesting thermal behaviour.[63] These ylides were designed such that the alkyne obtained by FVP, could react further in secondary fragmentation processes The formation of more complex and synthetically useful molecules could therefore be directed.

FVP of the ylides **59** at 700 °C affords the alkynes **60**. However at 850 °C the extrusion of phosphine oxide is accompanied by the loss of a
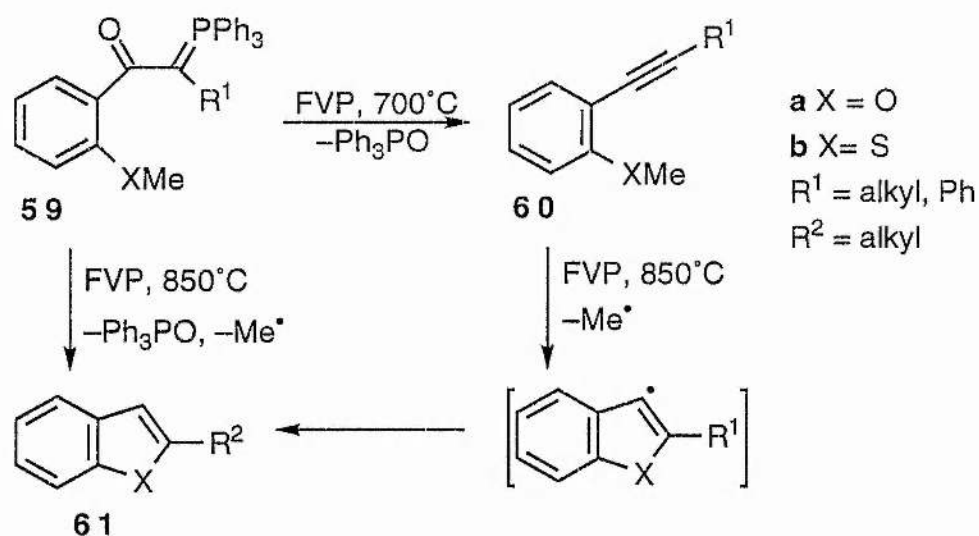
methyl radical. A radical mechanism is invoked to explain cyclisation to the 2-substituted benzofurans **61** and benzothiophenes and this method has recently been extended to tandem cyclisations.[64]

Two indirect methods of obtaining aliphatic alkynes from oxo ylides should be noted. In these instances traditional pyrolysis fails. The first route[65]

relies on the reaction of trifluoromethanesulphonic anhydride with the ylide **13** to form the triflate **62**. Reduction of the latter by sodium amalgam provides the alkyne **41**. triphenylphosphine and sodium triflate, which may be recovered.
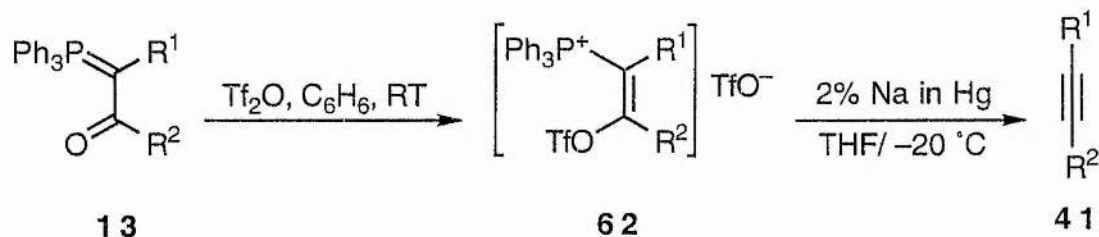
In contrast the second route[66] uses oxidation of acyl ylides to generate the alkyne. The products of oxidation, the 1.2 diketones are converted into bis-hydrazones **63**. Oxidation of the hydrazone with O_2/CuCl in pyridine releases the alkyne **41**.
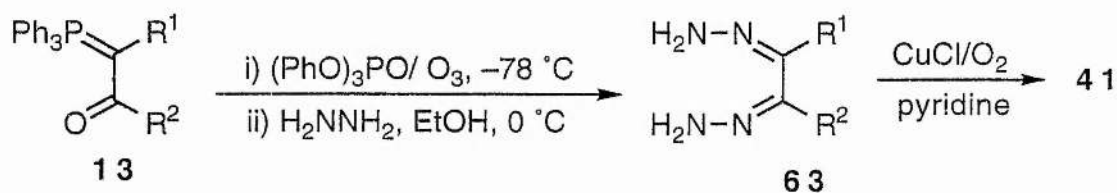
Although this methodology provided access to aliphatic alkynes, the two extra steps required (compared to the pyrolysis route) limited the overall yields obtained.

D   Oxidation of β-Oxo Ylides as Route to Carbonyl Compounds

1. General Background

The vicinal polycarbonyl system is a functional group aggregate incorporating powerful electrophilic sites at the carbon-oxygen double bonds. Therefore it is not surprising that such compounds have been known and

studied for over a century. Since the first reported synthesis of a 1,2,3-trione,[67] chemists have been curious about how many carbonyl groups may be juxtaposed. It is certain that such an unusual structure would have interesting properties. For the purposes of this discussion only the linear analogues will be focused on.

There has recently been renewed interest in *vic*-polycarbonyl compounds due to the occurrence of this functionality in the potent immunosuppressant FK-506[68] and the related antifungal antibiotics rapamycin[69] and 29-demethoxyrapamycin.[70] The C_1-C_{15} α-,β-diketoamide subunit **64** of FK-506, which is of interest is shown.
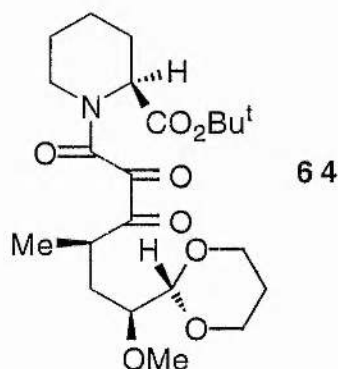
More recently Wasserman[71] has exploited *vic*-tricarbonyl compounds for the preparation of several natural products and natural product precursors. This

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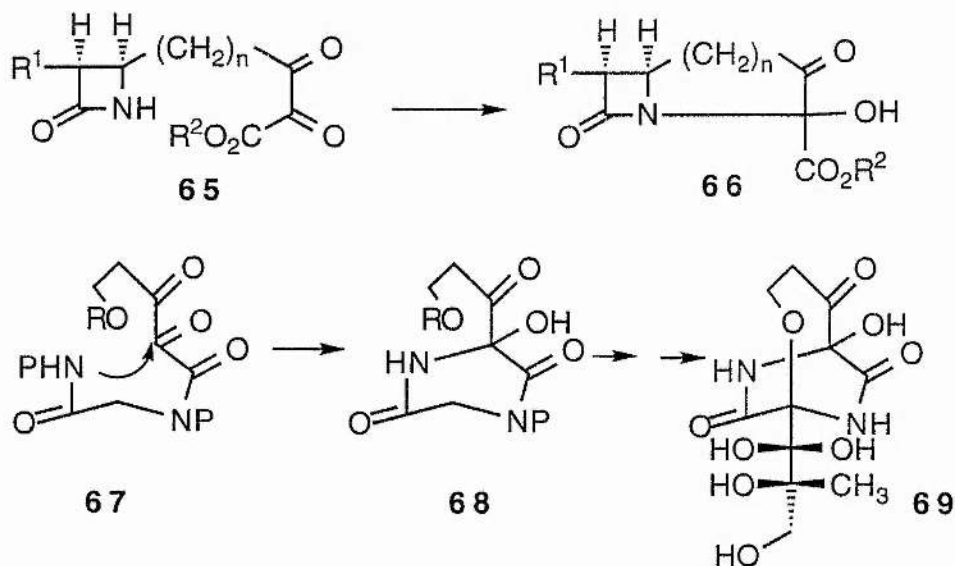
may be illustrated by the formation of carbapenams and carbacephams **66** from the β-lactam precursors **65**.[72] The latter were easily obtained from *vic*-tricarbonyl compounds. The key intermediate **68** in the Yoshimura synthesis of bicyclomycin **69**, was also successfully obtained from a *vic*-trione **67**.[73]

2. Structure and Reactivity

The first documented examples of vicinal polyketones (i.e. more than two carbonyl groups) were croconic acid **70** and rhodizonic acid **71**.[74] However their structure was only established later. The first examples of linear vicinal tricarbonyl compounds were diphenyl triketone **72**,[67] dimethyl triketone **73**[75] and diphenyl tetraketone **74**.[76]
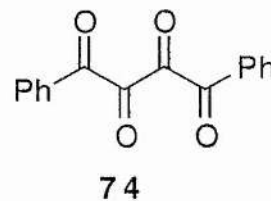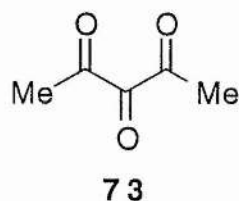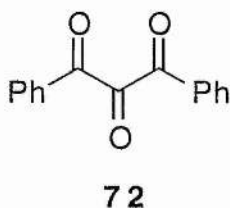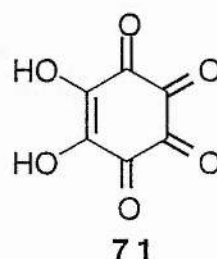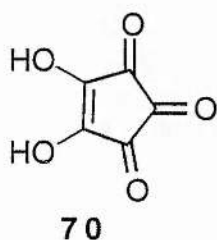
While polyketones can be obtained in their anhydrous keto form **75**, they are extraordinarily moisture sensitive and readily form molecular hydrates due to the enhanced reactivity of the central carbonyl groups. In fact the hydrated analogues are often desired as illustrated previously. The structures of the hydrates of the triketones are accepted as that of the gem-diol **76** and it has been confirmed that hydration and other reactions occur at the central carbonyl group.[77] Dehydration of the pale coloured hydrates to the attractive deeply coloured ketones is achieved by either distillation, sublimation or treatment with dehydrating materials such as phosphorus

pentoxide or molecular sieves. Numerous examples of linear vicinal triketones exist and their chemistry has been well researched.[78]

75

76

77

78
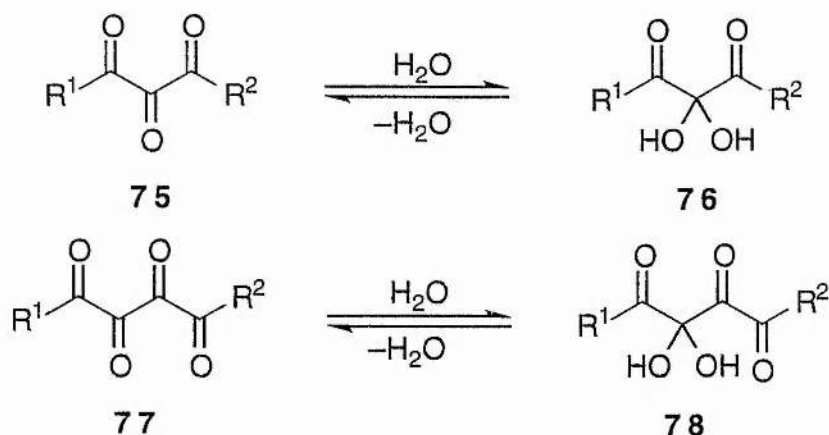
The structure of the hydrates of vicinal tetraketones was assumed to be that of the gem-diols **78**. Due to its unsymmetrical nature, two resonances were obtained in the ^{1}H NMR spectrum of the di-*t*-butyl compound.[79] Diphenyl tetraketone **74** and its hydrate have been studied, and detailed structural information was obtained from X-ray studies.[80] Apart from the diaryl examples and the di-*t*-butyl compound **77** ($R^1 = R^2 = Bu^t$),[81] linear tetraketones, especially non-symmetrical examples, are poorly represented in the literature. Moreover very little information on the nature of their structure and chemical reactivity is available.

As described in part 5 of this section, the only higher examples to have been prepared are two *vic*-pentaketones.

3. Synthesis of Carbonyl Compounds by the Oxidation of Phosphorus Ylides

The oxidative cleavage of the ylidic carbon–phosphorus bond has been widely explored since this provides a convenient route to carbonyl compounds. A variety of oxidising reagents have been developed for this purpose since the first reports in the1960s.[82] These communications showed that oxidation of the stabilised ylides **13** to give the corresponding carbonyl compounds was specific and high yielding.

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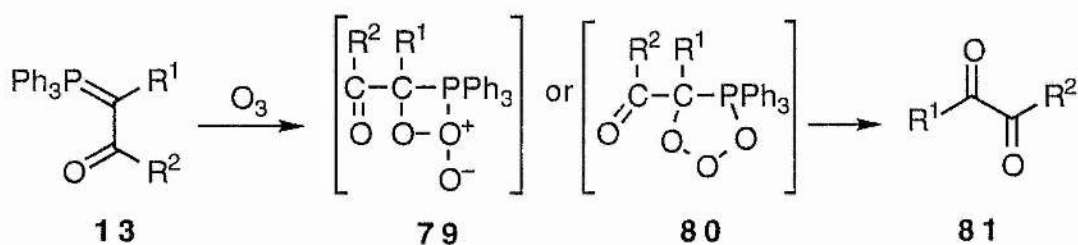
The mechanism postulated involved the initial addition of ozone across the P–C ylide bond. The intermediate (**79** or **80**) formed decomposes into the dicarbonyl product and a peroxidic phosphine oxide which in turn collapses to form phosphine oxide and molecular oxygen.

Recently, good results have been achieved by Wassermann.[71] Several vicinal tricarbonyl compounds **75** have been prepared by the ozonolysis of β,β'-dioxo ylides **82**. These vicinal tricarbonyl compounds were important reagents in the synthesis of several natural products.
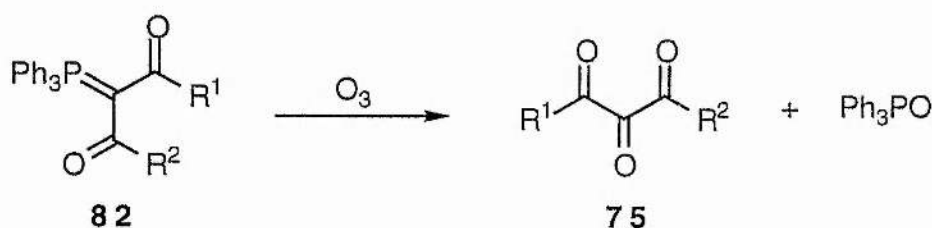
Singlet oxygen was found to bring about the same transformation.[83] Previous workers[84] found that singlet oxygen reacts with ester stabilised ylides **83** to give good yields of α-keto esters **86**. However when R=H, dimethyl fumarate and maleate were isolated. The mechanism of the oxidation was assumed to be an electrophilic attack by singlet oxygen on the ylidic carbanion centre of **83** to create the zwitterionic peroxide **84**. Ring closure then occurs to give **85**, followed by cleavage to form the product and phosphine oxide.
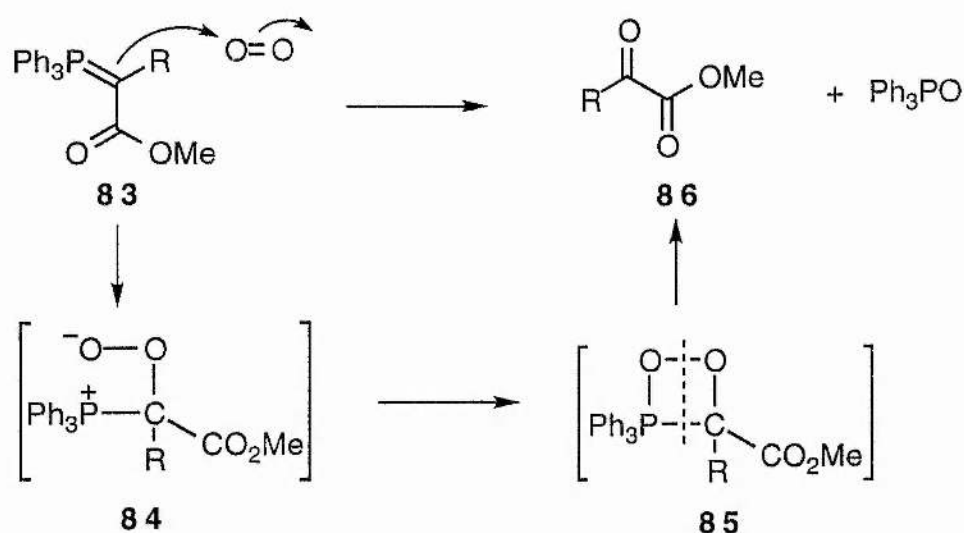
The smooth oxidation of ylides is accomplished by phosphite-ozone adducts.[85] Thus the oxidation of the disubstituted ylides by triphenyl phosphite ozonide leads to high yields of the ketones, triphenyl phosphate and triphenylphosphine oxide.

This technique has been successfully applied to the oxidation of trimethylsilyl ylide **87** and the bis(trimethylsilyl) ylide **89** to provide the benzoylsilane **88** and the previously unknown bis-silyl ketone **90**.[85] The bis-silyl ketone is extremely labile and reacts with air to form the ester **91**.
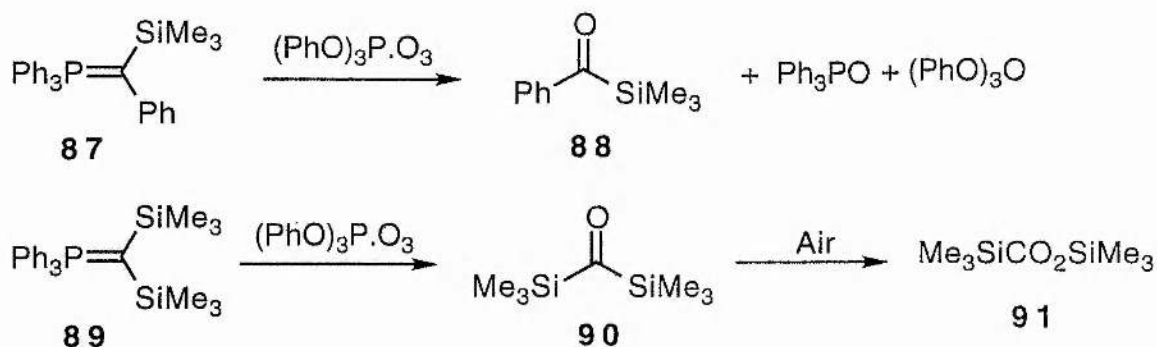
This reagent is superior to singlet oxygen and ozone because of the ease of measuring the exact quantities required and the excellent yields obtained. A possible disadvantage could be that the adduct decomposes into singlet oxygen and triphenyl phosphate at temperatures above −35 °C.

Two accounts have described the oxidative cleavage of the ylidic bond in a two phase system by $KMnO_4$. Six examples of β-oxo ylides possessing aliphatic substituents were oxidised to ketones in 18-75% yield.[86] More recent studies have extended the scope of this reaction to include aromatic β-oxo ylides.[87] In this way several unsymmetrical benzils and 1-aryl-1,2-diones were obtained. The combination of ylide formation and oxidation in a "one-pot" method gave satisfactory results.

Other reagents have found use in this transformation of phosphonium ylides. Early research investigated oxidants such as ethyl nitrite,[88] lead tetraacetate,[89] lead dioxide[89] and iodobenzene diacetate.[89] Oxone, a commercial version of potassium peroxymonosulphate, was recently shown to be useful in the selective oxidation of P–C bonds in the presence of alkene functionalities.[90] In another approach, 1,2-dicarbonyl compounds were prepared by the action of sodium periodate.[91] Under the conditions employed, the α-ketoaldehydes that were produced did not participate in a Wittig reaction with the parent ylide. Recently, N-sulphonyloxaziridines were reported to be effective oxidants.[92] Early exploratory studies using peracids and dibenzoyl peroxide indicated that these reagents were of limited utility.[93, 94]

Another aspect of the oxidation, hinted at earlier, is the possible Wittig reaction of the carbonyl product with the starting ylide which produces a symmetrical alkene. It has been observed in several independent experiments that oxidation of mono substituted ylides always results in alkene formation. These alkenes may be regarded as "dimers" of the carbanion part of the parent ylide.

Alkene formation is a useful reaction in itself and has been deliberately promoted by the use of half an equivalent of oxidant.[95] Some interesting systems that have been designed are trans-β-carotene[96] **92** and cyclic alkenes **94** and **95** were similarly formed from the bisylide **93**.[97]

92

93   **94**   +   **95**
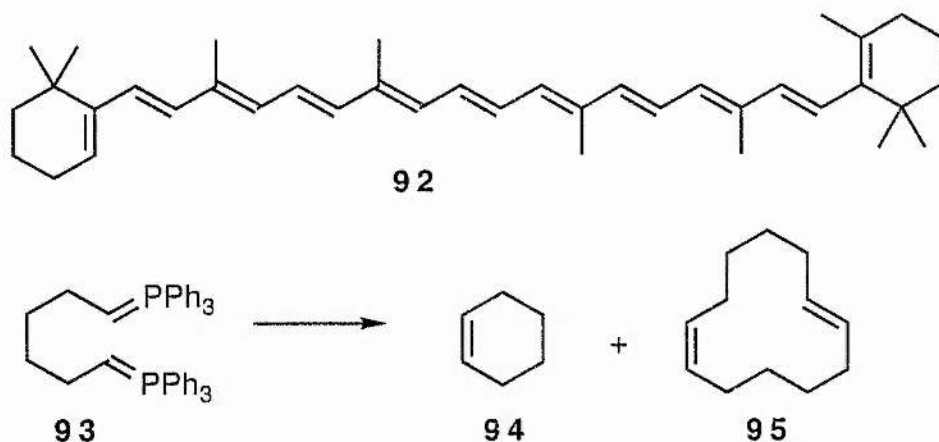
4. Synthesis of Carbonyl Compounds by the Oxidation of Sulphonium, Pyridinium and Iodonium ylides

It is not surprising that, in view of their electronic similarity to phosphorus ylides, sulphonium, pyridinium and iodonium ylides react with oxidants to form carbonyl compounds.

(Dimethylsulphonio)diacylmethylides **96** are oxidatively cleaved by equimolar amounts of ozone in an aprotic medium to yield vicinal triketones and DMSO.[98]

96   **75**
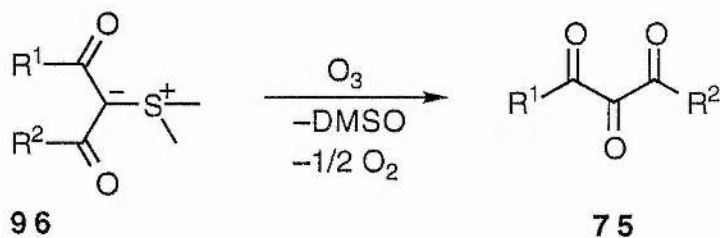
The reaction mechanism is said to involve the addition of ozone across the C–S ylidic bond. The intermediate **97** probably ring opens to form the zwitterionic structure **98**. Loss of DMSO from either intermediate affords **99** which is resonance stabilised. While the hybrids **99** and **100** may be possible, the cyclic structure **101** is considered unlikely.

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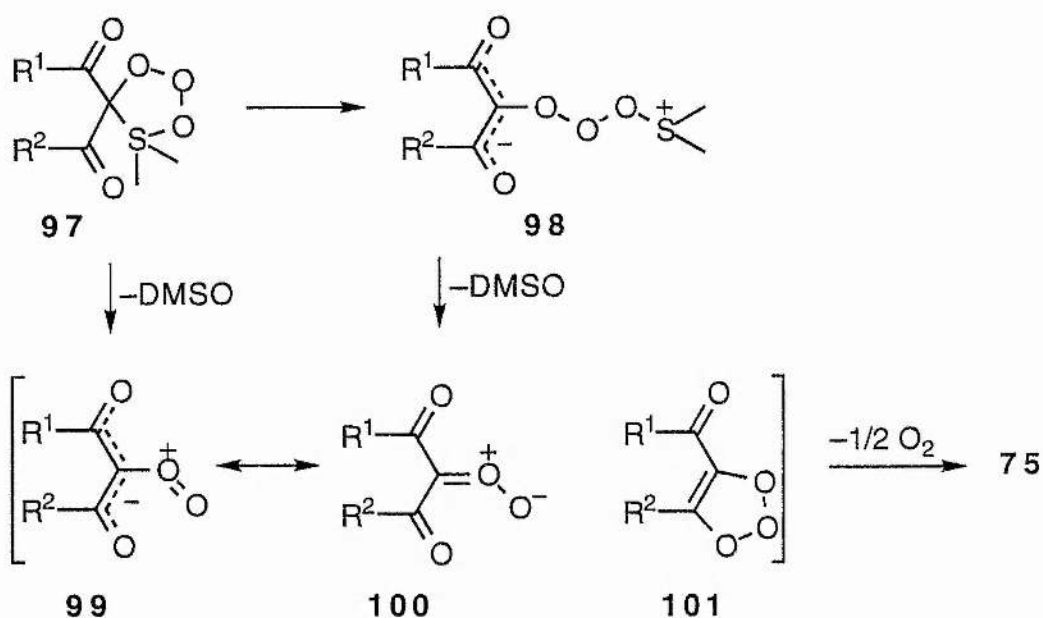
The closely related pyridinium ylides **102** also react with ozone to produce vic-tricarbonyl compounds.[99] The reaction proceeds with an initial attack at the ylidic carbanion to give the intermediate **103**. Completion of the reaction occurs with the elimination of pyridine and dioxygen.
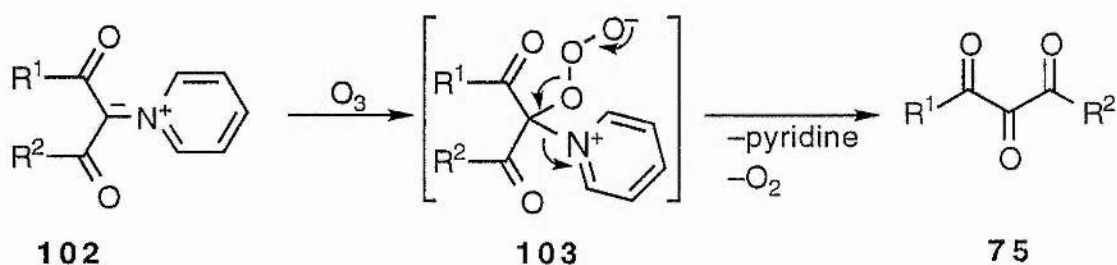
A similar intermediate **105** is suggested in the mechanism of the ozonolysis of phenyl iodonium ylides **104**.[100] Together with the carbonyl compound, iodobenzene and dioxygen were the only products. In all three situations no peroxidic products were observed.

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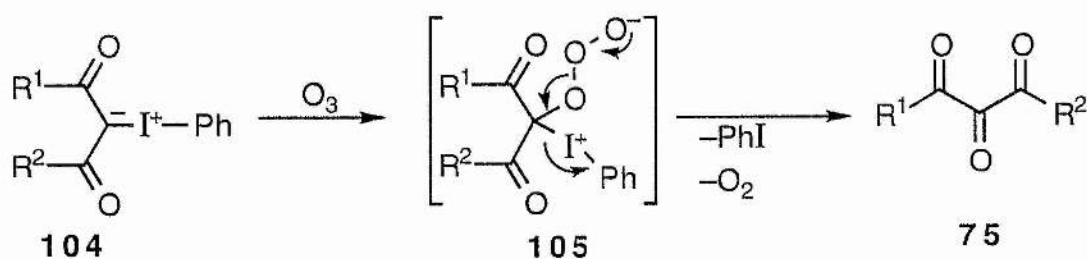
The immediate advantage of this methodology is the simplified work-up. All the unwanted non-gaseous products of the reaction, DMSO, pyridine, or iodobenzene, are easily removed under vacuum.

An earlier paper[101] showed that the analogous oxidation of sulphonium and pyridinium ylides by singlet oxygen leads to the formation of DMSO and pyridine respectively, together with the carbonyl compound.

5. Oxidation of Other Functionalities

The literature concerning the oxidation of functions such as C=C, C=N, N=N and C=S as a direct route to carbonyl compounds is extensive. Of interest is the oxidation of derivatives of ketones as a route to vicinal tri- and higher polycarbonyl compounds.

A well known example of C=C oxidation is in the synthesis of alloxan hydrate 107.[102] The oxidation of 106 is performed with chromium trioxide in acetic acid.
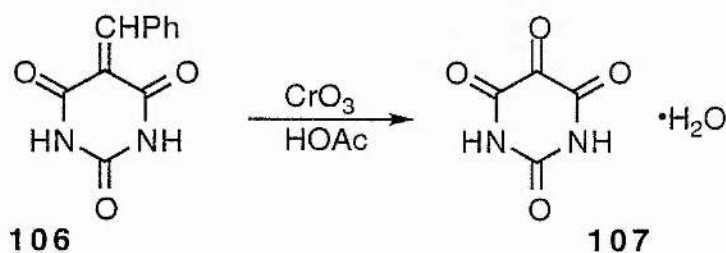
The successful cleavage of (methoxymethylene)-Meldrums acid and derivatives 108 by ozone in an aprotic medium is assumed to proceed via the

ozonides **109**.[103] Deoxygenation of the intermediates **109** with PCl3 yields the trioxo compounds **110**.

R1, R2 structures **108** → (O3) → **109** → (PCl3, –POCl3, –HCO2Me) → **110**
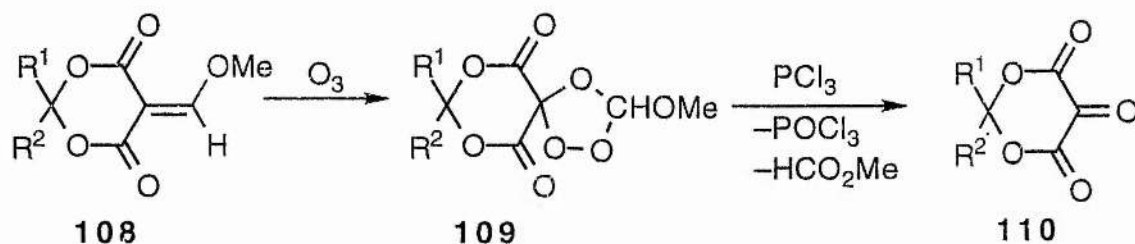
Analogous reactions of α-diazo β-diketones were successfully applied to the synthesis of both linear and cyclic triketones.[104]

The cleavage of C=N2 to prepare carbonyl compounds has culminated in the recent preparation of the first two examples of vicinal pentaketones and

111 → (p-Me-C6H4-SO2N3 /Et3N, MeCN) → **112** → (Bu'OCl /HCOOH)

113 → (P2O5) → **114**

R^1 = Ph, ^tBu
R^2 = Ph
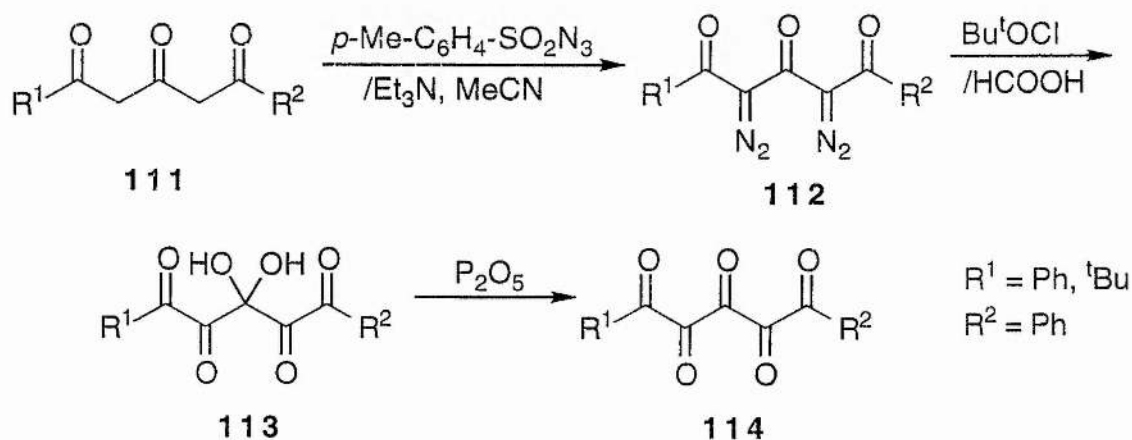
their hydrates.[105] This is surprising since the bis-diazo compound **112** and its readily available precursor had been known since 1969.[106]

The trione **111** was readily converted to the bis-diazo compound **112**. Reaction of **112** with t-butyl hypochlorite in formic acid provided the hydrates **113**. Dehydration of the latter was achieved in chloroform with phosphorus pentoxide to give a characteristic deep purple solution of the pentaketones **114**.

28

The significant structural parameters of the vicinal pentaketones were obtained from X-ray crystallography data.[107] The structures showed three central carbonyl groups in a cisoid arrangement while the two outer ones were in a transoid conformation. The short distance between C(1) and O(5) forces the C(1) and C(2) keto groups into pyramidalisation which explains the result obtained on reduction of **115** to give **116** as the sole product.

115   **116**
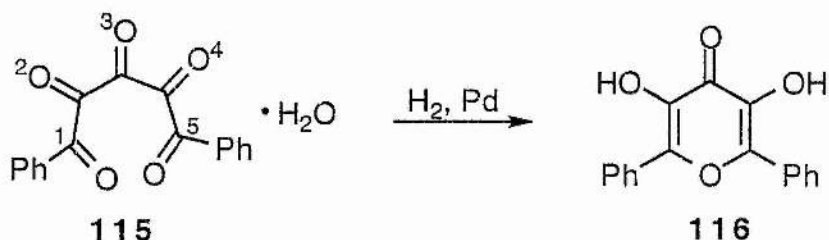
E   Ylides Containing Amino Functions

In an exploratory study ylides of this type were prepared by the reaction of *N*-phenylketeniminylidenetriphenylphosphorane **118** with *N,N*-diacylamino acids **117** to provide the intermediate **119** in good yield.[108] Elimination of the phenyl isocyanate moiety occurs, in some cases, with the formation of the ylide **120**. In other examples the pyrrolizidinediones **121** are isolated following a subsequent intramolecular Wittig reaction, the oxygen which is eliminated originating from the *N*-protecting group on the molecule.

117   **118**   **119**

120   **121**
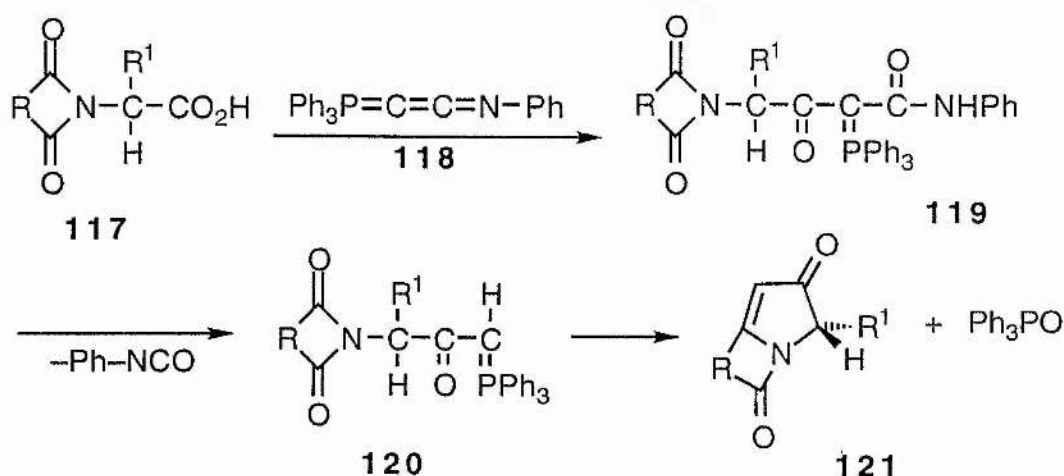
The decisive influence of R upon the product formation is reflected in the marked change in reaction time and yields obtained. Not only are the reaction times lengthy when groups other than phthalimido are employed (entries 4-5) but catalytic amounts of benzoic acid were also necessary.

Table 1: Yields of **120** and **121**

R	R^1	yield(%) 120	yield(%) 121	reaction time (h)
1,2-phenylene	H	85	56	12
1,2-phenylene	Me	—	60	12
1,2-phenylene	Bn	—	60	12
cyclohexane-1,2-diyl	H	84	28	200
ethylidene	Me	78	19	240

Analogous results were obtained in an earlier study in this laboratory involving the pyrolysis of α-phthalimidoacyl ylides **123**.[109] These ylides, derived from *N*-phthalimido amino acid chlorides **122** and (ethoxycarbonylmethylene)triphenylphosphorane, were subjected to FVP at 500 °C. Instead of the expected acetylenic products, benzopyrrolizidinediones

i) Ph$_3$P=CHCO$_2$Et, Et$_3$N
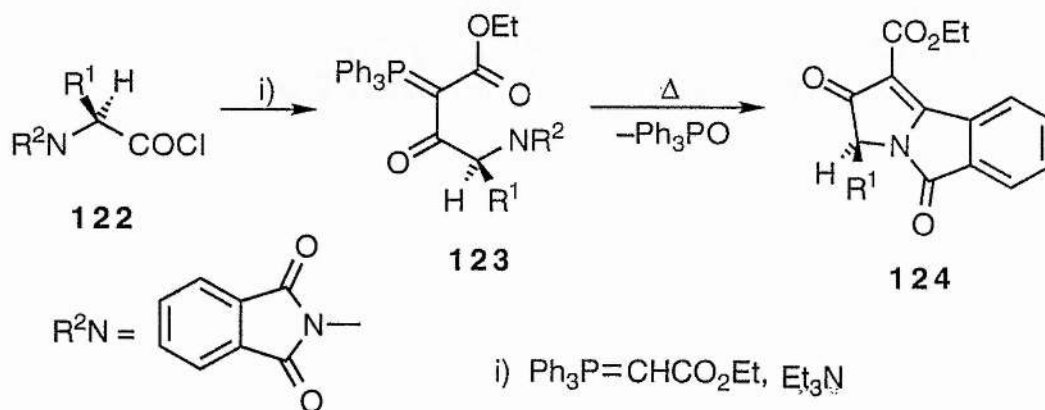
were formed by an intramolecular Wittig reaction between the ylide function and one carbonyl of the phthalimido group. The benzopyrrolizidinediones thus formed could not be separated from either triphenylphosphine oxide or tri-n-butylphosphine oxide. Characterisation was achieved through spectroscopic methods.

N-Trimethylsilylaminoacyl ylides **126** were readily accessible from the corresponding N,O-bis-silyl amino acids **125** and (trimethylsilyl methylene)triphenylphosphorane **28**.[36] These β-oxo ylides were prepared as precursors for the synthesis of ceramidin.
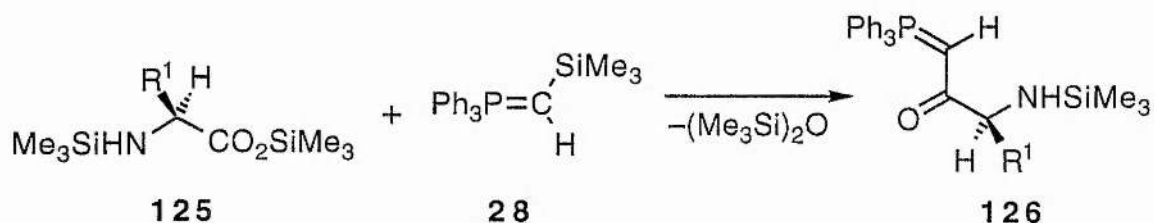
The discovery of preferential N-acylation instead of C-acylation in the reaction of acid chlorides with the ylide **126** was fortuitous. The intermediacy of the complex **127** in the mechanism seems likely since the enolate oxygen is more nucleophilic than the nitrogen. Elimination of trimethylsilyl chloride facilitates N-acylation.
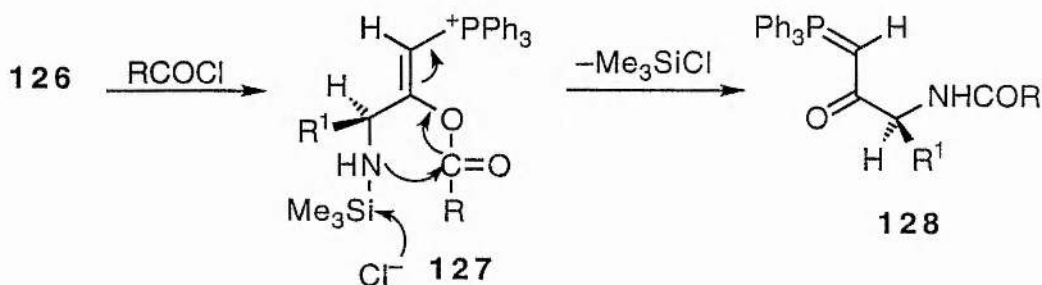
Reaction of unprotected amino acids, and acids in general, with the bis-silyl ylide **37** allows direct access to acyl ylides **129**.[29] Although only two examples, derived from glycine and alanine, were prepared the method could be applied to other amino acids. Treatment of the ylide **129** (R^1 = Me) with

Boc anhydride followed by a Wittig reaction with benzaldehyde affords *N*-protected merucathinone **130**. The free amino compound is a component of a drug.
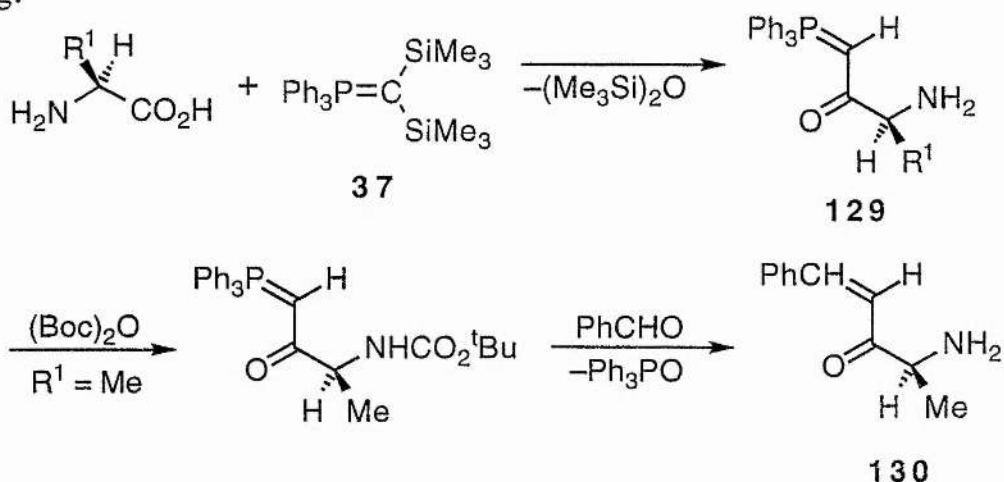
In another rather novel procedure, carbodiimides are reported to effect acylation reactions of ylides with carboxylic acids.[45] *N*-Protected amino acids **131** are coupled with stabilised ylides **132** in the presence of peptide coupling reagents, EDCI and PyBOP. Surprisingly, DCCI does not provide the keto ylides **133** and side reactions were reported. Studies with mono-, di- and tripeptides provided the corresponding ylides in good yields. Further modification of the ylides **133** by oxidative cleavage afforded the vicinal tricarbonyl compounds **134**. These triketones were shown to be potent inhibitors of serine proteases.

32
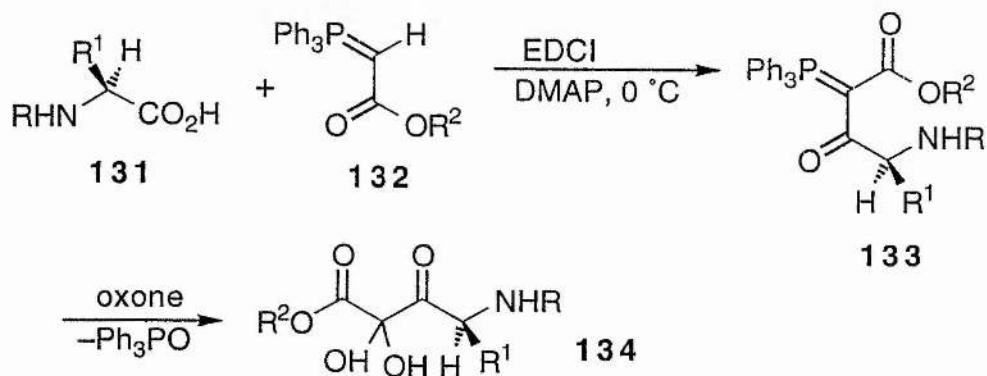
Other reports include a study on nucleophilic ring opening of aziridines by stabilised ylides.[110] A combination of three products were formed in the reaction of (ethoxycarbonylmethylene)triphenylphosphorane with the aziridines **135** of which the ylide **136** was preferred. In some cases (X= $COCF_3$, $COCH_2C_6H_4NO_2$-p) none of the desired ylide formed and **138** was the sole product isolated. From the results obtained, it was clear that the nature of the *N*-substituent determined the direction of the reaction and that the reaction was not specific. Subsequent Wittig reaction on the ylide **137** led to the optically pure unsaturated amino acids.

i) $Ph_3P=CHCO_2Et$

X = COR
R = CF_3, p-NO_2-$PhCH_2$
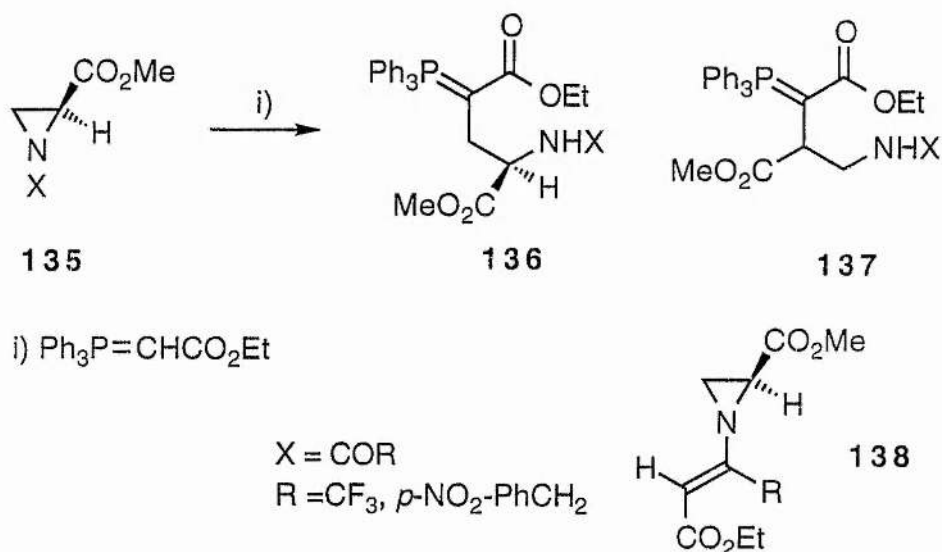
A special ylide was required for the synthesis of wybutine **142**.[111] The phosphonium salt **140** was prepared from the serine derivative **139** and triphenylphosphine in the usual way. Deprotonation and Wittig reaction with **141** gave the expected alkene **142** in a selective manner. However trace amounts of a rearranged product were also detected.
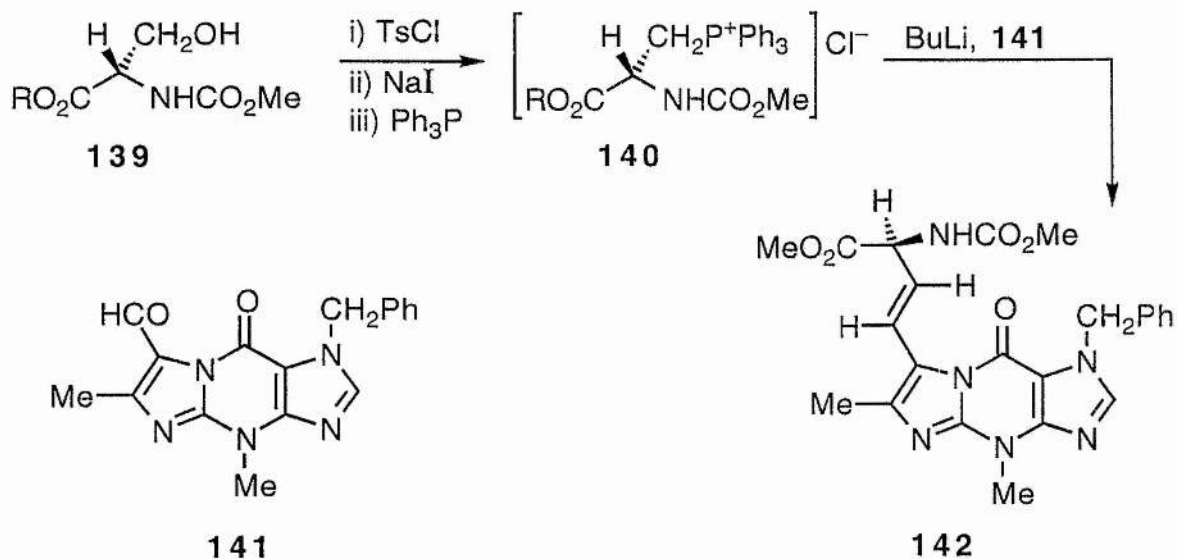
F Programme of Research

As described in section A of this Introduction, investigations of the structure and reactivity of β-oxo ylides have produced some interesting results over the last 35 years. Since the general synthetic routes to these compounds have been well developed, as discussed in section B, the preparation of new types of ylide was not expected to present major problems. At the outset of the work, a major objective was to prepare examples of higher polyoxo ylides. A promising preliminary study in this laboratory[112] had resulted in the synthesis of a few examples of the novel β,γ,β'-trioxoylides **143** and the extension of this study was considered to be of interest. At the same time, synthesis of the homologous tetraoxoylides **144** was envisaged and was expected to be reasonably straightforward. For both of these compound classes the structural and spectroscopic properties would make an interesting comparison with the data for the simpler systems already known. Perhaps more importantly, both the behaviour upon FVP and the possibility of oxidative cleavage to give *vic* polycarbonyl compounds would be of great interest in view of the results already observed in these areas and described in sections C and D earlier.

34
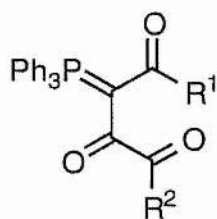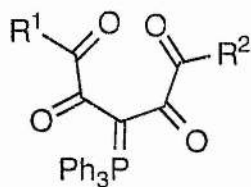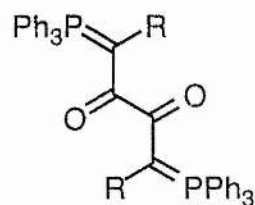
143 **144** **145**

The formation of oxalyl bis-ylides **145** had only been reported in a few cases and this was to be examined in more detail. The cases in which R contained one or two carbonyl groups would clearly be of particular interest both from the structural point of view and for pyrolysis and oxidation.

Although, as mentioned in section E, there has been a considerable amount of work on amino acid derived α-aminoacyl ylides **146**, the lucrative goal of pyrolytic extrusion of Ph₃PO from these to produce acetylenic amino acid analogues **147** had not been previously achieved and this formed the second major objective of the work.
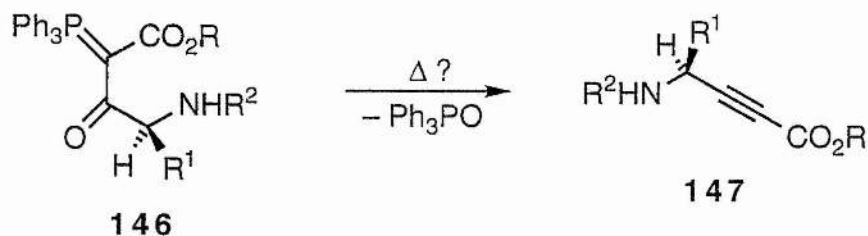
146 **147**

If it were possible to achieve this, the products would be of great interest as potential selective enzyme inhibitors with medicinal applications, as components of modified peptides, and as intermediates for synthesis of chiral compounds.

35

EXPERIMENTAL

A   Symbols and Abbreviations

b.p.	boiling point
br, s, d, t, q, m	broad, singlet, doublet, triplet, quartet, multiplet
CI	chemical ionisation
δ	chemical shift in parts per million
DCCI	dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
DMD	dimethyldioxirane
DMSO	dimethylsulphoxide
EI	electron impact
eq.	equivalent
ether	diethyl ether
EDCI	ethyl dimethylaminopropylcarbodiimide
FAB	fast atom bombardment
FVP	flash vacuum pyrolysis
GCMS	gas chromatography-mass spectrometry
h, min	hours, minutes
J	spin-spin coupling constant in Hertz
M	mol dm^{-3}
M$^+$	mass of molecular ion
m.p.	melting point
m/z	mass to charge ratio
mmol	millimoles
MS	mass spectrometry
ν_{max}	infra-red absorption frequency
NMR	nuclear magnetic resonance
PyBOP	benzotriazole-1-yloxytris(pyrrolidinyl)phosphonium hexafluorophosphate
RT	room temperature
THF	tetrahydrofuran
TLC	thin layer chromatography

B   Instrumentation and General Techniques

NMR Spectroscopy

^1H NMR

Routine spectra were obtained at 200 MHz on a Varian Gemini 200. High resolution were obtained at 300 MHz on a Bruker AM-300 spectrometer operated by the author and Mrs M. Smith.

^{13}C NMR

Spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by the author and Mrs M. Smith and at 50 MHz on a Varian Gemini 200.

All ^{13}C and ^1H spectra were obtained from solutions in deuteriochloroform except where indicated otherwise and chemical shifts are expressed in parts per million to high frequency of internal tetramethylsilane except for compounds containing $SiMe_3$ where CH_2Cl_2 at δ 5.30 was used.

^{31}P NMR

Spectra were obtained at 32 MHz on a Varian CFT-20 and a Bruker WP-80 or at 121 MHz on a Bruker AM-300 spectrometer operated by the author and Mrs M. Smith. Spectra are referenced to phosphoric acid as the external standard.

^{19}F NMR

Spectra were obtained at 282 MHz on a Varian Gemini 2000 operated by the author. Spectra are referenced to $CFCl_3$ as the external standard.

Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrophotometer or on a Perkin-Elmer 1710 fourier transform spectrophotometer. Solution spectra were run in methylene chloride using

matched sodium chloride cells of path length 0.1 mm. Spectra were calibrated with the polystyrene peak at 1603 cm^{-1}.

Mass Spectrometry

Mass spectra and Accurate mass measurements were obtained on an A.E.I./Kratos M.S.-50 spectrometer operated by Mr C. Millar. Unless otherwise indicated, the spectra were obtained using EI (70 eV). CI spectra were obtained on a VG Autospec using isobutane as the ionising gas. FAB spectra were obtained using 3-nitrobenzyl alcohol as the matrix.

Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry studies were carried out on a Hewlett-Packard 5890A gas chromatograph coupled to a Finnigan Incos mass spectrometer.

Elemental Analysis

Microanalyses for carbon, hydrogen and nitrogen were carried out on a Carlo-Erba 1106 elemental analyser operated by Mrs S. Smith.

Melting points

Melting points, both routine and for new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected.

Thin layer Chromatography

This was carried out using 0.2 mm layers of silica (Merck, Kieselgel 60F$_{254}$) on aluminium sheets. The components were observed under ultraviolet light.

Preparative Thin Layer Chromatography

This was carried out using 1.0 mm layers of silica (Merck, Kieselgel 60-80 mesh), containing 0.5% Woelm fluorescent green indicator, on glass plates. After locating the components with ultraviolet light, the bands were scraped off and the products removed from the support by soaking in dichloromethane for 30 min.

Column Chromatography

This was carried out using Fisons silica gel for chromatography (60-120 mesh), BDH "flash" grade silica and aluminium oxide (120 mesh) (pH 7.0).

Drying and Evaporation of Organic Solutions

Organic solutions were dried by standing over anhydrous magnesium sulphate and were evaporated under reduced pressure on a rotary evaporator.

Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise indicated. Where pure acetone was required the commercial Analytical Reagent (A.R.) grade solvent was used. Dry acetonitrile, ethanol and ethyl acetate were prepared by storing over molecular sieves. Dry ether and dry toluene were prepared by the addition of sodium wire. Extra dry ether was prepared by preliminary drying with sodium wire and then distilling from sodium benzophenone ketyl. Dry THF was prepared by preliminary drying with sodium wire and then distilling from potassium benzophenone ketyl. Dry dichloromethane was distilled from phosphorus pentoxide and stored over molecular sieves. Triethylamine was dried by heating under reflux with potassium hydroxide for 2 h. then distilling onto molecular sieves.

Flash Vacuum Pyrolysis

The apparatus used was based on the design of W. D. Crow, Australian National University. A similar set up is illustrated in a recent monograph by Brown.[58] The essential features of the apparatus are shown below. The sample was volatilised from a horizontal inlet tube, heated via an external heat source, through a 30 x 2.5 cm silica tube. This was heated at temperatures in the range of 400–600°C by a Carbolite Eurotherm Tube Furnace MTF-12/38A, the temperature being measured by a Pt/Pt-13% Rh thermocouple situated at the centre of the furnace. The non-volatile products were collected at the furnace exit and the volatile products collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} to 10^{-3} mmHg by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured on a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1–10 ms.
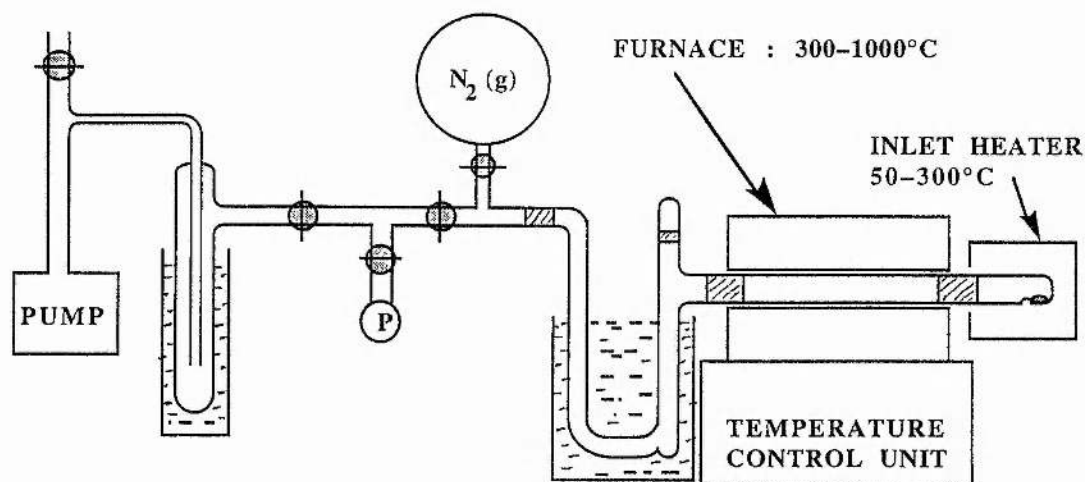
After the pyrolysis the system was isolated from the pump. The products were then dissolved out of the trap in deuteriochloroform, unless otherwise stated and analysed directly by NMR. Yields were estimated by adding a known amount of dichloromethane and comparing the NMR signals.

C   Preparation and Pyrolysis of Trioxo Ylides

1.   Preparation of Starting Phosphonium Salts and Ylides

These compounds and the succeeding ones were prepared by modification of the method of Michaelis and Gimborn.[1] An example is given below. The salts and precursor ylides were used directly without prior recrystallisation.

a. *(Benzoylmethyl)triphenylphosphonium bromide* **149** (R^1 = Ph)

To a solution of triphenylphosphine (30.0 g, 115 mmol) in dry toluene (200 cm^3) was added dropwise a solution of phenacyl bromide (22.84 g, 115 mmol) in dry toluene (20 cm^3). The mixture was then heated under reflux for 2 h and thereafter left to stir overnight. The off-white precipitate which formed was filtered off, washed with dry ether and dried to furnish the product (40.2 g, 76%) as a white powder, m.p. 265–266 °C (decomp) (lit.,[6] >250), δ_p + 25.3.

b. *(Trimethylacetylmethyl)triphenylphosphonium bromide* **149** (R^1 = Bu^t)

This was prepared as in a. using triphenylphosphine (40.0 g, 153 mmol) and 1-bromopinacolone (27.3 g, 153 mmol) to furnish the product (48.5 g, 72%) as a white powder, m.p. 216–217 °C (lit.,[113] 217–218 °C), δ_p + 21.7.

c. *(Acetylmethyl)triphenylphosphonium chloride* **149** (R^1 = Me)

This was prepared as in a. using triphenylphosphine (32.8 g, 125 mmol) and chloroacetone (10 cm^3, 11.6 g, 126 mmol) to furnish the product (40.1 g, 91%) as a white powder, m.p. 233–234 °C (lit.,[114] 235 °C), δ_p + 23.2.

d. *(Methoxycarbonylmethyl)triphenylphosphonium bromide* **149** (R^1 = OMe)

This was prepared as in a. using triphenylphosphine (40.0 g, 153 mmol) and methyl bromoacetate (14.5 cm^3, 23.4 g, 153 mmol) to furnish the product (49.3 g, 77.8%) as a white powder, m.p. 160–162 °C (lit.,[115] 162 °C)δ_p + 23.4.

e. *(Ethoxycarbonylmethyl)triphenylphosphonium bromide* **149** (R^1 = OEt)

This was prepared as in a. using triphenylphosphine (26.2 g, 100 mmol) and ethyl bromoacetate (11.1 cm^3, 16.7 g, 100 mmol) to furnish product (35.2 g, 82%) as a white powder, m.p. 155–158 °C (lit.,[115] 158 °C), δ_p +23.9.

f. *(Ethoxycarbonylmethylene)triphenylphosphorane* **150** (R^1 = OEt)

(Ethoxycarbonylmethyl)triphenylphosphonium bromide (15.0 g, 35 mmol) was dissolved in water (500 cm^3) and the solution extracted with toluene to remove any residual triphenylphosphine present. The aqueous phase was stirred vigorously as sodium hydroxide (1.4 g, 35 mmol) in water (60 cm^3) was added rapidly. The mixture was extracted with dichloromethane (2 x 100 cm^3) and the combined organic phase washed with water (1 x 100 cm^3), dried and evaporated to furnish the crude product (9.9 g, 81%) as a pale yellow solid, m.p. 162–163 °C (lit.,[115] 163 °C); δ_P +17.3 (lit.[116] δ_P +17.0).

g. *(Benzoylmethylene)triphenylphosphorane* **150** (R^1 = Ph)

This was prepared as in f. using (benzoylmethyl)triphenylphosphonium bromide (31.8 g, 69.0 mmol) to furnish (benzoylmethylene)triphenyl phosphorane (23.1 g, 87%) as pale yellow crystals; m.p. 178–180 °C (lit.,[19] 179–180 °C); δ_P +16.5 (lit.,[116] δ_P +16.2).

h. *(Trimethylacetylmethylene)triphenylphosphorane* **150** (R^1 = Bu^t)

This was prepared as in method f. using (trimethylacetylmethyl) triphenylphosphonium chloride (40.0 g, 91 mmol) to furnish (trimethylylacetylmethylene)triphenylphosphorane (24.2 g, 74%) as colourless crystals; m.p. 172–173 °C (lit.,[117] 175–173 °C); δ_P +15.8.

i. *(Acetylmethylene)triphenylphosphorane* **150** (R^1 = Me)

This was prepared as in method f. using (acetylmethyl) triphenylphosphonium chloride (42.0 g, 118.6 mmol) to furnish (acetylmethylene)triphenylphosphorane (31.7 g, 84%) as colourless crystals; m.p. 176–178 °C (lit.,[115] 178 °C); δ_P +14.1 (lit.,[115] δ_P +14.8).

j. *(Methoxycarbonylmethylene)triphenylphosphorane* **150** (R^1 = OMe)

This was prepared as in method f. using (methoxycarbonylmethyl) triphenylphosphonium bromide (9.2 g, 25.0 mmol) to furnish (methoxycarbonylmethylene)triphenylphosphorane (31.3 g, 87%) as colourless crystals; m.p. 160–162 °C (lit.,[115] 163 °C); δ_P +17.5. (lit.,[116] δ_P +17.8).

k. *(t-Butoxycarbonylmethylene)triphenylphosphorane* **150** (R^1 = OBu^t)

This was prepared as in f. using (t-butoxycarbonylmethyl) triphenylphosphonium bromide (prepared by a co-worker) (6.5 g, 15.8 mmol) to furnish (t-buoxycarbonylmethylene)triphenylphosphorane (5.2 g, 89%) as colourless crystals; m.p. 152–154 °C (lit.,[118] m.p. 151–152 °C), δ_P +17.2.

2. Preparation of α-oxo acid chlorides

a. *Phenylglyoxylyl chloride* **151** (R^2 = Ph)

Oxalyl chloride (5.1 cm^3, 7.5 g, 58.7 mmol) was added dropwise to a stirred suspension of benzoylformic acid sodium salt (10.0 g. 58.7 mmol) in dry ether (100 cm^3) under a nitrogen atmosphere. The mixture was stirred overnight, filtered under a nitrogen atmosphere and the filtrate evaporated under vacuum. The residue was Kugelrohr distilled to furnish phenylglyoxylyl chloride (4.7 g, 48%) as a yellow liquid, b.p.(oven temperature) 90–92 °C at 10 mmHg (lit.,[119] 55 °C at 1.5 mmHg).

b. *Pyruvyl chloride* **151** (R^2 = Me)

Oxalyl chloride (1 eq) was added dropwise to a stirred suspension of sodium pyruvate (1 eq) in dry ether (20 cm^3) at 0 °C under a nitrogen atmosphere. The mixture was stirred at RT for 6 h. The solids were filtered off under nitrogen and the filtrate used directly in the appropriate reaction.[119]

c. *Methyl oxalyl chloride* **151** (R^2 = OMe)

To a solution of oxalyl chloride (21.9 cm^3, 31.9 g, 298 mmol) in dry ether at 0 °C under a nitrogen atmosphere was added methanol (13.5 cm^3, 8.5 g, 265 mmol). The mixture was stirred at this temperature for 2 h and then distilled to furnish methyl oxalyl chloride (30.1 g, 93%) as a colourless liquid, b.p. (oven temperature) 120–122 °C (lit.,[120] 118–120 °C).

Ethyl oxalyl chloride **151** (R^2 = OEt) was commercially available.

3. Preparation of Trioxo ylides

General method

To a stirred solution of ylide (1 eq.) and triethylamine (1eq) in dry toluene was added the acid chloride (1 eq.) in dry toluene dropwise. The mixture was stirred at RT for 4 h, washed with water (2 x 20 cm^3) and the organic phase separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (2 x 50 cm^3) and the combined organic phase dried. The solvent was evaporated to furnish the crude product which was recrystallized from ethyl acetate.

a. *1,4-Diphenyl-3-triphenylphosphoranylidenebutane-1,2,4-trione* **143a**

Reaction as above using (benzoylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol) and phenylglyoxylyl chloride (0.89 g, 5.3 mmol) gave the title compound (2.21 g, 82%) as yellow crystals; m.p. 158–160 °C (Found: C, 79.4; H, 5.0. C$_{34}$H$_{25}$O$_3$P requires C, 79.7; H, 4.9%); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 3020, 1780, 1665, 1585, 1515, 1475, 1428, 1310, 1210, 1170, 1100, 995, 860 and 830; δ_H 8.15–7.0 (25 H, m, Ph); δ_C 193.5 (d, *J* 13, CO-CO-Ph), 193.4 (d, *J* 7, P=CCO-Ph), 190.3 (d, *J* 5, *CO*-CO-Ph), 141.9 (d, *J* 8, C-1 of Ph), 134.3 (C-1 of Ph), 133.4 (d, *J* 10, 6 x C-2 of P-Ph), 132.7 (Ph), 132.3 (d, *J* <2, 3 x C-4 of P-Ph), 130.6 (Ph), 129.0 (4C, Ph), 128.8 (d, *J* 13, 6 x C-3 of P-Ph), 127.9 (2 C, Ph), 127.5 (2 C, Ph), 124.1 (d, *J* 92, 3 x C-1 of P-Ph) and 84.2 (d, *J* 97, P=C); δ_P +16.5; *m/z* 512 (M$^+$, 0.5%), 456 (0.5), 407 (75), 379 (3), 277 (80), 262 (10), 234 (12), 183 (33), 129 (75), 105 (83) and 77 (100).

b. *1-Phenyl-2-triphenylphosphoranylidenepentane-1,3,4-trione* **143b**

Reaction as above using (benzoylmethylene)triphenylphosphorane (6.9 g, 18.1 mmol) and pyruvyl chloride (18.1 mmol) gave the title compound (4.79 g, 59%) as yellow crystals; m.p. 164–166 °C (Found: C, 77.4; H, 5.0. C$_{29}$H$_{23}$O$_3$P requires C, 77.3; H, 5.1%); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 1685, 1580,

1510, 1320, 1300, 1155. 1116, 1090, 1010, 985 and 858; δ_H 7.8–7.2 (20 H. m, Ph) and 1.98 (3 H. s. Me); δ_C 201.4 (d, J 11, COCO–Me), 193.5 (d, J 8, CO-Ph), 191.3 (d, J 5, COCO-Me), 143.2 (d, J 8, Ph), 133.5 (d, J 10, 6 x C-2 of P-Ph), 132.4 (d, J 3. 3 x C-4 of P-Ph), 131.0 (Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 128.6 (2 C, Ph). 128.1 (2 C, Ph), 124.1 (d, J 92, 3 x C-1 of P-Ph). 80.2 (d, J 99, P=C) and 25.6 (Me); δ_P +16.6; m/z (20 eV) 407 (M$^+$–MeCO. 2%), 277 (100), 262 (6). 201 (8), 172 (20), 157 (8), 129 (30) and 105 (26).

c. *Methyl 2,4-dioxo-4-phenyl-3-triphenylphosphoranylidenebutanoate* **143c**

Reaction as in above using (benzoylmethylene)triphenylphosphorane (3.0 g, 7.9 mmol) and methyl oxalyl chloride (0.97 g, 7.9 mmol) gave the title compound (2.6 g, 71%) as colourless crystals; m.p. 129–131 °C (Found: C. 74.7; H, 4.9. $C_{29}H_{23}O_4P$ requires C, 74.7; H, 5.0%); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 3000, 1714, 1580, 1520. 1472, 1420, 1338, 1302, 1195, 1170, 1122, 1092, 1014, 985 and 855; δ_H 7.8–7.3 (20 H, m, Ph) and 3.17 (3 H, s, Me); δ_C 192.9 (d, J 7, CO-Ph), 182.3 (d, J 6, COCO$_2$Me), 166.2 (d, J 15, COCO$_2$Me), 141.8 (d, J 8, Ph), 133.5 (d, J 10, 6 x C-2 of P-Ph), 132.4 (d, J 2, 3 x C-4 of P-Ph), 131.1 (Ph), 129.1 (2 C, Ph), 128.9 (d, J 13, 6 x C-3 of P-Ph), 127.9 (2 C, Ph), 124.1 (d, J 92, 3 x C-1 of P-Ph), 82.3 (d, J 100, P=C) and 51.4 (Me); δ_P +17.8; m/z 466 (M$^+$, 0.2%), 408 (5), 381 (2), 380 (2), 304 (2), 278 (33), 277 (76), 236 (6), 201 (12), 183 (11), 129 (12), 105 (29), 85 (66) and 84 (100).

d. *Ethyl 2,4-dioxo-4-phenyl-3-triphenylphosphoranylidenebutanoate* **143d**

Reaction as above using (benzoylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol) and ethyl oxalyl chloride (0.72 g, 0.8 cm^3, 5.3 mmol) gave the title compound (1.78 g, 70%) as colourless crystals; m.p. 172–175 °C (Found: C, 75.3; H, 5.4. $C_{30}H_{25}O_4P$ requires C, 75.0; H, 5.2%); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 1707, 1580, 1515, 1420, 1330, 1300, 1186, 1120, 1092, 1010, 985, 918 and 856; δ_H 7.85–7.2 (20 H, m, Ph), 3.58 (2 H, q, J 7, OCH$_2$) and 1.02 (3 H, t, J

7, Me); δ_C 193.0 (d, CO-Ph, J 7), 182.6 (d, J 6, COCO$_2$Et), 165.9 (d, J 15, COCO$_2$Et), 141.8 (d, J 8, Ph), 133.6 (d, J 10, 6 x C-2 of P-Ph), 132.4 (d, J 2, 3 x C-4 of P-Ph), 131.1 (Ph), 129.2 (2 C, Ph), 128.9 (d, J 13, 6 x C-3 of P-Ph), 128.0 (2 C, Ph), 124.1 (d, J 92, 3 x C-1 of P-Ph), 82.7 (d, J 100, P=C), 61.0 (OCH$_2$) and 13.6 (Me); δ_P +15.6; m/z 480 (M$^+$, 0.5%), 407 (7), 379 (2), 304 (2), 278 (45), 277 (100), 201 (25), 199 (22), 183 (25), 152 (18), 129 (33), 105 (32) and 77 (92).

e. *1-Phenyl-3-triphenylphosphoranylidenepentane-1,2,4-trione* **143e**

Reaction as above using (acetylmethylene)triphenylphosphorane (5.0 g, 15.7 mmol) and phenylglyoxylyl chloride (2.64 g, 15.7 mmol) gave the title compound (3.6 g, 51%) as brown crystals; m.p. 170–172 °C (Found: C, 77.4; H, 5.3. C$_{29}$H$_{23}$O$_3$P requires C, 77.3; H, 5.1%); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 3000, 1700, 1654, 1575, 1530, 1470, 1420, 1355, 1300, 1208, 1165, 1092, 987, 908 and 832; δ_H 8.0–7.25 (20 H, m, Ph) and 2.32 (3 H, d, J 4, Me); δ_C 195.2 (d, J 5, CO-Me), 193.4 (d, J 5, COCO-Ph), 190.2 (d, J 13, COCO-Ph), 133.8 (Ph), 133.5 (d, J 10, 6 x C-2 of P-Ph), 133.1 (Ph), 132.2 (d, J 2, 3 x C-4 of P-Ph), 129.7 (2 C, Ph), 128.7 (d, J 13, 6 x C-3 of P-Ph), 128.1 (2 C, Ph), 124.5 (d, J 92, 3 x C-1 of P-Ph), 86.3 (d, J 102, P=C) and 30.2 (Me); δ_P +15.6; m/z 450 (M$^+$, 0.5%), 345 (3), 303 (2), 278 (18), 277 (42), 201 (12), 199 (14), 183 (10), 105 (22) and 77 (100).

f. *Methyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate* **143f**

Reaction as above using (acetylmethylene)triphenylphosphorane (3.0 g, 9.4 mmol) and methyl oxalyl chloride (1.15 g, 9.4 mmol) gave the title compound as (2.98 g, 78%) yellow crystals; m.p. 130–132 °C (Found: C, 71.7; H, 5.3. C$_{24}$H$_{21}$O$_4$P requires C, 71.3; H, 5.2%); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 2930, 1710, 1535, 1470, 1414, 1352, 1280, 1190, 1092, 1033, 1015, 986, 918, 860 and 800; δ_H 7.75–7.4 (15 H, m, Ph), 3.44 (3 H, s, OMe) and 2.26 (3 H, s,

COMe); δ_C 195.0 (d, J 6, CO-Me), 182.4 (d, J 13, COCO$_2$), 167.1 (d, J 13, COCO_2), 133.4 (d, J 10, 6 x C-2 of P-Ph), 132.3 (d, J 2, 3 x C-4 of P-Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 124.6 (d, J 93, 3 x C-1 of P-Ph), 84.5 (d, J 104, P=C), 51.9 (OMe) and 29.5 (COMe); δ_P +16.2; m/z 404 (M$^+$, 1%), 376 (5), 375 (4), 345 (25), 318 (18), 303 (83), 277 (100), 201 (25), 183 (35) and 152 (16).

g. *Ethyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate* **143g**

Reaction as above using (acetylmethylene)triphenylphosphorane (5.00 g, 15.7 mmol) and ethyl oxalyl chloride (2.14 g, 15.7 mmol) gave the title compound (4.5 g, 68%) as yellow crystals; m.p. 138–140 °C (Found: C, 72.0; H, 5.7. C$_{25}$H$_{23}$O$_4$P requires C, 71.8; H. 5.5%); ν_{max} /cm^{-1} 1712, 1600, 1575, 1262, 1210, 1100, 1045, 861, 740, 720 and 690; δ_H 8.0–7.5 (15 H. m, Ph), 3.93 (2 H, q, J 7, OCH$_2$), 2.32 (3 H, s, COMe) and 1.22 (3 H, t, J 7, CH$_2Me$); δ_C 195.1 (d, J 6, CO–Me), 182.6 (d, J 13, COCO$_2$), 166.8 (d, J 5, COCO_2), 133.5 (d, J 10, 6 x C-2 of P-Ph), 132.2 (d, J 2, 3 x C-4 of P-Ph), 128.8 (d, J 12, 6 x C-3 of P-Ph), 124.8 (d, J 93, 3 x C-1 of P-Ph), 84.5 (d, J 105, P=C), 63.1 (OCH$_2$), 29.5 (COMe) and 13.8 (CH$_2Me$); δ_P +16.2; m/z 418 (M$^+$, 2%), 390 (15), 375 (2), 361 (2), 345 (100), 317 (10), 303 (83), 279 (37), 278 (37), 277 (78), 262 (22), 201 (23) and 183 (47).

h. *5,5-Dimethyl-1-phenyl-3-triphenylphosphoranylidenehexane-1,2,4-trione* **143h**

Reaction as above using (trimethylacetylmethylene)triphenyl phosphorane (2.0 g, 5.5 mmol) and phenylglyoxylyl chloride (0.93 g, 5.5 mmol) gave the title compound (2.13 g, 78%) as yellow crystals; m.p. 168–170 °C (Found: C, 77.8; H, 6.25. C$_{32}$H$_{29}$O$_3$P requires C, 78.0; H, 5.9%); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 1654, 1525, 1430, 1360, 1340, 1300, 1260, 1210, 1140, 1090, 832, 737, 702, 680 and 648; δ_H 7.75–7.15 (20 H, m, Ph) and 1.32 (9 H,

s, But); δ_C 206.9 (d, J 3, CO-CMe$_3$), 193.0 (d, J <2. CO-Ph), 185.1 (d, J 19, CO-COPh), 134.6 (C-4 of Ph). 133.7 (d, J 10, 6 x C-2 of P-Ph), 132.8 (Ph). 131.9 (d, J 3, 3 x C-4 of P-Ph). 129.9 (2 C, Ph), 128.4 (d, J 13. 6 x C-3 of P-Ph), 127.6 (2 C, Ph), 125.3 (d, J 93, 3 x C-1 of P-Ph), 85.9 (d, J 102, P=C), 43.9 (CMe$_3$) and 26.6 (CMe$_3$); δ_P +17.4; m/z 477 (M$^+$–Me, 0.2%), 436 (M$^+$–C$_4$H$_8$, 0.5), 435 (1), 387 (10), 303 (16), 277 (100). 201 (20), 183 (18), 158 (26) and 105 (50).

i. *Methyl 3,4-dioxo-4-phenyl-2-triphenylphosphoranylidenebutanoate* **143i**

Reaction as above using (methoxycarbonylmethylene)triphenyl phosphorane (2.5 g, 7.5 mmol) and phenylglyoxylyl chloride (1.26 g, 7.5 mmol) gave the title compound (3.0 g, 86%) as colourless crystals; m.p. 119–121 °C (Found: C, 74.8; H, 5.0. C$_{29}$H$_{23}$O$_4$P requires C, 74.7; H, 5.0%); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 2980, 1645, 1572, 1518, 1472, 1412. 1320, 1270, 1175, 1092, 1072, 1015, 988 and 960; δ_H 8.15–7.5 (20 H, m, Ph) and 3.21 (3 H, s, OMe); δ_C 194.5 (d, J 11, CO-Ph), 192.0 (d, J 4, $COCO$-Ph), 167.8 (d, J 14, CO_2), 133.7 (d, J 10, 6 x C-2 of P-Ph), 132.6 (Ph), 132.5 (d, J 3, 3 x C-4 of P-Ph), 129.1 (2 C, Ph), 128.8 (d, 6 x C-3 of P-Ph, J 13), 128.1 (d, 2 C, Ph), 124.3 (d, J 93, 3 x C-1 of P-Ph), 69.2 (d, J 109, P=C) and 50.1 (OMe); δ_P +15.7; m/z 438 (M$^+$-CO, 10%), 406 (4), 361 (2), 277 (100), 262 (8), 201 (8), 152 (8), 122 (27), 105 (27) and 92 (36).

j. *Methyl 3,4-dioxo-2-triphenylphosphoranylidenepentanoate* **143j**

Reaction as above using (methoxycarbonylmethylene)triphenyl phosphorane (3.60 g, 10.8 mmol) and pyruvyl chloride (10.8 mmol) gave the title compound (3.79 g, 87%) as colourless crystals; m.p. 153–155 °C (Found: C, 71.2; H, 5.3. C$_{24}$H$_{21}$O$_4$P requires C, 71.3; H, 5.2%); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 2925, 1690, 1650, 1600, 1470, 1412, 1338, 1290, 1172, 1090, 1060, 988, 941 and 872; δ_H 7.8–7.4 (15 H, m, Ph), 3.30 (3 H, s, OMe) and 2.38 (3 H, s,

COMe); δ_C 202.7 (d, J 11, CO-Me), 193.1 (d, J 4, $COCO$-Me). 168.1 (d, J 14, CO_2), 133.6 (d, J 10, 6 x C-2 of P-Ph), 132.5 (d, J 3, 3 x C-4 of P-Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 124.0 (d, J 93, 3 x C-1 of P-Ph), 66.2 (d, J 109, P=C), 50.1 (OMe) and 25.9 ($COMe$); δ_P +15.3; m/z 405 (M+H$^+$, 8%), 361 (8), 333 (24), 301 (30), 277 (100), 201 (25), 183 (44), 152 (18) and 77 (45).

k. *Dimethyl 2-oxo-3-triphenylphosphoranylidenebutanedioate* 143k

Reaction as above using (methoxycarbonylmethylene)triphenyl phosphorane (3.0 g, 9.0 mmol) and methyl oxalyl chloride (1.1 g, 9.0 mmol) gave the title compound (3.1 g, 82%) as colourless crystals; m.p. 148–150 °C (Found: C, 69.1; H, 5.2; M$^+$–CO_2Me, 361.0992. $C_{24}H_{21}O_5P$ requires C, 68.6; H, 5.0%; M$^+$–CO_2Me, 361.0994); v_{max} /cm^{-1} (CH$_2$Cl$_2$) 2970, 2930, 1715, 1650, 1540, 1470, 1415, 1350, 1270, 1180, 1095, 985 and 952; δ_H 7.75–7.4 (15 H, m, Ph), 3.83 (3 H, s, OMe) and 3.28 (3 H, s, OMe); δ_C 184.3 (d, J 6, $COCO_2$Me), 167.8 (d, J 15, CO_2Me), 167.5 (d, J 14, $COCO_2$Me), 133.6 (d, J 10, 6 x C-2 of P-Ph), 132.5 (d, J 2, 3 x C-4 of P-Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 124.0 (d, J 93, 3 x C-1 of P-Ph), 68.0 (d, J 111, P=C), 51.8 (OMe) and 50.3 (OMe); δ_P +16.3; m/z 420 (M$^+$, 0.5%), 361 (52), 301 (4), 277 (5), 201 (22), 183 (20) and 152 (10).

l. *1-Ethyl 4-methyl 2-oxo-3-triphenylphosphoranylidenebutanedioate* 143l

Reaction as above using (methoxycarbonylmethylene)triphenyl phosphorane (3.0 g, 9.0 mmol) and ethyl oxalyl chloride (1.22 g, 9.0 mmol) gave the title compound (3.20 g, 82%) as colourless crystals; m.p. 173–174 °C (Found: C, 68.8; H, 5.45. $C_{25}H_{23}O_5P$ requires C, 69.1; H, 5.3%); v_{max} /cm^{-1} (Nujol) 1728, 1663, 1582, 1440, 1432, 1350, 1278, 1180, 1153, 1101, 1088, 1021, 753, 710 and 691; δ_H 8.0–7.5 (15 H, m, Ph), 4.38 (2 H, q, J 7, OCH$_2$), 3.38 (3 H, s, OMe) and 1.38 (3 H, t, J 7, CH$_2$$Me$); δ_C 184.6 (d, J 6, $COCO_2$Et), 167.45 (d, J 13, $COCO_2$Et), 167.41 (d, J 15, CO_2Me), 133.6 (d, J

10, 6 x C-2 of P-Ph), 132.5 (d, J 2, 3 x C-4 of P-Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 124.1 (d, J 94, 3 x C-1 of P-Ph), 67.8 (d, J 111, P=C), 61.0 (OCH$_2$), 50.3 (OMe) and 14.2 (CH$_2$*Me*); δ_P +16.5; m/z 434 (M$^+$, 1%), 375 (4), 362 (23), 361 (100), 301 (5), 293 (16), 201 (6), 183 (17), 165 (8) and 77 (12).

m. *Ethyl 3,4-dioxo-4-phenyl-2-triphenylphosphoranylidenebutanoate* **143m**

Reaction as above using (ethoxycarbonylmethylene)triphenyl phosphorane (2.0 g, 5.7 mmol) and phenylglyoxylyl chloride (0.97 g, 5.7 mmol) gave the title compound (1.95 g, 71%) as colourless crystals; m.p. 168–169 °C (Found: C, 74.4; H, 5.9; M$^+$–CO, 452.1551. C$_{30}$H$_{25}$O$_4$P requires C, 75.0; H, 5.2%; M$^+$–CO, 452.1541); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 1640, 1530, 1470, 1425, 1353, 1327, 1270, 1200, 1160, 1090 and 980; δ_H 8.15–7.45 (20 H, m, Ph), 3.76 (2 H, q, J 7, OCH$_2$) and 0.59 (3 H, t, J 7, Me); δ_C 194.5 (d, J 11, *C*O-Ph), 192.0 (d, J 4, *C*OCO-Ph), 167.0 (d, J 14, CO$_2$), 134.7 (Ph), 133.7 (d, J 10, 6 x C-2 of P-Ph), 133.6 (Ph), 132.5 (d, J 2, 3 x C-4 of P-Ph), 129.3 (2 C, Ph), 128.8 (d, J 12, 6 x C-3 of P-Ph), 128.3 (2 C, Ph), 124.4 (d, J 93, 3 x C-1 of P-Ph), 69.0 (d, J 109, P=C), 59.2 (OCH$_2$) and 13.2 (Me); δ_P +15.6; m/z 452 (M$^+$–CO, 10%), 376 (26), 375 (100), 301 (9), 277 (20) and 262 (62).

Ethyl 3,4-dioxo-2-triphenylphosphoranylidenepentanoate **143n**

Reaction as above using (ethoxycarbonylmethylene)triphenyl phosphorane (12.6 g, 36.0 mmol) and pyruvyl chloride (36.0 mmol) gave the title compound (8.4 g, 56%) as colourless crystals; m.p. 138–140 °C (Found: C, 72.4; H, 5.5; M$^+$–COMe, 375.1118. C$_{25}$H$_{23}$O$_4$P requires C, 71.8; H, 5.5%; M$^+$–COMe, 375.1150); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 1690, 1638, 1532, 1468, 1415, 1355, 1320, 1250, 1146 and 1092; δ_H 7.8–7.4 (15 H, m, Ph), 3.83 (2 H, q, J 7, OCH$_2$), 2.32 (3 H, s, Me) and 0.78 (3 H, t, J 7, CH$_2$*Me*); δ_C 202.8 (d, J 10, *C*O–Me), 193.2 (d, J 4.5, *C*OCO-Me), 167.9 (d, J 13, CO$_2$), 133.6 (d, J 10, 6

x C-2 of P-Ph), 132.5 (d, J 3, 3 x C-4 of P-Ph), 128.9 (d, J 14, 6 x C-3 of P-Ph), 124.2 (d, J 93, 3 x C-1 of P-Ph), 66.0 (d, J 108, P=C), 59.1 (OCH$_2$), 26.0 (COMe) and 13.6 (CH$_2Me$); δ_P +15.2; m/z 418 (M$^+$, 0.2%), 375 (M$^+$–COMe, 100), 347 (5), 303 (28), 301 (36), 277 (67), 262 (70), 201 (37), 183 (86) and 165 (40).

o. *4-Ethyl-1-methyl 2-oxo-3-triphenylphosphoranylidenebutanedioate* **143o**

Reaction as above using (ethoxycarbonylmethylene)triphenyl phosphorane (3.0 g, 8.6 mmol) and methyl oxalyl chloride (1.1 g, 8.6 mmol) gave the title compound (3.38 g, 90%) as colourless crystals; m.p. 115–118 °C (Found: C, 69.45; H, 5.6. C$_{25}$H$_{23}$O$_5$P requires C, 69.1: H, 5.3%); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 2940, 1718, 1648, 1548, 1360, 1260, 1190, 1163, 1094, 1080 and 988; δ_H 7.75–7.4 (15 H, m, Ph), 3.85 (3 H, s, OMe), 3.83 (2 H, q, J 7, OCH$_2$) and 0.77 (3 H, t, J 7, CH$_2Me$); δ_C 184.3 (d, J 6, COCO$_2$Me), 167.8 (d, J 14, CO$_2$Me), 167.2 (d, J 13, COCO$_2$Me), 133.6 (d, J 10, 6 x C-2 of P-Ph), 132.5 (d, J 3, 3 x C-4 of P-Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 124.2 (d, J 93, 3 x C-1 of P-Ph), 67.8 (d, J 110, P=C), 59.1 (OCH$_2$), 51.7 (OMe) and 13.7 (CH$_2Me$); δ_P +16.2; m/z 434 (M$^+$, 0.2%), 376 (18), 303 (3), 301 (1), 278 (20), 277 (42), 201 (8), 183 (6), 91 (22), 85 (67) and 84 (100).

p. *Diethyl 2-oxo-3-triphenylphosphoranylidenebutanedioate* **143p**

Reaction as above using (ethoxycarbonylmethylene)triphenyl phosphorane (8.7 g, 25 mmol) and ethyl oxalyl chloride (3.4 g, 25 mmol) gave the title compound (9.4 g, 84%) as colourless crystals; m.p. 136–138 °C (Found: C, 70.0; H, 5.6. C$_{26}$H$_{25}$O$_5$P requires C, 69.6; H, 5.6%); ν_{max} /cm^{-1} 1735, 1725, 1672, 1540, 1438, 1342, 1278, 1190, 1095, 1020, 760, 745, 718 and 698; δ_H 8.0–7.5 (15 H, m, Ph), 4.38 (2 H, q, J 7, OCH$_2$), 3.89 (2 H, q, J 7, OCH$_2$), 1.37 (3 H, t, J 7, Me) and 0.78 (3 H, t, J 7, Me); δ_C 184.7 (d, J 6, COCO$_2$Et), 167.5 (d, J 15, CO$_2$Et), 167.2 (d, J 13, COCO$_2$Et), 133.6 (d, J 10,

6 x C-2 of P-Ph), 132.4 (d, J 2, 3 x C-4 of P-Ph), 128.7 (d, J 13, 6 x C-3 of P-Ph), 124.2 (d, J 93, 3 x C-1 of P-Ph), 67.6 (d, J 111, P=C), 60.9 (OCH_2), 59.1 (OCH_2), 14.1 (Me) and 13.7 (Me); δ_P +16.2; m/z 448 (M^+, 0.2%), 403 (0.2), 376 (16), 375 (100), 347 (4), 303 (12), 279 (4), 201 (6), 195 (3), 183 (11) and 165 (8).

4. Flash Vacuum Pyrolysis of Trioxo Ylides

a. *Pyrolysis of 1-phenyl-2-triphenylphosphoranylidenepentane-1,3,4-trione*

FVP of the ylide **143b** (124 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which proved by ^1H and ^{31}P NMR to be a mixture of Ph_3PO and Ph_3P, and in the cold trap a liquid which was shown by GCMS to contain a complex mixture of products including acetaldehyde, acetophenone, benzoic acid, 1-phenylpent-1-ene-3,4-dione and 1-phenylpent-2-ene-1,4-dione. The desired acetylbenzoylacetylene was not present.

Acetophenone : m/z (GCMS) 120 (M^+, 25%), 105 (100), 103 (85), 77 (54), 51 (23) and 43 (29).

1-phenylpent-1-ene-3,4-dione and 1-phenylpent-2-ene-1,4-dione: m/z (GCMS) 174 (M^+, 3%), 165 (5), 131 (100), 103 (85), 77 (54), 51 (23) and 43 (21).

Benzoic acid : m/z (GCMS) 122 (M^+, 9%), 105 (100), 77 (9) and 51 (45).

b. *Pyrolysis of 1-phenyl-3-triphenylphosphoranylidenepentane-1,2,4-trione*

FVP of ylide **143e** (106 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be Ph_3PO and in the cold trap a solid which was shown by ^1H NMR and GCMS to contain mainly benzaldehyde (17%) and benzoic acid (45%) (δ_H as in F2b.) with further minor unidentified components. The expected acetylbenzoylacetylene was not present.

c. *Pyrolysis of methyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate*

FVP of ylide **143f** (121 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be mainly Ph_3PO accompanied by ≈5% Ph_3P. The material in the cold trap was shown by ^{1}H NMR and GCMS to contain mainly methanol with further minor unidentified components. The expected methyl 3-acetylpropynoate was not present.

d. *Pyrolysis of ethyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate*

FVP of ylide **143g** (142 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph_3PO and in the cold trap ethyl 4-oxopent-2-ynoate **152g** (67%) as a colourless liquid; δ_H 4.26 (2 H, q, *J* 7, OCH_2), 2.36 (3 H, s, COMe) and 1.30 (3 H, t, *J* 7, CH$_2$*Me*); δ_C 182.5 (CO), 152.2 (CO_2), 80.8 ($C{\equiv}CCO_2$), 78.0 ($C{\equiv}CCO_2$), 63.0 (OCH_2), 32.3 (CO*Me*) and 13.9 (CH$_2$*Me*); *m/z* 140 (M$^+$, 1%), 125 (21), 111 (3), 95 (28), 80 (8), 67 (9) and 53 (100), accompanied by ethanol (≈20%).

e. *Pyrolysis of 5,5-dimethyl-1-phenyl-3-triphenylphosphoranylidenehexane-1,2,4-trione*

FVP of ylide **143h** (92 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph_3PO. The yellow liquid in the cold trap contained several unidentified components but the major one was the desired benzoylpivaloylacetylene **152h** (43%); δ_H 8.2-8.0 (2 H, m, Ph), 7.7-7.5 (3 H, m, Ph) and 1.34 (9 H, s, 3 x Me), δ_C 188.8 (CO), 176.5 (CO), 135.7 (C-1 of Ph), 135.1 (C-4 of Ph), 129.6 (2 C, Ph), 128.9 (2 C, Ph), 85.4 ($C{\equiv}C$), 78.2 ($C{\equiv}C$), 45.2 (CMe_3) and 25.6 (C*Me*$_3$); *m/z* (GCMS) 199 (M$^+$–Me, 1%), 159 (6), 158 (84), 130 (5), 105 (42), 102 (28), 77 (45) and 57 (100).

f. *Pyrolysis of methyl 3,4-dioxo-2-triphenylphosphoranylidenepentanoate*

FVP of ylide **143j** (140 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr. inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO and in the cold trap methyl 4-oxopent-2-ynoate **152j** (38%) as a colourless liquid; δ_H 3.80 (3 H, s) and 2.40 (3 H, s); δ_C 182.6 (CO), 152.7 (CO$_2$), 81.0 ($C\equiv$CCO$_2$), 77.5 (C$\equiv$$CCO_2$), 53.4 (OMe) and 32.3 (COMe), accompanied by methanol ($\approx$40%).

D   Preparation β,γ-Dioxo Phosphonium Salts

1. Preparation of Bromocarbonyl compounds

a. *1-Bromo-3-phenyl-1,2 propanedione* **168** (R^1 = Ph)

A mixture of 1-phenylpropane-1,2-dione (3.0 g, 20.2 mmol) and pyridine (0.2 cm^3, 0.2 g, 2.4 mmol) was warmed to 40–50 °C. Bromine (1.04 cm^3, 3.2 g, 20.2 mmol) was added dropwise until HBr evolution was observed. The heat was removed and and the remainder of the bromine added over 90 min. The mixture was stirred for a further hour while N$_2$ was passed through to remove HBr. The crude mixture was distilled to furnish the title compound (4.2 g, 92%) as a yellow oil, b.p. (oven temperature) 110 °C at 4 mmHg (lit.,[122] 145 °C at 10 mmHg); δ_H 8.05–7.98 (2 H, m, Ph), 7.70–7.57 (1 H, m, Ph), 7.54–7.49 (2 H, m, Ph) and 4.40 (2 H, s, CH$_2$Br).

b. *Methyl bromopyruvate* **168** (R^1 = OMe)

This compound was prepared as above using methyl pyruvate (20.0 g, 196 mmol), pyridine (0.5 cm^3, 0.5 g, 6 mmol) and bromine (10.1 cm^3, 31 g, 196 mmol) to furnish the title compound (25.6 g, 72%) as a yellow oil, b.p. (oven temperature) 64–65 °C at 4 mmHg (lit.,[121] 103–107 °C at 10 mmHg); δ_H 4.45 (3 H, s, OCH$_3$) and 4.44 (2 H, s, CH$_2$Br).

c. Ethyl bromopyruvate **168** (R^1 = OEt)

This compound was prepared as above using ethyl pyruvate (10.0 g, 86 mmol), pyridine (0.5 cm^3, 0.5 g, 6 mmol) and bromine (4.5 cm^3, 13.8 g, 86 mmol) to furnish the product (10.1 g, 59%) as a yellow oil, b.p. (oven temperature) 68–70 °C at 4 mmHg (lit.,[121] 98–105 °C at 9 mmHg); δ_H 4.45 (2 H, q, *J* 7, OCH$_2$), 4.44 (2 H, s, CH$_2$Br) and 1.41 (3 H, t, *J* 7, CH$_2$Me).

2. Preparation of Dioxo Phosphonium Salts

a. (2,3-Dioxo-3-phenylpropyl)triphenylphosphonium bromide **162**

A solution of 3-bromo-1-phenyl-1,2 propanedione (4.0 g, 17.6 mmol) in dry toluene (10 cm^3) was added dropwise to a solution of triphenylphosphine (4.60 g, 17.6 mmol) in dry toluene (50 cm^3) and the mixture stirred under a nitrogen atmosphere for 3 h. The mixture was evaporated and the residue triturated with dry ether to give the title compound in quantitative yield as a yellow powder, m.p. 108–110 °C (lit.,[123] 104–105 °C); v_{max}/cm^{-1} (Nujol) 1765, 1580, 1440, 1275, 1220, 1105, 990, 890, 810, 725 and 690; This proved by ^{1}H and ^{13}C NMR to consist of a mixture of tautomeric forms whose spectroscopic assignment is described in the discussion. δ_H 13.8 (1 H, br s, OH), 8.05–7.11 (20 H, m, Ph) and 6.45 (3 H, br d, *J* 13); δ_C (see Table 6 in Discussion); δ_P +22.3 (keto form) and +17.4 (enol form)

b. (2-methoxycarbonyl-2-oxoethyl)triphenylphosphonium bromide **163**

Reaction as in a. using methyl bromopyruvate (4.0 g, 22 mmol) and triphenylphosphine (5.7 g, 22 mmol) gave the title compound in quantitative yield as a white powder, m.p. 152–153 °C (Found: C, 59.5; H, 4.5. C$_{22}$H$_{20}$BrO$_3$P requires C, 59.6; H, 4.5%); v_{max}/cm^{-1} (Nujol) 1740, 1620,

1440, 1245, 1140, 1110, 890, 830, 750 and 690. This proved by ^{1}H and ^{13}C NMR to consist of a mixture of tautomeric forms whose spectroscopic assignment is described in the discussion. δ_H 8.9 (br s, OH). 8.00–7.52 (15 H, m, Ph), 7.19 (d, J 13), 6.30 (d, J 12), 6.01 (d, J 16), 3.94 (s, Me), 3.86 (s, Me) and 3.41 (s, Me); δ_C (see Table 6 in Discussion); δ_P +21.1 (10%), +17.2 (54%) and +15.0 (36%).

c. (2-Ethoxycarbonyl-2-oxoethyl)triphenylphosphonium bromide **164**

Reaction as in a. using ethyl bromopyruvate (4.5 g, 23 mmol) and triphenylphosphine (6.05 g, 23.1 mmol) gave the title compound in quantitative yield as a white powder, m.p. 160–161 °C (Found: C, 60.4; H, 4.8. $C_{27}H_{22}BrO_3P$ requires C, 60.4; H, 4.8%); v_{max} /cm^{-1} (Nujol) 1735, 1620, 1430, 1250, 1145, 1105, 1020, 830, 745 and 690; This proved by ^{1}H and ^{13}C NMR to consist of a mixture of tautomeric forms whose spectroscopic assignment is described in the discussion. δ_H 13.3 (br s, OH). 11.9 (br s, OH), 7.94–7.51 (15 H, m, Ph), 7.18 (d, J 13), 6.33 (d, J 12), 5.98 (d, J 16), 4.44 (q, J 7, OCH$_2$), 4.33 (q, J 7, OCH$_2$), 3.84 (q, J 7, OCH$_2$), 1.45 (t, J 7, Me), 1.37 (t, J 7, Me) and 1.02 (t, J 7, Me); δ_C (see Table 6 in Discussion); δ_P +21.2 (15%), +17.3 (46%) and +15.0 (39%).

d. 2,3-Dioxobutane-1,4-ylidene bis(triphenylphosphonium bromide) **171**

A solution of 1,4-dibromobutane-2,3-dione (5.0 g, 20.5 mmol) in acetone (40 cm^3) was added dropwise over 1 h to a solution of triphenylphosphine (12.0 g, 45.8 mmol) in acetone (80 cm^3) and the mixture stirred for 4 h at RT. The precipitate was filtered off to give an off-white powder. The crude product was redissolved in acetone, heated under reflux for 5 min. and left to cool. The precipitate which formed was filtered off to yield the pure product (1.6 g, 32%) as pale yellow crystals, m.p. 260–261 °C (decomp.) (lit.,[124] 238–240 °C); (Found: C, 62.7; H, 4.7. $C_{40}H_{34}Br_2O_2P_2$

requires C, 62.5; H, 4.5%); v_{max} /cm^{-1} (Nujol) 4000–2000, 1730, 1680, 1320, 1110, 1140, 1000, 830, 760, 750, 720 and 690; δ_H 11.20 (1 H, br s, OH), 9.31 (1 H, m), 8.79 (1 H, m) and 8.72–7.00 (m, 31 H, Ph); δ_C (see Table 6 in Discussion); δ_P +22.0, +21.1, +20.37 (d, ^5J $_{P-P}$ 3.3) and +15.02 (d, ^5J $_{P-P}$ 3.3).

e. *(2,3-Dioxo-4-triphenylphosphoranylidenebutyl)triphenylphosphonium bromide* 173

To a stirred solution of the bis-phosphonium salt **171** (2.0 g, 2.6 mmol) in water (25 cm^3) was added sodium hydroxide (0.21 g, 5.2 mmol) in water (5 cm^3). The mixture was extracted with dichloromethane (2 x 25 cm^3) and the combined organic phase washed with water (25 cm^3), dried and evaporated to furnish the crude product as a yellow solid. Recrystallisation from ethyl acetate gave the title compound (1.54 g, 86%) as yellow crystals; m.p. 158–161 °C; (Found: C, 69.5; H, 5.2. C$_{40}$H$_{33}$BrO$_2$P$_2$ requires C, 69.9; H, 4.8%); v_{max} /cm^{-1} (Nujol) 4000–2000, 1635, 1400, 1105, 990, 870, 830, 750, 735 and 690; δ_H 8.72–7.00 (m, 30 H, Ph), the position of the remaining 3 H was uncertain; δ_C (see Table 6 in Discussion); δ_P +16.7 and +12.8.

E   Preparation and FVP of β,γ-Dioxo Ylides

1.   Preparation

a. *1-Phenyl-3-triphenylphosphoranylidenepropane-1,2-dione* 174

A solution of 3-bromo-1-phenylpropane-1,2-dione (4.0 g, 17 mmol) in dry toluene (10 cm^3) was added dropwise to a solution triphenylphosphine (4.6 g, 17 mmol) in dry toluene (50 cm^3) and the mixture stirred under a nitrogen atmosphere for 3 h. Dichloromethane was added until all the

precipitated phosphonium salt dissolved, then a solution of NaOH (0.92 g) in water (20 cm^3) was added in one portion. The mixture was stirred rapidly for a few minutes and the organic phase was separated, dried and evaporated to give the title compound (7.0 g, 98%) as yellow crystals; m.p. 160–161 °C (lit.,[123] 164–165 °C) (Found: C, 79.7; H, 5.3. $C_{27}H_{21}O_2P$ requires C, 79.4; H, 5.2%); ν_{max} /cm^{-1} (Nujol) 1650, 1534, 1440, 1230, 1160, 1100, 985, 870, 750, 720 and 670; δ_H 8.15 (2 H, d. J 7, Ph) 7.74–7.67 (6 H, m, Ph), 7.63–7.52 (3 H, m, Ph), 7.48–7.14 (9 H, m, Ph) and 4.47 (1 H, br s, CH); δ_C 195.7 (d, J 17, COPh), 183.5 (d, J <2, COCOPh), 135.0 (C-1 of Ph), 133.0 (d, J 10, 6 x C-3 of P-Ph), 132.7 (C-4 of Ph), 132.6 (d, J 3, 3 x C-4 of P-Ph), 130.3 (2 C, Ph), 129.0 (d, J 12, 6 x C-2 of P-Ph), 128.0 (2 C, Ph), 125.6 (d, J 92, 3 x C-1 of P-Ph) and 54.8 (d, J 105, P=C); δ_P +17.4; m/z (CI) 409 (M+H$^+$, 100%), 279 (100), 263 (41), 149 (12), 73 (9) and 59 (19).

b. Methyl 2-oxo-3-triphenylphosphoranylidenepropionate **175**

Reaction as above using methyl bromopyruvate (10.4 g, 57.5 mmol), triphenylphosphine (15.0 g, 57.5 mmol) and NaOH (2.30 g, 57.3 mmol) gave the title compound (15.5 g, 75%) as off-white crystals; m.p. 175–178 °C (lit.,[125] m.p. 178–179 °C); ν_{max} /cm^{-1} (Nujol) 1700, 1550, 1230, 1105, 750, 720 and 690; δ_H 7.76–7.45 (15 H, m, Ph), 5.72 (1 H, br s, CH) and 3.75 (3 H, s, OMe); δ_C 171.2 (CO), 164.7 (d, J 19, CO_2Me), 133.1 (d, J 10, 6 x C-3 of P-Ph), 133.0 (3 x C-4 of P-Ph), 129.4 (d, J 13, 6 x C-2 of P-Ph), 123.3 (d, J 92, 3 x C-1 of P-Ph), 63.7 (d, J 103, P=C) and 52.4 (OCH$_3$); δ_P +16.8; m/z (CI) 363 (M+H$^+$, 32%), 317 (6), 279 (93) and 263 (100).

c. Ethyl 2-oxo-3-triphenylphosphoranylidenepropionate **176**

Reaction as above using ethyl bromopyruvate (4.5 g, 23 mmol), triphenylphosphine (6.0 g, 23 mmol) and NaOH (0.92 g, 23 mmol) gave the title compound (6.2 g, 72%) as off-white crystals; m.p. 166–168 °C (lit.,[125]

m.p. 169–171 °C); ν_{max} /cm^{-1} (Nujol) 1700, 1550, 1440, 1218, 1300, 750, 720 and 700; δ_H 7.75–7.35 (15 H, m, Ph), 5.20 (1 H, br s, CH), 4.23 (2 H, q, J 7, OCH$_2$) and 1.31 (3 H, t, J 7, CH$_3$); δ_C 173.9 (d, J 5, CO), 165.6 (d, J 20, CO$_2$Et), 133.1 (d, J 10, 6 x C-3 of P-Ph), 132.7 (d, J <2, 3 x C-4 of P-Ph), 129.1 (d, J 12, 6 x C-2 of P-Ph), 125.1 (d, J 92, 3 x C-1 of P-Ph), 61.2 (OCH$_2$), 57.5 (d, J 107, P=C) and 14.2 (CH$_3$); δ_P +16.3; m/z (CI) 377 (M+H$^+$, 100%), 349 (5), 319 (8), 303 (18), 279 (25) and 263 (17).

2. Pyrolysis of Dioxo Ylides

a. *Pyrolysis of 1-Phenyl-3-triphenylphosphoranylidenepropane-1,2-dione*

FVP of the ylide **174** (299 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO and Ph$_3$P in a ratio of 47:53, and in the cold trap a white solid which was shown by ^{1}H and ^{13}C NMR to contain benzoic anhydride, m.p. 34–35 °C (lit.,[126] 42 °C); δ_H 8.12 (2 H, d), 7.59 (1 H, m) and 7.12 (2 H, m); δ_C 171.7 (CO), 133.8 (C-4), 130.3 (C-2), 129.1 (C-1) and 128.5 (C-3). The desired benzoylacetylene was not present.

FVP of the ylide **174** (302 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO and Ph$_3$P in a ratio of 86:14, and in the cold trap a white solid which was shown by ^{1}H and ^{13}C NMR to contain benzoic anhydride, data as in a.. The desired benzoylacetylene was not present.

b. *Pyrolysis of Methyl 2-oxo-3-triphenylphosphoranylidenepropionate*

FVP of the ylide **175** (484 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, Ph$_3$P and unreacted starting material in a ratio of 39:52:9, and in the cold trap a

yellow oil which was shown by ^{1}H and ^{13}C NMR to contain mainly methanol, a small amount of the desired methyl propiolate and unidentified products.

FVP of the ylide **175** (401 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph_3PO, Ph_3P and starting material in a ratio of 78:18:4, and in the cold trap a colourless oil which was shown by ^{1}H and ^{13}C NMR to contain a small amount of methanol and unidentified products and the desired methyl propiolate (30%); δ_H 3.81 (3 H, s, OMe) and 2.87 (1 H, s, $\equiv$CH); δ_C 153.2 (CO_2), 75.0 ($C\equiv$CH), 74.5 ($\equiv$CH) and 52.9 (OMe).

c. *Pyrolysis of Ethyl 2-oxo-3-triphenylphosphoranylidenepropionate*

FVP of the ylide **176** (415 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph_3PO, Ph_3P and unreacted starting material in a ratio of 41 : 58 : 3. and in the cold trap an oil which was shown by ^{1}H and ^{13}C NMR to contain mainly ethanol and a small amount of the desired ethyl propiolate and unidentified products.

FVP of the ylide **176** (260 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph_3PO and Ph_3P in a ratio of 86 : 14, and in the cold trap a colourless oil which was shown by ^{1}H and ^{13}C NMR to contain a small amount of ethanol and unidentified products and the desired ethyl propiolate (28%); δ_H 4.24 (2 H, q, J 7, OCH_2), 2.89 (1 H, s, $\equiv$CH) and 1.21 (3 H, t, J 7, OMe); δ_C 153.0 (CO_2), 74.9 ($C\equiv$CH), 74.6 ($\equiv$CH), 62.5 (OCH_2) and 14.0 (CH_2Me).

F   Preparation and Pyrolysis of Tetraoxo Ylides

1.   Preparation of Tetraoxo Ylides

General Method

A solution of the β,γ-dioxo ylide (5.3 mmol) and triethylamine (5.3 mmol) in dry toluene was stirred at RT while a solution of the appropriate α-oxo-acid chloride (5.3 mmol) in dry toluene was added dropwise. The mixture was stirred at RT for 3 h then poured into water (50 cm^3). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 x 25 cm^3). The combined organic extracts were dried and evaporated to give the desired product.

a. *1,5-Diphenyl-3-triphenylphosphoranylidenepentane-1,2,4,5-tetraone* **144a**
Reaction above using *1-phenyl-3-triphenylphosphoranylidenepropane-1,2-dione* (2.0 g, 4.9 mmol), triethylamine (0.68 cm^3, 0.49 g, 4.9 mmol) and phenylglyoxylyl chloride (0.82 g, 4.9 mmol) gave the title compound (2.40 g, 92%) as yellow crystals; m.p. 223–224 °C (Found: C, 77.6; H, 4.5. $C_{35}H_{25}O_4P$ requires C, 77.8; H, 4.7%); v_{max}/cm^{-1} (Nujol) 1665, 1585, 1545, 1310, 1275, 1220, 1100, 990, 875, 750, 720 and 690; δ_H 7.83–7.26 (25 H, m, Ph); δ_C 193.2 (d, *J* 5, 2 x CO*C*OPh), 191.3 (d, *J* 9, 2 x *C*OCOPh), 133.9 (d, *J* 10, 6 x C-2 of P-Ph), 133.7 (2 x C-1 of Ph), 133.2 (2 C, Ph), 132.8 (d, *J* 2, 3 x C-4 of P-Ph), 129.7 (4 C, Ph), 128.9 (d, *J* 13, 6 x C-3 of P-Ph), 128.1 (4 C, Ph) and 83.6 (d, *J* 102, P=C); δ_P +15.5; *m/z* (FAB) 541 (M+H$^+$, 86%), 435 (38), 303 (15), 262 (13), 154 (89), 136 (60) and 105 (92).

b. Methyl 5-phenyl-2,4,5-trioxo-3-triphenylphosphoranylidenepentanoate
144b

Reaction as above using methyl 2-oxo-3-triphenylphosphoranylidene propionate (3.0 g, 8.3 mmol), triethylamine (1.2 cm^3, 0.84 g, 8.3 mmol) and phenylglyoxylyl chloride (1.4 g, 8.3 mmol) gave the title compound (2.96 g, 72%) as yellow crystals; m.p. 142–143 °C (Found: C. 72.8; H, 4.6. $C_{30}H_{23}O_5P$ requires C, 72.9; H, 4.7%); v_{max} /cm^{-1} (Nujol) 1730, 1655, 1590, 1550, 1310, 1220, 1150, 1100, 900, 850, 720, 690 and 650; δ_H 7.97–7.27 (20 H, m, phenyl) and 3.49 (3 H, s, OMe); δ_C 192.6 (d, J 5, COPh), 190.7 (d, J 9, COCOPh) 183.1 (d, J 9, COCO$_2$Me), 166.0 (d, J 9, COCO$_2$Me), 134.2 (Ph), 133.6 (Ph), 133.8 (d, J 10, 6 x C-3 of P-Ph), 132.8 (d, J 3, 3 x C-4 of P-Ph), 129.7 (2 C, Ph), 129.0 (d, J 13, 6 x C-2 of P-Ph), 128.1 (2 C. Ph), 122.7 (d, J 92, 3 x C-1 of P-Ph), 82.4 (d, J 103, P=C) and 52.0 (OMe); δ_P +16.2; m/z 494 (5), 435 (12), 389 (22), 361 (100), 301 (21), 277 (70), 201 (29) and 183 (30).

c. Ethyl 5-phenyl-2,4,5-trioxo-3-triphenylphosphoranylidenepentanoate **144c**

Reaction as above using ethyl 2-oxo-3-triphenylphosphoranylidene propionate (2.0 g, 5.3 mmol), triethylamine (0.73 cm^3, 0.54 g, 5.3 mmol) and phenylglyoxylyl chloride (0.89 g, 5.3 mmol) gave the title compound (2.08 g, 77%) as brown crystals; m.p. 139–140 °C (Found: C, 73.1; H, 5.1. $C_{31}H_{25}O_5P$ requires C, 73.2; H, 5.0%); v_{max} /cm^{-1} (Nujol) 1710, 1655, 1590, 1540, 1285, 1220, 1095, 1010, 750, 710, 690 and 650; δ_H 7.79–7.33 (20 H, m, Ph), 3.91 (2 H, q, J 7, OCH$_2$) and 1.15 (3 H, t, J 7, Me); δ_C 192.7 (d, J 6, COPh), 190.8 (d, J 9, COCOPh), 183.4 (d, J 9, COCO$_2$Et), 165.8 (d, J 9, COCO$_2$Et), 133.8 (d, J 10, 6 x C-3 of P-Ph), 132.8 (d, J 2, 3 x C-4 of P-Ph), 129.0 (d, J 13, x C-2 of P-Ph), 122.9 (d, J 102, 3 x C-1 of P-Ph), 82.3 (d, J 103, P=C), 61.5 (OCH$_2$) and 13.8 (Me); δ_P +16.3; m/z (CI) 509 (M+H$^+$, 22%)

405 (19), 383 (18), 361 (11), 317 (11), 279 (100), 363 (41), 249 (16), 145 (75), 127 (93) and 105 (9).

d. *Dimethyl 2,4-dioxo-3-triphenylphosphoranylidenepentanedioate* **144d**

Reaction as as above using methyl 2-oxo-3-triphenylphosphoranylidene propionate (3.0 g, 8.3 mmol), triethylamine (1.2 cm^3, 0.84 g, 8.3 mmol) and methyl oxalyl chloride (0.88 g, 8.29 mmol) gave the title compound (3.12 g, 81%) as colourless crystals; m.p. 203–205 °C (Found: C, 67.1; H, 4.7. C$_{25}$H$_{21}$O$_6$P requires C, 67.0; H, 4.7%); ν_{max} /cm^{-1} (Nujol) 1740. 1610, 1565, 1320, 1220, 1160, 1105, 110, 810, 765 and 700; δ_H 7.80–7.69 (6 H, m, Ph), 7.68–7.59 (3 H, m, Ph), 7.58–7.47 (6 H, m, Ph) and 3.62 (6 H, s, 2 x OMe); δ_C 182.6 (d, *J* 9, 2 x CO*CO*$_2$Me). 165.6 (d, *J* 9, 2 x CO*CO*$_2$Me), 133.6 (d, *J* 10, 6 x C-2 of P-Ph), 132.8 (d, *J* 2, 3 x C-4 of P-Ph), 129.0 (d, *J* 13, 6 x C-3 of P-Ph), 122.8 (d, *J* 93, 3 x C-1 of P-Ph), 81.2 (d, *J* 105, P=C) and 52.2 (2 x OMe); δ_P +17.2; *m/z* (CI) 449 (M+H$^+$, 10%), 279 (100) and 263 (95).

e. *Ethyl methyl 2,4-dioxo-3-triphenylphosphoranylidenepentanedioate* **144e**

Reaction as above using ethyl 2-oxo-3-triphenylphosphoranylidene propionate (1.0 g, 2.7 mmol), triethylamine (0.27 g, 0.37 cm^3, 2.7 mmol) and methyl oxalyl chloride (0.25 cm^3, 0.3.3 g, 2.7 mmol) gave title compound (1.08 g, 88%) as colourless crystals; m.p. 164–165 °C (Found: C, 67.8; H, 5.3. C$_{26}$H$_{23}$O$_6$P requires C, 67.5; H, 5.0%); ν_{max} /cm^{-1} (Nujol) 1730, 1610, 1560, 1320, 1220, 1160, 1100, 1020, 770, 730 and 700; δ_H 7.76–7.69 (6 H, m, Ph), 7.67–7.57 (3 H, m, Ph), 7.53–7.47 (6 H, m, Ph), 4.00 (2 H, q, *J* 7, OCH$_2$), 3.61 (3 H, s, OMe) and 1.24 (3 H, t, *J* 7, CH$_2$*Me*); δ_C 182.8 (d, *J* 9, CO), 182.7 (d, *J* 9, CO), 165.7 (d, *J* 7, *CO*$_2$Me), 165.3 (d, *J* 9, *CO*$_2$Et), 133.7 (d, *J* 10, 6 x C-3 of P-Ph), 132.8 (d, *J* 2, 3 x C-4 of P-Ph), 129.0 (d, *J* 13, 6 x C-2 of P-Ph), 122.9 (d, *J* 93, 3 x C-1 of P-Ph), 81.2 (d, *J* 104, P=C), 61.6 (OCH$_2$),

52.2 (OMe) and 13.8 (CH$_2$*Me*); δ_P +17.4; *m/z* (CI) 463 (M+H$^+$. 9%), 279 (100) and 189 (12).

Alternatively the same compound could be prepared using methyl 2-oxo-3-triphenylphosphoranylidene propionate (3 g, 8.3 mmol), triethylamine (1.2 cm^3, 0.84 g, 8.3mmol) and ethyl oxalyl chloride (1.1 g, cm^3. 8.3 mmol) to give the title compound (3.12 g, 81%) as colourless crystals; m.p. 165–166 °C, which has identical spectroscopic properties as those listed above.

f. *Diethyl 2,4-dioxo-3-triphenylphosphoranylidenepentanedioate* **144f**

Reaction as above using ethyl 2-oxo-3-triphenylphosphoranylidene propionate (2.0 g, 5.3 mmol), triethylamine (0.54 g, 0.74 cm^3, 5.3 mmol) and ethyl oxalyl chloride (0.60 cm^3, 0.73 g, 5.3 mmol) gave the title compound (1.82 g, 73%) as colourless crystals; m.p. 158–159 °C (lit.,[127] m.p. 160–161 °C) (Found: C, 67.8; H, 5.4. C$_{27}$H$_{25}$O$_6$P requires C, 68.1; H, 5.3%); ν_{max} /cm^{-1} (Nujol) 1725, 1620, 1560, 1320, 1220, 1180, 1160, 1100, 1020, 720 and 700; δ_H 7.77–7.69 (6 H, m, Ph), 7.64–7.61 (3 H, m, Ph), 7.60–7.46 (6 H, m, Ph), 4.00 (4 H, q, *J* 7, OCH$_2$) and 1.24 (6 H, t, *J* 7, Me); δ_C 182.9 (d, *J* 9, 2 x CO*CO$_2$Et), 165.3 (d, *J* 9, 2 x CO*CO$_2$*Et*), 133.7 (d, *J* 10, 6 x C-3 of P-Ph), 132.7 (3 x C-4 of P-Ph), 128.9 (d, *J* 13, 6 x C-2 of P-Ph), 123,0 (d, *J* 93, 3 x C-1 of P-Ph), 80.9 (d, *J* 104, P=C), 61.6 (2 x OCH$_2$) and 13.8 (2 x Me); δ_P +17.3; *m/z* (CI) 477 (M+H$^+$, 100%), 423 (8), 377 (22), 279 (40), 263 (15), 233 (21), 177 (31), 133 (12), 57 (46) and 43 (15).

2. FVP and Conventional Pyrolysis of Tetraoxo Ylides

a. Pyrolysis of 1,5-Diphenyl-3-triphenylphosphoranylidenepentane-1,2,4,5-tetraone

i.   FVP of the ylide **144a** (308 mg. 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a red solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a mixture which was shown by ^{1}H NMR to contain mainly benzoic anhydride (data as in E2a.), and benzaldehyde. The desired alkyne was not present.

Benzaldehyde: δ_H 10.2 (1 H, s. CHO), 7.96 (2 H, m, Ph), 7.62 (1 H, m, Ph) and 7.51 (2 H, m, Ph).

ii.   Conventional pyrolysis of the ylide **144a** (500 mg, 200 °C, 1.0 x 10^{-2} Torr) in a Kugelrohr gave a brown solid residue in the reaction flask which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the receiver a mixture which was shown by ^{1}H and ^{13}C NMR to contain benzoic anhydride, data as in E2a. The desired alkyne was not present.

b. Pyrolysis of Methyl 5-phenyl-2,4,5-trioxo-3-triphenylphosphoranylidene pentanoate

i.   FVP of the ylide methyl **144b** (305 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a red solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a mixture which was shown by ^{1}H and ^{13}C NMR to contain benzaldehyde (data as in ai.) and methanol (as the major products) and some benzoic acid, and other, unidentified, material. The desired alkyne was not present.

Benzoic acid: δ_H 12.2 (1 H, s, CO$_2$H), 8.15 (2 H, m), 7.65 (1 H, m) and 7.48 (2 H, m).

ii.   Conventional pyrolysis of the ylide **144b** (488 mg, 200 °C, 1.0 x 10^{-2} Torr) in a Kugelrohr gave a solid residue in the reaction flask which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the receiver a mixture which was shown by ^{1}H and ^{13}C NMR to contain benzaldehyde. δ$_H$ as in ai. The desired alkyne was not present.

c. *Pyrolysis of Ethyl 5-phenyl-2,4,5-trioxo-3-triphenylphosphoranylidene pentanoate*

i.   FVP of the ylide **144c** (301 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a red solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a mixture which was shown by ^{1}H and ^{13}C NMR to contain benzaldehyde, δ$_H$ as in ai.; ethanol (as the major products) and benzoic acid (δ$_H$ as in F2b), and other, unidentified, compounds. The desired alkyne was not present.

ii.   Conventional pyrolysis of the ylide **144c** (502 mg, 200 °C, 1.0 x 10^{-2} Torr) in a kugelrohr gave a brown solid residue in the reaction flask which proved by ^{1}H and ^{31}P NMR to be mainly Ph$_3$PO, and in the receiver a mixture which was shown by ^{1}H and ^{13}C NMR to contain benzaldehyde. δ$_H$ as in ai. The desired alkyne was not present.

d. *Pyrolysis of Dimethyl 2,4-dioxo-3-triphenylphosphoranylidenepentane dioate*

i.   FVP of the ylide **144d** (382 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a yellow oil which was shown by ^{1}H and ^{13}C NMR to contain methanol. None of the desired alkyne **189** was present.

ii.   Conventional pyrolysis of the ylide **144d** (518 mg, 200 °C, 1.0 10^{-2} Torr) in a Kugelrohr gave a brown solid residue in the reaction flask which

proved by ^{1}H and ^{31}P NMR to be mainly Ph$_3$PO, and in the receiver a yellow oil which was shown by ^{1}H and ^{13}C NMR to contain the desired alkyne **189**. Chromatography on silica (ethyl acetate/hexane, 1:1) gave *dimethyl 4-oxopent-2-ynedioate* (77 mg, 39%) as a yellow oil (Found: M+H$^+$, 171.0301. C$_7$H$_6$O$_5$ requires M+H$^+$, 171.0293); v_{max} /cm^{-1} 1765, 1745. 1725 and 1700; δ_H 3.97 (3 H, s, OMe) and 3.89 (3 H, s, OMe); δ_C 167.8 (CO$_2$COC≡C), 158.1 (CO$_2$COC≡C), 151.9 (C≡CCO$_2$Me), 83.4 (C≡CCO$_2$Me), 79.1 (C≡CCO$_2$Me), 54.1 (OMe) and 53.7 (OMe); m/z (CI) 171 (M+H$^+$, 100%), 143 (28), 73 (67) and 59 (30).

e. Pyrolysis of Ethyl methyl 2,4-dioxo-3-triphenylphosphoranylidenepentane dioate

i.   FVP of the ylide **144e** (299 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a white solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a yellow oil which was shown by ^{1}H and ^{13}C NMR to contain a small amount of the desired alkynes, **190** and **191**, data as in ii. below, as well as other unidentified products.

ii.   Conventional pyrolysis of the ylide **144e** (504 mg, 200 °C, 1.0 x 10^{-2} Torr) in a Kugelrohr gave a brown solid residue in the reaction flask which proved by ^{1}H and ^{31}P NMR to be mainly Ph$_3$PO, and in the receiver a yellow oil which was shown by ^{1}H and ^{13}C NMR to contain a 1:1 mixture of the alkynes **190** and **191**. Chromatography on silica (ethyl acetate/hexane, 1:1) gave a mixture of 1-ethyl 5-methyl- and 5-ethyl 1-methyl 4-oxopent-2-ynedioate (94 mg, 47%) as a yellow oil. (Found: M+H$^+$, 185.0248. C$_8$H$_8$O$_5$ requires M+H$^+$, 185.0450); v_{max} /cm^{-1} 1765, 1745, 1725 and 1700; m/z (CI) 553 [(Mx3)+H$^+$, 94%)], 369 [(Mx2)+H$^+$, 100%)]; m/z (EI) 185 (M+H$^+$, 19%), 156 (20), 153 (27), 139 (38), 125 (62), 111 (100), 97 (33), 59 (73), 53 (82) and 45 (22).

1-Ethyl 5-methyl-4-oxopent-2-ynedioate **190**: δ_H 4.35 (2 H, q, *J* 7, OCH$_2$), 3.90 (3 H, s, OMe) and 1.37 (3 H, t, *J* 7, CH$_2$*Me*); δ_C 167.9 (MeCO$_2$COC≡C), 158.1 (Me*C*O$_2$COC≡C), 151.9 (C≡C*C*O$_2$Et), 83.2 (*C*≡CCO$_2$Et), 79.2 (C≡*C*CO$_2$Et), 63.5 (OCH$_2$), 53.7 (OMe) and 13.9 (CH$_2$*Me*).

5-Ethyl 1-methyl-4-oxopent-2-ynedioate **191**: δ_H 4.42 (2 H, q, *J* 7, OCH$_2$), 3.99 (3 H, s, OMe) and 1.41 (3 H, t, *J* 7, CH$_2$*Me*); δ_C 168.3 (EtCO$_2$COC≡C), 157.7 (Et*C*O$_2$COC≡C), 151.4 (C≡C*C*O$_2$Me), 83.8 (*C*≡CCO$_2$Me), 78.8 (C≡*C*CO$_2$Me), 64.0 (OCH$_2$), 54.1 (OMe) and 13.9 (CH$_2$*Me*).

f. *Pyrolysis of Diethyl 2,4-dioxo-3-triphenylphosphoranylidenepentanedioate*

i.   FVP of the ylide **144f** (311 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr) gave a solid at the furnace exit which proved by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a yellow oil which was shown by ^{1}H and ^{13}C NMR to contain ethanol. None of the desired alkyne **192** was present.

ii.   Conventional pyrolysis of the ylide **144f** (504 mg, 200 °C, 1.0 x 10^{-2} Torr) in a Kugelrohr gave a brown solid residue in the reaction flask which proved by ^{1}H and ^{31}P NMR to be mainly Ph$_3$PO, and in the receiver a yellow oil which was shown by ^{1}H and ^{13}C NMR to contain the desired alkyne **192**. Chromatography on silica (ethyl acetate/hexane, 1:1) gave *diethyl 4-oxopent-2-ynedioate* (88 mg, 42%) as a yellow oil (lit.,[127] yellow oil) (Found: M+H$^+$, 199.0600. C$_7$H$_6$O$_5$ requires 199.0606); ν_{max} /cm^{-1} 1765, 1745, 1725 and 1700; δ_H 4.42 (3 H, q, *J* 7, CH$_2$), 4.35 (3 H, q, *J* 7, CH$_2$), 1.41 (3 H, t, *J* 7, CH$_2$*Me*) and 1.36 (3 H, t, *J* 7, Me); δ_C 168.4 (*C*O$_2$COC≡C), 157.7 (*C*O$_2$COC≡C), 151.4 (C≡C*C*O$_2$Et), 83.7 (*C*≡CCO$_2$Et), 78.9 (C≡*C*CO$_2$Et), 64.0 (OCH$_2$), 63.4 (OCH$_2$) and 13.9 (2 x CH$_2$*Me*); *m/z* (CI) 199 (M+H$^+$, 56%), 147 (28), 113 (100), 97 (53) and 73 (63).

G   Preparation and FVP of Oxalyl Bis-Ylides

1.   Preparation of Precursor Phosphonium salts

a. *(4-Chlorobenzyl)triphenylphosphonium chloride*

A solution of 4-chlorobenzyl chloride (10.0 g, 62.1 mmol) and triphenylphosphine (16.3 g, 62.1 mmol) in dry toluene (150 cm^3) was heated under reflux for 3 d. The precipitate which formed was filtered off, washed with ether and dried to afford the title salt (23.3 g, 89%) as a white powder, m.p. 285–286 °C (decomp.) (lit.,[128] 289 °C); δ_P +23.1.

b. *(4-Bromobenzyl)triphenylphosphonium bromide.*

This was prepared as above using 4-bromobenzyl bromide (15.0 g, 60 mmol) and triphenylphosphine (16.0 g, 60.0 mmol) to afford the title salt (27.5 g, 88%) as white powder, m.p. 276–278 °C (lit.,[129] 278 °C); δ_P +22.9.

2.   Preparation of Oxalyl Bis-Ylides from Non-stabilized Ylides

a. *1,4-Bis(triphenylphosphoranylidene)-1,4-bis(4-chlorophenyl)butane-2,3-dione* **201**

To a suspension of (4-chlorobenzyl)triphenylphosphonium chloride (10.0 g, 23.6 mmol) in dry THF (150 cm^3) at RT and under a nitrogen atmosphere, was added a solution of n-butyl lithium in hexane (9.3 cm^3, 23.6 mmol). The mixture was stirred for 30 min and oxalyl chloride (0.75 g, 5.9 mmol) in dry THF (10 cm^3) was added dropwise. The mixture was stirred at RT for 3 hours then poured into water and extracted with ethyl acetate (3 x 50 cm^3). The combined organic phase was dried and evaporated give to the title compound (2.2 g, 45%) as yellow crystals; m.p. 135 °C (Found: C, 75.1; H, 4.6; M+H$^+$, 827.1819, C$_{52}$H$_{38}$Cl$_2$O$_2$P$_2$ requires C, 75.5; H, 4.6%; M+H$^+$,

827.1802); v_{max} /cm^{-1} 1500, 1435, 1375, 1323, 1188. 1100. 963, 835, 750.
722 and 693; δ_H 7.2–7.7 (30 H, m. Ph) and 6.91 (8 H, s. Ph); δ_C 187.9 (d d. J
5, 13, 2 x CO), 137.0 (d, J 4, 4 C, C-2 of p-Cl-Ph), 135.5 (d, J 12, 2 C,C-1 of
p-Cl-Ph), 133.6 (d, J 10, 12 x C-2 of P-Ph), 131.4 (d, J <2. 6x C-4 of P-Ph),
130.6 (2 C, C-4 of p-Cl-Ph), 128.4 (d, J 12, 12 x C-3 of P-Ph), 127.1 (4 C, C-
3 of p-Cl-Ph), 126.0 (d, J 90, 6 x C-1 of P-Ph) and 67.8 (d, J 104, 2 x P=C);
δ_P +14.5; m/z (FAB) 827 (^{35}Cl$_2$-M+H$^+$, 10%), 415 (^{37}Cl-M$^+$/2. 36), 413
(^{35}Cl-M$^+$/2, 100), 279 (6), 262 (9), 201 (7) and 183 (15).

b. *1,4-Bis(triphenylphosphoranylidene)-1,4-bis(4-bromophenyl)butane-2,3-dione* **202**

Reaction as for the chloro analogue using (4-bromobenzyl)
triphenylphosphonium bromide (20.0 g, 39.0 mmol). and oxalyl chloride
(0.84 cm^3, 1.23 g, 9.86 mmol) gave the title compound (0.96 g, 11%) as
yellow crystals; correct elemental analysis could not be obtained due to partial
hydrolysis and decomposition on attempted recrystallisation; v_{max} /cm^{-1} 1705,
1435, 1195, 1180, 1096, 1063, 961, 748, 711 and 688; δ_H 7.5-7.2 (30 H, m),
and 7.05 and 6.83 (8 H, AB pattern, J 9); δ_C 185.5 (d d, J 4, 12, 2 x CO),
137.2 (d, J 4, 4 C, p-Br-Ph), 133.6 (d, J 10, 12 x C-2 of P-Ph), 131.8 (d, J <2,
6 x C-4 of P-Ph), 128.5 (d, J 12, 12 x C-3 of P-Ph), 124.9 (d, J 90, 6 x C-1 of
P-Ph) and 70.7 (d, J 102, 2 x P=C) (note: 3 signals from p-Br-Ph group could
not be assigned unambiguously); δ_P +14.7; m/z 457 (M$^+$/2, 0.2%), 379 (1),
350 (1), 278 (48), 277 (100), 271 (2), 269 (2), 262 (3), 201 (30), 199 (15),
185 (9), 183 (10) and 152 (6).

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3. Preparation of Bis-Ylides from Stabilized Ylides

General method

Oxalyl chloride (1 eq) in dry toluene (10 cm^3) was added dropwise to a solution of ylide (2 eq) and triethylamine (2 eq.) in dry toluene (150 cm^3) at RT. After 24 h the mixture was added to water (250 cm^3) and extracted with ethyl acetate (3 x 50 cm^3). The combined organic phase was dried and evaporated to afford the crude product which was recrystallised from ethyl acetate.

a. *2,5-Bis(triphenylphosphoranylidene)-1,6-diphenylhexane-1,3,4,6-tetraone* **203**

Reaction as above using (benzoylmethylene)triphenylphosphorane (5.0 g, 13.2 mmol), oxalyl chloride (0.84 g, 6.6 mmol) and triethylamine (1.3 g, 13.2 mmol) gave the title compound (3.4 g, 64%) as yellow crystals; m.p. 146–148 °C (Found: C, 80.0; H, 5.3; M$^+$–Ph$_3$PO, 536.1492. C$_{54}$H$_{40}$O$_4$P$_2$ requires C, 79.6; H, 4.9%; M$^+$–Ph$_3$PO, 536.1541); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 2990, 1583, 1512, 1410, 1345, 1305, 1196, 1150, 1120, 1092, 1047, 955 and 860; δ_H 7.65–7.15 (40 H, m, Ph); δ_C 191.7 (d d, *J* 4, 14, COCO), 191.6 (d, *J* 12, 2 x COPh), 144.2 (d, *J* 5, 2 x C-1 of Ph), 133.5 (d, *J* 10, 12 x C-2 of P-Ph), 131.4 (d, *J* <2, 6 x C-4 of P-Ph), 129.4 (2 C, C-4 of Ph), 128.7 (4 C, Ph), 128.5 (d, *J* 13, 12 x C-3 of P-Ph), 127.7 (4 C, Ph), 125.5 (d, *J* 92, 6 x C-1 of P-Ph) and 82.4 (d, *J* 99, 2 x P=C) ; δ_P +17.6; *m/z* 536 (M$^+$–Ph$_3$PO, 33%), 508 (2), 452 (3), 431 (6), 403 (4), 301 (8), 277 (100) and 262 (35).

b. *Dimethyl 2,5-bis(triphenylphosphoranylidene)hexane-3,4-dione-1,6-dioate* **204**

Reaction as above using (methoxycarbonylmethylene)triphenyl phosphorane (5.0 g, 15 mmol), oxalyl chloride (0.95 g, 7.5 mmol) and

triethylamine (1.5 g, 15 mmol) gave the title compound (3.7 g, 69%) as colourless crystals; m.p. 273–274 °C (Found: C, 73.3; H, 5.4; $M^+/2$, 361.0964. $C_{44}H_{36}O_6P_2$ requires C, 73.1; H, 5.0%: $M^+/2$, 361.0993); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 1660, 1545, 1350, 1300, 1190, 1107, 1091 and 910; δ_H 7.85–7.75 (12 H, m, Ph), 7.5–7.35 (18 H, m, Ph) and 3.30 (6 H, s, 2 x Me); δ_C 193.3 (d, J 3, 11, 2 x CO), 167.7 (d, J 16, 2 x CO$_2$), 133.7 (d, J 10, 12 x C-2 of P-Ph), 131.7 (d, J <2, 6 x C-4 of P-Ph), 128.4 (d, J 13, 12 x C-3 of P-Ph), 126.0 (d, J 93, 6 x C-1 of P-Ph), 66.1 (d, J 111, 2 x P=C) and 49.8 (2 x Me); δ_P +16.4; m/z (20 eV) 444 (M$^+$–Ph$_3$PO, 0.2%), 361 (M$^+$/2, 30), 301 (3), 277 (18), 262 (100) and 183 (9).

c. *Diethyl 2,5-bis(triphenylphosphoranylidene)hexane-3,4-dione-1,6-dioate*
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Reaction as above using (ethoxycarbonylmethylene)triphenyl phosphorane (5.0 g, 14.4 mmol), oxalyl chloride (0.91 g, 7.2 mmol) and triethylamine (1.45 g, 14.4 mmol) gave the title compound (3.9 g, 73%) as colourless crystals; m.p. 243–245 °C (lit.,[28] 248–249 °C) (Found: C, 73.6; H, 5.5. $C_{46}H_{40}O_6P_2$ requires C, 73.6; H, 5.4%); ν_{max} /cm^{-1} 1668, 1545, 1436, 1372, 1301, 1206, 1103, 1078, 756, 720 and 692; δ_H 7.9–7.75 (12 H, m, Ph), 7.5–7.3 (18 H, m, Ph), 3.81 (4 H, q, J 7, 2 x OCH$_2$) and 0.70 (6 H, t J 7, 2 x CH$_2$*Me*); δ_C 193.6 (d d, J 4, 11, 2 x CO), 167.3 (d, J 15, 2 x CO$_2$), 133.8 (d, J 10, 12 x C-2 of P-Ph), 131.5 (d, J <2, 6 x C-4 of P-Ph), 128.3 (d, J 13, 12 x C-3 of P-Ph), 126.4 (d, J 93, 6 x C-1 of P-Ph), 65.8 (d, J 112, 2 x P=C), 58.2 (2 x OCH$_2$) and 14.1 (2 x Me); δ_P +16.0; m/z 722 (M$^+$–28, 0.2%), 417 (0.7), 400 (1), 376 (100), 302 (12), 279 (38), 277 (90), 263 (76), 201 (17), 199 (8) and 183 (35).

d.   *3,6-Bis(triphenylphosphoranylidene)-1,8-diphenyloctane-1,2,4,5,7,8-hexaone* **207**

Reaction as above using 1-phenyl-3-triphenylphosphoranylidene propane-1,2-dione (2.0 g, 4.9 mmol), oxalyl chloride (0.31 g, 2.4 mmol) and triethylamine (0.50 g, 4.9 mmol) gave the title compound (0.82 g, 39%) as yellow crystals; m.p. 223–224 °C (Found: C, 77.05; H, 4.55. $C_{56}H_{40}O_6P_2$ requires C, 77.2; H, 4.6%); v_{max} /cm^{-1} (Nujol) 1770, 1600, 1560, 1535, 1260, 1220, 1120, 1010, 730 and 690; δ_H 7.84–7.44 (15 H, m, Ph), 7.41–7.38 (5 H, m, Ph), 7.36–7.21 (15 H, m, Ph) and 7.20–7.16 (5 H, m, Ph); δ_C 192.4 (d, J 5, 2 x CO), 191.1 (m, 2 x CO), 190.7 (m, 2 x CO), 134.6 (2 x C-1 of Ph), 133.8 (d, J 10, 12 x C-2 of P-Ph), 132.1 (2 x C-4 of Ph) 131.8 (d, J <2, 6 x C-4 of P-Ph), 129.8 (4C, Ph), 128.4 (d, J 13, 12 x C-3 of P-Ph), 127.7 (4C, Ph), 124.9 (d, J 93, 6 x C-1 of P-Ph) and 81.1 (d, J 103, 2 x P=C); δ_P +15.6; *m/z* (FAB) 871 (M+H$^+$, 6%), 765 (8), 721 (10), 435 (92), 303 (33), 262 (23), 183 (20), 154 (18), 129 (82) and 105 (96).

e.   *Dimethyl 3,6-bis(triphenylphosphoranylidene)octane-2,4,5,7-tetraone-1,8-dioate* **208**

Reaction as above using methyl 2-oxo-3-triphenyl phosphoranylidene-propionate (3.0 g, 8.3 mmol), oxalyl chloride (0.52 g, 0.36 cm^3, 4.1 mmol) and triethylamine (0.84 g, 8.3 mmol) gave the title compound (1.0 g, 32%) as colourless crystals; m.p. 212–213 °C (decomp.) (Found: C, 70.0; H, 5.0. $C_{46}H_{36}O_8P_2$ requires C, 70.9; H, 4.7%); v_{max} /cm^{-1} (Nujol) 1745, 1720, 1600, 1630, 1315, 1255, 1210, 1185, 1150, 1100, 1020, 725 and 690; δ_H 7.68–7.60 (12 H, m, Ph), 7.48–7.45 (6 H, m, Ph), 7.41–7.35 (12 H, m, Ph) and 3.65 (6 H, s, 2 x Me); δ_C 189.1 (m, 2 x CO), 183.9 (d, J 8, 2 x CO), 166.4 (d, J 12, 2 x CO$_2$), 133.5 (d, J 10, 12 x C-2 of P-Ph), 131.7 (d, J 2, 6 x C-4 of P-Ph), 128.5 (d, J 13, 12 x C-3 of P-Ph), 125.1 (d, J 93, 6 x C-1 of P-Ph), 79.7 (d, J

104, 2 x P=C) and 51.9 (2 x Me); δ_P +16.8; m/z (FAB) 389 (M$^+$/2. 3%), 375 (1), 361 (100), 303 (13), 262 (12) and 183 (10).

f.   *Diethyl 3,6-bis(triphenylphosphoranylidene)octane-2,4,5,7-tetraone-1,8-dioate* **209**

Reaction as above using ethyl 2-oxo-3-triphenylphosphoranylidene-propionate (3.0 g, 8.0 mmol), oxalyl chloride (0.4 g, 4.0 mmol) and triethylamine (0.81 g, 8.0 mmol) gave the title compound (0.94 g, 29%) as colourless crystals; m.p. 184–185 °C (decomp); (Found: C, 63.3: H, 4.25. $C_{48}H_{40}O_8P_2$ + $CDCl_3$ requires C, 63.5; H, 4.5%); v_{max}/cm^{-1} (Nujol) 1730, 1710, 1600, 1550, 1315, 1250, 1200, 1150, 1020, 750, 730 and 690: δ_H 7.76–7.51 (12 H, m, phenyl), 7.50–7.46 (6 H, m, phenyl), 7.45–7.7.31 (12 H, m, Ph), 4.04 (4 H, q, *J* 7, 2 x CH_2) and 1.24 (6 H, t, *J* 7, 2 x Me); δ_C 189.0 (m. 2 x CO), 184.1 (d, *J* 8, 2 x CO), 166.0 (d, *J* 11, 2 x CO_2), 133.5 (d, *J* 10, 12 x C-2 of P-Ph), 131.7 (d, *J* 2, 6 x C-4 of P-Ph), 128.5 (d, *J* 13, 12 x C-3 of P-Ph), 125.2 (d, *J* 93, 6 x C-1 of P-Ph), 79.5 (d, *J* 104, 2 x P=C), 61.0 (2 x OCH_2) and 14.0 (2 x Me); δ_P +17.1; m/z (FAB) 807 (M+H$^+$, 0.2%), 733 (2), 689 (0.3), 529 (0.3), 375 (100), 303 (30), 262 (16) and 183 (17).

4.   FVP of Oxalyl Bis-Ylides

a.   *Pyrolysis of 1,4-bis(triphenylphosphoranylidene)-1,4-diphenylbutane-2,3-dione* **200**

FVP of the bis-ylide **200** (prepared by a co-worker) at 850 °C and below gave only partial reaction and some unchanged ylide was recovered. FVP of the bis-ylide (100 mg, 900 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO and in the cold trap 1,4-diphenylbutadiyne **212** (45 mg, 64%) as colourless crystals, m.p. 85–86 °C (lit.,[130] 87–88°C); δ_H 7.5–7.4 (4 H, m) and

7.3–7.2 (6 H, m); δ_C 132.5 (4 C, Ph), 129.2 (2 C, Ph), 128.4 (4 C, Ph), 121.8 (2 C, Ph), 81.5 (C≡C) and 73.9 (C≡C).

b. *Pyrolysis of 1,4-Bis(triphenylphosphoranylidene)-1,4-bis(4-chloro--phenyl)butane-2,3-dione* **201**

FVP of the bis-ylide **201** (309 mg, 900 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to contain Ph_3PO and the desired diyne. These were separated using flash chromatography (SiO_2, Et_2O-hexane, 1:1) to give slightly impure 1,4-bis(4-chlorophenyl)butadiyne **213** (4.8 mg, 10%) as an waxy solid (lit.,[131] m.p. 258 °C); δ_H 7.45 and 7.32 (8 H, AB pattern, J 8.5); δ_C 135.6 (2 C), 133.7 (4 C), 128.9 (4 C), 120.1 (2 C), 80.8 (C≡C) and 74.6 (C≡C).

c. *Pyrolysis of 1,4-Bis(triphenylphosphoranylidene)-1,4-bis(4-bromo--phenyl)butane-2,3-dione* **202**

FVP of the bis-ylide **202** (302 mg, 900 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to contain Ph_3PO. The desired diyne was not obtained.

d. *Pyrolysis of 2,5-bis(triphenylphosphoranylidene)-1,6-diphenylhexane-1,3,4,6-tetraone* **203**

FVP of the bis-ylide **203** (285 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph_3PO and in the cold trap a solid which was shown by ^{1}H and ^{13}C NMR and GCMS to contain benzoic anhydride δ_H and δ_C as in E2a. The desired diyne was not obtained.

e.   *Pyrolysis of Dimethyl 2,5-bis(triphenylphosphoranylidene)hexane-3,4-dione-1,6-dioate* **204**

FVP of the bis-ylide **204** (265 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO, and in the cold trap a liquid which was shown by ^{1}H NMR and GCMS to contain mainly methanol. The desired diyne was not obtained.

f.   *Pyrolysis of Diethyl 2,5-bis(triphenylphosphoranylidene) hexane-3,4-dione-1,6-dioate* **46**

FVP of the bis-ylide **46** (398 mg, 500 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO and in the cold trap a liquid which was shown by ^{1}H NMR and GCMS to contain mainly ethanol and acetaldehyde. The desired diyne was not obtained.

H   Oxidation of Ylides

1. Preparation of Starting Materials

a. *1,2-Diphenyl-2-(triphenylphosphoranylidene)ethanone* **229**

To a suspension of benzyltriphenylphosphonium chloride (10.0 g, 25.7 mmol) in dry THF (50 cm^3) at RT and under a nitrogen atmosphere, was added a solution of n-butyl lithium in hexane (10.3 cm^3, 25.7 mmol). The mixture was stirred for 30 min and benzoyl chloride (1.80 g, 12.9 mmol) in dry THF (10 cm^3) was added dropwise. The mixture was stirred at RT for 3 hours then poured into water and extracted with ethyl acetate (3 x 50 cm^3). The combined organic phase was dried and evaporated to give the product (1.3 g, 22%) as yellow crystals; m.p. 187–189 °C (lit.,[132] 192–194 °C); δ_H

8.16–7.14 (25 H, m, Ph): δ_C 184.3 (d, J 5, CO), 141.4 (d, J 12, C-1 of P=C–Ph), 138.0 (d, J 11, C-1 of COPh), 134.8 (2 C, d, J 4, C-2 of P=C–Ph), 133.6 (d, J 9, 6 x C-2 of P-Ph), 131.4 (d, J 2, 3 x C-4 of P-Ph), 129.0 (2 C, Ph), 128.5 (d, J 12, 6 x C-3 of P-Ph), 128.2 (1 C, Ph), 127.7 (d, J 91, 3 x C-1 of P-Ph), 127.5 (2 C, Ph), 127.1 (2 C, Ph), 124.8 (Ph) and 73.3 (d, J 108, P=C); δ_P +16.6.

b. *1,3-Diphenyl-2-(triphenylphosphoranylidene)propane-1,3-dione* **230**

A solution of (benzoylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol) in dry toluene (50 cm^3) was heated under reflux while benzoyl chloride (0.5 g, 0.4 cm^3, 2.6 mmol) in dry toluene (5cm^3) was added dropwise. The mixture was heated under reflux for 8 h and the resulting white precipitate was fitered off. The filtrate was concentrated under vacuum to furnish a yellow oil which formed the title compound (1.2 g, 91%) as pale yellow crystals on cooling, m.p.191–192 °C (lit.,[26] 191–192 °C); δ_H 7.82–6.94 (25 H, m, Ph); δ_C 193.2 (d, J 6, CO-Ph), 142.0 (d, J 9, 2 x C-1 of Ph), 133.7 (d, J 11, 6 x C-2 of P-Ph), 132.1 (d, J 2, 3 x C-4 of P-Ph), 129.7 (2 C, C-4 of Ph), 129.1 (4 C, Ph), 128.9 (d, J 13, 6 x C-3 of P-Ph), 127.5 (4 C, Ph), 126.4 (d, J 93, 3 x C-1 of P-Ph) and 83.3 (d, J 103, P=C); δ_P +18.8.

c. *3-(Triphenylphosphoranylidene)pentane-2,4-dione*

A mixture of (acetylmethylene)triphenylphosphorane (2.0 g, 6.3 mmol) and acetic anhydride (0.64 g, 6.3 mmol) in dry toluene (50 cm^3) was heated at reflux for 12 h. The solvent was removed and the resulting oil was triturated with ether to give brown crystals. Recrystallisation from ethyl acetate afforded the title compound (1.54 g, 68%) as amber crystals; m.p. 191–192 °C (lit.,[26] 192–194 °C); δ_H 7.76–7.61 (6 H, m, Ph), 7.51–7.42 (9 H, m, Ph) and 2.27 (6 H, s, Me); δ_C 193.1 (d, J 8, CO), 133.0 (d, J 10, 6 x C-2 of P-Ph),

131.5 (d, J 2, 3 x C-4 of P-Ph), 128.6 (d, J 12, 6 x C-3 of P-Ph), 126.8 (d, J 92, 3 x C-1 of P-Ph), 88.8 (d, J 102, P=C) and 30.5 (d, J 6, Me); δ_P +16.6.

2. Oxidation of Ylides with Oxone

a. *Oxidation of 1,4-Diphenyl-3-triphenylphosphoranylidenebutane-1,2,4-trione* **143a**

Oxone (3 mmol) was added in one portion to a solution of ylide **143a** (1 g, 2 mmol) in THF (10 cm^3) and water (5 cm^3). The resulting mixture was stirred vigorously at RT. When the consumption of the starting material was complete (as shown by TLC) the reaction mixture was diluted with water (5 cm^3) and extracted with ethyl acetate (3 x 15 cm^3). The combined organic extract was dried and evaporated to furnish the crude product. The latter was purified by chromatography (1:2 ethyl acetate/hexane) to afford benzoic acid (δ_H as in F2b.) and triphenylphosphine oxide. None of the desired diphenyl tetraketone was isolated.

b. *Oxidation of Ethyl 3-(4-methylphenyl)-3-oxo-triphenylphosphoranylidene propanoate* **220**

Reaction as in a. using **220** (prepared by a co-worker) (1.0 g, 2.2 mmol) gave ethyl 2,2-dihydroxy-3-(4-methylphenyl)-3-oxopropanoate (0.33 g, 66%) as colourless crystals; m.p. 74–75 °C; δ_H 7.95 (2 H, d, Ar), 7.21 (2 H, d, Ar), 4.16 (2 H, q, J 7, OCH$_2$), 2.39 (3 H, s, *Me*-Ar) and 1.04 (3 H, t, J 7, Me); δ_C 191.5 (CO), 170.1 (CO$_2$Et), 146.0 (C-4 of Ar), 130.3 (2 C, Ar), 130.0 (C-1 of Ar), 129.5 (2 C, Ar), 91.5 (C(OH)$_2$), 63.1 (OCH$_2$), 21.8 (Ar*Me*) and 13.7 (CH$_2$*Me*).

Ethyl 2,3-dioxo-3-(4-methylphenyl)propanoate **222**

A CDCl$_3$ solution of the hydrate was dried over P$_2$O$_5$ to give a bright yellow solution of the title compound, δ_H 7.86 (2 H, d, Ar), 7.30 (2 H, d, Ar), 4.44 (2 H, q, *J* 7, OCH$_2$), 2.41 (3 H, s, Me) and 1.04 (3 H, t, *J* 7, CH$_2$*Me*); δ_C 189.8 (CO), 183.9 (CO), 160.4 (CO$_2$), 147.0 (C-4 of Ar), 130.1 (2 C, Ar), 129.8 (2 C, Ar), 129.0 (C-1 of Ar), 63.0 (OCH$_2$), 21.8 (Ar*Me*) and 13.8 (CH$_2$*Me*).

c. *Oxidation of 1-phenyl-3-triphenylphosphoranylidenepentane-1,2,4-trione* **143b**

Reaction as in a. using **143b** (0.5 g, 1.1 mmol) gave a yellow oil (after dehydration with P$_2$O$_5$) (0.11 g) which was shown spectroscopically to contain some of the desired product, 1-phenylpentane-1,2,3,4-tetraone; δ_H 7.02–8.30 (5 H, m, Ph) and 2.28 (3 H, s, Me); δ_C 192.3 (CO), 170.7 (CO), 134.4 (2 C, Ph), 130.6 (1 C, Ph), 129.0 (2 C, Ph), 127.8 (1 C, Ph) and 21.1 (Me).

d. *Oxidation of ethyl 2,4-dioxo-4-phenyl-3-triphenylphosphoranylidene butanoate* **143d**

Reaction as in a. using **143d** (0.5 g, 1.1 mmol) gave ethyl 4-phenyl-2,3,4-trioxobutanoate as the hydrate and as a colourless oil (0.09 g, 18.5%); δ_H 7.12-8.18 (5 H, m, Ph), 4.48 (2 H, q, *J* 7, OCH$_2$) and 1.49 (3 H, t, *J* 7, Me); δ_C (hydrate) 179.8 (CO), 171.6 (CO), 158.0 (CO), 134.7 (Ph), 130.2 (2 C, Ph), 128.8 (Ph), 128.6 (2 C, Ph), 92.1 (C(OH)$_2$), 63.5 (OCH$_2$) and 13.9 (Me).

Ethyl 4-phenyl-2,3,4-trioxobutanoate **227d**

A CDCl$_3$ solution of the hydrate was dried over P$_2$O$_5$ to give a bright yellow solution of the title compound; δ_C (ketone) 179.9 (CO), 171.7 (CO), 158.9 (CO), 158.0 (CO), 133.9 (Ph), 130.1 (2 C, Ph), 128.8 (Ph), 128.4 (2 C, Ph), 63.5 (OCH$_2$) and 13.7 (Me).

e. *Oxidation of methyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate* **143f**

Reaction as in a. using **143f** (0.5 g, 1.2 mmol) gave methyl 2.3,4-trioxopentanoate **227f** as the hydrate and as a colourless oil (0.04 g, 18%); δ_H 3.62 (3 H, s, OMe) and 2.06 (3 H, s, Me); δ_C 177.9 (CO), 169.0 (CO). 168.4 (CO), 90.5 (C(OH)$_2$), 54.8 (OMe) and 22.2 (Me).

f. *Oxidation of methyl 3,4-dioxo-4-phenyl-2-triphenylphosphoranylidene butanoate* **143i**

Reaction as in a. using **143i** (0.5 g, 1 mmol) gave methyl 4-phenyl-2,3,4-trioxobutanoate (hydrate) as a yellow oil (0.08 g, 15.4%); δ_H 8.15 (2 H), 7.52 (3 H) and 3.72 (3 H, s, OMe); δ_C 191.4 (CO), 171.9 (CO), 170.3 (CO), 134.6 (Ph), 130.1 (2 C, Ph), 129.1 (Ph), 128.3 (2 C, Ph), 91.7 (C(OH)$_2$) and 54.1 (OMe).

Dehydration as in b. gave a yellow solution of the ketone **227i**; δ_H 7.18-8.36 (5 H, m, Ph) and 3.95 (3 H, s, OMe); δ_H as above; δ_C 191.3 (CO), 190.0 (CO), 183.3 (CO), 170.3 (CO) and 53.4 (OMe).

g. *Oxidation of diethyl 2-oxo-3-triphenylphosphoranylidenebutanedioate* **143p**

Reaction as in a. using **143p** (0.5 g, 1 mmol) gave a yellow oil (0.04 g, 8.9%); δ_H 4.48 (4 H, q, J 7, 2 x OCH$_2$) and 1.41 (6 H, t, J 7, 2 x Me); δ_C 180.5 (CO), 158.2 (CO), 63.8 (OCH$_2$) and 13.9 (Me). Note that these signals may not necessarily arise from one compound. None of the desired tetraketone was isolated (refer to p85).

3. Oxidation of Ylides with Ozone

a. *Oxidation of 1,4-Diphenyl-3-triphenylphosphoranylidenebutane-1,2,4-trione* **143a**

Ozone was bubbled through a solution of ylide **143a** (1.0 g) in methylene chloride (50 cm^3) at –78 °C until all the starting material was consumed as indicated by TLC. The solvent was removed and the mixture chromatographed (1:3 ethyl acetate/hexane) to furnish the hydrate as colourless crystals. The tetraketone **74** was obtained by dehydration of the hydrate using P$_2$O$_5$. δ_H and δ_C as in H4c. below.

b. *Oxidation of Ethyl 3-(4-methylphenyl)-3-oxo-triphenyl phosphoranylidene--propanoate* **221**

Reaction as in a. using **221** (prepared by a co-worker) (1.0 g, 2.2 mmol) gave ethyl 2,2-dihydroxy-3-(4-methylphenyl)-3-oxopropanoate, the hydrate of **222**, (0.10 g, 20%) as colourless crystals. δ_H and δ_C as in H2b.

4. Oxidation of Ylides with Dimethyldioxirane

a. *Preparation of Dimethyldioxirane solution* **228**

This was based on the method of Adam *et al.*[133] A mixture of water (20 cm^3), acetone (13 cm^3, 0.177 mol) and sodium bicarbonate (12 g), was stirred in a flask equipped with a condenser, cooled to 10 °C, and a receiving flask (25 cm^3) cooled to –78 °C. While applying a slight vacuum (ca. 20 mmHg, water aspirator), solid oxone (25 g, 0.041 mol) was added in three portions while stirring vigorously at 0 °C. The yellow dioxirane-acetone solution (7 cm^3) was collected in the receiving flask.

b. Assays for Dioxirane Content

i. Reaction with phenyl methyl sulfide.

A solution of dimethyldioxirane in acetone (1.0 cm^3) was mixed with an acetone-d_6 solution of phenyl methyl sulfide (0.4 cm^3, 0.55 M). The solution was allowed to stand at RT for 5 min and the ^{1}H NMR spectrum taken. From the integration of the signals due to the sulfoxide phenyl protons ($\delta7.6$-7.9) vs those of the sulfide ($\delta7.1$-7.3) the concentration could be calculated.

ii. By ^{1}H NMR.

The height of the integral of the methyl proton signal of the dioxirane (at δ_H 1.65) was compared to that of acetone.

c. *Oxidation of 1,4-Diphenyl-3-triphenylphosphoranylidenebutane-1,2,4-trione* **143a**

A solution of dimethyldioxirane in acetone (3 eq. per ylide function) was added in 3 portions (8 hour intervals) to a solution of the ylide **143a** (1 eq) in acetone and the mixture stirred at RT for 3 days. The solvent was evaporated under vacuum and the residue chromatographed (silica, ethyl acetate/ hexane, 2:3) to afford Ph$_3$PO, benzoic acid (δ_H as in F2b.), and 3.3-dihydroxy-1,4-diphenylbutane-1,2,4-trione (0.19 g, 37%) as colourless crystals m.p. 78–83 °C (lit.,[134] 83–87 °C); δ_H 6.82-8.24 (10 H, m, Ph); δ_C 192.2 (CO), 191.1 (CO), 189.4 (CO), 134.5 (2 C, Ph), 130.4 (4 C, Ph), 129.1 (2 C, Ph), 128.8 (4 C, Ph) and 94.1 (C(OH)$_2$).

1,4-Diphenyl butane-1,2,3,4-tetraone **74**

This was obtained by dehydration of a solution of the hydrate in CDCl$_3$ using P$_2$O$_5$; δ_C 188.4 (CO) and 187.8 (CO), 134.5 (2 C, Ph), 130.4 (4 C, Ph), 129.1 (2 C, Ph), 128.8 (4 C, Ph).

d. *Oxidation of Ethyl 3-(4-methylphenyl)-3-oxo-triphenyl phosphoranylidene--propanoate* **221**

Reaction as in c. using **221** (1.0 g, 2.2 mmol) gave some unreacted starting material and ethyl 2,2-dihydroxy-3-(4-methylphenyl)-3-oxopropanoate, the hydrate of **222**, (0.30 g, 60%) as colourless crystals. δ_H and δ_C as in H2b.

The following experiments are part of a preliminary study and all conclusions are based on the spectra of the crude reaction mixtures.

e. *Oxidation of 1,2-diphenyl-2-(triphenylphosphoranylidene)ethanone* **229**

Reaction as in c. using **229** (0.5 g, 1 mmol) gave a small amount of rearranged product and benzil as the major product; δ_C 194.5 (CO), 134.9 (C-4 of Ph), 132.8 (C-1 of Ph), 129.8 (2 C, C-2 of Ph) and 128.8 (2 C, C-3 of Ph).

f. *Oxidation of 1,3-Diphenyl-2-(triphenylphosphoranylidene)propane-1,3-dione* **230**

Reaction as in c. using **230** (0.5 g, 1 mmol) gave some unreacted starting material, a small amount of rearranged product, benzoic acid (δ_H as in F2b.) and diphenyl triketone hydrate **231** as the major product; δ_C 192.4 (CO), 135.0 (C-4 of Ph), 132.5 (C-1 of Ph), 130.1 (2 C, C-2 of Ph) 128.7 (2 C, C-3 of Ph) and 95.4 (C(OH)$_2$), .

g. *Oxidation of 1,5-Diphenyl-3-triphenylphosphoranylidenepentane-1,2,4,5-tetraone* **144a**

Reaction as in c. using **144a** (0.5 g, 0.9 mmol) gave some unreacted starting material, a large amount of rearranged product, benzoic acid (δ_H as in F2b.), and diphenyl pentaketone as the hydrate; (The phenyl signals are masked by Ph$_3$PO signals) δ_C 193.3 (CO), 193.2 (CO) and 92.1 (C(OH)$_2$).

h. *Oxidation of 2,5-Bis(triphenylphosphoranylidene)-1,6-diphenylhexane-1,3,4,6-tetraone* **203**

Reaction as in c. using **203** (1.0 g, 1 mmol) gave unreacted starting material and a large amount of rearranged product (benzoic acid; δ_H as in F2b.). None of the hexaketone was obtained.

i. *Oxidation of 3,6-Bis(triphenylphosphoranylidene)-1,8-diphenyloctane-1,2,4,5,7,8-hexaone* **207**

Reaction as in c. using **207** (1.0 g, 1 mmol) gave unreacted starting material and a large amount of rearranged product (benzoic acid; δ_H as in F2b.). None of the octaketone was obtained.

j. *Preparation of an authentic sample of Diethyl dioxosuccinate monohydrate* **234** *and dihydrate* **235**

HCl gas was bubbled through a suspension of disodium dihydroxy tartrate (2 g, 7.58 mmol) in ethanol (25 cm^3) at 0 °C. The resultant mixture was then left in the refrigerator for 3 days, after which the excess solvent was removed to yield the crude product (1.02 g, 67%) as a pale yellow oil (lit., oil[135]) and as a mixture of title mono and dihydrate; δ_H 6.30–5.69 (2 H, br s. OH), 4.66–4.12 (4 H, q, 2 x CH$_2$) and 1.09 (6 H, t, 2 x Me); δ_C 185.4 (CO), 169.3 (CO), 167.6 (CO), 159.5 (CO), 94.1 (C(OH)$_2$), 91.3 (C(OH)$_2$), 63.6 (OCH$_2$), 63.5 (OCH$_2$), 63.4 (OCH$_2$) and 13.9 (2 x Me).

I   Reactions of Phosphorus Ylides with NO$_2$

1. Oxidation Reactions

A stock solution of NO$_2$ in dry CH$_2$Cl$_2$ was prepared by adding a weighed amount of the liquid gas from a cylinder. This brown solution was stored over Na$_2$CO$_3$ at RT and in the dark.

a. *Oxidation of (Benzoylmethylene)triphenylphosphorane* **150** (R^1 = Ph)

NO$_2$ (3 eq.) in CH$_2$Cl$_2$ was added dropwise to a solution of ylide **150** (R^1 = Ph) (0.5 g, 1.3 mmol) in dry CH$_2$Cl$_2$. The mixture was stirred at RT until all the starting material was consumed (monitored by ^{31}P NMR). The solvent was removed to give pale yellow crystals and a yellow oil which were identified as Ph$_3$P$^+$OH NO$_3^-$ (quantitative yield) and benzoyl cyanide; ν_{max} /cm^{-1} (mixture) (CH$_2$Cl$_2$) 3060, 2220 (CN), 1680 (CO), 1635, 1600, 1390, 1290, 1120, 1070 and 950.

Ph$_3$P$^+$OH NO$_3^-$: m.p. 68–70 °C, (Found: C, 63.8; H, 4.75; N, 4.3. C$_{18}$H$_{16}$NO$_4$P requires C, 63.3; H, 4.7; N, 4.1%); δ_H 17.72 (1H, br s, OH), 7.26–8.01 (15 H, m, Ph); δ_C 132.9 (d, *J* 3, 3 x C-4 of Ph), 132.1 (d, *J* 11, 6 x C-2 of Ph), 129.5 (d, *J* 108, 3 x C-1 of Ph) and 128.9 (d, *J* 13, 6 x C-3 of Ph); δ_P +34.6.

Benzoyl cyanide: *m/z* (GCMS) 131 (M$^+$, 49%), 105 (100), 77 (81) and 51 (60).

b. *Oxidation of (Acetylmethylene)triphenylphosphorane* **150** (R^1 = Me)

Reaction as in a. using **150** (R^1 = Me) (0.5 g, 1.5 mmol) and NO$_2$ (4.5 mmol) gave a yellow mixture of crystals and oil which were identified as Ph$_3$P$^+$OH NO$_3^-$ (quantitative yield) and pyruvonitrile; ν_{max} /cm^{-1} (mixture) (CH$_2$Cl$_2$) 3060, 2220, 1750, 1630, 1375, 1290, 1120, 1070, 950 and 850.

Ph₃P⁺OH NO₃⁻: yellow crystals obtained after triturating the mixture with dry ether; δ_H 17.48 (1 H, br s, OH) and 7.81–7.40 (15 H. m. Ph);δ_C as in a.; δ_P +34.9.

Pyruvonitrile: δ_H 2.28 (3 H, s).

c. *Oxidation of (methoxycarbonylmethylene)triphenyl phosphorane* **150** (R¹ = OMe)

Reaction as in a. using **150** (R¹ = OMe) (0.5 g, 1.5 mmol) and NO₂ (4.5 mmol) gave a yellow mixture of crystals and oil which were identified as Ph₃P⁺OH NO₃⁻ (quantitative yield), and methyl cyanoformate ; v_{max} /cm⁻¹ (mixture) (CH₂Cl₂) 3060, 2220, 1750, 1630, 1375, 1290, 1120. 1070, 950 and 850.

Ph₃P⁺OH NO₃⁻ yellow crystals obtained after triturating the mixture with dry ether, m.p. 80–82 °C; δ_H 17.65 (1 H, br s, OH) and 7.81–7.40 (15 H, m, Ph); δ_C as in a.; δ_P +34.1.

methyl cyanoformate δ_H 3.88 (3 H, s); δ_C 164.3, 117.8 and 54.6; *m/z* (GCMS) 86 (M+H⁺, 0.5%), 84 (10), 59 (19), 54 (100), 45 (37), 41 (73), 31 (91) 29 (70) and 15 (90).

d. *Oxidation of 1,2-diphenyl-2-(triphenylphosphoranylidene)ethanone* **229**

Reaction as in a. using the ylide **229** (1.0 g, 2 mmol) gave Ph₃P⁺OH NO₃⁻ as a minor product, δ_H and δ_C as in a. and Ph₃PO, benzoic acid and 2,4-dinitrobenzonitrile as the major products.

Benzoic acid: δ_H as in F2b.

Chromatography (ether/pet. ether, 1:1) afforded *2.4-dinitrobenzonitrile* **254** (0.1 g, 35%) as yellow crystals; m.p. 103.5–105 °C (lit.,[136] 104 °C); δ_H 9.18 (1 H, d, *J* 2), 8.70 (1 H, m) and 8.23 (1 H, d *J* 9); δ_C 150.0 (4ry), 149.3 (4ry), 137.1, 128.5, 120.9 and 113.2 (C≡N), *m/z* (GCMS) 193 (M⁺, 8%), 147 (2), 100 (15), 75 (20), 50 (29) and 46 (5).

e. *Oxidation of 3-triphenylphosphoranylidenepentane-2.4-dione*

Reaction as in a. using the title ylide (0.7 g, 1.9 mmol) and NO_2 (5.8 mmol) gave a yellow mixture of crystals and oil which was identified as $Ph_3P^+OH\ NO_3^-$ (near quantitative yield) and other unidentified material; v_{max} /cm^{-1} (mixture) (CH_2Cl_2) 3000, 1710, 1350, 1270, 1155, 1120, 995 and 945. *$Ph_3P^+OH\ NO_3^-$*: δ_H 11.99 (1 H, br s, OH) and 7.81–7.42 (15 H, m, Ph); δ_C as in a.; δ_P +33.4.

f. *Oxidation of diethyl 2-oxo-3-triphenylphosphoranylidenebutanedioate* **143p**

Reaction as in a. using **143p** (1.0 g, 2.2 mmol) and NO_2 (6.72 mmol) gave complete reaction after 8 days to furnish a mixture of $Ph_3P^+OH\ NO_3^-$, diethyl dioxosuccinate and a nitrile; v_{max} /cm^{-1} (mixture) (CH_2Cl_2) 3660, 3460, 3050, 2960, 2400, 1735, 1620, 1435, 1345, 1290, 1110, 1060, 945 and 850.

A portion of the sample was washed with ether and the ether evaporated to afford diethyl dioxosuccinate as colourless crystals; δ_H 4.31 (OCH_2) and 1.30 (CH_2Me); δ_C 158.8 (CO), 63.2 (OCH_2) and 13.9 (CH_2Me); *m/z* (GCMS) 202 (M^+, 1%), 102 (2), 74 (4) and 29 (100).

Ethyl cyanoformate : *m/z* (GCMS) 98 (M^+–1, 1%), 97 (82), 81 (9) and 55 (100); δ_C 101.4 (C≡N).

The insoluble material was identified as $Ph_3P^+OH\ NO_3^-$ isolated as yellow waxy crystals; δ_H 10.38 (1 H, br s, OH) and 7.38–7.89 (15 H, m, Ph); δ_C as in a.; δ_P +35.2.

g. *Oxidation of 1-phenyl-1-triphenylphosphoranylidenepropan-2-one*

Reaction as in a. using the title ylide (0.5 g, 1.3 mmol) and NO_2 (3.8 mmol) gave pale yellow crystals and a yellow oil which was identified as $Ph_3P^+OH\ NO_3^-$ (quantitative yield), benzoic acid and other, unidentified, material. *$Ph_3P^+OH\ NO_3^-$*: δ_H, δ_C and δ_P as in a.

h. *Oxidation of 1,4-Bis(triphenylphosphoranylidene)-1,4-diphenylbutane-2,3-dione* **200**

Reaction as in a. using **200** (1.0 g, 1.3 mmol) and NO_2 (3.9 mmol) gave a yellow mixture of crystals and oil which was identified as the Ph_3P^+OH NO_3^- adduct (quantitative yield), an isomer of nitrobenzonitrile and benzonitrile; v_{max} /cm^{-1} (mixture) (CH_2Cl_2) 3500, 3060, 2250, 1700, 1635, 1525, 1350, 1290, 1120, 1060, 960, 900 and 650.

Ph$_3$P$^+$OH NO$_3^-$: δ_H 16.20 (1 H, br s, OH) and 7.82–7.41 (15 H, m, Ph); δ_C as in a.; δ_P +35.0

Nitrobenzonitrile: m/z (GCMS) 148 (M–H$^+$, 27%), 122 (4), 102 (100), 90 (25) and 75 (42).

Benzonitrile: δ_H 8.35–8.20 (2 H, m); m/z (GCMS) 103 (M$^+$, 100) and 76 (44).

i. *Oxidation of 2,5-bis(triphenylphosphoranylidene)-1,6-diphenylhexane-1,3,4,6-tetraone* **203**

Reaction as in a. using **203** (0.5 g, 0.6 mmol) and NO_2 (1.8 mmol) gave a yellow mixture of crystals and oil which was identified as Ph_3P^+OH NO_3^- (quantitative yield), benzoyl cyanide and benzoic acid; v_{max}/cm^{-1} (mixture) (CH_2Cl_2) 3500, 3040, 2250, 2220, 1670, 1635, 1600, 1475, 1450, 1380, 1120, 1070, 950, 900 and 780.

Ph$_3$P$^+$OH NO$_3^-$: δ_H 16.3 (1 H, br s, OH) and 7.82–7.41 (15 H, m, Ph); δ_C as in a.; δ_P +36.1.

Benzoyl cyanide: δ_H 8.17–8.11 (2 H, m); δ_C 170.8, 136.6, 130.0, 129.2, 128.1 and 112.5; m/z (GCMS) 131 (M,$^+$ 34%), 105 (100), 77 (73) and 51 (43).

Benzoic acid : δ_H and δ_C as in E2a.; m/z (GCMS) 122 (M$^+$, 7%), 105 (100), 77 (91) and 51 (40).

j. Oxidation of diethyl 2.5-Bis(triphenylphosphoranylidene)hexane-3,4-dione-1,6-dioate **46**

Reaction as in a. using **46** (1.0 g, 1.3 mmol) and NO_2 (4.0 mmol) gave a yellow mixture of crystals and oil which were identified as $Ph_3P^+OH \ NO_3^-$ (near quantitative yield) and unidentified acidic material; v_{max} /cm-1 (mixture) (CH_2Cl_2) 3940, 3750, 3680, 3400. 2820. 2520, 2300, 1750. 1420, 1270, 1120 and 895.

$Ph_3P^+OH \ NO_3^-$: δ_H 15.66 (1 H, br s, OH) and 7.82–7.41 (15 H, m, Ph) δ_C as in .a.; δ_P +31.9;

Unidentified acidic material: δ_H 4.38 (2 H, q, *J* 7) and 1.39 (3 H, t, *J* 7).

2. Authentic Preparation of Adducts

a. *Reaction of triphenylphosphine oxide*

Reaction as in 1a. using triphenylphosphine oxide (0.5 g, 1.32 mmol) and NO_2 (3.97 mmol) gave pale yellow crystals (near quantitative yield), m.p. 80–81 °C (Found: C, 66.7; H, 5.2; N, 2.3. $C_{18}H_{16}NO_4P$ requires C, 63.3; H, 4.7, N, 4.1%); v_{max} /cm^{-1} (Nujol) 3440, 1590, 1440, 1390, 1190, 1120, 1070, 990, 748, 720 and 690; δ_H 11.5 (1 H, br s) and (15 H, Ph); δ_C 131.8 (d, *J* 3, 3 x C-4 of Ph), 131.3 (d, *J* 13, 6 x C-3 of Ph), 130.5 (d, *J* 106, 3 x C-1 of Ph) and 128.1 (d, *J* 10, 6 x C-2 of Ph); δ_P +30.8.

b. *Reaction of triphenylphosphine*

Reaction as in 1a. using triphenylphosphine (1.0 g, 3.82 mmol) and NO_2 (3 eq) gave $(Ph_3P)_2.HNO_3$ (and a small amount of Ph_3PO) as waxy yellow crystals, m.p. 130–135 °C (Found: C, 74.9; H, 5.5; N, 1.5. $C_{36}H_{31}NO_3P_2$ requires C, 73.6; H, 5.3, N, 2.4%); v_{max} /cm^{-1} (Nujol) 1300, 1190, 1120, 1070, 990, 750, 720 and 690; δ_H 5.20 (1 H, br s, OH) and (30 H, m, Ph); δ_C

133.0 (d, J 3, 6 x C-4 of Ph), 131.5 (d, J 10, 12 x C-2 of Ph), 131.4 (d, J 104. 6 x C-1 of Ph) and 128.1 (d, J 13, 12 x C-3 of Ph); δ_P +20.7.

c. *Hydroxytriphenylphosphonium nitrate* 258

Concentrated nitric acid (68%) (0.20 cm^3, 3.6 mmol) was added in portion to a solution of triphenylphosphine oxide (0.5 g, 1.8 mmol) in methylene chloride and the mixture stirred vigorously for 10 min. then diluted with methylene chloride (20 cm^3). The mixture was dried and the solvent evaporated to give the title compound (near quantitative yield), m.p. 80–82 °C (Found: C, 63.3; H, 4.6; N, 4.1. C$_{18}$H$_{16}$NO$_4$P requires C, 63.3; H. 4.7; N, 4.1%); v_{max}/cm^{-1} (Nujol) 3400, 1625. 1420, 1285, 1248, 1120, 1050. 948, 725, 690 and 650; δ_H 13.25 (1 H, br s, OH) and 7.81–7.26 (15 H, m. Ph); δ_C 133.2 (d, J 3, 3 x C-4 of Ph), 132.2 (d. J 11, 6 x C-2 of Ph), 129.0 (d. J 13, 6 x C-3 of Ph) and 128.9 (d, J 108, 3 x C-1 of Ph); δ_P +36.9.

d. 2 : 1 *Adduct of Ph₃PO with nitric acid* 259

Reaction as in 2c using triphenylphosphine oxide (0.5 g, 1.8 mmol) and HNO$_3$ (68%) (0.05 cm^3, 0.90 mmol) gave [Ph$_3$PO]$_2$.HNO$_3$ (near quantitative yield) as waxy yellow crystals; m.p. 68–70 °C (Found: C, 68.4; H, 4.7; N, 2.4. C$_{36}$H$_{31}$NO$_5$P$_2$ requires C, 69.8; H, 5.0; N, 2.3%); v_{max}/cm^{-1} (Nujol) 1620, 1440, 1220, 1170, 948, 750, 725 and 690; δ_H 13.34 (1 H, br s, OH) and 7.82–7.27 (30 H, m, Ph); δ_C 132.5 (d, J 3, 6 x C-4 of Ph), 132.1 (d, J 10, 12 x C-2 of Ph), 130.8 (d, J 106, 6 x C-1 of Ph) and 128.7 (d, J 12, 12 x C-3 of Ph); δ_P +32.1.

e. *Triphenylphosphonium nitrate* 261

Reaction as in 2c. using triphenylphosphine (1.0 g, 3.8 mmol) and HNO$_3$ (68%) (0.22 cm^3, 3.8 mmol) gave Ph$_3$PH$^+$ NO$_3^-$ (near quantitative yield) as waxy yellow crystals; m.p. 68–70 °C (Found: C, 58.85; H, 4.9; N,

4.3. $C_{18}H_{16}NO_3P$ requires C, 66.6: H, 5.0: N, 5.5%); v_{max} /cm^{-1} (Nujol) 3440, 1630, 1440, 1290, 1250, 1120. 1050, 950, 730, 690 and 650: δ_H 11.69 (1 H, br s) and 7.77–7.31 (15 H, m, Ph); δ_C 133.8 (d. J 14, 6 x C-3 of Ph), 133.3 (d, J <2, 3 x C-4 of Ph), 129.9 (d, J 11, 6 x C-2 of Ph) and 122.6 (d, J 52, 3 x C-1 of Ph); δ_P +35.2.

f.   2 : 1 Adduct of Ph₃P with nitric acid 262

Reaction as in 2c using triphenylphosphine (1.0 g, 3.8 mmol) and HNO$_3$ (68%) (0.11 cm^3, 1.9 mmol) gave [Ph$_3$P]$_2$.HNO$_3$ (near quantitative yield) as waxy yellow crystals; m.p. 67–70 °C (Found: C, 73.1 H. 5.3 N, 2.3. $C_{36}H_{31}NO_3P_2$ requires C, 73.6; H, 5.3, N, 2.4 %); v_{max} /cm^{-1} (Nujol) 3440, 1620, 1435, 1310, 1120, 1070, 1020, 990, 940, 740, 725 and 690; δ_H 7.79–7.19 (30 H, m, Ph) and 6.58 (1 H, br s); δ_C 133.7 (d, J 88, 6 x C-1 of Ph), 133.7 (d, J 13, 12 x C-3 of Ph), 129.5 (d, J 3, 6 x C-4 of Ph) and 128.7 (d. J 7, 12 x C-2 of Ph); δ_P +34.5.

J   Preparation and Pyrolysis of Aminoacyl Ylides

1.   Preparation of *N*-Protected Amino Acids

a. *(S)-N-(Trimethylsilyl)alanine (trimethylsilyl)ester* **125** (R^1 = Me)

A solution of trimethylsilyl chloride (2.44 g, 22.5 mmol) in dry dichloromethane (5 cm^3) was added dropwise to a stirred suspension of (S)-alanine (1.00 g, 11.2 mmol) in dichloromethane (20 cm^3) under a nitrogen atmosphere and the mixture heated under reflux for 2 h. Dry triethylamine (2.27 g, 22.4 mmol) was then added dropwise and the mixture heated under reflux for a further 10 min. The solvent was then removed and the residue extracted with dry ether. The ether extract was concentrated and distilled to

afford the title compound (2.2 g, 85%) as a colourless liquid, b.p. 48 °C at 2 mmHg (oven temp) (lit.,[137] 73 °C at 10 mmHg); δ_H 3.72–3.20 (1 H. m, NHCH), 1.28 (3 H, d, J 6, CH$_3$), 1.10 (1 H, d, J 8, NH), 0.25 (9 H, s, NSiMe$_3$) and 0.08 (9 H, s, OSiMe$_3$).

b. *(S)-N-(Trimethylsilyl)leucine (trimethylsilyl)ester* **125** (R^1 = Bu^i)

This was prepared as in a. using (S)-leucine (1.31 g, 10 mmol) and trimethlylsilyl chloride (2.17 g, 20 mmol) to the title compound (1.81 g, 66%) as a colourless liquid, b.p. 78 °C at 2 mmHg (oven temp) (lit.,[137] 105 °C at 12 mmHg); δ_H 3.52–3.24 (1 H, m, CHNH), 1.85–1.15 (3 H, m, CHCH$_2$), 1.10 (1 H, d, J 8, NH), 0.90 (6 H, d, J 6, CHMe_2), 0.25 (9 H, s, NSiMe$_3$) and 0.01 (9 H, s, OSiMe$_3$).

c. *(S)-N-(Trimethylsilyl)phenylalanine (trimethylsilyl)ester* **125** (R^1 = Bn)

This was prepared as in a. using (S)-phenylalanine (5.0 g, 30 mmol) and trimethlylsilyl chloride (4.8 cm^3, 8.2 g, 76 mmol) to afford the title compound (5.6 g, 60%) as a colourless liquid, b.p. 117 °C at 2 mm Hg (oven temp) (lit.,[138] 110 °C at 1.1 mmHg); δ_H 7.11–7.36 (5 H, m, Ph), 3.72–3.52 (1 H, m, NHCH), 3.00–2.76 (2 H, m, CH$_2$), 1.01 (1 H, d, J 8, NH), 0.28 (9 H. s, NSiMe$_3$) and 0.01 (9 H, s, OSiMe$_3$).

d. *5-Methyl (S)-glutamate hydrochloride*

(S)-Glutamic acid (5.0 g, 34.0 mmol) was suspended in dry methanol (100 cm^3) under a nitrogen atmosphere while trimethylsilyl chloride (9.5 cm^3, 8.1 g, 75 mmol) was added dropwise. After 15 min the solution was evaporated and the colourless solid recrystallised from methanol/ether to give 5-methyl (S)-glutamate hydrochloride (5.9 g, 88%) as colourless crystals; m.p. 157–158 °C (lit.,[139] m.p. 157–158 °C).

e. 4-Methyl (S)-aspartate hydrochloride

This was prepared as in (d) using (S)-aspartic acid (5.0 g, 37.6 mmol) and trimethylsilyl chloride (10.5 cm^3, 9.0 g, 82.7 mmol) to give 4-methyl (S)-aspartate hydrochloride (5.8 g, 85%) as colourless crystals; m.p. 192–193 °C (lit.,[140] m.p. 192–193 °C).

Note: In the spectroscopic data for the following N-alkoxycarbonylamino acids the signals due to the minor carbamate rotamer are denoted by * where these can be identified.

Preparation of N-benzoxycarbonyl and N-ethoxycarbonyl Protected Amino Acids

f. N-*Benzoxycarbonyl-(S)-alanine* 298a

To a stirred solution of (S)-alanine (10.0 g, 112 mmol) in 2M NaOH (56 cm^3, 112 mmol) at 0 °C was added simultaneously benzyl chloroformate (16.0 cm^3, 19.2 g, 112 mmol) and 2M NaOH (56 cm^3, 112 mmol) dropwise. The mixture was stirred at 0 °C for 3h then washed with ether (20 cm^3). The aqueous phase was acidified with 2M HCl and extracted with ethyl acetate (3 x 50 cm^3). The combined organic phase was dried and the solvent evaporated to furnish the title compound (17.1 g, 68%) as colourless crystals; m.p. 82–84 °C (lit.,[141] m.p. 83–84 °C); δ_H 10.84 (1 H, br s, OH), 7.38 (5 H, s, Ph), 6.69* and 5.58 (1 H, 2 x d, J 8, NH), 5.17 (2 H, s, OCH_2Ph), 4.41 (1 H, m, CH) and 0.74 (3 H, d, J 6, Me); δ_C 177.5 (CO$_2$H), 155.9 (NHCO), 136.0 (C-1 of Ph), 128.5 (Ph), 128.2 (Ph), 128.0 (Ph), 67.1 (OCH_2Ph), 49.4 (CH) and 18.2 (Me).

g. N-*benzoxycarbonyl-(±)-alanine*

Reaction as in f. using (±)-alanine (10.0 g, 112 mmol) and benzyl chloroformate (16.0 cm^3, 19.2 g, 112 mmol) gave the title compound (17.1 g. 68%) as colourless crystals; m.p. 114–115 °C (lit.,[142] m.p. 114–115 °C).

h. N-*Benzoxycarbonyl-(S)-valine* **298b**

Reaction as in f. using (S)-valine (5.0 g, 42 mmol) and benzyl chloroformate (6.1 cm^3, 7.3 g, 42 mmol) gave the title compound (6.15 g. 58 %) as colourless crystals; m.p. 60–62 °C (lit.,[143] m.p. 66–67 °C): δ_H 10.90 (1 H, br s, OH), 7.41 (5 H, s, Ph), 6.64* and 5.60 (1 H, 2 x d, *J* 8, NH), 5.18 (2 H, s, OC*H*$_2$Ph), 4.22* and 4.43 (1 H, 2 x m. C*H*NH), 2.18 (1H, m, CH), 1.12 (3 H, d, *J* 7, Me) and 0.98 (3 H, d, *J* 6, Me): δ_C 176.4 (CO$_2$H), 156.5 (NHCO). 136.0 (C-1 of Ph), 128.4 (Ph), 128.2 (Ph), 128.1 (Ph), 67.2 (OCH$_2$Ph), 58.8 (NCH), 31.0 (*C*HMe$_2$), 19.0 (Me) and 17.3 (Me).

i. N-*Benzoxycarbonyl-(S)-leucine* **298c**

Reaction as in f. using (S)-leucine (10.0 g, 76.3 mmol) and benzyl chloroformate (10.9 cm^3, 13.0 g, 76.3 mmol) gave the title compound (12.4 g, 61%) as a straw coloured oil (lit.,[141] colourless oil); δ_H 10.15 (1 H, br s, OH), 7.34 (5 H, s, Ph), 6.33* and 5.28 (1 H, 2 x d, *J* 8, NH), 5.11 (2 H, s, OC*H*$_2$Ph), 4.43 and 4.25* (1 H, 2 x m, CH), 1.61 (3 H, m, CH$_2$CH), 0.94 (3 H, d, *J* 4, Me) and 0.93 (3 H, d, *J* 4, Me); δ_C 178.0 (CO$_2$H), 156.2 (NHCO), 136.0 (C-1 of Ph), 128.5 (Ph), 128.2 (Ph), 128.1 (Ph), 67.1 (OCH$_2$Ph), 52.3 (CHNH), 41.4 (*C*H$_2$CH), 24.7 (*C*HMe$_2$), 22.8 (Me) and 21.7 (Me).

j. N-*Benzoxycarbonyl-(S)-phenylalanine* **298d**

Reaction as in f. using (S)-phenylalanine (10.0 g, 60.6 mmol) and benzyl chloroformate (9.0 cm^3, 10.8 g, 63.0 mmol) gave the title compound (12.3 g, 68%) as colourless crystals; m.p. 87–88 °C (lit.,[141] 88–89 °C); δ_H 11.05 (1 H,

br s, OH), 7.11–7.31 (10 H, m, Ph), 5.34 and 6.45*(1 H, 2 x d, J 8, NH), 5.07 (2 H, s, OCH_2Ph), 4.65 (1 H, m, CH) and 3.18 and 3.04 (2 H, AB pattern of d. J 16, 6, CHCH_2Ph); δ_C 176.2 (CO$_2$H), 156.9 (NHCO), 136.0 (C-4 of Ph), 135.5 (C-4 of Ph), 129.3 (2 C, Ph), 128.6 (2 C, Ph), 128.5 (2 C, Ph), 128.2 (Ph), 128.1 (2 C, Ph), 127.2 (Ph), 67.2 (OCH$_2$Ph), 54.5 (CH) and 37.7 (CHCH$_2$Ph).

k. N-*Benzoxycarbonyl-(S)-proline* **300a**

Reaction as in f. using (S)-proline (5.0 g, 43 mmol) and benzyl chloroformate (4.2 cm^3, 4.7 g, 43 mmol) gave the title compound (6.30 g, 77%) as colourless crystals; m.p. 60–61 °C (lit.,[141] m.p. 77 °C); δ_H 10.01 (1 H, br s, OH), 7.31 and 7.26 (5 H, 2 x s, Ph), 5.09 (2 H, m, OCH$_2$), 4.35 (1 H, m, CHNH), 3.46 (2 H, m, CH$_2$) and 2.05 (4 H, m, CH$_2$CH$_2$); δ_C 176.7 and 176.3 (CO$_2$H), 155.4 and 154.7 (NCO), 136.3 (C-1 of Ph), 128.4 and 128.3 (2 C, Ph), 127.9 (1 C, Ph), 127.8 and 127.5 (2 C, Ph), 67.3 and 67.2 (OCH$_2$), 59.1 and 58.7 (CHN), 46.6 and 46.5 (CH$_2$), 30.7 and 29.7 (CH$_2$) and 24.1 and 23.3 (CH$_2$).

l. N-*Ethoxycarbonylglycine* **298e**

Reaction as in f. using glycine (10.0 g, 85 mmol) and ethyl chloroformate (8.2 cm^3, 9.2 g, 85 mmol) gave the title compound (11.2 g, 70%) as a colourless oil (lit.,[143] m.p. 73–74), δ_H 9.66 (1 H, br s, OH), 6.85* and 5.50 (1 H, 2 x br s, NH), 4.33 (2 H, m, CH$_2$$H$NH), 4.15 and 4.00 (2 H, 2 x q, J 7, OCH$_2$) and 1.25 (3 H, t, J 7, Me); δ_C 174.4 and 173.7* (CO$_2$H), 157.2 (NHCO), 62.4* and 61.8 (OCH$_2$), 43.2* and 42.6 (CH$_2$) and 14.6 (CH$_2$$Me$).

m. N-*Ethoxycarbonyl-(S)-alanine* **298f**

Reaction as in f. using (S)-alanine (10.0 g, 112 mmol) and ethyl chloroformate (11.0 cm^3, 12.5 g, 112 mmol) gave the title compound (12.85

g, 71%) as a colourless oil (lit., [144] pale yellow oil); δ_H 10.26 (1 H, br s. OH), 6.77* and 5.58 (1 H, 2 x d, J 7. NH), 4.33 (1 H, m, CHNH), 4.07 (2 H. q, J 7, OCH_2), 1.40 (3 H, d, J 7, CHMe) and 1.19 (3 H, t, J 7, CH$_2Me$); δ_C 177.2 (CO_2H), 156.5 (NHCO), 61.4 (OCH_2). 49.4 (CHNH), 18.4 (CHMe) and 14.5 (CH$_2Me$).

n. N-*Ethoxycarbonyl-(±)-alanine*

Reaction as in f. using (±)-alanine (10.0 g, 112 mmol) and ethyl chloroformate (11.0 cm^3, 12.5 g, 112 mmol) gave the title compound (12.85 g, 71%) as colourless crystals; m.p. 80–82 (lit., [145] 84 °C).

o. N-*Ethoxycarbonyl-(S)-valine* **298g**

Reaction as in f. using (S)-valine (10.0 g, 85.0 mmol) and ethyl chloroformate (8.2 cm^3, 9.2 g, 85.0 mmol) gave the title compound (11.2 g, 70%) as a colourless oil (lit., [146] colourless oil); δ_H 10.80 (1 H, br s. OH), 6.54* and 5.52 (1 H, 2 x d, J 8, NH), 4.33 (1 H, m, CHNH), 4.16 (2 H, q, J 7, OCH_2), 2.23 (1H, m, CH), 1.25 (3 H, t, J 7, CH$_2Me$), 1.00 (3 H, d, J 7, CHMe) and 0.94 (3 H, d, J 7, CHMe); δ_C 176.3 (CO_2H), 157.0 (NHCO), 61.5 (OCH_2), 58.8 (CHNH), 31.1 (*C*HMe$_2$), 19.0 (CHMe), 17.4 (CHMe) and 14.5 (CH$_2Me$).

p. N-*Ethoxycarbonyl-(S)-leucine* **298h**

Reaction as in f. using (S)-leucine (10.0 g, 76.3 mmol) and ethyl chloroformate (7.3 cm^3, 8.2 g, 76.3 mmol) gave the title compound (10.75 g, 69%) as a colourless oil (lit., [147] oil); δ_H 11.11 (1 H, br s, OH), 6.38* and 5.31(1 H, 2 x d, J 8, NH), 4.37 (1 H, m, CHNH), 4.13 (2 H, q, J 7, OCH_2), 1.64 (3 H, m, CH_2CH), 1.25 (3 H, t, J 7, CH$_2Me$) and 0.96 (6 H, d, J 6, CHMe_2); δ_C 178.0 (CO_2H), 156.6 (NHCO), 61.4 (OCH_2), 52.3 (CHNH), 41.4 (CH_2), 24.7 (*C*HMe$_2$), 22.9 (CHMe), 21.7 (CHMe) and 14.5 (CH$_2Me$).

q. N-*Ethoxycarbonyl-(S,S)-isoleucine* **298i**

Reaction as in f. using (S,S)-isoleucine (5.0 g, 38 mmol) and ethyl chloroformate (3.6 cm^3, 4.1 g, 38 mmol) gave the title compound (5.56 g, 72%) as a colourless oil; δ_H 9.47 (1 H, br s, OH), 6.36* and 5.32 (1 H, 2 x d, J 8, NH), 4.36 (1 H, m, C*H*NH), 4.13 (2 H, q, J 7, OCH$_2$), 1.95 (1 H, m, C*H*CH$_3$), 1.49 (2 H, m, CH$_2$), 1.26 (3 H, t, J 7, OCH$_2$*Me*), 0.98 (3 H, d, J 7, CH*Me*) and 0.93 (3 H, t, J 7, CH$_2$*Me*); δ_C 176.7 (CO$_2$H), 156.6 (NHCO), 61.4 (OCH$_2$), 58.2 (CHNH), 37.8 (Me*C*H), 24.8 (CH*C*H$_2$), 15.5 (CH*Me*), 14.5 (OCH$_2$*Me*) and 11.6 (CHCH$_2$*Me*).

r. N-*Ethoxycarbonyl-(S)-phenylalanine* **298j**

Reaction as in f. using (S)-phenylalanine (10.0 g, 60.6 mmol) and ethyl chloroformate (6.0 cm^3, 7.1 g, 61 mmol) gave the title compound (8.4 g, 58%) as colourless crystals; m.p. 83–84 °C (lit.,[148] 83–85 °C); δ_H 11.58 (1 H, br s, OH), 7.43–7.16 (5 H, m, Ph), 6.58* and 5.27 (1 H, 2 x d, J 8, NH), 4.68 and 4.49* (1 H, 2 x m, CH), 4.08 (2 H, q, J 7, OCH$_2$), 3.15 (2 H, m, C*H*$_2$Ph) and 1.21 (3 H, t, J 7, Me); δ_C 176.3 (CO$_2$H), 156.4 (NHCO), 135.8 (C-1 of Ph), 129.5 (2 C, Ph), 128.7 (2 C, Ph), 127.3 (Ph), 61.6 (OCH$_2$), 54.6 (CH), 37.9 (*C*H$_2$Ph) and 14.6 (Me).

s. N-*Ethoxycarbonyl-(R)-phenylglycine* **298k**

Reaction as in f. using (R)-phenylglycine (5.0 g, 33.1 mmol) and ethyl chloroformate (3.2 cm^3, 3.6 g, 33 mmol) gave the title compound (4.9 g, 64%) as colourless crystals; m.p.142–143 °C (lit.,[149] (±)-analogue m.p. 121–122 °C); δ_H 10.71 (1 H, br s, OH), 8.04* and 5.80 (1 H, 2 x d, J 6, NH), 7.42 (5 H, m, Ph), 5.40* and 5.26(1 H, 2 x d, J 2, C*H*NH), 4.05 (2 H, m, OCH$_2$) and 1.24* and 1.07 (3 H, t, J 7, CH$_2$*Me*); δ_C 175.0* and 173.6 (CO$_2$H), 157.4 and 155.8* (NHCO), 137.5 and 136.2* (C-1 of Ph), 129.0 and 128.8 (2 C,

Ph), 128.6 and 128.2 (2 C, Ph), 127.1 (1 C, Ph), 62.1 and 61.6* (OCH$_2$), 58.4 and 57.7* (CHNH) and 14.5* and 14.2 (Me).

t. N-*Ethoxycarbonyl-(S)-proline* **300b**

Reaction as in f. using (S)-proline (5.0 g, 43 mmol) and ethyl chloroformate (4.2 cm^3, 4.7 g, 43 mmol) gave the title compound (6.30 g, 77%) as a colourless crystals; m.p. 59–60 °C, (lit.,[150] m.p. 62–63 °C); δ_H 10.68 (1 H, br s, OH), 4.24 (1 H, m, NH), 4.07 (2 H, m, OCH$_2$). 3.39 (2 H, m, CH$_2$), 2.11 (2 H, m, CH$_2$), 1.80 (2 H, m, CH$_2$) and 1.13 (3 H, m, Me); δ_C 177.0 and 176.4 (CO$_2$H), 155.9 and 155.1 (NCO), 61.8 and 61.7 (OCH$_2$), 59.1 and 58.7 (CHN), 46.8 and 46.5 (CH$_2$), 30.9 and 29.7 (CH$_2$). 24.3 and 23.5 (CH$_2$) and 14.7 and 14.6 (Me).

u. N,N'-*bis(Ethoxycarbonyl)-(S)-ornithine* **298l**

Reaction as in f. using 3 equivalents of base, (S)-ornithine hydrochloride (10.0 g, 59.3 mmol) and ethyl chloroformate (22.6 cm^3, 25.6 g, 119 mmol) gave the title compound (11.3 g, 71%) as a colourless oil (lit.,[151] oil); δ_H 10.84 (1 H, br s, OH), 6.48* and 5.78 (1 H, d, J 8, NH), 5.37 (1 H, d, J 8, NH), 4.35 (1 H, m, CHNH), 4.12 (4 H, q, J 7, OCH$_2$), 3.19 (2 H, m, CHCH$_2$), 2.09–1.48 (4 H, m, CH$_2$CH$_2$) and 1.28 (6 H, m, Me); δ_C 175.5 (CO$_2$H), 157.3 (NHCO), 156.7 (NHCO), 61.3 (OCH$_2$), 61.0 (OCH$_2$), 53.3 (CHNH), 40.4 (CH$_2$), 29.6 (CH$_2$), 25.8 (CH$_2$), 14.6 (Me) and 14.5 (Me).

v. N,N'-*bis(Ethoxycarbonyl)-(S)-lysine* **298m**

Reaction as in f. using using 3 equivalents of base, (S)-lysine hydrochloride (5.0 g, 27 mmol) and ethyl chloroformate (5.2 cm^3, 5.9 g, 55 mmol) gave the title compound (3.56 g, 64%) as a colourless oil (lit.,[147] oil); δ_H 10.86 (1 H, br s, OH), 6.49 (1 H, d, J 8, NH), 5.75 (1 H, d, J 8, NH), 4.35 (1 H, m, CHNH), 4.13 (4 H, m, OCH$_2$), 3.16 (2 H, m, CHCH$_2$), 1.81 (2 H, m,

1.81 (2 H, m, CH$_2$), 1.50 (4 H, m, CH$_2$CH$_2$) and 1.28 (6 H, m, 2 x Me); δ_C 175.8 and 175.6 (CO$_2$H), 158.63 and 158.59 (NHCO), 156.7 (NHCO), 61.3 (OCH$_2$), 61.0 (OCH$_2$), 53.3 (CHNH), 40.4 (CH$_2$), 31.9 (CH$_2$) 29.6 (CH$_2$), 22.3 (CH$_2$), 14.6 (Me) and 14.5 (Me).

w. N-*Ethoxycarbonyl-α–aminoisobutyric acid* 301

Reaction as in f. using α–aminoisobutyric acid (2.0 g, 19 mmol) and ethyl chloroformate (1.9 cm^3, 2.1 g, 19 mmol) gave the title compound (2.55 g, 75%) as colourless crystals; m.p. 84–86 °C (lit.,[147] 78–80); δ_H 10.73 (1 H, br s, OH), 5.51 (1 H, br s, NH), 4.04 (2 H, q, J 7, OCH$_2$), 1.45 (6 H, s, 2 x Me) and 1.15 (3 H, t, J 7, Me); δ_C 180.0 (CO$_2$H), 156.1 (NHCO), 61.5 (4ry C), 56.6 (OCH$_2$), 25.5 (2 x Me) and 14.8 (CH$_2$Me).

x. N-*Ethoxycarbonyl-(S)-methionine* 298n

Reaction as in f. using (S)-methionine (5.0 g, 33.5 mmol) and ethyl chloroformate (3.2 cm^3, 3.64 g, 33.5 mmol) gave the title compound (4.30 g, 62%) as a colourless oil (lit.,[147] oil); δ_H 10.49 (1 H, br s, OH), 6.82* and 5.50 (1 H, 2 x d, J 8, NH), 4.51 (1 H, m, CHNH), 4.18 (2 H, q, J 7, OCH$_2$), 2.60 (2 H, m, CH$_2$), 2.15 (3 H, s, SMe), 2.05 (2 H, m, CH$_2$) and 1.28 (3 H, t, J 7, Me); δ_C 176.1 (CO$_2$H), 153.7 (NHCO), 61.5 (OCH$_2$), 53.1 (CHNH), 31.6 (CH$_2$), 29.9 (CH$_2$), 15.3 (SMe) and 14.4 (Me).

y. N-*Ethoxycarbonyl-(S)-asparagine* 298o

Reaction as in f. using (S)-asparagine monohydrate (5.0 g, 33 mmol) and ethyl chloroformate (3.2 cm^3, 3.6 g, 33 mmol) gave the title compound (4.67 g, 69%) as colourless crystals; m.p. 169–170 °C (lit.,[152] m.p. 169–170 °C); δ_H 10.26 (1 H, br s, OH), 7.43 and 6.95 (2 H, 2 x d, J 8, CONH$_2$), 7.26 (1 H, d, J 8, NH), 4.29 (1 H, m, CHNH), 3.97 (2 H, q, J 7, OCH$_2$), 2.50 (2 H,

m, CH$_2$) and 1.16 (3 H, t, J 7, Me); δ_C 173.2 (CO), 171.2 (CO), 155.8 (NHCO$_2$), 59.7 (OCH$_2$), 50.4 (CHNH), 36.6 (CH$_2$) and 14.5 (Me).

z. N-*Ethoxycarbonyl-(S)-glutamic acid* γ-*methyl ester* **298p**

Reaction as in f. using 3 equivalents of base, 5-methyl (S)-glutamate hydrochloride (5.0 g, 25 mmol) and ethyl chloroformate (2.4 cm^3, 2.8 g, 25 mmol) gave the title compound (3.3 g, 55%) as a colourless oil; δ_H 10.00 (1 H, br s, OH), 6.19* and 5.95 (1 H, m, NH), 4.37 (1 H, m, NCH), 4.14 (2H, m, OCH$_2$), 3.69 (3 H, s, OMe), 2.46 (2H, m, CH$_2$), 2.17 (2H, m, CH$_2$) and 1.25 (3 H, t, J 7, CH$_2$*Me*); δ_C 179.6 (CO$_2$H), 174.7 (*C*O$_2$Me), 156.5 (NHCO), 61.8 (OCH$_2$), 55.7 (CH), 51.6 (OMe), 29.8 (CH$_2$), 26.9 (CH$_2$) and 14.1 (CH$_2$*Me*).

aa. N-*Ethoxycarbonyl-(S)-aspartic acid* β-*methyl ester* **298q**

Reaction as in f. using 3 equivalents of base, 4-methyl (S)-aspartate hydrochloride (5.0 g, 25 mmol) and ethyl chloroformate (2.4 cm^3, 2.8 g, 25 mmol) gave the title compound (3.3 g, 58%) as a colourless oil (lit.,[153] oil); δ_H 10.00 (1 H, br s, OH), 5.95 (1 H, m, NH), 4.31 (1 H, m, NCH), 4.10 (2 H, q, J 7, OCH$_2$), 3.68 (3 H, s, OMe), 2.79 (2 H, m, CH$_2$) and 1.23 (3 H, t, J 7, CH$_2$*Me*); δ_C 180.4 (*C*O$_2$H), 174.8 (*C*O$_2$Me), 156.4 (NHCO), 61.2 (OCH$_2$), 52.4 (CH), 51.8 (OMe), 29.6 (CH$_2$) and 14.3 (CH$_2$*Me*).

bb. N-*Ethoxycarbonyl-(S)-glutamic acid* **298r**

Reaction as in f. using 3 equivalents of base, (S)-glutamatic acid (10.0 g, 68 mmol) and ethyl chloroformate (6.5 cm^3, 7.4 g, 68 mmol) gave the title compound (2.9 g, 20%) as a colourless oil (lit.,[147] oil); δ_H 12.57 (2 H, br s, 2 x OH), 7.69 (1 H, d, J 8, NH), 4.01 (3 H, m, OCH$_2$ and NCH), 2.19 (2H, m, CH$_2$), 1.96 (2H, m, CH$_2$) and 1.18 (3 H, t, J 7, CH$_2$*Me*); δ_C 173.8 (CO$_2$H), 173.6 (*C*O$_2$H), 156.3 (NHCO), 59.9 (OCH$_2$), 52.9 (CH), 30.1 (CH$_2$), 26.1 (CH$_2$) and 14.2 (CH$_2$*Me*).

cc. N-*Ethoxycarbonyl-β-alanine* **302**

Reaction as in f. using β-alanine (5.0 g, 33.5 mmol) and ethyl chloroformate (3.20 cm^3, 3.64 g, 33.5 mmol) gave the title compound (4.30 g, 62%) as colourless crystals; m.p. 57–59 °C (lit.,[154] 57–59 °C); δ_H 10.88 (1 H, br s, OH), 7.17* and 6.42 (1 H, 2 x br d, J 8, NH), 5.80* and 5.59 (1 H, 2 x m, CHNH), 4.14 (2 H, q, J 7, OCH$_2$), 3.46 (2 H, m, NHCH$_2$), 1.52 (2 H, t, CH$_2$) and 1.28 (3 H, t, J 7, Me); δ_C 177.2 (CO$_2$H), 157.4 (NHCO), 61.5 (OCH$_2$), 36.7 (CH$_2$NH), 34.6 (CH$_2$) and 14.9 (Me).

dd. N-*t-Butoxycarbonyl-(S)-alanine* **298s**

Reaction as in f. using (S)-alanine (2.5 g, 28 mmol) and di-t-butyl pyrocarbonate (3.0 g, 28 mmol) gave the title compound (4.38 g, 79%) as colourless crystals; m.p. 81–83 °C (lit.,[155] 82–83 °C); δ_H 11.08 (1 H, br s, OH), 6.84* and 5.25 (1 H, 2 x br s, NH), 4.27 (1 H, m, CHNH) and 1.38 (12 H, m, CH*Me* and CMe$_3$); δ_C 177.8* and 177.3 (CO$_2$H), 156.9* and 155.4 (NHCO), 81.7* and 80.2 (CMe$_3$), 50.1* and 49.2 (CHNH), 28.3 (C*Me$_3$*) and 18.4 (CH*Me*).

ee. N-*Isobutoxycarbonyl-(S)-alanine* **298t**

Reaction as in f. using (S)-alanine (2.5 g, 28 mmol) and isobutyl chloroformate (1.5 g, 28 mmol) gave the title compound (3.86 g, 69%) as colourless crystals; m.p. 83–85 °C; δ_H 10.15 (1 H, br s, OH), 7.01* and 5.45 (1 H, 2 x br s, NH), 4.25 (1 H, m, CHNH), 3.91 (2 H, m, CH$_2$), 1.94 (1 H, m, CH*Me$_2$*), 1.48 (3 H, d, J 6, CH*Me*) and 0.96 (6 H, d, J 7, CH*Me$_2$*); δ_C 177.9* and 177.3 (CO$_2$H), 157.9* and 156.9 (NHCO), 72.0* and 72.6 (OCH$_2$), 50.5 and 49.9* (CHN), 28.2 (CHMe$_2$), 19.4 (CH*Me$_2$*) and 18.9 (CH*Me*).

2. Attempted Preparation of Aminoacyl ylides from silyl ylides

a. *(Trimethylsilylmethylene)triphenylphosphorane* 28

To a suspension of methyltriphenylphosphonium bromide (10.0 g, 28 mmol) in dry THF (140 cm^3) at RT and under a nitrogen atmosphere was added Bu^{n}Li (11.2 cm^3, 28 mmol) dropwise. The bright orange solution was stirred for 30 min before trimethylsilyl chloride (1.8 cm^3, 14 mmol) was added to the ylide and the mixture heated under reflux for 5 h, cooled and the THF phase separated from the solid. Evaporation of the solvent afforded a yellow waxy solid (4.8 g, 91%); δ_P(C$_6$D$_6$) +19.5 (lit.,[44] δ_P +19).

b. *Attempted preparation of 3-amino-1-triphenylphosphoranylidenebutan-2-one*

A solution of (trimethylsilylmethylene)triphenylphosphorane (2.0 g, 5.8 mmol) and *N*-trimethylsilyl-(S)-alanine trimethylsilyl ester (1.43 g, 5.8 mmol) in dry THF (25 cm^3) was heated under reflux under a nitrogen atmosphere for various lengths of time. (The most promising reaction time was 3 days.) The mixture was dissolved in water and extracted with CH$_2$Cl$_2$. The organic layer was dried and the solvent was removed to furnish a sticky residue. Recrystallisation of a portion of this residue was attempted but this yielded Ph$_3$PO and other, unidentifiable compounds. Reprecipitation of the crude mixture afforded off-white crystals (1.0 g, 44%), m.p. 154-158 °C The desired compound **129** (R = Me) should have had a m.p. of 170-173 °C.[29]

3. Preparation of β-aminoacyl phosphorus ylides

a. *Ethyl 4(S)-benzoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene-pentanoate* **303a**

To a stirred solution of (ethoxycarbonylmethylene)triphenyl phosphorane (1.82 g, 5.2 mmol) and *N*-benzoxycarbonyl-(S)-alanine (1.16 g, 5.2 mmol) in dry methylene chloride (25 cm³) at 0 °C was added EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol). The mixture was stirred at this temperature for 30 min then allowed to warm up to RT. Once all the starting material was consumed (indicated by TLC) the mixture was poured into brine, extracted with CH_2Cl_2 (3 x 20 cm³) and the combined organic extracts dried. The solvent was removed under reduced pressure to furnish the crude product. Chromatography (ethyl acetate/hexane, 1:2) yielded the desired compound which was recrystallised from ethyl acetate to afford the title compound (1.21 g, 46%) as colourless crystals; m.p. 140–142 °C (Found: C, 71.9; H, 5.7; N, 2.5. $C_{33}H_{32}NO_5P$ requires C, 71.6; H, 5.7; N. 2.5%); $[\alpha]_D^{20}$ +20.3 (*c* 1.005 in CH_2Cl_2); v_{max} /cm⁻¹ (Nujol) 3450, 1700, 1645, 1560, 1475, 1270, 1220, 1090, 1080, 1040, 750 and 690; δ_H 7.78–7.61 (5 H, m, Ph), 7.55–7.41 (10 H, m, Ph), 7.41–7.25 (5 H, m, Ph), 5.88 (1 H, d. *J* 7. NH), 5.51 (1 H, m, CH), 5.05 (2 H, s, OC*H₂*Ph), 3.79 (2 H, m, OCH₂), 1.54 (3 H, d, *J* 6, CHC*H₃*) and 0.74 (3 H, t, *J* 7, Me); δ_C 194.8 (P=C–*C*O), 166.7 (d, *J* 14, *C*O₂Et), 155.5 (NH*C*O), 137.1 (C-1 of Ph), 133.0 (d, *J* 10, 6 x C-2 of P-Ph), 131.8 (d, *J* <2, 3 x C-4 of P-Ph), 128.6 (d, *J* 12, 6 x C-3 of P-Ph), 128.3 (2 C, Ph), 127.7 (3 C, Ph), 126.0 (d, *J* 93, 3 x C-1 of P-Ph), 68.8 (d, *J* 111, P=C), 65.9 (O*C*H₂Ph), 58.7 (O*C*H₂), 52.5 (d, *J* 8, NH*C*H), 20.4 (CH*Me*) and 13.8 (OCH₂*Me*); δ_P +17.5; *m/z* (CI) 554 (M+H⁺, 100%), 508 (20), 446 (18), 375 (31), 279 (11), 263 (17), 184 (8) and 91 (10).

The racemic compound was prepared using *N*-benzoxycarbonyl-(±)-alanine and had m.p. 142–143 °C.

b. *Ethyl 4(S)-benzoxycarbonylamino-5-methyl-3-oxo-2-triphenylphosphoran--ylidenehexanoate* **303b**

Reaction as in a. using *N*-benzoxycarbonyl-(S)-valine (1.31 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.48 g, 49%) as colourless crystals; m.p. 88–91 °C (Found: C, 72.4; H, 6.4; N, 2.35. $C_{35}H_{36}NO_5P$ requires C, 72.3; H, 6.2; N, 2.4%); $[\alpha]_D^{20}$ +28.7 (*c* 0.995 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3390, 1710, 1640, 1550, 1275, 1220, 1090, 1065, 1000, 740, 710 and 680; δ_H 7.80–7.63 (5 H, m, Ph), 7.51–7.40 (10 H, m, Ph), 7.39–7.20 (5 H, m, Ph), 5.68 (1 H, d, *J* 9, NH), 5.54 (1 H, m, C*H*NH), 5.06 (2 H, s, OC*H*$_2$Ph), 3.74 (2 H, m, OCH$_2$), 2.44 (1 H, br m, CH), 1.09 (3 H, d, *J* 6, CH*Me*), 0.72 (3 H, t, *J* 7, CH$_2$*Me*) and 0.68 (3 H, d, *J* 7, CH*Me*); δ_C 194.1 (d, *J* 2, P=C–*C*O), 166.8 (d, *J* 14, *C*O$_2$Et), 156.6 (NHCO), 137.1 (C-1 of Ph), 133.0 (d, *J* 10, 6 x C-2 of P-Ph), 131.8 (d, 3 x C-4 of P-Ph), 128.5 (d, *J* 12, 6 x C-3 of P-Ph), 127.6 (3 C, Ph), 126.0 (d, *J* 94, 3 x C-1 of P-Ph), 69.8 (d, *J* 110, P=C), 66.0 (OCH$_2$Ph), 60.4 (d, *J* 8, CHNH), 58.6 (OCH$_2$), 32.3 (*C*HMe$_2$), 20.7 (CH*Me*), 15.9 (CH*Me*) and 13.8 (OCH$_2$*Me*); δ_P +17.8; *m/z* (FAB) 582 (M+H$^+$, 16%), 492 (5), 375 (100), 303 (39), 262 (14) and 183 (14).

c. *Ethyl 4(S)-benzoxycarbonylamino-6-methyl-3-oxo-2-triphenyl phosphoran--ylideneheptanoate* **303c**

Reaction as in a. using *N*-benzoxycarbonyl-(S)-leucine (1.38 g, 5.2 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.36 g, 44 %) as colourless crystals; m.p. 152–154 °C (Found: C, 72.8; H, 6.5; N, 2.3. $C_{34}H_{34}NO_5P$ requires C, 72.6; H, 6.4; N, 2.4%); $[\alpha]_D^{20}$ +21.7 (*c* 0.975 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3390, 3400, 1695, 1655, 1535, 1500, 1290, 1250, 1094, 1080, 1045, 730 and 680; δ_H 7.67–7.61 (5 H, m,

Ph), 7.64–7.44 (10 H, m, Ph), 7.30–7.26 (5 H, m, Ph), 5.61 (2 H, m, NH and CH), 5.07 (2 H, s, OCH_2Ph), 3.81 (2 H, m, OCH_2), 1.77 (2 H, m, CH_2CH), 1.36 (1 H, m, CH_2CH), 1.12 (3 H, d, J 6, CHMe), 0.94 (3 H, d, J 6, CHMe) and 0.72 (3 H, t, J 7, CH$_2$$Me$); δ_C 195.2 (d, J 3, P=C–CO), 166.8 (d, J 15, CO$_2$Et), 156.2 (NHCO), 137.1 (C-1 of Ph), 128.5 (d, J 12, 6 x C-3 of P-Ph), 133.1 (d, J 10, 6 x C-2 of P-Ph), 131.8 (d, J 2, 3 x C-4 of P-Ph), 128.3 (2 C, Ph), 127.7 (3 C, Ph), 126.2 (d, J 94, 3 x C-1 of P-Ph), 69.3 (d, J 110, P=C), 66.1 (OCH$_2$Ph), 58.7 (OCH$_2$), 55.1 (d, J 8, CHNH), 43.6 (CH$_2$CH), 25.1 (CHMe) and 21.9 (CHMe), 21.8 (CHMe) and 13.9 (OCH$_2$$Me$); δ_P +17.5; m/z (CI) 596 (M+H$^+$, 100%), 550 (44), 506 (6), 488 (19), 416 (30), 375 (23), 319 (7), 292 (12), 279 (17), 263 (41), 225 (36), 187 (11), 156 (12) and 91 (19).

d. *Ethyl 4(S)-benzoxycarbonylamino-3-oxo-5-phenyl-2-triphenyl phosphoran-ylidenepentanoate* **303d**

Reaction as in a. using *N*-benzoxycarbonyl-(S)-phenylalanine (1.54 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.05 g, 40%) as colourless crystals; m.p. 128–130 °C (Found: C, 74.6; H, 5.7; N, 2.15. C$_{39}$H$_{36}$NO$_5$P requires C, 74.4; H, 5.7; N, 2.2 %); $[\alpha]_D^{20}$ +27.9 (*c* 0.985 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} (Nujol) 3280, 1705, 1664, 1540, 1290, 1255, 1192, 1155, 1095, 1080, 1020, 990, 920, 905, 880, 840, 780, 745 and 680; δ_H 7.74–7.19 (25 H, m, Ph), 5.98 (1 H, m, CH), 5.72 (1 H, br d, J 9, NH), 5.72 (2 H, s, OCH_2Ph), 3.75 (2 H, m, OCH_2CH$_3$), 3.43 (1 H, dd, J 14, 5), 2.86 (1 H, dd, J 14, 8) and 0.65 (3 H, t, J 7, OCH$_2$$Me$); δ_C 193.5 (d, J 4, P=C–CO), 166.7 (d, J 14, CO$_2$Et), 155.5 (NHCO), 138.1 (C-1, Ph), 136.9 (C-1 of Ph), 132.9 (d, J 9, 6 x C-2 of P-Ph), 131.7 (3 x C-4 of P-Ph), 129.6 (2 C, Ph), 128.4 (d, J 12, 6 x C-3 of P-Ph), 128.0 (3 C, Ph), 127.8 (2 C, Ph), 127.4 (3 C, Ph), 125.9 (Ph), 125.7 (d, J 93, 3 x C-1 of P-Ph), 69.3 (d, J 109, P=C), 65.7 (OCH$_2$Ph), 58.4 (OCH$_2$CH$_3$), 57.1 (d, J 8, CH), 39.6 (CH$_2$Ph) and 13.6 (Me);

δ_P +17.7; m/z 449 (M$^+$–180, 0.5%), 375 (11), 358 (3), 303 (4), 277 (41), 262 (23), 216 (4), 201 (11), 183 (33), 152 (12), 108 (26) and 91 (100).

e. (N-*benzoxycarbonyl-(S)-prolinoyl(ethoxycarbonyl)methylene)triphenyl-* *-phosphorane* **304a**

Reaction as in a. using N-benzoxycarbonyl-(S)-proline (0.65 g, 2.6 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (0.91 g, 2.6 mmol), EDCI (0.5 g, 2.6 mmol) and DMAP (0.02 g, 0.13 mmol) yielded the product as an equal mixture of isomers (0.70 g, 49%) as colourless crystals; m.p. 129–130 °C (Found: C, 72.5; H, 6.15; N, 2.3. $C_{34}H_{34}NO_5P$ requires C, 72.5; H, 5.9; N, 2.4%); $[\alpha]_D^{20}$ –45 (c 1.03 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3350, 1675, 1605, 1580, 1440, 1295, 1000, 1050, 760 and 690; δ_H 7.88–7.14 (20 H, m, Ph), 5.71 and 5.64* (1 H, dd, J 9, 3, CH), 5.08 (2 H, m, OCH$_2$Ph), 3.72 (2 H, m, OCH$_2$), 3.49 (2 H, m, CH$_2$), 2.40 and 2.04 (2 H, 2 x m, CH$_2$), 1.73 (2 H, m, CH$_2$) and 0.66 (3 H, t, J 7, Me); δ_C 195.6 and 195.1* (d, J 3, P=C–CO), 167.51 and 167.46* (d, J 15, CO$_2$Et), 154.54 and 154.51* (NCO), 137.4 (C-1 of Ph), 133.3 and 132.9* (d, J 10, 6 x C-2 of P-Ph), 131.6 and 131.5* (d, J 4, 3 x C-4 of P-Ph), 128.8 (d, J 13, both isomers, 6 x C-3 of P-Ph), 128.2 (2 C, Ph), 127.6 (Ph), 126.6 (2 C, Ph), 126.4 and 126.2* (d, J 94, 3 x C-1 of P-Ph), 69.2 and 68.9* (d, J 111, P=C), 66.3 and 66.0* (OCH$_2$Ph), 62.9 and 62.4* (d, J 8, CHN), 58.4 and 58.3* (OCH$_2$), 47.4 and 46.9* (CH$_2$), 31.8 and 30.7* (CH$_2$), 23.8* and 23.0 (CH$_2$) and 13.7 (Me); δ_P +17.6 and 17.4*; m/z 567 (M$^+$, 0.7%), 553 (2.8), 525 (8), 465 (2.3), 375 (27), 279 (20), 181 (23), 149 (25), 105 (29) and 91 (100).

f. *Ethyl 4-ethoxycarbonylamino-3-oxo-2-triphenylphosphoranylidenebutyrate* **303e**

Reaction as in a. using N-ethoxycarbonylglycine (0.77 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI

(1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.27 g, 51%) as colourless crystals; m.p. 147–149 °C (Found: C, 68.2; H, 6.0: N, 2.8. $C_{27}H_{28}NO_5P$ requires C, 67.9; H, 5.9; N; 2.9); ν_{max} /cm^{-1} (Nujol) 3400, 1700, 1650, 1570, 1510, 1300, 1235, 1170, 1105, 1090, 770 and 690: δ_H 7.70–7.61 (6 H, m, Ph), 7.60–7.50 (3 H, m, Ph), 7.49–7.43 (6 H, m, Ph), 5.68 (1 H, br m, NH), 4.56 (2 H, d, J 3, CH$_2$), 4.09 (2 H. m, OCH$_2$), 3.78 (2H, m, OCH$_2$), 1.17 (3 H, t, J 7, Me) and 0.76 (3 H, t, J 7, Me); δ_C 190.6 (P=C–CO), 167.4 (d, J 15, CO$_2$Et), 156.6 (NHCO), 133.2 (d. J 10, 6 x C-2 of P-Ph), 131.9 (d, J 2, 3 x C-4 of P-Ph), 128.6 (d, J 13, 6 x C-3 of P-Ph), 125.9 (d, J 94, 3 x C-1 of P-Ph), 68.9 (d, J 112, P=C), 60.4 (OCH$_2$), 58.7 (OCH$_2$), 49.2 (d, J 8, CH$_2$NH), 14.7 (Me) and 13.9 (Me); δ_P +17.8; m/z (CI) 478 (M+H$^+$, 100%), 432 (52), 386 (8), 375 (19), 365 (11), 319 (6), 279 (26), 263 (29), 218 (14), 187 (9), 172 (20) and 47 (8).

g. *Ethyl 4(S)-ethoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene-pentanoate* **303f**

Reaction as in a. using *N*-ethoxycarbonyl-(S)-alanine (0.84 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.09 g, 50 %) as colourless crystals; m.p. 68–69 °C (Found: C, 68.4; H, 5.8; N, 2.8. $C_{28}H_{30}NO_5P$ requires C, 68.4; H, 6.2; N, 2.9%); $[\alpha]_D^{20}$ +17.5 (*c* 0.98 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} (Nujol) 3400, 1710, 1650, 1570, 1340, 1280, 1230, 1100, 1070 and 690; δ_H 7.81–7.62 (6 H, m, Ph), 7.60–7.53 (3 H, m, Ph), 7.53–7.42 (6 H, m, Ph), 5.66 (1 H, br d, J 9, NH), 5.48 (1 H, br m, CHN), 4.06 (2 H, q, J 7, OCH$_2$), 3.79 (2 H, m, OCH$_2$), 1.45 (3 H, d, J 6, CH*Me*), 1.16 (3 H, t, J 7, CH$_2$*Me*) and 0.75 (3 H, t, J 7, CH$_2$*Me*); δ_C 195.1 (P=C–CO), 166.8 (d, J 15, CO$_2$Et), 155.9 (NHCO), 133.1 (d, J 10, 6 x C-2 of P-Ph), 131.8 (d, J 2, 3 x C-4 of P-Ph), 128.6 (d, J 13, 6 x C-3 of P-Ph), 126.2 (d, J 94, 3 x C-1 of P-Ph), 68.8 (d, J 111, P=C), 60.2 (OCH$_2$), 58.7 (OCH$_2$), 52.4

(d, J 8, CHNH), 20.5 (CHMe), 14.7 (CH$_2Me$) and 13.8 (CH$_2Me$); δ_P +18.0; m/z (CI) 492 (M+H$^+$, 100%), 446 (76), 375 (54), 303 (8), 279 (9), 263 (34), 232 (8), 186 (21), 116 (8) and 47 (11).

The racemic compound was prepared using N-ethoxycarbonyl-($\pm$)-alanine and had m.p. 80–82 °C.

h. *Ethyl 4(S)-ethoxycarbonylamino-5-methyl-3-oxo-2-triphenyl phosphoran-ylidenehexanoate* **303g**

Reaction as in a. using N-ethoxycarbonyl-(S)-valine (0.90 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.23 g, 45%) as colourless crystals; m.p. 128–129 °C (Found: C, 69.3; H, 6.5; N, 2.6. C$_{30}$H$_{34}$NO$_5$P requires C, 69.4; H, 6.6; N, 2.7%); $[\alpha]_D^{20}$ +22.6 (c 0.975 in CH$_2$Cl$_2$); v_{max}/cm^{-1} (Nujol) 3385, 1730, 1660, 1575, 1380, 1290, 1220, 1100, 1070 and 690; δ_H 7.74–7.61 (6 H, m, Ph), 7.59–7.51 (3 H, m, Ph), 7.49–7.42 (6 H, m, Ph), 5.69 (1 H, br d, NH), 5.17 (1 H, br m, CHNH), 4.06 (2 H, q, J 7, OCH_2), 3.79 (2 H, m, OCH_2), 2.41 (1 H, br s, CHMe$_2$), 1.18 (3 H, t, J 7, CH$_2Me$), 1.06 (3H, d, J 7, CHMe), 0.75 (3 H, t, J 7, CH$_2Me$) and 0.62 (3 H, d, J 7, CHMe); δ_C 194.4 (P=C–CO), 166.9 (d, J 15, CO$_2$Et), 157.0 (NHCO), 133.2 (d, J 10, 6 x C-2 of P-Ph), 131.8 (d, J 2, 3 x C-4 of P-Ph), 128.5 (d, J 13, 6 x C-3 of P-Ph), 126.1 (d, J 94, 3 x C-1 of P-Ph), 70.0 (d, J 110, P=C), 60.4 (OCH$_2$), 60.3 (d, J 8, CHNH), 58.8 (OCH$_2$), 32.3 (CHMe$_2$), 20.7(CHMe), 15.9 (CHMe), 14.6 (CH$_2Me$) and 13.9 (CH$_2Me$); δ_P +17.8; m/z (CI) 520 (M+H$^+$, 100%), 474 (31), 375 (34) and 263 (31).

i. *Ethyl 4(S)-ethoxycarbonylamino-6-methyl-3-oxo-2-triphenyl phosphoran-ylideneheptanoate* **303h**

Reaction as in a. using N-ethoxycarbonyl-(S)-leucine (1.06 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol),

EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.23 g, 45%) as colourless crystals; m.p. 105–107 °C (Found: C, 69.6; H, 7.0; N, 2.5. $C_{30}H_{34}NO_5P$ requires C, 69.8; H, 6.8; N, 2.6%); $[\alpha]_D^{20}$ +17.1 (c 0.935 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3360, 3260, 1720, 1670, 1580, 1260, 1100, 1050 and 690; δ_H 7.75–7.61 (6 H, m, Ph), 7.56–7.50 (3 H, m, Ph), 7.48–7.42 (6 H, m, Ph), 5.56 (1 H, m, NH), 5.41 (1 H, m, CHNH), 4.04 (2 H, q, J 7, OCH$_2$), 3.72 (2 H, m, OCH$_2$), 1.78 (2 H, m, CH$_2$CH), 1.34 (1 H, m, CHMe$_2$), 1.17 (3 H, t, J 7, CH$_2$Me), 1.11 (3 H, d, J 5, CHMe), 0.93 (3 H, d, J 6, CHMe) and 0.73 (3 H, t, J 7, CH$_2$Me); δ_C 195.4 (P=C–CO), 166.8 (d, J 15, CO$_2$Et), 156.6 (NHCO), 133.1 (d, J 10, 6 x C-2 of P-Ph), 131.7 (d, J 2, 3 x C-4 of P-Ph), 128.5 (d, J 13, 6 x C-3 of P-Ph), 126.3 (d, J 94, 3 x C-1 of P-Ph), 69.2 (d, J 110, P=C), 60.3 (OCH$_2$), 58.7 (OCH$_2$), 54.9 (d, J 8, CHNH), 43.7 (NCHCH$_2$), 25.1 (CHMe$_2$), 24.0 (CHMe), 21.8 (CHMe), 14.6 (CH$_2$Me) and 13.9 (CH$_2$Me); δ_P +17.9; m/z (CI) 534 (M+H$^+$, 100%), 488 (93), 431 (14), 412 (7), 375 (30), 319 (5), 274 (20), 263 (39), 228 (28), 185 (8), 158 (8) and 47 (9).

j. *Ethyl 4(S)-ethoxycarbonylamino-5(S)-methyl-3-oxo-2-triphenyl phosphor--anylideneheptanoate* **303i**

Reaction as in a. using *N*-ethoxycarbonyl-(S,S)-isoleucine (1.06 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.34 g, 48%) as colourless crystals; m.p. 148–149 °C (Found: C, 69.4; H, 6.8; N, 2.5. $C_{31}H_{36}NO_5P$ requires C, 69.8; H, 6.8; N, 2.6%); $[\alpha]_D^{20}$ +5.9 (c 1.0 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3390, 1695, 1650, 1580, 1470, 1440, 1340, 1298, 1280, 1220, 1098, 1065, 750 and 690; δ_H 7.78–7.61 (6 H, m, Ph), 7.59–7.50 (3 H, m, Ph), 7.47–7.31 (6 H, m, Ph), 5.55 (1 H, m, NH), 5.46 (1 H, m, CHN), 4.03 (3 H, q, J 7, OCH$_2$), 3.78 (2 H, m, OCH$_2$), 1.68 (1 H, m, CH), 1.17 (3 H, t, J 7, OCH$_2$Me), 1.10–0.91 (3 H, m, CH$_2$Me), 0.87 (2 H, m,

CHCH_2), 0.74 (3 H, t, J 7, OCH$_2$$Me$) and 0.58 (3 H, d, J 7, CHMe); δ_C 194.5 (P=C–CO), 166.8 and 166.7* (d, J 14, CO$_2$Et), 156.9 (NHCO), 133.1 (d, J 10, 6 x C-2 of P-Ph), 131.6 (d, J <2, 3 x C-4 of P-Ph), 128.5 (d, J 12, 6 x C-3 of P-Ph), 126.2 and 126.15* (d, J 93, 3 x C-1 of P-Ph), 70.3 and 69.8* (d, J 110, P=C), 60.3 (OCH$_2$), 58.7 (OCH$_2$), 60.5 and 57.2* (d, J 8, CHNH), 39.4 and 38.8* (NCHCH), 27.8 and 22.8* (CHCH_2), 16.8 (CHMe), 14.6 (OCH$_2$$Me$), 13.9 (OCH$_2$$Me$) and 12.9 and 12.1* (CHCH$_2$$Me$); δ_P +18.7, 18.6*; m/z (CI) 534 (M+H$^+$, 75%), 458 (9), 412 (6), 375 (11), 326 (17), 312 (11), 294 (5), 281 (22), 266 (23), 215 (48) and 236 (100).

k. *Ethyl 4(S)-ethoxycarbonylamino-3-oxo-5-phenyl-2-triphenyl phosphoran-ylidenepentanoate* **303j**

Reaction as in a. using N-ethoxycarbonyl-(S)-phenylalanine (1.24 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) afforded the product (0.94 g, 32%) as colourless crystals; m.p. 145–147 °C (Found: C, 72.1; H, 6.2; N, 2.5. C$_{34}$H$_{34}$NO$_5$P requires C, 71.9; H, 6.0; N, 2.5%); [α]$_D^{20}$ +29.0 (c 1.015 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} (Nujol) 3410, 1715, 1650, 1580, 1500, 1295, 1240, 1095, 1080, 1050, 752, 735 and 690; δ_H 7.69–7.16 (20 H, m, Ph), 5.82 (1 H, m, CH), 5.45 (1 H, d, NH, J 9), 3.95 (2 H, q, J 7, OCH$_2$), 3.76 (2 H, q, J 7, OCH$_2$), 3.40 (1 H, half AB pattern of d, J 13, 4), 2.83 (1 H, half AB pattern of d, J 13, 8), 1.14 (3 H, t, J 7, Me) and 0.68 (3 H, t, J 7, Me); δ_C 193.7 (d, J 3, P=C–CO), 167.9 (d, J 14, CO$_2$Et), 156.0 (NHCO), 138.1 (C-1 of Ph), 133.2 (d, J 10, 6 x C-2 of P-Ph), 131.8 (d, J 2, 3 x C-4 of P-Ph), 129.7 (2 C, Ph), 128.6 (d, J 13, 6 x C-3 of P-Ph), 127.9 (2 C, Ph), 126.0 (1 C, Ph), 125.9 (d, J 94, 3 x C-1 of P-Ph), 64.5 (d, J 107, P=C), 60.2 (OCH$_2$), 58.7 (OCH$_2$), 56.7 (CH, J 9), 39.9 (CH_2Ph), 14.6 (Me) and 13.7 (Me); δ_P +17.7; m/z (CI) 567 (M$^+$, 0.6%), 522 (4), 476 (1), 430 (2), 375 (53), 347 (15), 303 (3), 262 (100), 214 (2), 183 (32), 152 (3), 108 (10) and 91 (2).

l. *Ethyl 4(R)-ethoxycarbonylamino-3-oxo-4-phenyl-2-triphenyl phosphoran--ylidenebutyrate* **303k**

Reaction as in a. using *N*-ethoxycarbonyl-(R)-phenylglycine (1.16 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded a nearly racemic product (1.30 g, 45%) as colourless crystals; m.p. 144–145 °C (Found: C, 71.9; H, 5.8; N, 2.5. $C_{33}H_{32}NO_5P$ requires C, 71.6; H. 5.8; N, 2.5%); $[\alpha]_D^{20}$ +0.6 (*c* 1.035 in CH_2Cl_2); ν_{max}/cm^{-1} (Nujol) 3400. 1700, 1640, 1320, 1220, 1165, 1105, 1090, 1045, 750, 700 and 690; δ_H 7.67–7.20 (20 H, m, Ph), 6.74 (1 H, d, *J* 8, NH), 6.21 (1 H, br d, *J* 8, NCH), 4.00 (2 H, m, OCH$_2$,), 3.71 (2 H, m, OCH$_2$), 1.10 (3 H, t, *J* 7, Me) and 0.67 (3 H. t, *J* 7, Me); δ_C 191.3 (P=C–*C*O), 166.6 (d, *J* 14, *C*O$_2$Et), 155.6 (NHCO), 140.6 (C-1 of Ph), 133.0 (d, *J* 10, 6 x C-2 of P-Ph), 131.8 (d, *J* 2, 3 x C-4 of P-Ph), 128.5 (d, *J* 13, 6 x C-3 of P-Ph), 128.0 (3 C, Ph), 127.1 (2 C, Ph), 125.7 (d, *J* 93, 3 x C-1 of P-Ph), 69.6 (d, *J* 111, P=C), 60.3 (d, *J* 8, CHNH), 60.0 (OCH$_2$), 58.9 (OCH$_2$), 14.6 (Me) and 13.8 (Me); δ_P +18.1; *m/z* 554 (CI) (M+H$^+$, 100%), 508 (57), 375 (22), 294 (9), 263 (22), 248 (18), 178 (9) and 47 (8).

m. (*N-Ethoxycarbonyl-(S)-prolinoyl(ethoxycarbonyl)methylene)triphenyl--phosphorane* **304b**

Reaction as in a. using *N*-ethoxycarbonyl-(S)-proline (0.98 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.19 g, 44%) as colourless crystals; m.p. 112–114 °C (Found: C, 69.8; H, 6.5; N, 2.4. $C_{30}H_{32}NO_5P$ requires C, 69.6; H, 6.2; N, 2.7%); $[\alpha]_D^{20}$ –33.8 (*c* 0.96 in CH_2Cl_2); ν_{max}/cm^{-1} (Nujol) 1650, 1560, 1440, 1290, 1095, 1080, 750 and 690; δ_H 7.68–7.55 (6 H, m, Ph), 7.55–7.38 (9 H, m, Ph), 5.52 and 5.61 (1 H, ddd, *J* 13, 9, 2, CH), 4.04 (2 H, m, OCH$_2$), 3.72 (2 H, m, OCH$_2$), 3.40 (2 H,

m, CH$_2$), 2.36 and 2.04 (2 H, 2 x m, CH$_2$), 1.71 (2 H, m, CH$_2$), 1.18 (3 H, m, Me) and 0.68 (3 H, t, J 7, Me); δ_C 195.5 (d, J 3, P=C–CO), 195.4* (P=C–CO), 167.54 and 167.49* (d, J 15, CO_2Et), 155.0 and 154.9* (NHCO), 133.4 and 133.1* (d, J 10, 6 x C-2 of P-Ph), 131.6 and 131.5* (d, J <2, 3 x C-4 of P-Ph) 128.5 and 128.4* (d, J 13, 6 x C-2 of P-Ph), 126.7 (d, J 94, 3 x C-1 of P-Ph), 69.3 (d, J 111, P=C), 68.9* (d, J 110, P=C), 60.6 and 60.5* (OCH$_2$), 62.7 and 62.4* (d, J 8, CHNH), 58.4 and 58.3* (OCH$_2$), 47.2 and 46.9* (CH$_2$), 31.9 and 30.7* (CH$_2$), 23.8* and 22.9 (CH$_2$), 14.8 (Me) and 13.8 and 13.7* (Me); δ_P +17.4 and 17.2*; m/z (CI) 518 (M+H$^+$, 100%), 472 (95), 449 (9), 400 (42), 375 (71), 319 (9), 290 (58), 279 (73), 244 (14), 212 (49), 187 (32), 142 (52) and 47 (16).

n. *(±)Ethyl 4,7-bis(ethoxycarbonylamino)-3-oxo-2-triphenyl phosphoranyl-*
-ideneheptanoate **303l**

Reaction as in a. using racemic N,N'-bis-(ethoxycarbonyl)ornithine (1.14 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.23 g, 45%) as colourless crystals; m.p. 125–128 °C (Found: C, 65.5; H, 4.5; N, 4.65. C$_{33}$H$_{39}$N$_2$O$_5$P requires C, 65.3; H, 6.5; N, 4.6%); v_{max}/cm^{-1} (Nujol) 3320, 1710, 1645, 1550, 1260, 1020, 1030 and 690; δ_H 7.70–7.61 (6 H, m, Ph), 7.57–7.52 (3 H, m, Ph), 7.51–7.33 (6 H, m, Ph), 5.72 (1 H, br s, CH), 5.54 (2 H, br d, J 6, 2 x NH), 4.06 (4 H, m, 2 x OCH$_2$), 3.71 (2 H, m, OCH$_2$), 3.38 (2 H, m, CH$_2$), 2.11 (2 H, br m, CH$_2$), 1.64 (2 H, br m, CH$_2$), 1.17 (6 H, m, 2 x Me) and 0.63 (3 H, t, J 7, Me); δ_C 194.7 (P=C–CO), 167.1 (d, J 14, CO_2Et), 156.8 (NHCO), 156.6 (NHCO), 133.1 (d, J 10, 6 x C-2 of P-Ph), 131.9 (d, J <2, 3 x C-4 of P-Ph), 128.6 (d, J 12, 6 x C-3 of P-Ph), 126.0 (d, J 94, 3 x C-1 of P-Ph), 68.9 (d, J 109, P=C), 60.3 (2 x OCH$_2$), 58.6 (OCH$_2$), 55.0 (d, J 8, CHNH), 39.4 (NCHCH_2), 31.6 (CH$_2$), 25.6 (CH$_2CH_2$CH$_2$), 14.7 (Me), 14.6 (Me) and 13.6 (Me); δ_P +17.8; m/z (FAB)

607 (M+H+, 32%), 449 (11), 375 (7), 301 (10), 279 (24), 263 (35) 225 (100) and 47 (10).

o. *Ethyl 4(S),8-bis(ethoxycarbonylamino)-3-oxo-2-triphenyl phosphoranyli-*
-deneoctanoate **303m**

Reaction as in a. using N,N'-bis-(ethoxycarbonyl)-(S)-lysine (1.52 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.36 g, 42%) as a white foam (Found: C, 65.5; H, 6.8; N, 4.55. $C_{34}H_{41}N_2O_7P$ requires C, 65.8; H, 6.7; N, 4.5%) ; $[\alpha]_D^{23}$ +26.5 (c 0.50 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3320, 1700, 1655, 1525, 1250, 1070, 745 and 690; δ_H 7.81–7.62 (6 H, m, Ph), 7.61–7.51 (3 H, m, Ph), 7.49–7.42 (6 H, m, Ph), 5.62 (1 H, br m, NH), 5.49 (1 H, br m, NH), 5.07 (1H, br m, CH), 4.08 (4 H, m, 2 x OCH_2), 3.75 (2 H, m, OCH_2), 3.17 (2 H, m, CH_2), 1.50 (4 H, m, 2 x CH_2), 1.21 (8 H, m, CH_2 and 2 x Me) and 0.68 (3 H, t, J 7, Me); δ_C 194.5 (P=C–CO), 166.8 (d, J 14, CO_2Et), 156.8 (NHCO), 156.6 (NHCO), 133.1 (d, J 10, 6 x C-2 of P-Ph), 131.9 (d, J 2, 3 x C-4 of P-Ph), 128.5 (d, J 12, 6 x C-3 of P-Ph), 126.0 (d, J 93, 3 x C-1 of P-Ph), 69.2 (d, J 109, P=C), 60.4 (2 x OCH_2), 58.7 (OCH_2), 55.7 (d, J 8, CHNH), 40.9 (CH_2), 34.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 14.7 (Me), 14.6 (Me) and 13.7 (Me); δ_P +18.3; m/z (FAB) 621 (M+H+, 13%), 575 (8), 529 (9), 375 (100), 303 (37), 262 (21) and 183 (120).

p. *Ethyl 4(S)-ethoxycarbonylamino-3-oxo-7-thia-2-triphenyl phosphoranyli-*
-deneoctanoate **303n**

Reaction as in a. using N-ethoxycarbonyl-(S)-methionine (1.08g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.52 g, 53%) as pale pink crystals; m.p. 120–122 °C (Found: C, 65.6; H, 5.9;

N, 2.4. $C_{29}H_{30}NO_5PS$ requires C, 65.3; H, 6.2; N, 2.5%); $[\alpha]_D^{20}$ +3.1 (c 1.035 in CH_2Cl_2); ν_{max} /cm^{-1} (Nujol) 3420, 1724, 1702, 1655, 1580. 1503. 1301, 1267, 1220, 1170, 1003, 1084, 1060, 754 and 690; δ_H 7.78–7.61 (6 H. m, Ph), 7.58–7.52 (3 H, m, Ph), 7.50–7.43 (6 H, m, Ph), 5.66 (1 H, br d, NH), 5.54 (1 H, m, CH), 4.04 (2 H, q, J 7, OCH_2), 3.75 (2 H, m, OCH_2), 2.63 and 1.81 (2 H, AB pattern of m, CH_2), 2.46 (2 H, m, CH_2), 2.10. (3 H, s, SMe), 1.18 (3 H, t, J 7, Me) and 0.73 (3 H, t, J 7, Me); δ_C 193.5 (P=C–CO), 166.8 (d, J 14, CO_2Et), 156.5 (NHCO), 133.1 (d, J 9, 6 x C-2 of P-Ph), 131.9 (d, J 2, 3 x C-4 of P-Ph), 128.6 (d, J 12, 6 x C-3 of P-Ph), 125.9 (d. J 93, 3 x C-1 of P-Ph), 69.3 (d, J 112, P=C), 60.4 (OCH_2), 58.8 (OCH_2), 56.2 (d, J 8, CHNH), 35.0 (CHCH_2), 30.5 (CH_2S). 15.6 (SMe), 14.6 (Me) and 13.8 (Me); δ_P +18.4; m/z (CI) 552 (M+H$^+$, 24%), 391 (54), 381 (28), 351 (26), 308 (24), 292 (14), 279 (48), 266 (61), 250 (84), 221 (9) and 187 (10).

q. *1-Ethyl 6-methyl 4(S)-ethoxycarbonylamino-3-oxo-2-triphenyl phosph-oranylidenehexane-1,6-dioate* **303o**

Reaction as in a. using *N*-ethoxycarbonyl-(S)-aspartic acid β-methyl ester (0.49 g, 2.6 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (0.91 g, 2.6 mmol), EDCI (0.5 g, 2.6 mmol) and DMAP (0.02 g, 0.13 mmol) yielded the product (0.57 g, 40%) as a white foam. Correct microanalysis could not be obtained on this material; ν_{max} /cm^{-1} (Nujol) 3400, 1700, 1650, 1570, 1510, 1300, 1235, 1170, 1105, 1090, 770 and 690; δ_H 7.76–7.61 (6 H, m, Ph), 7.60–7.51 (3 H, m, Ph), 7.50–7.42 (6 H, m, Ph), 5.72 (2 H, br m, CHNH), 4.04 (2 H, m, OCH_2), 3.71 (2H, m, OCH_2), 3.56 (3 H, s, OMe) 3.05 (1 H, half AB pattern of d, J 16), 2.73 (1 H, half AB pattern of d, J 16, 8), 1.14 (3 H, t, J 7, Me) and 0.69 (3 H, t, J 7, Me); δ_C 192.2 (P=C–CO), 171.6 (CO_2Me), 166.9 (d, J 14, CO_2Et), 156.1 (NHCO), 133.2 (d, J 10, 6 x C-2 of P-Ph), 131.9 (d, J <2, 3 x C-4 of P-Ph), 128.6 (d, J 12, 6 x C-3 of P-Ph), 125.8 (d, J 94, 3 x C-1 of P-Ph), 69.4 (d, J 110, P=C), 60.5 (OCH_2), 58.9

(OCH$_2$). 53.6 (d, *J* 8, CH*N*H), 51.6 (OMe), 38.7 (CH*C*H$_2$). 14.6 (Me) and 13.7 (Me); δ_P +18.4; *m/z* 518 (M$^+$–OMe, 19%), 445 (18), 376 (100), 348 (48), 303 (68), 277 (67), 262 (89), 201 (26) and 183 (52).

r. *1-Ethyl 7-methyl 4(S)-ethoxycarbonylamino-3-oxo-2-triphenyl phosph-oranylideneheptane-1,7-dioate* **303p**

Reaction as in a. using *N*-ethoxycarbonyl-(S)-glutamic acid γ-methyl ester (0.52 g, 2.6 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (0.91 g, 2.6 mmol), EDCI (0.5 g, 2.6 mmol) and DMAP (0.02 g, 0.13 mmol) yielded the product (0.54 g, 38%) as a colourless foam. Correct microanalysis could not be obtained on this material; v_{max} /cm^{-1} (Nujol) 3400, 1700, 1650, 1570, 1510, 1300, 1235, 1170, 1105, 1090, 770 and 690; δ_H 7.70–7.62 (6 H, m, Ph), 7.57–7.52 (3 H, m, Ph), 7.49–7.40 (6 H, m, Ph), 5.62 (1 H, br m, NH), 5.49 (1 H, br m, CH), 4.04 (2 H, q, *J* 7, OCH$_2$), 3.71 (2 H, m, OCH$_2$), 3.66 (3H, s, OMe), 2.41 (2 H, m, CH$_2$), 2.09 (2 H, m, CH$_2$), 1.16 (3 H, t, *J* 7, Me) and 0.71 (3 H, t, *J* 7, Me); δ_C 193.6 (P=C–*C*O), 174.4 (*C*O$_2$Me), 166.7 (d, *J* 14, *C*O$_2$Et), 156.4 (NH*C*O), 133.1 (d, *J* 10, 6 x C-2 of P-Ph), 131.9 (3 x C-4 of P-Ph, *J* <2), 128.6 (d, 6 x C-3 of P-Ph, *J* 12), 125.9 (d, *J* 94, 3 x C-1 of P-Ph), 69.3 (d, *J* 110, P=C), 60.4 (OCH$_2$), 58.8 (OCH$_2$), 55.8 (d, *J* 9, *C*HNH), 51.4 (OMe), 31.1 (CH$_2$), 30.1 (CH$_2$), 14.6 (Me) and 13.7 (Me); δ_P +18.3; *m/z* 517 (M$^+$–EtOH, 58%), 431 (31), 375 (100), 302 (31), 279 (10), 262 (34), 201 (10) and 183 (34).

s. *Reaction of* N-*ethoxycarbonyl-(S)-glutamic acid*

Reaction as in a. using *N*-ethoxycarbonyl-(S)-glutamic acid (0.57 g, 2.6 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded a near 1:1 mixture of mono and bis ylides (1.2 g) as colourless crystals; (Found: C, 68.65; H, 5.7; N, 1.6. C$_{81}$H$_{81}$N$_2$O$_{15}$P$_3$ requires C, 68.7; H, 5.8; N, 1.6); v_{max}

/cm^{-1} (Nujol) 3480, 3420, 1780, 1745, 1715, 1660, 1560, 1295, 1190, 1100, 1080, 760, 720 and 690.

The mixture was rechromatographed to furnish some pure mono ylide and a mixture that was enriched in the bis ylide.

1-Ethyl 7-hydrogen 4(S)-ethoxycarbonylamino-3-oxo-2-triphenyl phosph-oranylideneheptane-1,7-dioate **303q**

δ_H 7.70–7.62 (6 H, m, Ph), 7.58–7.49 (3 H, m, Ph), 7.46–7.38 (7 H, m, Ph +OH), 5.92 (1 H, d, J 9, NH), 5.26 (1 H, br m, CH), 4.18 (2 H, m, OCH$_2$), 3.73 (2 H, m, OCH$_2$), 3.05 and 2.16 (2 H, m, CH$_2$), 2.41 (2 H, m, CH$_2$), 1.22 (3 H, t, J 7, Me) and 0.64 (3 H, t, J 7, Me); δ_C 192.8 (d, J 4, P=C–CO), 174.5 (CO$_2$H), 167.4 (d, J 14, CO$_2$Et), 151.6 (NHCO), 133.1 (d, J 10, 6 x C-2 of P-Ph), 132.0 (d, J <2, 3 x C-4 of P-Ph), 128.5 (d, J 12, 6 x C-3 of P-Ph), 125.9 (d, J 94, 3 x C-1 of P-Ph), 68.7 (d, J 110, P=C), 62.1 (OCH$_2$), 58.5 (OCH$_2$), 62.5 (d, J 9, CHNH), 31.4 (CH$_2$), 23.2 (CH$_2$), 14.2 (Me) and 13.7 (Me); δ_P +17.6.

Diethyl 2,8-bis(triphenylphosphoranylidene)-3,7-dioxo-4(S)-ethoxycarbonyl-aminononane-1,9-dioate **305**

δ_H 7.80–7.37 (30 H, m, Ph), 5.89 (1 H, d, J 9, NH), 5.56 (1 H, br m, CH), 4.01 (2 H, m, OCH$_2$), 3.76 (4 H, m, OCH$_2$), 3.01 (2 H, m, CH$_2$), 2.41 (2 H, m, CH$_2$), 1.14 (3 H, t, J 7, Me) and 0.76 (6 H, m, Me); δ_C 197.3 (d, J 4, P=C–CO), 195.0 (P=C–CO), 167.5 (d, J 16, CO$_2$Et), 166.6 (d, J 15, CO$_2$Et), 156.7 (NHCO), 133.0 (d, J 10, 12 x C-2 of P-Ph), 132.1 (d, J <2, 3 x C-4 of P-Ph), 131.9 (d, J 3, 3 x C-4 of P-Ph), 128.5 (d, J 12, 6 x C-3 of P-Ph), 128.4 (d, J 12, 6 x C-3 of P-Ph), 127.1 (d, J 94, 3 x C-1 of P-Ph), 126.3 (d, J 93, 3 x C-1 of P-Ph), 70.5 (d, J 112, P=C), 69.4 (d, J 112, P=C), 62.0 (OCH$_2$) 58.5 (OCH$_2$), 58.4 (OCH$_2$), 56.5 (d, J 9, CHNH), 36.8 (d, J 6, CH$_2$), 29.3 (CH$_2$), 14.6 (Me) and 13.7 (2 x Me); δ_P +18.0 and +17.7.

t. *Ethyl 5-ethoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene-pentanoate* **306**

Reaction as in a. using *N*-ethoxycarbonyl-β-alanine (0.84 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.34 g, 52%) as colourless crystals; m.p. 94–95 °C (Found: C, 68.1; H, 6.1; N, 2.8. $C_{28}H_{30}NO_5P$ requires C, 68.4; H, 6.2; N, 2.9%); v_{max}/cm^{-1} (Nujol) 3230, 1700, 1650, 1535, 1320, 1255, 1230, 1120, 1105, 1100, 1080, 1030, 750 and 690; δ_H 7.80–7.42 (15 H, m, Ph), 5.31 (1 H, br m, NH), 4.08 (2 H, q, *J* 7, OCH$_2$), 3.72 (2 H, q, *J* 7, OCH$_2$), 3.42 (2 H, m, CH$_2$N), 3.12 (2 H, t, *J* 7, CH$_2$), 1.25 (3 H, t, *J* 7, Me) and 0.69 (3 H, t, *J* 7, Me); δ_C 196.0 (P=C–*C*O), 167.9 (d, *J* 15, *C*O$_2$Et), 156.6 (NHCO), 133.0 (d, *J* 10, 6 x C-2 of P-Ph), 131.7 (d, *J* 2, 3 x C-4 of P-Ph), 128.6 (d, *J* 13, 6 x C-3 of P-Ph), 126.5 (d, *J* 94, 3 x C-1 of P-Ph), 71.4 (d, *J* 111, P=C), 60.2 (OCH$_2$), 58.5 (OCH$_2$), 40.0 (d, *J* 6, *C*H$_2$CH$_2$N), 37.4 (CH$_2$*C*H$_2$N), 14.8 (Me) and 13.7 (Me); δ_P +18.1; *m/z* (CI) 492 (M+H$^+$, 100%), 446 (12), 391 (29), 279 (39) and 263 (5).

u. *Ethyl 4(S)-t-butoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene-pentanoate* **303r**

Reaction as in a. using *N*-t-butyloxycarbonyl-(S)-alanine (0.90 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.05 g, 55 %) as colourless crystals; m.p. 184–185 °C (Found: C, 69.6; H, 6.8; N, 2.8. $C_{30}H_{34}NO_5P$ requires C, 69.4; H, 6.6; N, 2.7%); $[\alpha]_D^{20}$ +4.1 (*c* 0.5 in CH$_2$Cl$_2$); v_{max}/cm^{-1} (Nujol) 3380, 1720, 1650, 1550, 1300, 1105, 760 and 690; δ_H 7.81–7.64 (6 H, m, Ph), 7.56–7.50 (3 H, m, Ph), 7.48–7.42 (6 H, m, Ph), 5.76 (1 H, br d, *J* 7, NH), 5.42 (1 H, m, CH), 4.06 (2 H, q, *J* 7, OCH$_2$), 1.45 (3 H, d, *J* 6, CH*Me*), 1.15 (3 H, t, *J* 7, Me) and 1.11 (9 H, s, CMe$_3$); δ_C 194.4 (P=C–*C*O), 166.2 (d, *J* 14, *C*O$_2$Et), 155.8 (NHCO), 132.9

(d, J 10, 6 x C-3 of P-Ph), 131.7 (d, J 2, 3 x C-4 of P-Ph), 128.6 (d, J 12, 6 x C-2 of P-Ph), 126.4 (d, J 93, 3 x C-1 of P-Ph), 79.1 (CMe_3), 69.0 (d, J 109, P=C), 60.1 (OCH_2), 52.1 (d, J 7, NCH), 28.1 (3 C, CMe_3), 20.8 ($CHMe$) and 14.7 (CH_2Me) ; δ_P +17.7; m/z (CI) 520 ($M+H^+$, 100%), 474 (21), 446 (17), 420 (20), 403 (26), 347 (6), 319 (5), 303 (10), 279 (15) and 263 (14).

v. *Ethyl 4-(S)-isobutoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene--pentanoate* **303s**

Reaction as in a. using *N*-isobutyloxycarbonyl-(S)-alanine (0.90 g, 5.2 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (1.82 g, 5.2 mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.2 g, 45%) as colourless crystals; m.p. 103–104 °C (Found: C, 69.1; H, 6.5; N, 2.7. $C_{30}H_{34}NO_5P$ requires C, 69.4; H, 6.6; N, 2.7%); $[\alpha]_D^{20}$ +13.8 (*c* 0.5 in CH_2Cl_2); v_{max} /cm^{-1} (Nujol) 3490, 1710, 1650, 1545, 1320, 1255, 1230, 1120, 1105, 1100, 1090, 1050, 750 and 690; δ_H 7.81–7.62 (6 H, m, Ph), 7.57–7.52 (3 H, m, Ph), 7.49–7.42 (6 H, m, Ph), 5.76 (1 H, br d, J 7, NH), 5.46 (1 H, m, CH), 3.77 (4 H, m, 2 x CH_2), 1.83 (1 H, m, CH), 1.46 (3 H, d, J 7, $CHMe$), 0.85 (6 H, d, J 6, $CHMe_2$) and 0.75 (3 H, t, J 7, Me); δ_C 194.5 (P=C–CO), 166.4 (d, J 14, CO_2), 155.5 (NHCO), 132.5 (d, J 10, 6 x C-3 of P-Ph), 131.5 (3 x C-4 of P-Ph), 128.1 (d, J 13, 6 x C-2 of P-Ph), 125.5 (d, J 93, 3 x C-1 of P-Ph), 68.4 (d, J 110, P=C), 69.9 (OCH_2), 58.2 (OCH_2), 51.9 (d, J 8, CHN), 27.5 ($CHMe_2$), 20.6 ($CHMe$), 18.6 (2 C, $CHMe_2$) and 13.3 (CH_2Me); δ_P +18.0; m/z (CI) 520 ($M+H^+$, 100%), 474 (10), (13), 375 (12), 263 (19) and 187 (15).

w. *(±)-t-Butyl 4-ethoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene--pentanoate* **307a**

Reaction as in a. using racemic *N*-ethoxycarbonylalanine (0.84 g, 5.2 mmol), (t-butoxycarbonylmethylene)triphenylphosphorane (1.96 g, 5.2

mmol), EDCI (1.0 g, 5.2 mmol) and DMAP (0.03 g, 0.26 mmol) yielded the product (1.54 g, 54%) as colourless crystals; m.p. 160–162 °C (Found: C, 69.2; H, 6.6; N, 2.6. $C_{30}H_{34}NO_5P$ requires C, 69.4; H, 6.6; N, 2.7%); ν_{max} /cm^{-1} (Nujol) 3450, 1700, 1670, 1550, 1290, 1105, 1090, 1050, 760 and 690; δ_H 7.71–7.54 (6 H, m, Ph), 7.53–7.46 (3 H, m, Ph), 7.45–7.35 (6 H, m, Ph), 5.45 (1 H, m, NH), 5.39 (1 H, m. CH), 3.89–3.65 (2 H. m, OCH$_2$), 1.42 (3 H, d, J 7, CHMe), 1.37 (9 H, s, CMe_3) and 0.74 (3 H, t, J 7, Me); δ_C 195.5 (P=C–CO), 166.7 (d, J 15, CO$_2$), 155.3 (NHCO), 133.0 (d, J 9, 6 x C-2 of P-Ph), 131.7 (d, J <2, 3 x C-4 of P-Ph), 128.6 (d, J 13, 6 x C-3 of P-Ph), 126.2 (d, J 93, 3 x C-1 of P-Ph), 78.3 (CMe$_3$), 68.9 (d, J 112, P=C), 58.6 (OCH$_2$), 52.0 (d, J 8, CHNH), 28.4 (3 C, CMe_3), 20.2 (CHMe) and 13.8 (Me); δ_P +17.9; m/z (CI) 520 (M+H$^+$, 12%), 446 (5), 375 (100), 347 (8), 303 (22) and 262 (8).

x. t-Butyl *4(S)-t-butoxycarbonylamino-3-oxo-2-triphenylphosphoranylidene-pentanoate* **307b**

Reaction as in a. using *N*-t-butyloxycarbonyl-(S)-alanine (0.45 g, 2.6 mmol), (t-butoxycarbonylmethylene)triphenylphosphorane (0.98 g, 2.6 mmol), EDCI (0.50 g, 2.6 mmol) and DMAP (0.02 g, 0.16 mmol) yielded the product (0.76 g, 53%) as colourless crystals; m.p. 165–166 °C (Found: C, 70.2; H, 7.05; N, 2.5. $C_{32}H_{38}NO_5P$ requires C, 70.2; H, 7.0; N, 2.6%); $[\alpha]_D^{20}$ +5.5 (*c* 0.50 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} (Nujol) 3410, 1705, 1675, 1590, 1350, 1160, 1100, 1080, 1040, 720 and 690; δ_H 7.77–7.64 (6 H, m, Ph), 7.58–7.41 (9 H, m, Ph), 5.58 (1 H, br d, J 7, NH), 5.36 (1 H, m, CH), 1.42 (3 H, d, J 7, CHCH_3), 1.38 (9 H, s, Me$_3$) and 1.12 (9 H, s, NHCO$_2$Me$_3$); δ_C 194.8 (P=C–CO), 166.2 (d, J 15, CO$_2$), 155.2 (NHCO), 132.9 (d, J 10, 6 x C-3 of P-Ph), 131.6 (d, J 2, 3 x C-4 of P-Ph), 128.5 (d, J 12, 6 x C-2 of P-Ph), 126.5 (d, J 93, 3 x C-1 of P-Ph), 79.0 (CCH$_3$), 78.1 (CCH$_3$), 69.0 (d, J 109, P=C), 51.8 (d, J 8, CH), 28.4 (3 C, CMe_3), 28.2 (3 C, CMe_3) and 20.7 (CHMe); δ_P +17.7;

m/z 403 (M$^+$–CH(Me)NHCO$_2$Bu^t, 42%), 347 (100). 303 (27), 262 (13) and 183 (12).

4. FVP of γ-Amino β-Oxo Ylides: Preparation of Acetylenic *N*-Alkoxycarbonyl Amino Acid Esters

a. *Ethyl 4(S)-(benzoxycarbonylamino)pent-2-ynoate* **308a**

FVP of the ylide **303a** (500 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (72 mg, 29%) as a yellow oil; (Found: C, 65.7; H, 6.6; N, 5.4; M+H$^+$, 276.1226. C$_{15}$H$_{17}$NO$_4$ requires C, 65.4; H, 6.2; N, 5.1%; M+H$^+$, 276.1236); [α]$_D^{23}$ –30.3 (*c* 0.615 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} 3318, 2983, 2245, 1709, 1526, 1254, 1064, 770 and 708; δ_H 7.38 (5 H, s, Ph), 5.11 (2 H, s, OC*H$_2$*Ph), 4.99 (1 H, br d, N*H*), 4.70 (1 H, m, C*H*), 4.22 (2 H, q, *J* 7, OCH$_2$), 1.47 (3 H, d, *J* 7, CH*Me*) and 1.30 (3 H, t, *J* 7, Me); δ_C 155.0 (CO$_2$), 153.2 (NHCO), 136.0 (C-1 of Ph), 128.6 (2 C, Ph), 128.3 (1 C, Ph), 128.2 (2 C, Ph), 86.8 (OC*C*≡C), 74.4 (OCC≡*C*), 67.2 (O*C*H$_2$Ph), 62.2 (O*C*H$_2$Me), 38.8 (N*C*H), 21.6 (CH*Me*) and 14.0 (OCH$_2$*Me*); *m/z* (CI) 276 (M+H$^+$, 26%), 232 (100), 147 (8) and 91 (9).

b. *Ethyl 4(S)-(benzoxycarbonylamino)-5methylhex-2-ynoate* **308b**

FVP of the ylide **303b** (509 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (81 mg, 30%) as a yellow oil (Found: C, 65.6; H, 7.2; N, 6.3; M+H$^+$, 304.1551. C$_{17}$H$_{21}$NO$_4$ requires C, 67.3; H, 7.0; N, 4.6%; M+*H*, 304.1549); [α]$_D^{23}$ –34.4

(c 0.545 in CH_2Cl_2); ν_{max} /cm^{-1} 3330, 2970, 2240, 1715, 1535, 1302, 1260, 1050, 750 and 690; δ_H 7.38 (5 H, s, Ph), 5.14 (2 H, s, OCH_2Ph), 5.02 (1 H, br d, NH), 4.55 (1 H, m, NHCH), 4.24 (2 H, q, J 7, OCH_2), 1.99 (1 H, m, CHMe$_2$), 1.33 (3 H, t, J 7, Me) and 1.03 (6 H, d, J 7, CHMe_2); δ_C 155.5 (CO$_2$), 153.3 (NHCO), 136.1 (C-1 of Ph), 128.6 (2 C, Ph), 128.3 (1 C, Ph), 128.2 (2 C, Ph), 85.2 and 81.6* (OC$C\equiv$C), 76.0 and 75.8* (OCC$\equiv C$), 67.3 (OCH_2Ph), 62.1 (OCH_2Me), 49.2 (NCH), 33.0 (CHMe$_2$), 18.6 (CHMe), 17.9 (CHMe) and 14.0 (OCH$_2$$Me$); m/z (CI) 304 (M+H$^+$, 51%), 360 (92), 232 (100), 188 (14) and 171 (16).

c. *Ethyl 4(S)-(benzoxycarbonylamino)-6-methylhept-2-ynoate* **308c**

FVP of the ylide **303c** (361 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (68 mg, 30%) as a yellow oil.(Found: C, 68.0; H, 8.1; N, 4.5; M+H$^+$, 318.1707. $C_{18}H_{23}NO_4$ requires C, 68.1; H, 7.3; N, 4.4%; M+H$^+$, 318.1705): $[\alpha]_D^{22}$ –26.7 (c 0.49 in CH_2Cl_2); ν_{max}/cm^{-1} 3320, 2960, 2240, 1710, 1530, 1245, 1030, 750 and 700; δ_H 7.35 (5 H, s, Ph), 5.12 (2 H, s, OCH_2Ph), 4.93 (1 H, br s, NH), 4.68 (1 H, m, NHCH), 4.22 (2 H, q, J 7, OCH_2), 1.78 (1 H, m, CH_2CH), 1.62 (2 H, m, CHCH_2), 1.30 (3 H, t, J 7, Me) and 0.94 (6 H, d, J 7, CHMe_2); δ_C 155.3 (CO$_2$), 153.3 (NHCO), 136.1 (C-1 of Ph), 128.6 (2 C, Ph), 128.3 (1 C, Ph), 128.2 (2 C, Ph), 86.5 and 83.4* (OC$C\equiv$C), 75.0 and 71.2* (OCC$\equiv C$), 67.2 (OCH_2Ph), 62.1 (OCH_2Me), 44.3 (CH$_2$), 41.8 (NCH), 24.9 (CHMe$_2$), 22.4 (CHMe), 22.1 (CHMe) and 14.0 (OCH$_2$$Me$); m/z (CI) 318 (M+H$^+$, 26%), 274 (100), 246 (13) and 202 (10).

d. Ethyl 3-((S)-(1-benzoxycarbonylpyrrolidin-2-yl)propynoate 311a

FVP of the ylide **304a** (352 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph_3PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (90 mg, 48%) as a pale yellow oil; (Found: C, 68.0; H, 6.6; N, 4.6. $C_{17}H_{19}NO_4$ requires C, 67.8; H, 6.4; N, 4.7%); $[\alpha]_D^{22}$ –114.4 (c 1.01 in CH_2Cl_2); ν_{max} /cm^{-1} 3400, 2980, 2240, 1705, 1410, 1355, 1250, 1180, 1120, 1090, 750 and 700; δ_H 7.34 (5 H, m, Ph), 5.18 (2 H, m, OCH_2Ph), 4.68 (1 H, m, CHN), 4.22 (2 H, q, J 7, OCH$_2$), 3.44 (2 H, m, CHCH_2), 2.12 (4 H, m, CH$_2$CH$_2$) and 1.30 (3 H, t, J 7, Me); δ_C 154.4 and 154.1* (NCO), 153.3 (CO$_2$). 136.5 (C-1 of Ph), 128.4 (2 C, Ph), 128.0 (1 C, Ph), 127.9 (1 C, Ph), 127.8 (1 C, Ph), 87.0 and 86.8* (OC$C{\equiv}$C). 74.3 and 70.3* (OCC${\equiv}C$), 67.1 (OCH$_2$Ph), 62.0 (OCH$_2$Me), 48.4 and 47.9* (NCH), 46.3 and 45.9 (CH$_2$), 33.2 and 32.2* (CH$_2$), 24.6 and 23.8* (CH$_2$) and 14.0 (OCH$_2$$Me$); m/z (CI) 302 (M+H$^+$, 61%), 272 (11), 258 (33), 168 (12), 147 (27), 111 (28), 97 (53), 86 (32). 71 (37) and 59 (100).

e. Ethyl 4-(ethoxycarbonylamino)but-2-ynoate 308d

FVP of the ylide **303e** (202 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph_3PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (33 mg, 39%) as a yellow oil; (Found: C, 54.0; H, 6.9; N, 8.0; M+H$^+$, 200.0913. $C_9H_{13}NO_4$ requires C, 54.3; H, 6.5; N, 7.0%; M+H$^+$, 200.0922); ν_{max} /cm^{-1} 3340, 2980, 2240, 1705, 1520, 1360, 1240, 750 and 720; δ_H 4.25 (7 H, m, 3 x CH$_2$ and NH), 1.28 (3 H, t, J 7, Me) and 1.23 (3 H, t, J 7, Me); δ_C 156.0 (CO$_2$), 153.2 (NHCO), 83.5 (OC$C{\equiv}$C), 75.1 (OCC${\equiv}C$), 62.2 (OCH$_2$), 61.5 (OCH$_2$), 30.7 (NCH$_2$), 14.6 (CH$_2$$Me$) and 14.0 (CH$_2$$Me$); m/z (EI) 199 (M$^+$,

7%), 171 (6), 154 (45), 127 (100), 98 (83), 84 (82), 66 (47), 54 (68) and 49 (93).

f. Ethyl 4(S)-(ethoxycarbonylamino)pent-2-ynoate 308e

FVP of the ylide **303f** (476 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (78 mg, 32%) as a yellow oil; (Found: C, 56.6; H. 7.2; N, 6.6; M+H$^+$, 214.1083. C$_{10}$H$_{15}$NO$_4$ requires C, 56.3; H, 7.1; N, 6.6%; M+H$^+$, 214.1079); $[\alpha]_D^{20}$ –91 (c 0.695 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} 3300, 2960, 2210, 1695, 1520, 1430, 1355, 1235, 1165, 1109 and 1044; δ_H 4.99 (1 H. br s, NHCH), 4.69 (1 H, m. NHCH), 4.23 (2 H, q, J 7, OCH$_2$), 4.14 (2 H, q, J 7, OCH$_2$), 1.47 (3 H, d, J 7, CHMe), 1.31 (3 H, t, J 7, CH$_2Me$) and 1.25 (3 H, t, J 7, CH$_2Me$) ; δ_C 155.3 (CO$_2$), 153.3 (NHCO), 87.1 (OCC≡C), 74.2 (OCC≡C), 62.1 (OCH$_2$), 61.4 (OCH$_2$), 38.6 (NCH), 21.6 (CHMe), 14.5 (OCH$_2Me$) and 14.0 (OCH$_2Me$); m/z (CI) 214 (M+H$^+$, 79%), 168 (100) and 142 (16).

g. Ethyl 4(S)-(ethoxycarbonylamino)-5-methylhex-2-ynoate 308f

FVP of the ylide **303g** (501 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:1) gave the pure product (79 mg, 34%) as a yellow oil; (Found: C, 61.0; H, 7.7; N, 7.0; M+H$^+$, 242.1400. C$_{12}$H$_{19}$NO$_4$ requires C, 59.7; H, 7.9; N, 5.8%; M+H$^+$, 242.1392); $[\alpha]_D^{20}$ –49.5 (c 0.91 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} 3350, 2960, 2240, 1700, 1540, 1460, 1360, 1240, 1090, 1030 and 740; δ_H 4.92 (1 H, br d, J 8, NHCH), 4.51 (1 H, m, NHCH), 4.22 (2 H, q, J 7, OCH$_2$), 4.14 (2 H, q, J 7, OCH$_2$), 1.96 (1 H, m, CH), 1.31 (3 H, t, J 7, Me), 1.26 (3 H, t, J 7, Me) and 1.02 (6 H, d, J 7,

CHMe_2); δ_C 156.0 and 156.6* (CO$_2$), 153.6* and 153.4 (NHCO), 86.9* and 85.6 (OCC≡C), 75.9 and 75.2* (OCC≡C), 62.1 and 62.0* (OCH$_2$), 61.4* and 60.1 (OCH$_2$), 49.7 and 47.7* (NCH), 33.3* and 33.2 (CHMe$_2$), 18.8* and 18.6 (CHMe), 18.0 and 17.8* (CHMe), 14.5 (OCH$_2Me$) and 14.0 (OCH$_2Me$); m/z (CI) 242 (M+H$^+$, 92%), 224 (9), 213 (21), 196 (1000, 170 (27), 153 (21) and 57 (44).

h. Ethyl 4(S)-(ethoxycarbonylamino)-6-methylhept-2-ynoate 308g

FVP of the ylide **303h** (450 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:1) gave the pure product (77 mg, 36%) as a yellow oil; (Found: C, 61.8; H, 8.2; N, 6.9; M+H$^+$, 256.1556. C$_{13}$H$_{21}$NO$_4$ requires C, 61.2; H, 8.3; N, 5.5%; M+H$^+$, 256.1549); $[\alpha]_D^{20}$ –74.5 (c 0.865 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} 3340, 2460, 2240, 1700, 1530, 1370, 1245, 1050 and 760; δ_H 5.15 and 5.31 (1 H, 2 x br d, NH CH), 4.64 and 4.81 (1 H, m, NHCH), 4.22 (2 H, q, J 7, OCH$_2$), 4.17 (2 H, q, J 7, OCH$_2$), 1.78 (1 H, m, CH$_2$CH), 1.48 (2 H, t, J 7, CH$_2$), 1.31 (3 H, t, J 7, Me), 1.26 (3 H, t, J 7, Me) and 0.95 (6 H, d, J 7, CHMe_2); δ_C 156.0* and 155.7 (CO$_2$), 153.6* and 153.4 (NHCO), 88.2* and 86.9 (OCC≡C), 74.8 and 74.4 (OCC≡C), 62.1 and 62.0* (OCH$_2$), 61.9* and 61.4 (OCH$_2$), 44.6* and 44.3 (CH$_2$CH), 41.6* and 40.2 (NCH), 24.9* and 24.8 (CHMe$_2$), 22.5* and 22.3 (CHMe), 22.1 (CHMe), 14.5 (OCH$_2Me$) and 14.0 (OCH$_2Me$); m/z (CI) 256 (M+H$^+$, 98%), 228 (11), 210 (100), 198 (12), 167 (15) and 57 (23).

i. Ethyl 4(S)-(ethoxycarbonylamino)-5-(S)-methylhept-2-ynoate 308h

FVP of the ylide **303i** (440 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product.

Chromatography on silica (ether/hexane, 1:1) gave the pure product (80 mg, 38%) as a yellow oil; (Found: C, 61.3; H, 9.3; N, 5.7; M+H+ 256.1547. $C_{13}H_{21}NO_4$ requires C, 61.2; H, 8.3; N, 5.5%; M+H+, 256.1549); $[\alpha]_D^{20}$ +9.1(c 0.52 in CH_2Cl_2); ν_{max} /cm^{-1} 3310, 2960, 2230, 1710, 1530, 1240, 1040 and 750; δ_H 5.34 and 5.06 (1 H, 2 x m, NHCH), 4.79 and 4.62 (1 H, 2 x m, NHCH), 4.24 (2 H, m, OCH$_2$), 4.15 (2 H, m, OCH$_2$), 1.76-1.58 (1 H, m, HCH), 1.27 (5 H, m, MeCHCH_2), 1.00 (3 H, d, J 7, Me) and 0.94 (3 H, t, J 7, Me); δ_C 155.9* and 155.7 (CO$_2$), 153.4 and 153.3* (NHCO), 86.1 and 85.3* (OC$C\equiv$C), 76.0* and 75.6 (OCC$\equiv$$C$), 62.1 and 62.0* (OCH$_2$), 61.4 (OCH$_2$), 47.8* and 47.6 (N$C$H), 39.6* and 39.4 (NCH$C$H), 25.8* and 25.2 (CH$CH_2$), 15.1 and 14.7* (CH$Me$), 14.5 (OCH$_2$$Me$), 14.0 (OCH$_2$Me) and 11.5 and 11.4* (CHCH$_2$$Me$); m/z (CI) 256 (M+H+, 67%), 228 (37), 210 (31) and 184 (11).

j. Ethyl 3-((S)-(1-ethoxycarbonylpyrrolidin-2-yl)propynoate 311b

FVP of the ylide **304b** (501 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (110 mg, 48%) as a yellow oil; (Found: C, 60.9; H, 7.6; N, 6.8; M+H+, 240.1226. $C_{12}H_{17}NO_4$ requires C, 60.2; H, 7.2; N, 5.9%; M+H+, 240.1236); $[\alpha]_D^{20}$ –137.7 (c 0.535 in CH_2Cl_2); ν_{max} /cm^{-1} 2960, 2220, 1700, 1410, 1330, 1250, 1120, 1090, 770 and 750; δ_H 4.68 (1 H, m, NCH), 4.59 (2 H, m, OCH$_2$), 4.16 (2 H, m, OCH$_2$), 3.44 (2 H, m, CH$_2$), 2.13 (4 H, m, CH$_2$CH$_2$) and 1.29 (6 H, t, J 7, 2 x Me); δ_C 154.7* and 154.5 (NCO), 153.5 (CO$_2$), 87.1 (OC$C\equiv$C), 74.1 and 70.1* (OCC$\equiv$$C$), 62.0 (OCH$_2$), 61.5 (OCH$_2$), 48.2* and 47.7 (N$C$H), 46.1 and 45.8* (CH$_2$), 33.2 and 32.4* (CH$_2$), 24.6* and 23.8 (CH$_2$) 14.7 (OCH$_2$$Me$) and 14.0 (OCH$_2$$Me$); m/z (CI) 240 (M+H+, 55%), 212 (98), 194 (70), 167 (100), 138 (77), 94 (33) and 70 (39).

k. *Ethyl 4(S)-(isobutoxycarbonylamino)pent-2-ynoate* **308i**

FVP of the ylide **303s** (500 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (77 mg, 33%) as a pale yellow oil; (Found: C, 57.7; H. 8.4; N, 5.1; M+H$^+$, 242.1392. $C_{12}H_{19}NO_4$ requires C, 59.7; H. 7.9; N, 5.8%, M+H$^+$, 242.1401); $[\alpha]_D^{23.4}$ –9.1 (*c* 0.615 in CH$_2$Cl$_2$); ν_{max} /cm^{-1} 3320. 2970, 2250, 1715, 1530, 1470, 1370, 1255, 1055, 1025, 780 and 755; δ_H 4.97 (1 H, m, NH), 4.69 (1 H, m, NCH), 4.23 (2 H, q, *J* 7, OCH$_2$), 3.86 (2 H. d, *J* 6, C*H*$_2$CH), 2.92 (1H, m, C*H*Me$_2$), 1.48 (3 H, d, *J* 7, CH*Me*), 1.31 (3 H. t, *J* 7, CH$_2$*Me*) and 0.93 (6 H, d, *J* 7, Me); δ_C 155.5 (CO$_2$), 153.3 (NHCO). 87.1 (OC*C*≡C), 74.3 (OCC≡*C*). 71.6 (NHCO$_2$*C*H$_2$), 62.1 (OCH$_2$), 38.7 (NCH), 28.0 (*C*HMe$_2$), 19.2 (2 x Me) 21.6 (NCH*Me*) and 14.0 (OCH$_2$*Me*); *m/z* (CI) 242 (M+H$^+$, 100%).

l. *Ethyl 5-(ethoxycarbonylamino)pent-2-ynoate* **312**

FVP of the ylide **306** (504 mg, 600 °C. 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave a mixture of solid and oil at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ether/hexane, 1:2) gave the pure product (107 mg, 49%) as a pale yellow oil. (Found: C, 56.6; H, 7.3; N, 6.4. $C_{10}H_{15}NO_4$ requires C, 56.3; H, 7.1; N, 6.6%); ν_{max} /cm^{-1} 3330, 2980, 2240, 1700, 1540, 1360, 1250, 1070, 1030 and 750; δ_H 5.16 (1 H, br s, NH), 4.22 (2 H, q, *J* 7, OCH$_2$), 4.12 (2 H, q, *J* 7, OC*H*$_2$), 3.38 (2 H, q, *J* 7, NHC*H*$_2$), 2.57 (2 H, t, *J* 7, CH$_2$), 1.31 (3 H, t, *J* 7, Me) and 1.24 (3 H, t, *J* 7, Me); δ_C 156.5 (CO$_2$), 153.5 (NHCO), 87.1* and 86.1 (OC*C*≡C), 74.3 and 74.2* (OCC≡*C*), 62.0 (OCH$_2$), 61.1 (OCH$_2$), 38.9 (≡C*C*H$_2$), 20.3 (N*C*H$_2$), 14.6 (CH$_2$*Me*) and 14.0 (CH$_2$*Me*); *m/z* 213 (M$^+$, 15%), 185 (20), 168 (40), 141 (14), 122 (31), 102 (100), 84 (29) and 66 (22).

5. Reactions of Acetylenic Amino Acid Esters

Hydrobromination

a. *(E) and (Z)-Ethyl 3-bromo-4(S)-(ethoxycarbonylamino)pent-2-enoate* **313**

To a solution of ethyl 4(S)-(ethoxycarbonylamino)pent-2-ynoate **308e** (0.12 g, 0.56 mmol) in dry methylene chloride (5 cm^3) was added a solution of hydrobromic acid in acetic acid (45% w/v) (0.20 cm^3, 1.1 mmol) and the mixture stirred overnight at RT. The solvent was evaporated under vacuum and the residue was chromatographed (SiO$_2$, Ethyl acetate/hexane, 1:1) gave the pure product (0.13 g, 80%) as a yellow oil (Found: ^{79}Br–M+H$^+$, 294.0347. C$_{10}$H$_{16}$BrNO$_4$ requires M+H, 294.0340); v_{max} /cm^{-1} 3320, 2980, 1710, 1625, 1520, 1445, 1330, 1300, 120, 1170, 1090, 1050, 1030, 865 and 750; δ_H 6.57 and 6.36* (1 H, 2 x s, CH), 5.74 and 5.61 (1 H, 2 x s, NH), 5.73 and 4.49 (1 H, 2 x s, NHC*H*), 4.14 and 4.10 (2 H, m, OCH$_2$), 4.041 and 4.042 (2 H, m, OCH$_2$), 1.29 (3 H, d, *J* 7, Me), 1.21 and 1.16 (3 H, t, *J* 7, Me) and 1.14 (3 H, t, *J* 7, Me); δ_C 164.1 and 163.6 (*C*O$_2$Et), 155.4 (2 x NHCO), 151.7 and 143.4* (=*C*Br), 123.5 and 119.6 (=CH), 61.2 and 61.0 (OCH$_2$), 54.9 and 48.6 (NCH), 20.3 and 19.6 (CH*Me*), 14.6 (CH$_2$*Me*) and 14.2 (CH$_2$*Me*); *m/z* 294 (^{79}Br–M+H$^+$, 94%), 146 (26), 116 (35), 99 (34), 90 (48), 73 (85), 59 (53) and 46 (5).

Hydrogenation: Preparation of GABA Analogues

b. *Ethyl 4(S)-aminopentanoate* **314a**

To a solution of ethyl 4(S)-(benzoxycarbonylamino)pent-2-ynoate **308a** (80 mg, 0.29 mmol) in methanol (10 cm^3) was added Pd/C catalyst (80 mg) and the mixture stirred under a hydrogen atmosphere. After stirring overnight the mixture was filtered through a celite pad and the solvent

removed. Chromatography on silica (methanol/ether, 2:1) gave the pure product (31 mg, 74%) as a yellow oil; $[\alpha]_D^{25.5}$ −2.5 (c 0.50 in MeOH) (Found: M+H$^+$, 146.1179. $C_7H_{15}NO_2$ requires M+H, 146.1181); v_{max} /cm^{-1} (Nujol) 3400, 1730, 1600, 1505, 1275. 1188 and 1020; δ_H 7.52 (2 H, br s, NH$_2$), 4.14 (2 H, q, J 7, OCH$_2$), 3.47 (1 H, m, CH), 2.51 (2 H. t. J 7, COCH$_2$), 2.17 and 1.98 (1 H, 2 x m, CH$_2$), 1.43 (3 H, d, J 5, CHMe) and 1.25 (3 H. t, J 7, OCH$_2$Me); δ_C 172.7 (CO$_2$), 60.8 (OCH$_2$), 47.8 (CH), 30.4 (COCH$_2$), 29.7 (CH$_2$CH), 18.5 (CHMe) and 14.2 (Me); m/z (CI) 146 (M+H$^+$, 100%).

(±)-Ethyl 4-aminopentanoate

This was prepared as in b. using ethyl (±)-4-(benzoxycarbonyl-amino)pent-2-ynoate the racemic analogue of **308a**) (100 mg, 0.36 mmol) and Pd/C catalyst (100 mg) to give the title compound (38 mg. 72%) as an oil. Spectroscopic properties are identical to the non-racemic compound.

c. Ethyl 4(R)-amino-5-methylhexanoate 314b

This was prepared as b. using ethyl 4(S)-(benzoxycarbonylamino)-5-methylhex-2-ynoate **308b** (88 mg, 0.29 mmol) and Pd/C catalyst (88 mg) to give the title compound (40 mg, 72%) as colourless crystals; m.p. 101–102 °C; $[\alpha]_D^{25.5}$ +7.2 (c 0.50 in MeOH); (Found: M+H$^+$, 174.1498. $C_9H_{19}NO_2$ requires M+H, 174.1494); v_{max} /cm^{-1} (Nujol) 3340, 1725, 1640, 1540, 1260, 1180, 1100,1040 and 800; δ_H 7.96 (2 H, br s, NH$_2$), 4.13 (2 H, q, J 7, CH$_2$), 3.14 (1 H, m, NCH), 2.62 (2 H, t, J 7, COCH$_2$), 2.02 (3 H, m, CH + CH$_2$), 1.25 (3 H, t, J 7, OCH$_2$Me), 1.10 (3 H, d, J 5, CHMe) and 1.08 (3 H, d, J 5, CHMe); δ_C 172.5 (CO$_2$), 60.7 (OCH$_2$), 57.3 (NCH), 30.52 (CH), 30.48 (COCH$_2$), 25.0 (CH$_2$CH), 18.1 (CHMe), 18.0 (CHMe) and 14.2 (OCH$_2$Me); m/z (CI) 174 (M+H$^+$, 100%), 128 (8) and 102 (6).

d. *Ethyl 4(R)-amino-6-methylheptanoate* **314c**

This was prepared as in b. using ethyl 4(S)-(benzoxycarbonylamino)-6-methylhept-2-ynoate **308c** (94 mg, 0.30 mmol) and Pd/C catalyst (94 mg) to give the title compound (39 mg, 70%) as colourless crystals; m.p. 124–125 °C; $[\alpha]_D^{25.5}$ +6.9 (*c* 0.50 in MeOH); (Found: M+H$^+$, 188.1644. $C_{10}H_{21}NO_2$ requires M+H, 188.1650); ν_{max} /cm^{-1} (Nujol) 3390, 1730, 1600, 1510, 1275, 1190 and 1020; δ_H 8.93 (2 H, br s, NH$_2$), 4.14 (2 H, q, *J* 7, OCH$_2$), 3.37 (1 H, m, NCH), 2.59 (2 H, t, *J* 7, COCH$_2$), 2.04 (2 H, m, CH$_2$), 1.88 and 1.70 (2 H, 2 x m, CH$_2$), 1.49 (1 H, m, CH), 1.25 (3 H, t, *J* 7, OCH$_2$*Me*) and 0.95 (6 H, d, *J* 7, CH*Me$_2$*); δ_C 172.5 (CO$_2$), 60.7 (OCH$_2$), 50.2 (NCH), 42.1 (CH*C*H$_2$), 30.1 (CO*C*H$_2$), 28.2 (CH$_2$), 24.4 (CH), 22.4 (CH*Me*), 22.2 (CH*Me*) and 14.2 (OCH$_2$*Me*); *m/z* (CI) 188 (M+H$^+$, 100%).

e. *Ethyl 3-((S)-pyrrolidin-2-yl)propanoate* **315**

This was prepared as b. using ethyl 3-((S)-1-benzoxycarbonyl--pyrrolidin-2-yl)propynoate **311a** (90 mg, 0.30 mmol) and Pd/C catalyst (90 mg) to give the title compound (40 mg, 78%) as a yellow oil; $[\alpha]_D^{25.5}$ –8.6 (*c* 1.0 in MeOH); (Found: M+H$^+$, 172.1339. $C_9H_{17}NO_2$ requires M+H, 172.1338); ν_{max} /cm^{-1} 3440, 2960, 2750, 2500, 1730, 1630, 1450, 1420, 1375, 1280, 1190 and 1025; δ_H 8.90 (1 H, br s, NH), 4.09 (2 H, q, *J* 7, OCH$_2$), 3.61 (1 H, m, NCH), 3.40 (2 H, m, CH$_2$), 2.57 (2 H, t, *J* 8, COCH$_2$), 2.05 (5 H, m, 2 x CH$_2$ and 1 H of C*H$_2$*CH), 1.71 (1 H of C*H$_2$*CH, m) and 1.26 (3 H, t, *J* 7, Me); δ_C 172.3 (CO$_2$), 60.8 (OCH$_2$), 59.8 (NCH), 44.6 (CH$_2$), 31.5 (CH$_2$), 30.3 (CH$_2$), 27.1 (CH$_2$), 23.4 (CH$_2$) and 14.2 (Me); *m/z* (CI) 172 (M+H$^+$, 100%) and *m/z* (EI) 170 (M–H$^+$, 6%), 126 (14), 84 (6) and 70 (100).

6. Preparation of Mosher Acid Derivatives

These derivatives were prepared by a modification of the method by Mosher and co-workers[156] as illustrated by the example below. The * denotes the minor diastereomer

a. Derivative of Ethyl 4(S)-aminopentanoate 314a

A solution of (S)-α-methoxy-α-trifluoromethylphenylacetyl chloride **316** (156 mg, 0.62 mmol) in dry toluene (2 cm^3) under a nitrogen atmosphere was cooled to 0 °C. DMAP (76 mg, 0.62 mmol) and **314a** (30 mg, 0.21 mmol) in dry toluene (2 cm^3) were then added and the mixture stirred at RT for 2 h. The reaction mixture was recooled to 0 °C and washed sucessively with 1M HCl (1 cm^3) and saturated NaHCO$_3$ (1 cm^3). The organic phase was dried and concentrated under vacuum to give the Mosher's acid derivative which was analysed without further purification; δ_H 7.59 (2 H, m, Ph), 7.50 (3 H, m, Ph), 6.81 and 6.74* (1 H, d, *J* 8, NH), 4.05 (3 H, m, NCH + OCH$_2$), 3.41 and 3.38* (3 H, d, *J* 2, OMe), 2.28 (2 H, m, COCH$_2$), 1.81 (2 H, m, CH$_2$), 1.25 (3 H, t, *J* 7, OCH$_2$*Me*) and 1.20 and 1.17* (3 H, d, *J* 6, CH*Me*) ; δ_C 173.3 and 173.2* (CO), 165.8 and 165.78* (CO$_2$), 132.7 (d, *J* 17, C-1 of Ph,), 129.5 (1 C, Ph), 128.6 (2 C, d, *J* 4, Ph), 127.7 (2 C, d, *J* 5, Ph), 124.0 (q, *J* 290, CF$_3$) 84.1 (q, *J* 26, *C*CF$_3$), 60.6 (OCH$_2$), 54.9 (OMe), 45.4 (NCH), 31.4 and 31.3* (CH$_2$), 31.0 (CH$_2$), 20.85 and 20.77* (CH*Me*) and 14.2 (OCH$_2$*Me*); δ_F –70.46 and –70.51*; e.e. = 70%.

Derivative of (±)-Ethyl 4-aminopentanoate

This was prepared as above using (±)-ethyl 4-aminopentanoate (30 mg, 0.21 mmol), **316** (156 mg, 0.62 mmol) and DMAP (76 mg, 0.62 mmol) to give the Mosher's acid derivative as an oil; δ_H, δ_C and δ_F as above.

b. *Derivative of Ethyl 4(S)-amino-5-methylhexanoate* **314b**

This was prepared as in a. using **314b** (20 mg, 0.12 mmol), **316** (88 mg, 0.35 mmol) and DMAP (42 mg, 0.35 mmol) to give the Mosher's acid derivative as an oil; δ_H 7.56 (2 H, m, Ph), 7.40 (3 H, m, Ph), 6.69 and 6.56* (1 H, br d, J 8, NH), 4.06 (2 H, m, OCH$_2$), 3.82 (1 H, m, CHN), 3.44 and 3.39* (3 H, d, J 2, OMe), 2.20 (2 H, m, COCH$_2$), 1.84 (2 H, m, CH$_2$), 1.63 (1 H, m, CH), 1.20 (3 H, t, J 7, Me), 0.94 (3 H, d, J 6, CHMe) and 0.92 (3 H, d, J 6, CHMe); δ_C 173.6 (CO), 166.4 (CO$_2$), 133.1 (d, J 17, C-1 of Ph), 129.6 (Ph), 128.7 (2 C, d, J 4, Ph), 127.7 (2 C, d, J 5, Ph), 124.0 (q, J 290, CF$_3$), 84.2 (q, J 26, CCF$_3$), 60.6 (OCH$_2$), 55.2 (NCH), 54.2 (OMe), 39.5 (CH), 32.0 (CH$_2$), 29.8 (CH$_2$), 19.0 (CHMe), 17.8 (CHMe) and 14.2 (OCH$_2Me$); δ_F –69.68 and –69.86*; e.e. = 85%.

c. *Derivative of Ethyl 4(S)-amino-6-methylheptanoate* **314c**

This was prepared as in a. using **314c** (20 mg, 0.11 mmol), **316** (88 mg, 0.35 mmol) and DMAP (42 mg, 0.35 mmol) to give the Mosher's acid derivative as an oil; δ_H 7.53 (2 H, m, Ph), 7.31 (3 H, m, Ph), 6.64 (1 H, br s, NH), 4.07 (3 H, m, CHN and OCH$_2$), 3.39 and 3.38* (3 H, d, J 2, OMe), 2.32 (1 H, m, COCH$_2$), 1.89 (2 H, m, CH$_2$), 1.64 (1 H, m, CH), 1.41 (2 H, m, CH$_2$), 1.21 (3 H, t, J 7, OCH$_2Me$), 0.94 (3 H, d, J 6, CHMe) and 0.92 (3 H, d, J 6, CHMe); δ_C 173.9 (CO), 166.3 (CO$_2$), 132.4 (d, J 17, C-1 of Ph), 129.4 (Ph), 128.5 (2 C, d, J 4, Ph), 127.4 (2 C, d, J 5, Ph), 123.2 (q, J 288, CF$_3$) 84.1 (q, CCF$_3$, J 26), 60.8 (OCH$_2$), 55.5 (OMe), 47.6 (NCH), 44.4 (CHCH$_2$), 30.8 (CH$_2$), 30.3 (CH$_2$), 24.9 (CH), 23.0 (CHMe), 22.0 (CHMe) and 14.1 (OCH$_2Me$); δ_F –69.68 and –69.86*; e.e. >85%.

d. *Derivative of Ethyl 3-((S)-1-pyrrolidin-2-yl)propanoate* **315**

This was prepared as in a. using **315** (20 mg, 0.12 mmol), **316** (88 mg, 0.35 mmol) and DMAP (42 mg, 0.35 mmol) gave the Mosher's derivative as

an oil and as one isomer; δ_H 7.54 (2 H, m, Ph), 7.34 (3 H, m. Ph). 4.18 (3 H, m, CHN + OCH$_2$), 3.46 (1 H, m, CH), 3.42 (3 H, d, J <2, OMe). 2.36 (4 H, m), 1.85 (2 H. m), 1.70 (2 H, m), 1.59 (2 H, m) and 1.26 (3 H. t. J 7. Me); δ_C 173.6 (CO), 164.6 (CO$_2$), 132.3 (C-1 of Ph), 130.6 (Ph), 128.7 (2 C, d, J 4. Ph), 127.9 (2 C, d, J 5, Ph), 124.1 (q, J 290, CF$_3$) 84.3 (q, J 26. CCF$_3$), 60.8 (OCH$_2$), 58.4 (NCH), 55.4 (OMe), 46.1 (CHCH$_2$), 31.5 (CH$_2$). 28.5 (CH$_2$), 27.5 (CH$_2$), 24.4 (CH$_2$) and 14.2 (Me); δ_F −71.96; e.e. >95%.

7. Preparation and Pyrolysis of *N*-deprotected aminoacyl ylides

a. *(±)-Ethyl 4-amino-3-oxo-2-triphenylphosphoranylidenepentanoate* **320a**

To a solution of racemic ylide **303a** (0.40 g, 0.72 mmol) in methanol (15 cm^3) was added the Pd/C catalyst (0.1 g) and the mixture stirred under a hydrogen atmosphere for several hours. The mixture was filtered through a celite pad and the filtrate concentrated to afford the crude product. Recrystallisation from ethyl acetate yielded the product (0.26 g. 86%) as colourless crystals; m.p. 203–204 °C (Found: M$^+$−MeCHNH$_2$, 375.1158. C$_{25}$H$_{26}$NO$_3$P requires, 375.1150); ν_{max} /cm^{-1} (Nujol) 3400, 1660, 1550, 1300, 1235, 1100, 740, 710 and 690; δ_H 8.10 (2 H, br s, NH$_2$), 7.70–7.61 (6 H, m, Ph), 7.60–7.43 (9 H, m, Ph), 5.04 (1 H, br s, CH), 3.71 (2 H, m, OCH$_2$), 1.55 (3 H, d, J 7, CHMe) and 0.64 (3 H, t, J 7, OCH$_2$$Me$); δ_C 190.6 (d, J 4, P=CCO), 166.9 (d, J 13, CO$_2$), 133.4 (d, J 10, 6 x C-2 of P-Ph), 132.4 (d, J 2, 3 x C-4 of P-Ph), 129.1 (d, J 11, 6 x C-3 of P-Ph), 125.1 (d, J 94, 3 x C-1 of P-Ph), 69.7 (d, J 110, P=C), 59.1 (OCH$_2$), 52.2 (d, J 10, NCH), 17.9 (CHMe) and 13.6 (OCH$_2$$Me$); δ_P +18.1; m/z 375 (M$^+$−MeCHNH$_2$, 75%), 303 (14), 279 (23), 262 (17), 183 (10), 167 (43) and 149 (100).

b. *Ethyl 4(S)-amino-5-methyl-3-oxo-2-triphenylphosphoranylidenehexanoate* **320b**

Reaction as in a. using **303b** (0.3 g, 0.30 mmol) gave, after recrystallisation, the product (0.21 g, 89%) as colourless crystals; m.p. 120–122 °C (Found: M+H⁺, 448.2050. $C_{27}H_{30}NO_3P$ requires M+H. 448.2042): v_{max} /cm⁻¹ (Nujol) 3380, 1655, 1575, 1300, 1275, 1100, 750, 720 and 690: δ_H 8.09 (2 H, br s, NH₂), 7.81–7.63 (6 H, m, Ph), 7.61–7.48 (9 H, m, Ph). 5.00 (1 H, br s, CH), 3.75 (2 H, m, OCH₂), 2.61 (1 H. m, C*H*Me₂), 1.29 (3 H. d, *J* 7, CH*Me*), 0.81 (3 H, d, *J* 7, CH*Me*) and 0.69 (3 H. t, *J* 7, OCH₂*Me*); δ_C 189.1 (d, *J* 5, P=C–CO), 166.5 (d, *J* 13, CO₂), 133.3 (d, *J* 10, 6 x C-2 of P-Ph), 132.2 (d, *J* <2, 3 x C-4 of P-Ph), 128.8 (d. *J* 13. 6 x C-3 of P-Ph), 124.9 (d, *J* 94, 3 x C-1 of P-Ph), 70.5 (d, *J* 110, P=C), 60.5 (d, *J* 9, NCH), 59.0 (OCH₂), 30.4 (CHMe₂), 20.4 (CH*Me*), 15.1 (CH*Me*) and 13.7 (OCH₂*Me*); δ_P +18.7; *m/z* (CI) 448 (M+H⁺, 10%) and 402 (100).

c. *Ethyl 3-oxo-3-((S)-(pyrrolidin-2-yl)-2-triphenylphosphoranylidene propanoate* **321**

Reaction as in a. using ylide **304a** (0.30 g, 0.53 mmol) gave, after recrystallisation, the product (0.21 g, 90%) as colourless crystals, m.p. 105–106 °C ((Found: M+H⁺, 446.1876. $C_{27}H_{28}NO_3P$ requires M+H. 446.1885); v_{max} /cm⁻¹ (Nujol) 3480, 3410, 1660, 1545, 1300, 1240, 1165, 1100, 990, 750 and 690; δ_H 11.56 (1 H, br s, NH), 7.74–7.59 (9 H, m, Ph), 7.58–7.45 (6 H, m, Ph), 5.36 (1 H, br s, CH), 3.74 (2 H, m, OCH₂), 3.49 (1 H. m, 1 H of CH₂), 3.15 (1 H, m, 1 H of CH₂), 2.77 (1 H, m, 1 H of CH₂), 2.08 (2 H, m, CH₂), 1.68 (1 H, m, 1 H of CH₂) and 0.71 (3 H, t, *J* 7, Me); δ_C 188.1 (d, *J* 5, P=C*C*O), 166.3 (d, *J* 13, CO₂), 133.1 (d, *J* 10, 6 x C-2 of P-Ph), 132.6 (d, *J* 2, 3 x C-4 of P-Ph), 129.0 (d, *J* 11, 6 x C-3 of P-Ph), 124.9 (d, *J* 93, 3 x C-1 of P-Ph), 69.6 (d, *J* 110, P=C), 63.6 (d, *J* 10, NCH), 59.3 (OCH₂), 46.6

(CH$_2$), 32.0 (CH$_2$), 24.7 (CH$_2$) and 13.7 (OCH$_2$Me); δ_P +18.1; m/z (CI) 400 (M+H$^+$, 57%).

d. (±)-5-Methyl-3-triphenylphosphoranylidenepyrrolidine-2,4-dione 322a

FVP of the racemic ylide **320a** (202 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave ethanol in the cold trap and a white solid at the furnace exit. Recrystallisation of the crude product from ethyl acetate gave pure **322a** (120 mg, 68%) as colourless crystals; m.p. 218–219 °C. (Found: C, 74.6; H, 5.85; N, 5.0, M+H$^+$, 374.1306. C$_{23}$H$_{20}$NO$_2$P requires C, 74.0; H, 5.4; N, 3.8%, M+H, 374.1309); v_{max} /cm^{-1} (Nujol) 3320, 1600, 1310, 1260, 1200, 1100, 750, 720 and 690; δ_H 7.82–7.56 (9 H, m, Ph), 7.56–7.38 (6 H, m, Ph), 5.51 (1 H, br s, NH), 4.43 (1 H, m, CH) and 1.32 (3 H, d, J 7, Me); δ_C 197.7 (d, J 7, P=CCO), 176.3 (d, J 16, NCO), 134.0 (d, J 11, 6 x C-2 of P-Ph), 133.0 (d, J 2, 3 x C-4 of P-Ph), 128.9 (d, J 13, 6 x C-3 of P-Ph), 122.8 (d, J 93, 3 x C-1 of P-Ph), 63.2 (d, J 122, P=C), 58.2 (d, J 13, NCH) and 18.5 (Me); δ_P +10.8; m/z (CI) 374 (M+H$^+$, 100%) and 279 (5).

e. 5(S)-Isopropyl-3-triphenylphosphoranylidenepyrrolidine-2,4-dione 322b

FVP of the ylide **320b** (100 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave ethanol in the cold trap and a white solid at the furnace exit. Recrystallisation of the crude product from ethyl acetate gave pure **322b** (65 mg, 72%) as colourless crystals; m.p. 240–241 °C. (Found: C, 74.5; H, 6.0; N, 3.4. C$_{25}$H$_{24}$NO$_2$P requires C, 74.8; H, 6.0; N, 3.5%); v_{max} /cm^{-1} (Nujol) 3310, 1590, 1100, 720 and 690; δ_H 7.72–7.57 (9 H, m, Ph), 7.56–7.45 (6 H, m, Ph), 5.09 (1 H, br s, NH), 3.78 (1 H, dd, J 2, 1, NCH), 2.22 (1 H, m, CH), 1.00 (1 H, d, J 7, Me) and 0.91 (1 H, d, J 7, Me); δ_C 196.6 (d, J 7, P=CCO), 176.9 (d, J 17, NC=O), 134.1 (d, J 11, 6 x C-2 of P-Ph), 132.9 (d, J 2, 3 x C-4 of P-Ph), 128.8 (d, J 13, 6 x C-3 of P-Ph), 123.2 (d, J 93, 3 x C-1 of P-Ph),

67.4 (d, *J* 13, NCH), 64.6 (d, *J* 122, P=C), 29.8 (CH), 20.1 (Me) and 15.5 (Me); δ_P +10.8; *m/z* (CI) 402 (M+H$^+$, 100%), 279 (15), 263 (7) and 187 (15).

f. 5-(S)-3-Triphenylphosphoranylidene-1-azabicyclo[3.3.0]octane-2,4-dione 323

FVP of the ylide **321** (100 mg, 600 °C, 1.0–2.0 x 10^{-2} Torr, inlet 180–200 °C) gave ethanol in the cold trap and a white solid at the furnace exit. Recrystallisation of the crude product from ethyl acetate gave pure **323** (60 mg, 67%) as colourless crystals; m.p. 200–202 °C. (Found: M+H$^+$, 400.1456. $C_{25}H_{22}NO_2P$ requires M+*H*, 400.1466); ν_{max} /cm^{-1} (Nujol) 3310, 1590, 1100, 720 and 690; δ_H 7.83–7.56 (9 H, m, Ph), 7.56–7.38 (6 H, m, Ph), 4.04 (1 H, t, *J* 7, NCH), 3.8–3.7 (1 H, m), 3.01 (1 H, m), 2.04 (3 H, m) and 1.71 (1 H, m); δ_C 197.9 (d, *J* 8, P=C*C*O), 180.0 (d, *J* 16, N*C*O), 134.2 (d, *J* 11, 6 x C-2 of P-Ph), 133.2 (d, *J* <2, 3 x C-4 of P-Ph), 129.0 (d, *J* 13, 6 x C-3 of P-Ph), 123.0 (d, *J* 93, 3 x C-1 of P-Ph), 69.4 (d, *J* 13, NCH), 65.2 (d, *J* 116, P=C), 44.8 (CH$_2$), 28.4 (CH$_2$) and 27.2 (CH$_2$); δ_P 10.1; *m/z* (CI) 400 (M+H$^+$, 100) and 279 (5).

K   X-Ray Structure Determinations

The structure of **143b** was determined by Professor M. B. Hursthouse, EPSRC X-ray Crystallography Unit, University of Wales, Cardiff, while the structures of **144a**, **203** and **208** were determined by Dr P. Lightfoot, School of Chemistry, University of St. Andrews.

1. *1-Phenyl-2-triphenylphosphoranylidenepentane-1,3,4-trione* **143b**

A colourless crystal suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate – toluene. The following data were obtained:—

$C_{29}H_{23}O_3P$, $M = 450.44$, monoclinic space group P21/n; $a = 12.911(4)$, $b = 10.271(4)$, $c = 17.527(4)$ Å, $\beta = 101.36(2)$ °, $V = 2278.7(12)$ Å^3, $Z = 4$, $D_C = 1.313$ g cm^{-3}, R1 = 0.0408, wR2 = 0.1049 for 3397 data with $I > 2\sigma(I)$ and 299 parameters. Data were recorded at 120 K using Mo-Kα radiation and the structure was solved by direct metods and refined using full-matrix least squares analysis. The structure is illustrated in the Discussion and selected data are given in the Appendix.

2. *1,5-Diphenyl-3-triphenylphosphoranylidenepentane-1,2,4,5-tetraone* **144a**

A colourless block suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate. The following data were obtained:—

$C_{35}H_{25}O_4P$, $M = 540.58$, triclinic space group P$\overline{1}$ (#2); $a = 11.681(2)$, $b = 14.540(2)$, $c = 10.415(2)$ Å, $\alpha = 101.15(1)$, $\beta = 115.38(1)$, $\gamma = 91.95(1)$ °, $V = 1554.5(6)$ Å^3, $Z = 2$, $D_C = 1.231$ g cm^{-3}, R = 0.079, R$_W$ = 0.076 for 3569 data with $I > 3\sigma(I)$ and 406 parameters. Data were recorded at 293 K using Mo-Kα radiation and the structure was solved by direct metods and refined using full-matrix least squares analysis. The structure is illustrated in the Discussion and selected data are given in the Appendix.

3. *3,6-Bis(triphenylphosphoranylidene)-1,8-diphenyloctane-1,2,4,5,7,8-hexa-*
-one **208**

A colourless plate suitable for X-ray diffraction was obtained by slow
evaporation of a solution in $CDCl_3$. The structure showed that two molecules
of $CDCl_3$ of crystallisation were present. The following data were
obtained:—

$C_{46}H_{36}O_8P_2 \cdot 2CDCl_3$, $M = 1017.5$, triclinic space group P$\bar{1}$ (#2); a =
10.08(1), b = 14.23(2), c = 17.18(1) Å, $\alpha = 85.5(1)$, $\beta = 81.4(1)$, $\gamma = 76.20(7)$
°, V = 2364(4) Å^3, Z = 2, $D_C = 1.429$ g cm^{-3}, R = 0.054, $R_W = 0.055$ for
1999 data with $I > 3\sigma(I)$ and 578 parameters. Data were recorded at 293 K
using Mo-Kα radiation and the structure was solved by direct metods and
refined using full-matrix least squares analysis. The structure is illustrated in
the Discussion and selected data are given in the Appendix.

4. *2,5-Bis(triphenylphosphoranylidene)-1,6-diphenylhexane-1,3,4,6-tetraone*
203

A yellow crystal suitable for X-ray diffraction was obtained by
recrystallisation from ethyl acetate – toluene. The following data were
obtained:—

$C_{54}H_{40}O_4P_2$, $M = 814.86$, monoclinic space group Cc (#9); a = 32.65(1), b =
15.601(5), c = 19.141(8) Å, $\beta = 102.95(3)$ °, V = 9500(6) Å^3, Z = 8, $D_C =$
1.139 g cm^{-3}, R = 0.107, $R_W = 0.142$ for 3178 data with $I > 3\sigma(I)$ and 568
parameters. Data were recorded at 220 K using Mo-Kα radiation and the
structure was solved by direct methods and refined using full-matrix least
squares analysis. The structure is illustrated in the Discussion and selected
data are given in the Appendix.

DISCUSSION

A   Preparation and Pyrolysis of Trioxo Phosphorus Ylides

As described earlier, in section C of the Introduction, the pyrolyis of β-oxo phosphorus ylides **13** provides a versatile method for formation of a wide variey of alkynes. It was established at an early stage that for ylides **148** stabilised by both ester and keto carbonyl groups, extrusion of phosphine oxide involves the loss of the keto oxygen exclusively.[47] A probable explanation is that these compounds may exist entirely in the configuration shown with the keto carbonyl *syn* and the ester carbonyl *anti* to phosphorus.[14, 15]
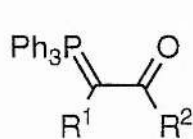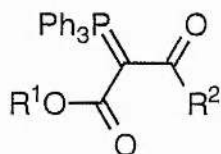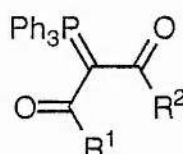
13   **148**   **82**

R^1, R^2 = Me, Ph

R^1 = H, R^2 = CF_3, C_2F_5, $C_3F_7^n$

Pyrolysis of β,β'-dioxo ylides has only been studied for a few compounds. Early work on the ylides **82** showed that selectivity was poor when R^1 and R^2 were different.[26] This observation was supported by more recent work on the fluoro compounds where a mixture of isomeric alkynes was formed.[157]

The thermal reactivity of the previously unknown higher homologues **143**, stabilised by an ester or keto function on one side of the ylide carbon and an α-diketo or α-keto ester group on the other would be valuable in understanding the structure and reactivity of oxo ylides.

1. Synthesis of β,γ,β'-Trioxo Phosphorus Ylides

Several examples of the trioxo compounds were previously synthesised by past members of the group.[158] These compounds were reprepared together with other new examples, and all the sixteen trioxo ylides were fully characterised for the first time.

The synthesis of the trioxo ylides **143** involved, initially, the preparation of a series of precursor phosphonium salts **149** and ylides **150**. These compounds were prepared by various modifications of the method reported by Michaelis and Gimborn.[1]
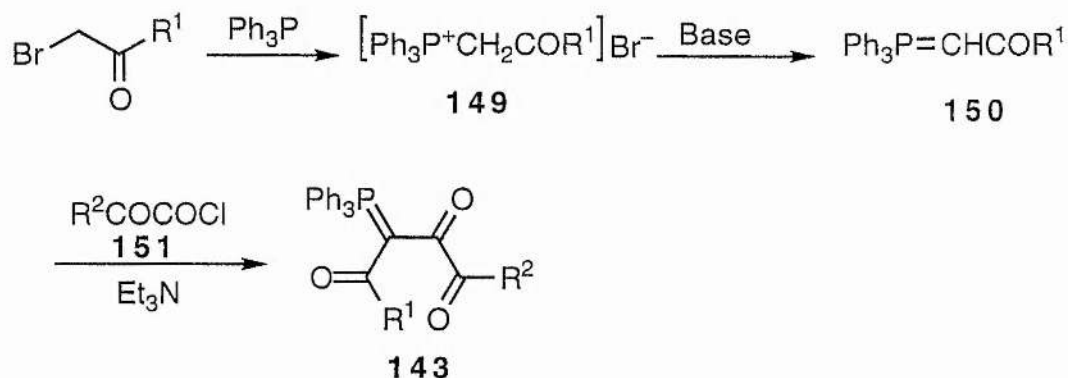
Once the mono substituted ylides **150** were obtained, the β,γ,β'-trioxo phosphorus ylides **143** were prepared by analogy with the known procedure for ylide acylation, described in section B of the Introduction. This involved the coupling of the starting phosphorane and one equivalent of the α-dioxo acid chloride **151** in dry toluene in the presence of triethylamine at room temperature. The triethylamine hydrochloride formed during the reaction was removed by washing with water. For $R^2 = Me$ it was preferable to use a solution of pyruvyl chloride in toluene prepared *in situ* by the reaction of sodium pyruvate with oxalyl chloride. Numerous attempts to obtain the pure compound where R^1 and R^2 were methyl were unsuccessful.

Sixteen examples were obtained in moderate to excellent yield as is illustrated in Table 2. All the compounds were crystalline and, because of the α-carbonyl groups, it is not surprising that these ylides were stable.

Table 2: Preparation of ylides **143**

	R^1	R^2	yield (%)	δ_P		R^1	R^2	yield (%)	δ_P
a	Ph	Ph	82	16.5	**i**	OMe	Ph	68	15.7
b	Ph	Me	58	16.6	**j**	OMe	Me	87	15.3
c	Ph	OMe	87	17.8	**k**	OMe	OMe	82	16.3
d	Ph	OEt	70	15.6	**l**	OMe	OEt	98	16.5
e	Me	Ph	51	15.6	**m**	OEt	Ph	71	15.5
f	Me	OMe	86	16.2	**n**	OEt	Me	56	15.2
g	Me	OEt	68	16.2	**o**	OEt	OMe	80	16.2
h	Bu^t	Ph	78	17.4	**p**	OEt	OEt	91	16.2

The spectroscopic properties exhibited by these phosphoranes **143** are of note. The ^{31}P NMR signals, at +15–18 ppm, were in agreement with a previous study[116] which investigated the ^{31}P NMR behaviour of the acyl methylenephosphoranes. The ^{31}P chemical shifts of the trioxo ylides **143** were equal or at a slightly higher frequency to the starting ylides **150**. This high frequency shift indicates a reduction in the electron density on the ylidic carbon which then deshields the adjacent phosphorus atom.

The IR spectra of these compounds were also examined and they are in agreement with the literature. A signal around 1500 cm^{-1}, is indicative of delocalisation of charge from the ylidic carbon through to substituents, in this

case the carbonyl group. This observation has been cited as further proof of single bond character of the carbonyl group.

The ^{13}C NMR spectra, especially the observed values of J_{P-C}, were more informative and the structures of the products were easily confirmed. The ^{13}C spectra of the series of ylides prepared are summarised in Table 3. As can be seen from the results in the Table, the chemical shift of the ylidic carbon, C-1, is very dependent on the nature of R^1. When R^1 is an acyl group (δ_C 80–86) (entries **a-h**), it is more effective at delocalising the charge, hence the higher chemical shift value of the ylidic carbon. Naturally the opposite effect may be seen with an α-ester group (entries **i-p**), where the ylidic carbon is more shielded (δ_C 66–70). Interestingly, the $^1J_{P-C}$ values in the latter group (110 Hz) are slightly larger than in the acyl series (100 Hz). Apparently R^2 is too far away to affect the ylidic carbon. Doubling of resonances caused by coupling to phosphorus is also observed throughout the P-phenyl groups and to the first carbon of R^1.

The effect of the phosphorus atom on the α-substituents in the molecule is reflected by their coupling constants and surprising trends are observed. In most of the examples, the assignments were based on the observed chemical shift values or by extrapolation across the series. Where uncertainty remained, the signals have been assigned to conform to the pattern of P–C coupling constants. In entries **a–d** (R^1 = Ph), the three-bond coupling to R^2CO is largest with smaller couplings to the other two carbonyls. The three-bond coupling, for **i–p** (R^1 = OMe, OEt), to R^2CO and the two-bond coupling to R^1CO are both large and the remaining value is small. A stark exception is observed with the ylides **e-h**, where R^1 = Me or Bu^t. The two-bond coupling to R^2COCO is now large and the remaining two values small. While there is no obvious explanation for this pattern, it may be related to substituent dependent electron distribution within the trioxo system.

Table 3: ^{13}C NMR Spectra of Trioxo Ylides **143**, δ_C (J_{P-C})

	R¹	R²	P=$\underline{C}$	$\underline{C}$O-R¹	$\underline{C}$O-COR²	CO-$\underline{C}$OR²	P–Phenyl C-1	C-2	C-3	C-4	R signals
a	Ph	Ph	84.2 (97)	193.4 (7)	190.3 (5)	193.5 (13)	124.1 (92)	133.4 (10)	128.8 (13)	132.3 (<2)	141 9 (8), 134.3, 132.7, 130.6, 129.0 (4 C), 127.9 (2 C), 127.5 (2 C)
b	Ph	Me	80.2 (99)	193.5 (8)	191.3 (5)	201.4 (11)	124.1 (92)	133.5 (10)	128.8 (13)	132.4 (3)	143.2 (8), 131.0, 128.6 (2 C), 128.1 (2 C), 25.6
c	Ph	OMe	82.3 (100)	192.9 (7)	182.3 (6)	166.2 (15)	124.1 (92)	133.5 (10)	128.9 (13)	132.4 (2)	141.8 (8), 131.1, 129.1 (2C), 127.9 (2 C), 51.4
d	Ph	OEt	82.7 (100)	193.0 (7)	182.6 (6)	165.9 (15)	124.1 (92)	133.6 (10)	128.9 (13)	132.4 (2)	141.8 (8), 131.1, 129.2 (2C), 128.0 (2 C), 61.0, 13.6
e	Me	Ph	86.3 (102)	195.2 (5)*	190.2 (13)	193.4 (5)*	124.5 (92)	133.5 (10)	128.7 (13)	132.2 (2)	133.8, 133.1, 129.7 (2 C), 128.1 (2 C), 30.2 (5)
f	Me	OMe	84.5 (104)	195.0 (6)	182.4 (13)	167.1 (6)	124.6 (93)	133.4 (10)	128.8 (13)	132.3 (2)	51.9, 29.5 (5)
g	Me	OEt	84.5 (105)	195.1 (6)	182.6 (13)	166.8 (5)	124.8 (93)	133.5 (10)	128.8 (12)	132.2 (2)	61.3, 29.5 (5), 13.8
h	Buᵗ	Ph	85.9 (102)	206.9 (3)	185.1 (19)	193.0 (<2)	125.3 (93)	133.7 (10)	128.4 (13)	131.9 (3)	134.6, 132.8, 129.9 (2 C), 127.6 (2C), 43.9 (5), 26.6 (3C)
i	OMe	Ph	69.2 (109)	167.8 (14)	192.0 (4)	194.5 (11)	124.3 (93)	133.7 (10)	128.8 (13)	132.5 (3)	134.7, 132.6, 129.1 (2 C), 128.4 (2 C), 50.1
j	OMe	Me	66.2 (109)	168.1 (14)	193.1 (4)	202.7 (11)	124.0 (93)	133.6 (10)	128.8 (13)	132.5 (3)	50.1, 25.9
k	OMe	OMe	68.0 (111)	167.8 (15)*	184.3 (6)	167.5 (14)*	124.0 (93)	133.6 (10)	128.8 (13)	132.5 (2)	51.8, 50.3
l	OMe	OEt	67.8 (111)	167.41 (15)*	184.6 (6)	167.45 (13)*	124.1 (94)	133.6 (10)	128.8 (13)	132.5 (3)	61.0, 50.3, 14.2
m	OEt	Ph	69.0 (109)	167.0 (14)	192.0 (4)	194.5 (11)	124.4 (93)	133.7 (10)	128.8 (12)	132.5 (2)	134.7, 133.6, 129.3 (2 C), 128.3 (2 C), 59.2, 13.4
n	OEt	Me	66.0 (108)	167.9 (13)	193.2 (4.5)	202.8 (10)	124.2 (93)	133.6 (10)	128.9 (14)	132.5 (3)	59.1, 26.0, 13.6
o	OEt	OMe	67.8 (110)	167.8 (14)*	184.3 (6)	167.2 (13)*	124.2 (93)	133.6 (10)	128.8 (13)	132.5 (3)	59.1, 51.7, 13.7
p	OEt	OEt	67.6 (111)	167.5 (15)*	184.7 (6)	167.2 (13)*	124.2 (93)	133.6 (10)	128.7 (13)	132.4 (2)	60.9, 59.1, 14.1, 13.7

* Assignments may be interchanged

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According to previous work in this laboratory,[159] the coupling constants between P and the α-carbonyl carbons provide valuable information about the likely reactivity of oxoylides towards pyrolysis. Only if $^2J_{C-P}$ is ≤ 10 Hz, is elimination of Ph_3PO between the ylide and that particular carbonyl possible. For the trioxo ylides also there may be some correlation between the magnitude of the coupling constants of R²COCO and behaviour during FVP.

2.   FVP of β,γ,β'-Trioxo Phosphorus Ylides

The ylides **143** were subjected to FVP at 500 °C and elimination of Ph_3PO occurred across the central position to afford the diacylalkynes **152**, separate from Ph_3PO in most cases (Table 4). Moreover no major contamination was detected, and more significantly, none of the isomeric product **154** was formed. This was expected for cases **i–p** since these compounds are assumed to exist predominantly in the form **153** indicated with the ester CO *anti* to phosphorus. The preference for product **152** rather than **154** is surprising for cases **a**, **c** and **d**.
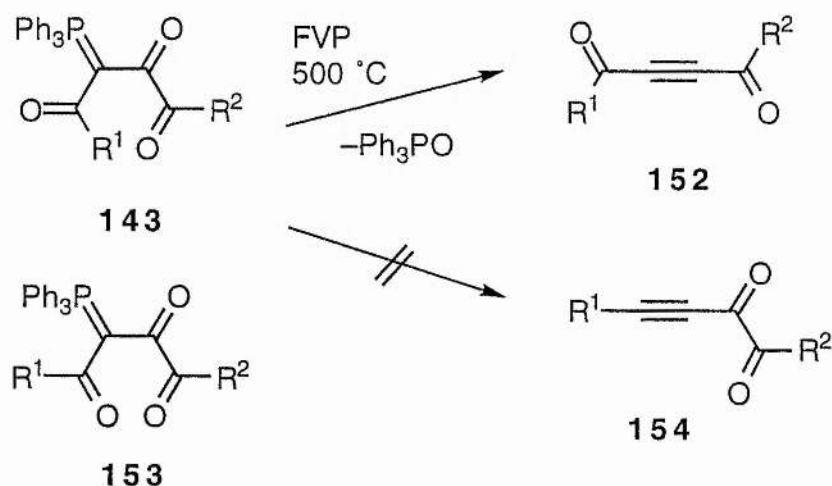
The ^{13}C NMR data of the diacylalkynes are not unusual and follow the normal pattern for compounds of this type.

Table 4: Formation, Yields and ^{13}C Data of Diacylalkynes **152**

	R^1	R^2	yield (%)	C≡C	C=O	R
a	Ph	Ph	40	85.8	176.5	135.8 (4ry), 135.2. 129.8 (2 C). 129.0 (2 C)
b	Ph	Me	0	–		
c	Ph	OMe	23	85.11. 80.08	176.0, 152.7	135.6 (4ry), 135.2. 129.8 (2 C). 129.0 (2 C), 53.4
d	Ph	OEt	44	80.5. 79.7	176.1, 152.2	135.6 (4ry), 135.2, 129.7 (2 C). 128.9 (2 C), 63.1, 14.0
e	Me	Ph	0	–		
f	Me	OMe	0	–		
g	Me	OEt	67	80.8. 78.0	182.5, 152.2	63.0, 32.3, 13.9
h	Bu^t	Ph	43	85.4. 78.2	188.8, 176.5	135.7 (4ry), 135.1. 129.6 (2C). 128.9 (2 C), 45.2, 25.6 (3 C)
i	OMe	Ph	67	(as in c)		
j	OMe	Me	38	81.0, 77.5	182.6, 152.7	53.4, 32.3
k	OMe	OMe	59	74.4	152.0	54.0
l	OMe	OEt	61	75.1, 74.3	152.3, 151.8	63.1, 53.5, 13.9
m	OEt	Ph	38	(as in d)		
n	OEt	Me	23	81.4, 78.5	183.1, 152.8	63.6, 33.0, 14.5
o	OEt	Ph	70	(as in l)		
p	OEt	OEt	63	74.7	151.8	63.1, 13.9

None of the desired alkynes were formed for **143b**, **e** and **f**. Instead indiscriminate fragmentation processes occurred, forming complex mixtures, including acetaldehyde and acetophenone (**b**), benzoic acid (**b**, **e**), benzaldehyde (**e**) and methanol (**f**). Negative results were expected for **e–f**

because of the high value of $^2J_{P-C}$ (> 10 Hz) to the central carbonyl. An extensive study in the group has shown that there is correlation between pyrolysis behaviour and $^2J_{P-C}$. FVP of stabilised ylides with a value of $^2J_{P-C}$ > 10 Hz may result in elimination of Ph$_3$P and does not generally yield the desired product. This theory does not hold for **143g** and **h** here, where $^2J_{P-C}$ is 13 Hz and 19 Hz respectively, and for **143b** ($^2J_{P-C}$ = 6 Hz). The pyrolysis was a success in the first two cases and not in the latter. Clearly, the pyrolysis behaviour of stabilised ylides in relation to $^2J_{P-C}$ values requires further investigation.

Although the method was not successful for all 16 ylides, it does allow convenient preparation of multigram quantities of some diacylalkynes. Previous work within the group has described the use of **152a** and **c** prepared in this way for cycloaddition with Bu$_3$P.CS$_2$.[14] Synthesis of a specifically ^{13}C labelled acetylenic diester **154**, which was required for a mechanistic study on the higher temperature fragmentation of acetylenic esters, was also readily achieved by this methodology.[160]

$$EtO_2C - {}^*C \equiv C - CO_2Me$$

154

$* = {}^{13}C$
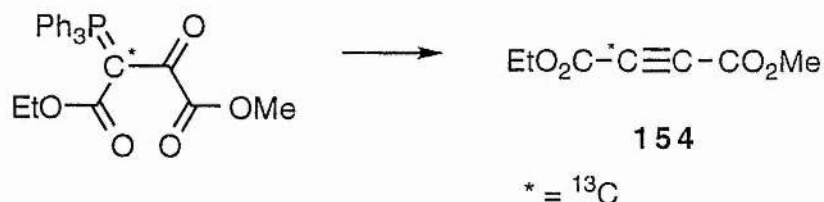
B β,γ-Dioxo Phosphonium Salts and Ylides

1. Tautomerism in β,γ-dioxo Phosphonium Salts

It is now accepted that while β-oxo ylides, the monosubstituted analogues **150** in particular, display isomerism due to restricted mobility, there is no evidence of this behaviour in the associated salts. Therefore

structure and bonding in these simple phosphonium salts has not been a controversial issue

The introduction of a second keto group in the β' position allows the 1,3-dioxo salt **156** to behave differently. Early work examined the relationship between the acidity and enolisation of different phosphonium salts.[161] Dioxophosphonium salts **156** were prepared by adding acids to the corresponding dioxo ylide **155**. It was found that the acidity of the dioxo salt **156** was substantially greater than in the monooxo salts.

$X = Cl, CF_3CO_2,$
$BF_4, ClO_4, B(Ph)_4$
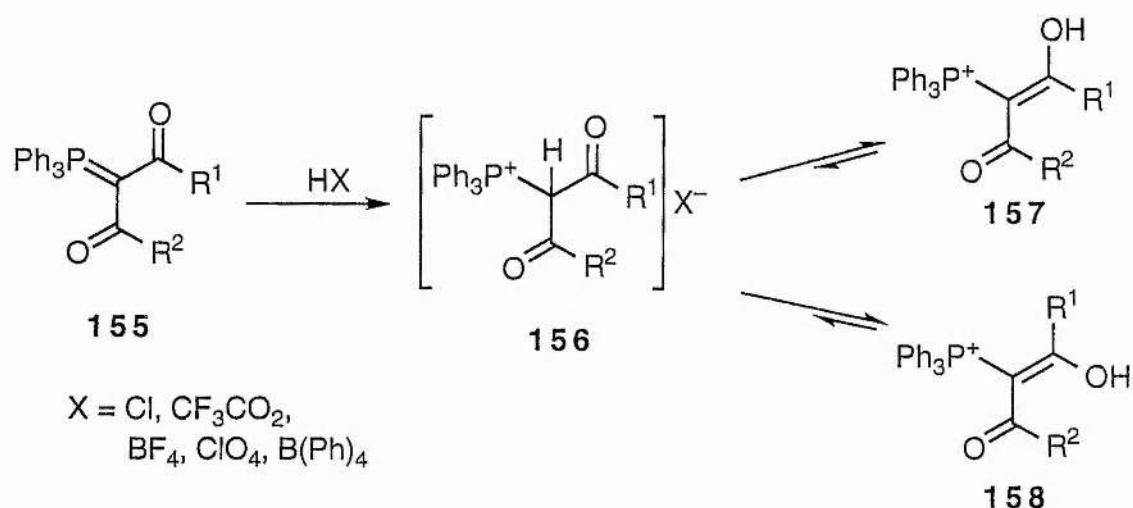
The proton NMR of the salts **156** was recorded at varying concentrations and the chemical shift of the hydroxyl group at approximately 12 ppm was found to be concentration dependent. The distinct absence of a P–C*H* signal indicated that the spectrum was of a pure enol form. This evidence together with IR data was interpreted as indicating intermolecular hydrogen bonds and that the geometry adopted is of the *Z* configuration **157**. The participation of the counter ion in hydrogen bonding was also questioned.

Further results from the same group[162] on the salt **159** found that it exists entirely in the enol form **160** both in solution and in the solid state. This *Z* configuration was confirmed by results obtained from X-ray structure

analysis on the chloro analogue. Interaction by the chloride anion provided further stabilisation.

159   **160**
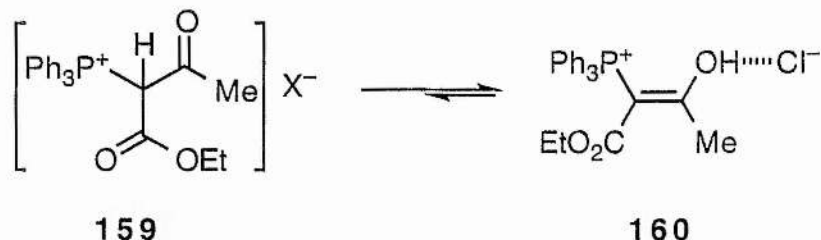
It was concluded that these α-(triphenylphosphonio)-substituted acetoacetic esters exist in the Z enol tautomeric form and display a characteristic resonance of 16–17 ppm in the ^{31}P spectrum.

The effect of different counter ions on the structure of these dioxo salts was investigated. Unexpected results were obtained with complex ions (such as BF$_4^-$, ClO$_4^-$ and BPh$_4^-$) which were not capable of forming strong hydrogen bonds. Information obtained from IR and proton NMR showed that these salts do exist in the Z enol form, however the integral of the signal arising from the hydroxyl proton corresponded to half the expected value. It was inferred that the enol structure of salts possessing complex anions is stabilised by a molecule of the conjugate base, the ylide. X-ray structure analysis of the tetrafluoroborate salt **161** provided conclusive evidence. The BF$_4^-$ anion does not participate in stabilising the enol form.

161
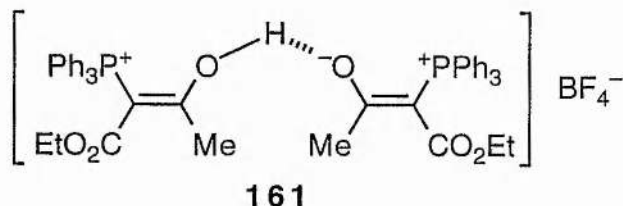
In the course of the present study on the synthesis of higher homologues of oxo ylides, the precursor, β,γ-dioxo phosphonium salts, **162-4** were required. Although reference to all three examples was found in the literature, none had been fully characterised. Only the melting point and IR of one

example 162[123] was recorded while no information on the other two, 163 and 164, was available.[125] Therefore it was pertinent to examine the NMR spectroscopic properties of the β,γ-dioxo salts and to compare them to the well researched β-oxo phosphonium salts 149.

$$\left[Ph_3P^+CH_2COCOR^1\right]Br^-$$

162 R^1 = Ph
163 R^1 = OMe
164 R^1 = OEt
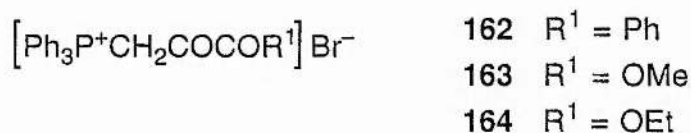
Dombrovskii[123] and co-workers reported on the elegant preparation of a range of substituted aryl β,γ-dioxo phosphonium salts and the corresponding ylides. A band at 3300–3200 in the IR spectra was attributed to possible enolisation of the dicarbonyl moiety. This was not very surprising since the system being considered is a 1,2-dioxo system and such compounds are known to exhibit keto-enol tautomerism. The structure 165 was suggested and possible E-Z geometrical isomerism was discussed. Further work from the same group showed that in the arylglyoxylylylide-γ-oxime 167 and its phosphonium salt 166 the carbonyl group participated in hydrogen bonding with the hydroxyl of the γ-oxime group.[163]

165   166   167
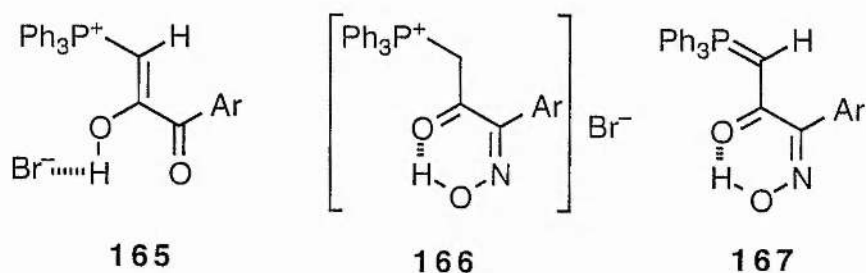
The required β, γ-dioxo phosphonium salts were readily synthesised by quarternisation of triphenylphosphine with the appropriate bromo 1,2-dioxo compound 168. The reaction, which was performed in dry toluene and at room temperature, provided the salts 162-4 in excellent yields. The salts are stable solids which display the expected analytical data.

BrCH₂COCOR¹ $\xrightarrow[\text{toluene, RT}]{\text{Ph}_3\text{P}}$ $\left[\text{Ph}_3\text{P}^+\text{CH}_2\text{COCOR}^1\right]$ Br⁻

168

162 $R^1 = Ph$
163 $R^1 = OMe$
164 $R^1 = OEt$
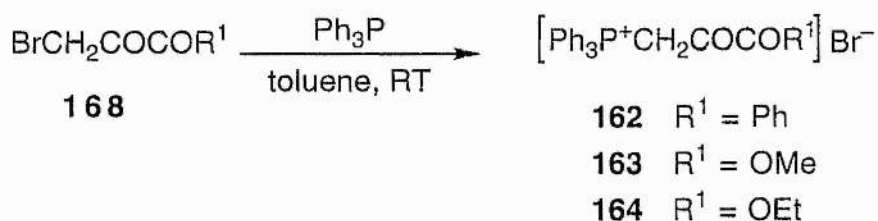
NMR spectroscopic analysis of analytically pure samples of each of the phosphonium salts clearly showed that in solution (CDCl₃) a mixture of compounds was present. This was pleasing because it provided support and conclusive evidence for the observations of the earlier workers.

The ³¹P, ¹H and ¹³C spectra were consistent with the structures proposed. Two sets of signals were observed in the ³¹P spectrum for the phenyl derivative and this was attributed to the keto form **162** and the enol structure **162a**. The enol is depicted as the Z isomer since only one enol was detected and it appears likely that steric hindrance may disfavor the alternative E enol **162b**. A broad singlet at 13.5 ppm in the ¹H NMR spectrum is consistent with the structure proposed.

In solution (CDCl₃) :

162b   **162**   **162a**
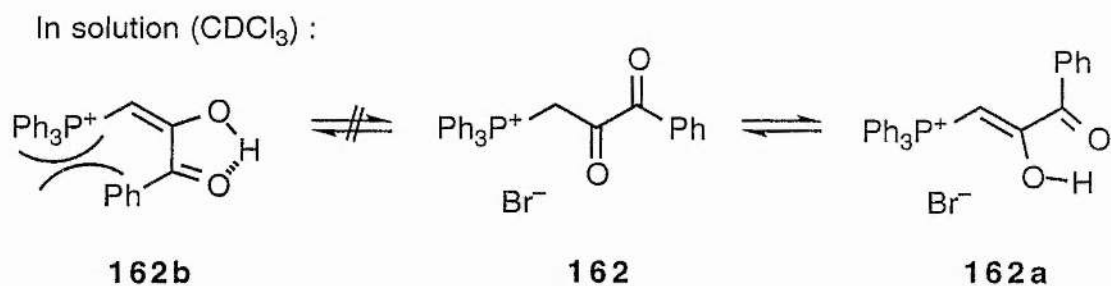
The salts bearing ester substituents behave slightly differently. Three sets of signals are observed and these have been rationalised in terms of the presence of the keto and E and Z enol forms, each of which give rise to separate NMR signals. Again both enol forms are favoured by hydrogen bonding but the unfavourable steric interaction is no longer present and indeed the E isomers **b** may be stabilised by hydrogen bonding from the alkoxy

oxygen as shown in form **c**. Two sets of broad singlets arising from the hydroxyl groups were observed in the ^{1}H NMR spectra of **163** and **164** at approximately 11.3 and 13.9 ppm arising from the two geometrical isomers.

In solution (CDCl$_3$) :

163 R^1 = OMe
164 R^1 = OEt
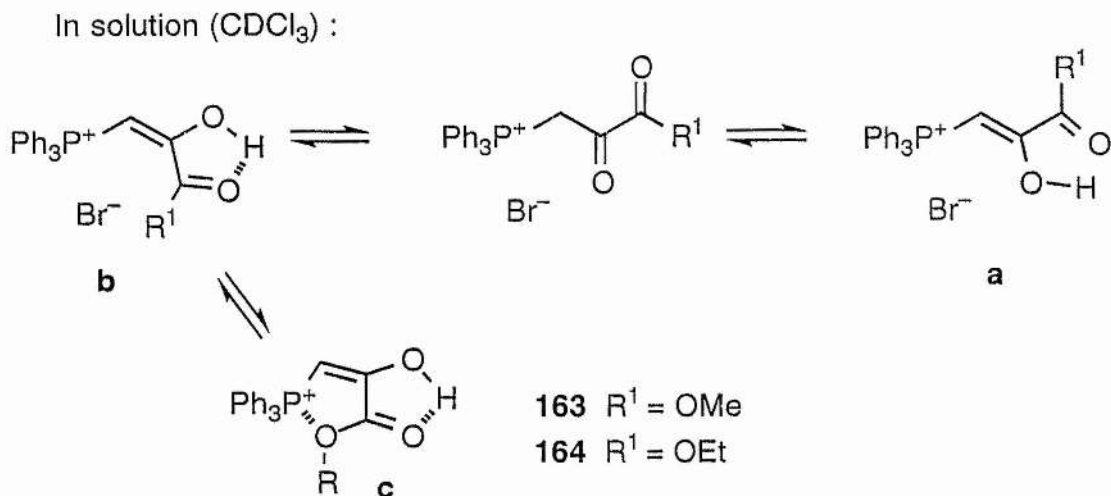
Table 5 lists the ^{31}P resonances and the isomer ratios obtained. These ratios are an averaged estimation because they were found to be dependent on concentration and temperature of the sample. A systematic study of the effect of these factors would be more informative.

Table 5: ^{31}P (CDCl$_3$) and isomer ratios of β, γ'-dioxo phosphonium salts

	R^1	δ_P (keto)	(ratio)	δ_P (Z-enol)	(ratio)	δ_P (E-enol)	(ratio)
162	Ph	22.3	42	16.7	58	—	
163	OMe	21.1	10	17.2	54	15.0	36
164	OEt	21.2	15	17.3	46	15.0	39

The ^{13}C NMR spectra were particularly interesting and provided ready confirmation of the expected structures (Table 6). Coupling with phosphorus extends throughout the P-phenyl groups and to both the carbonyl groups of the keto structure. Doublets arising from the α carbon (α to P) appear in the

151

Table 6: NMR Spectra of Phosphonium Salts **162–4**, **171** and **173**, δ_P and δ_C (J_{P-C})

	R	δ_P	δ_C			P–Phenyl				R signals
			C_α	C_β	C_γ	C–1	C–2	C–3	C–4	
162 (keto)	Ph	22.1	36.4 (56)	188.9 (21)	192.5	118.3 (89)	134.0 (10)	130.3 (13)	135.1 (2)	135.0, 133.3 (4ry), 131.5 (2C), 128.7 (2C)*
162 (Z-enol)	Ph	17.3	80.4 (106)	171.8	171.6	121.4 (94)	133.5 (11)	129.6 (13)	134.0 (3)	134.7, 130.8 (4ry), 130.4 (2C), 128.4 (2C)*
163 (keto)	OMe	21.1	37.0 (58)	185.5 (5)	159.5 (6)	117.7 (89)	133.9 (10)	130.4 (14)	135.2	54.0
163 (Z-enol)	OMe	17.2	83.2 (105)	162.3	161.0 (16)	121.5 (95)	133.4 (11)	129.9 (14)	134.2 (2)	53.8*
163 (E-enol)	OMe	15.0	82.5 (95)	162.3	164.2 (7)	119.1 (93)	134.0 (11)	130.4 (14)	135.0	53.3*
164 (keto)	OEt	21.3	36.9 (57)	185.5 (5)	159.6 (6)	117.7 (89)	134.0 (11)	130.4 (13)	135.2	63.9, 13.9
164 (Z-enol)	OEt	17.3	83.1 (105)	162.7	160.6 (16)	121.8 (95)	133.4 (11)	129.8 (13)	134.1	63.9, 14.2*
164 (E-enol)	OEt	15.1	82.1 (95)	162.7	163.8 (7)	119.3 (93)	133.1 (10)	130.4 (13)	135.0	63.1, 13.6*
171a keto end		20.4	40.2 (60)	190.8 (6)	—	118.4 (89)	134.6 (11)	130.6 (13)	135.3 (2)	—
enol end		15.0	85.8 (92)	167.9 (13)	—	120.4 (93)	133.8 (11)	129.9 (13)	134.2 (2)	—
173 enol end		16.7	109.9 (89, 3)	158.5 (2)	—	117.5 (91)	133.6 (11)	130.8 (13)	135.7 (1)	—
ylide end		12.8	65.0 (104)	174.7 (18, 3)	—	124.4 (92)	133.0 (11)	129.3 (11)	132.9	—

* Assignments of R signals between the two isomeric forms are uncertain.

152

usual range, 36 ppm ($^1J_{P-C} = 56$) for **162**. Replacing the phenyl substituent by ester groups in **163** and **164** does not cause any change in the chemical shift or coupling constant. However, these values are slightly higher than in the β-oxo phosphonium salts **149** where the signal appears at a lower chemical shift (30 ppm, $^1J_{P-C} = 93$)

A lower chemical shift value of 117 ppm for C-1 of P-phenyl (C_{ipso}) and a marked higher chemical shift value (80 ppm) for the α carbon in the enol structure distinguishes this form from the keto form. The other quaternary carbon (C=COH) appears in the usual 150–165 ppm range.

An interesting feature in the IR spectrum is the position of the carbonyl groups in the 1735 cm^{-1} and 1620 cm^{-1} regions for **163** and **164** and 1765 cm^{-1} and 1580 cm^{-1} for the phenyl analogue **162**.

In order to obtain additional information on the effect of substituents on the keto-enol isomerism of dioxo phosphonium salts, the synthesis of the diacetyl derivative **169** was attempted. The experiment was performed in the usual manner by reacting triphenylphosphine and bromodiacetyl in dry toluene at room temperature. Spectroscopic analysis of the yellow crystalline material isolated revealed that several products were formed. Recrystallisation was attempted but without success. Perhaps the use of the exact literature procedure would have been advisable.[16]

169
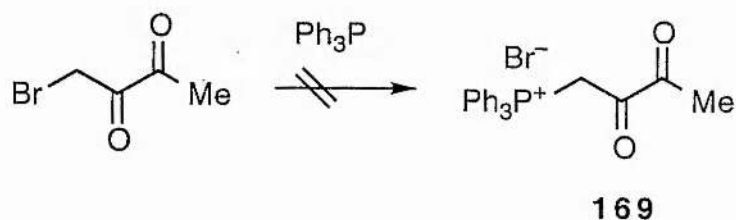
The analogous experiment with dibromodiacetyl and 2 equivalents of triphenylphosphine in toluene was also reported. The reaction was claimed to produce the unstable bis-enol-phosphonium salt **170** which did not isomerise into the diketo bisphosphonium salt **171** even after lengthy reaction times at

room temperature or when heated in toluene. Isomerisation into the stable diketo bisphosphonium salt **171** only occurred when the initial salt **170** was heated briefly in acetone. Decomposition of the enol-phosphonium salt **170** into Ph3PO, diacetyl and HBr by atmospheric moisture was thought to support the structure proposed. The absence of IR signals arising from the carbonyl functions was interpreted as further proof. It is significant that no NMR analysis of the product was reported. Similiar enol phosphonium salts, termed "quasi phosphonium salts", are known.[164]
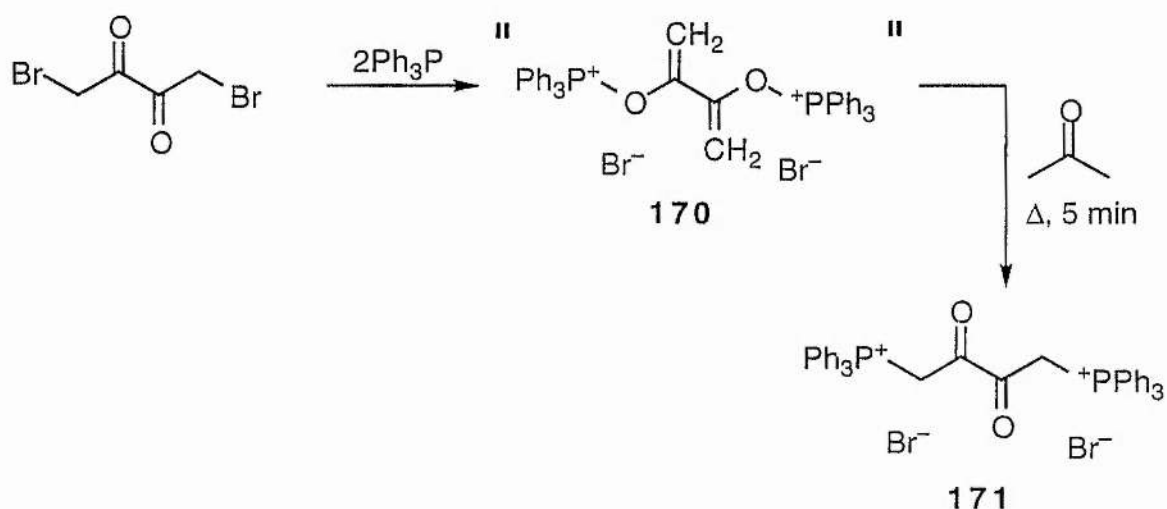
Thus, dibromodiacetyl and triphenylphosphine were reacted in toluene at room temperature. Analysis of the crystals isolated revealed **20 peaks** in the ^{31}P NMR spectrum while the ^{13}C spectrum was a forest of signals in the aromatic range (120–140 ppm). At this stage the product obtained corresponds to the "bis-enol-phosphonium salt" **170** obtained by the Russian group.[163] The next stage involved heating the initial product under reflux for 5 min in acetone. Pale yellow crystals formed on cooling (32% isolated yield) and the results of the NMR spectra and microanalysis were pleasingly in agreement with expectation for **171**. Clearly, some of the desired diketo-bis-phosphonium salt **171** was present in the original mixture and the second stage was an efficient method of purification. Although the experiment was repeated

several times, with different solvents, reaction times and temperatures, an alternative, more efficient route to the bis-phosphonium salt **171** was not found.

It is not surprising that the bis-phosphonium salt **171** also displays tautomeric behaviour in solution, i.e., it exists mainly in the structures **171a** or **171b** with one side in the keto form and the other in the enol form. Both the Z and E configurations seem possible, although the large size of the Ph$_3$P groups would tend to favour **171a** where steric hindrance is less.
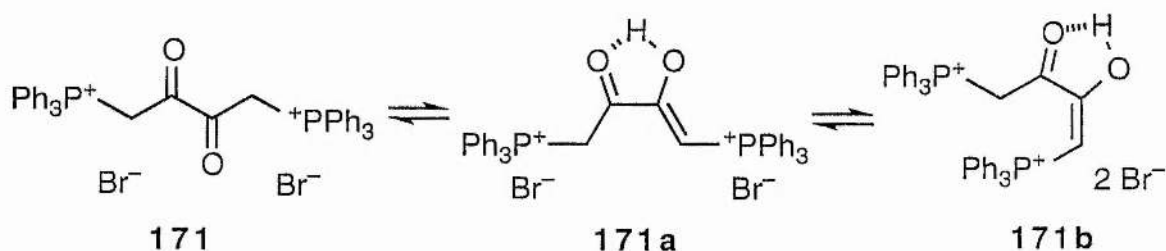
The ^{31}P spectrum contained two doublets at δ 20.4 and 15.0 ($^5J_{P-P}$ 3.3) which is consistent with one of the enol forms **171a** or **171b** and two additional signals at δ_P 22.0 and 21.1 in the range expected for the enol phosphonium functions. The ^{13}C signals expected for **171a** were present as shown in Table 6 but unfortunately the additional signals due to the species of δ_P 22.0 and 21.1 could not be unambiguously assigned.

The reaction of **171** with two equivalents of base, NaOH, was unexpected in that the desired bisylide **172** was not formed and instead the salt

155
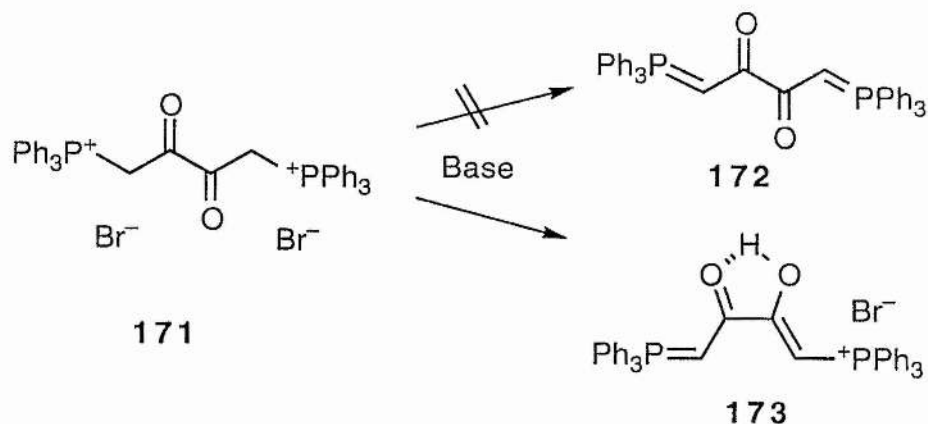
173 was isolated as the sole product. This should be expected if strong hydrogen bonds existed in the precursor molecule. The NMR spectra are unambiguous and fully support the structure 173. BuLi, a stronger base, was also ineffective in abstracting the proton.

The problem of the effect of substituents (electronic and steric effects) on enolisation of this class of phosphonium salts, may be better understood if more experiments including variable temperature solution NMR (in solvents with different polarities) and solid state NMR are undertaken. These experiments should be able to confirm the nature of the structure and bonding in solution and in the solid.

2. Preparation and Pyrolysis of β,γ-Dioxo Phosphorus Ylides

Having obtained the precursor salts 162-4, it was of interest to convert these to the corresponding ylides 174-176 and examine their pyrolysis behaviour.

$$Ph_3P=CH-C(=O)-C(=O)-R^1$$

174 R^1 = Ph
175 R^1 = OMe
176 R^1 = OEt
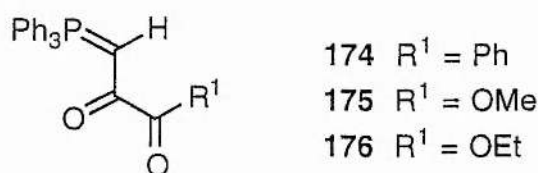
The original paper on the methyl and ethyl ester derivatives 175-6 included a report of the condensation of aldehydo-D-galactose pentaacetate with 175.[125] The product 177 is an unsaturated ketonononic acid and the

175
$$Ph_3P=CH-C(=O)-C(=O)-OMe$$

CHO
(CHOAc)$_4$
CH$_2$OAc
—Ph$_3$PO

→

177
CO$_2$Me
C=O
HC=CH
(CHOAc)$_4$
CH$_2$OAc
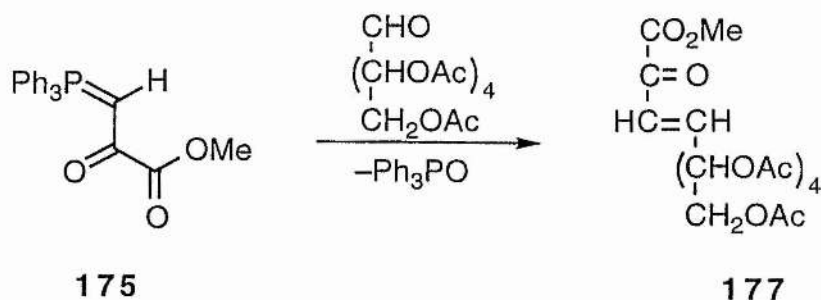
reaction serves to illustrate that it is possible to lengthen the carbon chain of carbohydrates by 3 carbon units in just a single step. Later, similar Wittig reactions with the ethyl ester ylide **176** were explored by another group.[165]

The reports on **174**, the phenylglyoxylyl analogue, have included discussions on its decomposition by water/alcohol and Wittig reactions.[123] In the hydrolysis reaction, **174** was heated under reflux for 32 hours in aqueous alcohol to afford Ph₃PO, acetaldehyde and benzoic acid. This was explained by initial formation of the hydroxy phosphonium salt **178** which fragments into benzoic acid and the phosphonium salt **179**. Rearrangement and subsequent decomposition would account for the other products, Ph₃PO and acetaldehyde.
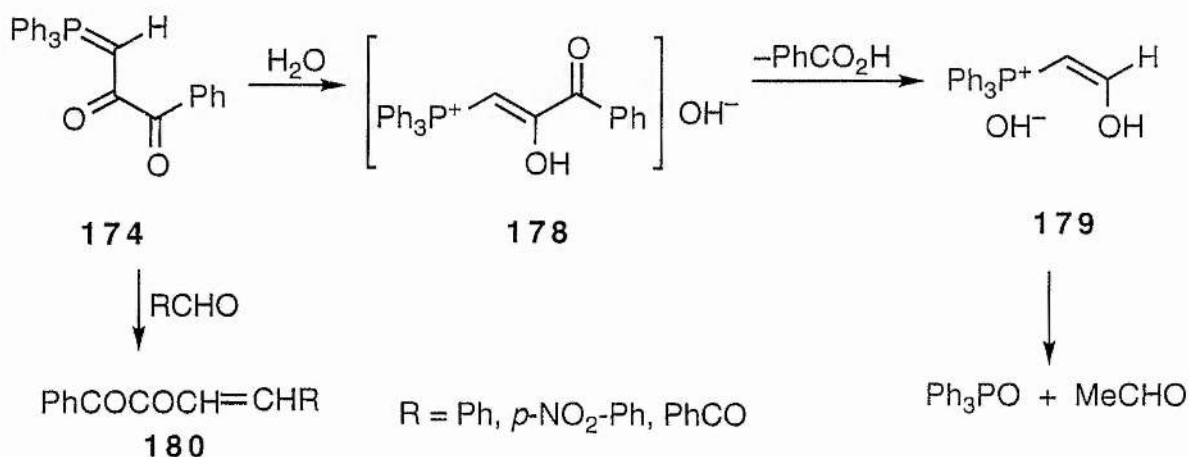
The Wittig reaction of **174** with aromatic aldehydes is uncomplicated and the unsaturated diketones such as **180** were readily obtained in moderate yield.

Another route to the ethoxy-β,γ-dioxo phosphorus ylide was later reported. Le Corre showed that the reaction of the nonstabilised ylide, methylenetriphenylphosphorane, with diethyl oxalate led to good yields of the desired compound **176** and the interesting amido ylide **181** was also prepared

in this way.[165] The substituted β, γ-dioxo ylide **182** is likewise accessible from the ethylidene ylide and dimethyl oxalate.[166]

176 R¹ = OEt
181 R¹ = NH₂

182
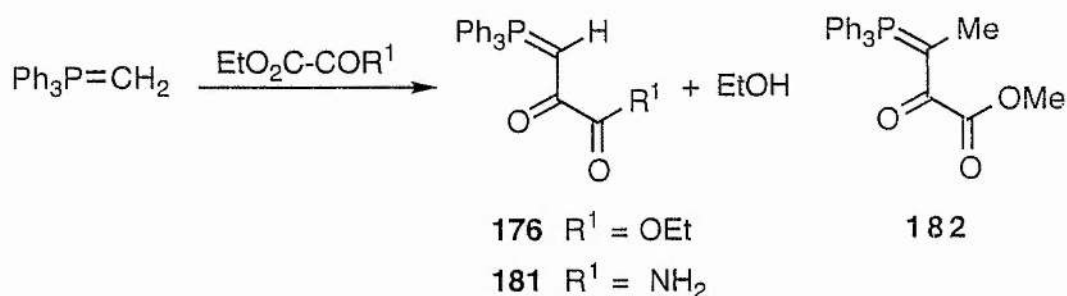
Reactions of **176** with aryl furandiones were recently shown to afford the cyclic oxalyl ylides **183**.[167] The latter were found to be resistant to Wittig reactions. The high degree of delocalisation possible for the electron density of the ylide carbon could account for this.

176

183
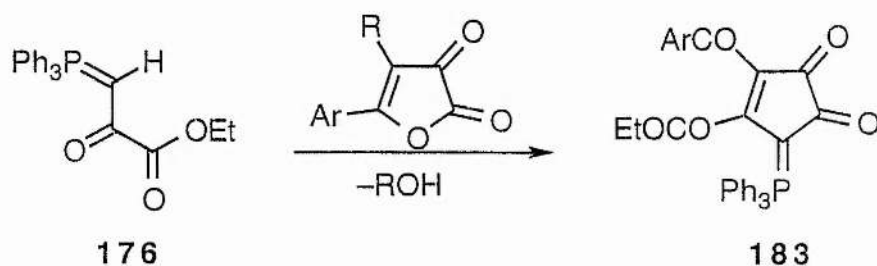
Treatment of **176** with hydrazine hydrate in ethanol furnished the hydrazide **184**. Again, no Wittig products were obtained in the reaction with aldehydes, instead the hydrazones **185** were formed. Reaction of **184** with the aryl furandiones gives the product **186** as a mixture of tautomers. Subsequent reaction with hydrazine hydrate provided **187**.

In the original reports, the β,γ-dioxo phosphorus ylides were prepared by reacting the precursor β,γ-dioxo phosphonium salts with a base.[123, 125] It was this method that was eventually employed here and good yields of the products **174-6** were obtained. Initially, the reaction of methylene
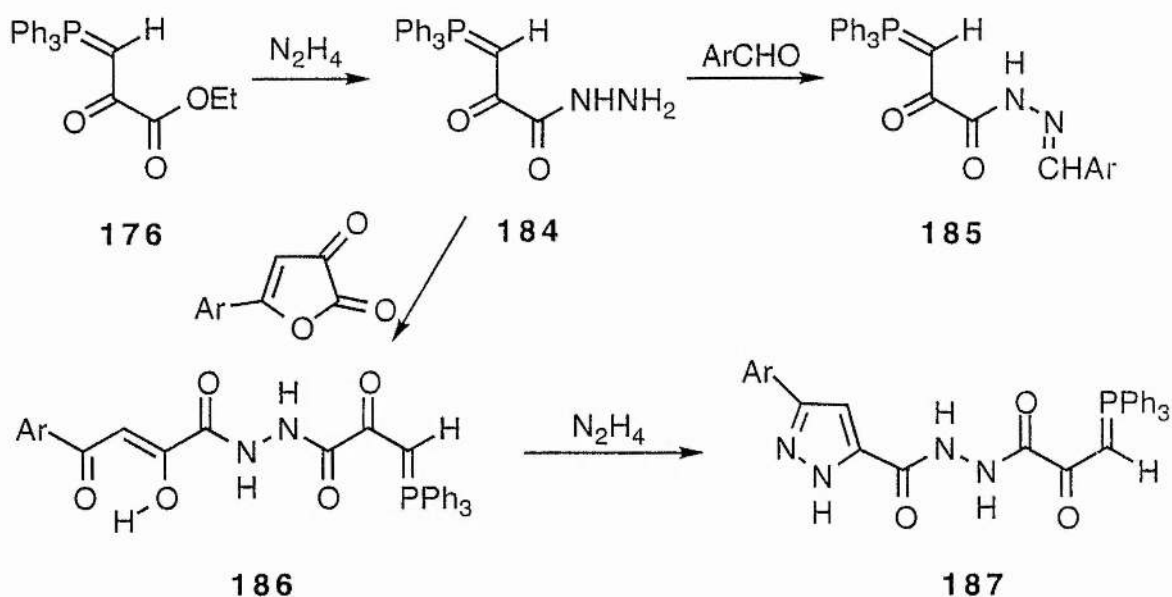
triphenylphosphorane and the α-dioxo acid chloride seemed promising. However, a brown intractable gum was isolated from the reaction and the NMR spectra showed a mixture of products to be present.
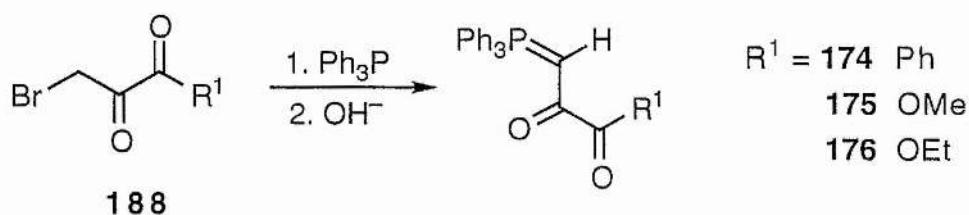
It is interesting that the melting points of the salts **162-164** are lower than the corresponding ylides **174-176**. The opposite is true for phosphonium salts such as **149** possessing one carbonyl and for their ylides **150**.

Although these three β,γ-dioxo ylides have been known for some time, their NMR spectroscopic properties were not previously recorded. The spectroscopic features of **174-6** differ significantly from the simple β-oxo ylides **150** in the position of the ylidic carbon which appears at higher chemical shift in the ^{13}C spectra (Table 7). Another interesting aspect is that the $^{3}J_{P-C}$ coupling (20 Hz) is far greater than the $^{2}J_{P-C}$ coupling. This

Table 7: 13C NMR Spectra of Ylides **174–6** and **144**, δ_C (J_{P-C})

	R^1	R^2	P=$\underline{C}$	$\underline{C}$OCOR^1	$\underline{C}$OR^1	$\underline{C}$OCOR^2	$\underline{C}$OR^2	P–Phenyl				R^1 and R^2 signals
								C-1	C-2	C-3	C-4	
174	Ph	—	54.8 (105)	183.5 (<2)	195.7 (17)	—	—	125.6 (92)	133.0 (10)	129.0 (12)	132.6 (3)	135.0, 132.7 (4ry), 130.3, 128.0
175	OMc	—	63.7 (103)	171.2 (<2)	164.7 (19)	—	—	123.3 (92)	133.1 (10)	129.4 (13)	133.0 (<2)	52.4
176	OEt	—	57.5 (107)	173.9 (5)	165.6 (20)	—	—	125.1 (92)	133.1 (10)	129.1 (12)	132.7 (2)	61.2, 14.2
144a	Ph	Ph	83.6 (102)	191.3 (9)	193.2 (5)	—	—	122.9 (92)	133.9 (10)	128.9 (13)	132.8 (2)	133.7 (4ry), 133.2, 129.7, 128.1
144b	OMe	Ph	82.4 (103)	183.1 (9)	166.0 (9)	190.7 (9)	192.6 (5)	122.7 (92)	133.8 (10)	129.0 (13)	132.8 (3)	133.6, 133.0, 129.7 (2), 128.1 (2C), 52.0,
144c	OEt	Ph	82.3 (103)	183.4 (9)	165.8 (9)	190.8 (9)	192.7 (6)	122.9 (92)	133.8 (10)	129.0 (13)	132.8 (2)	133.4,133.0,129.8 (2C), 128.1 (2C), 61.5, 13.8
144d	OMe	OMe	81.2 (105)	182.6 (9)	165.6 (9)	182.6 (9)	165.6 (9)	122.8 (93)	133.6 (10)	129.0 (13)	132.8 (2)	52.2
144e	OEt	OMe	81.2 (104)	182.7 (9)	165.3 (9)	182.7 (9)	165.3 (9)	122.9 (93)	133.7 (10)	129.0 (13)	132.8 (2)	61.6, 52.2, 13.8
144f	OEt	OEt	80.9 (104)	182.9 (9)	165.4 (9)	182.9 (9)	165.4 (9)	123.0 (93)	133.7 (10)	128.0 (13)	132.7 (<2)	61.6, 13.8

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assignment of the ^{13}C signals was based on the known chemical shift ranges for esters and ketones.

FVP of these β,γ-dioxo ylides was expected to lead to the formation of benzoylacetylene, for **174**, and methyl propiolate and ethyl propiolate for **175** and **176** respectively. Pyrolysis of **174** at 500 °C resulted in the extrusion of Ph₃PO and Ph₃P in equal amounts. The volatile component was identified as being benzoic anhydride. None of the required benzoylacetylene was detected. Increasing the temperature to 600 °C led to the selective extrusion Ph₃PO but benzoic anhydride was still the only other product. FVP of **175** and **176** at 500 °C resulted in the extrusion of Ph₃PO and Ph₃P in equal amounts and a small amount of unreacted starting material remained. A similar reaction at 600 °C gave mainly Ph₃PO and the corresponding acetylenic esters as the major elimination products. The extrusion of Ph₃P instead of Ph₃PO at the lower temperature was surprising.

$$\text{175 } R^1 = \text{OMe,} \quad \text{176 } R^1 = \text{OEt}$$
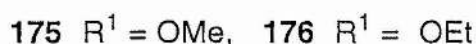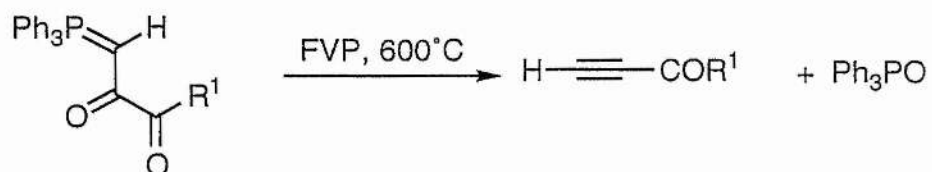
Table 8: Preparation and FVP of β,γ-dioxo Ylides **174-176**

	R¹	Yield (%)	δP	FVP at 600 °C Products	Yield
174	Ph	98	17.4	Ph₃PO, benzoic anhydride	—
175	OMe	75	16.8	Ph₃PO, methyl propiolate	30%
176	OEt	72	16.3	Ph₃PO, ethyl propiolate	28%

161

C   β,γ,β,γ'-Tetraoxo Phosphorus Ylides

1.   Preparation of Tetraoxo Phosphorus Ylides

Although the β,γ-dioxo ylides **175-6** were reported 30 years ago,[125] and the phenyl derivative **174** not long after,[123] only a few groups have used them in synthesis. This is surprising in view of the potentially rich chemistry of these compounds.

The reaction of the dioxo ylides **174-176** with acid chlorides has not been previously reported, except for one precedent.[127] the 1,5 bis-ethoxy tetraoxo ylide **144f**, which was reported while this work was being undertaken. For the purposes of this study, β,γ,β',γ'-tetraoxo ylides **144** were prepared for further studies on the relationship between structure and FVP reactivity of polyoxo ylides.

The reaction of the β,γ-dioxo ylides **174-176** and α-diketo or α-keto ester acid chlorides **151** proceeds in a similar way as described for the synthesis of the trioxo ylides. As expected the β,γ,β',γ'-tetraoxo ylides, obtained in good to excellent yield, are stable crystalline compounds and their ^{31}P signals appear in the +15–18 ppm range (Table 9).
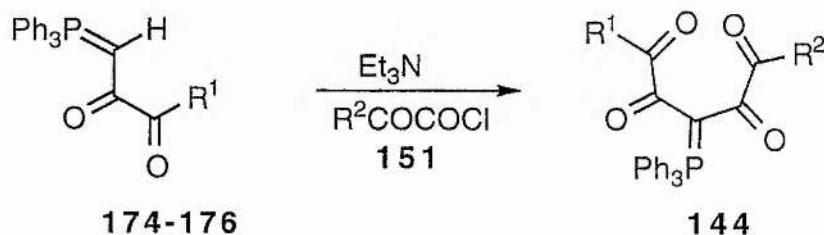
The structures were unambiguously assigned by analytical and spectroscopic data. Table 7 (page 160) lists the ^{13}C data together with the coupling constants. In comparison to the starting materials, the ylidic carbon

Table 9: Preparation of $\beta,\beta',\gamma,\gamma'$-Tetraoxo Ylides **144**

	R^1	R^2	Yield (%)	δ_P		R^1	R^2	Yield (%)	δ_P
a	Ph	Ph	92	15.5	**d**	OMe	OMe	84	17.2
b	Ph	OMe	72	16.2	**e**	OMe	OEt	88	17.4
c	Ph	OEt	78	16.3	**f**	OEt	OEt	72	17.3

resonates at a higher frequency and this reflects the decrease in electron density at that centre. The J_{P-C} coupling pattern is consistent and coupling is observed throughout the P-phenyl rings and extends across to the γ-carbonyl function in most cases. The $^2J_{P-C}$ values of <10 Hz for the β carbonyls indicate that pyrolysis is likely to be successful.

2. Pyrolysis of Tetraoxo Ylides

In order to ascertain the optimum temperature, the tetraoxo ylides **144** were subjected to FVP at various temperatures. Ph_3PO was eliminated at temperatures as low as 300 °C but none of the desired acetylenes were observed for any of the examples. It would appear that either these ylides or the products are extremely thermally labile and therefore do not survive under FVP conditions.

Following the example in the literature,[127] conventional pyrolysis at 220 °C in a Kugelrohr at 0.2 mmHg was performed. Successful results were achieved for ylides where both substituents were esters. The results of the pyrolyses are displayed in Table 10. For the mixed bis-ester, **144e**, there was no selectivity and both the expected products **190** and **191** are equally favoured.

Reaction scheme: **144d-f** → (200 °C, 0.2 mmHg, –Ph$_3$PO) → **189-192**

R^1, R^2 = OEt, OMe
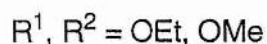
Table 10: Products identified upon Pyrolysis of Tetraoxo Ylides **144**

	R^1	R^2	product: conventional pyrolysis: 200 °C	product: 500 °C (FVP)
a	Ph	Ph	benzoic anhydride	benzoic anhydride, benzaldehyde
b	Ph	OMe	benzoic anhydride	benzaldehyde, methanol
c	Ph	OEt	benzoic anhydride	benzaldehyde, ethanol
d	OMe	OMe	**189**	**189** (trace amount)*, methanol
e	OMe	OEt	**190, 191**	methanol, ethanol
f	OEt	OEt	**192**	ethanol

* identified on one occasion only and could not be repeated

The trioxo alkynes **189-192** were isolated, after chromatography, as yellow oils with a pleasant, fruity fragrance. After a few days at room temperature the smell deteriorated and the colour deepened and the oils became viscous. Given the functionalities present in the molecule, it is probable that polymerisation would occur readily. Supporting evidence for this is the mass spectrum (CI probe) of a sample of the mixture of **190-191** which had been kept at room temperature for several days. The spectrum shows molecular ion fragments that correspond to 369 {(2 x M)+H} and 553 {(3 x M)+H}. The ^{13}C spectroscopic properties of the trioxoalkynes are listed in Table 11.

Table 11: ^{13}C NMR Spectra of Trioxoalkynes **189-192**

	R^1	R^2	CO	$COCO_2$	CO_2	$COC\equiv C$	$COC\equiv C$	R^1/R^2
189	OMe	OMe	167.8	158.1	151.9	83.4	79.1	51.4, 53.7
190	OMe	OEt	167.9	158.1	151.9	83.2	79.2	63.5, 53.7, 13.9
191	OEt	OMe	168.3	157.7	151.4	83.8	78.8	64.0, 54.1, 13.9
192	OEt	OEt	168.4	157.1	151.4	83.7	78.9	64.0, 63.4, 13.9

It is remarkable that highly functionalised molecules such as the trioxo alkynes **189-192** could be accessible in just 3 steps from readily available α-oxo acids. The versatility of these alkynes was elegantly illustrated by Sicker and co-workers' study on the bis-ethyl analogue **192**.[127] Thus, the Diels-Alder reaction with 1,3-diphenylisobenzofuran gave **193** and the heterocycles **194** and **195** were also readily obtained.
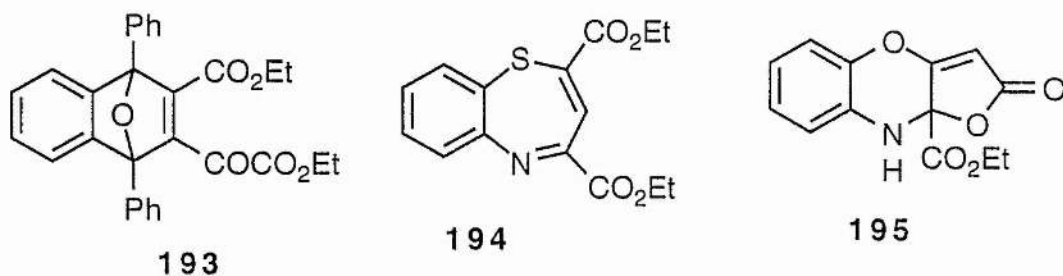
It is unfortunate that the pyrolysis of tetraoxo ylides bearing the phenyl group failed to produce the desired products. However, these studies demonstrate that traditional pyrolysis is not an outmoded technique.

D   Oxalyl Bis Phosphorus Ylides

The range of β-oxo ylides prepared was extended to include bis-ylides, for structure/reactivity studies in relation to pyrolysis and oxidation.

Early ylide chemistry describes several successful preparations of bis-ylides such as **196**,[168] and Bestmann *et al.*[95] have reported bis-ylides **197** where A is a variety of aromatic nuclei. Bis-ylides with a range of functional groups are also known. With the notable exception of Trippett's bis-ethoxycarbonyl bis-ylide **46**,[28] stabilised β-oxo ylides **145** linked by the oxalyl moiety are uncommon. Some recent examples (R = H. Me, Et) were prepared for coordination studies.[169] These bis-phosphonium ylides were prepared from bis-thioesters and the appropriate nonstabilised ylides. The subsequent complexation with transition metal comlpexes was then studied. An alternative route describes the formation of bis-ylide **145** (R = H) by the reaction of oxalic acid and the bis-silyl ylide **37**.[44]

$Ph_3PCH(CH_2)_nCHPPh_3$

n = 1,2

196

145

197
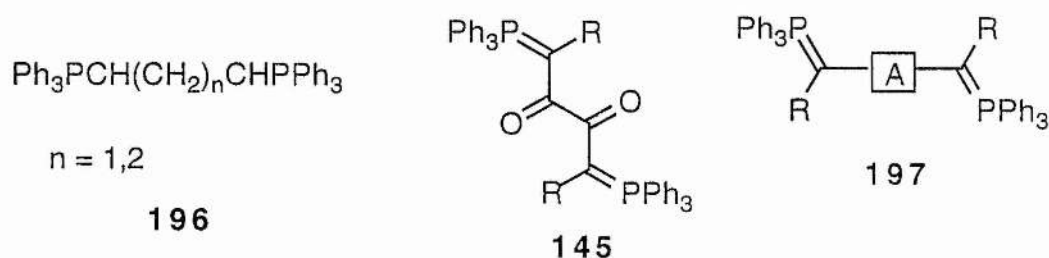
Pyrolysis of alkynoyl ylides **198** to provide access to 1,3-diynes **199** has been demonstrated as a sound route.[61, 170] Theoretically the simultaneous formation of triple bonds of similiar 1,3-diynes should be possible by the

198 $\xrightarrow[-Ph_3PO]{FVP}$ $R^1 \!-\!\!\equiv\!\!-\!\!\equiv\!\!-R^2$

199
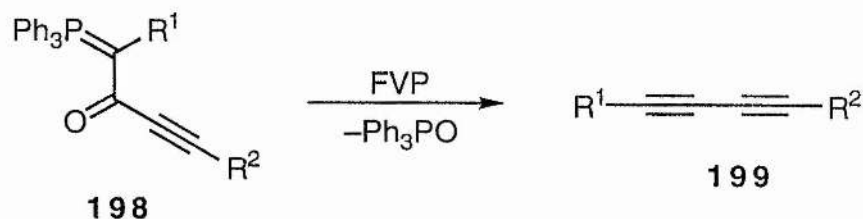
extrusion of 2 equivalents of Ph_3PO from the 1,4-bis(triphenylphosphoranylidene)butane-2,3-diones **145**. It was therefore of interest to prepare the bis-ylides of this type and test this hypothesis.

In previous work within the group, the reaction of a range of simple non-stabilised ylides $Ph_3P=CHR$ (R = Me, Et, Pr, Pr^i) with oxalyl chloride was attempted. Reaction at temperatures as low as −60 °C resulted in complex reactions and only Ph_3PO was isolated. Use of the semi-stabilised ylide $Ph_3P=CHPh$ proved more sucessful and led to the formation of **200**.

The current work continues this study and includes the semi-stabilised ylides **201** and **202** and also extends the reaction to stabilised ylides

1. Preparation of Oxalyl Bis Phosphorus Ylides

Coupling of the simple ylides with oxalyl chloride was uncomplicated. The examples **200-202** were synthesised by the reaction of the semi-stabilised ylides, generated *in situ* from the corresponding phosphonium salts and BuLi, with oxalyl chloride in THF. The reaction proceeds with transylidation to regenerate two equivalents of phosphonium salt. The desired bis ylides were isolated in disappointing yield and were difficult to obtain pure. This was due to partial hydrolysis and decomposion during the recrystallisation needed to remove all traces of the phosphonium salt.

$$Ph_3P=CHAr \xrightarrow{ClCOCOCl\ (0.25\ eq)} \text{bis-ylide} + [Ph_3P^+CH_2Ar]\ X^-$$

200 Ar = Ph
201 Ar = p-Cl-Ph
202 Ar = p-Br-Ph
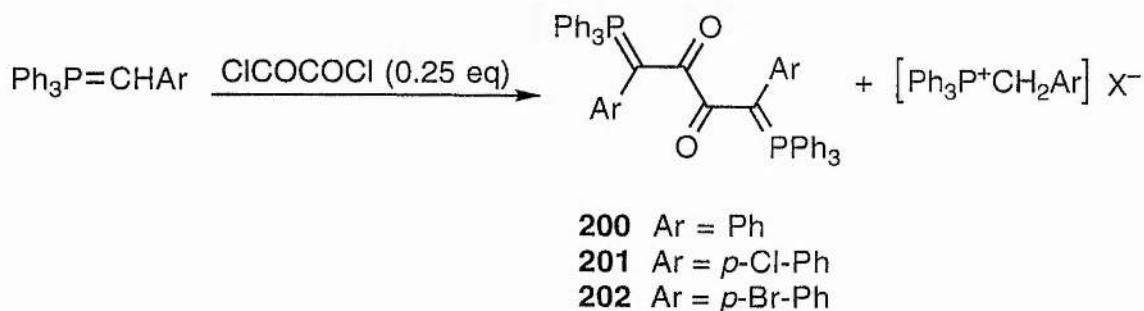
Despite this, spectroscopic examination revealed that the materials isolated did consist overwhelmingly of the desired compounds. In particular,

the ^{31}P NMR signals at δ_P +14.4–14.5 and the ^{13}C NMR data (Table 12) were in excellent agreement with the structures. In the latter spectra, the ylide carbon appears at 70 ppm (^1J $_{P-C}$ 102–105 Hz) and coupling to phosphorus is observed throughout the P-phenyl rings and across to the first two positions of the Ar groups. The carbonyl signals occurred as characteristic double doublets in the 185–190 ppm range. By analogy with similar compounds, particularly **143** the smaller coupling constant (4–5 Hz) was assigned to the two bond coupling to the nearer phosphorus and the larger value of 12–13 Hz to ^3J $_{P-C}$.

The original preparation of **46** used 4 equivalents of the precursor ylide with oxalyl chloride in the transylidation process.[28] While this route was successful, a more efficient method using triethylamine as the base afforded better yields. The compounds **203, 204** and **46** were prepared in moderate yield from 2 equivalents of the precursor ylide and 2 equivalents of Et$_3$N. The hydrochloride was readily removed during the aqueous workup. The physical characteristics of **46** were in perfect agreement with the literature[28] while those of **204** were not. Mehrotra and coworkers[169] reported a melting point of 136 °C for the latter and claimed that it was too insoluble and therefore no supporting NMR data was obtained. Contrary to this, the compound **204** prepared in this study was readily soluble in CDCl$_3$ and melted at 273–274 °C. All the analytical and spectroscopic properties (Table 12) were consistant with this structure. It may be concluded that the compound obtained by the Indian workers was not **204**.
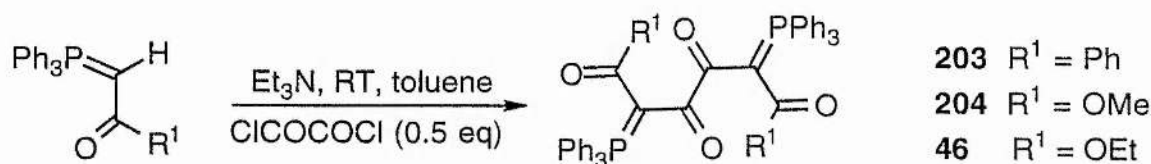
While this work was in progress Capuano *et al.*[171] described the reaction of Ph$_3$P=CHCOPh and oxalyl chloride to form the hygroscopic cyclic

Table 12: ^{13}C NMR Spectra of Oxalyl Bis Ylides, δ_C (J_{p-C})

	R	COCO (^2J, ^3J)	P=C	p-Phenyl				R signals
				C-1	C-2	C-3	C-4	
200	Ph	188.2 (5, 13)	68.5 (105)	125.4 (95)	133.7 (10)	128.2 (13)	130.2 (2)	136.7 (11), 136.0 (2C, 5), 127.2, 126.9 (2C)
201	p-Cl-Ph	187.9 (5, 13)	67.8 (104)	126.0 (90)	133.6 (10)	128.4 (13)	131.4 (<2)	137.0 (2 C, 4ry), 135.5 (12), 130.6, 127.1 (2C)
202	p-Br-Ph	185.5 (4, 12)	70.7 (102)	126.0 (90)	133.6 (10)	128.5 (12)	131.8 (<2)	137.2 (2 C, 4ry), 135.1 (11), —
203	COPh	191.7 (4, 14)	82.4 (99)	125.5 (92)	133.5 (10)	128.5 (13)	131.4 (<2)	191.6 (12), 144.2 (5), 129.4, 128.7 (2C),127.7 (2C)
204	CO₂Me	193.3 (3, 11)	66.1 (111)	126.0 (93)	133.7 (10)	128.4 (13)	131.7 (<2)	167.7 (16), 49.8
46	CO₂Et	193.6 (4, 11)	65.8 (112)	126.4 (93)	133.8 (10)	128.3 (13)	131.5 (<2)	167.3 (15), 58.2, 14.1
207	COCOPh	191.1 (m)	81.1 (103)	124.9 (93)	133.8 (10)	128.4 (13)	131.8 (<2)	192.4 (5), 190.7, 134.6, 132.1, 129.8 (2C), 127.7 (2C)
208	COCO₂Me	189.1 (m)	79.7 (104)	125.1 (93)	133.5 (10)	128.5 (13)	131.7 (2)	183.9 (8), 166.4 (12), 51.9
209	COCO₂Et	189.0(m)	79.5 (104)	125.2 (93)	133.5 (10)	128.5 (13)	131.7 (2)	184.1 (8), 166.0 (11), 61.0, 14.0

169

phosphonium salt **205**. The experiment is performed by the addition of one equivalent of the ylide to oxalyl chloride. This product does not occur when the order of the additions is reversed as described above. Hydrolysis of **201** occurs readily to afford **206**.
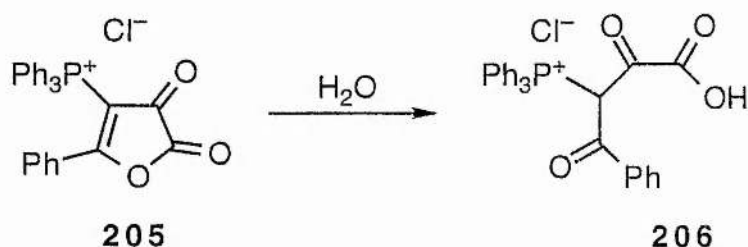
The exclusive formation of the attractive hexaoxo ylides **207–209** from the reaction of oxalyl chloride and β,γ-dioxoylides **174–176** in the presence of Et_3N further illustrates this. It was interesting to note that while compounds **208** and **209** were intially colourless, both in the solid and in solution they gradually developed a faint purple colouration upon storage. The spectroscopic characteristics were highly informative with ^{31}P signals occurring at 17-18 ppm and carbonyl frequencies in the IR spectrum reflecting the 3 different carbonyl functions in the molecule.

The fully assigned ^{13}C spectra, presented in Table 12, confirm the structures expected. Coupling constants have guided the assignments where some doubt may have existed. Multiplets arising from the "oxalyl" carbonyls make the individual $^2J_{P-C}$ and $^3J_{P-C}$ assignments impossible. Aside from this, the ^{13}C spectra are similar to the tetraoxo bis ylides.

207 R^1 = Ph
208 R^1 = OMe
209 R^1 = OEt
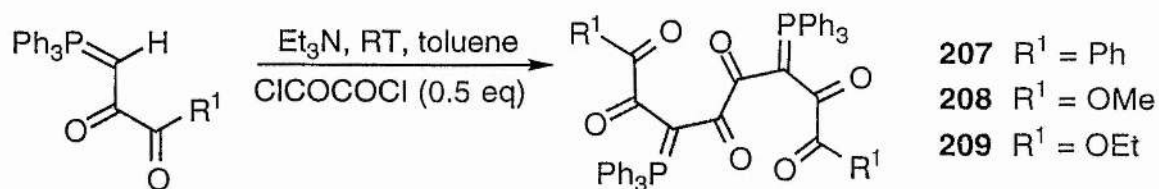
As far as we are aware these compounds are unique in that they are the first examples of compounds that contain a linear array of as many as **eight** C=X functions. Their conformation is of great interest as will be addressed in detail by X-ray structure determination of **208** in section H.

In order to add to the series of polyoxo bis ylides prepared, the bis ylide **211**, generated from the salt **210** and BuLi, was reacted with simple acid chlorides, α-oxo acid chlorides and oxalyl chloride. The ^{31}P NMR spectra of the products isolated clearly showed that the reactions had been complex giving rise to many different products and that pursuing this area further was unlikely to be productive.

R = Ph, PhCO
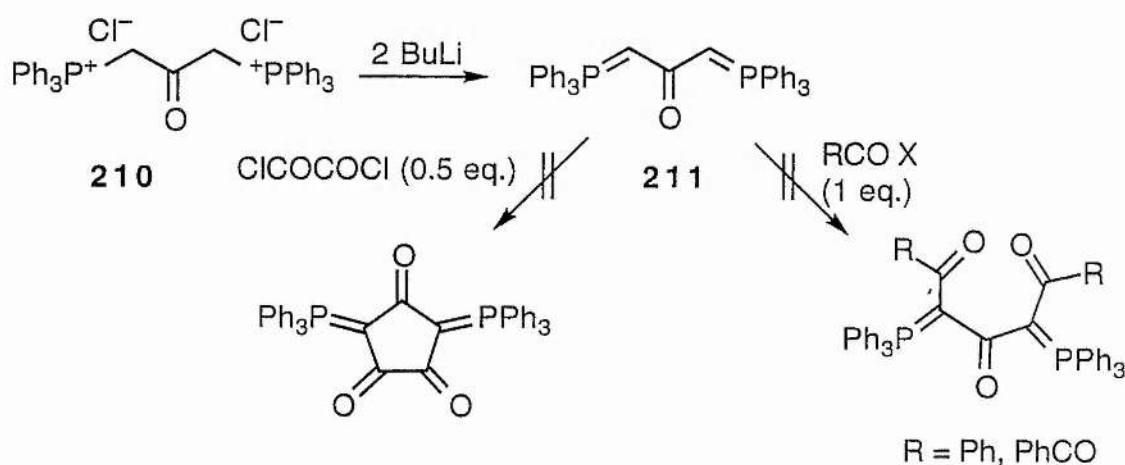
2. Pyrolysis of Oxalyl Bis Phosphorus Ylides

The bis ylides **200–202** proved to be extremely resistant towards extusion when subjected to FVP at temperatures up to 850 °C. Complete

212 Ar = Ph
213 Ar = *p*-Cl-Ph

200-201

171
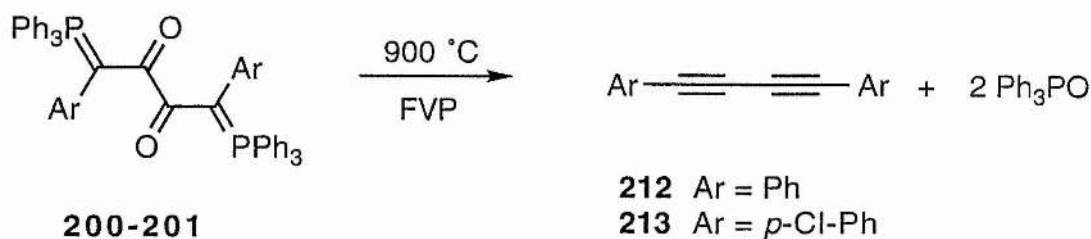
conversion to Ph₃PO only occurred at 900 °C. The diynes **212** and **213** could only be isolated from **200** and the chloro analogue **201**.

In contrast, the tetraoxo **203, 204** and **46**, as well as the hexaoxo bis ylide **207** underwent complete elimination upon FVP at 500 °C to yield Ph₃PO in excellent yields. Unfortunately none of the diynes were detected. The only products isolated were benzoic anhydride from **203**, methanol from **204**, ethanol and acetaldehyde from **46** and benzoic anhydride from **207**. It is probable that the expected diynes **214** and **215** may be formed but are not stable under the conditions used and rearrange and fragment by concerted and radical mechanisms to give the non volatile products.

203, 204, 46

214

207

215
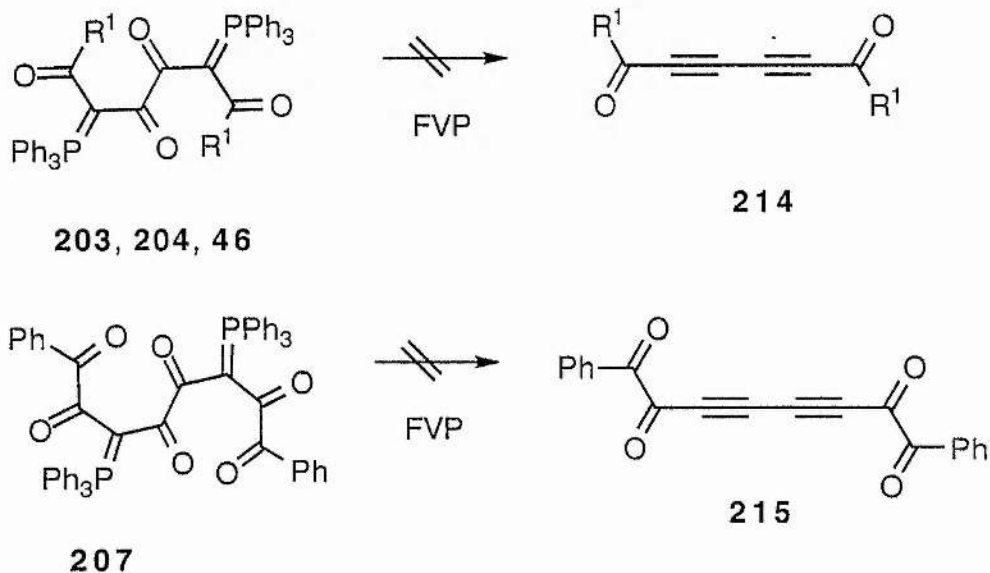
E   Reaction of Phosphorus Ylides with Oxidants

As described in section D of the Introduction, there are many examples of vicinal triketones and their use in synthesis has been elegantly described by Wasserman.[71-73] It is therefore anticipated that vicinal tetracarbonyl compounds could be similarly exploited as reagents in synthetic transformations. A literature survey established that while many examples of linear vicinal triketones exist, the tetraketones possessing alkyl groups are poorly represented. Therefore it seemed pertinent to synthesise these compounds. The precursors to these compounds, the β,γ,β'-trioxo phosphorus ylides **143**, were available from the work described in section A of this Discussion.

1.   Synthesis of Vicinal Tetraketones

With a few exceptions, *vic*-tetrones have been prepared from their dihydro derivatives. Linear diaryl and di-t-butyl tetraketones have been obtained by a procedure developed by Soderbaum *et al.*[172] α-Ketoaldehydes **216** undergo self-condensation in the presence of the cyanide ion to generate the ene-diol **217** which is then oxidised, most frequently with nitric acid, to the polycarbonyl **218**.
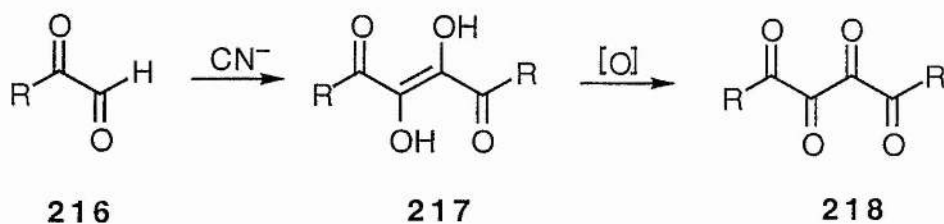
All these syntheses have produced symmetrical diaryl tetraketones with only one example of an aliphatic derivative, namely, di-t-butyl tetraketone.[77]

The method of choice to obtain samples for X-ray crystallographic[80] and spectroscopic studies[77,173] is that of Ruggli *et al.*[134] In this procedure benzoylformin **219** is oxidised to the ketone **74** in moderate yields.
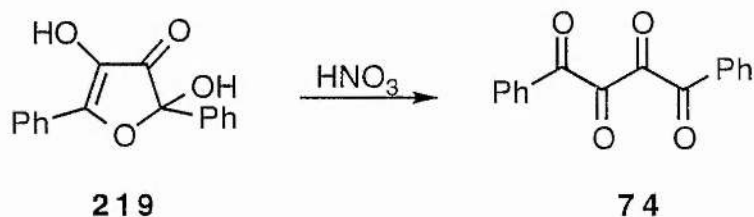
In a later procedure Wolfe and co-workers[174] synthesised diphenyl tetraketone **74** by treating diphenylbuta-1,3-diyne **220** with *N*-bromosuccinnimide in DMSO. However the product could not be isolated.
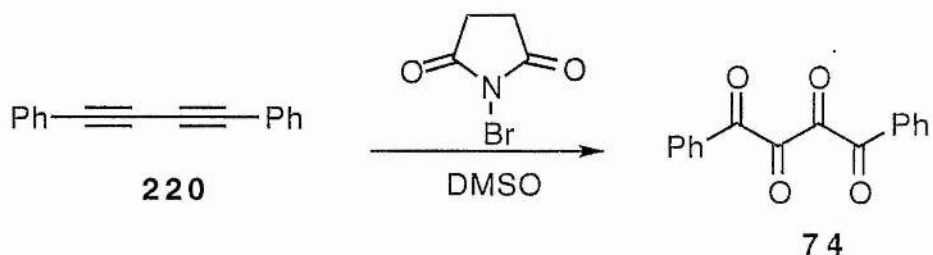
It is notable that no vicinal tetraones or higher homologues have been prepared by the oxidation of phosphorus ylides.

2. Oxidation of Phosphorus ylides

Three separate reagents were investigated and the results for each are described separately. Initial studies on the oxidation of phosphorus ylides for the synthesis of ketones began with the use of oxone.

a. Oxone

The preliminary oxidation studies were based on the methodology developed by Wasserman and co-workers.[90] The American group was interested in preparing the 1,2,3-tricarbonyl functional group for various synthetic applications leading to natural products. Among the procedures for vicinal tricarbonyl formation, the method involving the oxidative cleavage of the ylide bond in dioxo ylides **143**, with oxone is particularly attractive. It seems a convenient, general and mild procedure.

The β,β'-dioxoylide **221** and 1,4-diphenyl trioxo-ylide **143a** were selected as the substrates for the preliminary study. The use of the dioxo ylide was to test the method and the potential oxidation product, diphenyltetraketone **74** of the latter is a known compound. In a typical experimental procedure the polyketone was prepared by the oxidation of one equivalent of phosphorane with 1.5 equivalents of oxone in a THF/water solvent system. Although the exact structure of oxone is not fully understood, the reactive species is represented by the structure shown in the scheme.
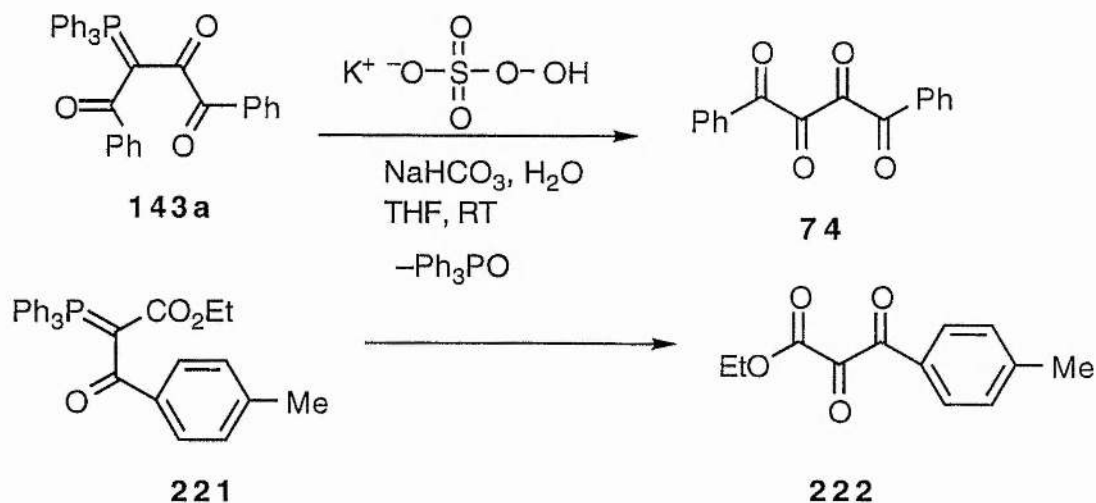
The trioxo product **222** was isolated as a mixture of hydrate and ketone forms in moderate yield. In the case of **143**, although the reaction evidently proceeded smoothly and no starting material could be detected, the yield was

175

yield was extremely disappointing. It was found that if all the starting material was allowed to react, the reaction time was approximately 5 days. A ^{13}C NMR spectrum of the crude reaction mixture revealed the presence of a very small amount of the expected product **74**, triphenylphosphine oxide, as well as two other compounds which contained the acid functionality.

A chromatographic separation of the reaction mixture confirmed that the side products were acids. These acids were easily characterised by ^{13}C NMR as being benzoic acid and 4-hydroxybutyric acid. The latter was formed as a result of the oxidation of the solvent, THF, to butyrolactone initially, and then hydrolysis to the acid. This was not surprising since *vic*-polyketones and their hydrates react readily in basic solution. The reaction appears to be analogous to the benzilic acid rearrangement of α–diketones. The addition of hydroxide ion to a central carbonyl group of polyketones or reaction of the weakly acidic hydrate with hydroxide ions furnishes the anion **223** which rearranges to benzoic acid.
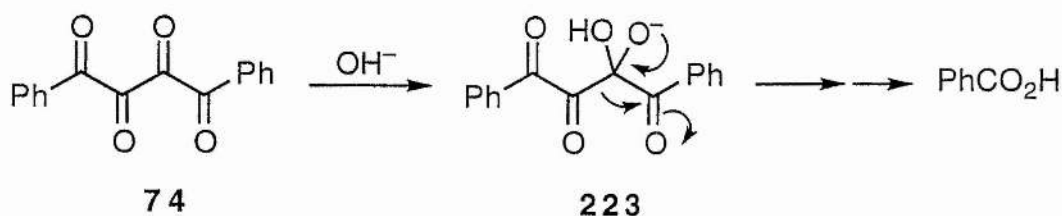
Although the scheme depicted is intended to represent a working hypothesis rather than a mechanistic proposal, it must be noted that there are formal precedents for it. Gray and Fuson[175] noted that dimesityl tetraketone **224** undergoes a complicated reaction which involves rearrangement and cleavage of the carbon chain in the presence of alkaline solutions. It was claimed that 2 acids, namely mesitylglycolic acid **225** and mesitylglyoxylic acid **226** were isolated from the reaction mixture as well as a third component which was not identified.

224 → **225** + **226** (−CO₂)
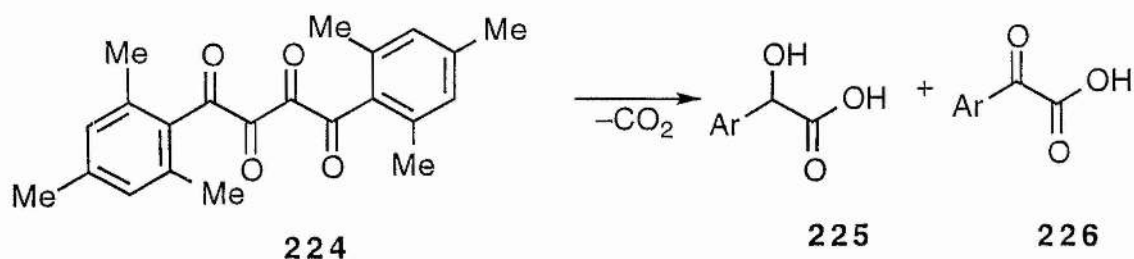
A subsequent study investigating the oxidation of acetylenes by NBS, found that diphenyltetraketone **74** readily decarbonylates to benzil.[174] This observation supports the earlier observation by Schönberg and Azzam.[176] It was proposed that the tetraketone undergoes fragmentation in a similar mechanism to the diphenyltriketone-benzoin rearrangement. This phenomenon poses a further constraint on the reaction conditions and work-up.

Although the poor yield of **74** suggested that the use of oxone was unlikely to be of much preparative use, the series of the β,β,γ-trioxo ylides **146** bearing other groups were oxidised using the same approach. Again, the desired tetraketones **227** were obtained in poor yield and purification was difficult due to decomposion during chromatography. The NMR spectra clearly display signals arising from acid functions. Another problem, mentioned earlier, was the oxidation of the solvent, THF. A range of alternative solvents were examined without any success.
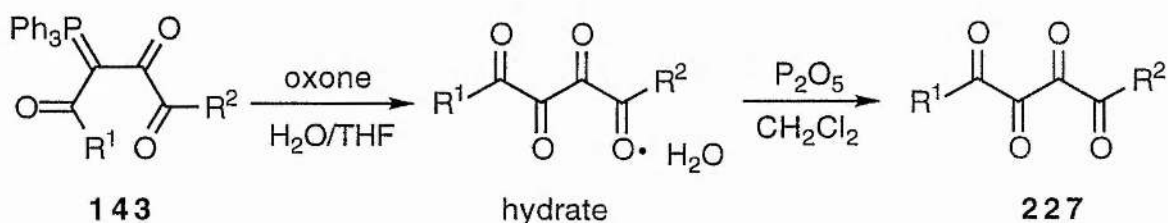
This study of the scope of oxidation of the trioxoylides **143** indicates that the conversion of these ylides to tetraketones with oxone in THF cannot be a general route to the elusive *vic*-polycarbonyls.

Table 13: Characteristic ^{13}C NMR Signals for Oxidation products of **221** and **143**

	R[1]	R[2]	Hydrate	Ketones **222** or **227**
221	—	—	191.5, 170.1, 91.5	189.9, 183.9, 160.4
143a	Ph	Ph	192.2, 191.1, 189.4, 94.1	188.4, 187.8
143d	Ph	OEt	179.8, 171.6, 158.0, 92.1	179.9, 171.7, 158.9, 158.0
143f	Me	OMe	177.9, 169.0, 168.4, 90.5	—
143i	OMe	Ph	191.4, 171.9, 170.3, 91.7	191.3, 190.0, 183.3, 170.3

b. Ozone

Again, the β,β'-dioxoylide **221** and 1,4-diphenyl-1,2,4-trioxo-3-triphenylphosphoranylidenebutane **143a** were selected as the substrates for the preliminary study. While the oxone methodology produced the pale coloured hydrates, ozonolysis of the ylide in dry methylene chloride yielded a bright yellow solution of the trioxo product and an attractive magenta solution of diphenyl tetraketone **74**. A ^{13}C NMR study of the crude reaction mixture confirmed that the desired products were present mainly in the ketone form.

The crude mixture was purified by column chromatography. Analysis of the ^{13}C NMR spectrum showed traces of decomposition products. However, this preliminary study looked encouraging since the hydrated species as well as the free ketone were isolated. Unfortunately the other examples of β,γ,β'-trioxophosphorus ylides gave rearranged products only.

c. Dimethyldioxirane

An alternative oxidising reagent, dimethyldioxirane[133] **228**, was also examined. Recently this reagent has found extensive use because of its selectivity and mild conditions. The preparation of this oxidant was achieved

by reacting oxone and acetone in a basic solution. Dimethyldioxirane (DMD) was then isolated as a solution in acetone. The concentration of DMD in the solution was approximately 0.1 M.
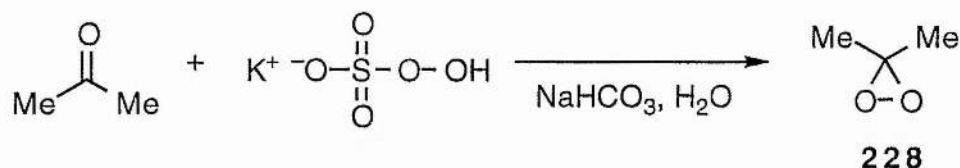
The β,β'-dioxoylide **221** was again selected for a test reaction. A solution of the ylide in methylene chloride and DMD (2.5 eq., added in 3 portions at 6 hour intervals) was stirred at room temperature and the course of the reaction was monitored by TLC. After 2 days the reaction mixture was analysed by ^{31}P and ^{13}C NMR which showed that some unreacted starting material was still present and a significant amount of the hydrate of **222** was also formed.

Subsequently oxidation of compounds **229**, **230**, **143a**, **144a**, **203** and **207** was investigated. The conversion of **229** and **230** to benzil and diphenyl triketone **72** respectively was encouraging. In the reactions of **143a** and **144a**
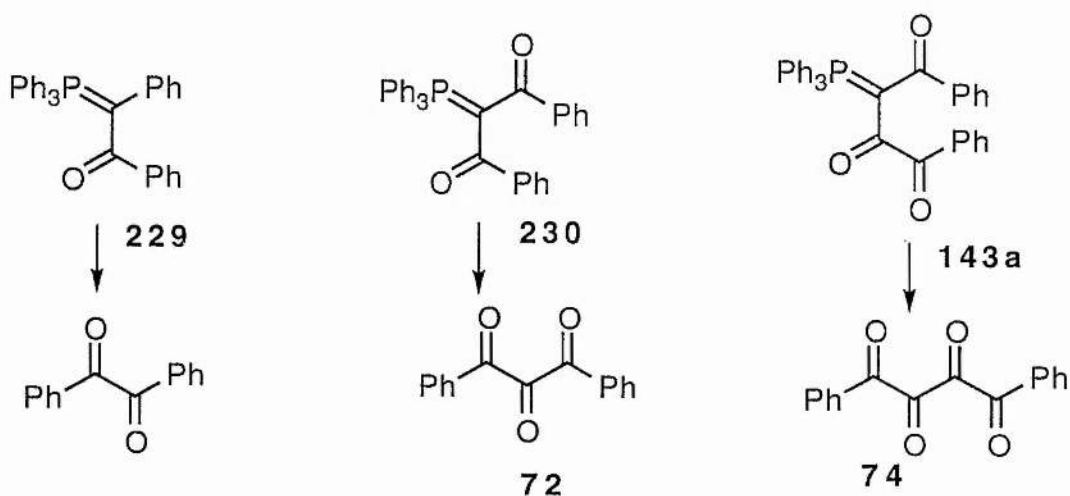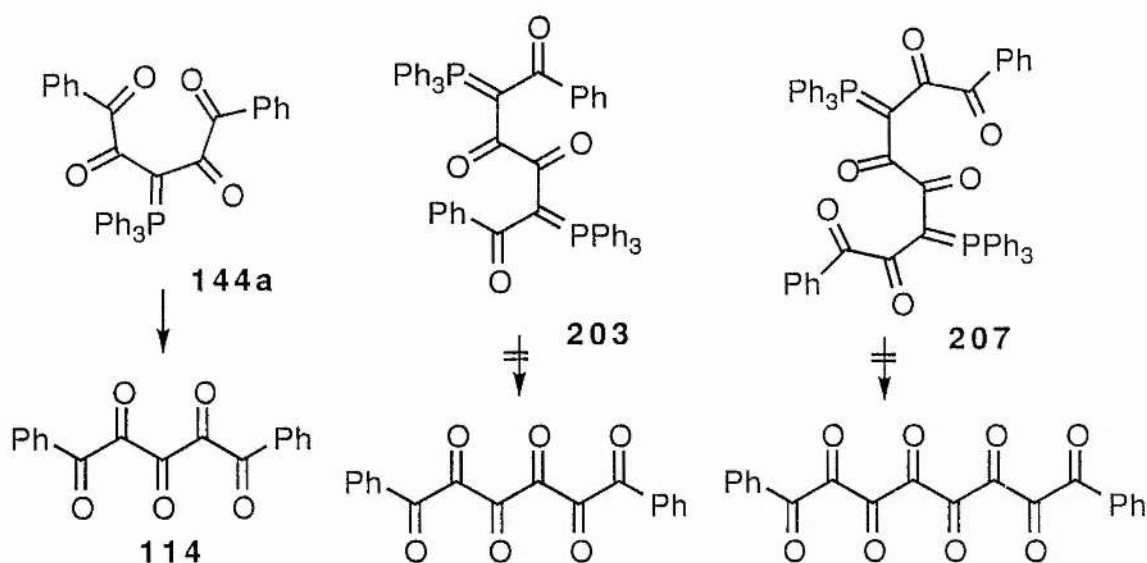
the desired polyketones **74** and **114**, together with a significant amount of rearranged products were formed. It is clear that DMD does effect the oxidation of ylides. However an anhydrous solution of the reagent is likely to be more successful, and this will form the basis of future studies in this laboratory.

d.   Reaction of vic-polyketones with water

Vicinal polyketones react extremely rapidly with water to form the hydrated derivatives. This observation was originally based on visual evidence, namely, that the colours of the polyketones disappear when they are exposed to air.

Since many syntheses of *vic*-carbonyl compounds involve aqueous conditions, the hydrates are the usual products obtained. Conversion to the free ketone is achieved by conventional methods.

It is not surprising that preferential reaction at the central carbonyl group of triketones has been observed since the maximum number of vicinal carbonyl interactions are relieved in this way. Spectroscopic data has established that the hydration of diphenyl triketone **72** provides the gem-

dihydroxy compound **231**.[79] The latter structure has generally been accepted as the correct representation for these hydrates.
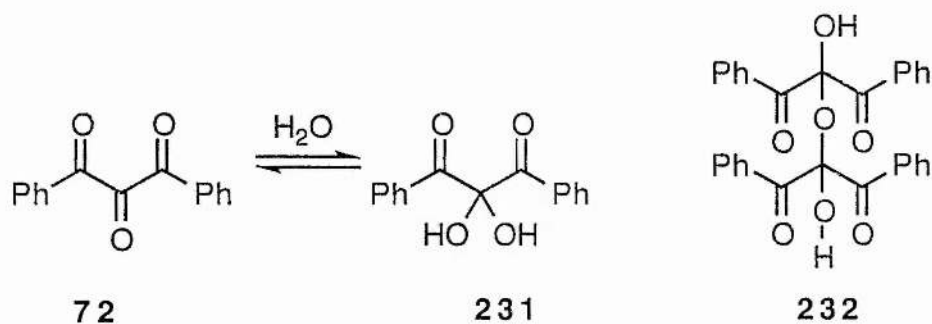
Further evidence has suggested that polyketones can also form hemihydrates.[177] It seems feasible, particularly in situations where the amount of water is limited, that the initial hydrate **231** can react to produce the hemihydrate **232**.

As mentioned in the Introduction the structures of hydrates of tetraketones have also been assumed to be of the simple gem-diol type. Dihydrates of tetraketones have been reported but without any precise information being provided about their structure. In order to gain some insight into the hydration of tetraketones, diethyl dioxosuccinate **233** was prepared according to an early report and the ^{13}C NMR spectra of the products recorded for te first time.[135] In this procedure, the disodium salt of dihydroxytartaric acid was esterified to the corresponding ester using ethanol and HCl gas. The ^{13}C spectrum of the crude compound showed two resonances at δ91.3 and 94.1. These chemical shift values have been assigned to quaternary carbons possessing gem-dihydroxy groups, namely those in the monohydrate **234** and the dihydrate **235**. The number of resonances for the carbonyl groups could be rationalised in a similar way. The monohydrate, being nonsymmetrical, displays three carbonyl resonances while the symmetrical dihydrate **235** displays only one.
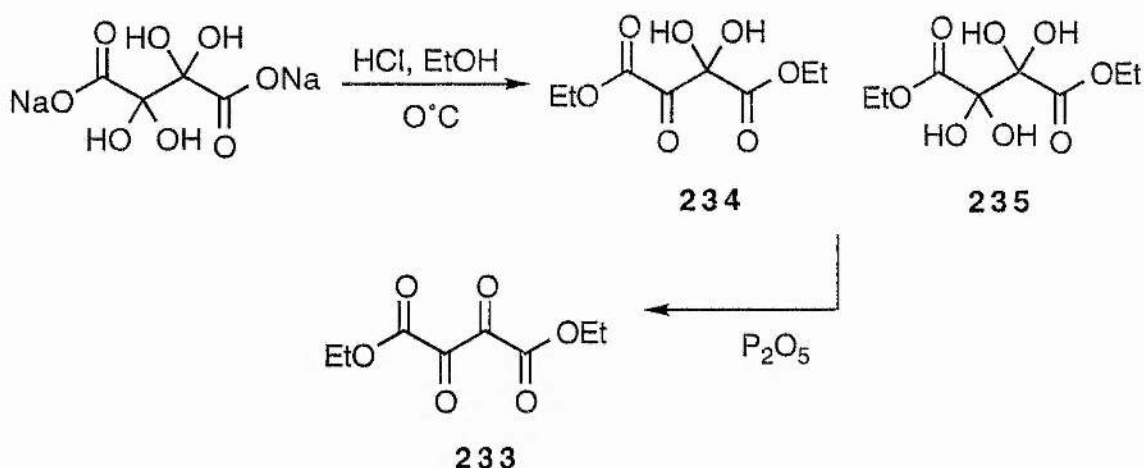
Attempts to obtain the free dioxoester by distillation resulted in decomposition. Elaboration and further work in this area is needed. It is important to ascertain the factors influencing the hydration and rearrangement of linear polyketones in order to isolate them successfully.

F   Reaction of β-oxo Ylides with NO₂

In an early paper on the reaction of phosphonium salts with ethyl nitrite, Zbiral and Fenz[88] demonstrated that the nature of the reaction products is directed by the substituents. It was established that the P–C bond in β-oxo salts **236** is oxidised to yield Ph₃PO and the corresponding α-oxonitrile. The reaction pathway involves the initial nucleophilic attack on the nitrogen followed by elimination of ethanol and HX to yield **237** and Ph₃PO.
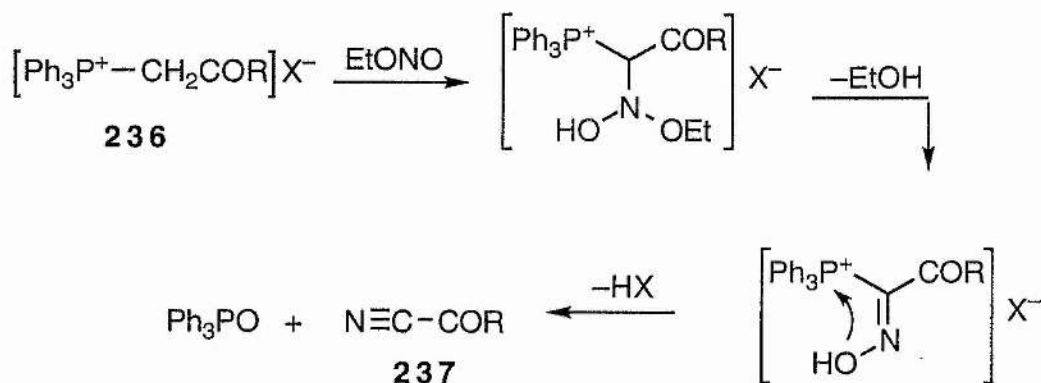
Similarly alkylphosphonium salts **238** were oxidised to nitriles for R^1 = H, R^2 = alkyl, and for R^1, R^2 = alkyl, the products formed are ketoxime ethers **239**.

$$\text{Ph}_3\text{P}^+\!\!-\!\!\underset{\underset{\text{O}}{\overset{|}{\text{N}}}\!\!-\!\!\text{OEt}}{\overset{\overset{\displaystyle R^1}{|}}{\text{C}}}\!\!-\!\!R^2 \quad\longrightarrow\quad \underset{R^2}{\overset{R^1}{\diagdown}}\!\!C\!\!=\!\!N\!-\!\text{OEt} \;+\; \text{Ph}_3\text{PO}$$

238   **239** R^1, R^2 = alkyl
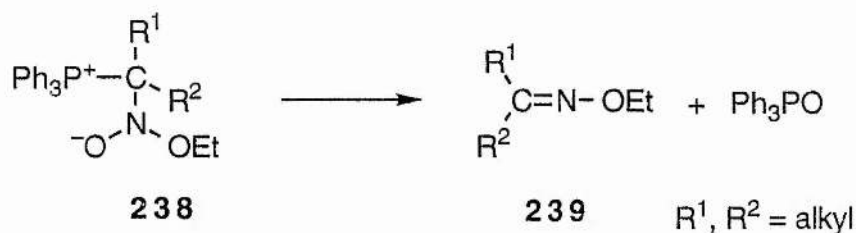
Further work on the oxidation of γ-acylpropenylphosphonium salts **240** with alkyl nitrites and nitrosyl chloride found that the substituents played a significant role in directing the course of the reaction.[178] The different products **241-244** were isolated depending on the substitution pattern.
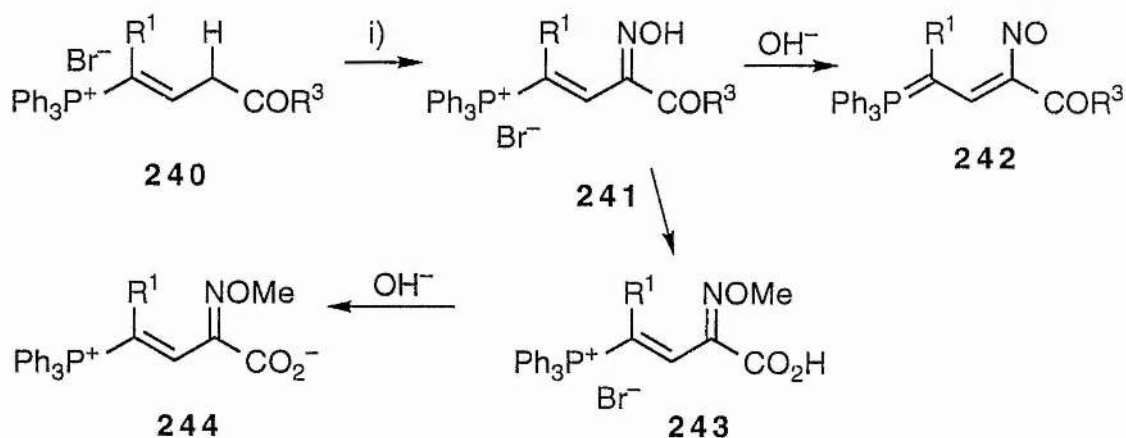
i) EtONO or NOCl

At the same time another group[179] found a similiar pattern in the reaction of β-oxo ylides and alkylidene phosphonium ylides. Thus, the reaction with nitrosyl chloride afforded α-oxonitriles and nitriles respectively. The reaction with nitric oxide was more complex with the formation of nitriles and aldehydes together with Ph_3PO.[180]

An extensive recent study on the reaction of nitrating agents with phosphorus ylides bearing a variety of functional groups was found to give an

183

interesting but complex pattern of reactivity.[181] A solution of NO_2 in THF forms a blue coloured complex and the reaction of this species with a range of ylides affords α-nitro-α-nitroso-carboxylates **245** (R^1 = alkyl, R^2 = CO_2Et), nitroles **246** (R^1 = Me, R^2 = H), nitriles (R^1 = alkyl, R^2 = H) and acylnitriles (R^1 = acyl, R^2 = H).
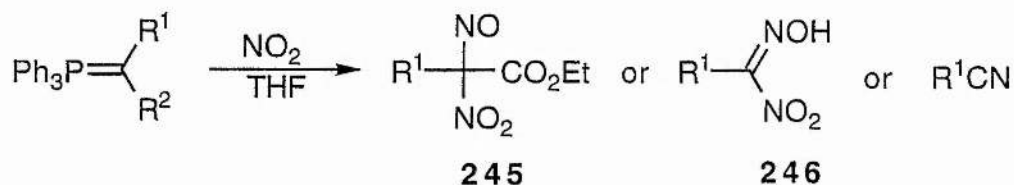
In accord with the original report on the phosphonium salts, the reaction was found to be influenced by the substituents borne by the ylide carbon. An interesting aspect of the experiment with ylides **247** is the nitration of the phenyl ring in the *para* position giving **248**. Complementary

184
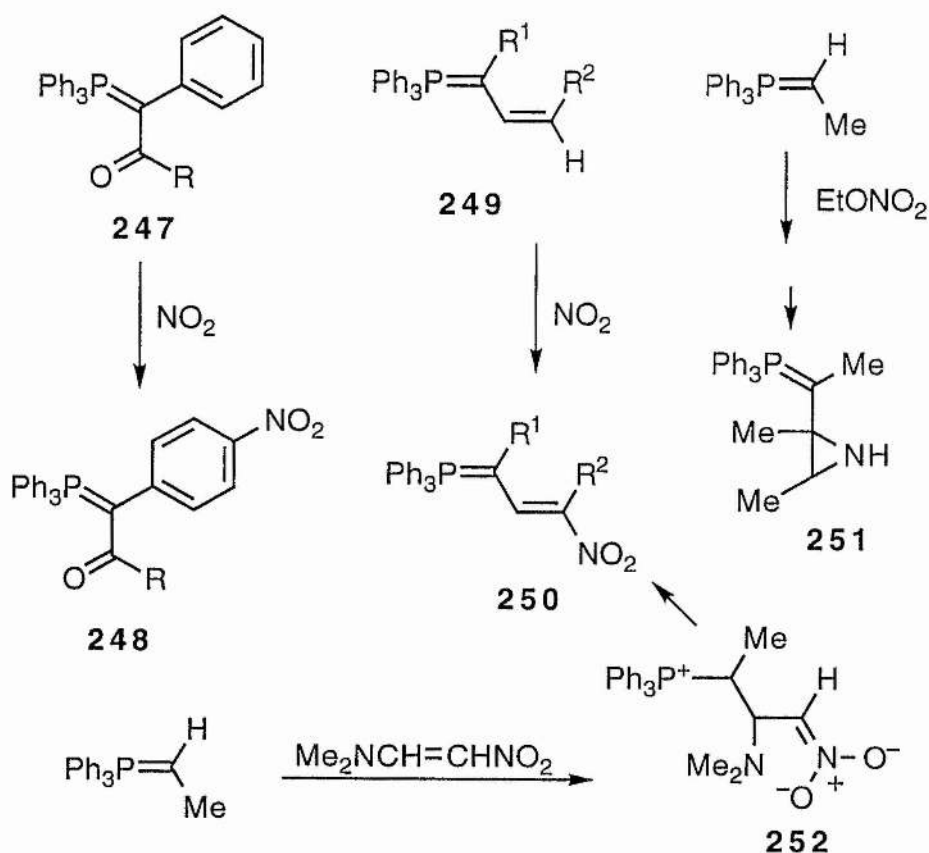
to Zbiral's work,[88] γ- nitration was observed in β,γ unsaturated side chains of ylides **249** to afford **250**. The same product is available when ethyl nitrate is used. Ethyl nitrate reacts with the ethylidene ylide in a complex reaction to afford the interesting aziridinyl-substituted ylide **251**. 1-Nitro-2-dimethylamino-ethylene reacts with ethylidenetriphenylphosphorane to yield **252** initially. Loss of dimethylamine provides alternative access to the β,γ-unsaturated nitro ylide **250** (R^1 = Me, R^2 = H).

In efforts to access polyketones, the oxidation of β-oxo ylides by NO_2 in methylene chloride was studied here. The experiments were performed by the addition of 3 equivalents NO_2 (in CH_2Cl_2) to a solution of ylide, also in CH_2Cl_2, at room temperature. The reaction was extremely exothermic and after a while the brownish solution turned green. A mixture of products was obtained and the identity of only some have been established (Table 14). The nitriles are formed by a mechanism similiar to the one proposed by Bestmann.[181] Surprisingly the reaction of the α-phenyl-α-benzoyl ylide **229** results in *ortho* and *para* nitration to give the ylide **253**. The latter reacts further with NO_2, and a Wittig reaction followed by rearangement affords 2,4-ditrobenzonitrile **254** and benzoic acid.
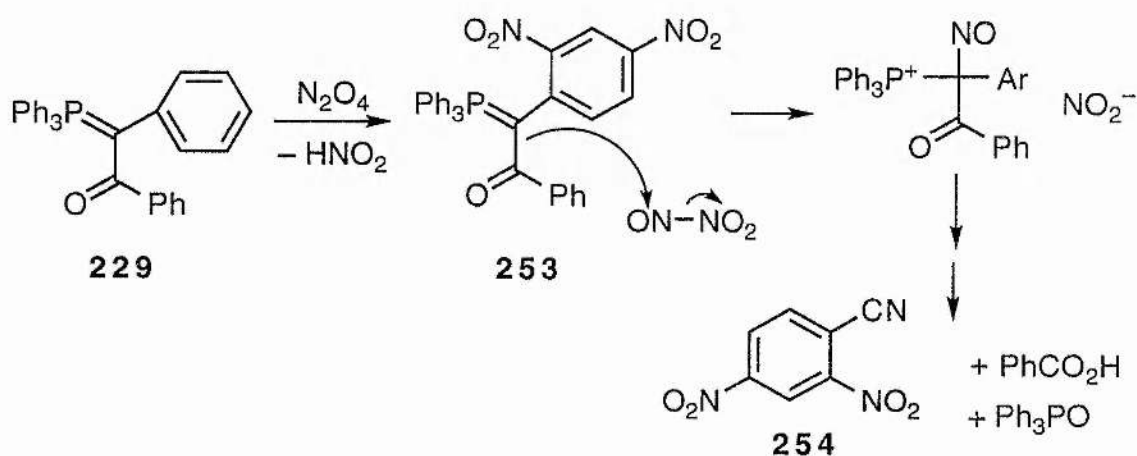
In contrast to the previous reports, phosphine oxide is not obtained in the free form but rather as its 1:1 adduct **255** with nitric acid. Recrystallisation of this adduct results in the formation of the 2:1 adduct **256**.

$$\text{Ylide} \xrightarrow{\text{NO}_2} \left[\text{Ph}_3\text{P}^+-\text{OH}\right]\text{NO}_3^- \xrightarrow{\text{Recryst.}} \left[\text{Ph}_3\text{P}^+-\text{O}-\text{H}\cdots\text{O}=\text{PPh}_3\right]\text{NO}_3^-$$

255   **256**
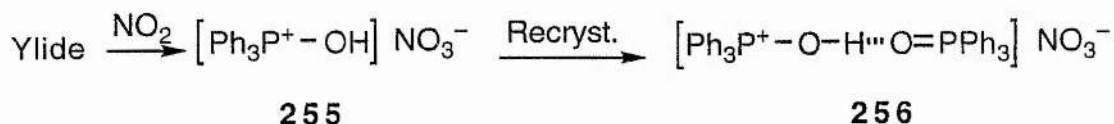
The identity of the adducts was established by elemental and spectroscopic analysis. In order to establish the exact structure of the adducts, Ph_3PO itself was reacted with NO_2. A yellow waxy solid which was not starting material was islolated. There is some uncertainty regarding the structure of the compound **257**.

13
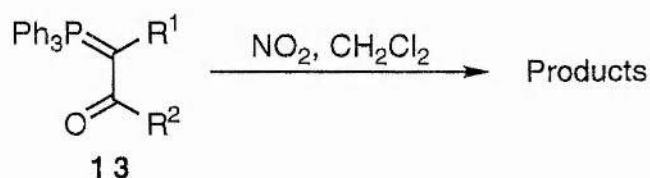
Table 14: Reaction of β-oxo ylides **13** with NO_2 in CH_2Cl_2

	R¹	R²	Products
a	H	Ph	**255**, PhCOCN
b	H	Me	**255**, CH₃COCN
c	H	OMe	**255**, MeOCOCN
d	Ph	Ph	**255**, 2.4-ditrobenzonitrile, benzoic acid
e	COMe	Me	**255**
f	CO₂Et	CO₂Et	**255**, EtOCOCN
g	Ph	Me	**255**, benzoic acid
h	Ph	COC(PPh₃)Ph	**255**, PhCOCN, benzoic acid
i	COPh	COC(PPh₃)COPh	**255**, PhCOCN, benzoic acid
j	CO₂Et	COC(PPh₃)CO₂Et	**255**

A more direct comparison would be a nitric acid adduct. Indeed, this type of compound is well known in the literature and is obtained from the reaction of Ph_3PO with acids.[182] The amount of acid used may be varied so that 1:1 adducts as well as 2:1 adducts are available. Several groups have shown that these adducts exhibit interesting electrophilic properties.[183] However, the NMR spectroscopic characteristics for the nitric acid adducts which were of interest were not available.

Thus the authentic adducts were prepared from Ph_3PO and the HNO_3. Ph_3PO was reacted with one equivalent and half an equivalent HNO_3 to give the desired adducts **258** and **259** respectively. The spectroscopic properties of the compounds prepared by this route compares well with the adduct **255**.
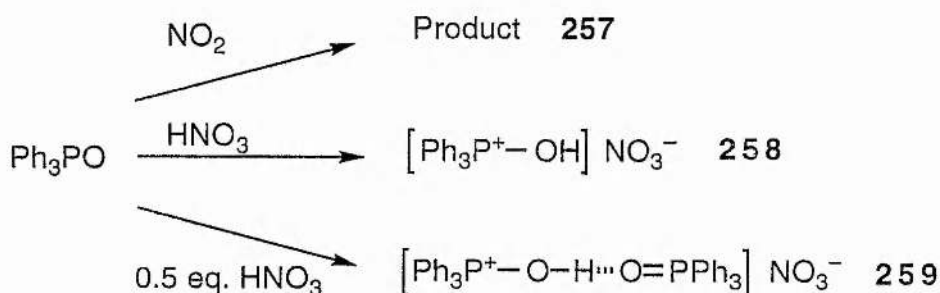
It was also of interest to examine the spectroscopic characteristics of the adducts of Ph_3P and NO_2, and Ph_3P and HNO_3. Again there is some uncertainty regarding the structure of **260**. Although suitable microanalysis could not be achieved for the compounds isolated from the reactions with HNO_3, structures **261** and **262** are not unreasonable.
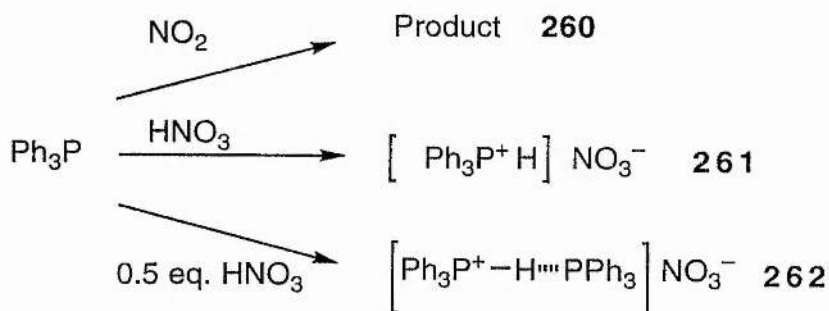
The interesting ^{13}C, ^{31}P and ^{1}H spectra (Table 15) support the structures proposed. The ^{31}P resonance is in agreement with a "salt" stucture while the OH signal at large chemical shift values is comparable with hydrogen bonded complexes. Doublets arising from coupling to P are observed throughout the P-phenyl rings. There is no obvious reason for the difference in the chemical shift values of the adducts isolated from the different reactions since they should all posess the same structure. A possible explanation is the difference in the concentration and temperature of the sample itself (in CDCl$_3$). The mass specta of the adducts was uninformative as no molecular ion and only peaks associated with Ph$_3$PO fragmentation were observed.

Table 15: ^{13}C NMR Spectra of Adducts **255-262**, δ_C (J $_{P-C}$)

	C–1	C–2	C–3	C–4	δ_P	(δ_H) OH
Ph$_3$PO	132.4 (94)	132.1 (10)	128.5 (10)	131.9 (<2)	28.6	
255	129.5 (107)	132.1 (11)	128.9 (13)	132.9 (3)	34.6	17.72
256	130.5 (106)	132.0 (10)	128.7 (13)	132.6 (3)	34.6	—
257	130.5 (106)	128.1 (10)	131.3 (13)	131.8 (3)	30.8	11.50
258	128.9 (108)	132.2 (11)	129.0 (13)	133.2 (3)	36.9	13.25
259	130.8 (106)	132.1 (10)	128.7 (12)	132.5 (3)	32.1	13.34
260	131.4 (104)	131.5 (10)	128.1 (13)	133.0 (3)	20.7	5.20
261	122.6 (52)	129.9 (11)	133.8 (14)	133.3(3)	35.2	11.69
262	133.7 (88)	128.7 (7)	133.7 (12)	129.5 (3)	34.5	6.58

G   Preparation and Reactions of Aminoacyl Phosphorus Ylides

1.   Acetylenic Amino Acid Derivatives

Unsaturated amines and amino acids are of interest because of their potential as specific irreversible enzyme inhibitors. Analogues of the natural amino acids in which the acid group is either replaced by C≡C or separated from the α centre by triple bonds are of special interest. It has been realized that amines and amino acid derivatives that contain carbon-carbon triple bonds act on enzymes that catalyse isomerisation, oxidation, elimination and transamination.[184] As a consequence considerable effort has been expended on the development of synthetic approaches to this class of compounds.

The principle action of the acetylenic compounds is dependent on the fact that they can be converted to conjugated allenes by enzymes. While acetylenes are not very reactive, allenes behave as good Michael acceptors. These compounds are described as "suicide substrates" because they become bound to the enzyme protein or co-factor as a result of the chemical modification.[185]

The α-acetylenic γ-amino acids are of particular interest since access to these compounds remains difficult.

a.   Preparation of Acetylenic amino acids and amines

The first general synthesis of α-acetylenic γ-, δ- and ε-amino acids was reported by Olomucki and Marszak.[186] They developed several routes to 4-dimethylaminobut-2-ynoic acid **263**, its homologues and esters. However, there was no attempt to study their potential biological activity.

$$Me_2N(CH_2)_nC \equiv C-CO_2R \qquad n = 1, 2 \qquad R = H, Et$$

263

189
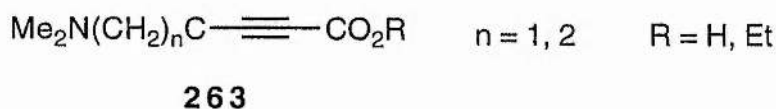
Subsequently, Hennion and Perrino[187] obtained 4,4-dimethyl-4-dimethylamino-2-butynoic acid **266** while investigating the reactions of α-acetylenic tertiary amines. It was found that the amine **265**, prepared from 3-chloro-3-methyl-1-butyne **264** and dimethylamine, reacted smoothly with sodamide and carbon dioxide to furnish the acetylenic amino acid **266**.
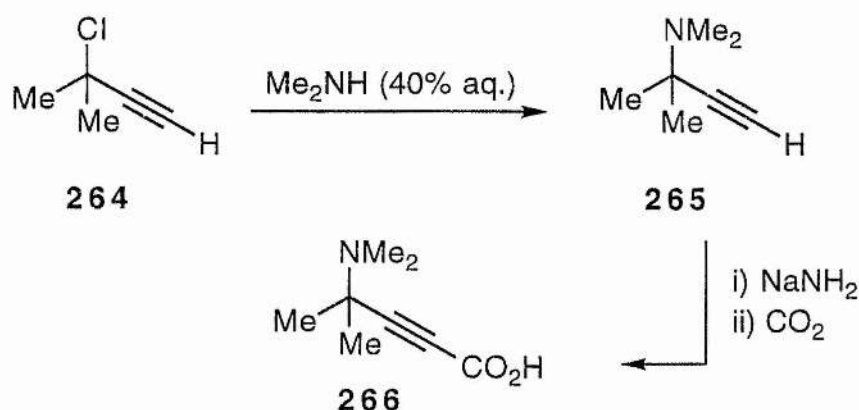
The first group to consider the potential biological activity of unsaturated γ-amino acids was that of Beart and Johnston.[188] 4-Aminotetrolic acid and some of its derivatives **270** were prepared because these compounds are simple, conformationally strained analogues of the neuromediator γ-aminobutanoic acid (GABA). The derivatives **270** were used to investigate the correlation between the structure and activity of the α-acetylenic γ-amino acids.

The preparation of the amino tetrolic acid derivatives, outlined below, began with the conversion of the diol **267** to the chloride **268**. Oxidation by CrO$_3$ furnished the chloro-acid **269**. Finally, a direct nucleophilic attack of the appropriate amine on **269** provided the product **270**. All of the γ-amino acids **270** proved to be inhibitors of the stimulation of central neurons, but they were not as active as GABA.

$$HOCH_2-\!\!\!\equiv\!\!\!-CH_2OH \xrightarrow{SO_2Cl} ClCH_2-\!\!\!\equiv\!\!\!-CH_2OH$$

267   **268**

$$\Big\downarrow CrO_3$$

$$R_2NCH_2-\!\!\!\equiv\!\!\!-CO_2H \xleftarrow{R_2NH} ClCH_2-\!\!\!\equiv\!\!\!-CO_2H$$

270   **269**

$NR_2 = NH_2,$ [morpholine], [piperazine] NH, [piperidine], [pyrrolidine]
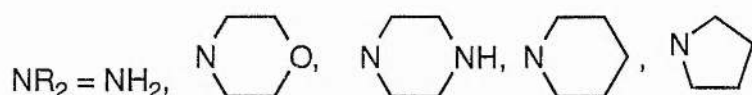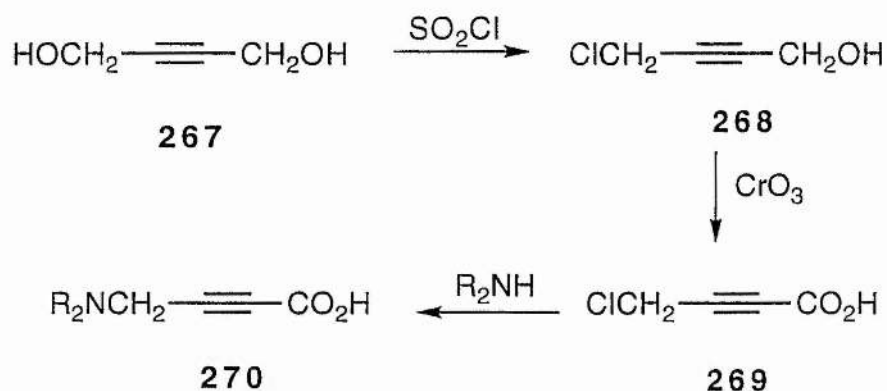
Further developments resulted in the aminoacetylenecarbonyl compounds **274** and analogues of γ-aminobutynoic acid being proposed for therapeutic treatment of alcoholism.[189] These compounds were prepared from the acetylenic amines **271** by replacing the acetylenic hydrogen with an aldehyde, carbonyl or amide function after initial protection of the amino group as in **272**. Subsequent acid hydrolysis under mild conditions gave the hydrochlorides of the desired compounds. Interestingly, some of the hydrochlorides **273** exhibited anti-tumour properties.[189]

$$\begin{array}{c} R \\ R^1 \end{array}\!\!\!>\!\!C-C\equiv CH \xrightarrow[\substack{Me_3Si\;\;\;\;SiMe_3 \\ |\;\;\;\;\;\;\;\;| \\ Cl\;\;\;\;\;\;\;Cl}]{Et_3N,\;CH_2Cl_2,\;0\,°C} \begin{array}{c} R \\ R^1 \end{array}\!\!\!>\!\!C-C\equiv CH$$

with NH_2 below on **271**; and N with Me_2Si—$SiMe_2$ ring on **272**.

i) BuLi, Et₂O, C₆H₁₄, −60 °C
ii) R²COX

$$\begin{array}{c} R \\ R^1 \end{array}\!\!\!>\!\!C-C\equiv C-COR^3 \xleftarrow{} \begin{array}{c} R \\ R^1 \end{array}\!\!\!>\!\!C-C\equiv C-COR^3 \xleftarrow{HCl} \begin{array}{c} R \\ R^1 \end{array}\!\!\!>\!\!C-C\equiv C-COR^3$$

274 (with NH₂)   **273** (with NH₃⁺Cl⁻)   **272** analog (with N–Me₂Si–SiMe₂ ring)
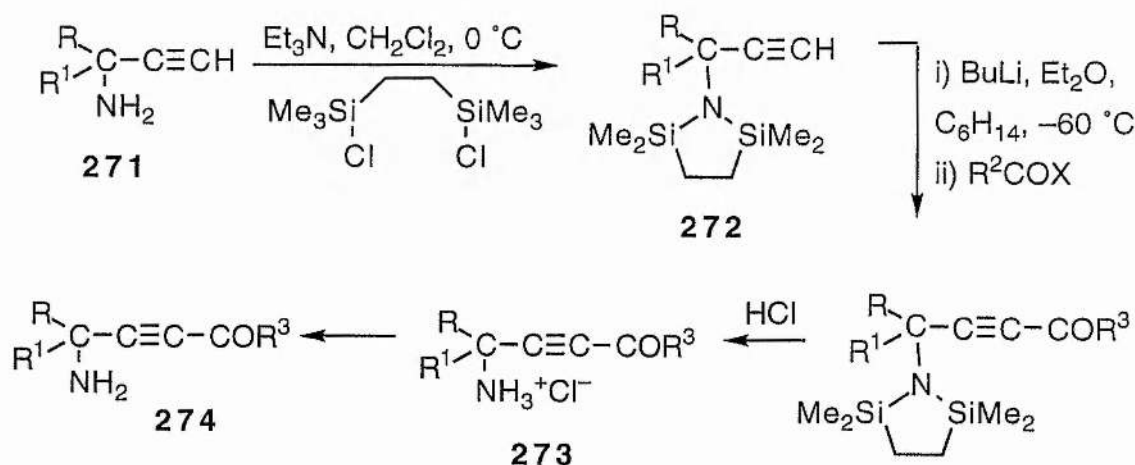
R, R¹ = hydrocarbon or heteroatom hydrocarbon groups
R, R¹ = cycloalkylene or heteroalkylene   R² = H, alkyl, NH₂

An attempt to access esters and amides of α-acetylenic hydroxyamino acids involved the amination of the epoxyacetylenic acid derivatives **275**.[184] It is surprising that the biological activity of compounds **276** and **277** were not investigated.
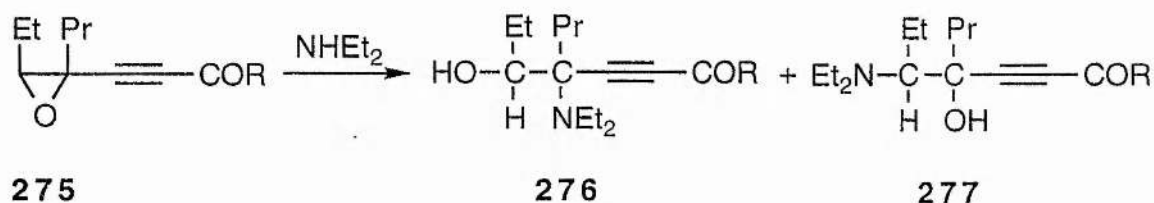
For general preparative purposes Abdulganeeva and co-workers[190] found it convenient to prepare *N*-substituted α-acetylenic-γ-amino acid esters by the oxidative alkoxycarbonylation of propargylic amines **278** with carbon monoxide under catalytic conditions. It was discovered that the amino acid esters **279** displayed fungicidal and antistaphylococcal activity.
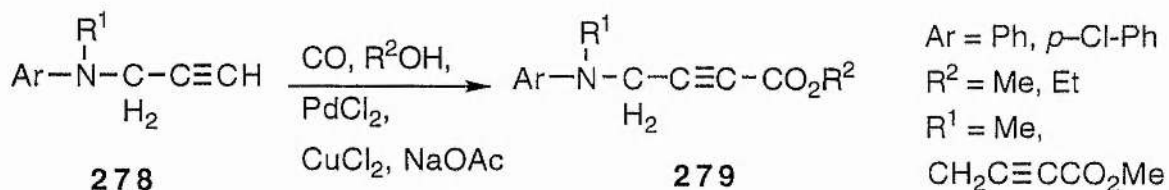
The synthesis of naturally ocurring and optically active acetylenic amino acids is of special interest due to the potential for biological activity. Apart from the examples presented, these compounds remain difficult to access. α-Acetylenic-3,4-dihydroxyphenylalanine **280**, was the first example of such compounds.[191] The regioselective alkylation of the synthon **281**, provided a series of substituted α–alkynyl amino acids **282**.[192] Deprotection of **281**, to give the parent amino acid **283**, was unsuccessful and led to the formation of the allenyl product **284**. The labile amino acid **283**, is known to inhibit alanine racemase, and was later isolated from *Streptomyces carenulae* as the *N*-acetyl derivative.[193]

280   **283**

282   **281**   **284**

deprotection
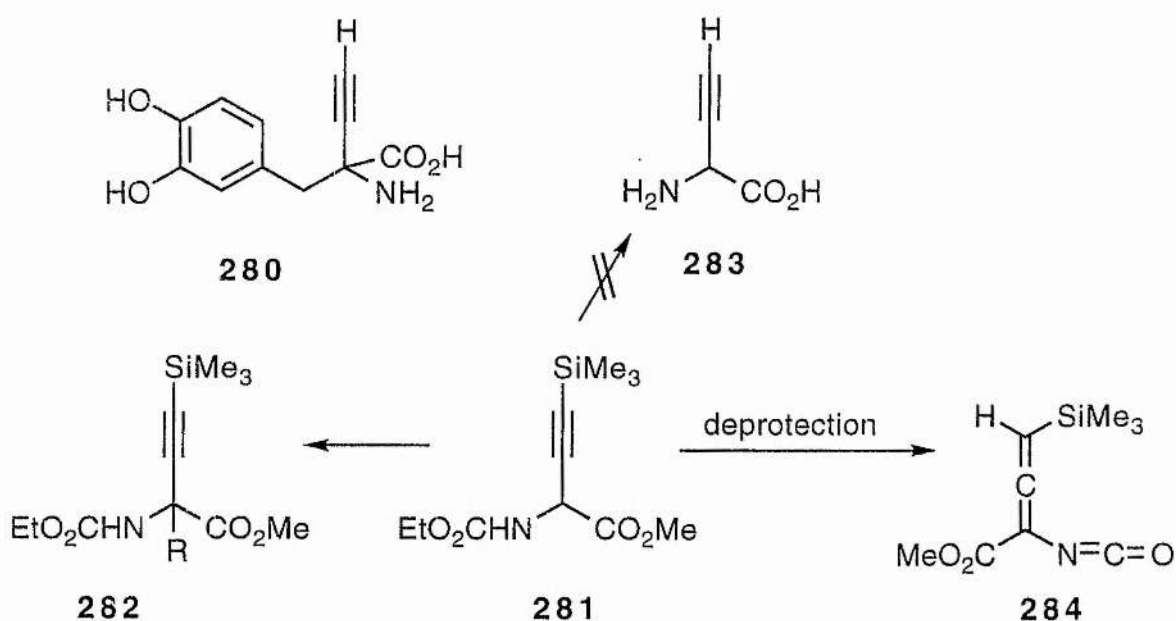
Similarly several derivatives of non-alkylated α-alkynyl-α-amino acids such as **286** were synthesised directly by carboxylation of the synthon **285**.[194] The allenylamino acid **287** was also a product of the reaction and was obtained in 20% yield.

i)LDA
ii) CO_2
iii) CH_2N_2

285   **286**   **287**
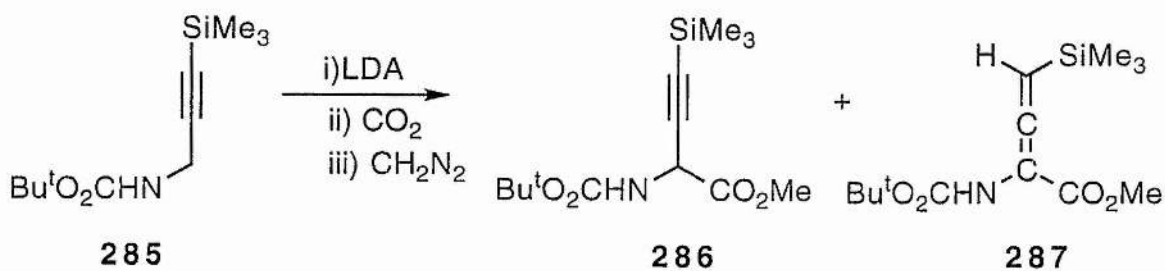
In an enantioselective synthesis, involving several steps, Holmes *et al.* prepared (S)-γ-acetylenic GABA **288**.[195] This inhibits GABA transaminase, an enzyme which has been linked to neurological disorders.

288
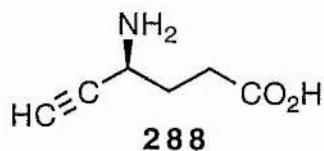
Recently, the first synthesis of ethynylglycine **283**, an antibiotic and an inhibitor of alanine racemase,[196] was reported.[197] The synthetic strategy involved the coupling of an alkynyltin reagent with an α-chloroglycinate **289** in the presence of zinc chloride. Deprotonation afforded the stable *N*-acetylethynylglycine **290**. The final step was performed enzymatically by rat liver acylase to produce the product **283** which could not be isolated from the fermentation medium.
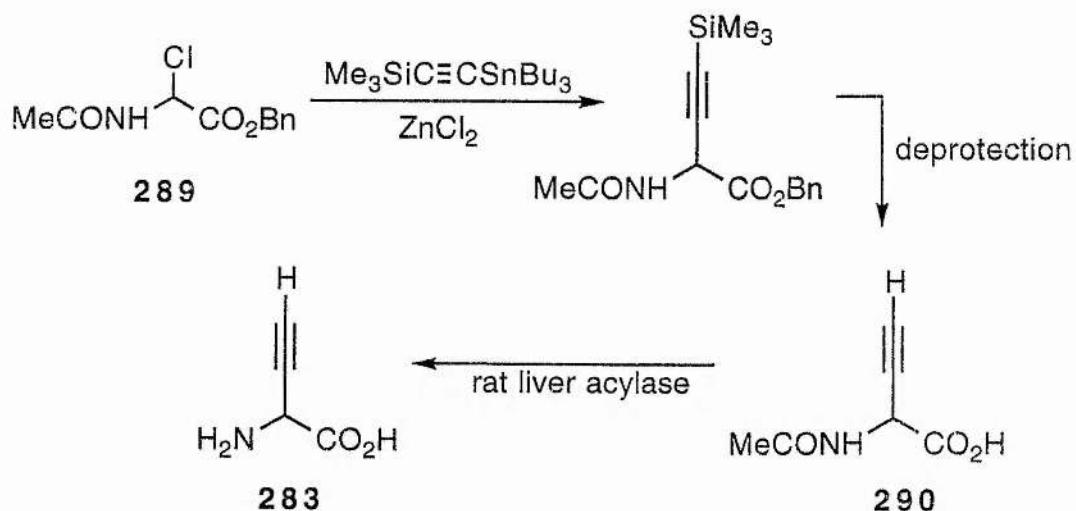
Since the first synthesis of the simple prop-2-ynylamine,[198] several approaches to higher homologues have been developed. One example is the asymmetric synthesis of (2R, 5R)-hept-6-yne-2,5-diamine **291** a potent, selective, irreversible inhibitor of the enzyme ornithine decarboxylase (O.D.C., E.C. 4.1.1.17).[199] Compound **291**, a monoamine oxidase resistant compound, is an analogue of (R)-hex-5-yne-1,4-diamine **292** which also inhibits O.D.C.

194
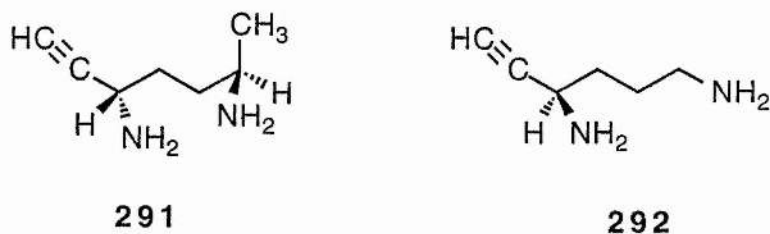
The key step in the synthesis involves the asymmetric alkylation of the *N,C*-diprotected acetylenic amine dianion, generated from the propargylamine **285** with excess base in the presence of excess TMEDA, and a chiral *N*–protected haloalkylamine **293**. The alkylated product **294** is deprotected to form **291**.[200]
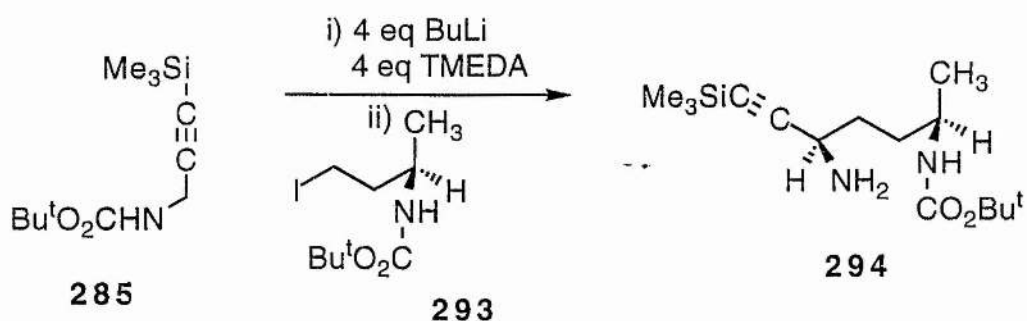
2.   **Preparation of β-aminoacyl ylides**

Although the acylation reaction of ylides is a well developed area, the recent work orginating from Bestmann's group provided access to the first β-aminoacyl ylides.[36] Two different methodologies for the synthesis of these ylides were examined and both required *N*-protected amino acids for the acylation of the corresponding phosphorus ylide. The starting optically-pure α-amino acids are readily available from the "chiral pool."

The acylation of ylides by amino acids is not uncomplicated, due to the competing nucleophilicity of the amine functionalty. The success of the reaction depends on its nucleophilicity being suppressed so that attack by the ylidic carbanion on the electrophilic carbonyl group of the amino acid is encouraged, that is, peptide formation is hindered.

The obvious and well understood solution is the protection of the NH$_2$ group. A choice of protecting groups are available for this purpose. The only limitation is the stablility of the protecting group in the conditions employed. Similarly, other functionalities present may be protected if it is necessary.

a. Attempted Acylation of Silyl Ylides

The reaction sequence in which the α-amino acid is first protected at the amine and acid functionalities before the reaction with the silylated phosphorane is known.[36] Use of silyl protection had an advantage since both the amino and acid functionalities could be protected in one step without racemisation occurring. It was envisaged that the γ-amino acetylenic compounds **296** would be produced on pyrolysis of the γ-amino β-oxoalkylidenephosphorane **295**. By varying R^1 a number of optically active γ-amino acetylenic compounds would be obtained in only 3 steps.
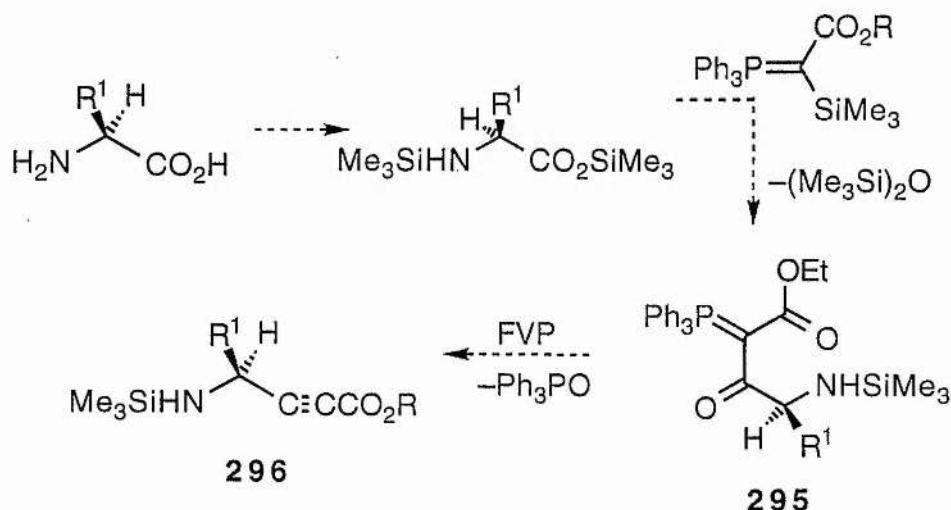
i. Synthesis of trimethylsilyl esters of *N*-(trimethylsilyl) amino acids

Numerous silylating reagents exist for the introduction of the organo-silicon group onto a variety of amines, alcohols and acids.[201] The only disadvantage is the lability of the Si–O and Si–N bonds to hydrolysis.

The silyl derivatives of the α-amino acids were prepared by a modification of the method reported by Kricheldorf.[202] This involved the reaction of an amino acid with excess trimethylsilyl chloride in the presence of triethylamine.

$R^1 = Me, Bu^i, Bn$
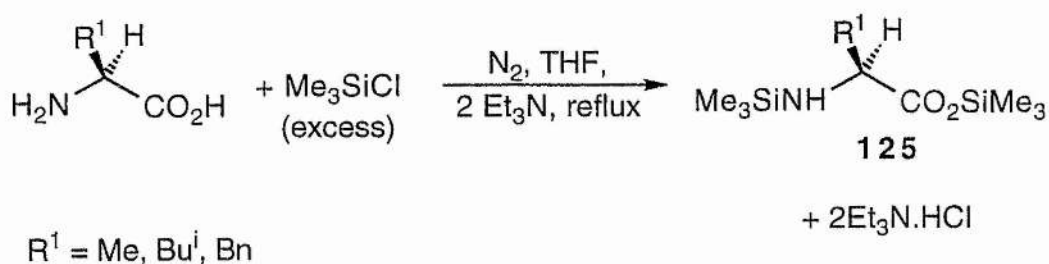
Initially the procedure described in the literature was followed. However, a mixture of the desired product, monosilylated compound and starting material was isolated. The separation of the required compound by distillation was futile since the difference in boiling points was not sufficient. By varying the amounts of trimethylsilyl chloride and reaction times, the ideal conditions were attained.

Surprisingly, the amino acid containing an aromatic group in the side chain, R, needed longer reaction times. The results are displayed in Table 16. More conclusive trends could be obtained by studying other α-amino acids.

Table 16: Preparation N,O-bis-trimethylsilyl amino acids **125**

	amino acid	R^1	reaction time (h)	yield (%)
a	alanine	Me	2	85
b	leucine	Bu^i	2.5	66
c	phenylalanine	Bn	4	60

ii.   Attempted acylation of Silyl Ylides

The reaction of the N,O-bis-silyl α-amino acid ester **125** and the silylated phosphorane **28** is known. However the use of the ester ylides in this way has not been investigated. Subsequently a literature search established that ylide **297** was not known. The original reason for using (ethoxycarbonyl

197

methylene)triphenylphosphorane was the discovery that FVP, at 750 °C, of ylides bearing this group leads to loss of CO_2Et as well as phosphine oxide and so provides access to terminal alkynes.

Numerous attempts to prepare the ylide **297** using the ethoxycarbonyl stabilised ylide and trimethylsilyl chloride were unsuccessful. The ylide was heated under reflux with trimethylsilyl chloride in the presence of triethylamine in various solvents at different reaction times. The only compound isolated was the starting material. It seems that the hydrogen on the ylide is not sufficiently activated and therefore requires a stronger silylating reagent.

$$Ph_3P=CHCO_2Et \xrightarrow{\quad Et_3N,\ Me_3SiCl \quad}\!\!\!\!/\!\!\!/\quad Ph_3P=\!\!\!<^{CO_2Et}_{SiMe_3}$$

297
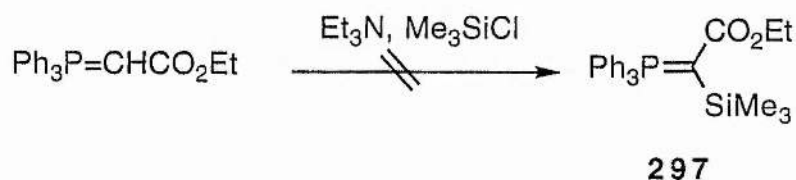
Bestmann's method[36] using the non-stabilised methylene ylide was an alternative route. The methyltriphenylphosphonium salt was suspended in dry THF and deprotonated with one equivalent of n-butyl lithium to form the ylide. The latter was then converted with half an equivalent of trimethylsilyl chloride to the silyl phosphorane **28** and phosphonium salt in the transylidation method.

$$2\left[Ph_3P^+\!\!-CH_3\right]X^- \xrightarrow[\text{ii)}]{\text{i)}} Ph_3P=\!\!\!<^{H}_{SiMe_3} + \left[Ph_3P^+\!\!-CH_3\right]X^-$$

28
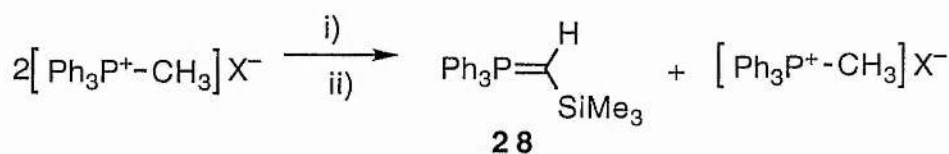
i) N_2, THF, n-BuLi, 0.5h, RT   ii) Me_3SiCl, 20h RT, 5h reflux

Initially, the yields obtained (<50%) were never comparable to the literature values due to the high reactivity of the ylide. The rigorous exclusion

of moisture and the use of freshly prepared dry solvent and reagents improved the yields considerably.

Once the phosphorane **28** was obtained, it was heated under reflux together with the protected amino acid **125** in dry THF for various lengths of time in order to establish the optimum reaction conditions. It seemed that the reaction had worked, but the product, an intractable viscous oil, partially decomposed during recrystallisation. Therefore suitable spectroscopic data could not be obtained. The melting point of this crude product was closer to that of the deprotected analogue.
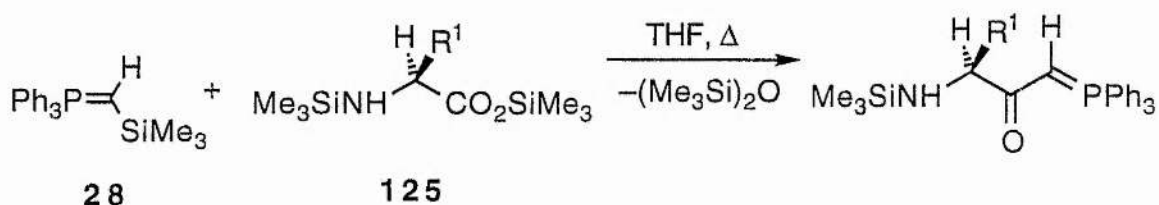
This route was abandoned due to the timely appearance of a paper by Wassermann.[73] In a rather novel procedure α-aminoacyl ylides were prepared from stabilised ylides and *N*-protected amino acids in the presence of a peptide coupling reagent.

3. Synthesis of β-aminoacyl Ylides mediated by Carbodiimides

a. Preparation of *N*-Alkoxycarbonyl Amino Acids

The popularity of the alkoxycarbonyl family of amine protecting groups in peptide synthesis is unquestionable. This is due to their stability, selective cleavability, and most significantly, immunity to racemisation. *N*-Alkoxycarbonyl derivatives, commonly referred to as carbamates or urethanes, may be regarded as both amides and esters. As amides, they posess low nucleophilic reactivity at nitrogen. Esters are known to be stable to acyl-

oxygen fission. However alkyl-oxygen fission can be promoted and deprotection occurs in this way with the formation of carbamic acids. Spontaneous decarboxylation of the latter regenerates the parent amine.

Thus, this choice of protecting group meets the requirements necessary for this study. The amino acids were readily converted to the alkoxycarbonyl derivatives **298** by standard techniques which involve the formation of the salt, followed by reaction with the appropriate chloroformate (R^2 = Et, Bn, Bu^i). t-Butoxycarbonyl protection was accomplished by using the anhydride **299**. As shown in Table 17 products with a range of substituents R^1 and R^2 were readily prepared.

Table 17: Preparation of *N*-alkoxycarbonyl amino acids **298**

	R^1	R^2	yield (%)	amino acid derived from		R^2	yield (%)
e	H	Et	70	glycine			
f	Me	Et	71	alanine	a	Bn	68
g	Pr^i	Et	70	valine	b	Bn	58
h	Bu^i	Et	69	leucine	c	Bn	61
i	Bu^s	Et	72	isoleucine			
j	Bn	Et	58	phenylalanine	d	Bn	68
300b	—	Et	77	proline	300a	Bn	77
k	Ph	Et	64	phenylglycine			
l	$(CH_2)_3NHCO_2Et$	Et	71	ornithine			
m	$(CH_2)_4NHCO_2Et$	Et	64	lysine			
p	—	Et	75	α-aminoisobutyric acid			
n	$(CH_2)_2SMe$	Et	62	methionine			
o	$(CH_2)_2CONH_2$	Et	69	asparagine			
p	$(CH_2)_3CO_2Me$	Et	55	methyl glutamate			
q	$(CH_2)_2CO_2Me$	Et	58	methyl aspartate			
r	$(CH_2)_3CO_2H$	Et	20	glutamic acid			
s	Me	Bu^t	79	alanine			
t	Me	Bu^i	69	alanine			
302	—	Et	62	β-alanine			
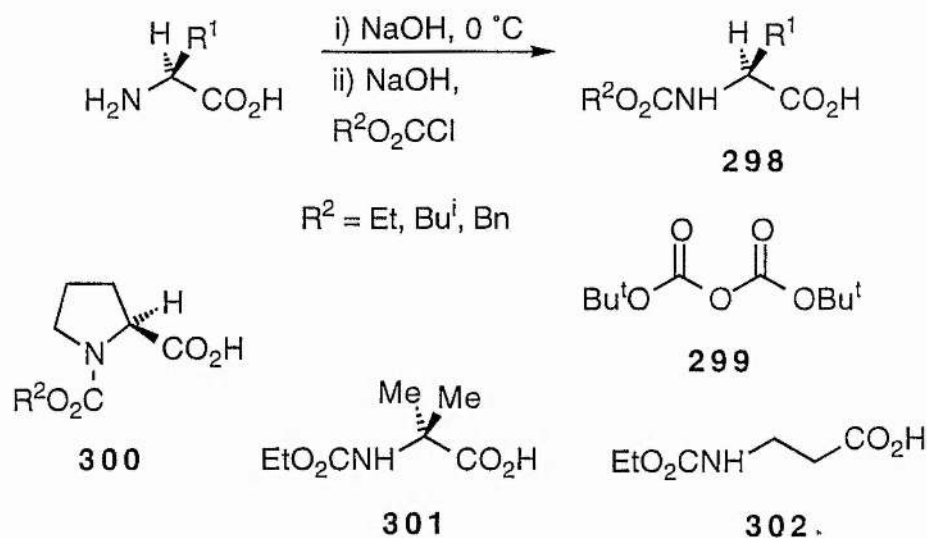
The effect of restricted rotation about the $N–CO_2R^2$ group on the ^{13}C NMR spectra may be seen in some examples. Proline is a classic example and derivatives of this amino acid are of special interest due to the E/Z isomerism that they display. Based on results from previous studies, the signals in the ^{13}C NMR spectrum arising from the ring carbons of each isomer can be assigned.
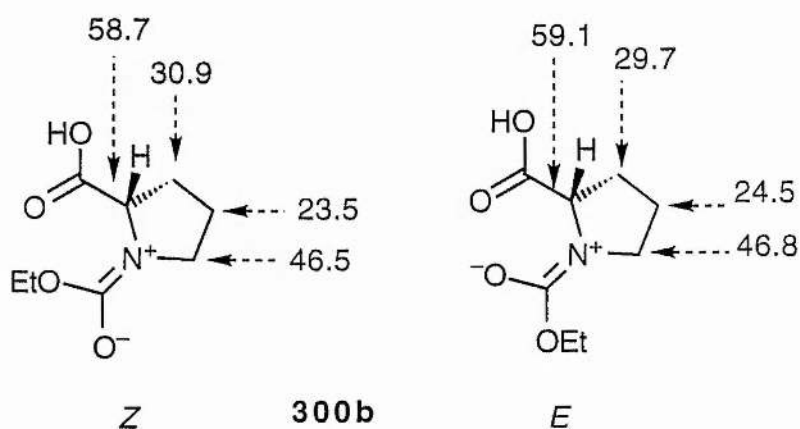
b. Synthesis of β-Oxo Ylides Derived from Amino Acids

A series of chiral stabilised γ-amino-β-oxophosphoranes **303** was now prepared by a simple procedure, by the acylation of the

(ethoxycarbonylmethylene)triphenylphosphorane with *N*–alkoxycarbonyl amino acids **298** in presence of the peptide coupling reagent, EDCI.[45] A catalytic amount of DMAP was found to enhance the reaction. The same products are formed with PyBOP mediated acylation. Since both EDCI and PyBOP are exorbitantly priced, the use of a more economically attractive peptide coupling reagent, dicylohexylcarbodiimide (DCCI), was investigated. Unfortunately, a complex mixture of products was formed and only a small amount of the required product was isolated. The urea, a byproduct of the reaction is not very water soluble and the desired product was isolated pure only after a second chromatographic separation. There is no obvious reason for the poor results of the DCCI mediated coupling.
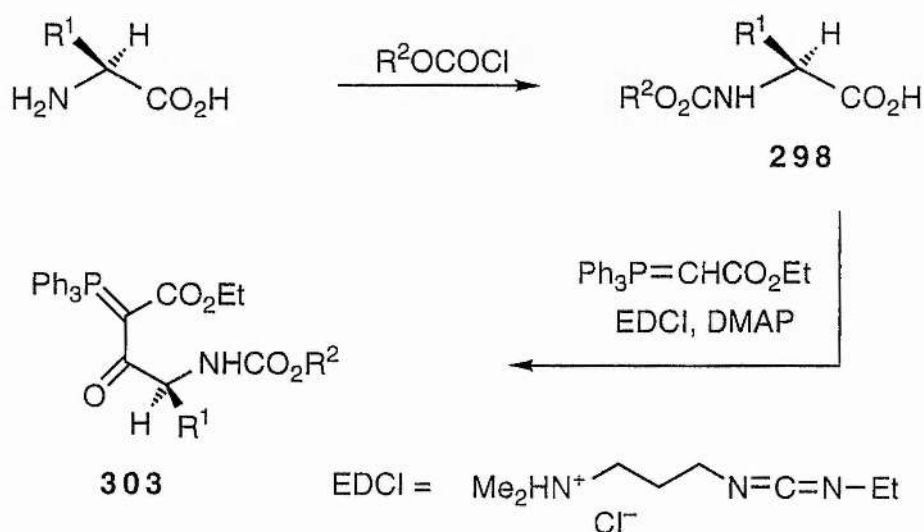
The proposed reaction pathway assumes that the acid and carbodiimide react initially with the formation of a reactive anhydride. Nucleophilic attack by the ylidic carbon affords the β-aminoacyl ylides. The ylides were obtained in moderate yield after chromatographic purification (Table 18) and most are colourless solids, except for the methionine derivative which was pale pink. This route was not expected to cause any racemisation since there is no precedent for this in the literature.

Table 18: γ-Amino-β-oxoylides **303** synthesised by the route shown.

	R^1	R^2	derived from	Yield %	δ_P	$[\alpha]_D$
a	Me	Bn	(Ala)	46	17.5	+20.3
b	Pr^i	Bn	(Val)	49	17.8	+28.7
c	Bu^i	Bn	(Leu)	44	17.5	+21.7
d	Bn	Bn	(Phe)	40	17.7	+27.9
304a	—	Bn	(Pro)	49	17.6/4[a]	−45
e	H	Et	(Gly)	51	17.8	—
f	Me	Et	(Ala)	50	18.0	+17.5
g	Pr^i	Et	(Val)	45	17.8	+22.6
h	Bu^i	Et	(Leu)	45	17.9	+17.1
i	Bu^s	Et	(Ile)	48	18.7/6[a]	+5.9
j	Bn	Et	(Phe)	32	17.7	+29.0
k	Ph	Et	(PhGly)	45	18.1	—
304b	—	Et	(Pro)	44	17.4/2[a]	−33.8
l	(CH$_2$)$_3$NHCO$_2$Et	Et	(Orn)	45	17.8	—
m	(CH$_2$)$_4$NHCO$_2$Et	Et	(Lys)	42	18.3	+26.5
n	(CH$_2$)$_2$SMe	Et	(Met)	53	18.4	+3.1
o	CH$_2$CO$_2$Me	Et	(Asp)	40	18.4	—
p	(CH2)$_2$CO$_2$Me	Et	(Glu)	38	18.3	—
q	(CH$_2$)$_2$CO$_2$H	Et	(Glu)	—	17.6	—
305	—	Et	(Glu)	—	18.0, 17.7	—
306	—	Et	(β-Ala)	52	18.1	—
r	Me	Bu^t	(Ala)	55	17.7	+4.1
s	Me	Bu^i	(Ala)	45	18.0	+13.8
307a	Me	Et	(Ala)	54	17.9	—
307b	Me	Bu^t	(Ala)	53	17.7	+5.5

a Two configurations due to restricted rotation about the N–CO$_2$R^2 group.

Ph₃P=C(CO₂Et)... 304

EtO₂C=C(PPh₃)... 305

Ph₃P=C(CO₂Et)... 306

...CO₂Buᵗ ...PPh₃ 307
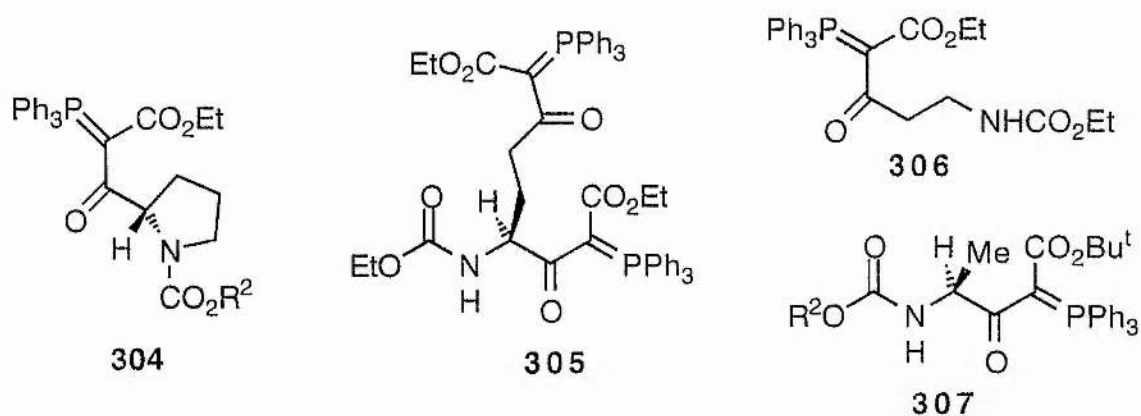
All attempts to prepare the aminoacyl ylides from *N*-protected α-amino isobutyric acid, serine and asparagine failed. Poor solubility of asparagine derivatives is a problem that is regularly encountered in peptide synthesis and it was not surprising that this amino acid was insoluble in CH_2Cl_2. More polar solvents such as DMF and DMSO were also tried but no useful results were obtained. In the case of serine, the hydroxyl group was free (unprotected) and there are two potential sites for reaction. This factor may account for the failure of the reaction. Prior protection of the hydroxyl function would be advisable in repeated studies. In principle there are no reasonable explanations why α-amino isobutyric acid does not react. Since both the ylide and the *N*-protected amino acid are isolated unchanged after 48 hours, a possible reason could be a very slow reaction. Clearly, there is a need for further study regarding the use of functionalised amino acids in this procedure.

An interesting result was obtained from *N*-ethoxycarbonyl glutamic acid where both the α and γ acid groups could react. The product obtained was a 1:1 mixture of the normal α-mono functionalised product and the α,γ-bis ylide **305**.

No ^{13}C spectroscopic information on compounds of this type could be found in the literature. The ^{13}C chemical shift values and the magnitude of the observed P–C coupling constants (Tables 19 and 20) are in agreement with the expected values. Doubling of signals arising from phosphorus coupling is

Table 19: ^{13}C NMR Spectra of N-Benzoxycarbonyl Ylides **303a-d** and **304a**, δ_C (J_{P-C})

				CO_2Et			CO_2CH_2Ph			P-Phenyl				
	CHN	P=C	COCN	CO	CH_2	CH_3	NCO_2	CH_2	Ph	C–1	C–2	C–3	C–4	R signals
a	52.5 (8)	68.8 (111)	194.8	166.7 (14)	58.7	13.8	155.5	65.9	137.1(4ry), 128.3, 127.7 (3C)	126.0 (93)	133.0 (10)	128.6 (12)	131.8 (<2)	20.4
b	60.4 (8)	69.8 (111)	194.1	166.8 (14)	58.6	13.8	156.6	66.0	137.1(4ry), 128.2, 127.6 (3C)	126.0 (94)	133.0 (10)	128.5 (12)	131.8 (<2)	32.3, 20.7, 15.9
c	55.1 (8)	69.3 (111)	195.2	166.8 (15)	58.7	13.9	156.6	66.1	137.1(4ry), 128.3, 127.7 (3C)	126.2 (94)	133.1 (10)	128.5 (12)	131.8 (2)	43.6, 25.1, 21.9, 21.8
d	57.1 (8)	69.3 (111)	193.5(4)	166.7 (14)	58.4	13.6	155.5	65.7	136.9(4ry), 128.0, 127.4 (3C)	125.7 (93)	128.4 (10)	132.9 (12)	131.7 (<2)	138.1, 129.6, 128.0, 125.9, 39.6
304a	62.9 (8)	69.2 (111)	195.6(3)	167.51 (15)	58.4	13.7	154.54	66.3	137.4, 128.2, 127.6 (3C)	126.4 (93)	128.8 (13)	133.3 (10)	131.6 (4)	46.9, 30.7, 23.8
	62.4 (8)	68.9 (111)	195.1(3)	167.46 (15)	58.3		154.51	66.0		126.2 (94)		132.9 (10)	131.5 (4)	47.4, 31.8, 23.0

For **304a** the signals for both carbamate rotamers are given where they differ

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Table 20: ^{13}C NMR Spectra of N-Ethoxycarbonyl Ylides: 303e-p, 304b, 305 and 306, δ_C ($J_{P, C}$)

	C–CO₂Et						N–CO₂Et			P–Phenyl				R signals
	$\underline{C}HN$	$P=\underline{C}$	$\underline{C}OCN$	CO	CH_2	CH_3	CO	CH_2	CH_3	C-1	C-2	C-3	C-4	
e	49.2 (8)	68.9 (112)	190.6	167.4 (15)	58.7	13.9	156.6	60.4	14.7	125.9 (94)	133.2 (10)	128.6 (13)	131.9 (2)	—
f	52.4 (8)	68.8 (111)	195.1	166.8 (15)	58.7	13.8	155.9	60.2	14.7	126.2 (94)	133.1 (10)	128.6 (13)	131.8 (2)	20.5
g	60.3 (8)	70.0(110)	194.4	166.9 (15)	58.8	13.9	157.0	60.4	14.6	126.1 (94)	133.2 (10)	128.5 (13)	131.8 (2)	32.3, 20.7, 15.9
h	54.9 (8)	69.2 (110)	195.4	166.8 (15)	58.7	13.9	156.6	60.3	14.6	126.3 (94)	133.1 (10)	128.5 (13)	131.7 (2)	43.7, 25.1, 24.0, 21.8
i	60.5 (8)	70.3 (110)	194.5	166.8 (14)	58.7	13.8	156.9	60.3	14.6	126.2 (93)	133.1 (10)	128.5 (12)	131.6 (<2)	39.4, 27.8, 16.8, 12.1
	57.2 (8)	69.8 (110)		166.7 (14)						126.15 (93)			38.8, 22.8 12.9	
j	56.7 (9)	64.5 (107)	193.7	167.9 (14)	58.7	13.7	156.0	60.2	14.6	125.9 (94)	133.2(10)	128.6 (13)	131.9 (2)	138.1(4ry), 131.8(2C), 129.7(2C), 126.0, 39.9
304b	62.7 (8)	69.3 (110)	195.5	167.54 (15)	58.4	13.8	155.0	60.6	14.8	126.7 (94)	133.4 (10)	128.5 (13)	131.6 (2)	47.2, 31.7, 22.9
k	60.3 (8)	69.6 (111)	191.3	166.6 (14)	58.9	13.8	155.6	60.0	14.6	125.7 (93)	133.0 (10)	128.5 (13)	131.8 (2)	140.6(4ry), 128.0, 127.1
l	55.0 (8)	68.9 (109)	194.7	167.1 (14)	58.6	13.6	156.8*	60.3	14.7*	126.0 (94)	133.1 (10)	128.6 (12)	131.9 (<2)	156.6*, 60.3, 39.4, 31.6, 25.6, 14.6*
m	55.7 (8)	69.2 (109)	194.5	166.8 (14)	58.7	13.7	156.8*	60.4	14.7*	126.0 (93)	133.1 (10)	128.5 (12)	131.9 (2)	156.6*, 60.4, 40.9, 34.4, 29.0, 22.7, 14.6*
n	56.2 (8)	69.3 (112)	193.5	166.8 (14)	58.8	13.8	156.5	60.4	14.6	125.9 (93)	133.1 (9)	128.6 (12)	131.9 (2)	35.0, 30.5, 15.6.
o	53.6 (8)	69.4 (110)	192.2	166.9 (14)	58.9	13.7	156.1	60.5	14.6	125.8 (94)	133.2 (10)	128.6 (12)	131.9 (<2)	171.6, 51.6, 38.7.
p	55.8 (9)	69.3 (110)	193.6	166.7 (14)	58.8	13.7	156.4	60.4	14.6	125.9 (94)	133.1 (10)	128.6 (12)	131.9 (<2)	174.4, 51.4, 31.1, 30.1.
q	62.5 (9)	68.7(110)	192.8	167.4 (14)	58.5	13.7	151.6	62.1	14.2	125.9 (94)	133.1 (10)	128.5 (12)	132.0 (<2)	174.5, 31.4, 23.2.
305	49.2 (8)	69.4 (112)	197.3	167.5 (16)	58.5	13.7	156.7	62.0	14.6	127.1 (94)	133.0 (10)	128.5 (12)	132.1 (2)	195.0, 166.5, 131.9(3), 128.4 (12), 126.3 (94), 69.4 (112), 58.4, 36.8, 29.3
306	—	71.4 (111)	196.0	167.9 (15)	58.5	13.7	156.6	60.2	14.8	126.5 (94)	133.0 (10)	128.6 (12)	131.7 (2)	40.0 (6), 37.4.

For 303i and 304b the signals for both carbamate rotamers are given where they differ.   Assignments for signals marked * may be interchanged.

observed throughout the P-phenyl groups and encompasses the ester carbonyl function and the γ-carbon of the acyl substituent. The value of ^2J $_{P-C}$ for the keto carbonyl is 6 Hz on average and this promises a successful FVP result. Similiarly, the ^{31}P spectra form a consistent pattern.

Many molecules show intramolecular mobility such as rotations about σ bonds. A typical example is N,N-dimethylformamide, which exists as an equilibrium mixture of cis and trans rotamers due to the partial π character of the N–CO bond. Rotation of the dimethylamino group is restricted at room temperature but occurs at higher temperatures.

The effect of restricted rotation about the N–CO bond on the ^{13}C NMR spectrum may be seen in the proline and isoleucine derivatives 304, 303i where certain resonances are doubled. The ^{31}P spectra illustrate this feature unambiguously. Proline occupies a unique place in peptide and protein structure because of the restricted mobility at the N–CO bond. The factors affecting E–Z equilibrium have received considerable interest.[203] In the ^{13}C spectrum of the prolinyl ylide, only the ring carbon resonances of the E and Z conformers can be identified unambiguously. Restricted rotation in isoleucine derivatives has not been documented.

304b
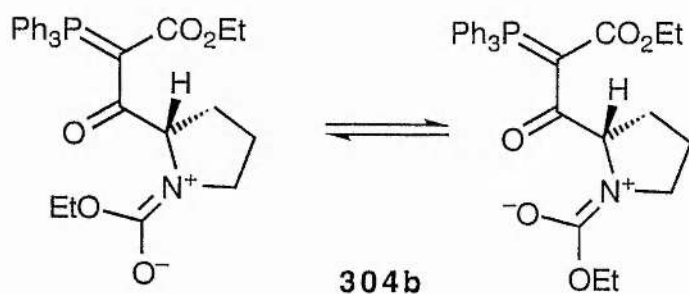
An equilibrium exists at room temperature and in both cases the two conformers are favoured equally. As with all equilibria, thermodynamic equations may be employed to describe the situation. The relevant equations are:

$$\Delta G^* = RT_c \, [22.96 + \ln(T_c/\delta_v)] \qquad \delta_v = (v_A - v_B)$$

where v_A-v_B is the separation of the signals of the two conformers. T_c is the temperature at which the signals merge and ΔG^* is the free energy barrier to rotation. A variable temperature NMR experiment was carried out by recording spectra were recorded at 10 °C intervals while the temperature was being increased. The NMR studies were performed both for ^{31}P and ^{13}C in d$_8$-toluene as the solvent.

The ΔG^* value calculated for both compounds are listed below.

		303i	304b
from ^{31}P:	Tc(K)	330	323
	δ_v (Hz)	4.5	10.5
	ΔG^* (kJmol^{-1})	74.8	70.9
from ^{13}C:	ΔG^*(kJmol^{-1})	—	71.5 ($\pm$ 2)

These values are typical for carbamates.

c. Pyrolysis β-Aminoacyl Ylides

As mentioned earlier FVP of the β-aminoacyl ylides **303** could potentially provide access to α,β-acetylenic γ-amino acid derivatives. These compounds are of considerable interest and as discussed at the beginning of this section relatively few compounds of this type have been previously prepared.

Thus, FVP of the β-keto ylides **303** was carried out at 600 °C and 1.0-2.0 x 10^{-2} Torr and resulted in the desired loss of Ph$_3$PO and the formation of the protected acetylenic amino acids **308** apparently without significant racemisation. The spectra of the crude pyrolysates showed that the reaction is obviously very clean with no secondary fragmentation products being formed.
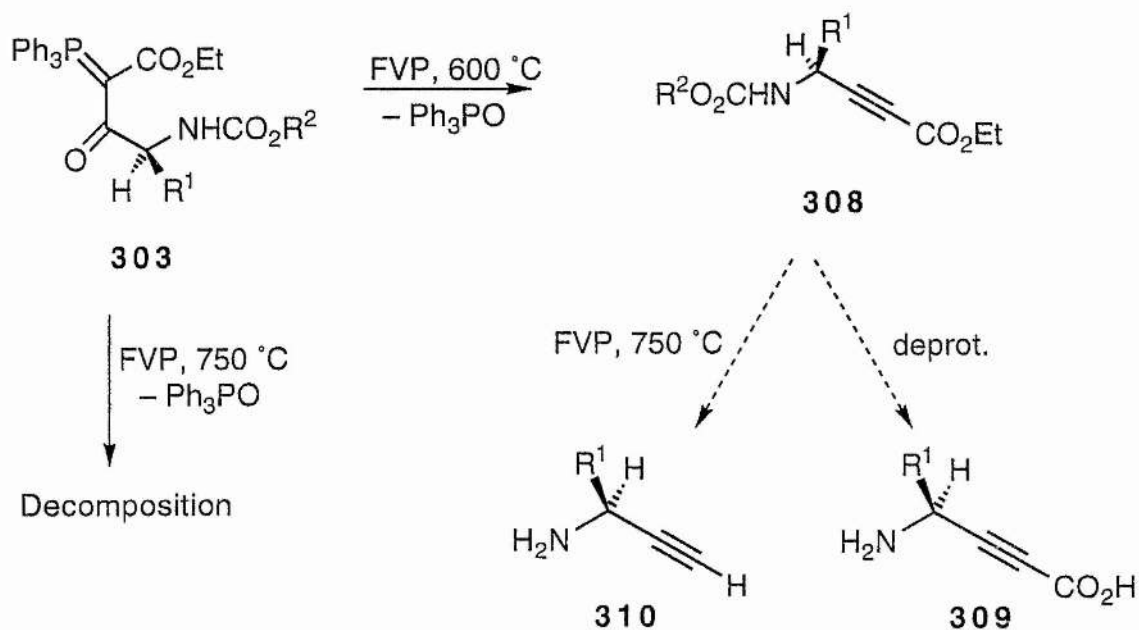
The products were purified by chromatography and obtained as yellow oils in yields of approximately 35–48%. These may be converted by simple deprotection methodology into the acetylenic amino acids **309**. Alternatively F.V.P. at a higher temperature is expected to lead to the loss of the ester function,[60] providing access to α-ethynylamines **310**. Attempts to access **310**

Table 21: Acetylenic compounds **308** prepared.

	R^1	R^2	derived from	Yield %	$[\alpha]_D$
a	Me	Bn	(Ala)	29	−30.3
b	Pr^i	Bn	(Val)	30	−34.4
c	Bu^i	Bn	(Leu)	30	−26.7
d	H	Et	(Gly)	39	—
e	Me	Et	(Ala)	32	−91.0
f	Pr^i	Et	(Val)	34	−49.5
g	Bu^i	Et	(Leu)	36	−74.5
h	Bu^s	Et	(Ile)	38	+9.1
i	Me	Bu^i	(Ala)	33	−9.1

311
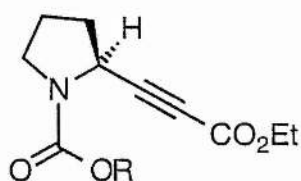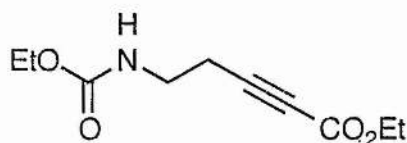
		yield	$[\alpha]_D$
a	R = Bn	48%	−114.4
b	R = Et	48%	−137.7

312

49%

directly by pyrolysis of the ylides at 750 °C led to decomposition. Compounds such as **309** may be of interest for the formation of modified peptides.

The successful pyrolysis results appear in Table 21. In the case of the derivatives not listed in the Table, only fragmentation products (some could be identified by NMR) and Ph$_3$PO were obtained.

It was hoped that groups such as R^2 = Bu^t and Bu^i would lead to automatic deprotection under FVP conditions. However, the Boc protected analogue led to complete decomposition while the Bu^i group remained intact in the formation of **308i**. Attempts to determine the enantiomeric excess of compounds **308** by ^{1}H NMR in the presence of the chiral lanthanide shift reagent Eu(hfc)$_3$ as well as by means of chiral stationary-phase HPLC were unsuccessful. These conditions have so far prevented the establishment of precise e.e. measurements although the substantial optical rotations obtained as shown in the Table suggest that they are certainly not racemic.

The structure of the acetylenic products was readily confirmed by their ^{13}C NMR spectra (Tables 22 and 23). Evidence of restricted rotation around the carbamate bond is also present in the ^{13}C spectra of some of these. For example restricted rotation around the *N*-alkoxycarbonyl part of the leucine derived acetylenic amino ester **308g** is thought to be responsible for the apparent peak doubling observed in that case.

Table 22: ^{13}C NMR Spectra of N-Benzoxycarbonyl Aminoacetylenic Esters **308a-c** and **311a**. δ_C (J_{P-C})

	$\underline{C}{\equiv}CCO_2$	$C{\equiv}\underline{C}CO_2$	$\underline{C}HNH$	$N\underline{C}O_2Bn$	$\equiv C\underline{C}O_2$	CH_2	CH_3	$\underline{C}H_2Ph$ Ph	R signals
308a	74.4	86.8	38.8	153.2	155.0	62.2	14.0	67.2	136.0 (4ry), 128.6 (2C), 128.3, 128.2 (2C)	21.6
308b	76.0	85.2	49.2	153.3	155.5	62.1	14.0	67.3	136.1 (4ry), 128.6 (2C), 128.3, 128.2 (2C)	33.0, 18.6, 17.9
	75.8	81.6								
308c	75.0	86.5	41.8	153.3	155.3	62.1	14.0	67.2	136.1 (4ry), 128.6 (2C), 128.3, 128.2 (2C)	44.3, 24.9, 22.4, 22.1
	71.2	83.4								
311a	74.3	87.0	—	153.4	154.4	62.0	14.0	67.0	136.5(4ry), 128.4 (2C), 128.0, 127.9	48.4, 46.3, 33.2, 24.6
	70.3	86.8	—		154.1					47.9, 45.9, 33.2, 23.8

The signals for both carbamate rotamers are given where they differ.

Table 23: ^{13}C NMR Spectra of N-Ethoxycarbonyl Aminoacetylenic Esters **308d-i, 311b** and **312.** δ_C ($J_{P,C}$)

	$\underline{C}{\equiv}CCO_2$	$C{\equiv}\underline{C}CO_2$	$\underline{C}HNH$	$N\underline{C}O_2Et$	${\equiv}C\underline{C}O_2Et$	CH_2	CH_3	CH_2	CH_3	R signals
308d	75.1, 75.0	83.5, 83.3	30.7, 29.8	153.2	156.0	62.2	14.6	61.5	14.0	—
308e	74.2	87.1	38.6	153.3	155.3	62.1	14.5	61.4	14.0	21.6
308f	75.9, 75.2	85.6, 86.9	49.7, 47.7	153.4, 153.6	156.0, 156.6	62.1, 62.0	14.5	60.1, 61.4	14.0	18.0, 18.6, 33.2 / 17.8, 18.8, 33.3
308g	74.8, 74.4	86.9, 88.2	40.2, 41.6	153.4, 153.6	155.7, 156.0	62.1, 60.0	14.5	61.9, 61.4	14.0	22.1, 22.3, 24.8, 44.3 / 22.1, 22.5, 24.9, 44.6
308h	75.6, 76.0	86.1, 85.3	47.6, 47.8	153.4, 153.3	155.9, 155.7	62.1, 62.0	14.5	61.9, 62.0	14.0	39.4, 25.2, 15.1, 11.5 / 39.6, 25.8, 14.7, 11.4
308i	74.3	87.1	38.7	153.3	155.5	62.1	14.0	—	—	71.6, 28.0, 19.0 (2C), 21.6
311b	74.1, 70.1	81.1, —	—	154.7, 154.5	153.5	62.0	14.7	61.5	14.0	47.7, 46.1, 33.2, 23.8 / 48.2, 45.8, 32.4, 24.6
312	74.3, 74.2	86.1, 87.1	—	153.5	156.5	62.0	14.6	61.1	14.0	38.9, 20.3

The signals for both carbamate rotamers are given where they differ.

212

308g
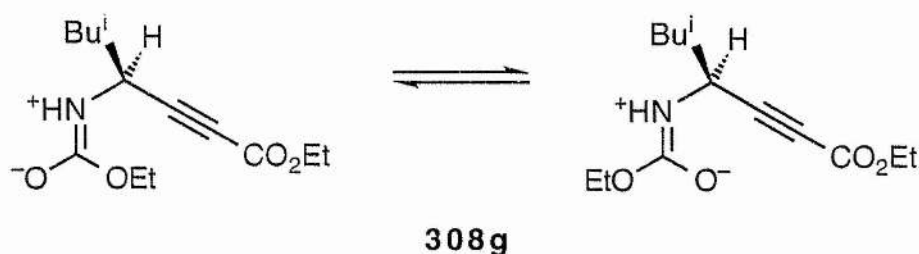
It is noteworthy that the ^{13}C NMR spectrum of the acetylenic amino ester **308h**, derived from isoleucine, has 4 sets of resonances for the acetylenic carbons due to the presence of the other diastereomer. If no racemisation had occurred one would have expected 2 sets of resonances (for the *E* and *Z* rotamers). From the relative intensity of these signals an approximate measure of the % d.e could be obtained and gave a value of 70%. This illustrates the mildness of the conditions used during pyrolysis.

4. Further Reactions of Acetylenic Amino Acids Derivatives

a. Addition Of HBr

A classical method for the deprotection of *N*-alkoxycarbonyl and benzoxycarbonyl groups is by the use of HBr in acetic acid and it was this procedure that was employed. A solution of the *N*-ethoxycarbonylalanine derivative **308e** in the HBr/acetic mixture was stirred at room temperature. Even after a lengthy reaction period, that protecting group remained intact, however HBr added across the triple bond to give **313** as an equal mixture of isomers.

308e   HBr/MeCO$_2$H   **313**
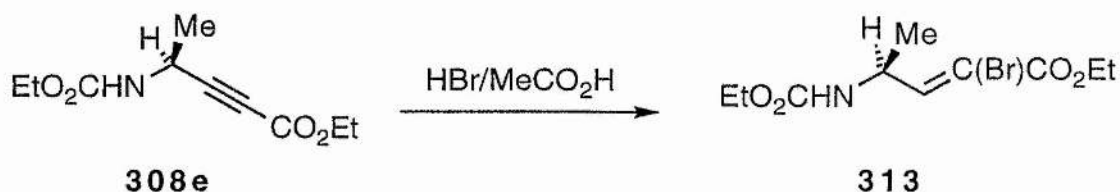
b. Catalytic Hydrogenation

Deprotection of *N*-benzoxycarbonyl groups by hydrogenation is another standard technique. Hydrogenation of the *N*-benzoxycarbonyl acetylenic amino esters **308** would not only remove the protecting group, but also provide access to chiral γ-aminobutyric acid GABA analogues by hydrogenation of the triple bond. GABA is a major neurochemical component in seisure inhibition and it is known that epileptic convulsions occur when GABA levels fall below a certain threshold in the brain.[204] An important treatment of epilepsy has focused on raising GABA levels by the irreversible inactivation of GABA transaminase. It is hoped that the chiral analogues could find use in this area and for the preparation of modified peptides.

The *N*-benzoxycarbonyl acetylenic amino esters **308a-c** and **311a** were therefore subjected to hydrogenation and the desired compounds **314** and **315** were isolated in good yields (Table 24).
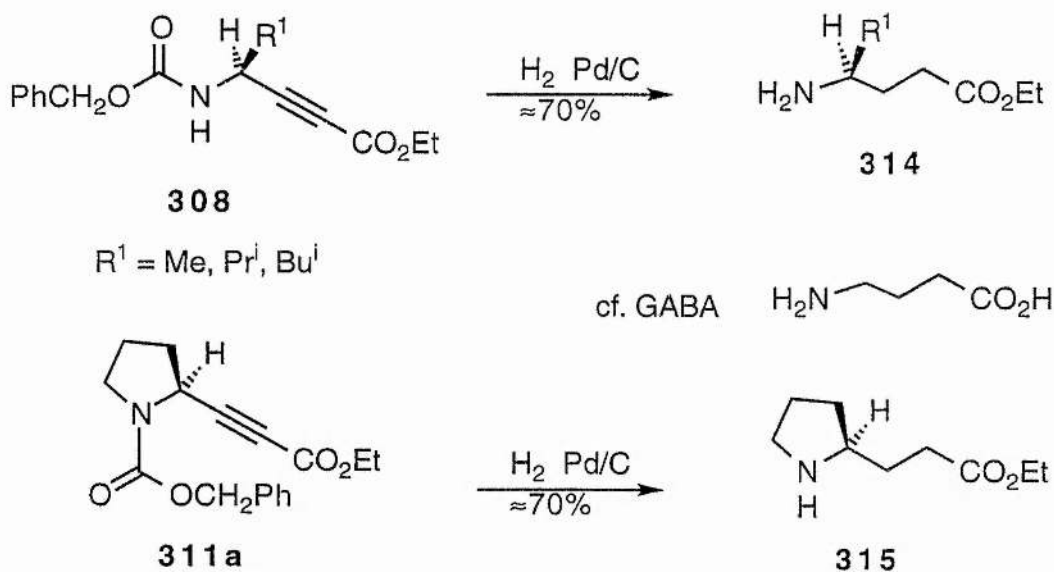
An indirect method for obtaining information on the degree of racemisation during FVP may be gained by derivatising **314** with Mosher's acid.[156] Thus the reaction of these compounds with the Mosher acid chloride

Table 24: Preparation of **314a-c** and **315**

	R^1	yield (%)	α_D	e.e. (%)
314a	Me	74	−2.5	70
314b	Pr^i	72	+7.2	85
314c	Bu^i	70	+6.9	>85
315	—	78	−8.6	>95

316 yields the diastereomer **317**. Careful analysis of the ^{13}C, ^{1}H and ^{19}F spectra allowed estimation of the e.e. values as shown in Table 24.
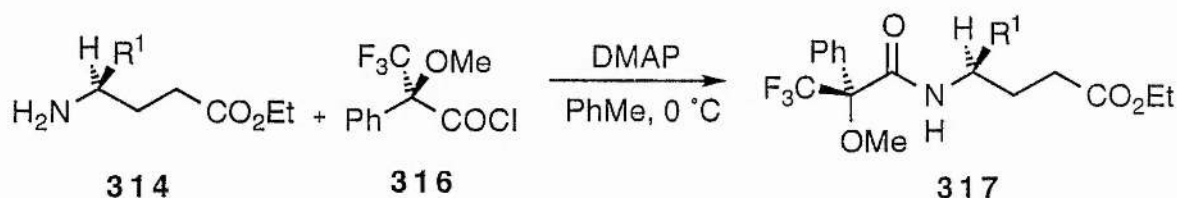
5. Preparation and Pyrolysis of *N*-unprotected Aminoacyl Ylides

Deprotection of the *N*-protected ylides **303** was expected to provided access to the free amino ylides and their pyrolysis was expected to provide direct access to the unprotected aminoesters. Therefore deprotection of the t-butoxycarbonyl derivatives **303r**, and **307a-b** was attempted using trifluoroacetic acid. None of the desired products **318** was obtained even after 4 hours of reaction time. Instead the phosphonium trifluoroacetate salts **319** were isolated.
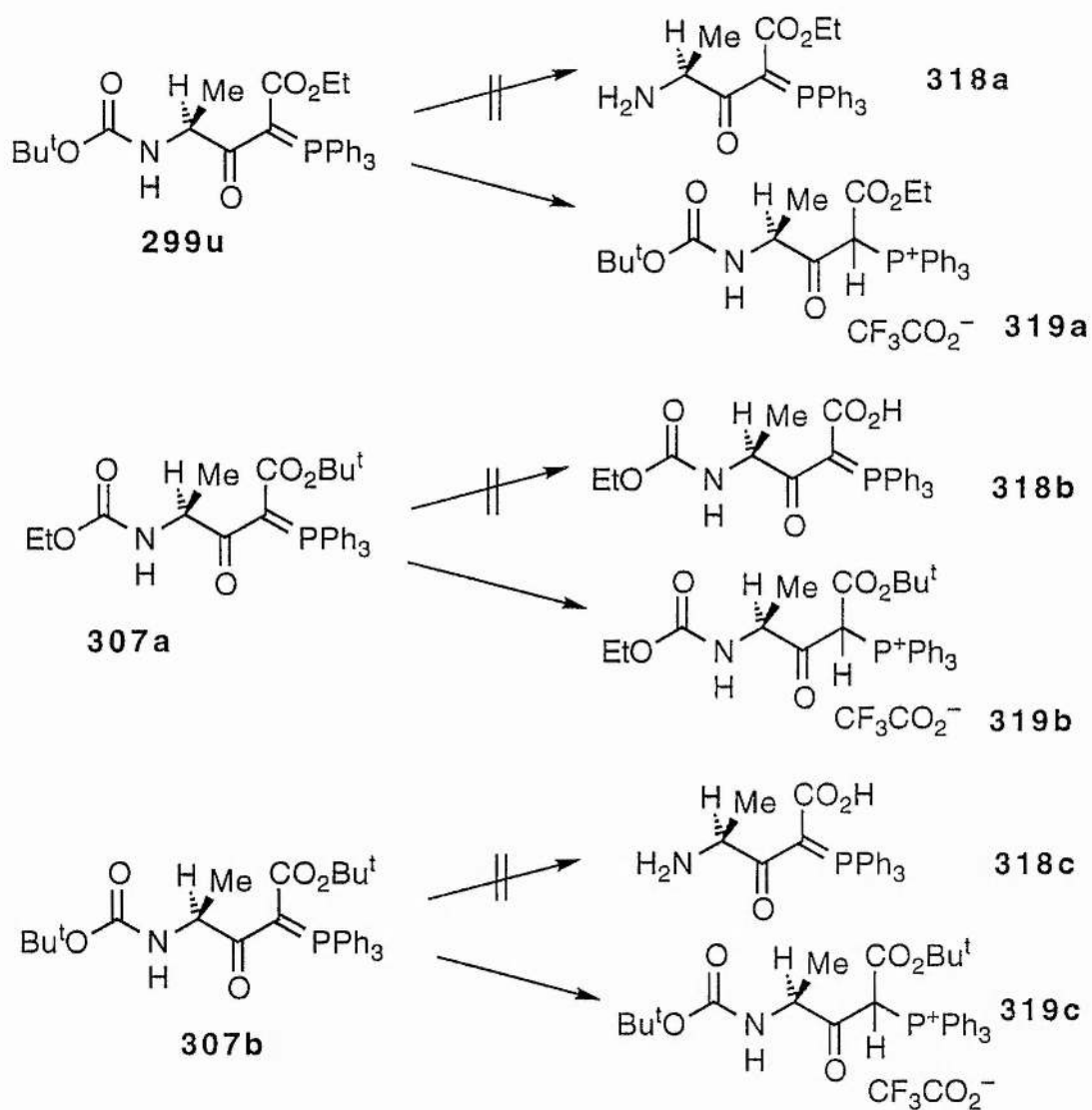
An alternative route employing the benzoxycarbonyl ylides **303a, b** and **304a** was investigated. Catalytic hydrogenation of the latter was expected to selectively cleave the benzoxycarbonyl group while the P=C bond remained intact. The hydrogenation proceeded smoothly to afford the deprotected ylides **320** and **321** in in good yields (Table 25). Surprisingly the pyrolysis of these ylides at 600 °C afforded the novel cyclic ylides **322** and **323** by loss of ethanol and none of the alkynes were formed.

These cyclic ylides possess the tetramic acid (pyrrolidine-2,4-dione) ring system. This structural unit is the component of many natural products
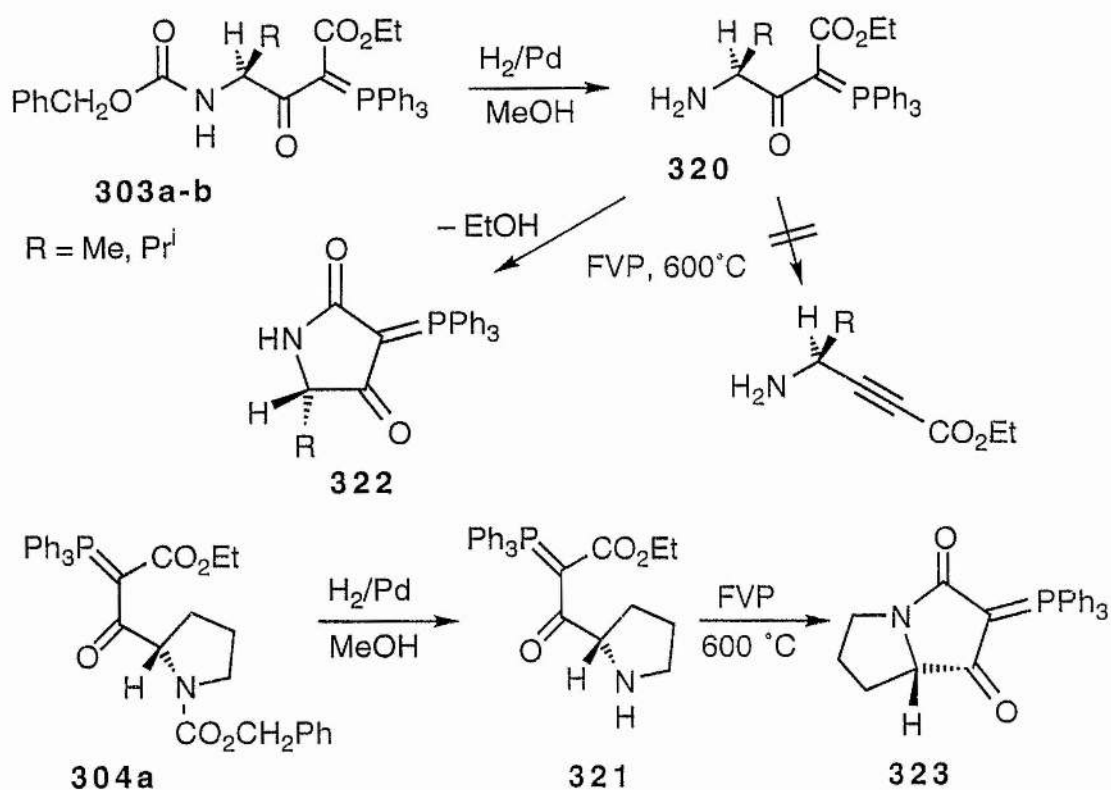
which exhibit biological activity.[205] Further transformation of these ylides is expected to provide a range of synthetically useful compounds. For example, FVP could result in the extrusion of Ph_3PO (note $^2J_{P-C} = 7$ Hz) while oxidation of the ylidic bond might provide the triketones. Most significantly, hydrolysis may directly give the tetramic acids.

Table 25: Preparation and pyrolysis of N-unprotected ylides

	R	yield (%)	δ_P	FVP product	yield (%)	δ_P
320a	Me	86	+18.1	**322a**	68	+10.8
320b	Pr^i	89	+18.7	**322b**	72	+10.8
321	—	90	+18.1	**323**	67	+10.1

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H. X-Ray Structure Determinations

Since a variety of novel ylides were available from the work described in earlier sections, it seemed worthwhile to examine the structures of representative examples by X-ray crystallography. The bond lengths would be expected to give a measure of the contribution from the phosphonium enolate type forms and the relative *syn* or *anti* conformation of the adjacent C=P and C=O bonds is of particular interest for the examples containing more oxo groups.

As described in the experimental section, suitable crystals were obtained for the trioxo ylide **143b**, the tetraoxo ylide **144a**, the hexaoxo bis-ylide **203** and the tetraoxo bis-ylide **208**. The resulting structures are shown in Figures 1–5 on the following pages.
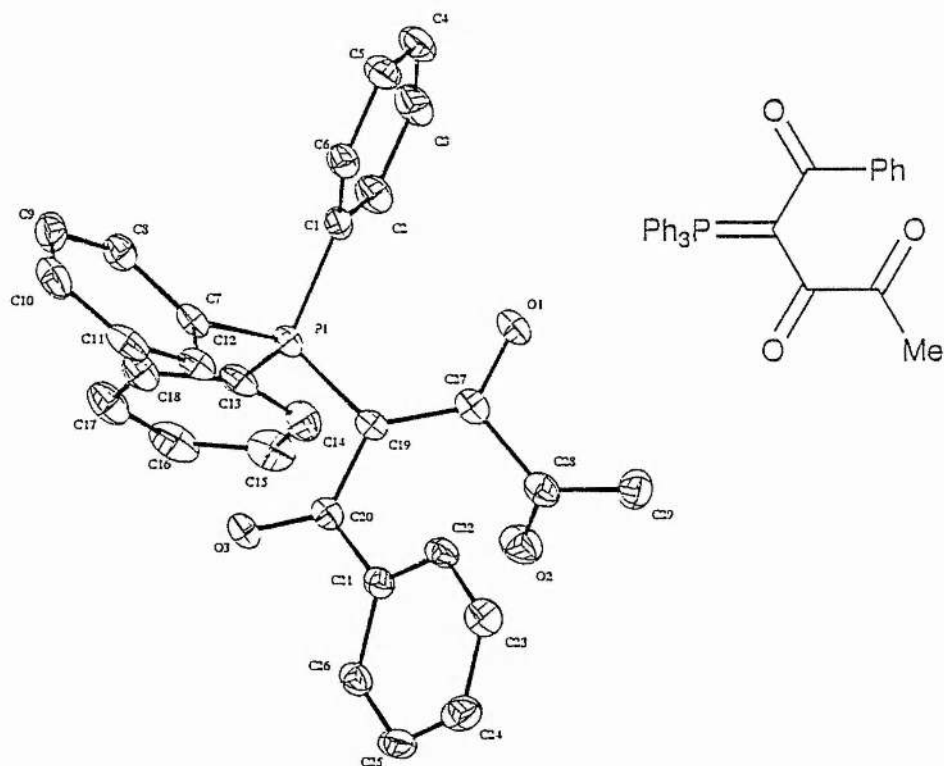
Figure 1: X-Ray structure of trioxo ylide **143b**. Selected bond lengths; P(1)–C(19) 1.760, C(19)–C(20) 1.443, C(20)–O(3) 1.239, C(19)–C(27) 1.430, C(27)–O(1) 1.239, C(27)–C(28) 1.530, C(28)–O(2) 1.2132 Å.
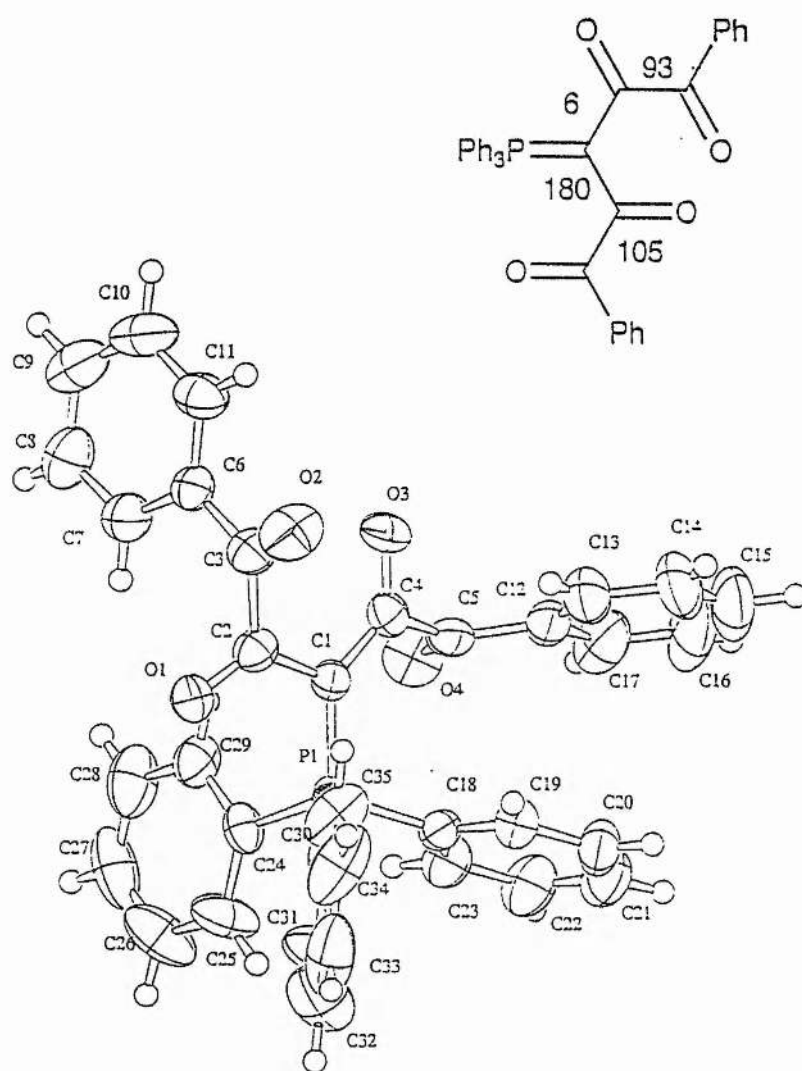
Figure 2: X-Ray structure of tetraoxo ylide **144a**. Selected bond lengths; P(1)–C(1) 1.758, C(1)–C(2) 1.422, C(2)–O(1) 1.237, C(2)–C(3) 1.540, C(3)–O(2) 1.217, C(1)–C(4) 1.437, C(4)–O(3) 1.239, C(4)–C(5) 1.530, C(5)–O(4) 1.213 Å; dihedral angles P(1)–C(1)–C(2)–O(1) 5.6, O(1)–C(2)–C(3)–O(2) 92.7, P(1)–C(1)–C(4)–O(3) 179.5, O(3)–C(4)–C(5)–O(4) 105.3 °.
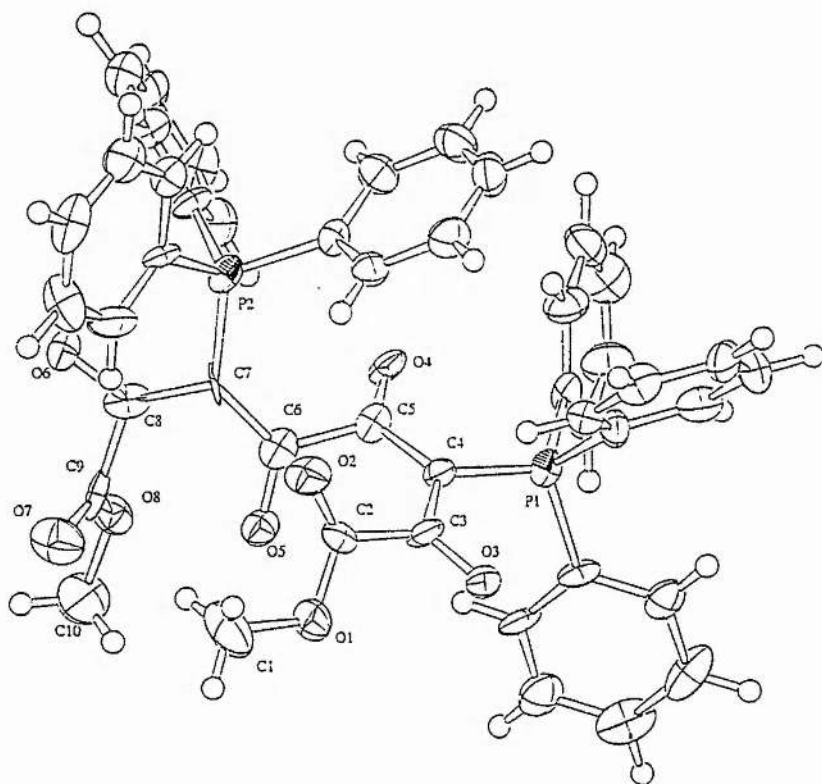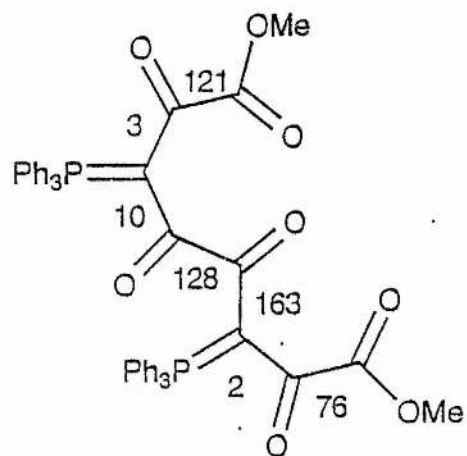
Figure 3: X-Ray structure of hexaoxo bis ylide **208**. Selected bond lengths; P(1)–C(4) 1.77, C(4)–C(3) 1.40, C(3)–O(3) 1.26, C(3)–C(2) 1.53, C(2)–O(2) 1.18, C(4)–C(5) 1.46, C(5)–O(4) 1.25, C(5)–C(6) 1.53, C(6)–O(5) 1.25, C(6)–C(7) 1.42, C(7)–P(2) 1.76, C(7)–C(8) 1.40, C(8)–O(6) 1.24, C(8)–C(9) 1.54, C(9)–O(7) 1.21 Å; dihedral angles P(1)–C(4)–C(3)–O(3) 3, O(3)–C(3)–C(2)–O(2) 121, P(1)–C(4)–C(5)–O(4) 10, O(4)–C(5)–C(6)–O(5) 128, O(5)–C(6)–C(7)–P(2) 163, P(2)–C(7)–C(8)–O(6) 2, O(6)–C(8)–C(9)–O(7) 76 °.

A
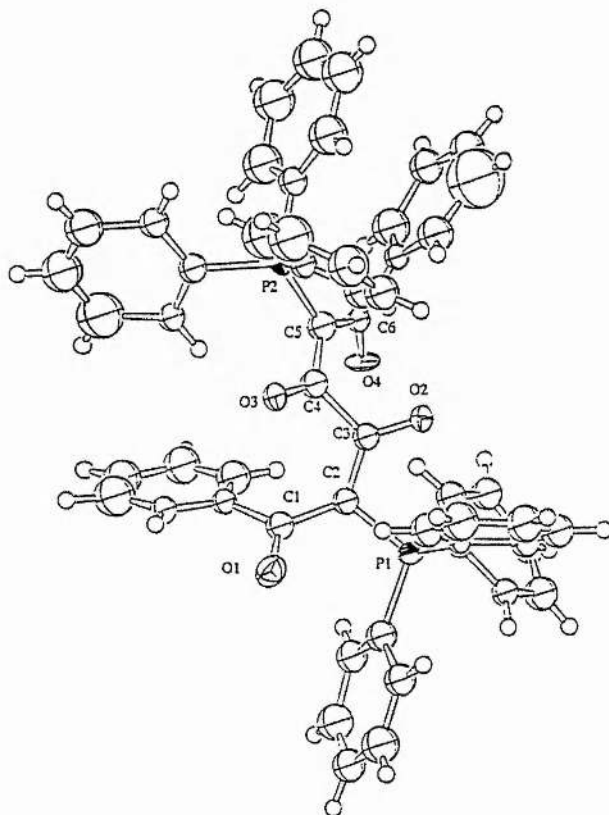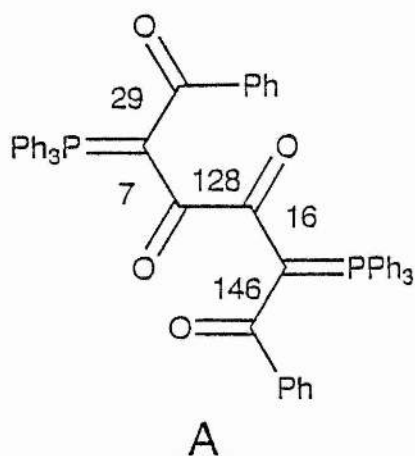
Figure 4: X-Ray structure of tetraoxo bis ylide **203**. Selected bond lengths; Molecule A

P(1)–C(2) 1.73, C(2)–C(1) 1.49, C(1)–O(1) 1.24, C(2)–C(3) 1.43, C(3)–O(2) 1.21, C(3)–C(4) 1.60, C(4)–O(3) 1.20, C(4)–C(5) 1.39, C(5)–P(2) 1.80, C(5)–C(6) 1.50, C(6)–O(4) 1.16 Å; dihedral angles P(1)–C(2)–C(1)–O(1) 29, P(1)–C(2)–C(3)–O(2) 7, O(2)–C(3)–C(4)–O(3) 128, O(3)–C(4)–C(5)–P(2) 16, P(2)–C(5)–C(6)–O(4) 146 °.
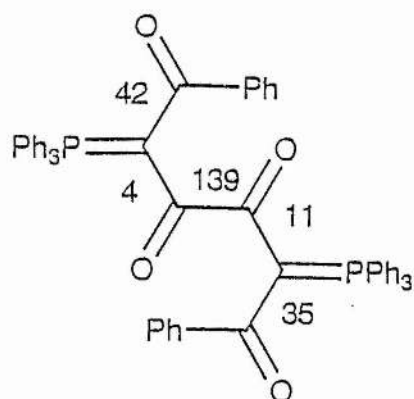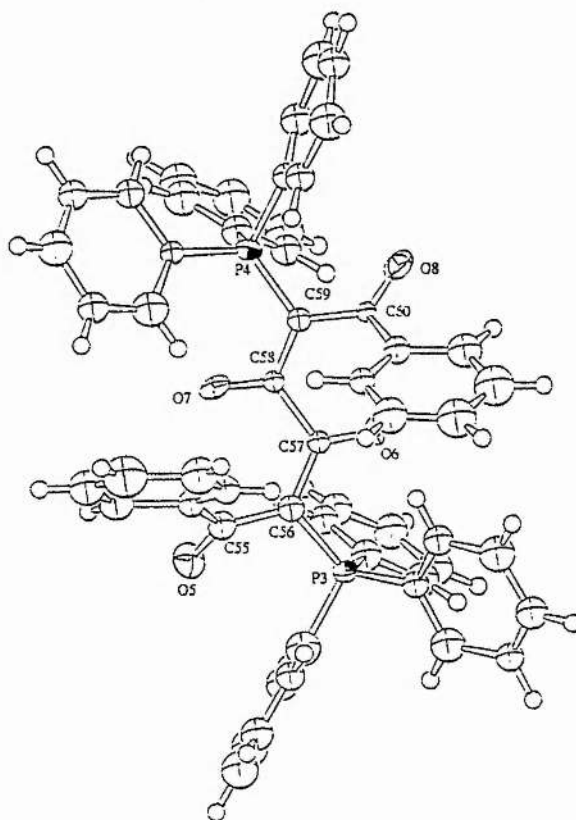
Figure 5: X-Ray structure of tetraoxo bis ylide **203**. Selected bond lengths; Molecule B

P(3)–C(56) 1.74, C(56)–C(55) 1.46, C(55)–O(5) 1.22, C(56)–C(57) 1.44, C(57)–O(6) 1.21, C(57)–C(58) 1.49, C(58)–O(7) 1.26, C(58)–C(59) 1.44, C(59)–P(4) 1.75, C(59)–C(60) 1.37, C(60)–O(8) 1.25 Å; dihedral angles P(3)–C(56)–C(55)–O(5) 42, P(3)–C(56)–C(57)–O(6) 4, O(6)–C(57)–C(58)–O(7) 139, O(7)–C(58)–C(59)–P(4) 11, P(4)–C(59)–C(60)–O(8) 35 °.

In general terms it might be assumed that compounds of the type $R(C=X)_nR$ would prefer to exist in a conformation with adjacent groups *anti* to each other to minimise dipole repulsions. In the case of β-oxo ylides however, the importance of the phosphonium enolate form in which there is electrostatic attraction between P and O means that the *syn* form may be preferred. In simpler cases it has previously been found that for ylides with β-keto and β'-ester carbonyls the first is *syn* and the second *anti* in the X-ray structures which have been determined.[15,109] The molecules studied here should give an idea just how far these principles can be extended.

The structure of **143b** shows the *syn* relationship of the ylide bond to each of the neighbouring carbonyls while the β- and γ-carbonyls are *anti* to each other. The bond lengths show clear evidence of the expected phosphonium enolate contributing form.

When it comes to the tetraoxo ylide **144a**, a most surprising result is observed. This time one β-carbonyl is *syn* to the ylide bond while the other is *anti* to it. The two γ-carbonyls are then at approximately 90 ° to the β-carbonyls. There is again considerable phosphonium enolate character and this is slightly greater for the *syn* group [C(1)–C(2) is slightly shorter than C(1)–C(4)].

We now consider the hexaoxo bis-ylide **208** and, as shown in Figure 3, the observed structure is again unexpected. At one ylide position the two adjacent carbonyls are *syn* but at the other one is *syn* and one *anti*. The outermost carbonyl groups are in a gauche relationship to those closer to the ylide functions. The central oxalyl function is also at an uneven angle as this is a pure single bond.

In view of these observations, the tetraoxo bis-ylide **203** gave a fascinating result. As shown in Figures 4 and 5 there are two different molecules in the unit cell and this made solving the structure rather challenging since, from a crystallographic point of view the size of the

molecule is effectively doubled from C_{54} to C_{108}. The two structures occur in a 1 : 1 ratio and differ only in the orientation of one of the outer carbonyls with respect to the ylide bond. In form A it is *anti* while in form B it is *syn*. Apart from this all other conformations are *syn* and again the central oxalyl unit is a purely single bond and so at an uneven angle.

The structures obtained here serve to illustrate that the energetic advantage associated with the *syn* conformation of the β-oxo ylide moiety is not very great, especially if there are already a number of such interactions elsewhere in the molecule concerned. Considerable delocalisation in the phosphonium enolate sense can also take place in the *anti* form. In some of the cases here it is clear that crystal packing forces are enough to override any such small structural preferences.

APPENDIX

Ray Structural Data for compounds **143b**, **144a**, **208** and **203**.

Table 26: Atomic coordinates and U_{eq} for **143b**

atom	x	y	z	U_{eq}
C(1)	0.7957(1)	0.2008(2)	0.8564(1)	19(1)
C(2)	0.8503(2)	0.0904(2)	0.8407(1)	25(1)
C(3)	0.8935(2)	0.0856(2)	0.7742(1)	29(1)
C(4)	0.8813(2)	0.1887(2)	0.7233(1)	29(1)
C(5)	0.8276(2)	0.2996(2)	0.7383(1)	26(1)
C(6)	0.7847(1)	0.3050(2)	0.8045(1)	22(1)
C(7)	0.6200(1)	0.3079(2)	0.9093(1)	19(1)
C(8)	0.5449(1)	0.2671(2)	0.8450(1)	23(1)
C(9)	0.4588(2)	0.3448(2)	0.8166(1)	28(1)
C(10)	0.4461(2)	0.4626(2)	0.8512(1)	29(1)
C(11)	0.5211(2)	0.5048(2)	0.9134(1)	25(1)
C(12)	0.6079(1)	0.4285(2)	0.9423(1)	22(1)
C(13)	0.7082(1)	0.0493(2)	0.9694(1)	21(1)
C(14)	0.7910(2)	−0.0214(2)	1.0132(1)	29(1)
C(15)	0.7743(2)	−0.1490(2)	1.0350(1)	35(1)
C(16)	0.6751(2)	−0.2037(2)	1.0149(1)	32(1)
C(17)	0.5926(2)	−0.1335(2)	0.9720(1)	30(1)
C(18)	0.6092(2)	−0.0074(2)	0.9488(1)	24(1)
C(19)	0.8244(1)	0.2875(2)	1.0205(1)	18(1)
C(20)	0.7739(1)	0.3081(2)	1.0860(1)	19(1)
C(21)	0.8194(1)	0.4050(2)	1.1481(1)	19(1)
C(22)	0.8734(1)	0.5153(2)	1.1313(1)	21(1)
C(23)	0.9080(2)	0.6080(2)	1.1880(1)	26(1)
C(24)	0.8879(2)	0.5917(2)	1.2621(1)	29(1)
C(25)	0.8319(2)	0.4836(2)	1.2792(1)	28(1)
C(26)	0.7977(1)	0.3909(2)	1.2226(1)	22(1)
C(27)	0.9346(1)	0.3019(2)	1.0207(1)	20(1)
C(28)	1.0145(1)	0.2926(2)	1.0991(1)	23(1)
C(29)	1.1070(2)	0.3822(2)	1.1111(1)	31(1)
O(1)	0.9777(1)	0.3076(1)	0.9635(1)	27(1)
O(2)	1.0054(1)	0.2041(1)	1.1428(1)	32(1)
O(3)	0.6868(1)	0.2583(1)	1.0882(1)	23(1)
P(1)	0.7384(1)	0.2134(1)	0.9421(1)	17(1)

Table 27: Bond lengths (Å) for **143b**

atom	atom	distance	atom	atom	distance
C(1)	C(2)	1.391(2)	C(1)	C(6)	1.393(2)
C(1)	P(1)	1.805(2)	C(2)	C(3)	1.389(2)
C(3)	C(4)	1.373(3)	C(4)	C(5)	1.386(3)
C(5)	C(6)	1.382(3)	C(7)	C(12)	1.389(3)
C(7)	C(8)	1.398(2)	C(7)	P(1)	1.806(2)
C(8)	C(9)	1.380(3)	C(9)	C(10)	1.378(3)
C(10)	C(11)	1.378(3)	C(11)	C(12)	1.379(2)
C(13)	C(18)	1.386(3)	C(13)	C(14)	1.391(2)
C(13)	P(1)	1.815(2)	C(14)	C(15)	1.393(3)
C(15)	C(16)	1.379(3)	C(16)	C(17)	1.381(3)
C(17)	C(18)	1.387(3)	C(19)	C(27)	1.430(3)
C(19)	C(20)	1.443(2)	C(19)	P(1)	1.760(2)
C(20)	O(3)	1.243(2)	C(20)	C(21)	1.506(2)
C(21)	C(22)	1.392(2)	C(21)	C(26)	1.396(2)
C(22)	C(23)	1.386(2)	C(23)	C(24)	1.383(2)
C(24)	C(25)	1.390(3)	C(25)	C(26)	1.383(3)
C(27)	O(1)	1.239(2)	C(27)	C(28)	1.549(2)
C(28)	O(2)	1.209(2)	C(28)	C(29)	1.490(3)

Table 28: Bond Angles(°) for **143b**

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(6)	119.2(2)	C(2)	C(1)	P(1)	121.96(13
C(6)	C(1)	P(1)	118.84(13)	C(2)	C(3)	C(1)	119.8(2)
C(4)	C(3)	C(2)	120.3(2)	C(3)	C(4)	C(5)	120.6(2)
C(6)	C(5)	C(4)	119.4(2)	C(5)	C(6)	C(1)	120.7(2)
C(12)	C(7)	C(8)	119.1(2)	C(12)	C(7)	P(1)	120.30(13
C(8)	C(7)	P(1)	120.25(13)	C(9)	C(8)	C(7)	119.9(2)
C(10)	C(9)	C(8)	120.4(2)	C(9)	C(10)	C(11)	119.9(2)
C(10)	C(11)	C(12)	120.4(2)	C(11)	C(12)	C(7)	120.2(2)
C(18)	C(13)	C(14)	119.6(2)	C(18)	C(13)	P(1)	123.78(13
C(14)	C(13)	P(1)	116.66(14)	C(13)	C(14)	C(15)	119.9(2)
C(16)	C(15)	C(14)	120.0(2)	C(15)	C(16)	C(17)	120.3(2)
C(16)	C(17)	C(18)	120.0(2)	C(13)	C(18)	C(17)	120.3(2)
C(27)	C(19)	C(20)	126.0(2)	C(27)	C(19)	P(1)	121.44(13
C(20)	C(19))	P(1)	111.70(13)	O(3)	C(20)	C(19)	121.1(2)
O(3)	C(20)	C(21)	118.4(2)	C(19)	C(20))	C(21)	119.9(2)
C(22)	C(21)	C(26)	118.9(2)	C(22)	C(21)	C(20)	121.64(14
C(26)	C(21)	C(20)	119.1(2)	C(23)	C(22)	C(21)	120.7(2)
C(24)	C(23)	C(22)	119.8(2)	C(23)	C(24)	C(25)	120.1(2)
C(26)	C(25)	C(24)	120.1(2)	C(25)	C(26)	C(21)	120.4(2)
O(1)	C(27)	C(19)	127.3(2)	O(1)	C(27)	C(28)	113.2(2)
C(19)	C(27)	C(28)	119.0(2)	O(2)	C(28)	C(29)	123.4(2)
O(2)	C(28)	C(27)	118.5(2)	C(29)	C(28)	C(27)	117.5(2)
C(19)	P(1)	C(1)	112.42(8)	C(19)	P(1)	C(7)	112.31(8)
C(1)	P(1)	C(7)	103.51(8)	C(19)	P(1)	C(13)	109.35(8)
C(1)	P(1)	C(13)	107.27(8)	C(7)	P(1)	C(13)	111.78(8)

Table 29: Atomic coordinates and B_{iso}/B_{eq} for **144a**

atom	x	y	z	B_{eq}
P(1)	0.83093(7)	0.20547(5)	0.32832(7)	3.05(2)
O(1)	1.0968(2)	0.2110(1)	0.3787(2)	4.50(5)
O(2)	1.0883(2)	0.2177(1)	0.0812(2)	5.89(6)
O(3)	0.8911(2)	0.3506(1)	0.0696(2)	4.94(5)
O(4)	0.7240(2)	0.4136(1)	0.2287(2)	5.40(6)
O(5)	0.2766(5)	0.0496(4)	0.2779(7)	21.5(2)
C(1)	0.8993(2)	0.2562(2)	0.2329(3)	3.22(6)
C(2)	1.0303(2)	0.2456(2)	0.2758(3)	3.44(6)
C(3)	1.0977(3)	0.2750(2)	0.1884(3)	3.89(7)
C(4)	0.8401(2)	0.3167(2)	0.1357(3)	3.63(6)
C(5)	0.7176(3)	0.3576(2)	0.1223(3)	3.88(6)
C(6)	1.1824(2)	0.3658(2)	0.2483(3)	3.65(6)
C(7)	1.2252(3)	0.4146(2)	0.3918(3)	4.59(7)
C(8)	1.3099(3)	0.4968(2)	0.4489(4)	6.01(9)
C(9)	1.3505(3)	0.5319(2)	0.3589(5)	6.49(10)
C(10)	1.3077(3)	0.4852(2)	0.2156(4)	6.11(10)
C(11)	1.2246(3)	0.4019(2)	0.1592(3)	4.85(8)
C(12)	0.6038(3)	0.3366(2)	-0.0210(4)	4.78(7)
C(13)	0.6022(3)	0.2752(2)	-0.1417(4)	6.38(9)
C(14)	0.4915(5)	0.2548(3)	-0.2744(4)	10.0(1)
C(15)	0.3835(5)	0.2971(4)	-0.2830(6)	12.6(2)
C(16)	0.3880(4)	0.3560(4)	-0.1642(7)	11.6(2)
C(17)	0.4946(3)	0.3771(2)	-0.0323(5)	7.3(1)
C(18)	0.6588(2)	0.2015(2)	0.2430(3)	3.30(5)
C(19)	0.5888(3)	0.1424(2)	0.1058(3)	4.25(6)
C(20)	0.4569(3)	0.1401(2)	0.0376(3)	5.36(8)
C(21)	0.3963(3)	0.1954(3)	0.1045(4)	6.12(9)
C(22)	0.4666(3)	0.2528(2)	0.2424(4)	6.01(9)
C(23)	0.5973(3)	0.2568(2)	0.3114(3)	4.54(7)
C(24)	0.8918(2)	0.2735(2)	0.5147(3)	3.56(6)
C(25)	0.8619(4)	0.2470(2)	0.6181(4)	6.19(10)
C(26)	0.9059(4)	0.3053(3)	0.7556(4)	7.6(1)
C(27)	0.9767(4)	0.3904(3)	0.7901(4)	7.2(1)
C(28)	1.0079(3)	0.4171(2)	0.6903(4)	6.57(9)
C(29)	0.9652(3)	0.3593(2)	0.5530(3)	4.70(7)
C(30)	0.8536(2)	0.0822(2)	0.3165(3)	4.11(6)
C(31)	0.8175(4)	0.0306(2)	0.3943(4)	6.70(10)
C(32)	0.8243(5)	-0.0656(3)	0.3778(5)	8.6(1)
C(33)	0.8671(4)	-0.1102(3)	0.2853(5)	8.1(1)
C(34)	0.9022(3)	-0.0623(3)	0.2059(5)	7.7(1)

Table 29: Atomic coordinates and B_{iso}/B_{eq} for **144a** (continued)

atom	x	y	z	B_{eq}
C(35)	0.8959(3)	0.0347(2)	0.2224(4)	6.00(9)
C(37)	0.3760(7)	0.0417(5)	0.3895(5)	14.7(2)
C(38)	0.4520(4)	0.0092(3)	0.3014(5)	10.4(1)
C(40)	0.1754(7)	-0.0709(4)	0.1347(7)	5.07(10)
C(41)	0.2043(8)	-0.0601(7)	0.1853(9)	12.0(3)
H(1)	1.1965	0.3913	0.4533	5.4988
H(2)	1.3382	0.5284	0.5464	7.1957
H(3)	1.4088	0.5881	0.3978	7.7014
H(4)	1.3346	0.5098	0.1535	7.4383
H(5)	1.1966	0.3686	0.0609	5.8049
H(6)	0.6765	0.2478	-0.1332	7.4957
H(7)	0.4916	0.2131	-0.3573	11.8074
H(8)	0.3099	0.2843	-0.3725	14.4870
H(9)	0.3138	0.3846	-0.1753	13.3888
H(10)	0.4934	0.4187	0.0499	9.0617
H(11)	0.6299	0.1032	0.0586	5.0728
H(12)	0.4070	0.0997	-0.0565	6.3990
H(13)	0.3067	0.1952	0.0558	7.2654
H(14)	0.4228	0.2886	0.2898	7.1550
H(15)	0.6457	0.2970	0.4062	5.4599
H(16)	0.8103	0.1889	0.5943	7.3732
H(17)	0.8878	0.2868	0.8271	8.9916
H(18)	1.0061	0.4309	0.8851	8.4529
H(19)	1.0566	0.4761	0.7150	7.7555
H(20)	0.9879	0.3786	0.4842	5.7793
H(21)	0.7839	0.0611	0.4578	8.1308
H(22)	0.7994	-0.0989	0.4341	10.2498
H(23)	0.8726	-0.1763	0.2764	9.9479
H(24)	0.9305	-0.0949	0.1395	9.4493
H(25)	0.9211	0.0690	0.1666	7.0576
H(26)	0.3740	-0.0048	0.4360	10.9523
H(27)	0.4233	0.0991	0.4516	10.9523
H(28)	0.2893	-0.0951	0.1997	9.7116
H(29)	0.1843	-0.0937	0.2535	9.7116
H(30)	0.4147	-0.0539	0.2363	10.8250
H(31)	0.4563	0.0500	0.2426	10.8250
H(32)	0.5402	0.0013	0.3647	10.8250
H(33)	0.0941	-0.0456	0.1257	4.8588
H(34)	0.1998	-0.0343	0.0752	4.8588
H(35)	0.1471	-0.1341	0.0735	4.8588

Table 30: Bond Lengths(Å) for **144a**

atom	atom	distance	atom	atom	distance
P(1)	C(1)	1.758(5)	P(1)	C(18)	1.810(5)
P(1)	C(24)	1.811(5)	P(1)	C(30)	1.809(5)
O(1)	C(2)	1.237(6)	O(2)	C(3)	1.217(6)
O(3)	C(4)	1.239(6)	O(4)	C(5)	1.213(6)
O(5)	C(37)	1.27(1)	O(5)	C(41)	1.67(2)
C(1)	C(2)	1.422(7)	C(1)	C(4)	1.437(7)
C(2)	C(3)	1.540(7)	C(3)	C(6)	1.474(7)
C(4)	C(5)	1.530(7)	C(5)	C(12)	1.478(8)
C(6)	C(7)	1.382(7)	C(6)	C(11)	1.394(7)
C(7)	C(8)	1.379(8)	C(8)	C(9)	1.383(9)
C(9)	C(10)	1.373(9)	C(10)	C(11)	1.382(9)
C(12)	C(13)	1.386(9)	C(12)	C(17)	1.392(8)
C(13)	C(14)	1.398(9)	C(14)	C(15)	1.40(2)
C(15)	C(16)	1.34(2)	C(16)	C(17)	1.37(1)
C(18)	C(19)	1.388(7)	C(18)	C(23)	1.387(7)
C(19)	C(20)	1.388(7)	C(20)	C(21)	1.370(9)
C(21)	C(22)	1.383(9)	C(22)	C(23)	1.375(8)
C(24)	C(25)	1.379(7)	C(24)	C(29)	1.375(7)
C(25)	C(26)	1.380(9)	C(26)	C(27)	1.36(1)
C(27)	C(28)	1.355(10)	C(28)	C(29)	1.377(8)
C(30)	C(31)	1.379(8)	C(30)	C(35)	1.363(7)
C(31)	C(32)	1.385(9)	C(32)	C(33)	1.34(1)
C(33)	C(34)	1.35(1)	C(34)	C(35)	1.395(9)
C(37)	C(38)	1.55(2)	C(40)	C(41)	0.48(3)

Table 31: Bond Angles(°) for **144a**

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	P(1)	C(18)	111.2(2)	C(1)	P(1)	C(24)	110.7(2)
C(1)	P(1)	C(30)	110.6(3)	C(18)	P(1)	C(24)	107.9(2)
C(18)	P(1)	C(30)	103.4(2)	C(24)	P(1)	C(30)	112.9(3)
C(37)	O(5)	C(41)	106(1)	P(1)	C(1)	C(2)	114.5(4)
P(1)	C(1)	C(4)	125.4(4)	C(2)	C(1)	C(4)	119.4(5)
O(1)	C(2)	C(1)	124.6(5)	O(1)	C(2)	C(3)	115.2(5)
C(1)	C(2)	C(3)	120.1(5)	O(2)	C(3)	C(2)	117.8(5)
O(2)	C(3)	C(6)	123.3(5)	C(2)	C(3)	C(6)	118.5(5)
O(3)	C(4)	C(1)	123.5(5)	O(3)	C(4)	C(5)	113.2(5)
C(1)	C(4)	C(5)	122.7(5)	O(4)	C(5)	C(4)	116.9(5)
O(4)	C(5)	C(12)	123.3(6)	C(4)	C(5)	C(12)	119.4(5)

Table 31: Bond Angles(°) for **144a** (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(3)	C(6)	C(7)	122.1(5)	C(3)	C(6)	C(11)	119.0(5)
C(7)	C(6)	C(11)	118.8(5)	C(6)	C(7)	C(8)	121.6(6)
C(7)	C(8)	C(9)	118.8(6)	C(8)	C(9)	C(10)	120.5(6)
C(9)	C(10)	C(11)	120.6(6)	C(6)	C(11)	C(10)	119.6(6)
C(5)	C(12)	C(13)	121.6(6)	C(5)	C(12)	C(17)	118.6(7)
C(13)	C(12)	C(17)	119.7(6)	C(12)	C(13)	C(14)	120.0(8)
C(13)	C(14)	C(15)	119.1(10)	C(14)	C(15)	C(16)	119.5(9)
C(15)	C(16)	C(17)	122(1)	C(12)	C(17)	C(16)	118.7(9)
P(1)	C(18)	C(19)	118.5(4)	P(1)	C(18)	C(23)	121.3(4)
C(19)	C(18)	C(23)	120.2(5)	C(18)	C(19)	C(20)	119.2(5)
C(19)	C(20)	C(21)	120.6(6)	C(20)	C(21)	C(22)	119.9(6)
C(21)	C(22)	C(23)	120.5(6)	C(18)	C(23)	C(22)	119.7(6)
P(1)	C(24)	C(25)	123.6(5)	P(1)	C(24)	C(29)	118.2(4)
C(25)	C(24)	C(29)	118.0(5)	C(24)	C(25)	C(26)	120.3(6)
C(25)	C(26)	C(27)	120.6(7)	C(26)	C(27)	C(28)	119.8(7)
C(27)	C(28)	C(29)	120.1(7)	C(24)	C(29)	C(28)	121.2(6)
P(1)	C(30)	C(31)	120.4(5)	P(1)	C(30)	C(35)	122.0(5)
C(31)	C(30)	C(35)	117.3(6)	C(30)	C(31)	C(32)	121.4(7)
C(31)	C(32)	C(33)	119.9(8)	C(32)	C(33)	C(34)	120.5(8)
C(33)	C(34)	C(35)	119.8(8)	C(30)	C(35)	C(34)	121.1(7)
O(5)	C(37)	C(38)	94.1(10)	O(5)	C(41)	C(40)	128(4)

Table 32: Torsion Angles(°) for **144a**

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
P(1)	C(1)	C(2)	O(1)	-5.6(7)	P(1)	C(1)	C(2)	C(3)	172.1(4)
P(1)	C(1)	C(4)	O(3)	-179.5(4)	P(1)	C(1)	C(4)	C(5)	10.2(7)
P(1)	C(18)	C(19)	C(20)	-178.6(4)	P(1)	C(18)	C(23)	C(22)	179.2(5)
P(1)	C(24)	C(25)	C(26)	-176.1(6)	P(1)	C(24)	C(29)	C(28)	176.0(5)
P(1)	C(30)	C(31)	C(32)	174.7(6)	P(1)	C(30)	C(35)	C(34)	-174.4(6)
O(1)	C(2)	C(1)	C(4)	165.3(5)	O(1)	C(2)	C(3)	O(2)	92.7(6)
O(1)	C(2)	C(3)	C(6)	-80.1(6)	O(2)	C(3)	C(2)	C(1)	-85.2(7)
O(2)	C(3)	C(6)	C(7)	-157.8(6)	O(2)	C(3)	C(6)	C(11)	19.8(8)
O(3)	C(4)	C(1)	C(2)	10.6(8)	O(3)	C(4)	C(5)	O(4)	-105.3(6)
O(3)	C(4)	C(5)	C(12)	67.6(6)	O(4)	C(5)	C(4)	C(1)	65.9(7)
O(4)	C(5)	C(12)	C(13)	177.1(6)	O(4)	C(5)	C(12)	C(17)	-5.3(9)
C(1)	P(1)	C(18)	C(19)	67.2(5)	C(1)	P(1)	C(18)	C(23)	-112.1(5)
C(1)	P(1)	C(24)	C(25)	-175.4(5)	C(1)	P(1)	C(24)	C(29)	9.0(5)
C(1)	P(1)	C(30)	C(31)	174.2(5)	C(1)	P(1)	C(30)	C(35)	-11.5(6)
C(1)	C(2)	C(3)	C(6)	102.0(6)	C(1)	C(4)	C(5)	C(12)	-121.2(5)

Table 32: Torsion Angles(°) for **144a** (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(2)	C(1)	P(1)	C(18)	-168.6(4)	C(2)	C(1)	P(1)	C(24)	71.5(4)
C(2)	C(1)	P(1)	C(30)	-54.4(4)	C(2)	C(1)	C(4)	C(5)	-159.7(5)
C(2)	C(3)	C(6)	C(7)	14.6(8)	C(2)	C(3)	C(6)	C(11)	-167.9(5)
C(3)	C(2)	C(1)	C(4)	-17.0(7)	C(3)	C(6)	C(7)	C(8)	176.5(6)
C(3)	C(6)	C(11)	C(10)	-177.7(5)	C(4)	C(1)	P(1)	C(18)	21.1(5)
C(4)	C(1)	P(1)	C(24)	-98.8(5)	C(4)	C(1)	P(1)	C(30)	135.3(4)
C(4)	C(5)	C(12)	C(13)	4.7(8)	C(4)	C(5)	C(12)	C(17)	-177.7(5)
C(5)	C(12)	C(13)	C(14)	178.0(6)	C(5)	C(12)	C(17)	C(16)	-178.5(7)
C(6)	C(7)	C(8)	C(9)	1(1)	C(6)	C(11)	C(10)	C(9)	0(1)
C(7)	C(6)	C(11)	C(10)	0.0(9)	C(7)	C(8)	C(9)	C(10)	0(1)
C(8)	C(7)	C(6)	C(11)	-1.1(9)	C(8)	C(9)	C(10)	C(11)	0(1)
C(12)	C(13)	C(14)	C(15)	0(1)	C(12)	C(17)	C(16)	C(15)	0(1)
C(13)	C(12)	C(17)	C(16)	0(1)	C(13)	C(14)	C(15)	C(16)	0(1)
C(14)	C(13)	C(12)	C(17)	0(1)	C(14)	C(15)	C(16)	C(17)	0(1)
C(18)	P(1)	C(24)	C(25)	62.7(6)	C(18)	P(1)	C(24)	C(29)	-112.8(4)
C(18)	P(1)	C(30)	C(31)	-66.7(6)	C(18)	P(1)	C(30)	C(35)	107.5(5)
C(18)	C(19)	C(20)	C(21)	0.0(9)	C(18)	C(23)	C(22)	C(21)	-1(1)
C(19)	C(18)	P(1)	C(24)	-171.2(4)	C(19)	C(18)	P(1)	C(30)	-51.4(5)
C(19)	C(18)	C(23)	C(22)	0.0(9)	C(19)	C(20)	C(21)	C(22)	-1(1)
C(20)	C(19)	C(18)	C(23)	0.6(8)	C(20)	C(21)	C(22)	C(23)	1(1)
C(23)	C(18)	P(1)	C(24)	9.5(5)	C(23)	C(18)	P(1)	C(30)	129.3(5)
C(24)	P(1)	C(30)	C(31)	49.6(6)	C(24)	P(1)	C(30)	C(35)	-136.1(5)
C(24)	C(25)	C(26)	C(27)	1(1)	C(24)	C(29)	C(28)	C(27)	0(1)
C(25)	C(24)	P(1)	C(30)	-50.9(6)	C(25)	C(24)	C(29)	C(28)	0.2(9)
C(25)	C(26)	C(27)	C(28)	-2(1)	C(26)	C(25)	C(24)	C(29)	0(1)
C(26)	C(27)	C(28)	C(29)	1(1)	C(29)	C(24)	P(1)	C(30)	133.6(4)
C(30)	C(31)	C(32)	C(33)	0(1)	C(30)	C(35)	C(34)	C(33)	0(1)
C(31)	C(30)	C(35)	C(34)	0(1)	C(31)	C(32)	C(33)	C(34)	0(1)
C(32)	C(31)	C(30)	C(35)	0(1)	C(32)	C(33)	C(34)	C(35)	1(1)
C(37)	O(5)	C(41)	C(40)	-156(4)	C(38)	C(37)	O(5)	C(41)	75(1)

Table 33: Atomic coordinates and B_{iso}/B_{eq} for **208**

atom	x	y	z	B_{eq}
Cl(1)	0.3626(5)	-0.3037(4)	0.7911(3)	9.4(2)
Cl(2)	0.1148(4)	-0.3617(3)	0.7730(2)	5.9(1)
Cl(3)	0.3151(7)	-0.4830(4)	0.8554(4)	14.3(3)
Cl(4)	0.5439(4)	-0.1580(3)	0.6720(2)	5.2(1)
Cl(5)	0.7780(6)	-0.2722(3)	0.5810(3)	8.7(2)
Cl(6)	0.7477(5)	-0.2939(3)	0.7503(3)	6.4(1)
P(1)	0.6047(4)	0.1852(3)	0.6292(2)	2.4(1)
P(2)	0.8980(4)	0.3181(3)	0.8538(2)	2.4(1)
O(1)	0.8479(9)	-0.0714(7)	0.8054(5)	3.5(3)
O(2)	0.9625(9)	0.0474(7)	0.7760(5)	3.4(3)
O(3)	0.7546(8)	-0.0044(6)	0.6631(5)	2.8(2)
O(4)	0.6326(9)	0.3077(6)	0.7669(5)	2.7(3)
O(5)	0.6854(8)	0.1109(6)	0.8833(5)	2.7(3)
O(6)	0.8479(9)	0.2683(6)	1.0164(5)	3.3(3)
O(7)	0.7842(10)	0.0739(7)	1.0475(6)	4.6(3)
O(8)	0.585(1)	0.1845(6)	1.0399(5)	3.0(3)
C(1)	0.939(2)	-0.113(1)	0.8633(9)	6.1(5)
C(2)	0.869(2)	0.0128(10)	0.7708(7)	2.2(4)
C(3)	0.766(1)	0.053(1)	0.7129(8)	2.6(4)
C(4)	0.697(1)	0.151(1)	0.7107(8)	2.3(4)
C(5)	0.687(1)	0.219(1)	0.7714(8)	2.2(4)
C(6)	0.727(1)	0.183(1)	0.8525(8)	2.5(4)
C(7)	0.798(1)	0.2350(9)	0.8923(8)	2.1(4)
C(8)	0.794(1)	0.2251(10)	0.9740(9)	2.5(4)
C(9)	0.723(2)	0.151(1)	1.0228(8)	2.6(5)
C(10)	0.510(2)	0.122(1)	1.0877(8)	5.3(5)
C(11)	0.475(1)	0.1146(8)	0.6328(9)	2.2(4)
C(12)	0.410(2)	0.0934(9)	0.7055(8)	3.0(4)
C(13)	0.298(2)	0.053(1)	0.7139(9)	3.9(5)
C(14)	0.253(1)	0.0321(10)	0.647(1)	4.1(5)
C(15)	0.319(2)	0.054(1)	0.571(1)	4.2(5)
C(16)	0.431(2)	0.0950(9)	0.5647(8)	3.0(4)
C(17)	0.511(2)	0.3102(9)	0.6257(8)	2.5(4)
C(18)	0.581(1)	0.383(1)	0.6057(8)	3.4(4)
C(19)	0.511(2)	0.479(1)	0.5994(8)	4.3(5)
C(20)	0.368(2)	0.502(1)	0.6150(9)	4.9(5)
C(21)	0.299(1)	0.431(1)	0.6317(8)	4.1(5)
C(22)	0.371(2)	0.336(1)	0.6382(7)	2.9(5)
C(23)	0.721(2)	0.1734(10)	0.5380(8)	2.5(4)
C(24)	0.672(1)	0.2138(9)	0.469(1)	3.2(4)

Table 33: Atomic coordinates and B_{iso}/B_{eq} for **208** (continued)

atom	x	y	z	B_{eq}
C(25)	0.759(2)	0.210(1)	0.3983(9)	3.5(5)
C(26)	0.895(2)	0.167(1)	0.3958(8)	3.6(5)
C(27)	0.948(1)	0.1261(9)	0.464(1)	3.5(5)
C(28)	0.860(2)	0.1305(9)	0.5347(8)	2.9(4)
C(29)	0.914(1)	0.342(1)	0.7489(7)	2.2(4)
C(30)	0.865(1)	0.431(1)	0.7138(9)	3.2(4)
C(31)	0.892(1)	0.448(1)	0.6340(10)	3.7(5)
C(32)	0.969(2)	0.375(1)	0.5870(8)	3.5(5)
C(33)	1.018(1)	0.285(1)	0.6188(9)	3.4(5)
C(34)	0.993(1)	0.2677(9)	0.6995(9)	2.6(4)
C(35)	0.824(2)	0.4347(9)	0.8966(7)	2.6(4)
C(36)	0.904(1)	0.491(1)	0.9150(8)	2.8(4)
C(37)	0.848(2)	0.581(1)	0.9458(8)	3.8(5)
C(38)	0.707(2)	0.616(1)	0.9523(8)	3.8(5)
C(39)	0.624(1)	0.561(1)	0.9323(8)	3.4(4)
C(40)	0.683(2)	0.470(1)	0.9052(8)	3.8(5)
C(41)	1.074(1)	0.2698(10)	0.8740(8)	2.2(4)
C(42)	1.114(2)	0.183(1)	0.9139(9)	3.7(5)‣
C(43)	1.251(2)	0.150(1)	0.9256(8)	4.0(5)
C(44)	1.347(1)	0.200(1)	0.8943(9)	3.7(5)
C(45)	1.310(2)	0.285(1)	0.8506(9)	3.8(5)
C(46)	1.175(2)	0.3176(9)	0.8405(7)	2.5(4)
C(47)	0.245(2)	-0.366(1)	0.8330(8)	5.6(5)
C(48)	0.718(1)	-0.2130(9)	0.6691(8)	4.2(4)
H(1)	0.9167	-0.1705	0.8864	7.4648
H(2)	1.0319	-0.1264	0.8383	7.4648
H(3)	0.9286	-0.0675	0.9030	7.4648
H(4)	0.4149	0.1532	1.0965	6.5861
H(5)	0.5207	0.0636	1.0613	6.5861
H(6)	0.5444	0.1069	1.1368	6.5861
H(7)	0.4431	0.1069	0.7512	3.8033
H(8)	0.2523	0.0397	0.7646	4.8918
H(9)	0.1762	0.0029	0.6511	5.0107
H(10)	0.2865	0.0399	0.5252	5.1640
H(11)	0.4763	0.1096	0.5143	3.8240
H(12)	0.6785	0.3668	0.5960	4.2890
H(13)	0.5602	0.5288	0.5850	5.2856
H(14)	0.3182	0.5676	0.6136	6.1195
H(15)	0.2013	0.4469	0.6393	5.1197
H(16)	0.3207	0.2872	0.6517	3.6665

Table 33: Atomic coordinates and B_{iso}/B_{eq} for **208** (continued)

atom	x	y	z	B_{eq}
H(17)	0.5777	0.2448	0.4698	4.0633
H(18)	0.7232	0.2372	0.3513	4.4222
H(19)	0.9544	0.1643	0.3472	4.4417
H(20)	1.0431	0.0956	0.4616	4.3984
H(21)	0.8965	0.1036	0.5816	3.6325
H(22)	0.8121	0.4822	0.7455	3.9757
H(23)	0.8574	0.5100	0.6110	4.5416
H(24)	0.9880	0.3877	0.5318	4.3856
H(25)	1.0692	0.2349	0.5859	4.2689
H(26)	1.0294	0.2054	0.7219	3.3008
H(27)	1.0017	0.4690	0.9064	3.5596
H(28)	0.9044	0.6181	0.9622	4.7633
H(29)	0.6669	0.6790	0.9709	4.7726
H(30)	0.5272	0.5855	0.9368	4.2187
H(31)	0.6262	0.4306	0.8924	4.6811
H(32)	1.0484	0.1450	0.9334	4.6772
H(33)	1.2777	0.0922	0.9560	4.9614
H(34)	1.4401	0.1761	0.9027	4.5404
H(35)	1.3769	0.3198	0.8279	4.7281
H(36)	1.1480	0.3751	0.8094	3.1381
H(37)	0.2016	-0.3368	0.8807	6.8359
H(38)	0.7671	-0.1639	0.6706	5.1437

Table 34: Bond Lengths(Å) for **208**

atom	atom	distance	atom	atom	distance
Cl(1)	C(47)	1.69(2)	Cl(2)	C(47)	1.77(2)
Cl(3)	C(47)	1.68(1)	Cl(4)	C(48)	1.74(1)
Cl(5)	C(48)	1.75(1)	Cl(6)	C(48)	1.75(1)
P(1)	C(4)	1.77(1)	P(1)	C(11)	1.82(1)
P(1)	C(17)	1.81(1)	P(1)	C(23)	1.80(1)
P(2)	C(7)	1.76(1)	P(2)	C(29)	1.80(1)
P(2)	C(35)	1.81(1)	P(2)	C(41)	1.82(1)
O(1)	C(1)	1.45(2)	O(1)	C(2)	1.35(1)
O(2)	C(2)	1.18(1)	O(3)	C(3)	1.26(1)
O(4)	C(5)	1.25(1)	O(5)	C(6)	1.25(1)
O(6)	C(8)	1.24(1)	O(7)	C(9)	1.21(1)
O(8)	C(9)	1.35(1)	O(8)	C(10)	1.44(1)
C(2)	C(3)	1.53(2)	C(3)	C(4)	1.40(2)
C(4)	C(5)	1.46(2)	C(5)	C(6)	1.53(2)

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Table 34: Bond Lengths(Å) for **208** (continued)

atom	atom	distance	atom	atom	distance
C(6)	C(7)	1.42(2)	C(7)	C(8)	1.40(2)
C(8)	C(9)	1.54(2)	C(11)	C(12)	1.37(2)
C(11)	C(16)	1.39(2)	C(12)	C(13)	1.37(2)
C(13)	C(14)	1.38(2)	C(14)	C(15)	1.41(2)
C(15)	C(16)	1.38(2)	C(17)	C(18)	1.38(2)
C(17)	C(22)	1.36(2)	C(18)	C(19)	1.39(2)
C(19)	C(20)	1.39(2)	C(20)	C(21)	1.34(2)
C(21)	C(22)	1.38(2)	C(23)	C(24)	1.39(2)
C(23)	C(28)	1.38(2)	C(24)	C(25)	1.38(2)
C(25)	C(26)	1.36(2)	C(26)	C(27)	1.38(2)
C(27)	C(28)	1.39(2)	C(29)	C(30)	1.38(2)
C(29)	C(34)	1.41(2)	C(30)	C(31)	1.37(2)
C(31)	C(32)	1.37(2)	C(32)	C(33)	1.36(2)
C(33)	C(34)	1.38(2)	C(35)	C(36)	1.35(2)
C(35)	C(40)	1.38(2)	C(36)	C(37)	1.38(2)
C(37)	C(38)	1.38(2)	C(38)	C(39)	1.37(2)
C(39)	C(40)	1.38(2)	C(41)	C(42)	1.37(2)
C(41)	C(46)	1.38(2)	C(42)	C(43)	1.39(2)
C(43)	C(44)	1.36(2)	C(44)	C(45)	1.37(2)
C(45)	C(46)	1.37(2)			

Table 35: Bond Angles(°) for **208**

atom	atom	atom	angle	atom	atom	atom	angle
C(4)	P(1)	C(11)	109.6(6)	C(4)	P(1)	C(17)	114.7(7)
C(4)	P(1)	C(23)	110.6(7)	C(11)	P(1)	C(17)	105.3(7)
C(11)	P(1)	C(23)	112.5(6)	C(17)	P(1)	C(23)	103.9(7)
C(7)	P(2)	C(29)	116.1(6)	C(7)	P(2)	C(35)	109.8(6)
C(7)	P(2)	C(41)	108.9(6)	C(29)	P(2)	C(35)	105.6(7)
C(29)	P(2)	C(41)	104.6(6)	C(35)	P(2)	C(41)	111.7(7)
C(1)	O(1)	C(2)	113(1)	C(9)	O(8)	C(10)	117(1)
O(1)	C(2)	O(2)	126(1)	O(1)	C(2)	C(3)	110(1)
O(2)	C(2)	C(3)	122(1)	O(3)	C(3)	C(2)	116(1)
O(3)	C(3)	C(4)	121(1)	C(2)	C(3)	C(4)	121(1)
P(1)	C(4)	C(3)	113(1)	P(1)	C(4)	C(5)	120(1)
C(3)	C(4)	C(5)	125(1)	O(4)	C(5)	C(4)	125(1)
O(4)	C(5)	C(6)	113(1)	C(4)	C(5)	C(6)	120(1)
O(5)	C(6)	C(5)	117(1)	O(5)	C(6)	C(7)	122(1)
C(5)	C(6)	C(7)	119(1)	P(2)	C(7)	C(6)	129(1)
P(2)	C(7)	C(8)	109(1)	C(6)	C(7)	C(8)	121(1)

Table 35: Bond Angles(°) for **208** (continued)

atom	atom	atom	angle	atom	atom	atom	angle
O(6)	C(8)	C(7)	127(1)	O(6)	C(8)	C(9)	111(1)
C(7)	C(8)	C(9)	120(1)	O(7)	C(9)	O(8)	123(1)
O(7)	C(9)	C(8)	123(1)	O(8)	C(9)	C(8)	113(1)
P(1)	C(11)	C(12)	117(1)	P(1)	C(11)	C(16)	121(1)
C(12)	C(11)	C(16)	120(1)	C(11)	C(12)	C(13)	121(1)
C(12)	C(13)	C(14)	118(1)	C(13)	C(14)	C(15)	120(1)
C(14)	C(15)	C(16)	119(1)	C(11)	C(16)	C(15)	118(1)
P(1)	C(17)	C(18)	120(1)	P(1)	C(17)	C(22)	122(1)
C(18)	C(17)	C(22)	117(1)	C(17)	C(18)	C(19)	121(1)
C(18)	C(19)	C(20)	118(1)	C(19)	C(20)	C(21)	120(1)
C(20)	C(21)	C(22)	120(1)	C(17)	C(22)	C(21)	122(1)
P(1)	C(23)	C(24)	119(1)	P(1)	C(23)	C(28)	122(1)
C(24)	C(23)	C(28)	118(1)	C(23)	C(24)	C(25)	121(1)
C(24)	C(25)	C(26)	120(1)	C(25)	C(26)	C(27)	120(1)
C(26)	C(27)	C(28)	119(1)	C(23)	C(28)	C(27)	120(1)
P(2)	C(29)	C(30)	123(1)	P(2)	C(29)	C(34)	118(1)
C(30)	C(29)	C(34)	117(1)	C(29)	C(30)	C(31)	121(1)
C(30)	C(31)	C(32)	120(1)	C(31)	C(32)	C(33)	120(1)
C(32)	C(33)	C(34)	119(1)	C(29)	C(34)	C(33)	120(1)
P(2)	C(35)	C(36)	121(1)	P(2)	C(35)	C(40)	119(1)
C(36)	C(35)	C(40)	118(1)	C(35)	C(36)	C(37)	121(1)
C(36)	C(37)	C(38)	118(1)	C(37)	C(38)	C(39)	120(1)
C(38)	C(39)	C(40)	119(1)	C(35)	C(40)	C(39)	120(1)
P(2)	C(41)	C(42)	122(1)	P(2)	C(41)	C(46)	118(1)
C(42)	C(41)	C(46)	118(1)	C(41)	C(42)	C(43)	118(1)
C(42)	C(43)	C(44)	121(1)	C(43)	C(44)	C(45)	120(1)
C(44)	C(45)	C(46)	118(1)	C(41)	C(46)	C(45)	122(1)
Cl(1)	C(47)	Cl(2)	112.1(8)	Cl(1)	C(47)	Cl(3)	113(1)
Cl(2)	C(47)	Cl(3)	108.7(8)	Cl(4)	C(48)	Cl(5)	109.7(8)
Cl(4)	C(48)	Cl(6)	111.2(7)	Cl(5)	C(48)	Cl(6)	110.8(7)

Table 36: Torsion Angles(°) for **208**

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
P(1)	C(4)	C(3)	O(3)	-3(1)	P(1)	C(4)	C(3)	C(2)	170.1(9)
P(1)	C(4)	C(5)	O(4)	-10(1)	P(1)	C(4)	C(5)	C(6)	160.6(9)
P(1)	C(11)	C(12)	C(13)	170(1)	P(1)	C(11)	C(16)	C(15)	-170(1)
P(1)	C(17)	C(18)	C(19)	177(1)	P(1)	C(17)	C(22)	C(21)	-176(1)
P(1)	C(23)	C(24)	C(25)	177(1)	P(1)	C(23)	C(28)	C(27)	-177.5(10)
P(2)	C(7)	C(6)	O(5)	163(1)	P(2)	C(7)	C(6)	C(5)	-22(1)
P(2)	C(7)	C(8)	O(6)	2(1)	P(2)	C(7)	C(8)	C(9)	-175(1)
P(2)	C(29)	C(30)	C(31)	172(1)	P(2)	C(29)	C(34)	C(33)	-174(1)
P(2)	C(35)	C(36)	C(37)	178(1)	P(2)	C(35)	C(40)	C(39)	-175(1)
P(2)	C(41)	C(42)	C(43)	178(1)	P(2)	C(41)	C(46)	C(45)	-177(1)
O(1)	C(2)	C(3)	O(3)	-50(1)	O(1)	C(2)	C(3)	C(4)	134(1)
O(2)	C(2)	O(1)	C(1)	10(1)	O(2)	C(2)	C(3)	O(3)	121(1)
O(2)	C(2)	C(3)	C(4)	-52(1)	O(3)	C(3)	C(4)	C(5)	170(1)
O(4)	C(5)	C(4)	C(3)	175(1)	O(4)	C(5)	C(6)	O(5)	128(1)
O(4)	C(5)	C(6)	C(7)	-46(1)	O(5)	C(6)	C(5)	C(4)	-44(1)
O(5)	C(6)	C(7)	C(8)	-16(1)	O(6)	C(8)	C(7)	C(6)	-177(1)
O(6)	C(8)	C(9)	O(7)	-76(1)	O(6)	C(8)	C(9)	O(8)	99(1)
O(7)	C(9)	O(8)	C(10)	-2(1)	O(7)	C(9)	C(8)	C(7)	101(1)
O(8)	C(9)	C(8)	C(7)	-82(1)	C(1)	O(1)	C(2)	C(3)	-177(1)
C(2)	C(3)	C(4)	C(5)	-15(1)	C(3)	C(4)	P(1)	C(11)	60(1)
C(3)	C(4)	P(1)	C(17)	178.4(10)	C(3)	C(4)	P(1)	C(23)	-64(1)
C(3)	C(4)	C(5)	C(6)	-13(1)	C(4)	P(1)	C(11)	C(12)	36(1)
C(4)	P(1)	C(11)	C(16)	-152(1)	C(4)	P(1)	C(17)	C(18)	73(1)
C(4)	P(1)	C(17)	C(22)	-110(1)	C(4)	P(1)	C(23)	C(24)	-167(1)
C(4)	P(1)	C(23)	C(28)	8(1)	C(4)	C(5)	C(6)	C(7)	141(1)
C(5)	C(4)	P(1)	C(11)	-114(1)	C(5)	C(4)	P(1)	C(17)	3(1)
C(5)	C(4)	P(1)	C(23)	121(1)	C(5)	C(6)	C(7)	C(8)	157(1)
C(6)	C(7)	P(2)	C(29)	0(1)	C(6)	C(7)	P(2)	C(35)	120(1)
C(6)	C(7)	P(2)	C(41)	-117(1)	C(6)	C(7)	C(8)	C(9)	4(1)
C(7)	P(2)	C(29)	C(30)	116(1)	C(7)	P(2)	C(29)	C(34)	-70(1)
C(7)	P(2)	C(35)	C(36)	142(1)	C(7)	P(2)	C(35)	C(40)	-42(1)
C(7)	P(2)	C(41)	C(42)	0(1)	C(7)	P(2)	C(41)	C(46)	172(1)
C(8)	C(7)	P(2)	C(29)	-179.5(9)	C(8)	C(7)	P(2)	C(35)	-59(1)
C(8)	C(7)	P(2)	C(41)	62(1)	C(8)	C(9)	O(8)	C(10)	-177(1)
C(11)	P(1)	C(17)	C(18)	-166(1)	C(11)	P(1)	C(17)	C(22)	10(1)
C(11)	P(1)	C(23)	C(24)	69(1)	C(11)	P(1)	C(23)	C(28)	-114(1)
C(11)	C(12)	C(13)	C(14)	1(2)	C(11)	C(16)	C(15)	C(14)	0(2)
C(12)	C(11)	P(1)	C(17)	-87(1)	C(12)	C(11)	P(1)	C(23)	160(1)
C(12)	C(11)	C(16)	C(15)	0(1)	C(12)	C(13)	C(14)	C(15)	-1(2)
C(13)	C(12)	C(11)	C(16)	0(2)	C(13)	C(14)	C(15)	C(16)	0(2)

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Table 36: Torsion Angles(°) for **208** (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(16)	C(11)	P(1)	C(17)	83(1)	C(16)	C(11)	P(1)	C(23)	-28(1)
C(17)	P(1)	C(23)	C(24)	-44(1)	C(17)	P(1)	C(23)	C(28)	131(1)
C(17)	C(18)	C(19)	C(20)	1(2)	C(17)	C(22)	C(21)	C(20)	-2(2)
C(18)	C(17)	P(1)	C(23)	-47(1)	C(18)	C(17)	C(22)	C(21)	0(2)
C(18)	C(19)	C(20)	C(21)	-3(2)	C(19)	C(18)	C(17)	C(22)	0(2)
C(19)	C(20)	C(21)	C(22)	3(2)	C(22)	C(17)	P(1)	C(23)	128(1)
C(23)	C(24)	C(25)	C(26)	0(2)	C(23)	C(28)	C(27)	C(26)	0(2)
C(24)	C(23)	C(28)	C(27)	-1(1)	C(24)	C(25)	C(26)	C(27)	0(2)
C(25)	C(24)	C(23)	C(28)	1(1)	C(25)	C(26)	C(27)	C(28)	0(2)
C(29)	P(2)	C(35)	C(36)	-91(1)	C(29)	P(2)	C(35)	C(40)	83(1)
C(29)	P(2)	C(41)	C(42)	-125(1)	C(29)	P(2)	C(41)	C(46)	47(1)
C(29)	C(30)	C(31)	C(32)	0(2)	C(29)	C(34)	C(33)	C(32)	1(2)
C(30)	C(29)	P(2)	C(35)	-5(1)	C(30)	C(29)	P(2)	C(41)	-123(1)
C(30)	C(29)	C(34)	C(33)	-1(1)	C(30)	C(31)	C(32)	C(33)	0(2)
C(31)	C(30)	C(29)	C(34)	0(1)	C(31)	C(32)	C(33)	C(34)	-1(2)
C(34)	C(29)	P(2)	C(35)	167(1)	C(34)	C(29)	P(2)	C(41)	49(1)
C(35)	P(2)	C(41)	C(42)	120(1)	C(35)	P(2)	C(41)	C(46)	-66(1)
C(35)	C(36)	C(37)	C(38)	-4(2)	C(35)	C(40)	C(39)	C(38)	-1(2)
C(36)	C(35)	P(2)	C(41)	21(1)	C(36)	C(35)	C(40)	C(39)	0(2)
C(36)	C(37)	C(38)	C(39)	3(2)	C(37)	C(36)	C(35)	C(40)	3(2)
C(37)	C(38)	C(39)	C(40)	0(2)	C(40)	C(35)	P(2)	C(41)	-163(1)
C(41)	C(42)	C(43)	C(44)	-4(2)	C(41)	C(46)	C(45)	C(44)	1(2)
C(42)	C(41)	C(46)	C(45)	-4(2)	C(42)	C(43)	C(44)	C(45)	0(2)
C(43)	C(42)	C(41)	C(46)	6(2)	C(43)	C(44)	C(45)	C(46)	0(2)

Table 37: Atomic coordinates and B_{iso}/B_{eq} for **203**

atom	x	y	z	B_{eq}
P(1)	0.0512(4)	0.0835(2)	0.4789	2.46(9)
P(2)	0.0504(4)	0.5062(2)	0.4313(2)	2.39(9)
P(3)	-0.1452(4)	0.2509(2)	0.1029(2)	2.55(9)
P(4)	-0.2060(4)	0.3152(2)	0.4130(2)	2.43(9)
O(1)	0.0830(5)	0.1204(5)	0.3399(5)	3.6(2)
O(2)	0.0267(5)	0.2491(5)	0.5109(4)	2.9(2)
O(3)	0.0527(5)	0.3398(5)	0.3710(4)	2.6(2)
O(4)	0.1035(5)	0.3463(5)	0.5872(4)	2.9(2)
O(5)	-0.1537(5)	0.4477(5)	0.1314(5)	3.3(2)
O(6)	-0.1616(5)	0.1881(5)	0.2346(4)	2.8(2)
O(7)	-0.1747(5)	0.3839(5)	0.2949(4)	2.5(2)
O(8)	-0.2017(5)	0.1266(5)	0.3784(5)	3.2(2)
C(1)	0.0929(6)	0.1737(8)	0.3888(7)	2.8(3)
C(2)	0.0718(6)	0.1760(8)	0.4503(6)	2.6(3)
C(3)	0.0513(6)	0.2495(8)	0.4720(7)	2.4(3)
C(4)	0.0566(6)	0.3393(8)	0.4347(7)	3.0(3)
C(5)	0.0633(6)	0.4084(8)	0.4815(7)	3.0(3)
C(6)	0.0805(6)	0.4000(8)	0.5610(6)	2.3(3)
C(7)	0.1315(6)	0.2285(7)	0.3917(6)	2.2(3)
C(8)	0.1448(6)	0.2445(8)	0.3300(6)	2.5(3)
C(9)	0.1792(7)	0.283(1)	0.3310(9)	5.6(4)
C(10)	0.2070(6)	0.3022(10)	0.3949(8)	4.8(4)
C(11)	0.1966(7)	0.2933(10)	0.4608(8)	5.1(4)
C(12)	0.1547(6)	0.2550(9)	0.4525(8)	4.4(3)
C(13)	0.0686(6)	0.0717(7)	0.5753(6)	2.1(2)
C(14)	0.0870(6)	0.1366(8)	0.6162(7)	3.2(3)
C(15)	0.1016(6)	0.1252(8)	0.6899(7)	3.5(3)
C(16)	0.0978(6)	0.0402(9)	0.7174(7)	4.1(3)
C(17)	0.0793(6)	-0.0252(9)	0.6796(7)	3.9(3)
C(18)	0.0623(6)	-0.0080(8)	0.6045(7)	2.6(3)
C(19)	0.0757(6)	-0.0097(8)	0.4452(7)	3.3(3)
C(20)	0.1182(6)	-0.0234(9)	0.4695(7)	3.7(3)
C(21)	0.1348(6)	-0.0995(10)	0.4471(8)	4.7(4)
C(22)	0.1116(6)	-0.1606(9)	0.4070(7)	4.0(3)
C(23)	0.0672(7)	-0.1464(10)	0.3826(8)	5.0(4)
C(24)	0.0480(6)	-0.0722(9)	0.4045(7)	3.6(3)
C(25)	-0.0057(6)	0.0767(7)	0.4519(6)	1.9(2)
C(26)	-0.0318(6)	0.0481(8)	0.4953(7)	3.2(3)
C(27)	-0.0744(6)	0.0476(9)	0.4703(7)	3.9(3)
C(28)	-0.0912(6)	0.0717(10)	0.4020(8)	4.9(4)

Table 37: Atomic coordinates and B_{iso}/B_{eq} for **203** (continued)

atom	x	y	z	B_{eq}
C(29)	-0.0656(7)	0.1030(10)	0.3603(9)	5.3(4)
C(30)	-0.0233(6)	0.1061(9)	0.3852(7)	4.0(3)
C(31)	0.0504(6)	0.6029(8)	0.4837(7)	2.9(3)
C(32)	0.0137(7)	0.646(1)	0.4891(8)	5.6(4)
C(33)	0.0114(7)	0.719(1)	0.5316(9)	6.1(4)
C(34)	0.0505(7)	0.748(1)	0.5641(9)	5.8(4)
C(35)	0.0919(7)	0.713(1)	0.5648(9)	6.0(4)
C(36)	0.0903(7)	0.6388(10)	0.5195(8)	5.3(4)
C(37)	-0.0009(6)	0.4944(8)	0.3754(6)	2.4(3)
C(38)	-0.0149(8)	0.548(1)	0.314(1)	7.8(5)
C(39)	-0.0549(8)	0.533(1)	0.279(1)	7.4(5)
C(40)	-0.0850(7)	0.474(1)	0.2929(9)	6.4(4)
C(41)	-0.0690(6)	0.4261(9)	0.3527(8)	4.4(3)
C(42)	-0.0265(6)	0.4373(9)	0.3981(7)	4.1(3)
C(43)	0.0886(6)	0.5375(8)	0.3794(7)	3.0(3)
C(44)	0.1234(6)	0.4851(8)	0.3884(6)	2.7(3)
C(45)	0.1593(7)	0.517(1)	0.3588(10)	7.4(5)
C(46)	0.1512(7)	0.588(1)	0.3152(9)	6.2(4)
C(47)	0.1175(7)	0.6347(9)	0.3055(8)	4.9(4)
C(48)	0.0853(6)	0.6119(8)	0.3421(7)	3.0(3)
C(49)	0.0620(6)	0.4639(7)	0.6081(6)	2.1(3)
C(50)	0.0904(7)	0.5026(10)	0.6614(9)	5.1(4)
C(51)	0.0761(7)	0.5638(9)	0.7100(7)	3.9(3)
C(52)	0.0364(7)	0.5699(9)	0.7047(8)	4.4(3)
C(53)	0.0049(9)	0.529(2)	0.651(1)	12.0(8)
C(54)	0.0193(7)	0.4758(10)	0.5970(8)	4.7(4)
C(55)	-0.1789(6)	0.3980(8)	0.1470(6)	2.5(3)
C(56)	-0.1705(6)	0.3070(7)	0.1596(6)	2.2(3)
C(57)	-0.1734(6)	0.2614(8)	0.2234(6)	1.6(2)
C(58)	-0.1858(6)	0.3065(7)	0.2845(6)	1.6(2)
C(59)	-0.2065(6)	0.2619(7)	0.3326(6)	1.9(2)
C(60)	-0.2146(5)	0.1755(7)	0.3263(6)	1.4(2)
C(61)	-0.2208(6)	0.4300(8)	0.1495(6)	2.3(3)
C(62)	-0.2282(6)	0.5212(8)	0.1560(7)	3.7(3)
C(63)	-0.2694(6)	0.5524(9)	0.1513(7)	4.0(3)
C(64)	-0.3016(7)	0.501(1)	0.1383(9)	6.0(4)
C(65)	-0.2960(7)	0.4104(10)	0.1312(8)	4.5(3)
C(66)	-0.2583(6)	0.3804(8)	0.1352(6)	2.6(3)
C(67)	-0.1715(6)	0.1597(7)	0.0623(6)	2.3(3)
C(68)	-0.2031(6)	0.1214(8)	0.0850(7)	3.0(3)

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Table 37: Atomic coordinates and B_{iso}/B_{eq} for **203** (continued)

atom	x	y	z	B_{eq}
C(69)	-0.2216(6)	0.0497(9)	0.0511(8)	4.4(3)
C(70)	-0.2108(6)	0.0162(9)	-0.0092(7)	3.6(3)
C(71)	-0.1812(6)	0.0532(8)	-0.0340(6)	2.7(3)
C(72)	-0.1618(6)	0.1300(9)	-0.0006(7)	3.9(3)
C(73)	-0.1428(6)	0.3169(8)	0.0292(7)	3.8(3)
C(74)	-0.1791(6)	0.3354(8)	-0.0208(6)	2.7(3)
C(75)	-0.1812(6)	0.3868(9)	-0.0778(7)	3.6(3)
C(76)	-0.1456(7)	0.4178(9)	-0.0905(8)	4.7(3)
C(77)	-0.1055(6)	0.4035(9)	-0.0434(8)	4.7(3)
C(78)	-0.1062(6)	0.3521(8)	0.0172(7)	3.3(3)
C(79)	-0.0902(6)	0.2254(8)	0.1505(7)	3.2(3)
C(80)	-0.0694(6)	0.1576(9)	0.1294(7)	3.8(3)
C(81)	-0.0287(6)	0.1427(9)	0.1641(7)	3.8(3)
C(82)	-0.0098(6)	0.1943(9)	0.2208(7)	3.6(3)
C(83)	-0.0303(6)	0.2604(8)	0.2391(7)	3.2(3)
C(84)	-0.0709(6)	0.2752(8)	0.2053(7)	2.6(3)
C(85)	-0.2355(5)	0.4112(7)	0.4036(6)	1.6(2)
C(86)	-0.2456(6)	0.4509(8)	0.4649(6)	2.6(3)
C(87)	-0.2726(6)	0.5197(8)	0.4552(6)	2.8(3)
C(88)	-0.2928(6)	0.5497(9)	0.3899(7)	3.8(3)
C(89)	-0.2861(6)	0.5122(8)	0.3276(7)	3.3(3)
C(90)	-0.2590(6)	0.4450(9)	0.3337(7)	3.9(3)
C(91)	-0.2333(6)	0.2533(7)	0.4671(6)	2.1(3)
C(92)	-0.2176(6)	0.2325(8)	0.5328(7)	3.3(3)
C(93)	-0.2405(7)	0.1886(9)	0.5760(8)	4.7(4)
C(94)	-0.2823(6)	0.1719(8)	0.5463(7)	3.3(3)
C(95)	-0.2982(6)	0.1872(9)	0.4765(8)	4.5(3)
C(96)	-0.2740(6)	0.2334(8)	0.4382(6)	2.8(3)
C(97)	-0.1556(6)	0.3306(8)	0.4647(7)	3.2(3)
C(98)	-0.1252(6)	0.2733(8)	0.4564(6)	2.9(3)
C(99)	-0.0855(7)	0.2761(10)	0.4993(8)	4.9(4)
C(100)	-0.0726(6)	0.3380(10)	0.5524(8)	4.6(3)
C(101)	-0.1041(7)	0.3999(9)	0.5575(8)	4.3(3)
C(102)	-0.1429(6)	0.3961(9)	0.5153(8)	4.2(3)
C(103)	-0.2456(6)	0.1397(8)	0.2626(6)	2.4(3)
C(104)	-0.2725(6)	0.1893(7)	0.2194(6)	2.2(2)
C(105)	-0.3008(6)	0.1554(9)	0.1629(7)	4.2(3)
C(106)	-0.3048(7)	0.0704(10)	0.1477(8)	5.0(4)
C(107)	-0.2765(7)	0.0200(10)	0.1928(8)	5.1(4)
C(108)	-0.2456(6)	0.0541(9)	0.2524(7)	3.6(3)

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Table 37: Atomic coordinates and B_{iso}/B_{eq} for **203** (continued)

atom	x	y	z	B_{eq}
C(109)	-0.1678(9)	-0.129(2)	0.257(1)	2.7(6)
C(110)	-0.1436(9)	-0.126(1)	0.204(1)	2.5(5)
C(111)	-0.1369(8)	-0.217(1)	0.185(1)	1.5(5)
C(112)	-0.1527(10)	-0.272(2)	0.226(1)	3.3(6)
C(113)	-0.1722(8)	-0.258(1)	0.269(1)	1.1(4)
C(114)	-0.1786(10)	-0.188(2)	0.282(1)	3.4(6)
C(115)	-0.125(2)	-0.071(3)	0.165(3)	11(1)

Table 38: Bond Lengths(Å) for **203**

atom	atom	distance	atom	atom	distance
P(1)	C(2)	1.73(3)	P(1)	C(13)	1.81(3)
P(1)	C(19)	1.84(3)	P(1)	C(25)	1.82(3)
P(2)	C(5)	1.80(3)	P(2)	C(31)	1.81(3)
P(2)	C(37)	1.78(3)	P(2)	C(43)	1.83(3)
P(3)	C(56)	1.74(3)	P(3)	C(67)	1.75(3)
P(3)	C(73)	1.76(3)	P(3)	C(79)	1.87(3)
P(4)	C(59)	1.75(3)	P(4)	C(85)	1.77(3)
P(4)	C(91)	1.79(3)	P(4)	C(97)	1.74(3)
O(1)	C(1)	1.24(3)	O(2)	C(3)	1.21(3)
O(3)	C(4)	1.20(3)	O(4)	C(6)	1.16(3)
O(5)	C(55)	1.22(3)	O(6)	C(57)	1.21(3)
O(7)	C(58)	1.26(3)	O(8)	C(60)	1.25(3)
C(1)	C(2)	1.49(4)	C(1)	C(7)	1.51(4)
C(2)	C(3)	1.43(4)	C(3)	C(4)	1.60(4)
C(4)	C(5)	1.39(4)	C(5)	C(6)	1.50(4)
C(6)	C(49)	1.56(4)	C(7)	C(8)	1.37(3)
C(7)	C(12)	1.31(4)	C(8)	C(9)	1.27(4)
C(9)	C(10)	1.38(4)	C(10)	C(11)	1.39(4)
C(11)	C(12)	1.47(5)	C(13)	C(14)	1.34(4)
C(13)	C(18)	1.40(4)	C(14)	C(15)	1.40(4)
C(15)	C(16)	1.44(4)	C(16)	C(17)	1.32(4)
C(17)	C(18)	1.45(4)	C(19)	C(20)	1.38(4)
C(19)	C(24)	1.44(4)	C(20)	C(21)	1.41(4)
C(21)	C(22)	1.34(4)	C(22)	C(23)	1.44(4)
C(23)	C(24)	1.42(4)	C(25)	C(26)	1.39(4)
C(25)	C(30)	1.36(4)	C(26)	C(27)	1.37(4)
C(27)	C(28)	1.35(4)	C(28)	C(29)	1.37(4)
C(29)	C(30)	1.36(4)	C(31)	C(32)	1.40(4)
C(31)	C(36)	1.44(4)	C(32)	C(33)	1.41(5)

Table 38: Bond Lengths(Å) for **203** (continued)

atom	atom	distance	atom	atom	distance
C(33)	C(34)	1.37(5)	C(34)	C(35)	1.45(5)
C(35)	C(36)	1.45(5)	C(37)	C(38)	1.43(5)
C(37)	C(42)	1.36(4)	C(38)	C(39)	1.35(5)
C(39)	C(40)	1.42(5)	C(40)	C(41)	1.37(5)
C(41)	C(42)	1.47(4)	C(43)	C(44)	1.38(4)
C(43)	C(48)	1.35(4)	C(44)	C(45)	1.50(5)
C(45)	C(46)	1.38(5)	C(46)	C(47)	1.30(5)
C(47)	C(48)	1.43(4)	C(49)	C(50)	1.36(4)
C(49)	C(54)	1.38(4)	C(50)	C(51)	1.48(4)
C(51)	C(52)	1.28(4)	C(52)	C(53)	1.43(6)
C(53)	C(54)	1.48(6)	C(55)	C(56)	1.46(4)
C(55)	C(61)	1.47(4)	C(56)	C(57)	1.44(3)
C(57)	C(58)	1.49(3)	C(58)	C(59)	1.44(3)
C(59)	C(60)	1.37(3)	C(60)	C(103)	1.51(4)
C(61)	C(62)	1.45(4)	C(61)	C(66)	1.42(4)
C(62)	C(63)	1.41(4)	C(63)	C(64)	1.30(4)
C(64)	C(65)	1.44(5)	C(65)	C(66)	1.30(4)
C(67)	C(68)	1.35(4)	C(67)	C(72)	1.39(4)
C(68)	C(69)	1.36(4)	C(69)	C(70)	1.38(4)
C(70)	C(71)	1.30(4)	C(71)	C(72)	1.44(4)
C(73)	C(74)	1.38(4)	C(73)	C(78)	1.38(4)
C(74)	C(75)	1.34(4)	C(75)	C(76)	1.33(4)
C(76)	C(77)	1.43(4)	C(77)	C(78)	1.41(4)
C(79)	C(80)	1.37(4)	C(79)	C(84)	1.34(4)
C(80)	C(81)	1.36(4)	C(81)	C(82)	1.38(4)
C(82)	C(83)	1.32(4)	C(83)	C(84)	1.36(4)
C(85)	C(86)	1.43(3)	C(85)	C(90)	1.48(4)
C(86)	C(87)	1.37(4)	C(87)	C(88)	1.36(4)
C(88)	C(89)	1.39(4)	C(89)	C(90)	1.36(4)
C(91)	C(92)	1.29(3)	C(91)	C(96)	1.36(4)
C(92)	C(93)	1.41(4)	C(93)	C(94)	1.38(4)
C(94)	C(95)	1.34(4)	C(95)	C(96)	1.39(4)
C(97)	C(98)	1.37(4)	C(97)	C(102)	1.40(4)
C(98)	C(99)	1.37(4)	C(99)	C(100)	1.40(4)
C(100)	C(101)	1.43(4)	C(101)	C(102)	1.34(4)
C(103)	C(104)	1.31(3)	C(103)	C(108)	1.35(4)
C(104)	C(105)	1.36(4)	C(105)	C(106)	1.36(4)
C(106)	C(107)	1.36(4)	C(107)	C(108)	1.44(4)
C(109)	C(110)	1.43(7)	C(109)	C(114)	1.13(7)
C(110)	C(111)	1.49(7)	C(110)	C(115)	1.4(1)

Table 38: Bond Lengths(Å) for **203** (continued)

atom	atom	distance	atom	atom	distance
C(111)	C(112)	1.33(7)	C(112)	C(113)	1.17(7)
C(113)	C(114)	1.15(7)			

Table 39: Bond Angles(°) for **203**

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	P(1)	C(13)	110(1)	C(2)	P(1)	C(19)	108(1)
C(2)	P(1)	C(25)	113(1)	C(13)	P(1)	C(19)	102(1)
C(13)	P(1)	C(25)	110(1)	C(19)	P(1)	C(25)	110(1)
C(5)	P(2)	C(31)	116(1)	C(5)	P(2)	C(37)	107(1)
C(5)	P(2)	C(43)	114(1)	C(31)	P(2)	C(37)	107(1)
C(31)	P(2)	C(43)	99(1)	C(37)	P(2)	C(43)	111(1)
C(56)	P(3)	C(67)	115(1)	C(56)	P(3)	C(73)	108(1)
C(56)	P(3)	C(79)	110(1)	C(67)	P(3)	C(73)	102(1)
C(67)	P(3)	C(79)	111(1)	C(73)	P(3)	C(79)	107(1)
C(59)	P(4)	C(85)	114(1)	C(59)	P(4)	C(91)	110(1)
C(59)	P(4)	C(97)	112(1)	C(85)	P(4)	C(91)	100(1)
C(85)	P(4)	C(97)	111(1)	C(91)	P(4)	C(97)	106(1)
O(1)	C(1)	C(2)	121(2)	O(1)	C(1)	C(7)	118(2)
C(2)	C(1)	C(7)	119(2)	P(1)	C(2)	C(1)	120(2)
P(1)	C(2)	C(3)	109(2)	C(1)	C(2)	C(3)	125(2)
O(2)	C(3)	C(2)	126(2)	O(2)	C(3)	C(4)	115(2)
C(2)	C(3)	C(4)	117(2)	O(3)	C(4)	C(3)	117(2)
O(3)	C(4)	C(5)	128(2)	C(3)	C(4)	C(5)	114(2)
P(2)	C(5)	C(4)	109(2)	P(2)	C(5)	C(6)	127(2)
C(4)	C(5)	C(6)	123(2)	O(4)	C(6)	C(5)	123(2)
O(4)	C(6)	C(49)	120(2)	C(5)	C(6)	C(49)	115(2)
C(1)	C(7)	C(8)	119(2)	C(1)	C(7)	C(12)	121(2)
C(8)	C(7)	C(12)	118(2)	C(7)	C(8)	C(9)	121(2)
C(8)	C(9)	C(10)	121(3)	C(9)	C(10)	C(11)	122(3)
C(10)	C(11)	C(12)	110(3)	C(7)	C(12)	C(11)	124(3)
P(1)	C(13)	C(14)	121(2)	P(1)	C(13)	C(18)	117(1)
C(14)	C(13)	C(18)	121(2)	C(13)	C(14)	C(15)	120(2)
C(14)	C(15)	C(16)	116(2)	C(15)	C(16)	C(17)	125(2)
C(16)	C(17)	C(18)	115(2)	C(13)	C(18)	C(17)	120(2)
P(1)	C(19)	C(20)	119(2)	P(1)	C(19)	C(24)	117(2)
C(20)	C(19)	C(24)	122(2)	C(19)	C(20)	C(21)	117(2)
C(20)	C(21)	C(22)	124(3)	C(21)	C(22)	C(23)	118(3)
C(22)	C(23)	C(24)	120(3)	C(19)	C(24)	C(23)	116(3)

Table 39: Bond Angles(°) for **203** (continued)

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	C(25)	C(26)	124(2)	P(1)	C(25)	C(30)	116(2)
C(26)	C(25)	C(30)	118(2)	C(25)	C(26)	C(27)	120(2)
C(26)	C(27)	C(28)	119(2)	C(27)	C(28)	C(29)	119(3)
C(28)	C(29)	C(30)	120(3)	C(25)	C(30)	C(29)	120(3)
P(2)	C(31)	C(32)	123(2)	P(2)	C(31)	C(36)	118(2)
C(32)	C(31)	C(36)	118(2)	C(31)	C(32)	C(33)	125(3)
C(32)	C(33)	C(34)	111(3)	C(33)	C(34)	C(35)	130(3)
C(34)	C(35)	C(36)	112(3)	C(31)	C(36)	C(35)	120(3)
P(2)	C(37)	C(38)	121(2)	P(2)	C(37)	C(42)	115(2)
C(38)	C(37)	C(42)	122(3)	C(37)	C(38)	C(39)	113(3)
C(38)	C(39)	C(40)	130(4)	C(39)	C(40)	C(41)	111(3)
C(40)	C(41)	C(42)	124(3)	C(37)	C(42)	C(41)	116(2)
P(2)	C(43)	C(44)	114(2)	P(2)	C(43)	C(48)	122(2)
C(44)	C(43)	C(48)	122(2)	C(43)	C(44)	C(45)	116(2)
C(44)	C(45)	C(46)	115(3)	C(45)	C(46)	C(47)	125(3)
C(46)	C(47)	C(48)	118(3)	C(43)	C(48)	C(47)	119(2)
C(6)	C(49)	C(50)	115(2)	C(6)	C(49)	C(54)	120(2)
C(50)	C(49)	C(54)	123(2)	C(49)	C(50)	C(51)	119(3)
C(50)	C(51)	C(52)	117(3)	C(51)	C(52)	C(53)	125(3)
C(52)	C(53)	C(54)	117(4)	C(49)	C(54)	C(53)	115(3)
O(5)	C(55)	C(56)	123(2)	O(5)	C(55)	C(61)	118(2)
C(56)	C(55)	C(61)	117(2)	P(3)	C(56)	C(55)	119(2)
P(3)	C(56)	C(57)	114(1)	C(55)	C(56)	C(57)	125(2)
O(6)	C(57)	C(56)	122(2)	O(6)	C(57)	C(58)	116(2)
C(56)	C(57)	C(58)	120(2)	O(7)	C(58)	C(57)	117(2)
O(7)	C(58)	C(59)	121(2)	C(57)	C(58)	C(59)	121(2)
P(4)	C(59)	C(58)	114(1)	P(4)	C(59)	C(60)	120(1)
C(58)	C(59)	C(60)	121(2)	O(8)	C(60)	C(59)	120(2)
O(8)	C(60)	C(103)	117(2)	C(59)	C(60)	C(103)	120(2)
C(55)	C(61)	C(62)	120(2)	C(55)	C(61)	C(66)	125(2)
C(62)	C(61)	C(66)	113(2)	C(61)	C(62)	C(63)	120(2)
C(62)	C(63)	C(64)	121(3)	C(63)	C(64)	C(65)	120(3)
C(64)	C(65)	C(66)	119(3)	C(61)	C(66)	C(65)	125(2)
P(3)	C(67)	C(68)	123(2)	P(3)	C(67)	C(72)	118(2)
C(68)	C(67)	C(72)	118(2)	C(67)	C(68)	C(69)	120(2)
C(68)	C(69)	C(70)	122(3)	C(69)	C(70)	C(71)	119(2)
C(70)	C(71)	C(72)	119(2)	C(67)	C(72)	C(71)	120(2)
P(3)	C(73)	C(74)	119(2)	P(3)	C(73)	C(78)	124(2)
C(74)	C(73)	C(78)	116(2)	C(73)	C(74)	C(75)	124(2)
C(74)	C(75)	C(76)	118(3)	C(75)	C(76)	C(77)	122(3)

Table 39: Bond Angles(°) for **203** (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(76)	C(77)	C(78)	115(3)	C(73)	C(78)	C(77)	122(2)
P(3)	C(79)	C(80)	120(2)	P(3)	C(79)	C(84)	119(2)
C(80)	C(79)	C(84)	120(3)	C(79)	C(80)	C(81)	118(2)
C(80)	C(81)	C(82)	119(2)	C(81)	C(82)	C(83)	120(3)
C(82)	C(83)	C(84)	120(2)	C(79)	C(84)	C(83)	120(2)
P(4)	C(85)	C(86)	120(1)	P(4)	C(85)	C(90)	123(1)
C(86)	C(85)	C(90)	114(2)	C(85)	C(86)	C(87)	119(2)
C(86)	C(87)	C(88)	123(2)	C(87)	C(88)	C(89)	120(2)
C(88)	C(89)	C(90)	118(2)	C(85)	C(90)	C(89)	123(2)
P(4)	C(91)	C(92)	124(2)	P(4)	C(91)	C(96)	117(2)
C(92)	C(91)	C(96)	118(2)	C(91)	C(92)	C(93)	123(3)
C(92)	C(93)	C(94)	117(2)	C(93)	C(94)	C(95)	120(2)
C(94)	C(95)	C(96)	118(3)	C(91)	C(96)	C(95)	121(2)
P(4)	C(97)	C(98)	117(2)	P(4)	C(97)	C(102)	125(2)
C(98)	C(97)	C(102)	116(2)	C(97)	C(98)	C(99)	121(2)
C(98)	C(99)	C(100)	123(3)	C(99)	C(100)	C(101)	114(3)
C(100)	C(101)	C(102)	121(3)	C(97)	C(102)	C(101)	122(3)
C(60)	C(103)	C(104)	121(2)	C(60)	C(103)	C(108)	117(2)
C(104)	C(103)	C(108)	120(2)	C(103)	C(104)	C(105)	120(2)
C(104)	C(105)	C(106)	124(3)	C(105)	C(106)	C(107)	114(3)
C(106)	C(107)	C(108)	122(3)	C(103)	C(108)	C(107)	117(2)
C(110)	C(109)	C(114)	126(6)	C(109)	C(110)	C(111)	106(4)
C(109)	C(110)	C(115)	142(6)	C(111)	C(110)	C(115)	111(6)
C(110)	C(111)	C(112)	112(4)	C(111)	C(112)	C(113)	129(5)
C(112)	C(113)	C(114)	119(6)	C(109)	C(114)	C(113)	126(6)

Table 40: Torsion Angles(°) for **203**

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
P(1)	C(2)	C(1)	O(1)	29(3)	P(1)	C(2)	C(1)	C(7)	-141(2)
P(1)	C(2)	C(3)	O(2)	7(3)	P(1)	C(2)	C(3)	C(4)	-164(1)
P(1)	C(13)	C(14)	C(15)	-177(2)	P(1)	C(13)	C(18)	C(17)	173(2)
P(1)	C(19)	C(20)	C(21)	174(2)	P(1)	C(19)	C(24)	C(23)	-176(2)
P(1)	C(25)	C(26)	C(27)	178(2)	P(1)	C(25)	C(30)	C(29)	179(2)
P(2)	C(5)	C(4)	O(3)	16(4)	P(2)	C(5)	C(4)	C(3)	-159(2)
P(2)	C(5)	C(6)	O(4)	-146(2)	P(2)	C(5)	C(6)	C(49)	38(3)
P(2)	C(31)	C(32)	C(33)	176(2)	P(2)	C(31)	C(36)	C(35)	-176(2)
P(2)	C(37)	C(38)	C(39)	-178(2)	P(2)	C(37)	C(42)	C(41)	-179(2)
P(2)	C(43)	C(44)	C(45)	-168(2)	P(2)	C(43)	C(48)	C(47)	176(2)
P(3)	C(56)	C(55)	O(5)	-42(3)	P(3)	C(56)	C(55)	C(61)	134(2)

Table 40: Torsion Angles(°) for **203** (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
P(3)	C(56)	C(57)	O(6)	-4(3)	P(3)	C(56)	C(57)	C(58)	167(1)
P(3)	C(67)	C(68)	C(69)	-179(2)	P(3)	C(67)	C(72)	C(71)	177(2)
P(3)	C(73)	C(74)	C(75)	178(2)	P(3)	C(73)	C(78)	C(77)	178(2)
P(3)	C(79)	C(80)	C(81)	177(2)	P(3)	C(79)	C(84)	C(83)	-177(2)
P(4)	C(59)	C(58)	O(7)	-11(3)	P(4)	C(59)	C(58)	C(57)	163(1)
P(4)	C(59)	C(60)	O(8)	-35(3)	P(4)	C(59)	C(60)	C(103)	132(2)
P(4)	C(85)	C(86)	C(87)	-172(2)	P(4)	C(85)	C(90)	C(89)	170(2)
P(4)	C(91)	C(92)	C(93)	175(2)	P(4)	C(91)	C(96)	C(95)	-178(2)
P(4)	C(97)	C(98)	C(99)	-174(2)	P(4)	C(97)	C(102)	C(101)	174(2)
O(1)	C(1)	C(2)	C(3)	-124(3)	O(1)	C(1)	C(7)	C(8)	25(3)
O(1)	C(1)	C(7)	C(12)	-148(3)	O(2)	C(3)	C(2)	C(1)	163(2)
O(2)	C(3)	C(4)	O(3)	-128(2)	O(2)	C(3)	C(4)	C(5)	49(3)
O(3)	C(4)	C(3)	C(2)	44(3)	O(3)	C(4)	C(5)	C(6)	-160(2)
O(4)	C(6)	C(5)	C(4)	30(4)	O(4)	C(6)	C(49)	C(50)	50(3)
O(4)	C(6)	C(49)	C(54)	-126(3)	O(5)	C(55)	C(56)	C(57)	124(3)
O(5)	C(55)	C(61)	C(62)	-19(3)	O(5)	C(55)	C(61)	C(66)	150(2)
O(6)	C(57)	C(56)	C(55)	-171(2)	O(6)	C(57)	C(58)	O(7)	139(2)
O(6)	C(57)	C(58)	C(59)	-35(3)	O(7)	C(58)	C(57)	C(56)	-32(3)
O(7)	C(58)	C(59)	C(60)	-172(2)	O(8)	C(60)	C(59)	C(58)	124(2)
O(8)	C(60)	C(103)	C(104)	153(2)	O(8)	C(60)	C(103)	C(108)	-24(3)
C(1)	C(2)	P(1)	C(13)	130(2)	C(1)	C(2)	P(1)	C(19)	19(2)
C(1)	C(2)	P(1)	C(25)	-104(2)	C(1)	C(2)	C(3)	C(4)	-8(4)
C(1)	C(7)	C(8)	C(9)	-172(2)	C(1)	C(7)	C(12)	C(11)	167(2)
C(2)	P(1)	C(13)	C(14)	12(2)	C(2)	P(1)	C(13)	C(18)	-166(2)
C(2)	P(1)	C(19)	C(20)	64(2)	C(2)	P(1)	C(19)	C(24)	-125(2)
C(2)	P(1)	C(25)	C(26)	-138(2)	C(2)	P(1)	C(25)	C(30)	38(2)
C(2)	C(1)	C(7)	C(8)	-163(2)	C(2)	C(1)	C(7)	C(12)	22(4)
C(2)	C(3)	C(4)	C(5)	-138(2)	C(3)	C(2)	P(1)	C(13)	-72(2)
C(3)	C(2)	P(1)	C(19)	176(1)	C(3)	C(2)	P(1)	C(25)	52(2)
C(3)	C(2)	C(1)	C(7)	64(3)	C(3)	C(4)	C(5)	C(6)	22(4)
C(4)	C(5)	P(2)	C(31)	172(2)	C(4)	C(5)	P(2)	C(37)	51(2)
C(4)	C(5)	P(2)	C(43)	-73(2)	C(4)	C(5)	C(6)	C(49)	-144(2)
C(5)	P(2)	C(31)	C(32)	-107(2)	C(5)	P(2)	C(31)	C(36)	74(2)
C(5)	P(2)	C(37)	C(38)	-160(2)	C(5)	P(2)	C(37)	C(42)	25(2)
C(5)	P(2)	C(43)	C(44)	-3(2)	C(5)	P(2)	C(43)	C(48)	-175(2)
C(5)	C(6)	C(49)	C(50)	-134(2)	C(5)	C(6)	C(49)	C(54)	48(3)
C(6)	C(5)	P(2)	C(31)	-10(3)	C(6)	C(5)	P(2)	C(37)	-130(2)
C(6)	C(5)	P(2)	C(43)	104(2)	C(6)	C(49)	C(50)	C(51)	-179(2)
C(6)	C(49)	C(54)	C(53)	172(3)	C(7)	C(8)	C(9)	C(10)	6(5)
C(7)	C(12)	C(11)	C(10)	3(4)	C(8)	C(7)	C(12)	C(11)	-6(4)

Table 40: Torsion Angles(°) for **203** (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(8)	C(9)	C(10)	C(11)	-9(5)	C(9)	C(8)	C(7)	C(12)	1(4)
C(9)	C(10)	C(11)	C(12)	4(4)	C(13)	P(1)	C(19)	C(20)	-51(2)
C(13)	P(1)	C(19)	C(24)	117(2)	C(13)	P(1)	C(25)	C(26)	-13(2)
C(13)	P(1)	C(25)	C(30)	163(2)	C(13)	C(14)	C(15)	C(16)	3(4)
C(13)	C(18)	C(17)	C(16)	4(4)	C(14)	C(13)	P(1)	C(19)	128(2)
C(14)	C(13)	P(1)	C(25)	-113(2)	C(14)	C(13)	C(18)	C(17)	-6(4)
C(14)	C(15)	C(16)	C(17)	-5(5)	C(15)	C(14)	C(13)	C(18)	1(4)
C(15)	C(16)	C(17)	C(18)	1(5)	C(18)	C(13)	P(1)	C(19)	-51(2)
C(18)	C(13)	P(1)	C(25)	66(2)	C(19)	P(1)	C(25)	C(26)	99(2)
C(19)	P(1)	C(25)	C(30)	-83(2)	C(19)	C(20)	C(21)	C(22)	-3(4)
C(19)	C(24)	C(23)	C(22)	6(4)	C(20)	C(19)	P(1)	C(25)	-169(2)
C(20)	C(19)	C(24)	C(23)	-7(4)	C(20)	C(21)	C(22)	C(23)	2(5)
C(21)	C(20)	C(19)	C(24)	5(4)	C(21)	C(22)	C(23)	C(24)	-4(4)
C(24)	C(19)	P(1)	C(25)	0(2)	C(25)	C(26)	C(27)	C(28)	2(4)
C(25)	C(30)	C(29)	C(28)	0(5)	C(26)	C(25)	C(30)	C(29)	-3(4)
C(26)	C(27)	C(28)	C(29)	-5(5)	C(27)	C(26)	C(25)	C(30)	1(4)
C(27)	C(28)	C(29)	C(30)	3(5)	C(31)	P(2)	C(37)	C(38)	73(2)
C(31)	P(2)	C(37)	C(42)	-100(2)	C(31)	P(2)	C(43)	C(44)	120(2)
C(31)	P(2)	C(43)	C(48)	-51(2)	C(31)	C(32)	C(33)	C(34)	4(5)
C(31)	C(36)	C(35)	C(34)	-4(4)	C(32)	C(31)	P(2)	C(37)	13(3)
C(32)	C(31)	P(2)	C(43)	129(2)	C(32)	C(31)	C(36)	C(35)	5(4)
C(32)	C(33)	C(34)	C(35)	-3(5)	C(33)	C(32)	C(31)	C(36)	-5(5)
C(33)	C(34)	C(35)	C(36)	4(5)	C(36)	C(31)	P(2)	C(37)	-164(2)
C(36)	C(31)	P(2)	C(43)	-48(2)	C(37)	P(2)	C(43)	C(44)	-126(2)
C(37)	P(2)	C(43)	C(48)	61(2)	C(37)	C(38)	C(39)	C(40)	1(7)
C(37)	C(42)	C(41)	C(40)	-5(5)	C(38)	C(37)	P(2)	C(43)	-34(3)
C(38)	C(37)	C(42)	C(41)	5(4)	C(38)	C(39)	C(40)	C(41)	0(6)
C(39)	C(38)	C(37)	C(42)	-4(5)	C(39)	C(40)	C(41)	C(42)	2(5)
C(42)	C(37)	P(2)	C(43)	151(2)	C(43)	C(44)	C(45)	C(46)	-10(4)
C(43)	C(48)	C(47)	C(46)	-7(4)	C(44)	C(43)	C(48)	C(47)	5(4)
C(44)	C(45)	C(46)	C(47)	8(6)	C(45)	C(44)	C(43)	C(48)	3(4)
C(45)	C(46)	C(47)	C(48)	0(6)	C(49)	C(50)	C(51)	C(52)	8(4)
C(49)	C(54)	C(53)	C(52)	5(6)	C(50)	C(49)	C(54)	C(53)	-4(5)
C(50)	C(51)	C(52)	C(53)	-7(5)	C(51)	C(50)	C(49)	C(54)	-2(5)
C(51)	C(52)	C(53)	C(54)	0(7)	C(55)	C(56)	P(3)	C(67)	-125(2)
C(55)	C(56)	P(3)	C(73)	-10(2)	C(55)	C(56)	P(3)	C(79)	107(2)
C(55)	C(56)	C(57)	C(58)	0(4)	C(55)	C(61)	C(62)	C(63)	173(2)
C(55)	C(61)	C(66)	C(65)	-173(2)	C(56)	P(3)	C(67)	C(68)	-16(2)
C(56)	P(3)	C(67)	C(72)	157(2)	C(56)	P(3)	C(73)	C(74)	-69(2)
C(56)	P(3)	C(73)	C(78)	110(2)	C(56)	P(3)	C(79)	C(80)	155(2)

Table 40: Torsion Angles(°) for **203** (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(56)	P(3)	C(79)	C(84)	-25(2)	C(56)	C(55)	C(61)	C(62)	164(2)
C(56)	C(55)	C(61)	C(66)	-26(3)	C(56)	C(57)	C(58)	C(59)	152(2)
C(57)	C(56)	P(3)	C(67)	66(2)	C(57)	C(56)	P(3)	C(73)	-178(2)
C(57)	C(56)	P(3)	C(79)	-60(2)	C(57)	C(56)	C(55)	C(61)	-59(3)
C(57)	C(58)	C(59)	C(60)	2(4)	C(58)	C(59)	P(4)	C(85)	66(2)
C(58)	C(59)	P(4)	C(91)	179(1)	C(58)	C(59)	P(4)	C(97)	-62(2)
C(58)	C(59)	C(60)	C(103)	-67(3)	C(59)	P(4)	C(85)	C(86)	165(2)
C(59)	P(4)	C(85)	C(90)	0(2)	C(59)	P(4)	C(91)	C(92)	127(2)
C(59)	P(4)	C(91)	C(96)	-58(2)	C(59)	P(4)	C(97)	C(98)	-27(2)
C(59)	P(4)	C(97)	C(102)	153(2)	C(59)	C(60)	C(103)	C(104)	-15(4)
C(59)	C(60)	C(103)	C(108)	166(2)	C(60)	C(59)	P(4)	C(85)	-131(2)
C(60)	C(59)	P(4)	C(91)	-19(2)	C(60)	C(59)	P(4)	C(97)	99(2)
C(60)	C(103)	C(104)	C(105)	-178(2)	C(60)	C(103)	C(108)	C(107)	177(2
C(61)	C(62)	C(63)	C(64)	-2(4)	C(61)	C(66)	C(65)	C(64)	3(4)
C(62)	C(61)	C(66)	C(65)	-3(4)	C(62)	C(63)	C(64)	C(65)	2(5)
C(63)	C(62)	C(61)	C(66)	2(3)	C(63)	C(64)	C(65)	C(66)	-2(5)
C(67)	P(3)	C(73)	C(74)	53(2)	C(67)	P(3)	C(73)	C(78)	-126(2)
C(67)	P(3)	C(79)	C(80)	26(2)	C(67)	P(3)	C(79)	C(84)	-155(2)
C(67)	C(68)	C(69)	C(70)	-3(4)	C(67)	C(72)	C(71)	C(70)	6(4)
C(68)	C(67)	P(3)	C(73)	-134(2)	C(68)	C(67)	P(3)	C(79)	110(2)
C(68)	C(67)	C(72)	C(71)	-8(4)	C(68)	C(69)	C(70)	C(71)	1(5)
C(69)	C(68)	C(67)	C(72)	6(4)	C(69)	C(70)	C(71)	C(72)	-3(4)
C(72)	C(67)	P(3)	C(73)	39(2)	C(72)	C(67)	P(3)	C(79)	-75(2)
C(73)	P(3)	C(79)	C(80)	-86(2)	C(73)	P(3)	C(79)	C(84)	92(2)
C(73)	C(74)	C(75)	C(76)	4(4)	C(73)	C(78)	C(77)	C(76)	1(4)
C(74)	C(73)	P(3)	C(79)	170(2)	C(74)	C(73)	C(78)	C(77)	0(4)
C(74)	C(75)	C(76)	C(77)	-4(5)	C(75)	C(74)	C(73)	C(78)	-2(4)
C(75)	C(76)	C(77)	C(78)	1(4)	C(78)	C(73)	P(3)	C(79)	-8(3)
C(79)	C(80)	C(81)	C(82)	1(4)	C(79)	C(84)	C(83)	C(82)	-3(4)
C(80)	C(79)	C(84)	C(83)	1(4)	C(80)	C(81)	C(82)	C(83)	-3(4)
C(81)	C(80)	C(79)	C(84)	0(4)	C(81)	C(82)	C(83)	C(84)	4(4)
C(85)	P(4)	C(91)	C(92)	-111(2)	C(85)	P(4)	C(91)	C(96)	63(2)
C(85)	P(4)	C(97)	C(98)	-157(2)	C(85)	P(4)	C(97)	C(102)	23(3)
C(85)	C(86)	C(87)	C(88)	4(4)	C(85)	C(90)	C(89)	C(88)	-1(4)
C(86)	C(85)	P(4)	C(91)	47(2)	C(86)	C(85)	P(4)	C(97)	-64(2)
C(86)	C(85)	C(90)	C(89)	4(4)	C(86)	C(87)	C(88)	C(89)	-1(4)
C(87)	C(86)	C(85)	C(90)	-5(3)	C(87)	C(88)	C(89)	C(90)	0(4)
C(90)	C(85)	P(4)	C(91)	-118(2)	C(90)	C(85)	P(4)	C(97)	129(2)
C(91)	P(4)	C(97)	C(98)	93(2)	C(91)	P(4)	C(97)	C(102)	-85(2)
C(91)	C(92)	C(93)	C(94)	-3(4)	C(91)	C(96)	C(95)	C(94)	8(4)

Table 40: Torsion Angles(°) for **203** (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(92)	C(91)	P(4)	C(97)	4(2)	C(92)	C(91)	C(96)	C(95)	-3(4)
C(92)	C(93)	C(94)	C(95)	8(4)	C(93)	C(92)	C(91)	C(96)	1(4)
C(93)	C(94)	C(95)	C(96)	-10(4)	C(96)	C(91)	P(4)	C(97)	179(2)
C(97)	C(98)	C(99)	C(100)	-1(5)	C(97)	C(102)	C(101)	C(100)	1(5
C(98)	C(97)	C(102)	C(101)	-4(4)	C(98)	C(99)	C(100)	C(101)	-1(4)
C(99)	C(98)	C(97)	C(102)	4(4)	C(99)	C(100)	C(101)	C(102)	1(4
C(103)	C(104)	C(105)	C(106)	2(5)	C(103)	C(108)	C(107)	C(106)	0(5)
C(104)	C(103)	C(108)	C(107)	0(4)	C(104)	C(105)	C(106)	C(107)	-2(5
C(105)	C(104)	C(103)	C(108)	0(4)	C(105)	C(106)	C(107)	C(108)	1(5)
C(109)	C(110)	C(111)	C(112)	-3(6)	C(109)	C(114)	C(113)	C(112)	0(11
C(110)	C(109)	C(114)	C(113)	0(12)	C(110)	C(111)	C(112)	C(113)	4(9)
C(111)	C(110)	C(109)	C(114)	1(9)	C(111)	C(112)	C(113)	C(114)	-2(11
C(112)	C(111)	C(110)	C(115)	175(6)	C(114)	C(109)	C(110)	C(115)	-177(1

Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 5.[1] Selective Extrusion of Ph₃PO from β,γ,β'-Trioxo Ylides to give Diacylalkynes

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Sixteen examples of the previously unknown trioxo ylides **7** have been prepared by acylation of stabilised phosphorus ylides **8** with α-oxo acid chlorides **9**. Extrusion of Ph₃PO from these is readily achieved using FVP at 500 °C in most cases, to afford the diacylalkynes **10** in moderate yield. Three examples failed to give the expected alkynes and the nature of the processes involved in these cases is uncertain. Fully assigned ¹³C NMR spectra are presented for the ylides and an unexpected pattern is observed in the value of J_{P-C} for the three carbonyl carbons depending on the nature of the substituents present. There is some correlation between the value of $^2J_{P-C}$ for the central carbonyl carbon and the success of the pyrolysis although this is not complete. The method has been used to prepare a specifically ¹³C labelled acetylenic diester **14**.

In previous papers in this series we have examined the use of flash vacuum pyrolysis (FVP) to bring about thermal extrusion of Ph₃PO from a variety of stabilised phosphorus ylides **1**, thus providing convenient synthetic methods for a variety of substituted alkynes $R^1C{\equiv}CR^2$. It has long been known that for ylides **2**, stabilised by both ester and keto carbonyl groups, phosphine oxide extrusion involves loss of oxygen exclusively from the latter to give acetylenic esters.[2] This is most probably due to these compounds existing predominantly in the configuration shown with the keto carbonyl *syn* to phosphorus and the ester carbonyl *anti* to it, as recently demonstrated in the solid state by an X-ray structure determination.[3] Pyrolysis of ylides stabilised by two keto or aldehyde carbonyls has only been examined in a few cases. For examples such as **3–5**[4] and **6**,[5] selectivity is poor and, unless the two groups are identical as in **3** and **4**, mixtures of the two isomeric alkynes, $R^1COC{\equiv}CR^2$ and

$$Ph_3P{=}CHCOR^1 \xrightarrow[\text{Et}_3\text{N}]{\underset{\textbf{9}}{R^2COCOCl}} \text{(7)}$$

8

Scheme 1   **7**
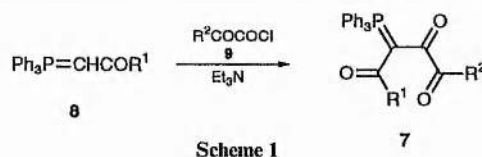
were stable crystalline solids which showed the expected analytical and spectroscopic properties including ³¹P NMR signals at δ_P +15–18. Their ¹³C NMR spectra, in particular, were highly informative and provided ready confirmation of the expected structures (Table 2). Doublets due to the ylide carbon are observed in the range δ_C 80–86 ($^1J_{P-C} \approx$ 100 Hz) for **7a–h** (R^1 = Ph, Me or Buᵗ) and at δ_C 66–70 ($^1J_{P-C} \approx$ 110 Hz) for **7i–p** (R^1 = OMe or OEt). Phosphorus coupling is also observed throughout the P-phenyl groups and to the first carbon of R^1.

The pattern of phosphorus coupling to the three carbonyl carbons is somewhat surprising, but does form a quite consistent pattern (Table 2). In most cases, the assignment of these signals could be made based on the observed chemical shifts or by extrapolation across the series. When ambiguity remained the signals have been assigned to conform to the pattern of observed P–C coupling constants. For **7a–d** (R^1 = Ph), the three-bond coupling to R^2CO is largest with smaller couplings to the other two carbonyls. For **7i–p** (R^1 = OMe or OEt), the three-bond coupling to R^2CO and the two-bond coupling to R^1CO are both large and the remaining value is small. A marked difference occurs for **7e–h** (R^1 = Me or Buᵗ), where the two-bond coupling to R^2COCO is now large and the remaining two values small. The reason for this pattern is not entirely clear but it presumably reflects the differing electron distribution in the trioxo ylide system depending on the groups present. As described below there is also a good correlation between the magnitude of the two-bond coupling to R^2COCO and the behaviour upon FVP.

When the ylides **7** were subjected to FVP at 500 °C, extrusion of Ph₃PO took place across the central position as shown in Scheme 2 to give diacylalkynes **10** in moderate yield in most cases (Table 3). Because of the small scale of operations, the boiling points of the liquid products, all well known compounds, were not determined but no significant impurities were detected by ¹H or ¹³C NMR and in no case was any of the isomeric product **11** detected. For **7i–p** this is as expected, since these compounds are assumed to exist predominantly in the form **12** with the ester CO *anti* to phosphorus, as is already well

1   **2**

3 $R^1 = R^2 = Me$
4 $R^1 = R^2 = Ph$
5 $R^1 = Me, R^2 = Ph$
6 $R^1 = H, R^2 = CF_3, C_2F_5, C_3F_7$

7
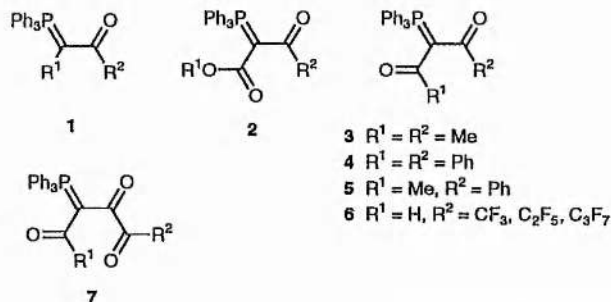
$R^1C{\equiv}CCOR^2$ are produced. In this paper we describe the preparation and behaviour upon FVP of the first examples of the higher homologues **7**, stabilised by an ester or keto group on one side of phosphorus and an α-diketone or α-keto ester group on the other.[6]

Results and Discussion

A total of 16 examples of the trioxo ylides **7** were obtained in good to excellent yield as shown in Scheme 1, by reaction of stabilised ylides **8** with 1 equiv. of the acid chlorides **9** in the presence of triethylamine in toluene at room temperature (Table 1). For $R^2 = Me$ it was found to be preferable to use a solution of pyruvoyl chloride in toluene prepared *in situ* by reaction of sodium pyruvate with oxalyl chloride. Repeated attempts to obtain **7** ($R^1 = R^2 = Me$) were unsuccessful. The new ylides

Table 1   Preparation of the ylides 7

	R^1	R^2	Yield (%)	δ_P		R^1	R^2	Yield (%)	δ_P
7a	Ph	Ph	82	16.5	7i	OMe	Ph	68	15.7
7b	Ph	Me	58	16.6	7j	OMe	Me	87	15.3
7c	Ph	OMe	87	17.8	7k	OMe	OMe	82	16.3
7d	Ph	OEt	70	15.6	7l	OMe	OEt	98	16.5
7e	Me	Ph	51	15.6	7m	OEt	Ph	71	15.6
7f	Me	OMe	86	16.2	7n	OEt	Me	56	15.2
7g	Me	OEt	68	16.2	7o	OEt	OMe	80	16.2
7h	Bu^t	Ph	78	17.4	7p	OEt	OEt	91	16.2

Table 3   Formation and ^{13}C NMR (δ_C) spectra of the diacylalkynes 10

	R^1	R^2	Yield (%)	C≡C	C=O	R signals
10a	Ph	Ph	40	85.8	176.5	135.8 (4ry), 135.2, 129.8 (2 C), 129.0 (2 C)
10b	Ph	Me	0	—		
10c	Ph	OMe	23	80.11, 80.08	176.0, 152.7	135.6 (4ry), 135.2, 129.8 (2 C), 129.0 (2 C), 53.4
10d	Ph	OEt	44	80.5, 79.7	176.1, 152.2	135.6 (4ry), 135.2, 129.7 (2 C), 128.9 (2 C), 63.1, 14.0
10e	Me	Ph	0	—		
10f	Me	OMe	0	—		
10g	Me	OEt	67	80.8, 78.0	182.5, 152.2	63.0, 32.3, 13.9
10h	Bu^t	Ph	43	85.4, 78.2	188.8, 176.5	135.7 (4ry), 135.1, 129.6 (2 C), 128.9 (2 C), 45.2, 25.6 (3 C)
10i	OMe	Ph	67	(as 10c)		
10j	OMe	Me	38	81.0, 77.5	182.6, 152.7	53.4, 32.3
10k	OMe	OMe	59	74.4	152.0	54.0
10l	OMe	OEt	61	75.1, 74.3	152.3, 151.8	63.1, 53.5, 13.9
10m	OEt	Ph	52	(as 10d)		
10n	OEt	Me	23	81.4, 78.5	183.1, 152.8	63.6, 33.0, 14.5
10o	OEt	OMe	70	(as 10l)		
10p	OEt	OEt	63	74.7	151.8	63.1, 13.9
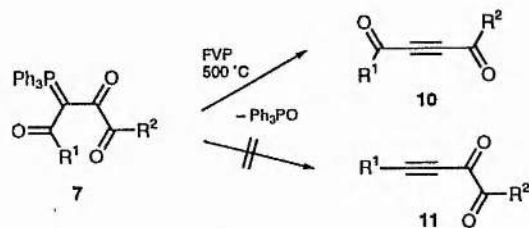
Scheme 2

known for the simpler analogues 2. The good selectivity for 10 as opposed to 11 is somewhat more surprising in cases 7a, c and d. The pattern of behaviour for the remaining compounds is harder to explain. For 7b, e and f none of the expected alkynes 10 were formed and the complex mixtures produced, including such components as acetaldehyde and acetophenone (7b), benzoic acid (7b, e) benzaldehyde (7e) and methanol (7f) indicate the occurrence of indiscriminate fragmentation processes. For 7e–h we had expected poor results owing to the high value of $^2J_{P-C}$ to the central carbonyl. In the course of an extensive study of the magnitude of this coupling in relation to the pyrolysis behaviour for very many stabilised ylides, we have observed a good correlation such that ylides with $^2J_{P-C} > 10$ Hz do not generally eliminate Ph$_3$PO to give alkynes while those with $^2J_{P-C} < 10$ Hz do. Based on this, pyrolysis of 7g and h should also have given poor results and FVP of 7b was expected to be successful. In fact, significant unidentified side-products were formed from 7h and the presence of a methyl group either as R^1 or R^2 seems to be undesirable explaining the failure of the pyrolysis of 7b and the formation of significant quantities of ethanol and methanol as by-products in the FVP of 7g and 7j, respectively. The dependence of the FVP behaviour on the values of R^1, R^2 and $^2J_{P-C}$ clearly needs further investigation.

Despite the problems encountered in some cases, this method
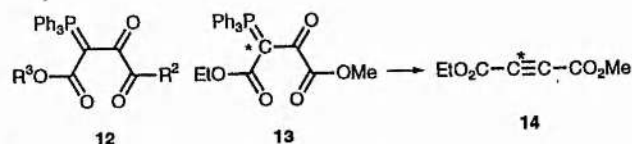
does allow convenient preparation of multigram quantities of diacylalkynes and we have already described the use of 10a and i prepared in this way for cycloaddition with Bu$_3$P·CS$_2$.[7] A further illustration of the value of this method is provided by the preparation of the specifically ^{13}C labelled unsymmetrical acetylene diester 14 which was required for a mechanistic study on the higher temperature fragmentation of acetylenic esters.[8] Beginning from ethyl bromoacetate labelled with 5% ^{13}C on the BrCH$_2$ carbon, the required labelled ylide 13 was readily prepared and, upon FVP, afforded the spectroscopically pure labelled diester (5 × enhancement of δ_C 75.1) in 55% yield. This labelled material could not be so readily prepared by other methods.

Experimental

M.p.s were recorded on a Kofler hot-stage microscope and are uncorrected. IR spectra were recorded for solids on Nujol mulls or solutions in CH$_2$Cl$_2$ and for liquids on thin films using a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^{1}H at 200 MHz and for ^{13}C at 50 MHz using a Varian Gemini instrument and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl$_3$ with internal Me$_4$Si as reference for ^{1}H and ^{13}C and external 85% H$_3$PO$_4$ as reference for ^{31}P. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. Mass spectra were obtained on an A. E. I. MS-902 spectrometer using electron impact at 70 eV. GC–MS data were obtained using a Hewlett Packard 5890A chromatograph

Table 2 ^{13}C NMR spectra [$\delta_C(J_{P-C})$], of the ylides 7

	R^1	R^2	P=C	CO-R^1	CO-COR^2	CO-COR^2	P-Phenyl				R signals
							C-1	C-2	C-3	C-4	
7a	Ph	Ph	84.2 (97)	193.4 (7)	190.3 (5)	195.5 (13)	124.1 (92)	133.4 (10)	128.8 (13)	132.3 (<2)	141.9 (8), 134.3, 132.7, 130.6, 129.0 (4 C), 127.9 (2 C), 127.5 (2 C)
7b	Ph	Me	80.2 (99)	193.5 (8)	191.3 (5)	201.4 (11)	124.1 (92)	133.5 (10)	128.8 (13)	132.4 (3)	143.2 (8), 131.0, 128.6 (2 C), 128.1 (2 C), 25.6
7c	Ph	OMe	82.3 (100)	192.9 (7)	182.3 (6)	166.2 (15)	124.1 (92)	133.5 (10)	128.9 (13)	132.4 (2)	141.8 (8), 131.1, 129.1 (2 C), 127.9 (2C), 51.4
7d	Ph	OEt	82.7 (100)	193.0 (7)	182.6 (6)	165.9 (15)	124.1 (92)	133.6 (10)	128.9 (13)	132.4 (2)	141.8 (8), 131.1, 129.2 (2C), 128.0 (2 C), 61.0, 13.6
7e	Me	Ph	86.3 (102)	195.2 (5)*	190.2 (13)	193.4 (5)*	124.5 (92)	133.5 (10)	128.7 (13)	132.2 (2)	133.8, 133.1, 129.7 (2 C), 128.1 (2 C), 30.2 (5)
7f	Me	OMe	84.5 (104)	195.0 (6)	182.4 (13)	167.1 (6)	124.6 (93)	133.4 (10)	128.8 (13)	132.3 (2)	51.9, 29.5 (5)
7g	Me	OEt	84.5 (105)	195.1 (6)	182.6 (13)	166.8 (5)	124.8 (93)	133.5 (10)	128.8 (12)	132.2 (2)	61.3, 29.5 (5), 13.8
7h	Bu^t	Ph	85.9 (102)	206.9 (3)	185.1 (19)	193.0 (<2)	125.3 (93)	133.7 (10)	128.4 (13)	131.9 (3)	134.6, 132.8, 129.9 (2C), 127.6 (2C), 43.9 (5), 26.6 (3 C)
7i	OMe	Ph	69.2 (109)	167.8 (14)	192.0 (4)	194.5 (11)	124.3 (93)	133.7 (10)	128.8 (13)	132.5 (3)	134.7, 132.6, 129.1 (2 C), 128.4 (2C), 50.1
7j	OMe	Me	66.2 (109)	168.1 (14)	193.1 (4)	202.7 (11)	124.0 (93)	133.6 (10)	128.8 (13)	132.5 (3)	50.1, 25.9
7k	OMe	OMe	68.0 (111)	167.8 (15)*	184.3 (6)	167.5 (14)*	124.0 (93)	133.6 (10)	128.8 (13)	132.5 (3)	51.8, 50.3
7l	OMe	OEt	67.8 (111)	167.41 (15)*	184.6 (6)	167.45 (13)*	124.1 (94)	133.6 (10)	128.8 (13)	132.5 (3)	61.0, 50.3, 14.2
7m	OEt	Ph	69.0 (109)	167.0 (14)	192.0 (4)	194.5 (11)	124.4 (93)	133.7 (10)	128.8 (12)	132.5 (2)	134.7, 133.6, 129.3 (2 C), 128.3 (2 C), 59.2, 13.4
7n	OEt	Me	66.0 (108)	167.9 (13)	193.2 (4.5)	202.8 (10)	124.2 (93)	133.6 (10)	128.9 (14)	132.5 (3)	59.1, 26.0, 13.6
7o	OEt	OMe	67.8 (110)	167.8 (14)*	184.3 (6)	167.2 (13)*	124.2 (93)	133.6 (10)	128.8 (13)	132.5 (3)	59.1, 51.7, 13.7
7p	OEt	OEt	67.6 (111)	167.5 (15)*	184.7 (6)	167.2 (13)*	124.2 (93)	133.6 (10)	128.7 (13)	132.4 (2)	60.9, 59.1, 14.1, 13.7

* Assignments may be interchanged.

coupled to a Finnigan Incos mass spectrometer. Toluene was dried over sodium.

The required stabilised ylides **8** are commercially available, with the exception of pivaloylmethylene(triphenyl)phosphorane (R^1 = Bu^t) which was prepared by reaction of Ph$_3$P with 1-bromopinacolone in boiling toluene followed by treatment of the resulting phosphonium salt with aqueous NaOH.

The acid chlorides **9** are commercially available (R^2 = OMe, OEt) or were prepared by treatment of the appropriate α-keto acid sodium salt with 1 equiv. of oxalyl chloride (R^2 = Ph, Me). In the first case the reaction was carried out in dry ether and was followed by filtration, evaporation and distillation of the product. In the last case the instability of the desired pyruvoyl chloride meant that it was preferable to perform the reaction in dry toluene, filter the solution under dry N$_2$ and use it directly for the ylide preparation.

Preparation of β,γ,β'-Trioxo Phosphorus Ylides.—A solution of the appropriate stabilised ylide **8** (10 mmol) and triethylamine (1.01 g, 10 mmol) in dry toluene (50 cm^3) was stirred at room temperature while a solution of the appropriate acid chloride **9** (10 mmol) in dry toluene (10 cm^3) was added dropwise to it. After the addition, the mixture was stirred for 3 h and then poured into water (100 cm^3). The organic phase was separated and the aqueous phase extracted with CH$_2$Cl$_2$ (2 × 50 cm^3). The combined organic phase and extracts were dried and evaporated to give the desired ylides which were recrystallised from ethyl acetate. Using this method the following were prepared.

1,4-Diphenyl-3-triphenylphosphoranylidenebutane-1,2,4-trione **7a**. Prepared as yellow crystals (82%), m.p. 158–160 °C (Found: C, 79.4; H, 5.0. C$_{34}$H$_{25}$O$_3$P requires C, 79.7; H, 4.9%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3020, 1780, 1665, 1585, 1515, 1475, 1428, 1310, 1210, 1170, 1100, 995, 860 and 830; δ$_H$ 8.15–7.0 (25 H, m); δ$_C$ see Table 2; δ$_P$ +16.5; m/z 512 (M$^+$, 0.5%), 456 (0.5), 407 (75), 379 (3), 277 (80), 262 (10), 234 (12), 183 (33), 129 (75), 105 (83) and 77 (100).

1-Phenyl-2-triphenylphosphoranylidenepentane-1,3,4-trione **7b** prepared as yellow crystals (58%), m.p. 164–166 °C (Found: C, 77.4; H, 5.0. C$_{29}$H$_{23}$O$_3$P requires C, 77.3; H, 5.1%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 1685, 1580, 1510, 1320, 1300, 1155, 1116, 1090, 1010, 985 and 858; δ$_H$ 7.8–7.2 (20 H, m) and 1.98 (3 H, s); δ$_C$ see Table 2; δ$_P$ +16.6; m/z (20 eV) 407 (M$^+$ − MeCO, 2%), 277 (100), 262 (6), 201 (8), 172 (20), 157 (8), 129 (30) and 105 (26).

Methyl 2,4-dioxo-4-phenyl-3-triphenylphosphoranylidenebutanoate **7c**. Prepared as colourless crystals (87%), m.p. 129–131 °C (Found: C, 74.7; H, 4.9. C$_{29}$H$_{23}$O$_4$P requires C, 74.7; H, 5.0%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3000, 1714, 1580, 1520, 1472, 1420, 1338, 1302, 1195, 1170, 1122, 1092, 1014, 985 and 855; δ$_H$ 7.8–7.3 (20 H, m) and 3.17 (3 H, s); δ$_C$ see Table 2; δ$_P$ +17.8; m/z 466 (M$^+$, 0.2%), 408 (5), 381 (2), 380 (2), 304 (2), 278 (33), 277 (76), 236 (6), 201 (12), 183 (11), 129 (12), 105 (29), 85 (66) and 84 (100).

Ethyl 2,4-dioxo-4-phenyl-3-triphenylphosphoranylidenebutanoate **7d**. Prepared as colourless crystals (70%), m.p. 123–125 °C (Found: C, 75.3; H, 5.4. C$_{30}$H$_{25}$O$_4$P requires C, 75.0; H, 5.2%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 1707, 1580, 1515, 1420, 1330, 1300, 1186, 1120, 1092, 1010, 985, 918 and 856; δ$_H$ 7.85–7.2 (20 H, m), 3.58 (2 H, q, J 7) and 1.02 (3 H, t, J 7); δ$_C$ see Table 2; δ$_P$ +15.6; m/z 480 (M$^+$, 0.5%), 407 (7), 379 (2), 304 (2), 278 (45), 277 (100), 201 (25), 199 (22), 183 (25), 152 (18), 129 (33), 105 (32) and 77 (92).

1-Phenyl-3-triphenylphosphoranylidenepentane-1,2,4-trione **7e**. Prepared as brown crystals (51%), m.p. 170–172 °C (Found: C, 77.4; H, 5.3. C$_{29}$H$_{23}$O$_3$P requires C, 77.3; H, 5.1%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 3000, 1700, 1654, 1575, 1530, 1470, 1420, 1355, 1300, 1208, 1165, 1092, 987, 908 and 832; δ$_H$ 8.0–7.25 (20 H, m) and 2.32 (3 H, d, J 4); δ$_C$ see Table 2; δ$_P$ +15.6; m/z

450 (M$^+$, 0.5%), 345 (3), 303 (2), 278 (18), 277 (42), 201 (12), 199 (14), 183 (10), 105 (22) and 77 (100).

Methyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate **7f**. Prepared as yellow crystals (86%), m.p. 130–132 °C (Found: C, 71.7; H, 5.3%; M − CO$_2$Me, 345.1056. C$_{24}$H$_{21}$O$_4$P requires C, 71.3; H, 5.2%; M − CO$_2$Me, 345.1044); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2930, 1710, 1535, 1470, 1414, 1352, 1280, 1190, 1092, 1033, 1015, 986, 918, 860 and 800; δ$_H$ 7.75–7.4 (15 H, m), 3.44 (3 H, s) and 2.26 (3 H, s); δ$_C$ see Table 2; δ$_P$ +16.2; m/z 404 (M$^+$, 1%), 376 (5), 375 (4), 345 (25), 318 (18), 303 (83), 277 (100), 201 (25), 183 (35) and 152 (16).

Ethyl 2,4-dioxo-3-triphenylphosphoranylidenepentanoate **7g**. Prepared as yellow crystals (68%), m.p. 138–140 °C (Found: C, 72.0; H, 5.7. C$_{25}$H$_{23}$O$_4$P requires C, 71.8; H, 5.5%); ν_{max}/cm^{-1} 1712, 1600, 1575, 1262, 1210, 1100, 1045, 861, 740, 720 and 690; δ$_H$ 8.0–7.5 (15 H, m), 3.93 (2 H, q, J 7), 2.32 (3 H, s) and 1.22 (3 H, t, J 7); δ$_C$ see Table 2; δ$_P$ +16.2; m/z 418 (M$^+$, 2%), 390 (15), 375 (2), 361 (2), 345 (100), 317 (10), 303 (83), 279 (37), 278 (37), 277 (78), 262 (22), 201 (23) and 183 (47).

5,5-Dimethyl-1-phenyl-3-triphenylphosphoranylidenehexane-1,2,4-trione **7h**. Prepared as yellow crystals (78%), m.p. 168–170 °C (Found: C, 77.8; H, 6.25. C$_{32}$H$_{29}$O$_3$P requires C, 78.0; H, 5.9%); ν_{max}/cm^{-1} 1654, 1525, 1430, 1360, 1340, 1300, 1260, 1210, 1140, 1090, 832, 737, 702, 680 and 648; δ$_H$ 7.75–7.15 (20 H, m) and 1.32 (9 H, s); δ$_C$ see Table 2; δ$_P$ +17.4; m/z 477 (M$^+$ − Me, 0.2%), 436 (M$^+$ − C$_4$H$_8$, 0.5), 435 (1), 387 (10), 303 (16), 277 (100), 201 (20), 183 (18), 158 (26) and 105 (50).

Methyl 3,4-dioxo-4-phenyl-2-triphenylphosphoranylidenebutanoate **7i**. Prepared as colourless crystals (68%), m.p. 205–207 °C (Found: C, 74.8; H, 5.0. C$_{29}$H$_{23}$O$_4$P requires C, 74.7; H, 5.0%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2980, 1645, 1572, 1518, 1472, 1412, 1320, 1270, 1175, 1092, 1072, 1015, 988 and 960; δ$_H$ 8.15–7.5 (20 H, m) and 3.21 (3 H, s); δ$_C$ see Table 2; δ$_P$ +15.7; m/z 438 (M$^+$ − CO, 10%), 406 (4), 361 (2), 277 (100), 262 (8), 201 (8), 152 (8), 122 (27), 105 (27) and 92 (36).

Methyl 3,4-dioxo-2-triphenylphosphoranylidenepentanoate **7j**. Prepared as colourless crystals (87%), m.p. 153–155 °C (Found: C, 71.2; H, 5.3. C$_{24}$H$_{21}$O$_4$P requires C, 71.3; H, 5.2%); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2925, 1690, 1650, 1600, 1470, 1412, 1338, 1290, 1172, 1090, 1060, 988, 941 and 872; δ$_H$ 7.8–7.4 (15 H, m), 3.30 (3 H, s) and 2.38 (3 H, s); δ$_C$ see Table 2; δ$_P$ +15.3; m/z 405 (M + 1$^+$, 8%), 361 (8), 333 (24), 301 (30), 277 (100), 201 (25), 183 (44), 152 (18) and 77 (45).

Dimethyl 2-oxo-3-triphenylphosphoranylidenebutanedioate **7k**. Prepared as colourless crystals (82%), m.p. 174–176 °C (Found: C, 69.1; H, 5.2%; M − CO$_2$Me, 361.0992. C$_{24}$H$_{21}$O$_5$P requires C, 68.6; H, 5.0%; M − CO$_2$Me, 361.0994); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 2970, 2930, 1715, 1650, 1540, 1470, 1415, 1350, 1270, 1180, 1095, 985 and 952; δ$_H$ 7.75–7.4 (15 H, m), 3.83 (3 H, s) and 3.28 (3 H, s); δ$_C$ see Table 2; δ$_P$ +16.3; m/z 420 (M$^+$, 0.5%), 361 (52), 301 (4), 277 (5), 201 (22), 183 (20) and 152 (10).

1-Ethyl 4-methyl 2-oxo-3-triphenylphosphoranylidenebutanedioate **7l**. Prepared as colourless crystals (98%), m.p. 173–174 °C (Found: C, 68.8; H, 5.45. C$_{25}$H$_{23}$O$_5$P requires C, 69.1; H, 5.3%); ν_{max}/cm^{-1} (Nujol) 1728, 1663, 1582, 1440, 1432, 1350, 1278, 1180, 1153, 1101, 1088, 1021, 753, 710 and 691; δ$_H$ 8.0–7.5 (15 H, m), 4.38 (2 H, q, J 7), 3.38 (3 H, s) and 1.38 (3 H, t, J 7); δ$_C$ see Table 2; δ$_P$ +16.5; m/z 434 (M$^+$, 1%), 375 (4), 362 (23), 361 (100), 301 (5), 293 (16), 201 (6), 183 (17), 165 (8) and 77 (12).

Ethyl 3,4-dioxo-4-phenyl-2-triphenylphosphoranylidenebutanoate **7m**. Prepared as colourless crystals (71%), m.p. 168–169 °C (Found: C, 74.4; H, 5.9%; M − CO, 452.1551. C$_{30}$H$_{25}$O$_4$P requires C, 75.0; H, 5.2%; M − CO, 452.1541); ν_{max}/cm^{-1} (CH$_2$Cl$_2$) 1640, 1530, 1470, 1425, 1353, 1327, 1270, 1200, 1160, 1090 and 980; δ$_H$ 8.15–7.45 (20 H, m), 3.76 (2 H, q, J 7) and 0.59 (3 H, t, J 7); δ$_C$ see Table 2; δ$_P$ +15.6; m/z 452 (M$^+$ − CO, 10%), 376 (26), 375 (100), 301 (9), 277 (20) and 262 (62).

Ethyl 3,4-dioxo-2-triphenylphosphoranylidenepentanoate **7n**.

Prepared as colourless crystals (56%), m.p. 138–140 °C (Found: C, 72.4; H, 5.5%; M − COMe, 375.1118. $C_{25}H_{23}O_4P$ requires C, 71.8; H, 5.5%; M − COMe, 375.1150); $v_{max}/cm^{-1}(CH_2Cl_2)$ 1690, 1638, 1532, 1468, 1415, 1355, 1320, 1250, 1146 and 1092; δ_H 7.8–7.4 (15 H, m), 3.83 (2 H, q, J 7), 2.32 (3 H, s) and 0.78 (3 H, t, J 7); δ_C see Table 2; δ_P +15.2; m/z 418 (M$^+$, 0.2%), 375 (M$^+$ − COMe, 100), 347 (5), 303 (28), 301 (36), 277 (67), 262 (70), 201 (37), 183 (86) and 165 (40).

4-*Ethyl* 1-*methyl* 2-*oxo*-3-*triphenylphosphoranylidenebutane-dioate* 7o. Prepared as colourless crystals (90%), m.p. 115–118 °C (Found: C, 69.45; H, 5.6. $C_{25}H_{23}O_5P$ requires C, 69.1; H, 5.3%); $v_{max}/cm^{-1}(CH_2Cl_2)$ 2940, 1718, 1648, 1548, 1360, 1260, 1190, 1163, 1094, 1080 and 988; δ_H 7.75–7.4 (15 H, m), 3.85 (3 H, s), 3.83 (2 H, q, J 7) and 0.77 (3 H, t, J 7); δ_C see Table 2; δ_P +16.2; m/z 434 (M$^+$, 0.2%), 376 (18), 303 (3), 301 (1), 278 (20), 277 (42), 201 (8), 183 (6), 91 (22), 85 (67) and 84 (100).

Diethyl 2-*oxo*-3-*triphenylphosphoranylidenebutanedioate* 7p. Prepared as colourless crystals (91%), m.p. 136–138 °C (Found: C, 70.0; H, 5.6. $C_{26}H_{25}O_5P$ requires C, 69.6; H, 5.6%); v_{max}/cm^{-1} 1735, 1725, 1672, 1540, 1438, 1342, 1278, 1190, 1095, 1020, 760, 745, 718 and 698; δ_H 8.0–7.5 (15 H, m), 4.38 (2 H, q, J 7), 3.89 (2 H, q, J 7), 1.37 (3 H, t, J 7) and 0.78 (3 H, t, J 7); δ_C see Table 2; δ_P +16.2; m/z 448 (M$^+$, 0.2%), 403 (0.2), 376 (16), 375 (100), 347 (4), 303 (12), 279 (4), 201 (6), 195 (3), 183 (11) and 165 (8).

Flash Vacuum Pyrolysis of the Ylides 7.—The apparatus used was as described previously.[9] All pyrolyses were conducted at pressures in the range 10^{-3}–10^{-1} Torr and were complete within 1 h for ⩽0.5 g of ylide or 3–4 h for 1–5 g ylide. Under these conditions the contact time in the hot zone was estimated to be ≈10 ms. In some cases Ph$_3$PO collected at the furnace exit and the more volatile products were recovered from the cold trap. Where necessary, in the case of less volatile products, the entire pyrolysate was washed out together and separated by preparative TLC or distillation. For small-scale pyrolyses yields were determined by calibration of the ^{1}H NMR spectra by adding an accurately weighed quantity of a solvent such as CH$_2$Cl$_2$ and comparing integrals, a procedure estimated to be accurate to ±10%. The apparently low overall yield of products in some cases is accounted for by the formation of gaseous products and/or by a substantial non-volatile polymeric residue in the inlet tube.

(a) FVP of the ylide 7a (5.0 g) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Chromatography on silica (ethyl acetate) gave pure dibenzoylacetylene 10a (0.9 g, 40%) as pale yellow crystals, m.p. 110–111 °C (lit.,[10] 112 °C); δ_H 8.4–8.2 (4 H, m) and 7.8–7.3 (6 H, m); δ_C see Table 3.

(b) FVP of the ylide 7b (124 mg) at 500 °C gave a solid at the furnace exit which proved to be a mixture of Ph$_3$PO and Ph$_3$P, and in the cold trap a liquid which was shown by ^{1}H and ^{13}C NMR and GCMS to contain a complex mixture of products including acetaldehyde, acetophenone, benzoic acid, 1-phenylpent-1-ene-3,4-dione and 1-phenylpent-2-ene-1,4-dione. The desired acetylbenzoylacetylene 10b was not present.

(c) FVP of the ylide 7c (200 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was methyl benzoylpropynoate 10c (23%); δ_H 8.12 (2 H, m), 7.75–7.45 (3 H, m) and 3.90 (3 H, s); δ_C see Table 3.

(d) FVP of the ylide 7d (215 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was ethyl benzoylpropynoate 10d (44%); δ_H 8.1–8.2 (2 H, m), 7.7–7.45 (3 H, m), 4.35 (2 H, q, J 7) and 1.38 (3 H, t, J 7); δ_C see Table 3.

(e) FVP of the ylide 7e (106 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO and in the cold trap a solid which was shown by ^{1}H NMR and GCMS to contain mainly benzaldehyde (17%) and benzoic acid (45%) with further minor unidentified components. The expected acetylbenzoylacetylene 10e was not present.

(f) FVP of the ylide 7f (121 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be mainly Ph$_3$PO accompanied by ≈5% Ph$_3$P. The material in the cold trap was shown by ^{1}H NMR and GCMS to contain mainly methanol with further minor unidentifed components. The expected methyl 3-acetylpropynoate 10f was not present.

(g) FVP of the ylide 7g (142 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO and in the cold trap ethyl 3-acetylpropynoate 10g (67%) as a colourless liquid; δ_H 4.26 (2 H, q, J 7), 2.36 (3 H, s) and 1.30 (3 H, t, J 7); δ_C see Table 3; m/z 140 (M$^+$, 1%), 125 (21), 111 (3), 95 (28), 80 (8), 67 (9) and 53 (100), accompanied by ethanol (≈20%).

(h) FVP of ylide 7h (92 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap contained several unidentified components but the major one was the desired benzoylpivaloylacetylene (43%); δ_H 8.2–8.0 (2 H, m), 7.7–7.5 (3 H, m) and 1.34 (9 H, s); δ_C see Table 3; m/z (GCMS) 199 (M$^+$ − Me, 1%), 159 (6), 158 (84), 130 (5), 105 (42), 102 (28), 77 (45) and 57 (100).

(i) FVP of the ylide 7i (1.0 g) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be a mixture of Ph$_3$PO and the desired product. Kugelrohr distillation gave methyl benzoylpropynoate 10i (0.27 g, 67%) as a colourless solid, m.p. 68–69 °C (lit.,[11] 65–66 °C); δ_H 8.4–8.2 (2 H, m), 7.8–7.5 (3 H, m) and 3.97 (3 H, s); δ_C see Table 3.

(j) FVP of the ylide 7j (140 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be Ph$_3$PO and in the cold trap methyl 3-acetylpropynoate 10j (38%) as a colourless liquid; δ_H 3.80 (3 H, s) and 2.40 (3 H, s); δ_C see Table 3, accompanied by methanol (≈40%).

(k) FVP of the ylide 7k (500 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was dimethyl butynedioate 10k (59%); δ_H 3.84 (6 H, s); δ_C see Table 3.

(l) FVP of the ylide 7l (503 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was ethyl methyl butynedioate 10l (61%); δ_H 4.37 (2 H, q, J 7), 3.89 (3 H, s) and 1.35 (3 H, t, J 7); δ_C see Table 3.

(m) FVP of the ylide 7m (500 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was ethyl benzoylpropynoate 10m (52%); δ_H 8.3–8.2 (2 H, m), 7.8–7.5 (3 H, m), 4.42 (2 H, q, J 7) and 1.39 (3 H, t, J 7); δ_C see Table 3.

(n) FVP of the ylide 7n (400 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was ethyl 3-acetylpropynoate 10n (23%); δ_H 4.32 (2 H, q, J 7), 2.45 (3 H, s) and 1.36 (3 H, t, J 7); δ_C see Table 3.

(o) FVP of the ylide 7o (1.10 g) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was ethyl methyl butynedioate 10o (88%); δ_H 4.28 (2 H, q, J 7), 3.82 (3 H, s) and 1.31 (3 H, t, J 7); δ_C see Table 3.

(p) FVP of the ylide 7p (503 mg) at 500 °C gave a solid at the furnace exit which was shown by ^{1}H and ^{31}P NMR to be pure Ph$_3$PO. The colourless liquid in the cold trap was diethyl butynedioate 10p (63%); δ_H 4.37 (2 H, q, J 7) and 1.35 (3 H, t, J 7); δ_C see Table 3.

(q) ^{13}C *Labelled ethyl methyl acetylenedicarboxylate* 14. This compound was prepared as for 10o by FVP of ylide 13 made

from (ethoxycarbonylmethylene)triphenylphosphorane derived from ethyl bromoacetate labelled with 5% ^{13}C at the BrCH$_2$ position. The product was obtained in 55% yield on the pyrolysis and had spectroscopic properties identical with those of the unlabelled compound **10o** above, except for a five times enhancement of the signal at δ_C 75.1.

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