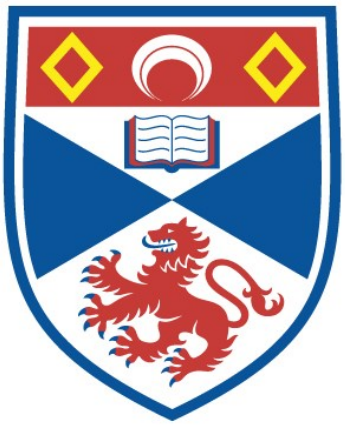
PREPARATION AND PYROLYSIS OF SOME SULPHINYL-STABILISED PHOSPHOROUS YLIDES

Bruce Martin Ryan

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



1996

PREPARATION AND PYROLYSIS OF SOME SULPHINYL-STABILISED PHOSPHORUS YLIDES

by

BRUCE MARTIN RYAN, B. Sc.

Thesis presented for the degree of
Doctor of Philosophy

University of St. Andrews

May, 1995

DECLARATIONS

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

Signed..... Date.....15th May 1995.....

I was admitted to the Faculty of Science of the University of St Andrews under Ordinance General number 12 on the 1st day of October 1989 and as a candidate for the degree of Ph. D. on 1st day of October 1990.

Signed..... Date...15th May 1995.....

I hereby certify that the candidate has fulfilled the conditions of the Resolution and regulations appropriate to the degree of Ph.D.

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TO ALYSSA, HANNAH AND EWAN

Maybe some day there'll be a decent world for you to enjoy.

ACKNOWLEDGEMENTS

I would like to thank Dr Alan Aitken for his valiant efforts to keep my nose to the grindstone and all my past and present colleages in Lab 434 for mopping up the blood. I am also extremely grateful to Stewart Leckie and Louise Yeoman for all their support, particularly during my Edinburgh sojourn and to the Forkenford crew (Charlie, Caroline, Dave, Duke, Gary, Henry, Neil, Rodney, Sherri, Shona, Simon and Stu) for welcoming me to Edinburgh.

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Finally, thanks are due to British Petroleum, my parents and the DSS for financial support.

LECTURE COURSES

The following are the courses attended during the period of research;

Organic Research Seminars	(3 years attendance)
Studies in Enzyme Mechanism	(Dr N. P. Botting)
Biological Chemistry	(Professor D. Gani)
Unusual Oxides and Sulphides of Carbon	(Dr R. A. Aitken)
Molecular Rearrangements	(Dr J. C. Walton)
Case Studies in Mechanistic Chemistry	(Dr A. R. Butler)
Computer Simulation of Solids	(Dr K. D. M. Harris)

ABSTRACT

The results of further investigation into the pyrolytic behaviour of alkane- and arenesulphinyl alkoxycarbonyltriphenylphosphoranes are reported. Flash vacuum pyrolysis (FVP) of these ylides at 600°C gives vinyl sulphides, sulphides and aldehydes. The vinyl sulphides and aldehydes are explained by assuming extrusion of $Ph_3P{=}O$, followed by C–H insertion in the resulting carbene to give a β-lactone. This can either lose CO_2 to give the vinyl sulphides or fragment in the opposite sense to give the aldehydes together with unknown products. The sulphides are explained by assuming extrusion of Ph_3P, followed by successive loss of CO and CO_2. A variable temperature study of $Ph_3P{=}C(CO_2Et)SOEt$ has revealed a complex pattern of interdependent restricted rotation of both ester and sulphinyl groups.

FVP of the alkanesulphinylbenzylidenetriphenylphosphoranes at 500°C gives the alkyl thiolobenzoates by oxygen transfer in the carbene formed by extrusion of Ph_3P. The first three examples of arenesulphinyl benzylidenetriphenylphosphoranes have been prepared. FVP of these at 500°C gives a mixture containing aryl thiolobenzoates formed as above together with ketones, sulphides, thiols, disulphides and stilbene. Mechanisms are suggested for the formation of these products.

Four new alkyl sulphonyldiazoacetates have been prepared. FVP of these at 600°C gives vinyl sulphones, while at lower temperatures, products resulting from transfer of oxygen in the carbenes formed by extrusion of N_2 predominate.

CONTENTS

INTRODUCTION

INTRODUCTION

A Flash Vacuum Pyrolysis

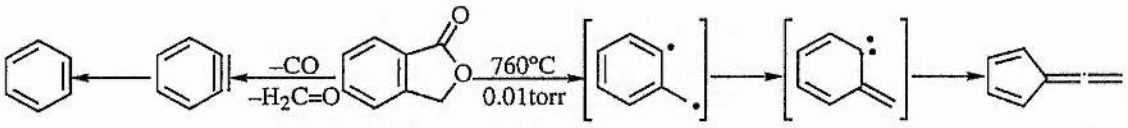
1 Techniques and apparatus

Since the earliest times, heat and fire have been used to change our surroundings and to illuminate our lives. It is no surprise that among the earliest techniques used by people to probe their surroundings were thermolysis and pyrolysis; "degradation (leading to analysis) by heat or by fire". However, as science moved on, there came an increasing necessity to fine-tune the tools. This necessity can be seen in Hurd's monograph which mentions every "organic" pyrolysis before 1929 and covers processes occuring at 125°C (decomposition of malonic acid) to 1100°C (decomposition of methane).[1] Originally, pyrolysis was carried out by heating the substrate in a vessel, maybe with exclusion of air, and analysing the result. This had the disadvantages that there were almost certainly secondary reactions of the products of the initial pyrolysis with air, the substrate and with itself, and further reactions between the products of these secondary reactions. Also, it would have been difficult to control the amount of energy each molecule would receive, so there was the possibility of several initial reactions in any pyrolysis. Even if none of these problems were serious, there would always be the difficulties of ensuring the reaction went to completion and separating the products at the end of the pyrolysis.

What was needed was for the pyrolytic reaction to take place away from the bulk of substrate and for the products to be collected elsewhere. A step

towards this was made with Hurd's apparatus for the generation of ketene in which acetone is vapourised by immersing the pyrolysis vessel in boiling water.[2] The vapour is led through a hot tube containing broken porcelain where the decomposition takes place and excess acetone is condensed from the gas stream by passage though a vertical water condenser.

In other cases, a vertical arrangement was used, e.g., for the conversion of ethyl acrylate to acrylic acid.[3] For compounds that were less volatile, the pyrolysis could be performed at reduced pressure; products that were more volatile than the substrate could be collected while the substrate itself was recycled through the hot zone (e.g. Williamson and co-workers' preparation of cyclohexenone from 2-acetylcyclohexanone).[4] Similarly Wiersum and Nieuwenhuis prepared fulvenallene **1** in 60–70% yield from phthalide **2**.[5] (There was a small amount of benzene in the pyrolysate, presumably from an alternative cleavage that gives benzyne.)

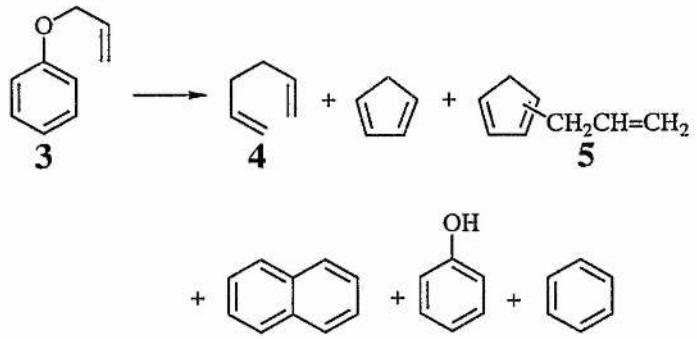


2 **1**

Spangler introduced the idea of sweeping the substrate along on a stream of nitrogen to prevent products from condensing around the hot zone.[6] Brown and Solly pyrolysed indanetrione in a stream of benzene through a vertical furnace to give biphenylene, naphthalene and acetylene.[7] These products were assumed to be formed via benzyne. Similarly, Cava and co-workers found that phthalic anhydride gave biphenylene on low pressure pyrolysis.[8]

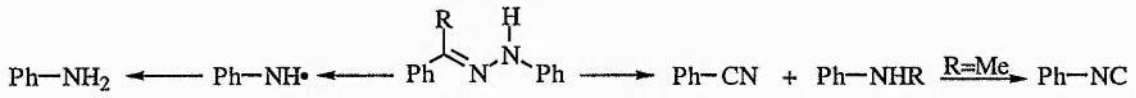
Finally, the desire to probe short-lived intermediates led several groups to the idea of flash vacuum pyrolysis (FVP). The idea is very similar to the acetone ⇒ ketene apparatus, except the pressure in the apparatus is kept very low (10^{-3} to 10^{-4} torr), and the substrate is sublimed through the hot zone under the influence of this vacuum and gentle heating of the substrate container. In all cases the idea is to supply a dilute stream of substrate into a hot zone where (unimolecular) reactions can occur. Products can be fed directly into analytical equipment or trapped on liquid nitrogen cold fingers, rare gas matrices, or collected for further work.

One of the first reports was from Hedaya and McNeil.[9] Their apparatus consisted of a quartz tube, surrounded by a wire heating element held in place with mastic, connected to a vacuum pump via a cold trap. They investigated the FVP of phenyl allyl ether **3** and found this produced hexa-1,5-diene **4** (13% at 954°C), cyclopentadiene (3%), allylcyclopentadiene **5** (36%), naphthalene (1%), phenol (7%) and benzene (1%). It is interesting to note that there was no sign of any Claisen-rearranged product.



3 **4** **5**

Crow and Solly used a similar system to pyrolyse phenyl hydrazones.[10] These gave aniline and phenylisocyanide. The apparatus was essentially similar to that shown at the beginning of the experimental section.



Brown introduced apparatus where a trapping agent could be injected into the reaction zone to react with the pyrolysis product.[11] Such apparatus is easily modified to collect samples for NMR directly from the cold trap.[12]

In many cases, comparisons have been made with mass spectral processes but the comparison may well be dubious due to changes in bond strength and the preferred geometry when an electron is removed.[13]

Twenty-five years on from these beginnings there is a large body of work on FVP. Techniques have improved (e.g. "firing" the product directly into a photo-electron spectrometer and "solution-spray FVP"[14]) but most of this work has simply been increasing the range of compounds fed into a simple hot tube.

2 FVP Reactions

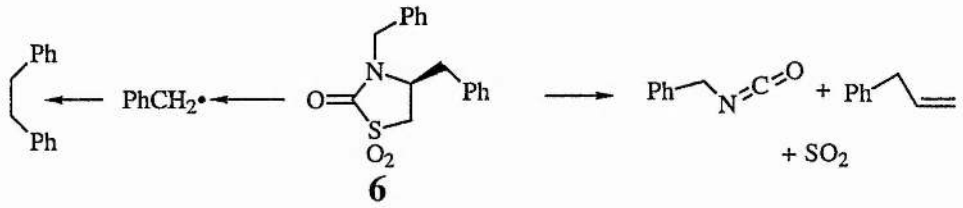
Reactions can be classified in several ways, depending on whether the important point is the product, the mechanism or the intermediates. The following is a necessarily brief outline of the major sorts of reaction that have been performed under FVP conditions.

a Extrusion of small molecules

i SO_2 extrusion

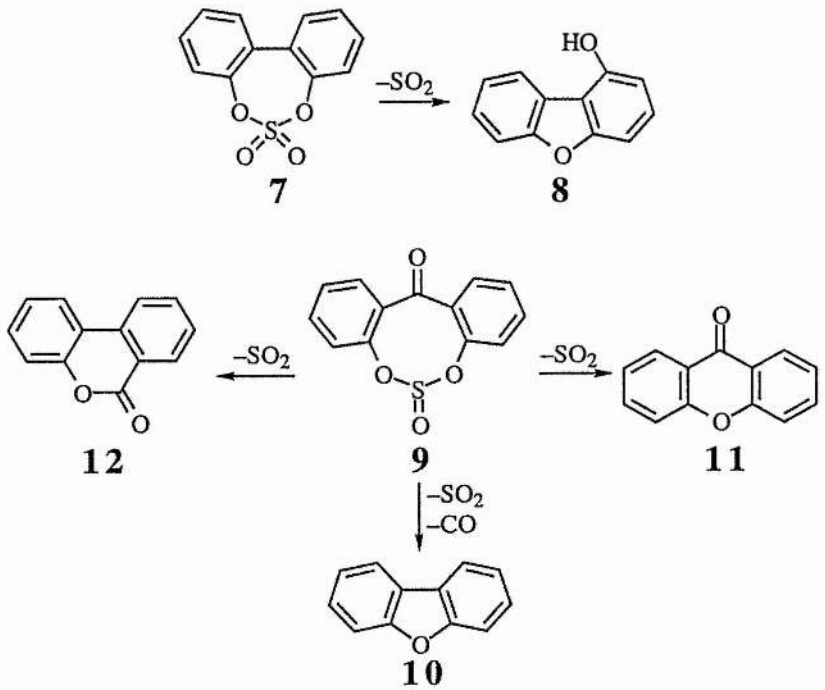
Probably the best known work in this area is Vogtle's work on the preparation of cyclophanes.[15] However SO_2 loss can happen in many ways and has recently been reviewed.[16] A few examples are given.

The thiazolidin-2-one-1,1-dioxide **6** loses SO_2 in an electrocyclic reaction to give benzyl isocyanate, allyl benzene and bibenzyl.[17]



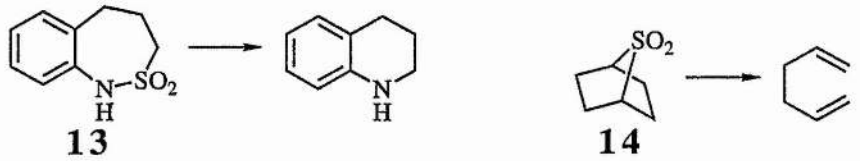
6

Similarly, the sulphate **7** gave hydroxydibenzofuran **8** whereas the related sulphite **9** gave dibenzofuran **10**, xanthone **11** and 3,4-benzocoumarin **12**.[18]



7 **8** **12** **9** **11** **10**

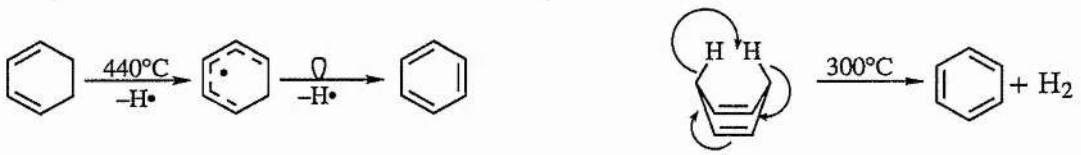
The benzothiazepine dioxide **13** gave the tetrahydroquinoline[19], and loss of SO_2 from the simple bicyclic system **14** gave 1,5-hexadiene.[20]



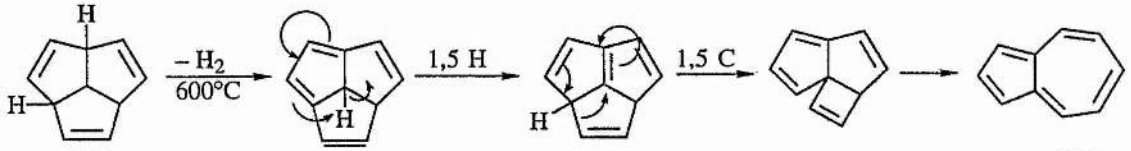
13 **14**

ii H_2 and alkane extrusion

There is a great contrast in ease of loss of H_2 from 1,3– and 1,4-cyclohexadiene. The former gives benzene via a radical mechanism; the latter goes by 1,4-elimination.[21] Similar effects occur with benzo-fused systems.[22]

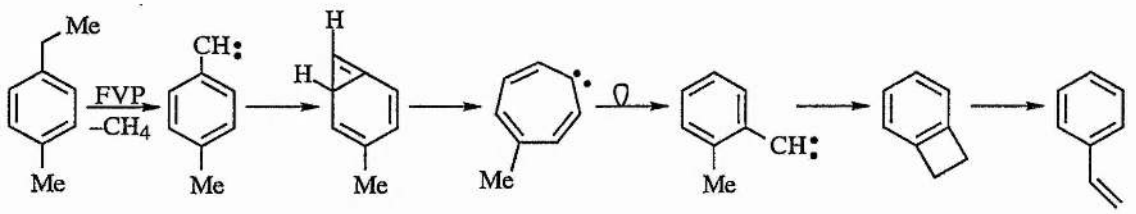


The dehydrogenation of triquinacene **15** to give azulene **16** involves an interesting series of rearrangements.[23]



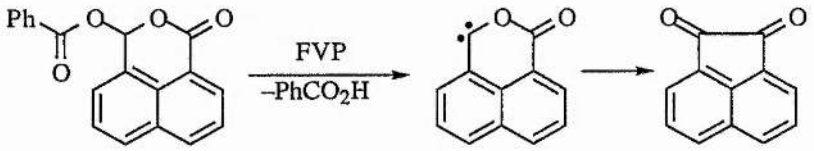
15 **16**

A striking reaction occurs in the pyrolysis of 4-ethyltoluene. The carbene "jumps" into the ring and styrene is given by an "aryl carbene walk" mechanism.[24]

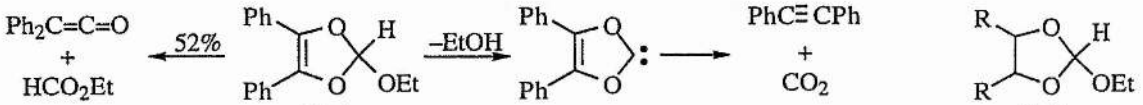


iii α-Elimination from esters

This has been observed in cases when β-elimination is not possible, such as the example noted by Brown.[25]



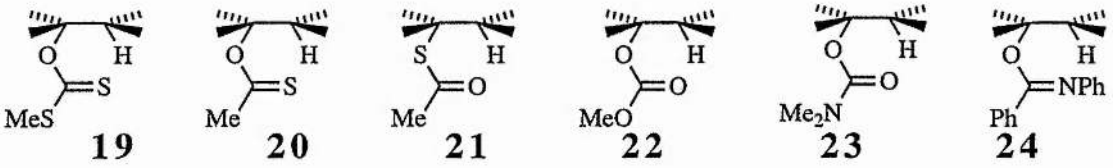
FVP of dioxole **17** gives the acetylene in 24% yield.[26] This is related to the conventional pyrolysis of dioxolanes **18** derived from 1,2-diols to give the corresponding alkenes.[27]



17 **18**

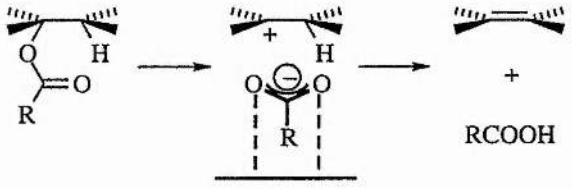
iv β-Elimination from esters and similar species

This is seen in systems that can give appropriate 6-membered transition states such as S-alkyl xanthates[28] **19**, thiono- **20** and thioloacetates[29] **21**, dialkylcarbonates[30] **22**, alkyl carbamates[31] **23** and imidates[32] **24**.

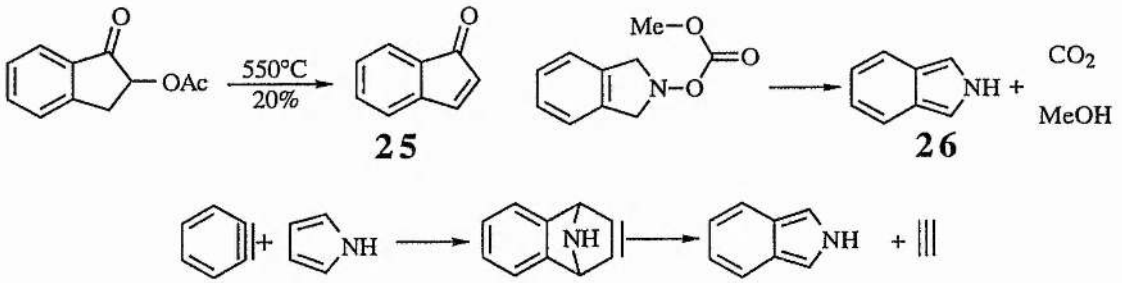


19 **20** **21** **22** **23** **24**

There is some argument over the amount of ion pair character in the TS, especially when the reaction is carried out in conditions where the reactor surface would stabilise such a pair.[33]



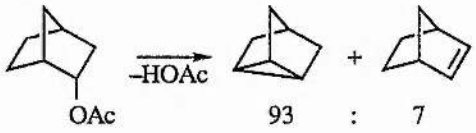
The pyrolytic preparations of indenone[34] **25** and isoindole[12] **26** are of synthetic interest but the latter has been superceded by Bornstein's retro Diels-Alder procedure.[35] It is interesting to note that benzyne can also be formed by FVP (e.g. of indanetrione) and to speculate on the possibility of linking the two steps in a tandem pyrolysis apparatus.

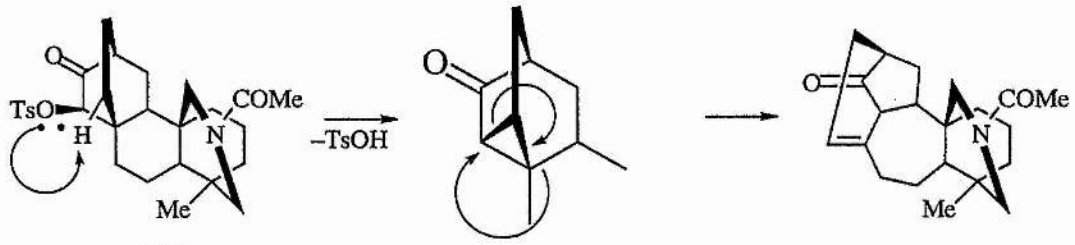


25 **26**

v γ-Eliminations from esters

This can accompany β-elimination, as seen below[36], and has been used to rearrange the atisine skeleton of **27** into the lycoctine-aconitine form.[37]





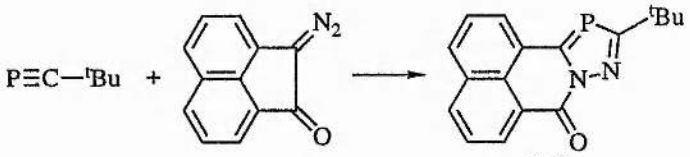
27

vi H-Hal elimation

A notable example is the synthesis of phospha-acetylene by FVP of $MePCl_2$.[38]

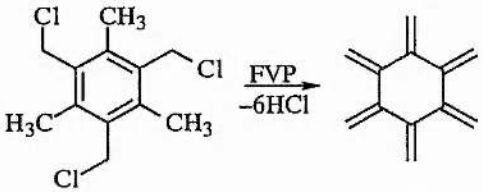
$$MePCl_2 \xrightarrow{1000°C} 2HCl + HC{\equiv}P$$

Substituted phospha-acetylenes, especially t-butyl phospha-acetylene, have a very rich chemistry. Highlights include cycloaddition with re-arrangement to give novel heterocycles such as **28**.[39]



28

The elimination of 3 equivalents of HCl from 2,4,6-tris(chloromethyl) mesitylene **29** by FVP at 660°C gives [6]radialene **30**.[40, 41]



29 **30**

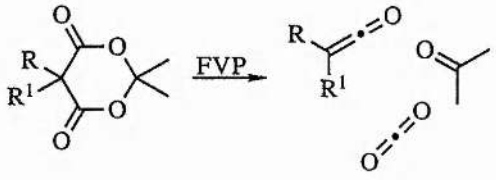
b Formation of reactive intermediates

i Ketenes

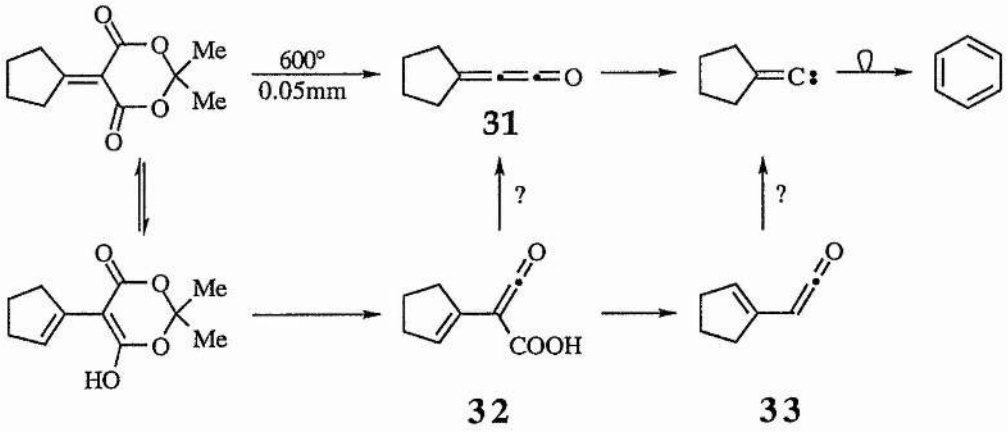
The most important use of ketene is in the production of acetic anhydride. In the industrial process, acetic acid is pyrolysed at 750°C. The gas stream is rapidly cooled to precipitate the extruded water and the ketene reacts with an incoming stream of acetic acid to produce the anhydride. This process is easily scaled down to lab FVP conditions.[42]

$$CH_3CO_2H \xrightarrow[(EtO)_3P=O\ cat.]{750°C} H_2C=C=O \xrightarrow{CH_3CO_2H} (MeCO)_2O$$
$$-H_2O$$

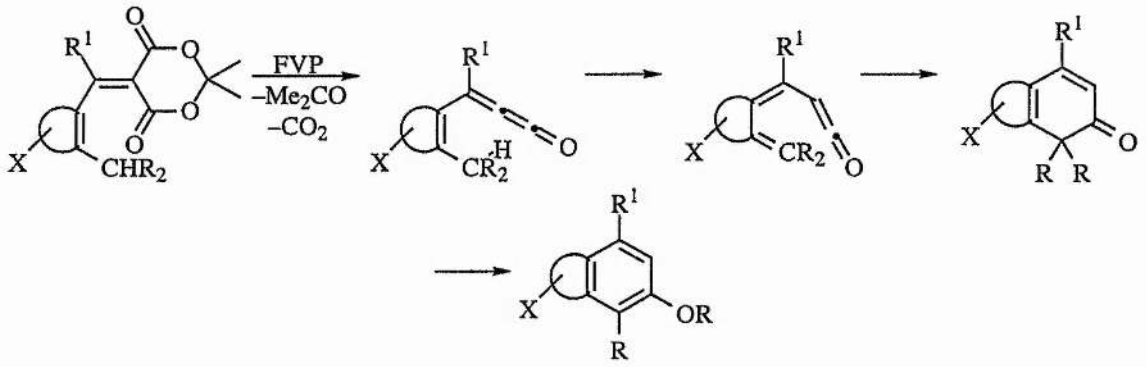
Brown has reviewed the work on the reactions of ketenes produced from Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives.[43]

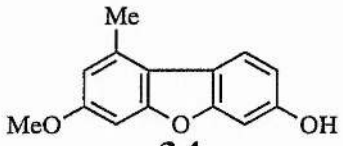


Recently, Wentrup and co-workers have shown that pyrolysis of 5-cyclopentylidene Meldrum's acid does not entirely follow this scheme. In addition to the formation of benzene via cyclopentylidene carbene, the ketenes **31**, **32** and **33** were observed by low temperature IR.[44]



Variations on the methyleneketene cyclisation (dubbed "the McMullen reaction") outlined below have been used to prepare substituted dibenzofurans such as **34**[45] and pyrrolones **35**[46] and **36**.[47]





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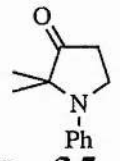

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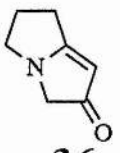
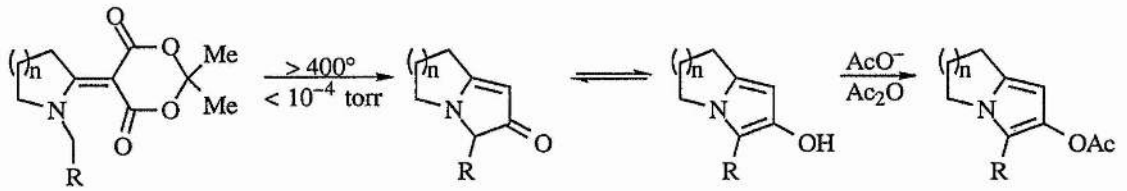
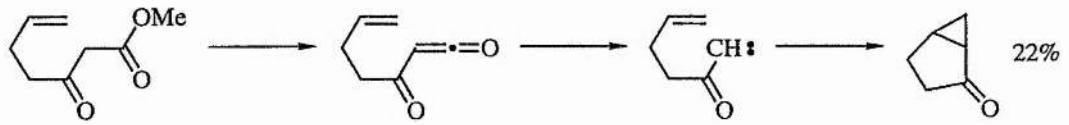


36

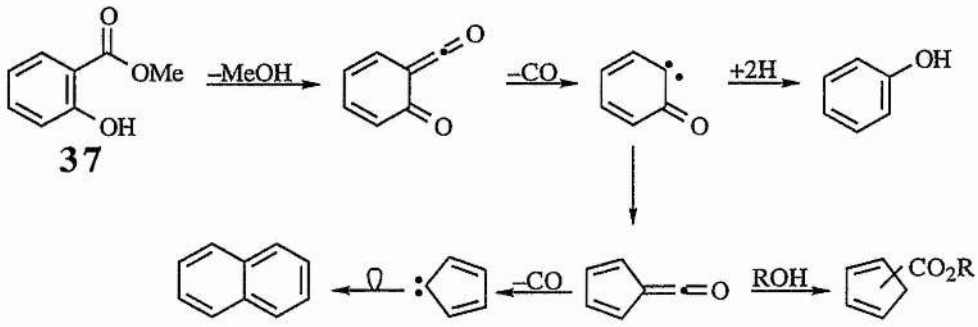
This approach has also been used to prepare bicyclic hydroxypyrazoles.[48]



Decarbonylation of ketenes to give carbenes is quite common[49] and ketenes can also be formed by 1,2- and 1,4-elimination of ROH from esters. Leyendecker used these ideas to prepare a fused cyclopentanone via a keto-carbene.[50]

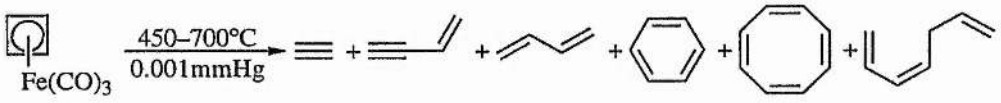


An example of a 1,4-elimination that serves to point towards some of the other types of reaction encountered in FVP work is the pyrolysis of 2-(methoxycarbonyl)phenol **37**. The ketene formed can be trapped with alcohol or left to undergo further reactions.[51]



ii Cyclobutadiene

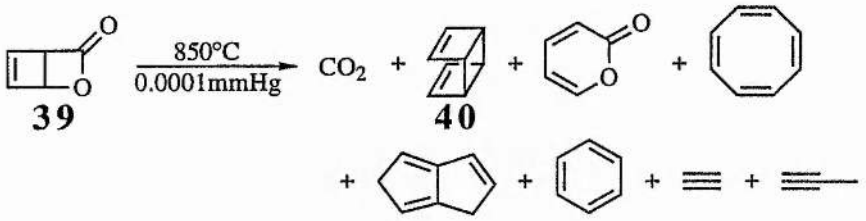
The history of the search for cyclobutadiene has been chronicled by Cava and Mitchell.[52] Although cyclobutadiene was first obtained by oxidation of the iron complex $Fe(CO)_3(C_4H_4)$ **38**[53], FVP syntheses are known. FVP of **38** gave acetylene, vinylacetylene, butadiene, benzene, cyclooctatetraene and styrene, and this product mixture is indicative, if not conclusive proof, that cyclobutadiene has been formed.[54]



38

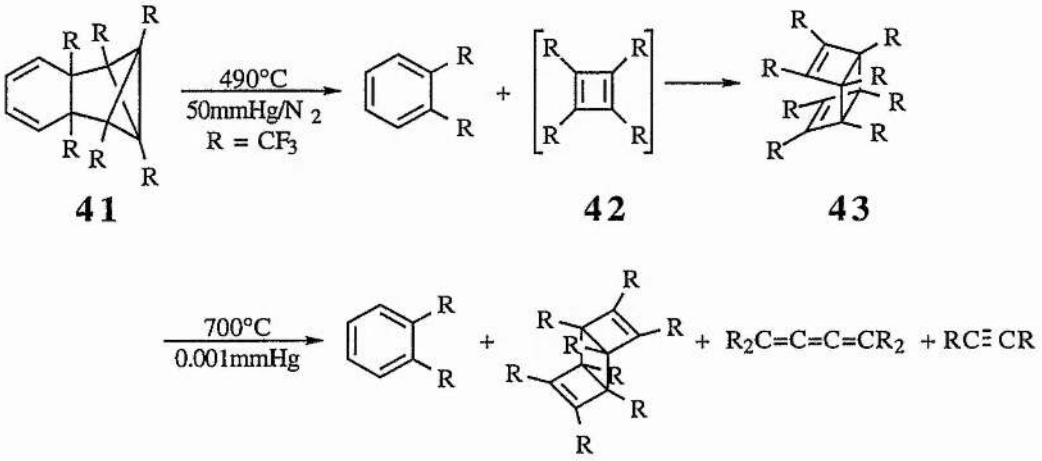
Hedaya pyrolysed photo-α-pyrone **39** and analysed the gas phase products directly by MS.[55] Cyclobutadiene was detected at m/z=52. Subsequently the pyrolysis was repeated in a normal FVP apparatus: the

product mixture, especially syn-tricyclo[4.2.0.0.^{2,5}]octa-3,7-diene **40**, left little doubt that cyclobutadiene had been formed.

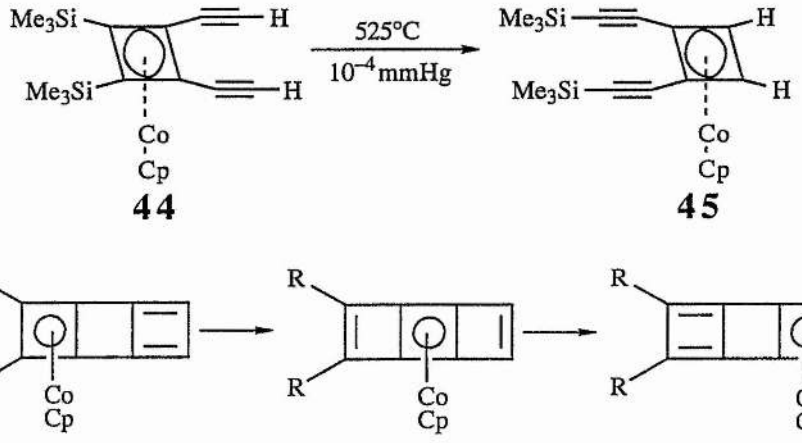


Later Chapman isolated benzocyclobutadiene in an argon matrix by FVP of cis-1,2-diiodobenzocyclobutene over zinc at 230°C/10^{-6}mmHg.[56]

Kobayashi has "conventionally" pyrolysed **41** to get the syn dimer **43** of tetrakis(trifluoromethyl)cyclobutadiene **42**[57], whereas Warrener found that FVP at 700°C of the same substrate gave the anti dimer of **42**, tetrakis(trifluoromethyl)butatriene and bis(trifluoromethyl) acetylene.[58]

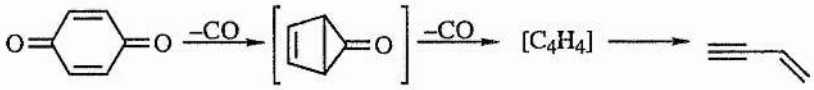


FVP of the complex **44** gives the isomer **45**. It was suggested that the two acetylene units undergo metathesis to give a transient tricyclo species. The CoCp unit then hops along the π-cloud and the now vacant cyclobutadiene opens up to form two acetylenes.[59]

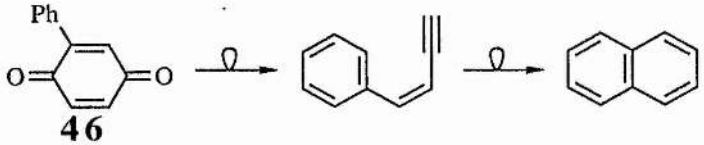


iii Cyclopentadienone and similar molecules

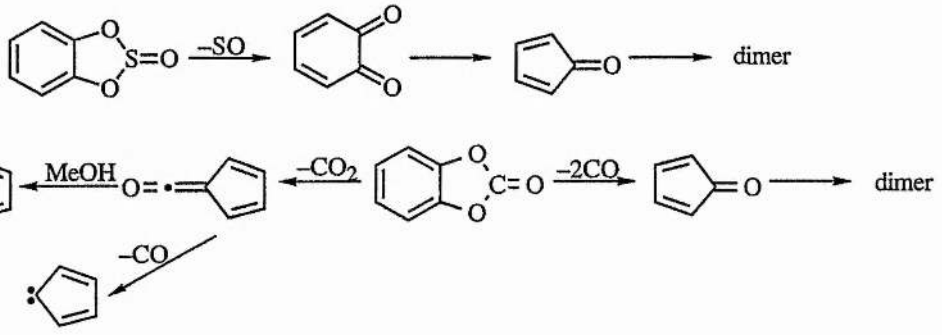
FVP of p-benzoquinone gives vinyl acetylene.[60] Dewar-cyclopentadienone has been postulated as an intermediate but no cyclopentadienone dimer was observed.



A synthetically useful process is decarbonylation of the quinone **46**. This presumably goes by the path shown and is thus able to lead to reliably labelled naphthalenes.[61]

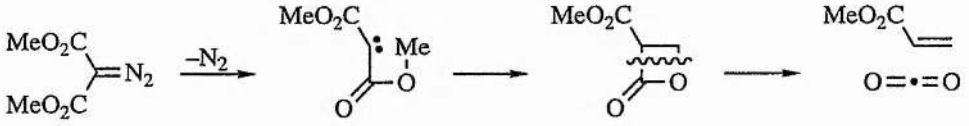


Similar decarbonylation processes are known for o-phenylene sulphite[18] and carbonate.[62] The sulphite reaction was discovered in an attempt to prepare cyclobutadiene.

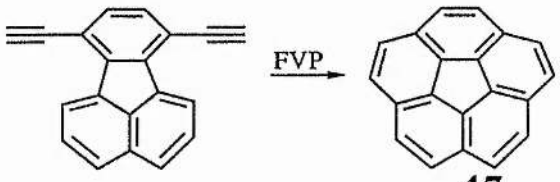


iv Carbenes

A major feature in FVP studies is the formation of carbenes. Some examples have been seen above but it is worthwhile considering some specific examples. A reaction that is pertinent to the present work is the intra-molecular insertion of bis(methoxycarbonyl)carbene. Extrusion of CO_2 from the resulting β-lactone then leads to the acrylate ester.[63]

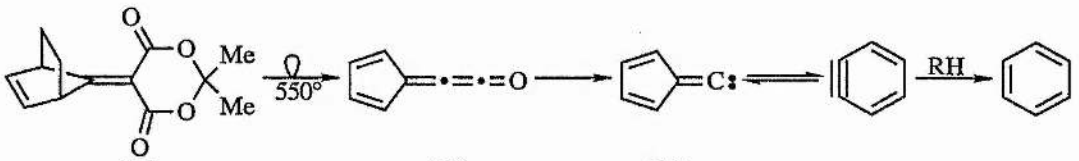


The most fascinating examples of carbene rearrangements are the reversible acetylene-carbene rearrangements (recently reviewed by Brown[64]) and the related "aryl carbene walk" and benzyne-cyclopentadi enylidene process. The former has recently been used by Scott to prepare corannulene **47**.[65]

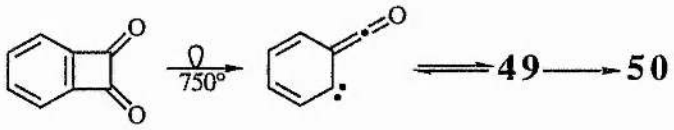


47

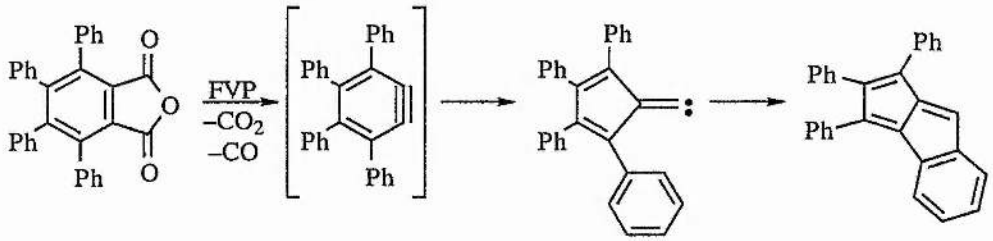
The transient existence of cyclopentadienylidene carbene **50** has been deduced from the formation of benzene and biphenylene by pyrolysis of norbornenylidene Meldrum's acid **48** over hydrogen-donating bitumen.[66] **50** had been postulated as an intermediate in the pyrolysis of benzocyclo butenedione.[67]



48 **49** **50**



Brown has performed some elegant hydrocarbon syntheses by fragmentation of substituted phthalic anhydrides. One such is triphenylbenzopentalene **51**.[68]

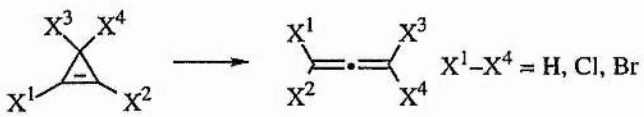


51

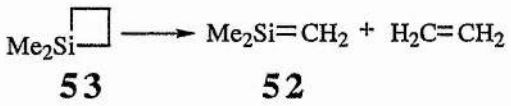
c Fragmentation of cyclic molecules

i Three and four-membered rings

Halocyclopropenes were observed to open cleanly on pyrolysis to the corresponding allenes.[69]

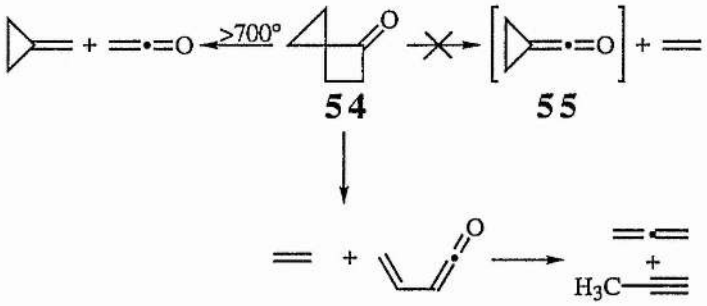


FVP comes into its own with the preparation of very unstable molecules in the gas phase. Thus silaethene **52** has been prepared and characterised by Barton and McIntosh by FVP of **53** and trapping the products at –196°C.[70]



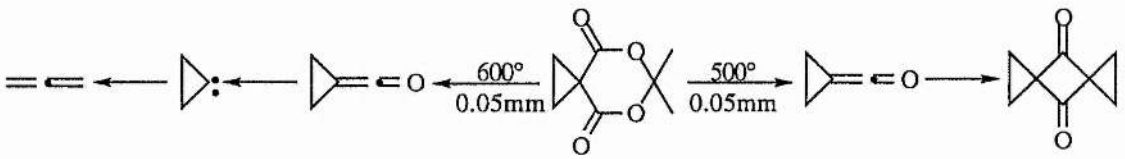
53 **52**

FVP of spiro [2,3] hexan-4-one **54** gives a complex mixture of products.[71]

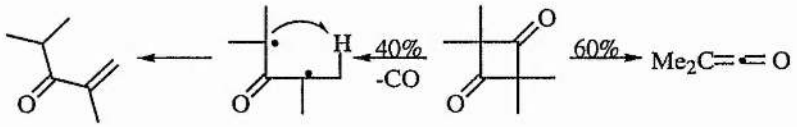


54 **55**

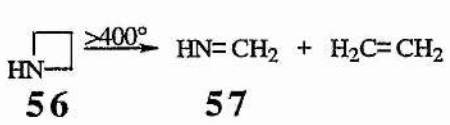
The desired product, carbonyl cyclopropane **55**, can be prepared by the pyrolysis of the appropriately substituted Meldrum's acid.[72]



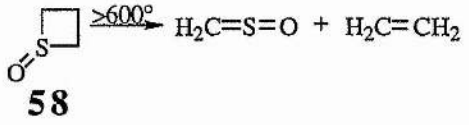
Pyrolytic preparation of alkyl ketenes was achieved by Brown and Baxter.[73]



FVP of azetidine **56** was used to produce methanimine **57**[74] and thietane and dithietane oxides **58** – **60**[75] have been pyrolysed to produce the relevant sulphines.



56 **57**



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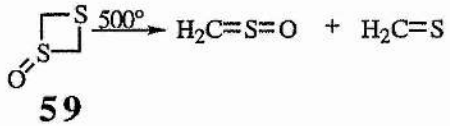
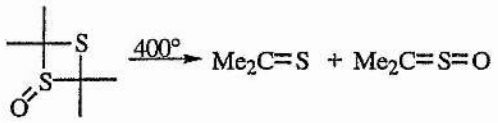
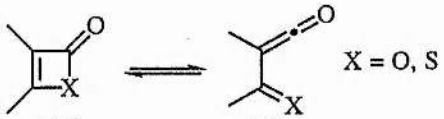


59



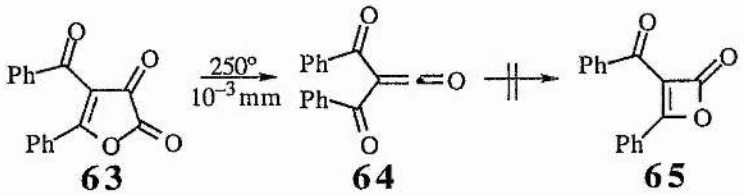
60

Wentrup has investigated the valence isomerism between **61** and **62**.[76]

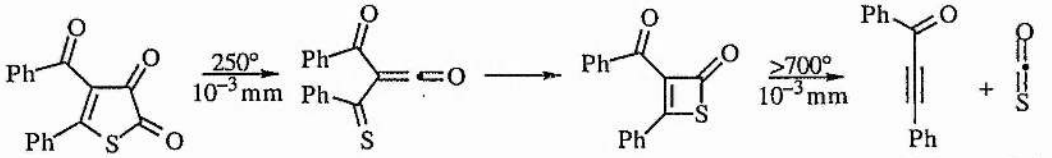


61 **62**

Pyrolysis of **63** causes decarbonylation to give **64**. No **65** was observed. However the corresponding sulphur species, **66**, gave both **67** (identified by IR) and **68** (identified by NMR). Pyrolysis of **66** above 700°C gave **69** and **70**.



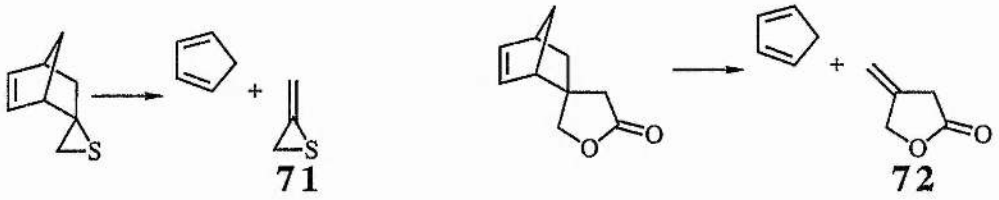
63 **64** **65**



66 **67** **68** **69** **70**

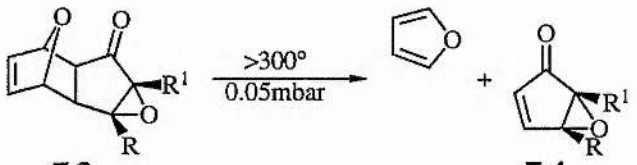
ii Retro Diels-Alder reactions

A number of interesting alkenes have been prepared by pyrolysis of substituted norbornenes. These include **71**[77] and **72**.[78]



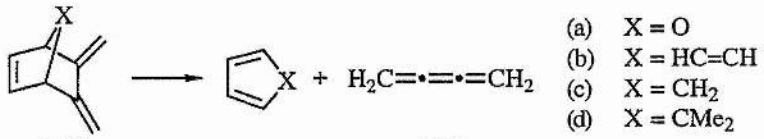
71 **72**

Pyrolysis of the related formal furan adducts **73** (obtained by alkaline peroxide oxidation of the corresponding enones) gave the relevant cyclopentadienone-epoxides **74**.[79]



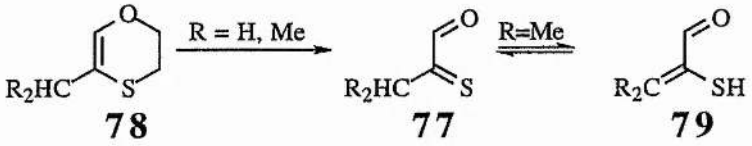
73 **74**

Roth and co-workers attempted to synthesise butatriene **75** from substituted norbornadienes and related compounds **76 a–d**. **76 a** and **b** gave the desired product in 80 and 100% yields respectively.[80]



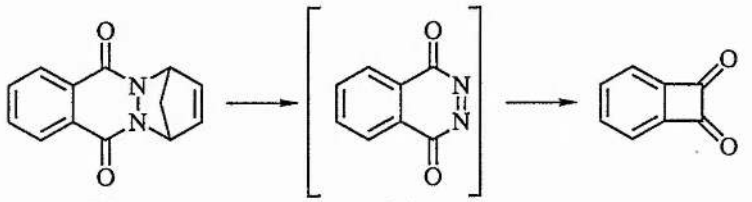
76 **75**

Bourdon, Ripoll and Vallée obtained **77** by FVP of **78**. The isopropyl compound mostly tautomerises to **79** while the parent compound stays as the ketone-thioketone tautomer.[81]



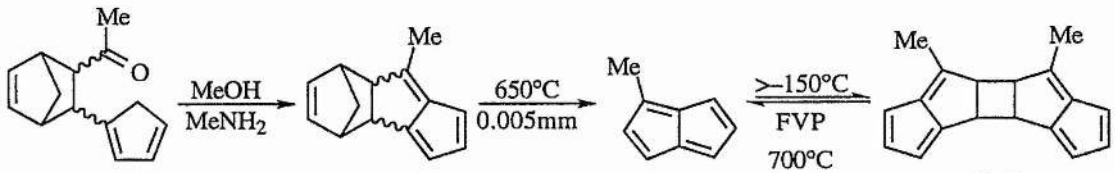
78 **77** **79**

Benzocyclobutanedione was prepared from **80** via the intermediate azocarbonyl compound **81**.[82]



80 **81**

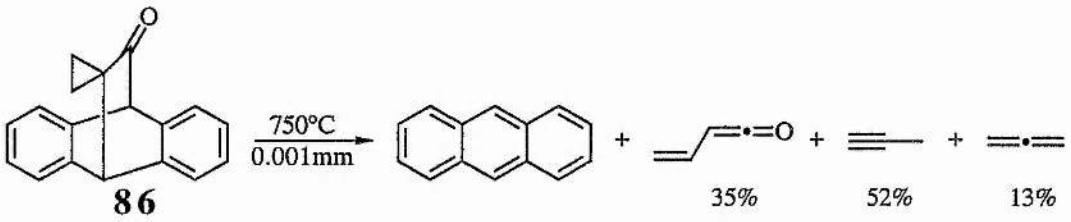
1-methylpentalene **82** was obtained by pyrolysing **83**, which was prepared by base-catalysed cyclisation of **84**. The dimer **85** can also be dissociated by FVP.[83]



84 **83** **82** **85**

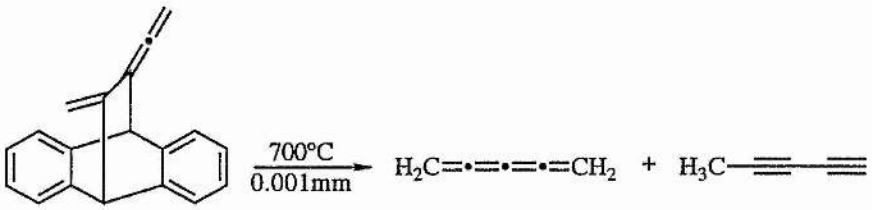
iii Elimination of aromatic residues

Another attempted route to carbonylcyclopropane was the pyrolytic cyclo-reversion of **86**. Again, the temperature needed to achieve the cycloreversion was too high and the products were vinyl ketene, methyl acetylene and allene.[84]

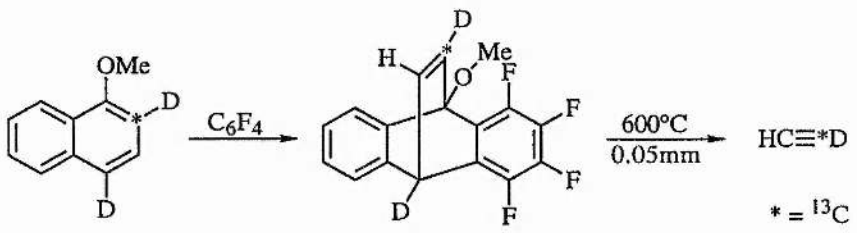


86

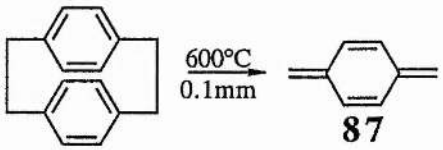
Rippoll and Thuillier were more succesful in their preparation of pentatetraene.[85] Pentatetraene is unstable, with a half-life of 20min in solution. Nevertheless, they recorded a 70% yield with the balance being pentadiyne.



Similarly, doubly labelled acetylene was produced by pyrolysis of the tetrafluorobenzyne-1-methoxynapthalene adduct.[86]

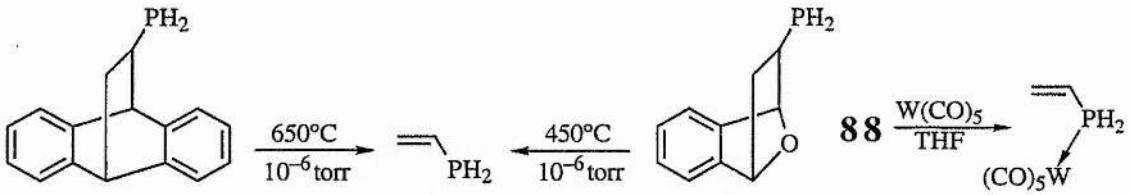


Pyrolysis of [2,2]paracyclophane gives p-xylylene **87**.[87] A strong coat of polymerised **87** ("Parylene") can be deposited directly on to subtrates from a gaseous stream of **87**.



87

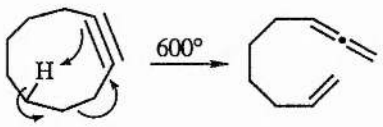
Ripoll and co-workers have obtained vinyl phosphine **88** by pyrolysis of the anthracene and isobenzofuran adducts **89** and **90**.[88] **88** was isolated as the tungsten adduct **91**.



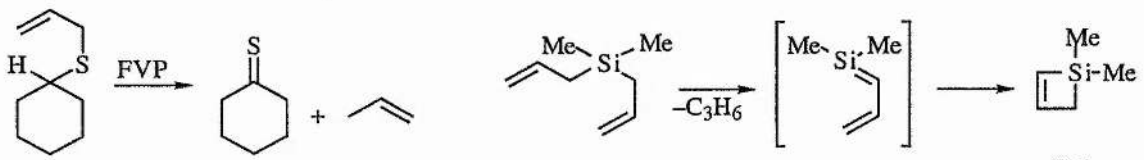
89 **88** **90** **91**

iv Retro-ene reactions

A 25% yield of (5-hexenyl)allene was obtained by pyrolysis of cyclononyne.[89]



Similarly, de Mayo has produced cyclohexanethione and other delicate thiocarbonyl compounds[90] by pyrolysis of allylic sulphides and Block and Reveille have prepared silacyclobutenes such as **92**.[91]

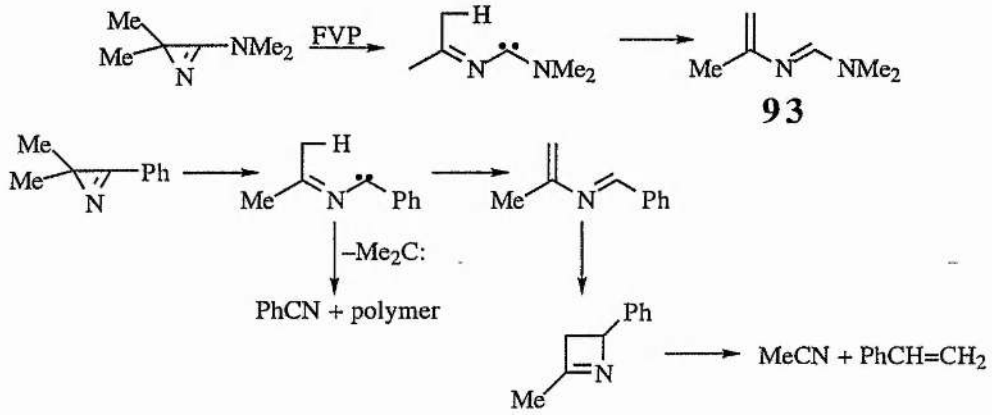


92

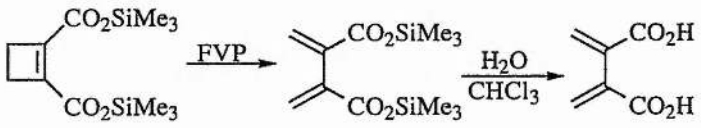
d Rearrangement without loss

Not all FVP reactions are destructive. Rearrangements that retain all the atoms include ring-opening and closure, Diels-Alder processes and ene reactions.

Ring opening of an aminoazirine gives the useful azadiene **93**[92] but fragmentation of the carbene from the corresponding arylazirine gives benzonitrile and a polymer and acetonitrile and styrene.[93]

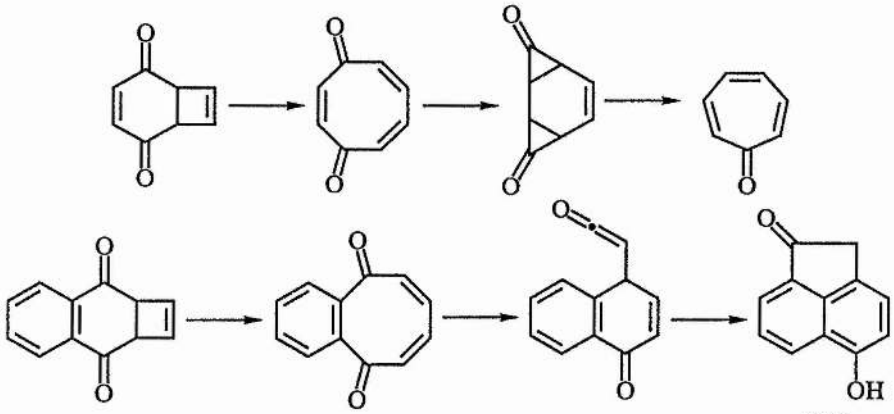


Butadiene-2,3-dicarboxylic acid **94** has been formed by FVP of the cyclobutene diester **95** followed by ester hydrolysis.[94]



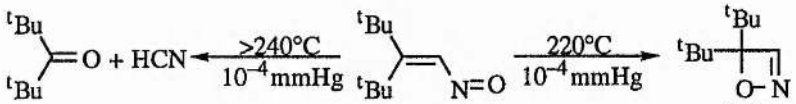
95 **94**

In a similar manner, ring opening reactions (which retain all the atoms), followed by decarbonylation or rearrangement have given tropone[95] and hydroxyacenaphthalenone **96**.[96]



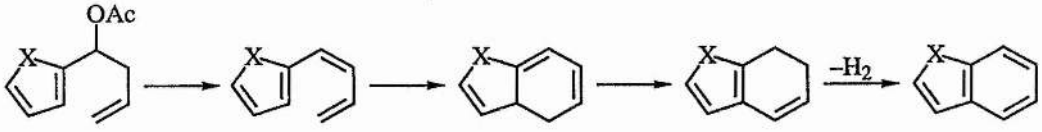
96

The following heterocyclic example of ring closure gives oxazete **97**. Pyrolysis at a slightly higher temperature leads to acyclic products.[97]

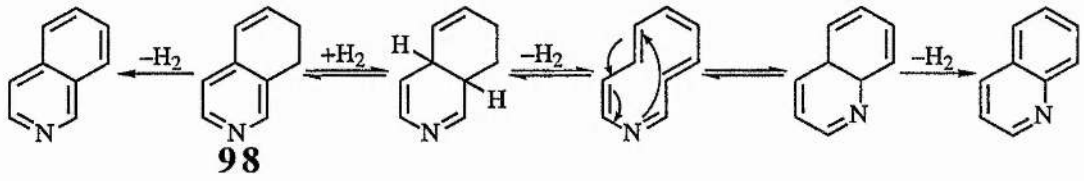


97

Formation of some relatively inaccessable heterocycles has been pioneered by Weber.[98] Arylbutadienes are formed by pyrolytic extrusion of acetic acid from 4-aryl-4-acetylbut-1-enes. Spontaneous rearrangement and loss of H_2 leads to the dihydrobicyclic and aromatised products.

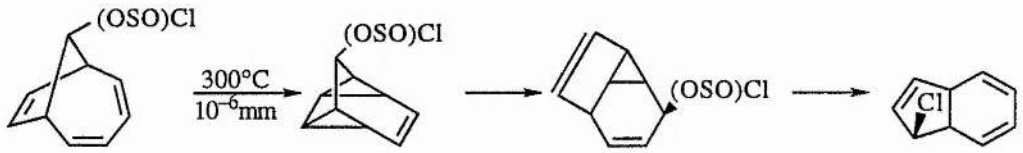


The pyrolysis of the 3-pyridyl species is interesting since the product mix includes a small amount of quinoline.[99] The rearrangment shown below, starting from the intermediate **98**, is postulated to account for this.

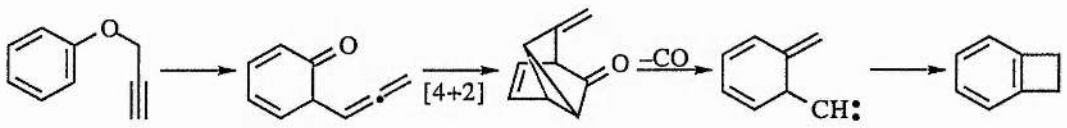


98

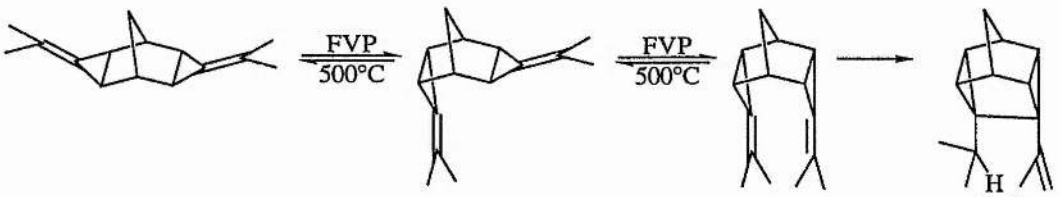
Examples of internal Diels-Alder reactions include Nomura's work on bicyclo[4.2.1]nona-trienes.[100]



Similarly, in Claisen rearrangement of allyl and propargyl aryl ethers, the resulting dienones can react intramolecularly.[101] The authors suggested that the minor product, 1,2-dihydrocyclobutene, was formed via a carbene.

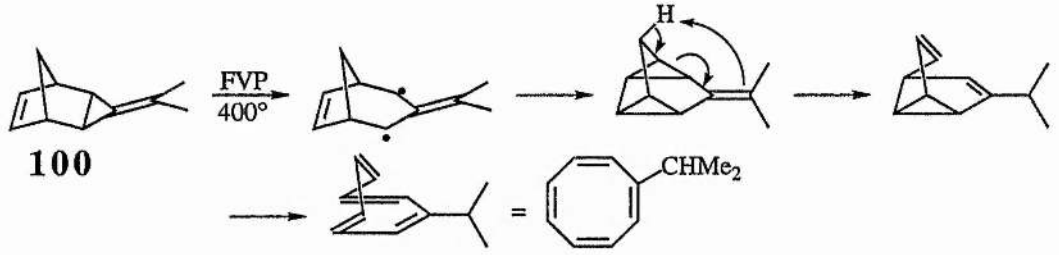


An elegant example of the ene reaction was reported by Bloch and Bortolussi.[102] The various isomers interconverted via diradicals but the endo, endo isomer underwent an ene reaction to give the compound **99**.



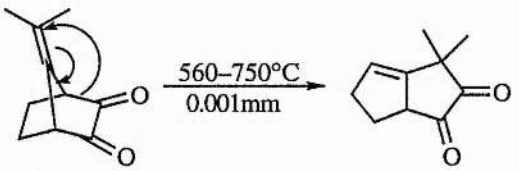
99

Another example of ring rearrangement occurs in the tricyclooctene **100**.[103]



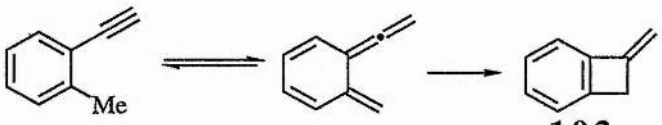
100

A case where an α-dicarbonyl compound does not decarbonylate is the pyrolysis of 7-isopropylidene-bicyclo[2.2.1]heptane-2,3-dione **101**.[104]



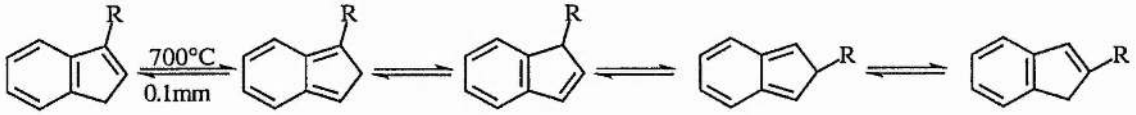
101

Temporary loss of aromaticity occurs in the formation of methylene-benzocyclobutene **102** from 2-ethynyltoluene.[105]

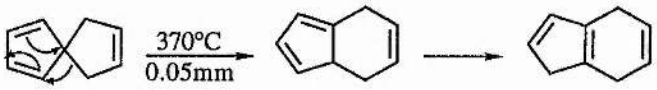


102

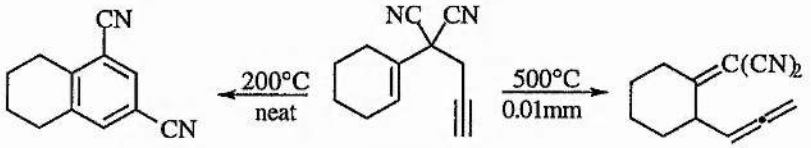
Brown and co-workers have investigated the interconversion of 2- and 3-substituted indenes and assume the intermediacy of isoindenes.[106]



Similarly, 1,5- shifts of spiro allyl groups have been noted.[107]

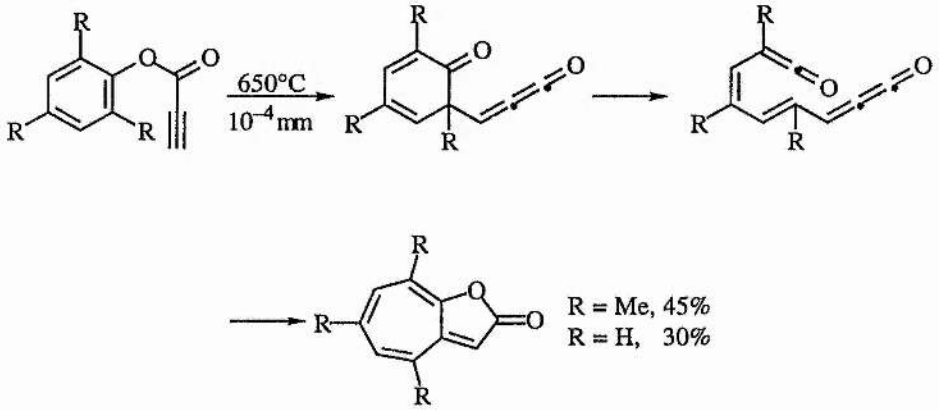


A Cope rearrangement that is best effected by FVP is the preparation of (2-dicyanomethyl)allenylcyclohexane from 4-(1-cyclohexenyl)-4,4-dicyanobut-1-yne **103**. Conventional pyrolysis of **103** gives only a mixture containing dicyanotetralin.[108]



103

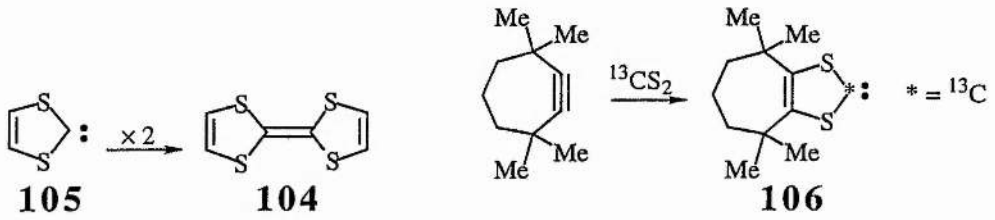
Trahanovsky and co-workers have studied the FVP of aryl propynoates and have come across an unexpected ring expansion.[109]



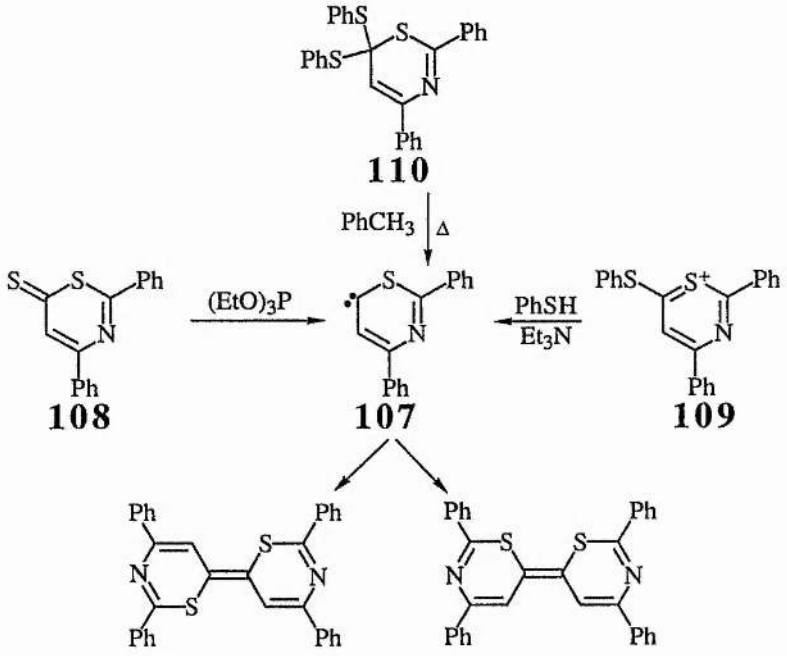
B Thio-, Sulphinyl- and Sulphonylcarbenes

1 Thiocarbenes

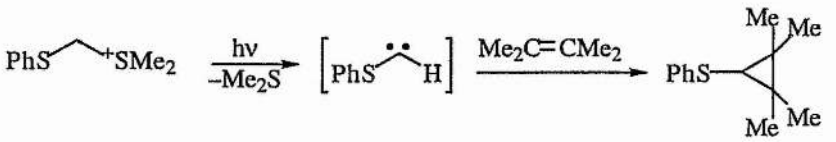
The most obvious desire for thiocarbenes is in the production of "organic metals" such as tetrathiafulvalene (TTF) **104**.[110] TTF is the formal dimer of **105** and the related species **106** has been detected at –50°C.[111]



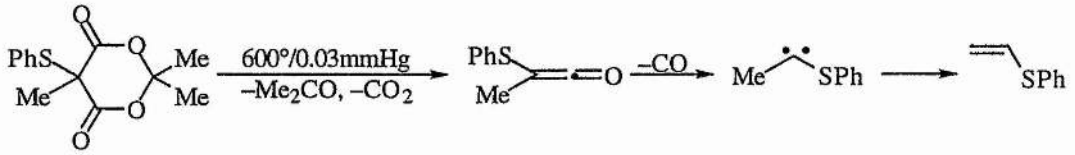
Production of thiocarbenes is best attempted under PTC conditions[112] but the carbene **107** has been produced by three methods. These start from thiono-thiazine **108** (60% yield of dimer), thiazinium salt **109** (80% yield of dimer) and bis(thio)thiazine **110** (95% yield of dimer).



Phenylthiocarbene **111** has been produced by photolysis of the sulphonium ylide **112**[113] and FVP of the Meldrum's acid derivative **113** gives the thiocarbene **114**. This then undergoes a 1,2-H shift to give vinyl sulphide **115**. (The ketene can be isolated as a stable product from FVP at lower temperatures.)[11]

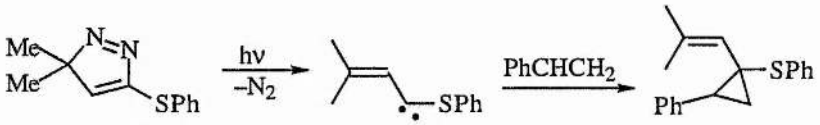


112 **111**



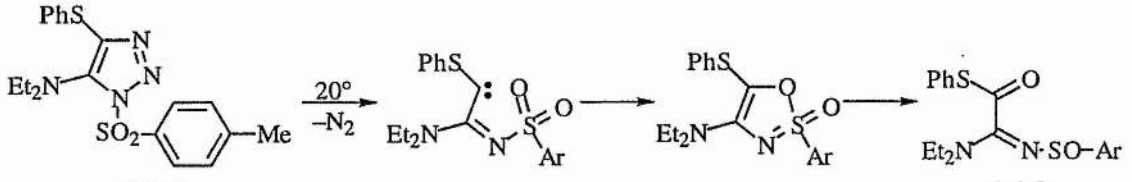
113 **114** **115**

Photolysis of the pyrazole **116** gives the carbene **117**. This is detected by trapping with styrene.[114]



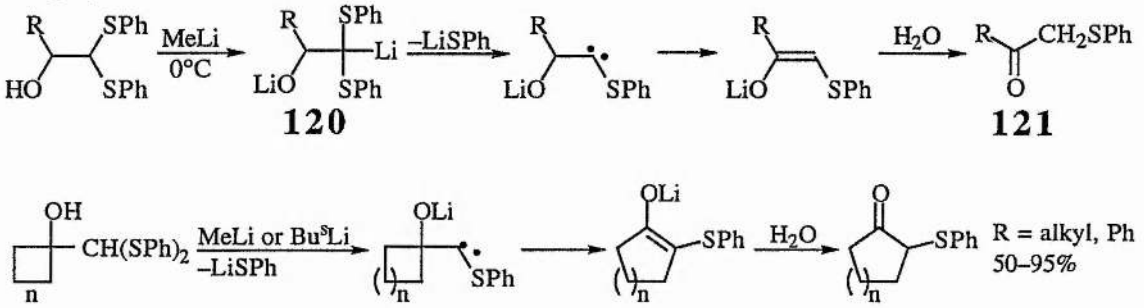
116 **117**

The triazole **118** also loses N_2 but the resulting carbene can extract oxygen from a neighbouring sulphonyl group to give the sulphinylimino-thioester **119**.[115]



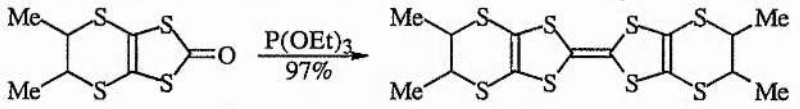
118 **119**

Bis-lithiated alcohols such as **120** can eliminate thiophenolate to give the ketones **121**.[116] This approach has been used to expand some small ring systems.[117]

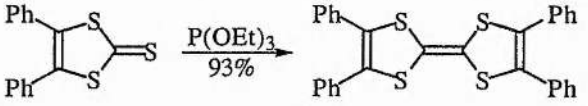


A large amount of work has gone into the production of bis(organothio) carbenes. As previously noted, their dimers, tetrathiafulvalenes were investgated as potential "organic metals" and some examples of the differing syntheses are given;

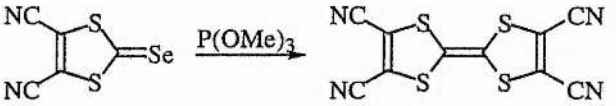
abstraction of O[118]:



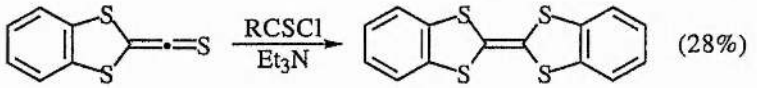
abstraction of S[119]:



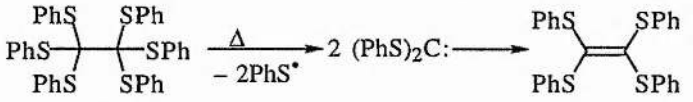
abstraction of Se[120]:



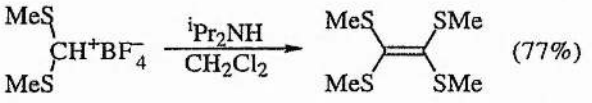
elimination of "C≡S"[121]:



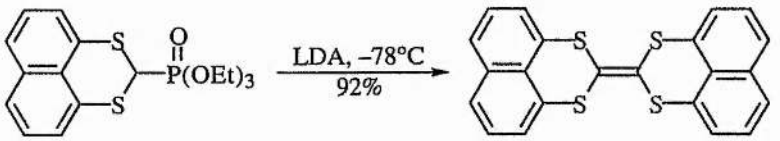
elimination of "RSSR"[122]:



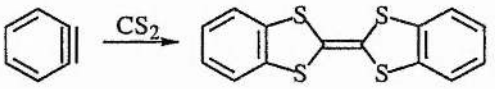
elimination of RH[123]:



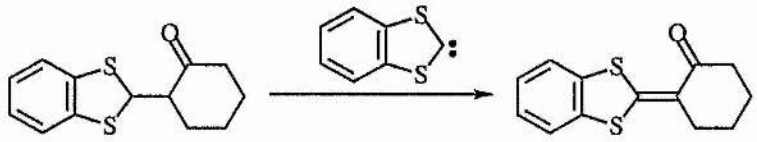
elimination of MX[124]:



CS_2 + "alkene/yne"[125]:

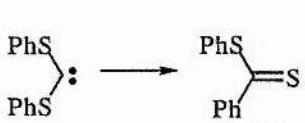


Carbenes have been used to dehydrogenate ketones such as **122**. [126]

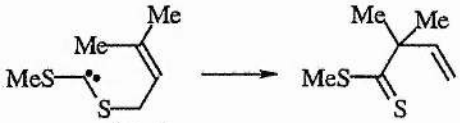


122

Bis(phenylthio)carbene undergoes a Wolff rearrangement to give the thioester **123**[125] and a nearly quantitative 2,3-sigmatropic rearrangment has been reported for **124**.[127]

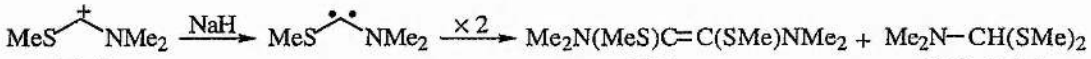


123



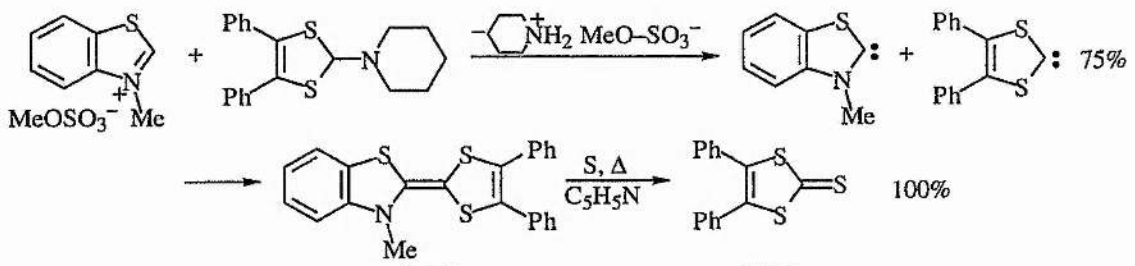
124

In the absence of trapping agents, **125** gives a mixture of the dimer and **126**.[128]



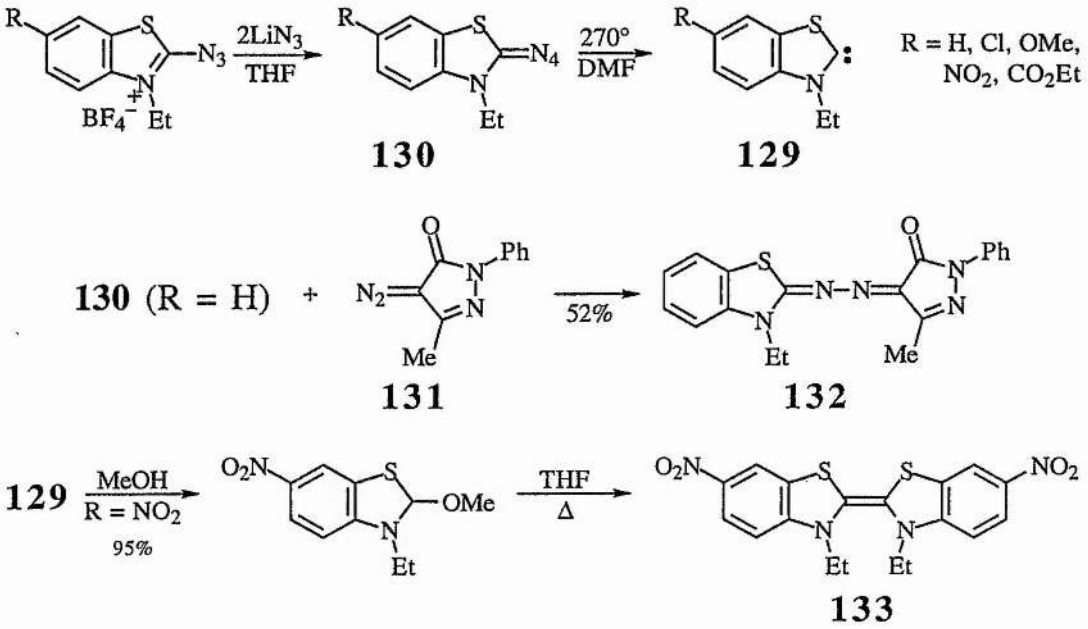
125 20% 52% **126**

A one-pot synthesis discovered by Buza and Krazuski involves forming two different nucleophilic carbenes in solution. Their addition product, **127**, is then reacted with sulphur to give the 2-thiono compound **128**.[129]



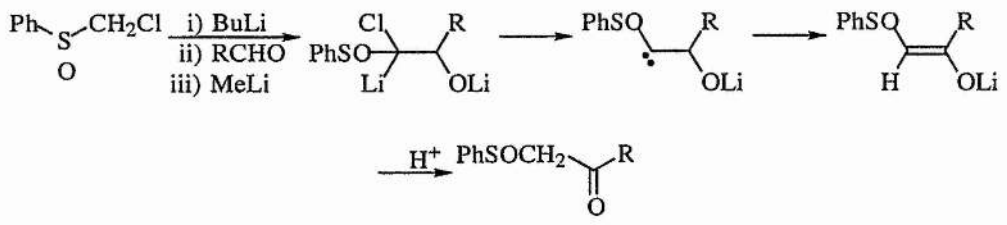
127 **128**

The carbenes **129** are formed by elimination of nitrogen from the azido-imines **130**. Diazo-coupling of the parent compound with **131** gives the azo-compound **132**. Addition of the nitro-variant of **129** to methanol followed by thermal re-elimination of methanol gives the dimer **133**.[130]

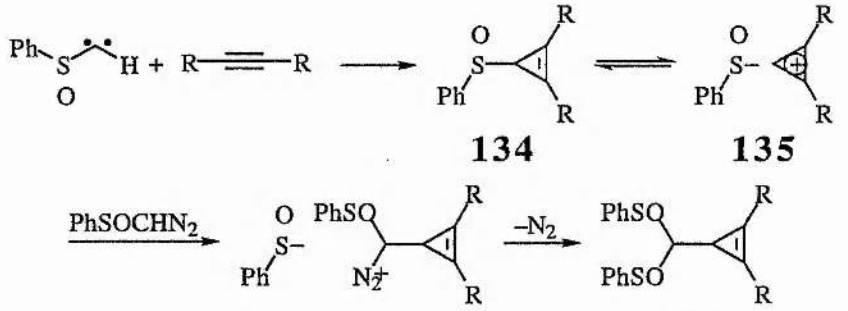


2 Sulphinylcarbenes

Thermolysis of phenylsulphinyldiazomethane in the presence of alkenes gives the corresponding cyclopropanes, predominantly the anti-isomer.[131] Sulphinyl carbenes are also implicated in a reaction of chloromethyl phenyl sulphoxide.[132]



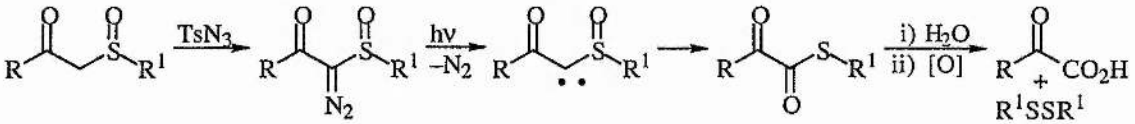
Phenylsulphinylcarbene reacts with alkynes in an unexpected manner. The expected adduct, **134**, ionises to **135**. Addition of **135** to a further mole of phenylsulphinyldiazomethane and loss of N_2 gives the 2:1 adduct, **136**.[133]



134 **135**

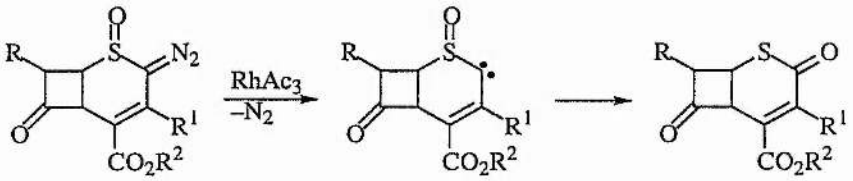
136

A reaction that is relevant to the present work is the formation of esters from carbonyl-substituted diazosulphinyl compounds.[134] Hydrolysis and oxidation of **137** gives the disulphides and keto-acids.

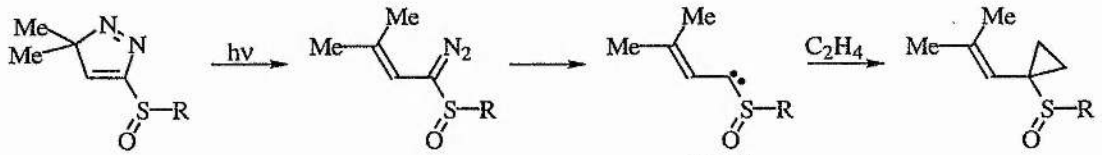


137

This sort of reaction has been used in the cephalosporin ring system.[135]

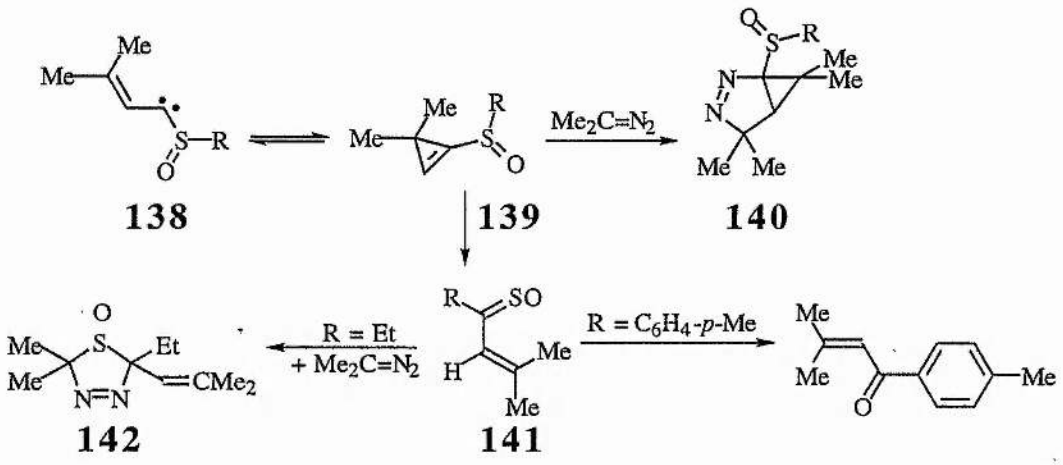


Addition of alkenylsulphinyl carbenes **138** to alkenes has been observed by Frank-Neumann and Lohmann.[136]

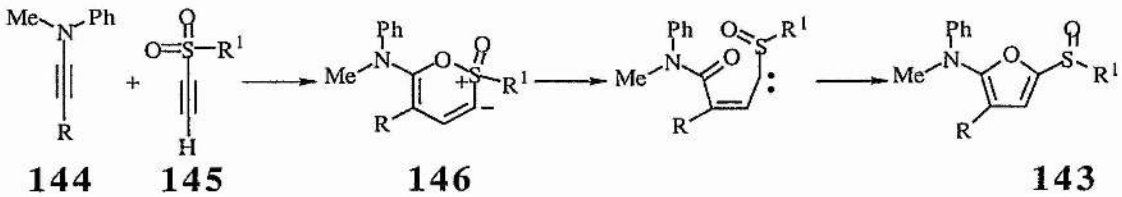


138

When no other alkene is available, **138** can react intramolecularly to give cyclopropane **139**. This may then add to excess 2-diazopropane (one of the components of the original diazene) to give the diazabicyclohexene **140** or rearrange to the sulphine **141**. Loss of sulphur gives the ketone and addition of a further molecule of 2-diazopropane to **141** gives the thiadiazoline-1-oxide **142**.[137]

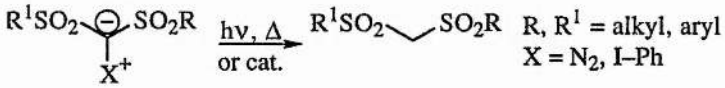


A synthesis of 2-amino-4-sulphinyl furans **143** was developed by Kossack and Himbert. They started from the yne-amine **144** and sulphonyl acetylene **145** which undergo cycloaddition to give **146**. This then undergoess an electrocyclic process to generate the sulphinyl carbene which goes on to form **143**.[138]

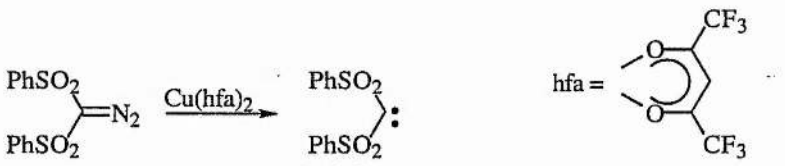


3 Sulphonyl carbenes

The formation of these carbenes is relatively simple. Photolysis and thermolysis of the relevant diazo species are the most widely used methods. However, bis-sulphonyl carbenes are easily produced by photolysis of the corresponding iodonium ylides.[139]

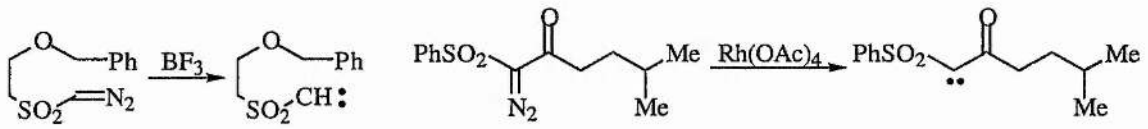


Thermolysis of bis(phenylsulphonyl) diazomethane in the presence of bis(hexafluoroacetoacetonyl)copper gives the carbenes **147**.[140]



147

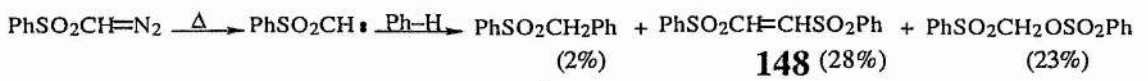
Loss of N_2 from diazomethane can also be catalysed by BF_3[141] or rhodium acetate, as shown below.[142]



The reactions of sulphonyl carbenes can be grouped as follows;

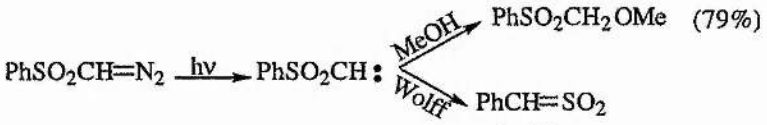
a dimerisation

This gives 1,2-sulphonylethenes, such as **148**.[143]

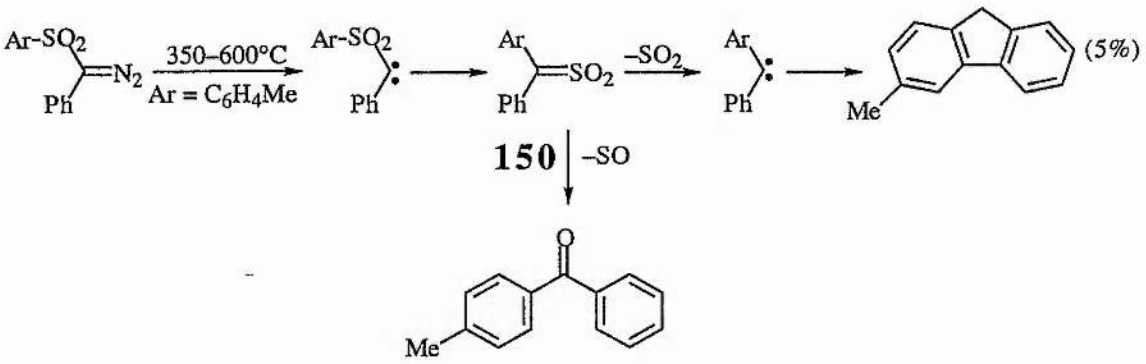


b Wolff-type rearrangements

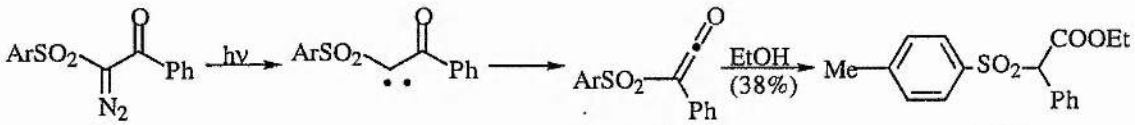
This leads to sulphenes, such as **149**[144] and **150**.[145] Trapping the original carbene with methanol gives the sulphone ether, while loss of SO from the sulphene **150** gives the ketone and loss of SO_2 gives the methylene carbene, which undergoes further reactions.



149



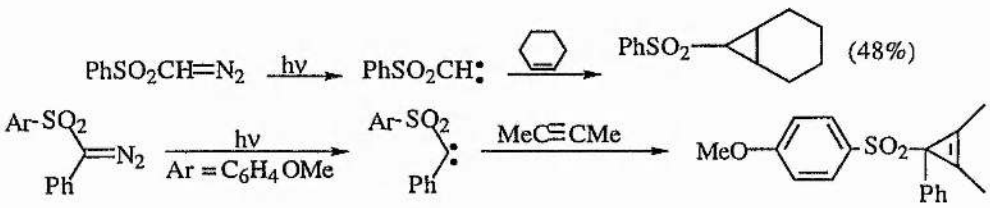
Wolff rearrangement, giving ketenes such as **151**, is the expected mode of reaction when the carbene centre is next to a carbonyl group. Trapping with ethanol gives the ester **152**.[146]



151 **152**

c addition to multiple bonds

Examples of trapping carbenes by addition to alkenes[144] and alkynes[147] have been reported, and typical examples are shown below.

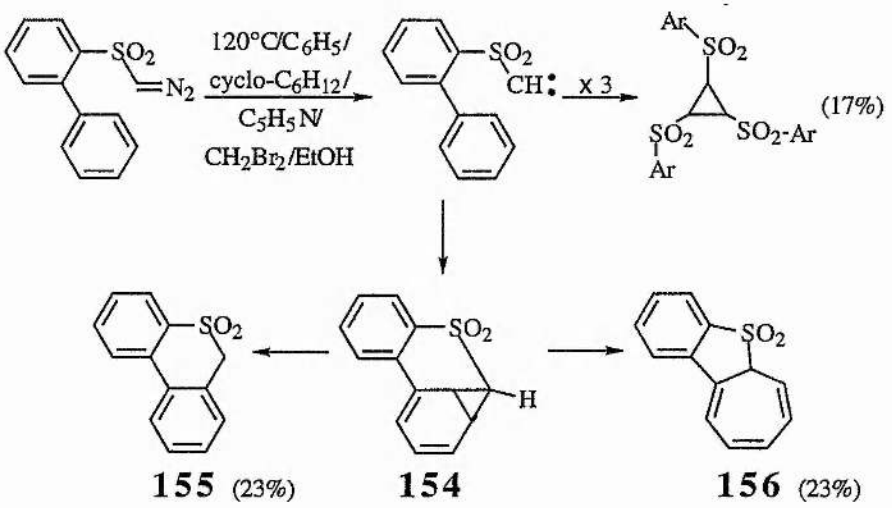


Under forcing conditions, α-metallated dichlorosulphones such as **153** eliminate metal halide to give carbenes which can be trapped by addition.[148]

153

d addition to aromatic rings

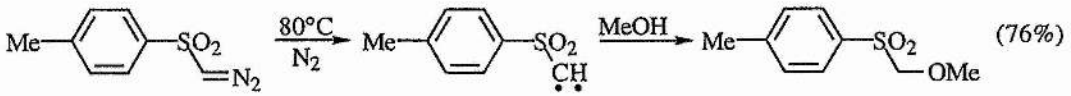
When a sulphonyl carbene is generated in proximity to an aromatic ring, addition to give bicyclic intermediate **154** is followed by ring opening to give both **155** and **156**. This example shows roughly equal amounts of each product and a smaller amount of the carbene trimer.[149]



155 (23%) **154** **156** (23%)

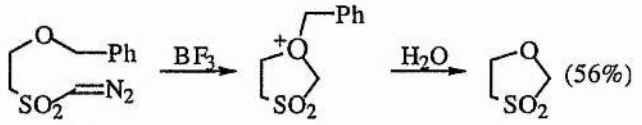
e insertion into OH

This reaction, giving ethers, is a "classical" method of detecting carbenes.[144]



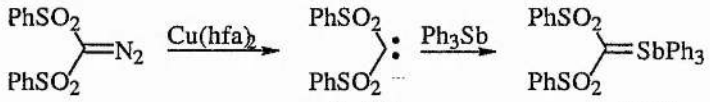
f reaction with nucleophiles

Intramolecular reaction of the carbene derived from **157** with the ether oxygen gives the oxonium species, **158**. Hydrolysis of **158**, leading to loss of benzyl cation, gives the sulphonyl ether, **159**.[143]



157 **158** **159**

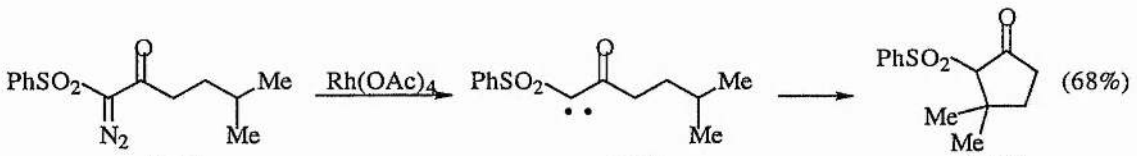
Bis-sulphonyl carbene **147** was reacted electrophilically with Ph_3Sb to give the ylide **160**.[142]



147 **160**

g insertion into C–H

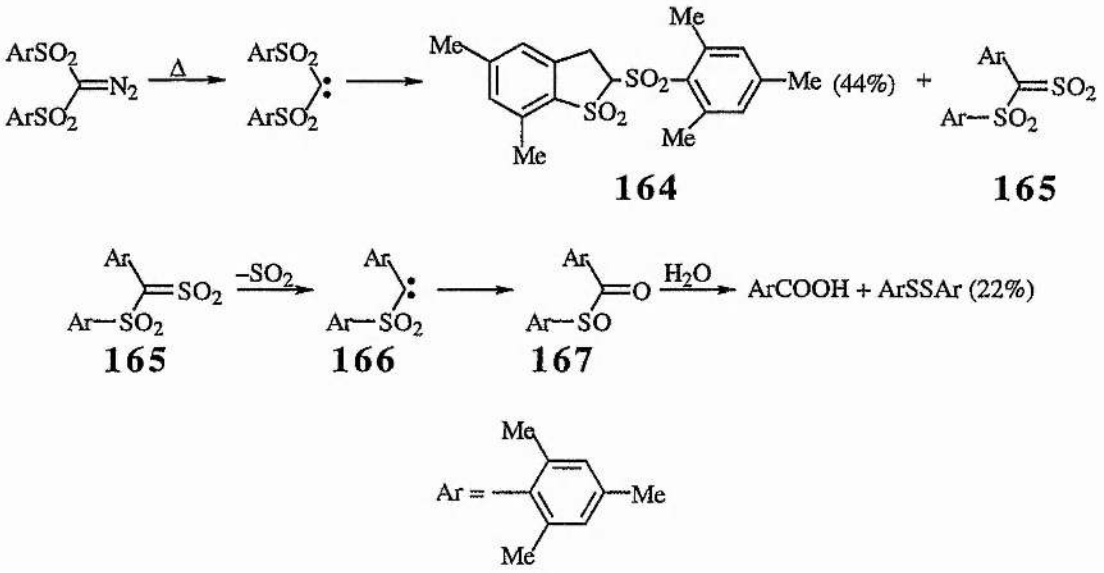
This is another classic carbene reaction. Rhodium acetate has been used to catalyse the elimination of N_2 from diazo compound **161** to give the carbene **162**. C–H insertion of the carbene then gives **163**.[144]



161 **162** **163**

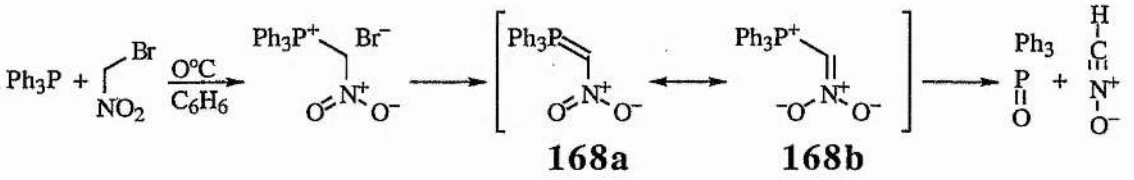
In the absence of any trapping agent, bis(mesitylsulphonyl)carbene can insert into one of the ortho-methyls to give **164**. This carbene also undergoes a Wolff rearrangment to give **165**, which loses SO_2 to generate

a second sulphonyl carbene **166**. This undergoes 1,2 oxygen transfer to give α-ketosulphoxide **167** which immediately hydrolyses to the corresponding benzoic acid and disulphide.[150]



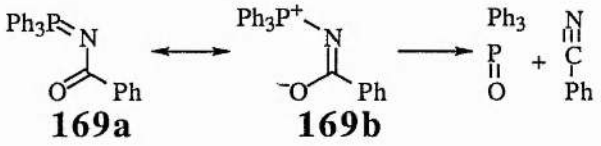
C Pyrolysis of phosphorus ylides

Modern interest in this area began in 1959 with Trippett and Walker's attempts to produce **168**.[151] An aqueous solution of nitromethyl triphenylphosphonium bromide immediately gave a quantitative precipitate of $Ph_3P{=}O$ on addition of alkali. Fulminate ion was detected in the solution and the authors hypothesised an internal Wittig reaction.

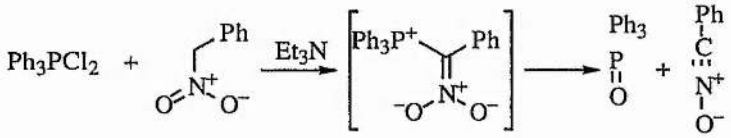


168a **168b**

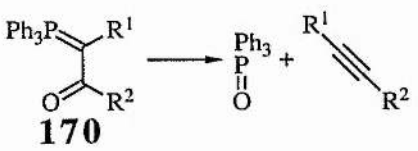
This was in line with Staudinger and Hauser's 1921 report that benzoyl iminotriphenylphosphorane **169** decomposed at 220°C to $Ph_3P{=}O$ and benzonitrile[152] and Horner and Oediger's 1958 finding that dichloro triphenylphosphorane reacted with phenylnitromethane to give benzonitrile oxide.[153]



169a **169b**



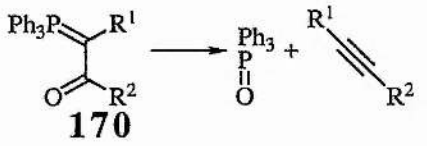
Following this lead, Trippett and Walker pyrolysed ylides **170**. They found that **170c** gave diphenylethyne quantitatively but **170a** and **b** gave no alkyne.



170

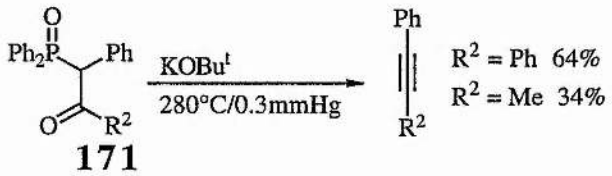
a $R^1 = H$, $R^2 = OMe$; no alkyne
b $R^1 = H$, $R^2 = OEt$; no alkyne
c $R^1 = Ph$, $R^2 = Ph$; ~100%

Trippett extended his work to other ylides in the hope of generalising production of alkynes.[154] He found that ylides **170d-f** pyrolysed at 280°C to give alkynes in 60–90% yield. Similarly, the phosphine oxides **171** gave alkynes in moderate yield but the phosphonate **172** gave only a trace of alkyne.



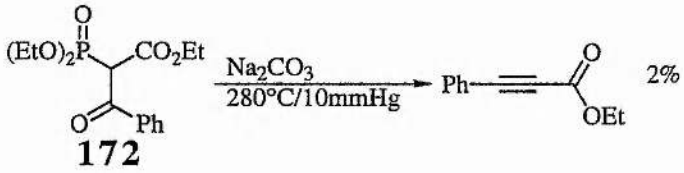
170

d $R^1 = CO_2Et$, R^2 = alkyl, 1-alkenyl
e R^1 = Ph, R^2 = Me
f R^1 = CN, $R^2 = {}^nPr$, Ph



171

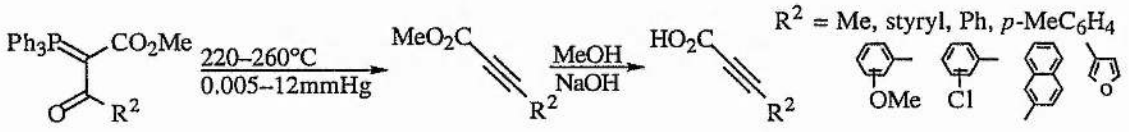
R^2 = Ph 64%
R^2 = Me 34%



172

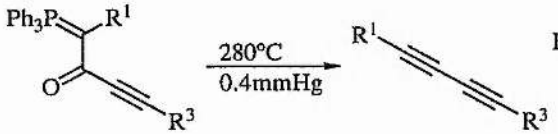
2%

Around the same time, Märkl prepared a range of acetylenic acids in 65–83% yield by vacuum pyrolysing the corresponding phosphoranes and hydrolysing the resulting esters.[155]



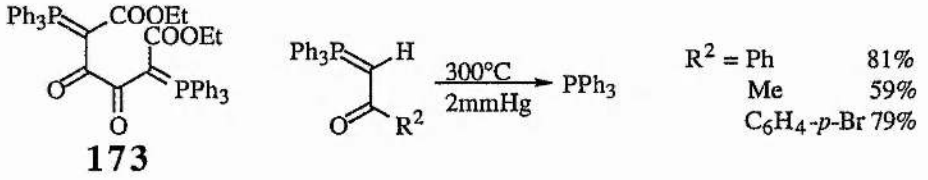
R^2 = Me, styryl, Ph, *p*-MeC_6H_4

The next paper by Trippett saw the extension of this work to the production of diacetylenes, albeit in less satisfactory yield.[156]

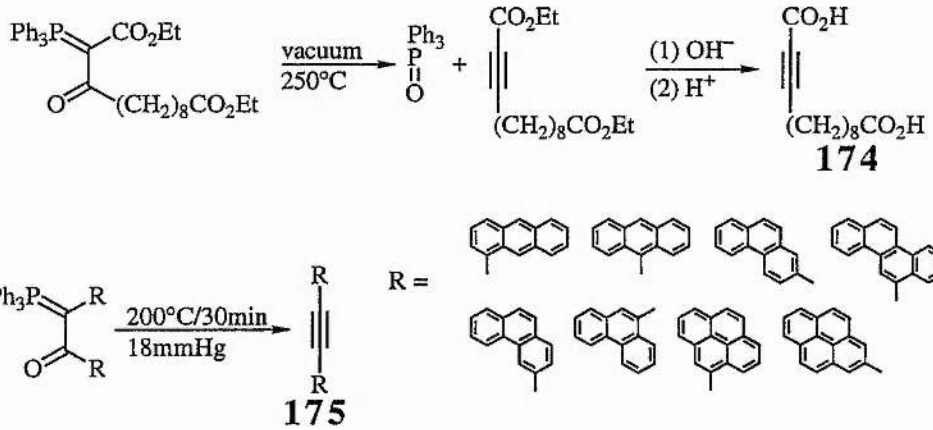


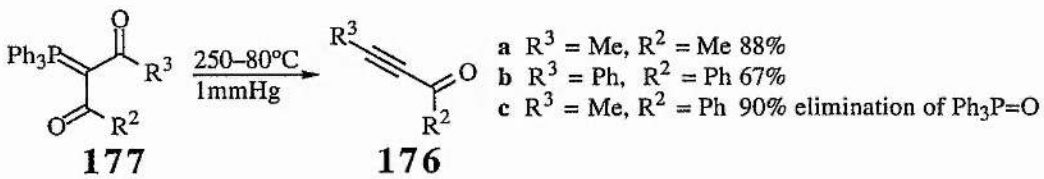
R^3 = Ph, R^1 = CN	30%	$R^3 = Bu^n$, R^1 = CN	23%
CO_2Et	9%	CO_2Et	16%
Ph	24%	Ph	23%

He also found that **173** did not give any diacetylene on pyrolysis; neither did phosphoranes **170** with R^1 = H. Instead, the acyl phosphoranes eliminated Ph_3P which distilled over, leaving an intractable black residue.



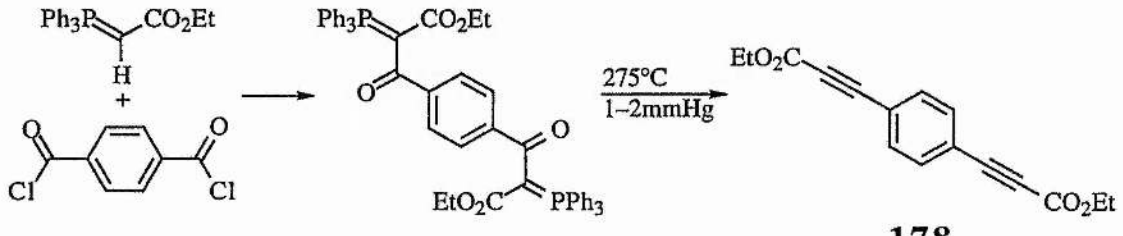
Later, the pyrolysis was used to prepare a diacid **174**[157], some diarylacetylenes **175**[158] and acetylenic ketones **176**.[159] For the non-symmetrical phosphorane **177c**, the product was a mixture of 1-phenylbut-1-yn-3-none and 4-phenylbut-3-yn-2-one (major component).



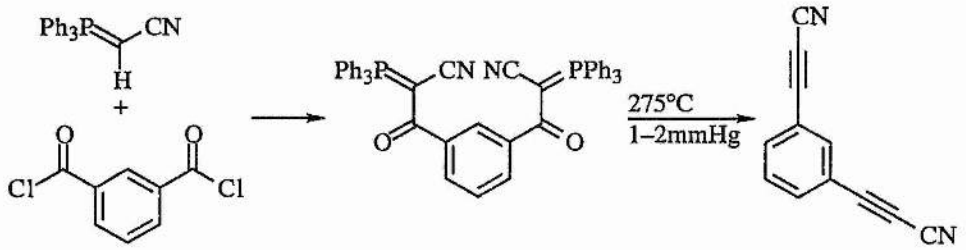


The bis-alkynyl benzenes **178** and **179** were produced by Henry as part of his research into polymer-forming Diels-Alder reactions. His

attempts to produce the 1,3- equivalent of **178** and bis(alkynyl)hexafluoro propanes were unsuccessful.[160]

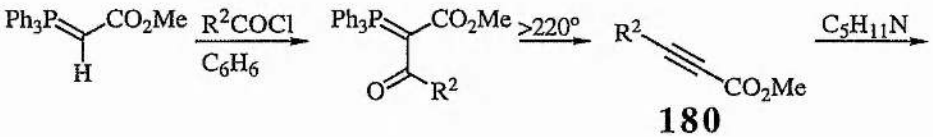


178

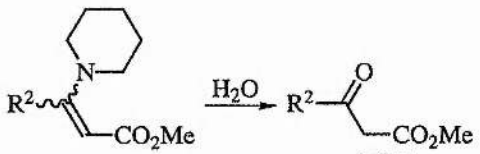


179

Bestmann and Geismann used the readily available methoxycarbonyl methylenetriphenylphosphorane and various acid chlorides to produce acetylenic esters **180**.[161] Reaction of these esters with piperidine, followed by hydrolysis, was used to prepare the β-ketoesters **181**.



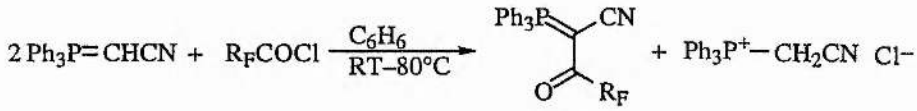
180



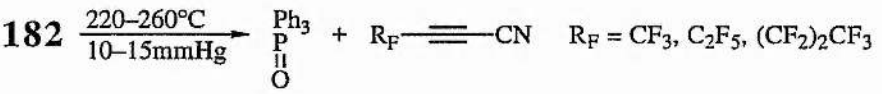
181

A chinese research group has had a long-standing interest in fluorine-containing organics as potential dipolarophiles and dienophiles. Pyrolysis

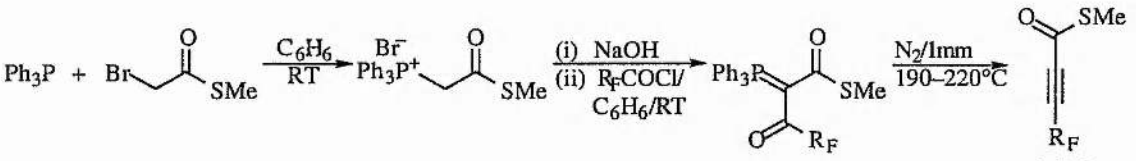
of cyano-stabilised ylides **182** gave perfluorinated acetylenic nitriles.[162] The ylides were synthesised from cyanomethylenetriphenylphosphorane and perfluoroalkyl chlorides and the pyrolyses were performed under nitrogen.



182



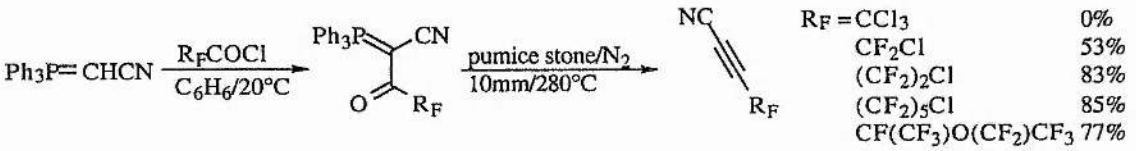
The range of acetylenes was extended in 1986 to include acetylenic thioesters **183**. The ylides were prepared in 72–90% overall yield and pyrolysed under nitrogen to give the alkynes in 69–80% overall yield.[163]



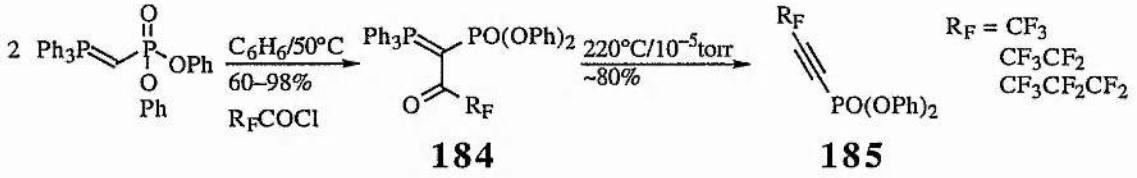
183

$R_F = C_2F_5$, $^nC_3F_7$, $^nC_7F_{15}$, $(CF_2)_3Cl$, $(CF_2)_5Cl$, $CF(CF_3)O(CF_2)_2CF_3$

The next paper reported on chlorofluoroylides and their pyrolysis to give acetylenic nitriles. The ylides were prepared in 77–90% yield and pyrolysed from powdered pumice stone to give the alkynes in 53–85% yield, except where R was trichloromethyl. No alkyne was obtained in this case.[164]

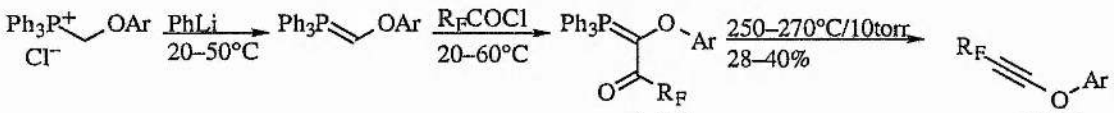


The work on perfluoro compounds was continued with the pyrolysis of perfluoroacyl(diphenylphosphonylmethylene)triphenylphosphoranes **184** to provide perfluoroalkynylphosphonates **185**.[165]



184 **185**

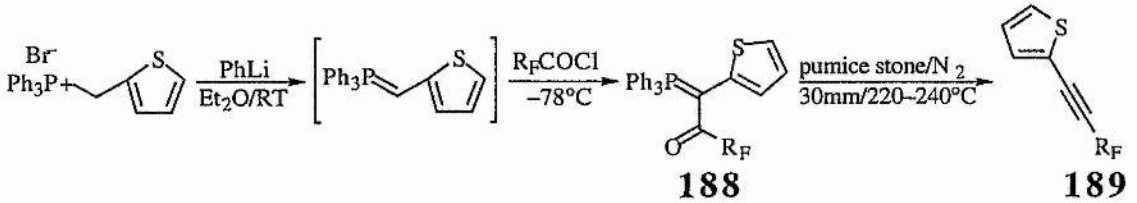
A publication in 1987 reported the production of aryloxy perfluoroalkynes **186**.[166] Pyrolysis of ylides **187**, which were obtained by the action of strong base on the phosphonium salts, at 250–270°C from powdered pumice stone gave **186** in 30–40% yield.



187 **186**

Ar = Ph, *p*-ClC_6H_4; R_F = C_2F_5, $CF_3CF_2CF_2$, $CF_3CF_2CF_2OCF(CF_3)_2$

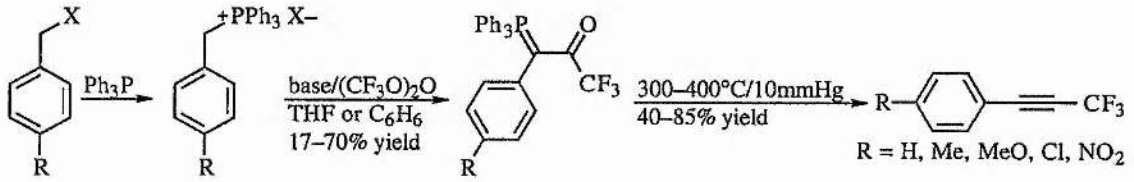
The thienyl ylides **188** were produced in 1988. The corresponding acetylenes **189** were obtained in good yield by pyrolysis from powdered pumice stone.[167]



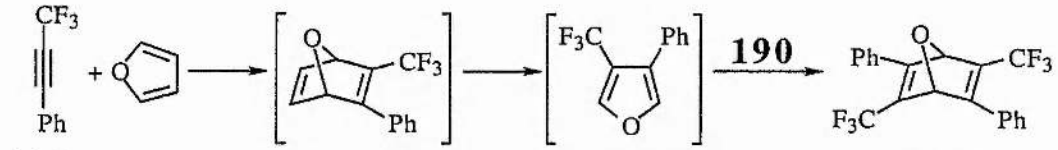
188 **189**

R_F = CF_3, C_2F_5, $^nC_3F_7$, $(CF_2)_3Cl$, $CF(CF_3)O(CF_2)_2CF_3$

In 1982, Kobayashi and co-workers synthesised aryl-trifluoromethyl alkynes, starting from phosphonium salts and trifluoracetic anhydride.[168]

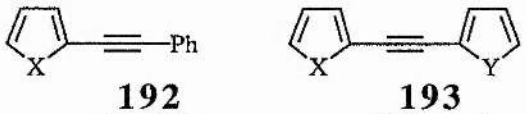


The authors also noted that 1-phenyl-3,3,3-trifluoropropyne **190** was less reactive than hexafluorobut-2-yne in Diels-Alder reactions. It gave a complex mixture of products, including **191**, at "elevated temperature" and no reaction at RT.

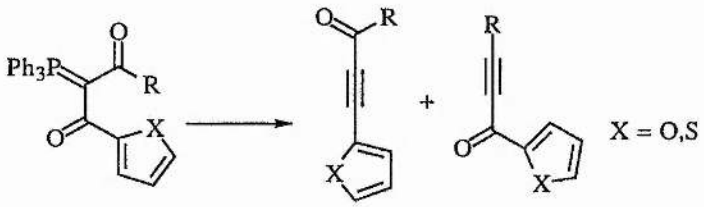


190 **191**

Recently, the 1-phenyl-2-heteroarylethynes **192** were produced in ~90% yield by pyrolysis of the corresponding ylides at 300°C in the presence of silica. Similar procedures gave the diheteroarylethynes **193** and mixtures of the isomeric aroylethynes **194** and **195**.[169]

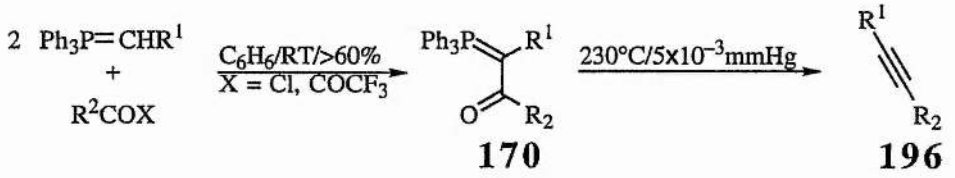


192 X = O,S **193** X,Y = O,S



194 **195**

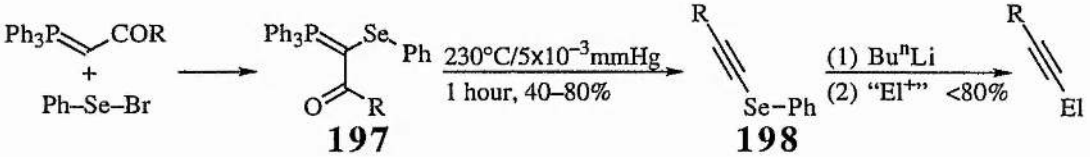
In 1984, Petragnani extended the range of alkynes accessible from ylides still further.[170] All successful pyrolyses of ylides **170** so far had had an electron-withdrawing group at R^1. Alkylthio groups, –SR, are known to stabilise carbanions and so the thioacetylenes **196** were prepared in yields of 40% for R^2 = alkyl and 70–80% for R^2 = CF_3, aryl.



170 **196**

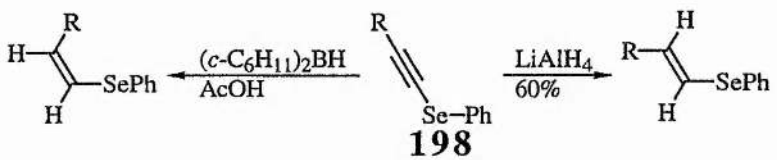
$R^1 = SR^3$; R^2 = Ph, *p*-MeC_6H_4, Me, ^tBu, $^nC_5H_{11}$; R^3 = Me, Ph

Petragnani also published a method of producing acetylenes which were otherwise inaccessible from phosphoranes **170** (i.e. where R^1 = alkyl).[171] This involved transylidation of acylphosphoranes with arylseleno bromides, followed by pyrolysis of the resulting α-acyl-α-(arylseleno) methylenetriphenylphosphoranes **197** to give arylselenoacetylenes **198**. Lithiation, followed by addition of electrophiles, gave the desired alkynes. Alternatively, borane reduction of **198** gave the Z-arylselenoalkenes and $LiAlH_4$ reduction gave the E-arylselenoalkenes



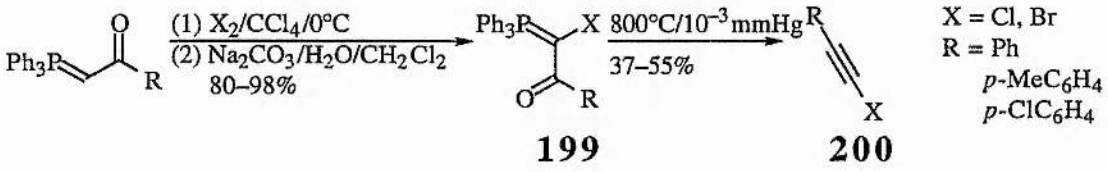
197 **198**

R = Ph, *p*-MeC_6H_4, *p*-Me-OC_6H_4, *p*-Cl-C_6H_4, *p*-O_2N-C_6H_4, CF_3, 2-thienyl
"El^+" = H_2O, MeI, MeCOMe, Ac



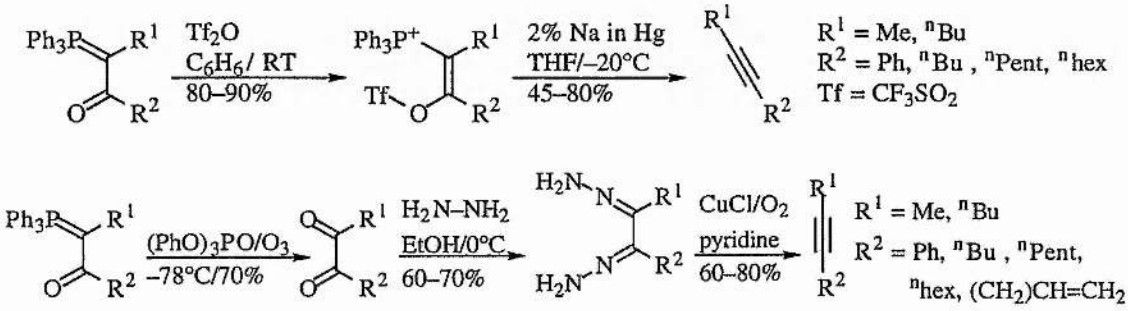
198

Braga and Comassetto extended their work on hetero-substituted ylides to α-halophosphoranes **199**.[172] These were produced by reacting the acylphosphoranes with halogen in CCl_4, followed by sodium carbonate work-up. FVP at 800°C gave the haloalkynes **200** in moderate yield.

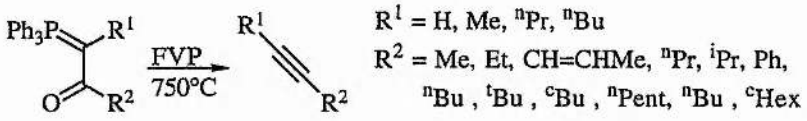


199 **200**

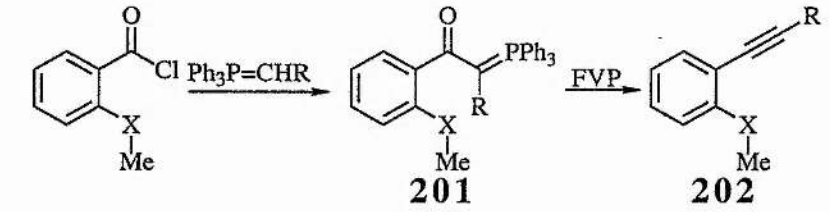
A long-standing limit to this "ylide ⟶ alkyne" route was that terminal and aliphatic alkynes were not directly accessible from phosphoranes. Bestmann had described two indirect routes to aliphatic alkynes. One involved O-triflation of the ylide followed by sodium amalgam reduction.[173] The other used the adduct of triphenylphosphite and ozone to give the diketone. This was then reacted with hydrazine to give the dihydrazone. Copper (I) chloride catalysed oxidation gave the acetylene.[174]

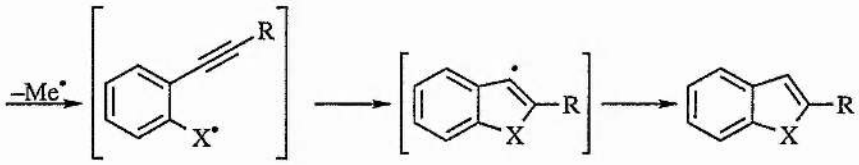


In earlier work in this laboratory, it was found that FVP of the ylides **170** gave aliphatic alkynes cleanly, separate from the phosphine oxide and in 60–85% yield.[175]



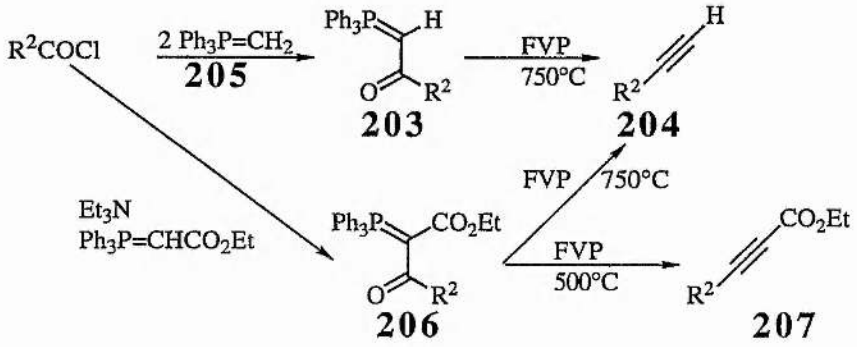
This work was extended to the ylides **201** in 1987.[176] These ylides were seen as potential precursors to benzofurans and benzothiophenes since aromatic methoxy groups were known to be labile.[177] In the event, FVP at 700°C gave the acetylenes **202** in good yield.



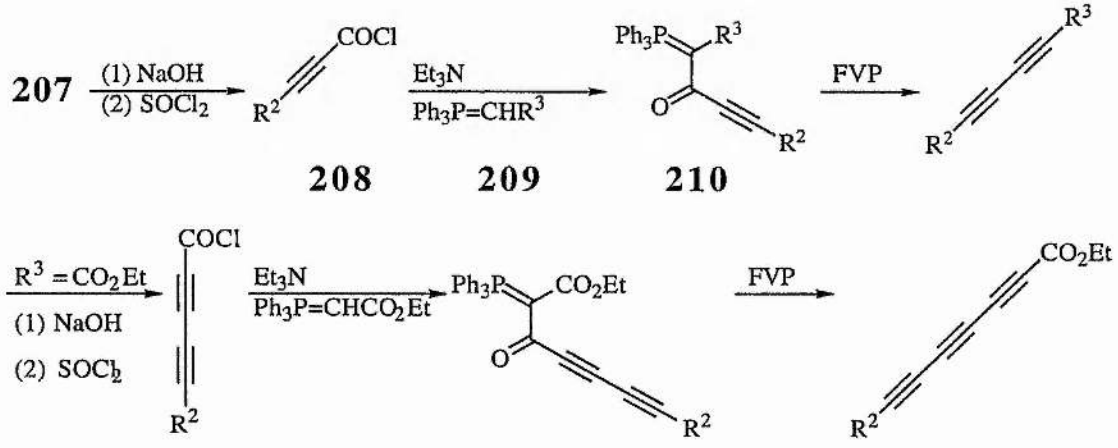


FVP at 850°C gave the cyclised products; 2-phenylbenzofuran was produced in 80% yield and 2-phenylbenzothiophene in 53% yield. However, for the species with aliphatic R, the cyclised products were obtained in moderate yield but R was found to have fragmented to methyl, ethyl and vinyl. In the case where R was Me, a radical mechanism, based on ideas from Barton[178] was proposed to explain the incorporation the methoxy carbon atom in the final product.

The route to terminal alkynes was improved in 1990.[179] Instead of pyrolysing **203** to get the alkyne **204**, so wasting one mole of starting material **205**, pyrolysis of the ethoxycarbonyl ylide **206** gave the ester **207** at 500°C and gave the terminal alkyne **204** directly upon simply raising the pyrolysis temperature to 750°C.

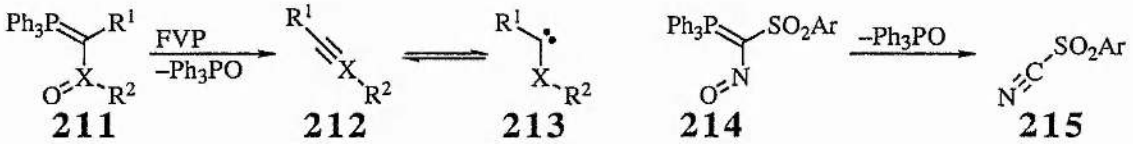


Hydrolysis of the acetylenic esters **207**, reaction with thionyl chloride and use of the resulting acid chloride **208** to acylate ylide **209** gave ylides **210**. FVP of these gave the di-ynes in moderate yield and the sequence was continued to the tri-yne in one case.[180]



D Programme of Research

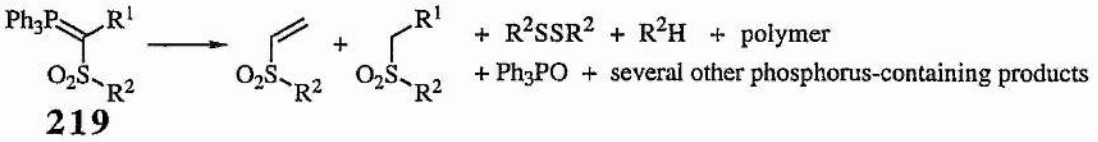
As mentioned in the previous section, the thermal extrusion of triphenylphosphine oxide from β-oxo phosphorus ylides to give alkynes has proved to be of considerable value over the last thirty years. The thermal behaviour of ylides **211** with other oxygen-containing functional groups in the α-position has been much less investigated. As already mentioned, α-nitro ylides were found to give nitrile oxides in two cases[151, 153] and α-nitroso ylides **214** were found to lose triphenylphosphine oxide spontaneously at –40°C to give sulphonyl cyanides **215**.[181] As shown, the product formed by loss of triphenylphosphine oxide from **211** can be regarded as either the triply-bonded form **212** or the heterocarbene **213**. While the latter would be the more normal representation of the species involved, the recent preparation of compounds such as **216**[182], **217**[183] and **218**[184] suggested that for suitable groups R^1, R^2 and X some genuine multiple bond character might be observed.



RC≡SF$_3$ **216** RS≡N **217** RS(=O)≡N **218**

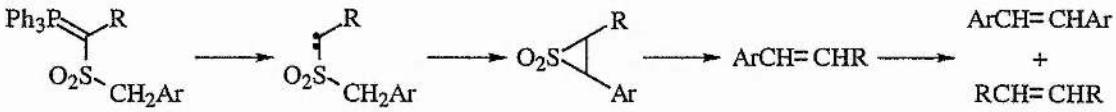
With this in mind, an earlier investigation in this laboratory[185] was concerned with the pyrolysis of sulphonyl ylides. The first system to be investigated was the arenesulphonyl ylides **219**. FVP of **219** at 500–750°C

a complex mixture of products, of which the major component was an intractable polymer.



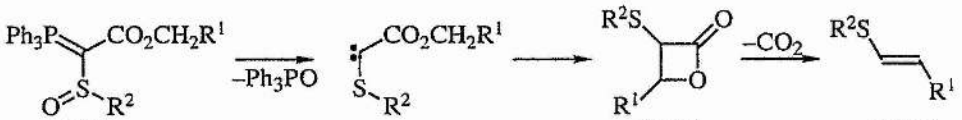
219

More interesting results were obtained for the arylmethanesulphonyl ylides **220**. They showed loss of triphenylphosphine to give products derived from the carbenes **221**.[186]



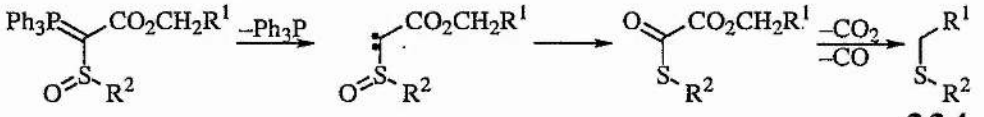
220 **221**

Attention then turned to the sulphinyl ylides **222**. FVP of these at 600° gave, for aromatic R^2, triphenylphosphine oxide (with a small amount of triphenylphosphine) and a mixture of the vinyl sulphide **223** (major component) and sulphide **224**, together with an unidentified carbonyl compound. For aliphatic R^2, the vinyl sulphide was the major product and the only phosphorus compound detected was triphenylphosphine. The vinyl sulphide was explained by assuming formation of β-lactone **225**, which then lost CO_2 to give **223**.



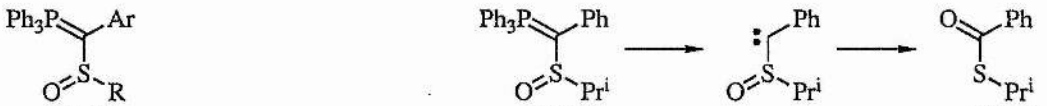
222 **225** **223**

Similarly, formation of **224** was explained by assuming loss of Ph_3P, CO_2 and CO. However this route could not be confirmed and further investigation was needed.



224

Finally, one representative of **226** had been synthesised. FVP of **227** gave Ph_3P and the thiolobenzoate **228**.



226 **227** **228**

The aim of the present work, therefore, was to examine the pyrolytic behaviour of sulphinyl ylides **222** in more detail in an attempt to elucidate the mechanistic pathways involved, and to conduct a thorough study of the thermal behaviour of a wide range of compounds **226**.

EXPERIMENTAL

A Symbols and Abbreviations

mmol	millimoles
M	mol dm^{-3}
h, min	hours, minutes
GCMS	gas chromatography-mass spectrometry
R_T	retention time (quoted in minutes)
TLC	thin layer chromatography
NMR	nuclear magnetic resonance
δ	chemical shift in parts per million
J	spin-spin coupling constant in Hz
4ry	quaternary
br, s, d, t, q, m	broad, singlet, doublet, triplet, quartet, multiplet
ν_{max}	infra-red absorbtion frequency in cm^{-1}
MS	mass spectroscopy
m/z	mass to charge ratio
M^+	mass of molecular ion
FVP	flash vacuum pyrolysis
m.p.	melting point
b.p.	boiling point
ether	diethyl ether
THF	tetrahydrofuran

B Instrumentation and General Techniques

1 N.M.R. Spectroscopy

All spectra were obtained from solutions in $CDCl_3$, except variable temperature studies where CD_2Cl_2 and $C_6D_5CD_3$ were used, and chemical shifts are expressed in parts per million to high frequency of internal TMS for ^1H and ^{13}C or 85% external H_3PO_4 for ^{31}P. Relative peak areas are given for multi-component mixtures and unidentified compounds thus: "δ_P = +28.1 (8) and –5.4 (12)" where (8) and (12) are the spectrometer's arbitrary units of peak height.

a ^1H NMR

Routine spectra were obtained at 60 MHz on a Varian EM-360 spectrometer. Spectra of new compounds were obtained at 80 MHz on a Bruker WP80 or at 200 MHz on a Varian Gemini 200. High resolution and variable temperature spectra were obtained at 300 MHz on a Bruker AM-300 spectrometer, operated by Mrs M. Smith or Mr P. Pogorzelec.

b ^{13}C NMR

Spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by Mrs M. Smith or Mr P. Pogorzelec and at 50 MHz on a Varian Gemini 200 spectrometer. Spectra were ^1H decoupled. Ylide spectra were assigned with reference to published values for analogues and DEPT spectra were taken where necessary to complete the assignment.

c ^{31}P NMR

Spectra were obtained at 32 MHz on a Varian CFT-20 or at 121 MHz on a Bruker AM-300 operated by Mrs M. Smith or Mr P. Pogorzelec.

2 Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrophotometer or on a Perkin-Elmer 1710 fourier transform spectrophotometer. Spectra of solids were run as nujol mulls and solution spectra were run in $CDCl_3$ using matched sodium chloride cells of path length 0.1 mm. Spectra were calibrated with the polystyrene peak at 1603 cm^{-1}.

3 Mass Spectrometry

Accurate mass measurements were obtained on an A.E.I. M.S.-902 instrument and mass spectra obtained on a Finnigan Incos 50 mass spectrometer, both operated by Mr C. Millar. Ionisation was by electron impact at 70 eV unless otherwise stated.

4 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 operated by Mr C. Miller. The column in the GC was a 25 m capilliary column (HR17 – stationary phase phenyl methyl silicone). The components are given in order of decreasing signal on the gas

chromatogram and the temperature ramp quoted as [initial temp. (°C) - rise per minute (°C) - final temp. (°C)]

5 Elemental Analysis

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

6 Melting points

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

7 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.

8 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.

9 Column Chromatography

This was carried out using Fisons silica gel for chromatography (60–120 mesh).

10 Drying and Evaporation of Organic Solutions

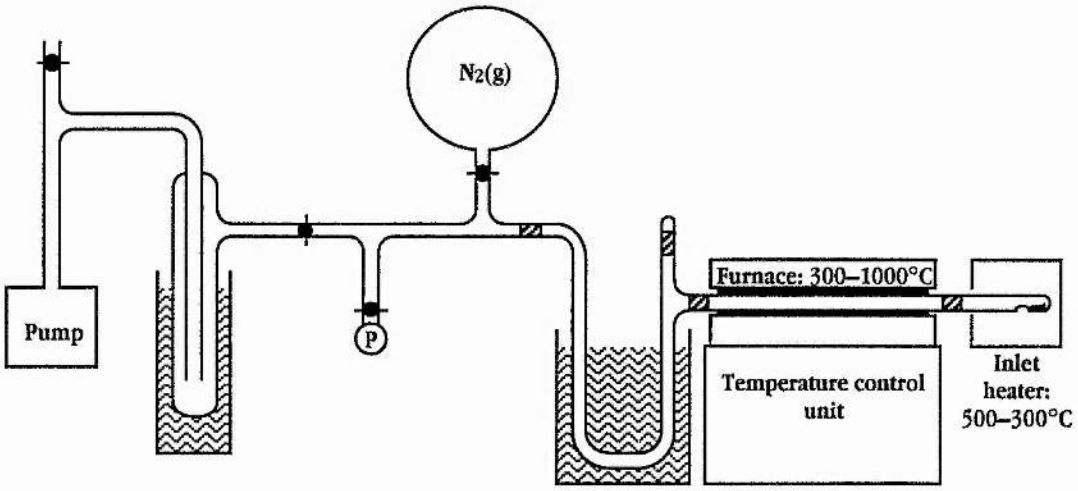
Organic solutions were dried by standing over anhydrous magnesium sulphate and were evaporated under reduced pressure on a rotary evaporator.

11 Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise indicated. Where pure acetone or carbon tetrachloride were required the commercial Analytical Reagent (A.R.) grade solvents were 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. Extra 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. Commercial solutions of n-butyl lithium in hexanes were used. Where necessary, the strength of these solutions was checked by titration with diphenylacetic acid under nitrogen.

12 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.[187] 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.

The pyrolysis conditions are quoted thus: "(weight of material volatilised, furnace temperature, pressure during the pyrolysis, inlet temperature)". Yields are quoted as percentages of theoretical yield.

C Alkane- and arenesulphinylalkoxycarbonylmethylene triphenylphosphoranes

1 Preparation

a Phosphonium salts

i Preparation of (ethoxycarbonylmethyl)triphenylphosphonium bromide **242**

A solution of ethyl bromoacetate (15.9 g, 95 mmol) and triphenylphosphine (25.0 g, 95 mmol) in dry toluene (175 ml) was heated under reflux for 12 h. The resulting precipitate was filtered off and washed with ether to give (ethoxycarbonylmethyl)triphenylphosphonium bromide **242** (40.2 g, 98%) as colourless crystals. m.p. 154°C (lit.,[188] 155–6°C); δ_P +20.6; δ_H (80 MHz) 7.6–8.2 (15H, m), 5.60 (2H, d, J = 15 Hz), 4.10 (2H, q, J = 7 Hz) and 1.18 (3H, t, J = 7 Hz).

ii Preparation of (t–butoxycarbonylmethyl)triphenylphosphonium chloride **243**

A solution of t-butyl chloroacetate (10.0 g, 66 mmol) and triphenylphosphine (17.4 g, 66 mmol) in dry toluene (175 ml) was stirred and heated under reflux for 3 days. The resulting precipitate was filtered off and washed with ether to give (t-butoxycarbonylmethyl)triphenyl phosphonium chloride **243** (22.8 g, 83%) as colourless crystals. m.p. 189°C (lit.,[189] 185°C) (Found: C, 70.5; H, 6.3. $C_{24}H_{26}ClO_2P$ requires C, 69.8; H, 6.3%); δ_P +20.6; δ_H (80 MHz) 7.8–8.2 (15H, m), 5.53 (2H, d, J =14 Hz) and 1.22 (9H, s); δ_C (75 MHz) 163.1 (d, J = 4 Hz, C=O), 135.1

(3C, d, ^4J_P = 3 Hz), 133.9 (6C, d, ^2J_P = 11 Hz), 130.2 (6C, d, ^3J_P = 13 Hz), 118.2 (3C, d, ^1J_P = 89 Hz), 84.5 ($\underline{C}Me_3$), 33.7 (d, ^1J_P = 54 Hz, CH_2) and 27.5; m/z 376 (M^+ – HCl, 8%), 319 (53), 301 (100), 275 (25), 262 (12), 183 (76) and 165 (48).

iii Preparation of (benzyloxycarbonylmethyl)triphenylphosphonium iodide **244**

A solution of chloroacetyl chloride (27.0 g, 240 mmol) in carbon tetrachloride (100 ml) was stirred while benzyl alcohol (28.2 g, 250 mmol) was added slowly and the reaction mixture was stirred for 1 h at room temperature, heated under reflux for 3 h, then left to cool for 12 h. The solvent was evaporated and the residue added to a solution of sodium iodide (37.5 g, 250 mmol) in AR acetone (150 ml). This mixture was stirred for 2 h then the solvent was evaporated and the residue partitioned between toluene and water. The toluene layer was dried, then triphenylphosphine (65.6 g, 250 mmol) was added and the solution stirred for one hour. The yellow precipitate was filtered off, washed with ether and recrystallised from toluene to give (benzyloxycarbonylmethyl)triphenylphosphonium iodide **244** (67.5 g, 51%) as yellow crystals. m.p. 129–30°C (Found: C, 60.2; H, 4.7. $C_{27}H_{24}O_2PI$ requires C, 60.2; H, 4.5%); δ_P +20.0; δ_H (200 MHz) 7.5–7.9 (15H, m), 7.0–7.3 (5H, m), 5.21 (2H, d, J =14 Hz) and 4.98 (2H, s); δ_C (75 MHz) 162.8 (d, J = 4 Hz, C=O), 134.6 (3C, d, ^4J_P = 2 Hz), 133.2 (6C, d, ^2J_P = 11 Hz), 129.6 (6C, d, ^3J_P = 13 Hz), 127.9 (3C), 127.8 (2C), 127.3 (4ry), 116.4 (3C, 4ry, d, ^1J_P = 89 Hz), 67.7 and 32.6 (d, J = 55

Hz); ν_{max} 2940, 1726, 1437, 1303, 1159, 1110, 737 and 692 cm^{-1}; m/z 411 (M^+ – I, 0.2%), 410 (0.5), 301 (8), 277 (100), 262 (23), 183 (26), 152 (8), 108 (13) and 91 (57).

b Phosphoranes

i Preparation of (ethoxycarbonylmethylene)triphenylphosphorane **245**

A solution of (ethoxycarbonylmethyl)triphenylphosphonium bromide (5.2 g, 12 mmol) in water (500 ml) was stirred vigorously by a mechanical stirrer. Aqueous sodium hydroxide (6 ml, 2 M, 12 mmol) was added dropwise to give a cloudy white precipitate. Dichloromethane (200 ml) was added and the mixture was transferred to a separating funnel, from which the organic layer was taken, washed with water, dried and evaporated to give (ethoxycarbonylmethylene)triphenylphosphorane **245** (3.5 g, 85%) as brown crystals. m.p. 118°C (lit.,[190] 116–117°C); δ_P +17.2; δ_H (80 MHz) 7.4–8.0 (15H, m), 3.92 (2H, q, J = 7 Hz), 2.90 (1H, br s) and 0.95 (3H, t, J = 7 Hz).

ii Preparation of (t–butoxycarbonylmethylene)triphenylphosphorane **246**

The procedure as above but using (t-butoxycarbonylmethyl)triphenyl phosphonium chloride (10.0 g, 23 mmol) and sodium hydroxide (11.7 ml, 2M, 23 mmol) gave (t-butoxycarbonylmethylene)triphenylphosphorane **246** (3.7 g, 51%) as colourless crystals. m.p. 150°C (lit.,[191] 154–5°C); δ_P +16.9; δ_H (80 MHz) 7.6–7.7 (6H, m), 7.35–7.5 (9H, m), 2.75 (1H, br s)

and 1.20 (9H, s); δ_C 171.0 (d, J = 9 Hz, C=O), 132.9 (6C, d, ^2J_P = 10 Hz), 131.7 (3C), 128.5 (6C, d, ^3J_P = 12 Hz), 128.3 (3C, 4ry, d, ^1J_P = 91 Hz), 76.3 ($\underline{C}Me_3$), 31.3 (d, J = 121 Hz) and 28.7 (3C).

iii Preparation of (benzyloxycarbonylmethylene)triphenylphosphorane **247**

The procedure as above but using (benzyloxycarbonylmethyl)triphenyl phosphonium iodide (30.0 g, 55 mmol) and sodium hydroxide (27.9 ml, 2M, 56 mmol), followed by recrystallisation from ethyl acetate gave (benzyloxycarbonylmethylene)triphenylphosphorane **247** as colourless crystals (11.3 g, 50%). m.p. 115–20°C; (Found: C, 77.3; H, 5.4; m/z = 410.1471. $C_{27}H_{23}O_2P$ requires C, 79.0; H, 5.6%; 410.1430); δ_P +17.4; δ_H (200 MHz) 7.0–7.7 (20H, m), 5.02 (2H, br s), 3.03 (1H, br s) [impurity ethyl acetate]; δ_C (50 MHz) 170.6 (d, J = 12 Hz, C=O), 138.5 (4ry), 132.7 (6C, d, ^2J_P = 10 Hz), 131.8 (3C, d, ^4J_P = 1 Hz), 128.6 (6C, d, ^3J_P = 12 Hz), 127.9 (2C), 127.6 (3C, d, ^1J_P = 93 Hz), 127.5 (2C), 126.9, 63.8 and 30.3 (d, J = 125 Hz); ν_{max} 1615, 1430, 1340, 1110, 1060, 872 and 690 cm^{-1}; m/z 410 (M^+, 0.1%), 379 (0.1), 301 (5), 277 (100), 262 (3), 201 (18), 183 (15), 152 (8), 108 (28), 91 (26) and 77 (18).

c Preparation of sulphinyl chlorides

These were prepared by the method of Youn and Herrmann.[192] Aromatic sulphinyl chlorides were usually not distilled due to danger of explosion or loss of the compound by polymerisation.

i Preparation of ethanesulphinyl chloride **236**

A mixture of ethanethiol (15.5 g, 250 mmol) and acetic acid (15.0 g, 250 mmol) was stirred below –45°C while sulphuryl chloride (68.8 g, 510 mmol) was added dropwise. The mixture was kept below –45°C for 30 min then left to warm up for 12 h. The mixture was then heated to 35°C and stirred at that temperature for 2 h, then allowed to cool to RT. Evaporation followed by kugelrohr distillation gave ethanesulphinyl chloride **236** (23.9 g, 85%), as a yellow, fuming oil. b.p. 60°C (oven temp.) at 3 mmHg (lit.,[192] 67°C at 26 mmHg); δ_H (200 MHz) 3.41 (2H, q, J = 7 Hz) and 1.47 (3H, t, J = 7 Hz); δ_C (50 MHz) 57.9 and 5.8.

ii Preparation of 2-propanesulphinyl chloride **237**

The procedure as above but using 2-propanethiol (19.0 g, 250 mmol), gave 2-propanesulphinyl chloride **237** as a yellow, fuming oil (30.0 g, 95%). b.p. 50°C (oven temp.) at 10 mmHg (lit.,[192] 49°C at 12 mmHg); δ_H (200 MHz) 3.33 (1H, septet, J = 7 Hz) and 1.45 (6H, d, J = 7 Hz).

iii Preparation of phenylmethanesulphinyl chloride **238**

The method as above, using phenylmethanethiol (31.1 g, 250 mmol), gave phenylmethanesulphinyl chloride **238** (10.1 g, 23%) as a yellow oil. b.p. 128°C (oven temp.) at 20 mmHg (lit.,[192] claimed not distillable); δ_H (200 MHz) 7.3–7.5 (5H, m) and 4.62 (2H, s).

iv Preparation of benzenesulphinyl chloride **239**

The method as above, using thiophenol (27.5 g, 250 mmol), gave benzenesulphinyl chloride **239** as an orange oil (11.7 g, 29%). b.p. 138°C (oven temp.) at 20 mmHg (lit.,[192] 65°C at 0.012 mmHg); δ_H (200 MHz) 7.8–7.9 (2H, m) and 7.5–7.7 (3H, m); δ_C (50 MHz) 148.5, 133.7, 129.5 (2C) and 123.7 (2C).

v Preparation of 4-methylbenzenesulphinyl chloride **240**

The method as above, using 4-methylthiophenol (5.0 g, 40 mmol), gave 4-methylbenzenesulphinyl chloride **240** as a yellow oil (6.5 g, 93%). b.p. not determined; δ_H (200 MHz) 7.75 and 7.37 (4H, AB pattern, J = 7 Hz) and 2.42 (3H, s); δ_C (75 MHz) 144.9, 130.1, 126.9 (2C), 123.7 (2C) and 21.7.

vi Preparation of 4-chlorobenzenesulphinyl chloride **241**

The method as above, using 4-chlorothiophenol (5.0 g, 35 mmol), gave 4-chlorobenzenesulphinyl chloride **241** as a yellow oil (5.1 g, 76%). b.p. not determined; δ_H (200 MHz) 7.2–8.0 (4H, m).

d Preparation of ylides

i Preparation of [(ethanesulphinyl)ethoxycarbonylmethylene]triphenyl phosphorane **248**

(Ethoxycarbonylmethylene)triphenylphosphorane **245** (12.4 g, 35 mmol) was stirred in dry toluene (100 ml) at 0°C under nitrogen. Ethanesulphinyl

chloride (1.9 g, 17 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. The mixture was filtered and evaporation and trituration with ethyl acetate (5 ml) gave yellow cubes of slightly impure [(ethanesulphinyl)ethoxycarbonylmethylene]triphenylphosphorane **248** (1.2 g, 16%). m.p. 141–2°C (Found: C, 69.4; H, 5.9; m/z = 408.1307. $C_{24}H_{25}O_3PS$ requires C, 67.9; H, 5.9%; $M^+ - O$, 408.1313); δ_P +27.5 (120) [impurities +22.1 (7) and 18.7 (3)]; δ_H (80 MHz) 7.4–8.0 (15H, m), 4.05 (2H, q, J = 7 Hz, $OC\underline{H}_2$), 2.25 (2H, q of d, J = 7 Hz, J_P = 2 Hz, $SC\underline{H}_2$), 0.95 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$) and 0.9–1.0 (3H, br s, $SCH_2C\underline{H}_3$) [minor impurities 4.0–4.4 (m) and 1.2–1.4 (m)]; δ_C (75 MHz) 172.2 (C=O), 133.8 (6C, d, ^2J_P = 10 Hz), 131.7 (3C, d, ^4J_P = 2 Hz), 130.8 (3C, 4ry, ^1J_P = 58 Hz), 128.3 (6C, d, ^3J_P = 12 Hz), 58.6 ($O\underline{C}H_2$), 37.0 (d, J = 120 Hz), 33.1 ($S\underline{C}H_2$), 13.9 ($OCH_2\underline{C}H_3$) and 13.4; ν_{max} 3040, 2970, 2920, 1640, 1595, 1482, 1436, 1365, 1230, 1190, 1170, 1100, 1070 and 865 cm^{-1}; m/z 408 ($M^+ - O$, 45%), 379 (100), 301 (7), 277 (8), 262 (37), 183 (38), 152 (5), 108 (14) and 77(4).

ii Preparation of [(benzenesulphinyl)ethoxycarbonylmethylene]triphenyl phosphorane **249**

(Ethoxycarbonylmethylene)triphenylphosphorane (3.0 g, 8.6 mmol) was stirred in dry toluene (100 ml) at 0°C under nitrogen. Benzenesulphinyl chloride (0.69 g, 4.3 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. The byproduct phosphonium salt was filtered off, then evaporation and trituration with ethyl acetate (5 ml) gave

colourless crystals of slightly impure [(benzenesulphinyl)ethoxycarbonyl methylene]triphenylphosphorane **249** (0.50 g, 25%). m.p. 167–70°C (Found: C, 72.8; H, 5.3; m/z, 456.1319. $C_{28}H_{25}O_3PS$ requires C, 71.2; H, 5.3%; $M^+ - O$, 456.1313); δ_P +28.1; δ_H (80 MHz) 7.0–7.9 (20H, m), 4.06 (2H, q, J =7 Hz) and 0.95 (3H, br t, J =7 Hz) [and a trace of toluene]; δ_C (75 MHz) 172.4 (C=O), 144.4, 133.7 (6C, d, ^2J_P = 10 Hz), 131.9 (3C, d, ^4J_P = 2 Hz), 128.3 (6C, d, ^3J_P = 12 Hz), 128.0 (4C, s), 124.8 (3C, 4ry, d, ^1J_P = 104 Hz), 124.1, 59.0 (OCH_2), 36.0 (d, J = 120 Hz), and 14.6 (br, $OCH_2\underline{C}H_3$) [and additional minor Ar-C peaks]; ν_{max} 1600, 1440, 1370, 1270, 1110, 1080, 740 and 690 cm^{-1}; m/z 456 ($M^+ - O$, 25%), 411 (3), 379 (4), 302 (7), 277 (100), 262 (78), 218 (7), 201 (20), 183 (42), 152 (13), 108 (15) and 77 (38).

iii Preparation of [(phenylmethanesulphinyl)ethoxycarbonylmethylene] triphenylphosphorane **250**

(Ethoxycarbonylmethylene)triphenylphosphorane (10.0 g, 29 mmol) and triethylamine (2.9 g, 29 mmol) were stirred in dry toluene (100 ml) at 0°C under nitrogen. Phenylmethanesulphinyl chloride (5.0 g, 29 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. The byproduct triethylammonium salt was filtered off, then evaporation and trituration with ethyl acetate (5 ml) gave a yellow powder of crude [(phenylmethanesulphinyl)ethoxycarbonylmethylene]triphenylphosphorane **250** (1.2 g, 8%). δ_P +23.1; δ_H (80 MHz) 7.0–7.6 (20H, m), 5.47 and 4.17 (2H, AB pattern, J =14 Hz), 3.98 (2H, m), 0.91 (3H, m); δ_C (75 MHz)

134.0, 133.8 (6C, d), 132.3 (3C, d), 130.5 (2C), 128.7 (2C), 128.5 (6C, d), 124.9 (3C, 4ry, ^1J_P = 93 Hz), 58.8, 56.6 (d, ^3J_P = 10 Hz) and 14.3 (4ry, C=O and ylide C not apparent). Recrystallisation from di-isopropyl ether/dichloromethane gave just triphenylphosphine oxide so no further characterisation was made.

iv Preparation of [(4-methylbenzenesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane **251**

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane **246** (4.0 g, 11 mmol) and triethylamine (1.1 g, 11 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. 4-Methylbenzenesulphinyl chloride (1.9 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 3 h. Filtration, evaporation and trituration with ethyl acetate gave slightly impure [(4-methylbenzenesulphinyl)-t-butoxycarbonylmethylene] triphenylphosphorane **251** as yellow crystals (1.02 g, 19%). m.p. 140°C (Found: C, 74.2; H, 5.8; m/z = 498.1815. $C_{31}H_{31}O_3PS$ requires C, 72.4; H, 6.1%; M^+ – O, 498.1782); δ_P +28.5; δ_H (80 MHz) 6.9–8.0 (19H, m), 2.25 (3H, m) and 1.15 (9H, s) [impurity toluene]; δ_C (75 MHz) 171.8 (C=O), 141.3, 133.8 (6C, d, ^2J_P = 10 Hz), 133.6, 131.8 (3C, d, ^4J_P = 2 Hz), 128.7 (2C), 128.2 (6C, d, ^3J_P = 12 Hz), 127.7 (3C, 4ry, d, ^1J_P = 89Hz), 126.0 (2C), 78.2 ($O\underline{C}Me_3$), 36.7 (d, J = 118 Hz), 28.4 (3C) and 20.9 [small signals in the aromatic region due to Ph_3P=O & toluene]; ν_{max} 1610, 1304, 1252, 1170, 1112, 1070, 815, 730 and 700 cm^{-1}; m/z 498 (M^+ – O, 0.1%),

427 (0.2), 303 (0.1), 301 (0.2), 277 (100), 246 (8), 201 (22), 199 (20) and 183 (18).

v Preparation of [(4-chlorobenzenesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane **252**

A solution of t-butoxycarbonylmethylenetriphenylphosphorane (1.5 g, 4 mmol) and triethylamine (0.4 g, 4 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. 4-Chlorobenzenesulphinyl chloride (0.8 g, 4 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 3 h. Filtration, evaporation and trituration with ethyl acetate gave [(4-chloro benzenesulphinyl)-t-butoxycarbonylmethylene]triphenylphosphorane **252** (0.45 g, 21%). m.p. 153°C (Found: C, 66.7; H, 5.0; m/z = 518.1204. $C_{30}H_{28}ClO_3PS$ requires C, 67.3; H, 5.3%; $M^+ - O$, 518.1236); δ_P +28.2; δ_H (80 MHz) 7.4–7.9 (15H, m), 7.22 (4H, s) and 1.13 (9H, s); δ_C (75 MHz) 170.6 (C=O), 133.8 (6C, d, ^2J_P = 9 Hz), 132.1 (4ry), 132.0 (3C), 128.6 (4ry), 128.3 (6C, d, ^3J_P = 12 Hz), 128.0 (4C), 127.5 (3C, 4ry, d, ^1J_P = 66 Hz), 78.6 ($O\underline{C}Me_3$), 36.3 (d, J = 118 Hz) and 28.4 (3C, $OC(\underline{C}H_3)$); ν_{max} 1645, 1246, 1161, 1106, 1064, 820, 760, 722 and 697 cm^{-1}; m/z 518 (^{35}Cl-$M^+ - O$, 5%), 462 (2), 445 (2), 318 (1), 301 (8), 277 (68), 262 (100), 183 (54), 144 (36) and 108 (50).

vi Preparation of [(ethanesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **253**

A solution of (benzyloxycarbonylmethylene)triphenylphosphorane **247** (1.5 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.4 g, 7.3 mmol) was added, followed by ethanesulphinyl chloride (0.41 g, 3.64 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave yellow cubes of [(ethanesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **253.** (0.31 g, 17%). m.p. 115–7°C (Found: C, 71.5; H, 5.6. $C_{29}H_{27}O_3PS$ requires C, 71.6; H, 5.6%); δ_P +27.5; δ_H (200 MHz) 7.1–7.7 (20H, m), 5.0 (2H, m), 2.18 (2H, q, J = 7 Hz) and 0.97 (3H, t, J = 7 Hz); δ_C (75 MHz) 172.0 (C=O), 133.8 (6C, d, ^2J_P = 10 Hz), 132.0, 131.8 (3C, d, ^4J_P = 2 Hz), 128.3 (6C, d, ^3J_P = 12 Hz), 127.9 (2C), 127.8 (2C), 127.8 (3C, 4ry, d, ^1J_P = 83 Hz), 127.0, 64.7 (OCH_2), 37.0 (d, J = 120 Hz), 33.2 (SCH_2) and 13.4; ν_{max} 1590, 1282, 1242, 1101, 1040, 908 and 750 cm^{-1}; m/z 470 (M^+ – O, 2%), 441 (3), 294 (7), 278 (40), 277 (100), 262 (8), 201 (18), 199 (14), 185 (14) and 183 (25).

vii Preparation of [(2-propanesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **254**

A solution of (benzyloxycarbonylmethylene)triphenylphosphorane (2.7 g, 6.6 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.7 g, 7 mmol) was added, followed by 2-propanesulphinyl chloride (0.83 g, 6.6 mmol) and the mixture was stirred for 12 h.

Filtration, evaporation and trituration with ethyl acetate (1 ml) gave slightly impure [(2-propanesulphinyl)benzyloxycarbonylmethylene]triphenyl phosphorane **254** (0.33 g, 10%). m.p. 122–5°C (Found: C, 72.5; H, 6.1; m/z = 484.1616. $C_{30}H_{29}O_3PS$ requires C, 72.0; H, 5.8%; $M^+ - O$, 484.1626); δ_P +24.1(60) [impurities +28.8 (8) and +27.2 (6)]; δ_H (20 MHz) 6.9–7.7 (20H, m), 5.02 and 4.88 (2H, AB pattern, J = 12 Hz), 4.35 (1H, m), 1.28 (3H, d, J = 8 Hz) and 1.02 (3H, d, J = 8 Hz) [impurities 3.08 (q), 2.35 (s) and 1.40 (t)]; δ_C (75 MHz) 166.4 (d, J = 11 Hz, C=O), 133.8 (6C, d, ^2J_P = 10 Hz); 132.4 (3C, d, ^4J_P = 2 Hz), 132.0 (4ry), 128.8 (6C, d, ^3J_P = 13 Hz), 128.1 (2C), 128.0 (2C), 127.3, 125.0 (3C, 4ry, d, ^1J_P = 93 Hz), 64.8 (OCH_2), 55.2 (d, J = 119 Hz), 49.8 (d, J = 9 Hz, S<u>C</u>HMe_2), 18.8 and 18.4 [impurities 136.9, 134.0, 133.5, 133.4, 132.1, 45.8 and 8.7]; ν_{max} 1620, 1320, 1275, 1112, 1063, 1012, 752, 730 and 700 cm^{-1}; m/z 484 ($M^+ - O$, 0.1%), 441 (0.3), 294 (0.5), 277 (35), 201 (7), 199 (5), 108 (18) and 91 (100).

viii Preparation of [(benzenesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **255**

A solution of (benzyloxycarbonylmethylene)triphenylphosphorane (1.5 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.4 g, 3.65 mmol) was added, followed by benzenesulphinyl chloride (0.59 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave [(benzenesulphinyl)benzyloxycarbonylmethylene]triphenylphosphorane

255 (0.12 g, 6%). m.p. 145–7°C (Found: m/z = 518.1462. $C_{33}H_{27}O_3PS$ requires [M^+ – O], 518.1469); δ_P +28.3; δ_H (200 MHz) 6.95–7.55 (25H, m) and 5.06 (2H, br s) [impurities CH_2Cl_2, 2.37 (s), 2.06 (s), 1.77 (br s) and 1.2–1.4 (m)]; δ_C (75 MHz) 172.0 (C=O), 144.3 (br, 4ry), 133.8 (6C, d, ^2J_P = 9 Hz), 132.1 (2C), 132.0 (3C), 131.9, 128.6, 128.4 (6C, d, ^3J_P = 12 Hz), 128.0 (2C), 127.9 (2C), 127.5 (3C, d, ^1J_P = 75 Hz), 125.6 (2C), 124.2, 65.0 and 36.7 (d, J = 120 Hz); ν_{max} 1603, 1440, 1260, 1105, 1050, 902, 752, 720 and 696 cm^{-1}; m/z 518 (M^+ – O, 1%), 441 (5), 427 (1), 411 (9), 383 (18), 339 (5), 303 (63), 273 (58), 262 (100) and 183 (84).

ix Preparation of [(4-methylbenzenesulphinyl)benzyloxycarbonyl methylene]triphenylphosphorane **256**

A solution of (benzyloxycarbonylmethylene)triphenylphosphorane (1.5 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.37 g, 3.65 mmol) was added, followed by 4-methyl benzenesulphinyl chloride (0.64 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave slightly impure [(4-methylbenzenesulphinyl)benzyloxycarbonyl methylene]triphenylphosphorane **256** (0.48 g, 24%). m.p. 160–2°C (Found: m/z = 532.1619. $C_{34}H_{29}O_3PS$ requires M^+ – O, 532.1626); δ_P +28.5; δ_H (200 MHz) 7.1–7.55 (20H, m), 7.05 and 6.88 (4H, AB pattern, J = 8 Hz), 5.07 (2H, br s) and 2.23 (3H, s) [impurities 1.2–1.3 (m)]; δ_C (75 MHz) 172.0 (C=O), 140.7, 133.7 (2C), 133.7 (6C, d, ^2J_P = 9 Hz), 131.8 (3C, d, ^4J_P = 2 Hz), 128.8 (2C), 128.5, 128.3 (6C, d, ^3J_P = 12 Hz), 127.9

(2C), 127.8, 127.0 (2C), 126.7 (3C, 4ry, d, ^1J_P = 91 Hz), 125.8, 64.8 (OCH_2), 36.8 (d, J = 122 Hz) and 20.9; ν_{max} 1605, 1268, 1110, 1052, 906, 757, 725 and 698 cm^{-1}; m/z 532 (M^+ – O, 97%), 441 (3), 425 (5), 397 (3), 303 (20), 262 (100) and 183 (22).

x Preparation of [(4-chlorobenzenesulphinyl)benzyloxycarbonyl methylene]triphenylphosphorane **257**

A solution of (benzyloxycarbonylmethylene)triphenylphosphorane (1.5 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.37 g, 3.65 mmol) was added, followed by 4-chlorobenzenesulphinyl chloride (0.71 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave [(4-chlorobenzenesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **257** (1.42 g, 68%). m.p. 133–5°C (Found: C, 70.2; H, 4.7; m/z = 552.1084. $C_{33}H_{26}ClO_3PS$ requires C, 69.7; H, 4.6%; ^{35}Cl-M^+ – O, 552.1080); δ_P +28.2; δ_H (200MHz) 7.15–7.6 (20H, m), 7.08 and 7.02 (4H, AB pattern, J = 9 Hz) and 5.05 (2H, br s); δ_C (75 MHz) 172.0 (C=O), 135.1, 133.8 (4ry), 133.7 (6C, d, ^2J_P = 9 Hz), 132.1 (3C, d, ^4J_P = 2 Hz), 132.0, 128.4 (6C, d, ^3J_P = 12 Hz), 128.4, 128.0 (2C), 127.9 (2C), 127.4 (3C, 4ry, d, ^1J_P = 59 Hz), 127.2 (2C), 126.8 (2C), 65.0 (OCH_2) and 36.4 (d, J = 121 Hz); ν_{max} 1604, 1266, 1106, 1086, 1010, 819, 750, 723 and 696 cm^{-1}; m/z 554 (^{37}Cl-M^+ – O, 7%,), 552 (^{35}Cl-M^+ – O, 20%), 303 (13), 301 (16), 262 (95), 183 (40), 108 (82) and 91 (100).

xi Attempted preparation of [(benzenesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (3.5 g, 9 mmol) was stirred in dry toluene (100 ml). Triethylamine (0.9 g, 9 mmol) and benzenesulphinyl chloride (1.6 g, 10 mmol) in dry toluene (10 ml) were added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a mixture which, in addition to the phosphonium salt, starting phosphorane and triphenylphosphine oxide, contained two major products, δ_P = +23.4 and +28.2 but these could not be isolated.

xii Attempted preparation of [(phenylmethanesulphinyl)benzyloxy carbonylmethylene]triphenylphosphorane

A solution of (benzyloxycarbonylmethyl)triphenylphosphorane (1.50 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.74 g, 7.3 mmol) was added, followed by phenylmethanesulphinyl chloride (0.64 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave an oil that had δ_P +28.9 (Ph_3P=O), +28.5 (possibly the desired product) and +18.9 (starting phosphorane); δ_H 6.9–7.6 (25H, m) and 5.0 (br s).

xiii Attempted preparation of [(4-chlorobenzenesulphinyl)ethoxycarbonyl methylene]triphenylphosphorane

(Ethoxycarbonylmethylene)triphenylphosphorane (2.5 g, 7.2 mmol) and 4-chlorobenzenesulphinyl chloride (0.70 g, 3.6 mmol) were stirred in dry toluene at 0°C for 12 h. Filtration, evaporation and trituration with ethyl acetate gave the starting phosphorane.

xiv Attempted preparation of [(ethanesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane

A solution of freshly prepared (t-butoxycarbonylmethylene)triphenyl phosphorane (9.1 g, 24 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. Ethanesulphinyl chloride (1.4 g, 12 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration and evaporation gave an oil whose mass spectrum showed evidence for the presence of the desired product (m/z = 436 [M^+ – O], 407 [M^+ – O, Et], 380 [M^+ – O, $H_2C{=}CMe_2$], 351, 319, 307, 277 and 262) but whose ^{31}P NMR spectrum (+27.9, +27.7 to +25.0, +21.6, +21.4 and +20.7) appeared too complex to make further purification possible and whose ^1H spectrum appeared very unpromising.

xv Attempted preparation of [(2-propanesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane

A solution of freshly prepared (t-butoxycarbonylmethylene)triphenyl phosphorane (9.14 g, 24 mmol) in dry toluene (100 ml) was stirred at 0°C

under nitrogen. 2-Propanesulphinyl chloride (1.5 g, 12 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave the starting phosphonium salt and in the residual oil a major component δ_P +26.2. Attempts to crystallise this failed.

xvi Attempted preparation of [(phenylmethanesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (9.1 g, 24 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. Phenylmethanesulphinyl chloride (2.1 g, 12 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 2 h. Filtration, evaporation and trituration with ethyl acetate gave the starting phosphorane and its conjugate phosphonium salt.

xvii Attempted preparation of [(benzenesulphinyl)-t-butoxycarbonyl methylene]triphenylphosphorane

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. Benzenesulphinyl chloride (0.4 g, 2.5 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave an oil contining triphenylphosphine oxide, the starting phosphorane, its conjugate phosphonium salt and what may have been the product (δ_P = +24.3). No crystals ever formed.

xviii Attempted preparation of [(4-chlorobenzenesulphinyl)-t-butoxy carbonylmethylene]triphenylphosphorane

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (4.0 g, 10.6 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. 4-Chlorobenzenesulphinyl chloride (1.0 g, 5.3 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 3 h. Filtration, evaporation and trituration with ethyl acetate gave just the phosphonium salt.

xix Attempted preparation of [(4-methylbenzenesulphinyl)-t-butoxy carbonylmethylene]triphenylphosphorane

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (3.2 g, 8.5 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. A solution of 4-methylbenzenesulphinyl chloride (0.74 g, 4.2 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 4 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals which contained several different products and no pure product could be isolated.

2 FVP of alkane- and arenesulphinylalkoxycarbonylmethylene triphenylphosphoranes

i FVP of [(ethanesulphinyl)ethoxycarbonylmethylene]triphenyl phosphorane **248**

FVP of the title compound (0.2105g) [600°C, 5 x 10^{-3} torr, 200°C] gave a colourless liquid in the cold trap [GCMS (40-20-300) and ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR indicated the presence of

ethyl 1-propenyl sulphide, (36% yield) R_T = 2.35, m/z 162 (61%), 87 (9), 73 (53) and 45 (100); δ_H 5.8–5.9 (1H, m), 5.4–5.9 (1H, m), 2.5–2.6 (2H, m), 1.6–1.7 (3H, m) and 1.1–1.3 (3H, m); δ_C (major component, hence presumably E- isomer) 124.9, 122.2, 25.7, 17.4 and 13.6; (Z- isomer) 124.4, 122.8, 26.6, 14.5 and 13.5.

acetaldehyde, (7% yield) δ_H 9.75 (1H, q, J = 4 Hz) and 2.15 (3H, d, J = 4 Hz)]; δ_C 198.9 and 29.9.];

and a yellow amorphous solid at the furnace exit [^{31}P NMR indicated the presence of Ph_3P, Ph_3P=O and Ph_3P=S in the ratio 84:9:7.

Ph_3P, δ_P –5.0.

Ph_3P=O, δ_P +28.5.

Ph_3P=S, δ_P +43.5.].

ii FVP of [(benzenesulphinyl)ethoxycarbonylmethylene]triphenyl phosphorane **249**

FVP of the title compound (0.10g) [600°C, 5 x 10^{-3} torr, 80°C] gave a colourless liquid in the cold trap [GCMS (40-20-300) and ^{1}H (80 MHz) and ^{13}C (75 MHz) NMR indicated the presence of

PhSSPh, (10% yield) R_T = 12.30, m/z 218 (42%), 185 (15), 154 (29) and 109 (100).

phenyl E- and Z-propenyl sulphide, (10% yield) R_T = 7.54, m/z 150 (100%), 135 (82), 121 (11), 109 (40) and 105 (58); δ_H 7.2–7.7 (5H, m), 5.9–6.3 (2H, m) and 1.85 (3H, d of m, J = 5 Hz); δ_C many Ar-C, 123.6, 121.7 (PhSCH=CHMe), 18.5 and 14.7 (PhSCH=CHMe)

ethyl phenyl sulphide, (5% yield) R_T = 7.01, m/z 138 (100%), 123 (80) and 110 (70); δ_H 2.95 (2H, q, J = 7 Hz) and 1.30 (3H, t, J = 7 Hz); δ_C 27.7 and 14.4.

unknown, R_T = 8.55, m/z 166 (15%), 137 (100), 121 (2) and 109 (50).

unknown (possibly 1,1-di(phenylthio)propane), R_T = 13.58, m/z 260 (5%), 218 (18), 184 (2), 151 (100), 137 (25) 123 (37) and 109 (62).

an aldehyde, δ_H 9.6 (d, J = 3 Hz) and δ_C 195.5.];

and a yellow solid at the furnace exit [^{13}C NMR indicated the presence of $Ph_3P{=}O$ and Ph_3P in the ratio 1:1.

Ph_3P, δ_C 137.1 (3C, d, ^1J_P = 10 Hz), 133.7 (6C, d, ^2J_P = 19 Hz), 128.5 (6C, d, ^3J_P = 15 Hz) and 128.4 (3C).

$Ph_3P{=}O$, δ_C 132.3 (3C, d, ^1J_P = 104 Hz), 132.1 (6C, d, ^2J_P = 10 Hz), 131.9 (3C, d, ^4J_P = 2 Hz) and 128.5 (6C, d, ^3J_P = 12 Hz).].

iii FVP of [(methanesulphinyl)methoxycarbonylmethylene]triphenyl phosphorane **270**

FVP of the title compound[185] (0.2153g) [600°C, 5 x 10^{-3} torr, 104°C] gave a colourless liquid in the cold trap [GCMS (60-20-300) and ^{1}H (300 MHz) and ^{31}P NMR indicated the presence of

methyl vinyl sulphide, (20% yield) R_T = 1.20, m/z 74 (9%), 73 (100), 59 (3) and 45 (22); δ_H 6.46 (1H, dd, J = 16 Hz, 10 Hz), 5.20 (1H, d, J = 10 Hz), 4.97 (1H, d, J = 16 Hz) and 2.27 (3H, s); ^{13}C 132.9, 108.4 and 13.6.

1,1-di(methylthio)ethane, R_T = 2.23, m/z 122 (33%), 105 (2) and 75 (100); δ_H 2.12 (6H, s), 2.09 (3H, d, J = 9 Hz) and 1.23 (1H, q, J = 9 Hz).

MeSSMe, R_T = 1.38, m/z 94 (58%), 79 (49), 61 (13), 47 (44) and 45 (100); δ_H 2.43.];

and brown droplets at the furnace exit [GCMS (60-20-300) and ^{31}P NMR indicated the presence of Ph_3P, $Ph_3P{=}O$ and $Ph_3P{=}S$ in the ratio 80:14:6.

Ph_3P, R_T = 9.58, m/z 262 (69%), 183 (100), 152 (15) and 108 (59); δ_P –5.5.

$Ph_3P{=}O$, R_T = 11.32, m/z 277 (65%), 199 (27), 103 (26), 152 (25) and 51 (100) [Most intense ion in molecular ion cluster at m/z 277 ($M^+ - 1$)]; δ_P +31.9.

$Ph_3P{=}S$, R_T = 11.56, m/z 294 (35%), 201 (11), 215 (9) and 183 (100); δ_P +43.1.].

iv FVP of [(2-propanesulphinyl)benzyloxycarbonylmethylene]triphenyl phosphorane **254**

FVP of the title compound (0.1103g) [500°C, 1.8 x 10^{-2} torr, 150°C] gave a colourless liquid in the cold trap [^1H NMR indicated the presence of benzyl alcohol, δ_H 7.4–7.1 (5H, m), 4.65 (2H, s,) and 3.0 (1H, br s).];

and brown droplets at the furnace exit [^{31}P NMR indicated the presence of $Ph_3P{=}O$, δ_P +28.9 (40).

$Ph_3P{=}S$, δ_P +43.1 (7).].

v FVP of [(benzenesulphinyl)benzyloxycarbonylmethylene]triphenyl phosphorane **255**

FVP of the title compound (0.0453g) [500°C, 1.8 x 10^{-2} torr, 150°C] gave a colourless liquid in the cold trap [^1H NMR indicated the presence of

benzyl alcohol, δ_H as above.];

and brown droplets at the furnace exit [^{31}P NMR indicated the presence of $Ph_3P{=}O$, δ_P +28.5].

vi FVP of [(4-chlorobenzenesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **257**

FVP of the title compound (0.1123g) [500°C, 1.8 x 10^{-2} torr, 150°C] gave a colourless liquid in the cold trap [GCMS (60-20-300) and ^1H (200 MHz) NMR indicated the presence of

benzyl alcohol, R_T = 4.02, m/z 108 (42%), 91 (12), 79 (100) and 77 (65); δ_H 7.4–7.1 (5H, m) and 4.70 (2H, s).

4-Cl-$C_6H_4SCH_2Ph$, R_T = 10.00, m/z 234 (1%), 165 (1), 143 (3) and 91 (100); δ_H 4.1 (s).

4-Cl-C_6H_4Me, R_T = 3.43, m/z 130 (2%), 128 (5%), 126 (15) and 91 (100)

unknown, R_T = 7.04, m/z 156 (3%), 129 (46), 115 (6) and 91 (88)

toluene, R_T = 1.50, m/z 92 (54%), 91 (100), 74 (2) and 65(18)

$PhCH_2CH_2Ph$, R_T = 7.34, m/z 182 (3%), 91 (100), 77 (6) and 65 (20).];

and brown droplets at the furnace exit [GCMS (60-20-300) and ^1H (200 MHz) NMR indicated the presence of

(4-Cl-$C_6H_4S)_2$, R_T = 11.41, m/z 290 (0.5%), 288 (1), 28 6 (2), 145 (30) and 143 (100); δ_H 7.41 and 7.30 (8H, AB pattern, J = 9 Hz).

$Ph_3P{=}O$, R_T = 14.21, m/z 277 (4%), 199 (5), 183 (5) and 77 (59)

vii FVP of [(4-methylbenzenesulphinyl)benzyloxycarbonylmethylene] triphenylphosphorane **256**

FVP of the title compound (0.1259g) [500°C, 3 x 10^{-3} torr, 150°C] gave brown droplets at the furnace exit and a colourless liquid in the cold trap. These were collected together [^{1}H (200 MHz) and ^{31}P NMR indicated the presence of

benzyl alcohol, δ_H 7.4–7.1 (5H, m) and 4.7 (2H, s).

$Ph_3P{=}O$, δ_H 7.7–7.4 (m); δ_P +28.6.].

viii FVP of [(4-methylbenzenesulphinyl)-t-butoxycarbonylmethylene] triphenylphosphorane **251**

FVP of the title compound (0.0950g) [500°C, 1.6 x 10^{-2} torr, 50°C] gave yellow droplets in the cold trap [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{13}C (75 MHz) NMR indicated the presence of

$(4\text{-}Me\text{-}C_6H_4S)_2$, R_T = 10.25, m/z 246 (26%), 182 (8), 123 (100) and 77 (64); δ_H 7.19 and 7.04 (8H, AB pattern, J = 8 Hz) and 2.32 (6H, s); δ_C 135.7 (2C), 132.2 (2C), 129.8 (4C), 128.5 (4C) and 20.9 (2C).];

and yellow droplets at the furnace exit [^{1}H (200 MHz) and ^{31}P NMR indicated the presence of Ph_3P and $Ph_3P{=}O$ in the ratio 7:30.

Ph_3P, δ_H 7.3 (m); δ_P –5.4.

$Ph_3P{=}O$, δ_H 7.8–7.4 (m); δ_P +29.3.

However, a GCMS taken 17 days later indicated the presence of

$Ph_3P{=}O$, R_T = 13.42, m/z 277 (18%), 199 (15), 186 (16) and 77 (100).

$Ph_3P{=}S$, R_T = 14.11, m/z 294 (10%), 263 (15), 183 (100) and 139 (38).

in the ratio 12:1].

ix FVP of [(4-chlorobenzenesulphinyl)-t-butoxycarbonylmethylene] triphenylphosphorane **252**

FVP of the title compound (0.0917g) [500°C, 2.3 x 10^{-2} torr, 52°C] gave a white solid in the cold trap [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{31}P NMR indicated the presence of

t-butanol, R_T = 1.16, m/z 74 (1%), 73 (1), 59 (100) and 31 (47); δ_H 2.3 (1H, br s) and 1.27 (9H, s); δ_C 69.3 and 31.2.

$(4\text{-Cl-}C_6H_4S)_2$, R_T = 11.13, m/z 290 (5%), 288 (25), 286 (30), 145 (23) and 143 (88); δ_H 7.20 (8H, s); δ_C 130.8 (4C) and 129.2 (4C).

and brown droplets at the furnace exit [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{31}P NMR indicated the presence of

$(4\text{-Cl-}C_6H_4S)_2$, R_T = 11.13, m/z 290 (4%), 288 (12), 286 (19), 222 (6), 145 (28), 143 (70) and 108 (100).

$Ph_3P{=}O$, R_T = 13.37, m/z 277 (28%), 199 (18), 183 (12) and 77 (100) (peak area 60 units); δ_P +29.2.

$Ph_3P{=}S$, R_T = 14.07, m/z 294 (33%), 278 (5), 203 (24) and 183 (100) (peak area 7 units).].

3 Preparation of authentic samples of FVP products

i Preparation of ethyl prop-2-enyl sulphide **280**

Sodium metal (2.3 g, 100 mmol) was stirred in ethanol (200 ml). Ethanethiol (6.2 g, 100 mmol) was added, followed by allyl bromide (13.3 g, 110 mmol) and the mixture was stirred for 12 h. The mixture was then added to water (450 ml), from which the product was extracted with ether (2 x 500 ml). Drying, evaporation and kugelrohr distillation gave ethyl prop-2-enyl sulphide **280** as a colourless liquid (5.2 g, 51%). b.p. 60°C (oven temp.) at 4.5 mmHg (lit.,[193] 115–6°C at 759 mmHg); δ_H (80 MHz) 5.9–5.6 (1H, m), 5.0–5.1 (2H, m), 3.13 (2H, d, J = 8 Hz), 2.47 (2H, q, J = 8 Hz) and 1.21 (3H, t, J = 8 Hz); δ_C (50 MHz) 134.9, 116.7, 34.6, 24.7 and 14.7.

ii Attempted preparation of ethyl prop-1-enyl sulphide **282**

Sodium metal (1.9 g, 83 mmol) was dissolved in dry ethanol (100 ml). Ethanethiol (5.1 g, 83 mmol) was added, followed by 1-bromoprop-1-ene (10.0 g, 83 mmol) and the mixture was stirred for 3 h. The mixture was then added to water (1000 ml), from which the product was extracted using ether (2 x 400 ml). Drying and evaporation gave a colourless liquid whose spectra showed no sign of the required double bond.

A repeat of this experiment, heating the reagents in a sealed tube at 120°C gave a clear liquid whose spectra showed no sign of the double bond.

Ethyl prop-2-enyl sulphide **280** (2.0 g, 20 mmol) and sodium hydroxide (5.0 g, 125 mmol) were stirred in water (50 ml) under nitrogen, while being heated under reflux for 12 h. Acidification with HCl (2M) and extraction with dichloromethane (2x100 ml) gave only the starting material.

iii Preparation of ethyl prop-2-enyl sulphoxide **281**

This was prepared by Johnson and Keiser's method.[194] Sodium metaperiodate (1.1 g, 5 mmol) was stirred in water (21 ml) at 0°C. Ethyl prop-2-enyl sulphide (0.5 g, 5 mmol) was added and the mixture was stirred for 12 h. Filtration, followed by extraction with dichloromethane (3 x 50 ml), drying over magnesium sulphate/ activated charcoal, evaporation and kugelrohr distillation gave ethyl prop-2-enyl sulphoxide **281** as a clear liquid (0.2 g, 34%). b.p. 140°C (oven temp.) at 20 mmHg (lit.,[195] 40°C at 0.02 mmHg); δ_H (80 MHz) 5.8–6.1 (1H, m), 5.3–5.6 (2H, m), 3.50 and 3.42 (2H, AB pattern of doublets, J_{AB} =13 Hz and J_d =7 Hz), 2.75 (2H, m) and 1.35 (3H, t); δ_C (50 MHz) 125.8, 123.4, 55.1, 44.2 and 6.6.

iv Preparation of methyl vinyl sulphide **284**

2-chloroethyl methyl sulphide (5.6 g, 51 mmol) was added to a solution of sodium (1.17 g, 51 mmol) in pentan-1-ol (100 ml) and heated at reflux for 30 min. Distillation, collecting all fractions boiling lower than 87°C, followed by kugelrohr distillation at 760 mmHg gave 1.5g clear liquid which was mostly pentanol but which did contain the desired product,

methyl vinyl sulphide **284** (0.4g by calculation from ^{1}H NMR, 11%). δ_H (300 MHz) 6.42 (1H, dd, J = 10 Hz, 16 Hz), 5.18 (1H, d, J = 10 Hz), 4.95 (1H, d, J = 16 Hz) and 2.22 (3H, s); δ_C (75 MHz) 132.9, 108.5 and 13.5.

v Preparation of methyl vinyl sulphoxide **285**

Half of the product of the preceding experiment was dissolved in dichloromethane (10 ml). This was added to a solution of sodium metaperiodate (0.6 g, 3 mmol) in water (10 ml) which was stirred for 12 h. Filtration, extraction with dichloromethane (2 x 100 ml), drying and evaporation gave a few droplets of methyl vinyl sulphoxide **285**. δ_H (200 MHz) 6.70 (1H, dd, J = 16 Hz, 10 Hz), 6.12 (1H, d, J = 16 Hz), 5.96 (1H, d, J = 10 Hz) and 2.64 (3H, s)

vi Preparation of O-ethyl-S-(4-chlorophenyl)thiocarbonate **268**

Triethylamine (1.9 g, 18 mmol) and 4-chlorothiophenol (2.7 g, 18 mmol) were stirred in extra dry ether (50 ml). Ethyl chloroformate (2.0 g, 18 mmol) in extra dry ether (20 ml) was added dropwise. Water (20 ml) was added and this mixture partitioned between water (200 ml) and ether (200 ml). The ether layer was dried. Evaporation of the ether and kugelrohr distillation gave O-ethyl-S-(4-chlorophenyl)thiocarbonate **268** as a colourless liquid. (2.4 g, 60%). b.p. 160°C (oven temp.) at 20 mmHg (lit.,[196] 142–3°C at 10 mmHg); δ_H (200 MHz) 7.40 and 7.33 (4H, AB pattern, J = 8 Hz), 4.27 (2H, q, J = 7 Hz), 1.30 (3H, t, J = 7 Hz); δ_C 168.8, 136.0 (2C), 135.8, 129.3 (2C), 126.4, 64.2 and 14.2.

D Attempted preparation of alkane- and arenesulphinyl and sulphenyl diazoacetates

1 Diazo-transfer reagents

i Preparation of tosyl azide **296**

Sodium azide (35.0 g, 556 mmol) in water (200 ml) was added to a solution of tosyl chloride (105.8 g, 556 mmol) in ethanol (500 ml) and stirred for 1 h. The mixture was poured into water (2000 ml), the product separated off, then washed with water (2 x 200 ml) and dried to give tosyl azide **296** as an off-white powder (83.5 g, 76%). m.p. 63–5°C (lit.,[197] 22°C); δ_H (80 MHz) 7.82 and 7.42 (4H, AB pattern, J = 10 Hz) and 2.47 (3H, s); δ_C (75 MHz) 146.4 (4ry), 135.5 (4ry), 130.4 (2C), 127.5 (2C) and 21.7; ν_{max} 2350 and 2130 cm^{-1}. The m.p. noted is far above the literature value. It is likely that the product had decomposed before the m.p. was taken.

ii Preparation of 4-(N-acetylamino)benzenesulphonyl azide **301**

This diazotransfer agent was supposed to have the distinction that the byproduct amide would be easily separated from the diazo-products.[198] A solution of sodium azide (3.9 g, 60 mmol) in water (30 ml) was added to a solution of 4-(N-acetylamino)benzenesulphonyl chloride (11.7 g, 50 mmol) in acetone (100 ml). This mixture was stirred for 12 h poured into water (1450 ml). These mixtures were stirred for 1 h, after which the product was filtered off. Recrystallisation from toluene gave 4-(N-acetylamino) benzenesulphonyl azide **301** as a white powder (9.1 g, 76%). m.p. 114°C

(lit.,[198] 113–5°C); δ_H (300 MHz) 8.32 (1H, s), 7.87 and 7.82 (4H, AB pattern, J = 10 Hz) and 2.25 (3H, s); δ_C (50 MHz) 169.7 (C=O), 144.2 (4ry), 132.3 (4ry), 128.9 (2C), 119.7 (2C) and 24.7; ν_{max} 3250, 3170, 2340, 2120, 1665 and 1580 cm^{-1}.

2 Alkane- and arenesulphenylacetates

a Preparation of (benzenesulphenyl)acetyl chloride

A solution of (benzenesulphenyl)acetic acid (10.0 g, 60 mmol) in thionyl chloride (100 ml) was heated under reflux for 6 h. Evaporation and kugelrohr distillation gave (benzenesulphenyl)acetyl chloride **133** as a dark brown oil (9.0 g, 81%). b.p. 140°C (oven temp.) at 0.5 mmHg; δ_H (200 MHz) 7.2–7.5 (5H, m) and 4.00 (2H, s); δ_C (50 MHz) 170.4 (C=O), 133.5 (4ry), 131.9 (2C), 130.0 (2C), 128.8 and 48.9. The product was used directly for reaction as below without further characterisation.

b Preparation of methyl (ethanesulphenyl)acetate 292

Sodium metal (2.1 g, 92 mmol) was dissolved in methanol (100 ml). Ethanethiol (4.8 g, 92 mmol) was added, followed by methyl chloroacetate (10.0 g, 77 mmol) and the mixture was stirred for 30 min. The mixture was evaporated and the residue taken up into dichloromethane. This solution was washed with water, dried, evaporated and kugelrohr distilled to give methyl (ethanesulphenyl)acetate **292** as a colourless liquid (4.1 g, 52%). b.p. 60°C (oven temp.) at 6 mmHg (lit.,[199] 106–8°C at 100 mmHg); δ_H (200 MHz) 3.74 (3H, s), 3.25 (2H, s), 2.67 (2H, q, J = 8 Hz) and 1.29

(3H, t, J = 8 Hz); δ_C (50 MHz), 171.0 (C=O), 52.3 (OCH_3), 33.1 (CH_2CO), 26.6 (SCH_2Me) and 14.2.

c Preparation of ethyl (ethanesulphenyl)acetate 294

Sodium metal (2.0 g, 87 mmol) was dissolved in ethanol (100 ml). Ethanethiol (5.1 g, 82 mmol) was added, followed by ethyl chloroacetate (10.0 g, 82 mmol) and the mixture was stirred for 30 min. The mixture was evaporated and the residue taken up in dichloromethane (200 ml). Washing with water (2 x 200 ml), drying, evaporation and kugelrohr distillation gave ethyl (ethanesulphenyl)acetate **294** as a colourless liquid (5.1 g, 42%). b.p. 100°C (oven temp.) at 4 mmHg (lit.,[200] 187–9°C at 759 mmHg); δ_H (200 MHz) , 4.19 (2H, q, J = 8 Hz), 3.22 (2H, s), 2.65 (2H, q, J = 8 Hz, SCH_2Me), 1.28 (3H, t, J = 8 Hz) and 1.27 (3H, t, J = 8 Hz); δ_C (50 MHz), 170.5 (C=O), 61.2 (OCH_2), 33.3 (CH_2CO), 26.6 (SCH_2Me) and 14.2 (2 x CH_3).

d Preparation of methyl (benzenesulphenyl)acetate 293

i A solution of (benzenesulphenyl)acetyl chloride (4.0 g, 21 mmol) in methanol (60 ml) was stirred for 12 h. Evaporation and kugelrohr distillation gave methyl (benzenesulphenyl)acetate **293** as a golden yellow liquid (2.5 g, 63%). b.p. 170°C (oven temp.) at 3 mmHg (lit.,[201] 262–3°C at 759.4 mmHg); δ_H (200 MHz) 7.2–7.5 (5H, m), 3.69 (3H, s) and 3.62 (2H, s); δ_C (50 MHz), 170.1 (C=O), 135.0 (4ry), 129.8 (2C), 129.0 (2C), 126.9, 52.4 (OCH_3) and 36.4 (SCH_2).

ii Sodium metal (2.1 g, 92 mmol) was dissolved in ethanol (100 ml) and thiophenol (10.1 g, 92 mmol) was added. Methyl chloroacetate (10.0 g, 92 mmol) was added dropwise and the mixture was stirred for 12 h. The mixture was evaporated and the residue taken up into dichloromethane. This solution was washed with water, dried, evaporated and kugelrohr distilled to give methyl (benzenesulphenyl)acetate **293** (12.4 g, 74%) as a colourless liquid. Spectra identical to those of the product of **d**i above.

e Preparation of ethyl (benzenesulphenyl)acetate

i Sodium metal (1.9 g, 82 mmol) was dissolved in ethanol (100 ml) and thiophenol (9.0 g, 82 mmol) was added. Ethyl chloroacetate (10.0 g, 82 mmol) was added dropwise and the mixture was stirred for 12 h. The mixture was evaporated and the residue taken up into dichloromethane. This solution was washed with water, dried, evaporated and kugelrohr distilled to give ethyl (benzenesulphenyl)acetate as a colourless liquid **295** (11.5 g, 72%). b.p. 130°C (oven temp.) at 2 mmHg (lit.,[201] 265°C at 759.4 mmHg); δ_H (200 MHz) 7.1–7.5 (5H, m), 4.12 (2H, q, J = 8 Hz), 3.62 (2H, s) and 1.20 (2H, t, J = 8 Hz); δ_C (50 MHz) 169.6 (C=O), 135.1 (4ry), 129.8 (2C), 129.0 (2C), 126.8, 61.4 (OCH_2), 36.6 (SCH_2) and 14.0.

ii A solution of (benzenesulphenyl)acetyl chloride (4.0 g, 21 mmol) in ethanol (100 ml) was stirred for 12 h. Evaporation and kugelrohr distillation gave ethyl (benzenesulphenyl)acetate **295** (2.44 g, 58%) as a

golden yellow liquid which had identical properties to the product of experiment ei above

3 Preparation of alkane- and arenesulphinylacetates

i Preparation of methyl (ethanesulphinyl)acetate **297**

Sodium metaperiodate (1.6 g, 7 mmol) was stirred in 20 ml deionised water. Methyl (ethanesulphenyl)acetate (1.0 g, 7 mmol) in methanol was added dropwise and the mixture was stirred for 12 h. The product was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave methyl (ethanesulphinyl)acetate **297** as a colourless oil (0.4 g, 36%). b.p. 150°C (oven temp.) at 0.1 mmHg; (Found: 150.0349. $C_5H_{10}O_3S$ requires 150.0351); δ_H (200 MHz) 3.77 (3H, s), 3.78 and 3.68 (2H, AB pattern, J = 18 Hz), 2.89 (2H, m) and 1.35 (3H, t, J = 7 Hz); δ_C (50 MHz) 166.2 (C=O), 55.2 and 53.0 (OCH_3 and $\underline{C}H_2CO$), 46.2 ($S\underline{C}H_2CH_3$) and 6.7 ($SCH_2\underline{C}H_3$); ν_{max} 1710, 1330, 1285, 1255, 1140 and 1086 cm^{-1}; m/z 150 (M^+, 3%), 134 (45), 122 (5), 105 (21), 89 (11), 75 (100), 61 (84), 59 (92) and 45 (61).

ii Preparation of ethyl (ethanesulphinyl)acetate **299**

Sodium metaperiodate (4.8 g, 22 mmol) was stirred in 20 ml deionised water. Ethyl (ethanesulphenyl)acetate (4.0 g, 27 mmol) in methanol (20 ml) was added dropwise and mixture was stirred for 12 h. The reaction mixture was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave ethyl (ethanesulphinyl)acetate

299 as a yellow oil (3.1 g, 85%). b.p. 105°C (oven temp.) at 0.3 mmHg; (Found: m/z [M^+ – O] 148.0570. $C_6H_{12}O_3S$ requires [M^+ – O] 148.0558); δ_H (200 MHz) 4.23 (2H, q, J = 8 Hz), 3.73 and 3.66 (2H, AB pattern, J = 18 Hz), 2.90 (2H, m), 1.36 (3H, t, J = 8 Hz) and 1.32 (3H, t, J = 8 Hz); δ_C (50 MHz) 165.6 (C=O), 62.4 (OCH_2), 55.6 ($\underline{C}H_2CO$), 46.5 ($S\underline{C}H_2CH_3$), 14.5 ($OCH_2\underline{C}H_3$) and 6.9 ($SCH_2\underline{C}H_3$); ν_{max} 1720, 1440, 1370, 1295, 1090 and 855 cm^{-1}; m/z = 148 (M^+ – O, 3%), 135 (3), 88 (9), 75 (31), 61 (10), 47 (32) and 29 (100).

iii Preparation of methyl (benzenesulphinyl)acetate **298**

Sodium metaperiodate (1.17 g, 5.5 mmol) was stirred in 20 ml deionised water. Methyl (benzenesulphenyl)acetate (1.0 g, 5.5 mmol) in methanol was added dropwise and mixture was stirred for 12 h. The reaction mixture was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave methyl (benzenesulphinyl) acetate **298** as a yellow oil (0.35 g, 32%). b.p. 200°C (oven temp.) at 1 mmHg; (Found: m/z = 198.0355. $C_9H_{10}O_3S$ requires 198.0351); δ_H (200 MHz) 7.70 (2H, m), 7.6–7.5 (3H, m), 3.86 and 3.74 (2H, AB pattern, J = 16 Hz) and 3.69 (3H, s); δ_C (50 MHz) 165.2 (C=0), 142.9 (4ry), 131.8, 129.4 (2C), 124.1 (2C), 61.3 (OCH_3) and 52.7; ν_{max} 1720, 1435, 1275, 1110, 1080, 1040, 900, 740 and 690 cm^{-1}; m/z = 198 (M^+, 22%), 182 (1), 167 (2), 138 (3), 125 (100), 109 (5), 97 (32) and 77 (38).

iv Preparation of ethyl (benzenesulphinyl)acetate **300**

Sodium metaperiodate (4.4 g, 21 mmol) was stirred in water (210 ml). Ethyl (benzenesulphenyl)acetate (4.0 g, 20 mmol) in methanol (20 ml) was added dropwise and mixture was stirred for 12 h. The reaction mixture was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave ethyl (benzenesulphinyl) acetate **300** as a yellow oil (1.9 g, 45%). b.p. 169°C (oven temp.) at 0.5 mmHg (Found: C, 54.1; H, 5.3; m/z 196.0561. $C_{10}H_{12}O_3S$ requires C, 56.6; H, 5.7%; $M^+ - O$ requires 196.0558); δ_H (200 MHz) 7.6–7.8 (2H, m), 7.55–7.45 (3H, m), 4.12 (2H, q, J = 7 Hz), 3.77 and 3.81 (2H, AB pattern, J = 10 Hz) and 1.15 (3H, t, J = 7 Hz); δ_C (50 MHz) 164.1 (C=O), 142.5 (4ry), 131.0, 128.7 (2C), 123.5 (2C), 61.1, 60.7 and 13.3; ν_{max} 1717, 1430, 1360, 1270, 1210, 1080, 1010, 735 and 680 cm^{-1}; m/z 196 ($M^+ - O$, 7%), 170 (19), 123 (32), 103 (62), 75 (68) and 47 (100).

4 Attempted preparation of alkane- and arenesulphinyl diazoacetates

a Preparation of ethyl (ethanesulphinyl)diazoacetate

Ethyl(ethanesulphinyl)acetate (2.0 g, 12 mmol), tosyl azide (2.7 g, 14 mmol) and triethylamine (1.2 g, 12 mmol) were stirred in dichloromethane (100 ml) for 3 days. The solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 1M) and extracted with ether (2 x 100 ml). This solution was dried and evaporated to give recovered tosyl azide.

b Preparation of methyl (benzenesulphinyl)diazoacetate

Methyl (benzenesulphinyl)acetate (2.0 g, 10 mmol), tosyl azide (2.3 g, 12 mmol) and triethylamine (1.0 g, 10 mmol) were stirred in dichloromethane (100 ml) for 3 days. The solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 1M) and extracted with ether (2 x 100 ml). This was dried and evaporated to give recovered tosyl azide.

c Preparation of ethyl (benzenesulphinyl)diazoacetate

i Following a method by Regitz[202], ethyl (benzenesulphinyl)acetate (0.5 g, 3 mmol), tosyl azide (0.5 g, 3 mmol) and triethylamine (0.2 g, 12 mmol) were stirred in dichloromethane (100 ml) for 3 days. The solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 1M) and extracted with ether (2 x 100 ml), dried and evaporated to give just tosyl azide.

ii An adaptation of the Davies *et al* diazo-transfer method was used.[198] Ethyl (benzenesulphinyl)acetate (3.0 g, 14 mmol), 4-(N-acetylamino) benzenesulphonyl azide (3.4 g, 14 mmol) and triethylamine (4.3 g, 42 mmol) were stirred in acetonitrile (100 ml) for 3 days. Evaporation gave a residue which was triturated with 1:1 dry ether:40–60 petroleum (100 ml). Filtration and evaporation gave just the starting sulphinyl ester.

5 Attempted preparation of benzenesulphinyl(phenyl) diazomethane

i triethylamine as base

Benzyl phenyl sulphoxide (5.0 g, 23 mmol), 4-(N-acetylamino)benzene sulphonyl azide (5.6 g, 26 mmol) and triethylamine (7.0 g, 69 mmol) were stirred in acetonitrile/ dichloromethane (60 ml) for 3 days. A deep orange colour was observed. The solvent was evaporated and the residue triturated with 1:1 dry ether:40–60 petroleum (100 ml). Filtration and evaporation gave just the starting sulphoxide.

ii n-butyl lithium as base

Benzyl phenyl sulphoxide (3.0 g, 14 mmol) was stirred in dry ether (60 ml) under nitrogen. n-Butyl lithium (5.6 ml, 2.5M, 14 mmol) was added to give a corn-yellow solution, followed by 4-(N-acetylamino)benzene sulphonyl azide (3.3 g, 14 mmol) in 1:1 acetonitrile:ether, whereupon the solution became a deeper yellow. The mixture was stirred for 3 h, then the solvent was evaporated and the residue triturated with 1:1 dry ether:40–60 petroleum (100 ml). Filtration and evaporation gave the starting sulphoxide.

6 Attempted preparation of alkyl (benzenesulphenyl) diazoacetates

a Preparation of methyl (benzenesulphenyl)diazoacetate

Methyl (benzenesulphenyl)acetate (2.0 g, 11 mmol) and triethylamine (1.1 g, 11 mmol, 1.5 ml) were stirred in acetonitrile (100 ml). A solution of tosyl azide (2.2 g, 11 mmol) in acetonitrile (10 ml) was added dropwise and the mixture was stirred for 64 hrs. After evaporation, the residue was taken up in ether (200 ml) and dried and evaporated to give just the starting materials.

b Preparation of ethyl (benzenesulphenyl)diazoacetate

i Ethyl (benzenesulphenyl)acetate (2.0 g, 5 mmol) and triethylamine (1.0 g, 10 mmol) were stirred in acetonitrile (100 ml). A solution of tosyl azide (2.0 g, 10 mmol) in acetonitrile (10 ml) was added dropwise and the mixture was stirred for 64 hrs. The mixture was washed evaporated and the residue taken up in ether (200 ml). This mixture was washed with aqueous potassium hydroxide solution, dried and evaporated to give just the starting materials.

ii Sodium hydride (60% dispersion in oil [0.2g ≡ 0.1g sodium hydride] 5 mmol) was washed with 40–60 petroleum to remove the oil and then dispersed in extra dry THF (50 ml). To this was added ethyl (phenylthio) acetate (1.0 g, 5 mmol) in dry THF (50 ml) and tosyl azide (5 mmol) in dry THF (1.0 g, 50 ml). This mixture was stirred for 72 h, then the THF

was evaporated, the residue partitioned between ether (200 ml) and aqueous potassium hydroxide (200 ml, 0.2M). The ether layer was dried and evaporated to give just the starting materials.

iii Lithium di-isopropylamide was prepared by adding n-butyl lithium (2.0 ml, 2.5M, 5 mmol) to a solution of di-isopropylamine (0.5 g, 5 mmol) in extra dry THF (20 ml) under nitrogen and stirring for 30 min. Ethyl (phenylthio)acetate (1.0 g, 5 mmol) in extra dry THF (7 ml) was added to give a yellow solution, followed by tosyl azide (1.0 g, 5 mmol) in extra dry THF (50 ml), whereupon the solution went bright red. This mixture was stirred for 3 days, then the mixture was added to ether (200 ml) and washed with aqueous sodium hydroxide (1M, 200 ml). The ether layer was dried and evaporated to give just the starting materials.

E Preparation and pyrolysis of (arenesulphinyl)benzylidene triphenylphosphoranes

1 Preparation

a Preparation of phosphonium salts $Ph_3P^+CH_2Ar\ Hal^-$

i Preparation of benzyltriphenylphosphonium chloride **315**

A solution of triphenylphosphine (25.0 g, 95 mmol) and benzyl chloride (13.1 g, 105 mmol) in toluene (250 ml) was heated under reflux for 24 h. The white precipitate was filtered off and washed with ether to give benzyltriphenyl phosphonium chloride **315** as a white powder (18.1 g,

48%). m.p. 282–3°C (lit.,[203] 287–8°C); δ_P +23.0; δ_H (80 MHz) 7.5–8.0 (15H, m), 7.1–7.4 (5H, m) and 5.55 (2H, d, J_{P-H} = 16 Hz).

ii Preparation of 4-nitrobenzyltriphenylphosphonium bromide **316**

A solution of triphenylphosphine (25.0 g, 95 mmol) and (4-nitrobenzyl) bromide (30.9 g, 143 mmol, 1.5eq) in toluene (250 ml) was heated to reflux for 24 h. The white precipitate was filtered off and washed with ether to give 4-nitrobenzyl triphenylphosphonium bromide **316** as a white powder (46.4 g, 83%). m.p. 263°C (lit.,[204] 261°C); δ_P +24.1; δ_H (200 MHz) 7.45–7.9 (19H, m) and 6.02 (2H, d, J = 20 Hz); δ_C (75 MHz) 147.2 (d, J = 2 Hz), 135.8 (d, J = 9 Hz), 135.1 (3C, d, ^4J_P = 3 Hz), 134.5 (6C, d, ^2J_P = 10 Hz), 133.0 (2C, d, J = 5 Hz), 130.1 (6C, d, ^3J_P = 13 Hz), 123.1 (2C, d, J = 3 Hz), 117.2 (3C, 4ry, d, ^1J_P = 86 Hz) and 29.6 (d, J = 46 Hz).

iii Preparation of 4-methoxybenzyltriphenylphosphonium bromide **317**

A solution of 4-methoxybenzyl alcohol (50.0 g, 362 mmol) in dichloromethane (100 ml) was stirred at 0°C while a solution of phosphorus tribromide (32.7 g, 121 mmol) in dichloromethane (50 ml) was added dropwise. The mixture was stirred for 90 min, added to water (100 ml) and the product extracted with ether. Drying and evaporation gave 4-methoxybenzyl bromide (68.0 g, 93%). δ_H (60 MHz) 7.2 and 6.8 (4H, AB pattern, J = 8 Hz), 4.5 (2H, s) and 3.7 (3H, s). The product was not purified further because it is a severe irritant.

The product from the previous reaction, 4-methoxybenzyl bromide (68.0 g, 338 mmol) was added to a solution of triphenylphosphine (88.6 g, 338 mmol) in toluene (200 ml). This mixture was heated under reflux for 6 h, then the white precipitate was filtered off and washed with ether to give 4-methoxybenzyltriphenylphosphonium bromide **317** as a white powder (140.8 g, 90%). m.p. 230–2°C (lit.,[205] 217°C); δ_P +22.1; δ_H (200 MHz) 7.6–7.9 (15H, m), 7.00 and 6.65 (4H, AB pattern, J = 10 Hz), 5.15 (2H, d, J = 16 Hz) and 3.73 (3H, s); δ_C (200 MHz) 159.6 (d, J = 4 Hz), 135.1 (3C, d, ^4J_P = 2 Hz), 134.3 (6C, d, ^2J_P = 10 Hz), 132.6 (2C, d, J = 10 Hz), 130.2 (6C, d, ^3J_P = 12 Hz), 118.4 (d, J = 4 Hz), 117.6 (3C, d, ^1J_P = 85 Hz), 114.2 (2C, d, J = 2 Hz), 55.3 and 30.0 (d, J = 47 Hz).

b Preparation of ylides

i Preparation of [(benzenesulphinyl)benzylidene]triphenylphosphorane **312**

Benzyltriphenylphosphonium chloride (10.2 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 11 ml, 28 mmol) was added and the mixture was stirred for 30 min. Benzenesulphinyl chloride (2.1 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of slightly impure [(benzenesulphinyl)benzylidene]triphenylphosphorane **312** (1.8 g, 29%). m.p. 172–4°C (Found: C, 76.8; H, 5.25, m/z = 460.1423. $C_{31}H_{25}OPS$ requires C, 78.1; H, 5.3%; M^+ – O, 460.1415); δ_P +20.4; δ_H (300 MHz)

7.4–7.8 (17H, m), 7.2–7.3 (2H, m), 7.1–7.2 (1H, m), 7.02 (2H, m), 6.75–6.85 (2H, m) and 6.70 (1H, m); δ_C (75 MHz) 147.7 (d, J = 16 Hz), 137.2 (d, J = 12 Hz), 134.3 (6C, d, ^2J_P = 10 Hz), 132.4 (3C, d, ^4J_P = 2 Hz), 129.7 (2C, d, J = 6 Hz), 128.8 (6C, d, ^3J_P = 12 Hz), 128.6, 127.8 (2C), 127.3 (2C), 126.8 (3C, d, ^1J_P = 89 Hz), 126.3 (2C), 122.7 and 52.2 (d, J = 122 Hz); ν_{max} 1735, 1590, 1485, 1440, 1245, 1100, 1000 and 930 cm^{-1}; m/z 460 (M^+ – O, 4%), 399 (1), 351 (1), 277 (13), 262 (24), 234 (2), 218 (42), 200 (42), 183 (13), 143 (15), 105 (50) and 91 (100).

ii Preparation of [(4-methylbenzenesulphinyl)benzylidene]triphenyl phosphorane **313**

Benzyltriphenylphosphonium chloride (6.4 g, 16 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 10.2 ml, 16 mmol) was added and the mixture was stirred for 30 min. A solution of 4-methyl benzenesulphinyl chloride (1.4 g, 8 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of [(4-methylbenzenesulphinyl)benzylidene]triphenylphosphorane **313** (1.8 g, 45%). m.p. 168–73°C (Found: C, 78.6; H, 5.5. $C_{32}H_{27}OPS$ requires C, 78.3; H, 5.6%;); δ_P +20.2; δ_H (80 MHz) 6.8–8.0 (24H, m) and 2.27 (3H, s); δ_C (75 MHz) 144.6 (4ry, d, J = 16 Hz), 137.7, 137.4 (4ry, d, J = 12 Hz), 134.3 (6C, d, ^2J_P = 10 Hz), 132.3 (3C), 132.0 (2C, d, J = 7 Hz), 128.8 (6C, d, ^3J_P = 12 Hz), 128.7 (2C), 128.0 (3C, 4ry, d, ^1J_P = 78 Hz), 127.3 (2C), 126.3 (2C), 122.6, 52.1 (d, J = 125 Hz) and 21.1; ν_{max} 1605, 1510, 1250,

1175, 1030, 835, 755 and 735 cm^{-1}; m/z 474 (M^+ – O, 0.2%), 394 (1), 379 (1), 277 (15), 262 (26), 241 (1), 228 (2), 183 (45), 105 (69), 91 (15) and 77 (100).

iii Preparation of [(4-chlorobenzenesulphinyl)benzylidene]triphenyl phosphorane **314**

Benzyltriphenylphosphonium chloride (10.0 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 16.1 ml, 26 mmol) was added and the mixture was stirred for 30 min. A solution of 4-chlorobenzenesulphinyl chloride (2.5 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of [(4-chlorobenzenesulphinyl)benzylidene]triphenylphosphorane **314** (2.1 g, 31%). m.p. 194–6°C (Found: C, 74.3; H, 5.1; m/z = 494.1020. $C_{31}H_{24}ClOPS$ requires C, 72.9; H, 4.7%; ^{35}Cl-M^+ – O, 494.1024); δ_P +19.7; δ_H (300 MHz) 6.6–7.8 (m) [plus ethyl acetate 4.13 (2H, q, J = 7 Hz), 2.01 (s, 3H), 1.35 (3H, t, J = 7 Hz)]; δ_C (75 MHz) 146.3 (4ry, d, J = 21 Hz), 145.1 (4ry), 133.9 (6C, d, ^3J_P = 9 Hz), 132.1 (d, J = 10 Hz), 131.9 (3C), 128.5 (6C, d, ^2J_P = 12 Hz), 127.9 (3C, 4ry, d, ^1J_P = 88 Hz), 127.9 (2C), 127.6 (2C), 125.3 (2C), 122.7 [ylide C and 2C not apparent]; ν_{max} 1590, 1450, 1250, 1190, 1100, 980, 820, 750 and 700 cm^{-1}; m/z 496 (^{37}Cl-M^+ – O, 0.5%), 494 (^{35}Cl-M^+ – O, 2), 383 (2), 309 (1), 277 (100), 262 (35), 233 (15), 183 (30), 152 (12), 121 (70), 108 (10), 91 (30) and 77 (305).

iv Attempted preparation of [(benzenesulphinyl)-4-methoxybenzylidene] triphenylphosphorane

A solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 13.5 ml, 22 mmol) was added and the mixture was stirred for 30 min. Benzenesulphinyl chloride (1.7 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave the starting salt.

v Attempted preparation of [(4-methylbenzenesulphinyl)-4-methoxy benzylidene]triphenylphosphorane

A solution of (4-methoxybenzyl)triphenylphosphonium bromide (9.0 g, 19 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 12.2 ml, 19 mmol) was added and the mixture was stirred for 30 min. 4-Methylbenzene sulphinyl chloride (1.7 g, 10 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave mainly triphenylphosphine oxide with none of the desired product.

vi Attempted preparation of [(4-chlorobenzenesulphinyl)-4-methoxy benzylidene] triphenylphosphorane

A solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 13.5 ml, 22 mmol) was added and the mixture was

stirred for 30 min. A solution of 4-chlorobenzenesulphinyl chloride (2.1 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave the starting phosphonium salt and 2 other products, δ_P +25.1 and 23.5.

vii Attempted preparation of [(4-methylbenzenesulphinyl)-4-nitro benzylidene]triphenylphosphorane

A solution of (4-nitrobenzyl)triphenylphosphonium bromide (10.0 g, 21 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 13.1 ml, 21 mmol) was added and the mixture was stirred for 30 min. A solution of 4-methylbenzenesulphinyl chloride (1.8 g, 10 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave triphenylphosphine oxide.

viii Attempted preparation of [(4-chlorobenzenesulphinyl)-4-nitro benzylidene]triphenylphosphorane

A solution of (4-nitrobenzyl)triphenylphosphonium bromide (10.0 g, 21 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 13.1 ml, 21 mmol) was added and the mixture was stirred for 30 min. A solution of 4-chlorobenzenesulphinyl chloride (1.8 g, 10 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave triphenylphosphine oxide.

2 FVP of [(arenesulphinyl)benzylidene]triphenyl phosphoranes

a FVP of [(benzenesulphinyl)benzylidene]triphenylphosphorane **312**

FVP of the title compound (0.21 g) [500°C, 5.0 x 10^{-2} torr, 100°C] gave a small droplet of blue liquid in the cold trap [GCMS (40-20-300) and ^{1}H (200 MHz) and ^{31}P NMR indicated the presence of

Ph_3P, R_T = 11.47, m/z 261 (11%), 183 (47), 152 (12) and 108 (100); δ_P –5.0 (24).

phenyl thiolobenzoate, (20% yield) R_T = 10.23, m/z 214 (1%), 152 (1), 105 (91) and 77 (100); δ_H as for authentic material prepared in **3di**.

diphenyl disulphide, (10% yield) R_T = 10.01, m/z 218 (9%), 185 (3), 154 (10) and 109 (100).

E-stilbene, (8% yield) R_T = 9.01, m/z 180 (63%), 179 (66), 165 (48), 152 (18) and 51 (100).

thiophenol, (8% yield) R_T = 3.34, m/z 110 (100%), 84 (38) and 77 (70); δ_H 3.55 (s).

$Ph_3P{=}O$, R_T = 15.01, m/z 277 (19%), 199 (14), 183 (10) and 157 (17); δ_P +29.4 (12).

phenyl benzyl sulphide, (4% yield) R_T = 9.08, m/z 200 (3%), 165 (1), 109 (5) and 91 (100).

$Ph_3P{=}S$, R_T = 15.41, m/z 294 (9%), 262 (4), 183 (55) and 139 (43); δ_P +43.7 (2).

unknown, R_T = 4.55, m/z 150 (91%), 135 (35), 110 (38) and 39 (100).

Z-stilbene, (2% yield) R_T = 7.46, m/z 180 (39%), 179 (43), 165 (35), 152 (18) and 51 (100).

unknown, R_T = 12.19, m/z 215 (1%), 167 (100), 152 (28) and 109 (26).].

In a separate run, stopped when half the substrate had been pyrolysed, the inlet tube was found to contain only a brown substance [GCMS (60-20-300) and ^1H (200 MHz) and ^{31}P NMR indicated the presence of

$Ph_3P=O$, R_T = 14.43, m/z 277 (10%), 199 (12), 183 (13) and 157 (14); δ_P +28.6 (21).

diphenyl disulphide, R_T = 9.57, m/z 218 (11%), 185 (9), 154 (12) and 109 (100).

Ph_3P, R_T = 11.44, m/z 262 (12%), 183 (45), 152 (16) and 108 (100); δ_P –5.4 (16).

$Ph_3P=S$, R_T = 15.23, m/z 294 (8%), 262 (15), 215 (8) and 183 (43).].

b FVP of [(4-methylbenzenesulphinyl)benzylidene]triphenylphosphorane **313**

FVP of the title compound (0.21 g) [500°C, 3.8 x 10^{-1} torr, 100°C] gave a small droplet of blue liquid in the cold trap [GCMS (60-20-300) and ^1H (200 MHz) and ^{31}P NMR indicated the presence of

Ph_3P, R_T = 11.46, m/z 262 (16%), 183 (62), 152 (16) and 108 (100); δ_P –5.0 (140)

$PhCOSC_6H_4Me$, (25% yield) R_T = 10.55, m/z 228 (1%), 184 (1), 105 (100) and 77 (89); δ_H and δ_C as for authentic material prepared in **3d**iii.

$Ph_3P=O$, R_T = 14.44, m/z 277 (18%), 199 (14), 183 (14) and 152 (12); δ_H 7.4–7.8 (m); δ_P +28.8 (26).

4-MeC_6H_4SH, (20% yield) R_T = 4.15, m/z 124 (37%), 91 (100), 77 (15) and 45 (44) δ_H 2.26 (s).

$(4\text{-}MeC_6H_4S)_2$, (6% yield) R_T = 11.04, m/z 246 (8%), 214 (1), 182 (4) and 123 (74).

$Ph_3P{=}S$, R_T = 15.28, m/z 294 (13%), 262 (5), 215 (5) and 183 (62); δ_H 7.3 (m); δ_P +43.5 (5).

$PhCOC_6H_4Me$, (5% yield) R_T = 9.29, m/z 196 (12%), 181 (6), 165 (4), 152 (4), 119 (100) and 105 (38).

benzaldehyde, (5% yield) R_T = 3.40, m/z 106 (55%), 105 (58), 77 (100) and 51 (80); δ_H 10.0 (s).]

and brown droplets at the furnace exit [GCMS (60-20-300) indicated the presence of

Ph_3P, R_T = 11.46, m/z 262 (16%), 183 (62), 152 (16) and 108 (100); δ_H 7.3 (m).

$PhCOSC_6H_4Me$, R_T = 10.55, m/z 228 (1%), 184 (1), 105 (100) and 77 (89).

$Ph_3P{=}O$, R_T = 14.44, m/z 277 (18%), 199 (14), 183 (14) and 152 (12).

$Ph_3P{=}S$, R_T = 15.28, m/z 294 (13%), 262 (5), 215 (5) and 183 (62).

$(4\text{-}MeC_6H_4S)_2$, R_T = 11.04, m/z 246 (8%), 214 (1), 182 (4) and 123 (74).

4-MeC_6H_4SH, R_T = 4.15, m/z 124 (37%), 91 (100), 77 (15) and 45 (44).

$PhCOC_6H_4Me$, R_T = 9.29, m/z 196 (12%), 181 (6), 165 (4), 152 (4), 119 (100) and 105 (38).].

c FVP of [(4-chlorobenzenesulphinyl)benzylidene]triphenylphosphorane **314**

FVP of the title compound (0.1812 g) [500°C, 1.0 x 10^{-3} torr, 100°C] gave a small droplet of blue liquid at the room temperature part of the trap and yellow droplets at the furnace exit. These were collected together [GCMS (60-20-300) and ^{1}H (200 MHz), ^{13}C (50 MHz) and ^{31}P NMR indicated the presence of

$Ph_3P{=}O$, R_T = 17.46, m/z 277 (100%), 201 (28), 183 (27) and 152 (10); δ_P +29.4 (24).

Ph_3P, –5.1 (9).

$Ph_3P{=}S$, R_T = 19.28, m/z 294 (91%), 262 (15), 217 (15) and 183 (100); δ_P +43.6 (2).

4-ClC_6H_4SH, (25% yield) R_T = 6.19, m/z 146 (36%), 144 (100) and 109 (50); δ_H 3.47 (1H).

$PhCOC_6H_4Cl$, (18% yield) R_T = 10.59, m/z 218 (18%), 216 (70), 181 (20), 141 (88) and 105 (100).

(4-$ClC_6H_4S)_2$, (17% yield) R_T = 13.22, m/z 290 (3%), 288 (32), 175 (2) and 143 (100)

$PhCOSC_6H_4Cl$, (9% yield) R_T = 12.33, m/z 250 (2%), 248 (6), 197 (1), 184 (1) and 105 (100).

$PhCH_2SC_6H_4Cl$, (7% yield) R_T = 11.22, m/z 236 (8%), 234 (22), 165 (2), 143 (10) and 91 (100); δ_H 4.04 (2H).

E-stilbene, (7% yield) R_T = 10.07, m/z 180 (100%), 165 (48), 152 (16) and 89 (25).

benzaldehyde, R_T = 4.31, m/z 106 (55%), 100 (100) and 77 (62)

3 Preparation and FVP of authentic samples of FVP products

a Preparation of benzophenones

i Preparation of 4-chlorobenzophenone **347**

A solution of 4-chlorobenzoic acid (6.3 g, 40 mmol) in thionyl chloride (97.9 g, 823 mmol, 60 ml) was heated under reflux for 12 h. Evaporation and kugelrohr distillation gave 4-chlorobenzoyl chloride as a yellow oil which was used immediately for further experiments.

Aluminium trichloride (2.2 g, 9 mmol) was added slowly to a solution of 4-chlorobenzoyl chloride (2.6 g, 15 mmol) in benzene (50 ml). The mixture was heated under reflux until HCl evolution had ceased then poured onto a mixture of concentrated HCl (100 ml) and ice (200g). The ice was allowed to melt, then the benzene layer was separated off and washed with aqueous sodium hydroxide (2M, 2 x 200 ml) and water (2 x 200 ml). Drying, evaporation and kugelrohr sublimation gave 4-chlorobenzophenone **347** as an off-white solid (2.7 g, 84%). m.p. 72–3°C (lit.,[206] 75.5–76°C); δ_H (200 MHz) 7.7–7.8 (4H, m) and 7.4–7.7 (5H, m); δ_C (50 MHz) 195.4 (C=O), 138.9 (C-Cl), 137.2 (4ry), 135.9 (4ry), 132.6, 131.4 (2C), 129.9 (2C), 128.6 (2C) and 128.4 (2C).

ii Preparation of 4-methylbenzophenone **348**

A solution of 4-methylbenzoic acid (5.0 g, 37 mmol) in thionyl chloride (81.5 g, 684 mmol, 50 ml) was heated under reflux for 12 h. Evaporation

and kugelrohr distillation gave 4-methylbenzoyl chloride as a clear oil (5.0 g, 88%) δ_H (60 MHz) 8.1 and 7.4 (4H, AB pattern, J = 8 Hz) and 2.5 (3H, s). The oil was used immediately for further experiments and so was not distilled.

Aluminium trichloride (2.2 g, 9 mmol) was added slowly to a solution of 4-methylbenzoyl chloride (2.6 g, 17 mmol) in benzene (50 ml). The mixture was heated under reflux until HCl evolution had ceased then poured onto a mixture of concentrated HCl (100 ml) and ice (200g). The ice was allowed to melt, then the benzene layer was separated off and washed with aqueous sodium hydroxide (2M, 2 x 200 ml) and water (2 x 200 ml). Drying, evaporation and kugelrohr sublimation gave 4-methylbenzophenone **348** as a yellow solid (1.7 g, 52%). m.p. 49–50°C (lit.,[207] 50–51°C); δ_H (200 MHz) 7.7–7.9 (4H, m), 7.4–7.6 (3H, m), 7.2–7.3 (2H, m) and 2.43 (3H, s); δ_C (75 MHz) 196.3 (C=O), 143.2 (<u>C</u>-CH_3), 137.9 (4ry), 134.9 (4ry), 132.1, 130.2 (2C), 129.9 (2C), 128.9 (2C), 128.2 (2C) and 21.6.

b FVP of benzophenones

i <u>FVP of 4-chlorobenzophenone</u> **347**

FVP of the title compound (0.5505 g) [500°C, 5 x 10^{-3} torr, 100°C] gave only the unchanged starting material.

ii <u>FVP of 4-methylbenzophenone</u> **348**

FVP of the title compound (0.3481 g) [500°C, 4 x 10^{-3} torr, 100°C] gave only the unchanged starting material (100%).

c Preparation of thiobenzophenones

These were prepared according to the method of Gattermann.[208]

i Preparation of thiobenzophenone

Phosphorus pentasulphide (4.9 g, 22 mmol) was stirred in xylene (10 ml). Benzophenone (2.0 g, 11 mmol) in xylene (20 ml) was added and the mixture heated under reflux for 12 h. Filtration and kugelrohr distillation gave thiobenzophenone **343** as a blue liquid (1.5 g, 69%). b.p. 170°C (oven temp.) at 0.1 mmHg (lit.,[209] 174°C at 14 mmHg); (Found: m/z = 198.0541. $C_{13}H_{10}S$ requires 198.0503); δ_H (200 MHz) 7.25–7.85 (m); δ_C (50 MHz) 238.3 (C=S), 147.2 (2C, 4ry), 131.9 (2C), 129.6 (4C) and 127.9 (4C); λ_{max} 570nm.

ii Preparation of 4-chlorothiobenzophenone **345**

Phosphorus pentasulphide (4.2 g, 18 mmol) was stirred in xylene (10 ml). 4-chlorobenzophenone (2.0 g, 9 mmol) in xylene (20 ml) was added and the mixture was heated under reflux for for 12 h. Filtration and kugelrohr distillation gave 4-chlorothiobenzophenone **345** as a blue liquid (0.43 g, 20%). b.p. 170°C (oven temp.) at 0.1 mmHg (lit.,[210] 145–6°C at 0.22 mmHg); (Found: m/z = 232.0102. $C_{13}H_9{}^{35}ClS$ requires 232.0113); δ_H (200 MHz) 7.2–7.8 (m); δ_C (50 MHz) 236.2 (C=S), 146.9 (4ry), 145.3 (4ry), 138.5 (4ry), 132.1, 130.8 (2C), 129.4 (2C), 128.2 (2C) and 128.0 (2C); λ_{max} 592nm.

iii Preparation of 4-methylthiobenzophenone **344**

Phosphorus pentasulphide (4.5 g, 20 mmol) was stirred in xylene (10 ml). 4-methylbenzophenone (1.0 g, 10 mmol) in xylene (20 ml) was added and the mixture heated under reflux for for 12 h. Filtration and kugelrohr distillation gave 4-methylthiobenzophenone **344** as a blue liquid (0.4 g, 37%). b.p. 170°C (oven temp.) at 0.1 mmHg (lit.,[210] 136–8°C at 0.3 mmHg); (Found: m/z = 212.0648. $C_{14}H_{12}S$ requires 212.0660); δ_H (200 MHz) 7.1–7.8 (m, 9H) and 2.38 (3H, s); δ_C (50 MHz) 237.7 (C=S), 147.6 (4ry), 144.8 (4ry), 143.1 (4ry), 131.7, 129.9 (2C), 129.5 (2C), 128.7 (2C), 127.9 (2C) and 21.6; λ_{max} 585nm

d Preparation of thiolobenzoates

i Preparation of phenyl thiolobenzoate **349**

Sodium metal (1.0 g, 45 mmol) was dissolved in ethanol (100 ml) and thiophenol (5.0 g, 45 mmol) was added, followed by benzoyl chloride (6.4 g, 45 mmol). The mixture was stirred for 30 min, then the ethanol was evaporated and the residue taken up in dichloromethane. This solution was washed with water. Drying, evaporation and recrystallisation of the residue from ethanol gave phenyl thiolobenzoate **349** as colourless flakes (7.3 g, 75%). m.p. 50–1°C (lit.,[211] 56°C); δ_H (200 MHz) 8.0 (2H, m) and 7.3–7.6 (8H, m)

ii Preparation of 4-chlorophenyl thiolobenzoate **350**

A solution of benzoyl chloride (9.7 g, 69 mmol) in dry toluene (30 ml) was added dropwise to a solution of 4-chlorothiophenol (10.0 g, 69 mmol) and triethylamine (7.0 g, 9.6 ml, 69 mmol) in dry toluene (100 ml) and the mixture was stirred for 30 min. The byproduct amine salt was filtered off and the toluene solution was washed with water. Drying and evaporation gave 4-chlorophenyl thiolobenzoate **350** as colourless crystals (2.9 g, 16%). m.p. 57-9°C (Found: C, 62.2; H, 4.0; m/z = 248.0057. $C_{13}H_9{}^{35}ClOS$ requires C, 62.8; H, 3.7%; 248.0063); δ_H (200 MHz) 8.0–8.15 (2H, m) and 7.2–7.7 (7H, m); δ_C (50 MHz) 190.0 (C=O), 136.9 (2C), 136.5 (C-Cl), 134.5, 130.1 (2C), 129.9 (4ry), 129.4 (2C), 128.1 (2C) and 126.4 (4ry); ν_{max} 1680, 1210, 1180, 1100, 1020, 900, 825, 780 and 690 cm^{-1}; m/z 250 (^{37}Cl-M^+, 3%), 248 (^{35}Cl-M^+, 10), 226 (4), 198 (2), 176 (4), 145 (6, $^{37}ClC_6H_4S^+$), 143 (18, $^{35}ClC_6H_4S^+$), 122, (6), 105 (100), 91 (75) and 77 (92).

iii Preparation of 4-methylphenyl thiolobenzoate **351**

A solution of benzoyl chloride (11.3 g, 80 mmol) in dry toluene was added dropwise to a solution of 4-methylthiophenol (10.0 g, 81 mmol) and triethylamine (8.2 g, 11.3 ml, 81 mmol) in dry toluene (100 ml) and the mixture was stirred for thirty minutes. Filtration, washing with water, drying and evaporation gave 4-methylphenyl thiolobenzoate **351** (8.4 g, 45%) as colourless crystals. m.p. 65°C (Found: C, 73.7; H, 5.6; m/z = 228.0612. $C_{14}H_{12}OS$ requires C, 73.7; H, 5.3%; 228.0609); δ_H (200 MHz)

8.02 and 7.18 (4H, AB pattern, J = 9 Hz), 7.35–7.55 (5H, m) and 2.34 (3H, s); δ_C (50 MHz) 191.0 (C=O), 140.3 (4ry), 137.3 (4ry), 135.7 (2C), 134.2, 130.7 (2C), 129.4 (2C), 128.1 (2C), 124.5 (4ry) and 22.0; ν_{max} (CH_2Cl_2) 3030, 2920, 2870, 1670, 1605, 1590, 1500, 1460, 1410, 1310, 1210, 1185, 1105, 1030, 910 and 820 cm^{-1}; m/z 228 (M^+, 15%), 123 (5), 105 (100), 91 (4) and 77 (65).

e FVP of thiolobenzoates

i FVP of 4-chlorophenyl thiolobenzoate **350**

FVP of the title compound (1.81 g) [500°C, 2 x 10^{-3} torr, 100°C] gave a colourless solid which was shown by ^1H and ^{13}C NMR to be the starting material (1.7 g, 96%) and toluene.

ii FVP of 4-methylphenyl thiolobenzoate **351**

FVP of the title compound (3.48 g) [500°C, 5 x 10^{-3} torr, 100°C] gave a pale yellow solid which was shown by ^1H and ^{13}C NMR to be the unchanged starting material (3.0 g, 87%).

f Reaction of triphenylphosphine and triphenylphosphine oxide with thiobenzophenones

i Triphenylphosphine and thiobenzophenone

Triphenylphosphine (0.03 g, 0.1 mmol) was added to an NMR tube containing thiobenzophenone (0.2 g, 10 mmol) in $CDCl_3$. The blue colour of the thioketone persisted, even after 4 days, but the ^{31}P NMR spectrum

showed that the phosphine had been almost entirely converted to triphenylphosphine sulphide (δ_P +42.8).

ii Triphenylphosphine oxide and 4-methylthiobenzophenone

4-methylthiobenzophenone (0.72 g, 3 mmol) was stirred in chloroform and triphenylphosphine oxide (1.0 g, 3 mmol) was added. There appeared to be no colour diminution after 16 h so a further equivalent of triphenylphosphine oxide was added. After 16 days the colour had disappeared. The solvent was evaporated to give a waxy solid which was separated by column chromatography (silica, 2 Et_2O:1 40–60 petroleum ether) into two components, triphenylphosphine oxide (δ_P +28.9) and 4-methylbenzophenone (δ_H identical to authentic sample spectra).

g FVP of sulphides

i FVP of benzyl 4-methylphenyl sulphide **353**

FVP of the title compound (0.2614 g) [500°C, 1.3 x 10^{-2} torr, 20C] gave a colourless band in the cold trap and a larger amount of colourless solid in the furnace exit. Both fractions were collected together and were shown by ^1H and ^{13}C NMR to be the unchanged starting compound (60% by calibration with CH_2Cl_2)

ii FVP of benzyl 4-chlorophenyl sulphide **352**

FVP of the title compound (0.3097 g) [500°C, 1.2 x 10^{-2} torr, 40C] to give a colourless band in the cold trap and a larger amount of colourless solid in

the furnace exit. Both fractions were collected together and were shown by ^{1}H and ^{13}C NMR to be the unchanged starting compound (85% by calibration with CH_2Cl_2)

F Preparation and pyrolysis of [(alkanesulphinyl)alkylidene]triphenyl phosphoranes

1 Preparation

i Preparation of [(ethanesulphinyl)benzylidene]triphenylphosphorane **355**

Benzyltriphenylphosphonium chloride (10.0 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 10.3 ml, 26 mmol) was added and the mixture was stirred for 30 min. Ethanesulphinyl chloride (1.5 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of [(ethanesulphinyl) benzylidene]triphenylphosphorane **355** (1.3 g, 23%). m.p. 169–72°C (Found: C, 75.4; H, 5.9; m/z = 412.1436. $C_{27}H_{25}OPS$ requires C, 75.7; H, 5.9%; $M^+ - O$, 412.1415); δ_P +19.7; δ_H (200 MHz) 6.9–7.7 (20H, m), 2.85 (2H, q, J = 8 Hz) and 1.07 (3H, t, J = 8 Hz); δ_C (75 MHz) 137.1 (d, J = 14 Hz), 134.2 (6C, d, $^{2}J_P$ = 10 Hz), 131.9 (3C, d, $^{4}J_P$ = 2 Hz), 131.5 (2C, d, J = 6 Hz), 128.6 (6C, d, $^{3}J_P$ = 12 Hz), 127.7 (3C, d, $^{1}J_P$ = 86 Hz), 127.8 (2C), 124.0, 47.9 (d, J = 126 Hz), 45.2 (d, J = 12 Hz) and 10.1; ν_{max} 1591, 1489, 1436, 1255, 1240, 1101, 1093, 999, 977 and 754 cm^{-1}; m/z 412 ($M^+ - O$, 5%), 383 (10), 351 (1), 300 (277), 262 (12%), 183 (32), 121 (100).

ii Preparation of [(2-propanesulphinyl)benzylidene] triphenylphosphorane **227**

Benzyltriphenylphosphonium chloride (10.0 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 10.3 ml, 26 mmol) was added and the mixture was stirred for 30 min. A solution of 2-propanesulphinyl chloride (1.6 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave orange crystals of (2-propanesulphinyl)benzylidene]triphenylphosphorane **227** (1.1 g, 19%). m.p. 145–8°C (Found: C, 75.6; H, 5.8. $C_{28}H_{27}OPS$ requires C, 76.0; H, 6.1%); δ_P +20.2; δ_H (200 MHz) 6.9–7.7 (20H, m), 3.08 (1H, septet of d, J = 8 Hz, J_P = 2 Hz), 1.25 (3H, dd, J = 8 Hz, 1 Hz) and 1.08 (3H, d, J = 8 Hz); δ_C (50 MHz) 137.3 (d, J = 11 Hz), 134.3 (6C, d, ^2J_P = 10 Hz), 132.0 (3C, d, ^4J_P = 2 Hz), 131.9 (2C, d, J = 5 Hz), 128.6 (6C, d, ^3J_P = 12 Hz), 127.7 (2C), 127.5 (3C, d, ^1J_P = 89 Hz), 124.1, 49.6 (d, J = 12 Hz), 47.2 (d, J = 123 Hz), 19.0 and 18.7; ν_{max} 1570, 1180, 1105, 1090, 980, 915, 745, 715 and 685 cm^{-1}; m/z 426 (M^+ – O, 1%), 400 (12), 399 (41), 263 (43), 262 (71), 183 (78), 121 (76) and 105 (100).

iii Preparation of [(phenylmethanesulphinyl)benzylidene]triphenyl phosphorane **356**

Benzyltriphenylphosphonium chloride (7.1 g, 18 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 7.3 ml, 18 mmol) was added and the mixture was stirred for 30 min.

Phenylmethanesulphinyl chloride (1.6 g, 9.1 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 2 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of slightly impure [(phenylmethanesulphinyl)benzylidene]triphenylphosphorane **356** (0.2 g, 4%). m.p. 159°C (Found: C, 75.1; H, 5.3. $C_{32}H_{27}OPS$ requires C, 78.6; H, 5.6%;); δ_P +18.7; δ_H (80 MHz) 7.0–8.0 (25H, m) and 4.60 (1H, half of AB pattern of d, J = 13 Hz, 2 Hz), 4.13 (1H, half of AB pattern, J = 13 Hz) [plus impurities of ethyl acetate and toluene]; δ_C (75 MHz) 138.3 (4ry, d, J = 12 Hz), 134.0 (6C, d, ^2J_P = 10 Hz), 133.2 (4ry), 132.1 (3C), 131.9 (2C, d, J = 5 Hz), 130.5 (2C), 128.6 (6C, d, ^3J_P = 12 Hz), 128.4 (2C), 127.9 (2C), 127.0 (3C, d, ^1J_P = 90 Hz), 127.0, 123.5, 56.3 (d, J = 12 Hz) and 47.1 (d, J = 128 Hz); ν_{max} 1580, 1430, 1300, 1250, 1180, 1100, 990, 925, 750, 710 and 685 cm^{-1}; m/z 455 (1%, impurity), 415 (3), 399 (M^+ – $PhCH_2$, 4), 398 (23), 382 (10), 366 (4), 351 (8), 303 (2), 294 (4), 277 (10), 262 (58), 183 (100), 152 (20), 105 (95) and 77 (98).

iv Attempted preparation of [(phenylmethanesulphinyl)ethylidene] triphenylphosphorane

Ethyltriphenylphosphonium bromide (10.0 g, 27 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 10.3 ml, 26 mmol) was added and the mixture was stirred for 20 min. Phenylmethanesulphinyl chloride (2.4 g, 14 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a few very small crystals δ_P +30.56.

Evaporation of the ethyl acetate gave a solid that was mostly triphenylphosphine oxide, δ_P 28.5, and triphenylphosphine, δ_P –5.5, with minor components δ_P 43.0 ($Ph_3P=S$), 35.7, 33.6 and 30.7.

v Attempted preparation of [(ethanesulphinyl)ethylidene]triphenylphosphorane

Ethyltriphenylphosphonium chloride (10.0 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 10.3 ml, 26 mmol) was added and the mixture was stirred for 20 min. Ethanesulphinyl chloride (1.5 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration and evaporation, followed by trituration with ethyl acetate, gave no crystals. The ethyl acetate was evaporated to give a residue which was mostly triphenylphosphine oxide and triphenylphosphine but had a minor component δ_P +33.4.

vi Attempted preparation of [(methanesulphinyl)benzylidene]triphenyl phosphorane

Benzyltriphenylphosphonium chloride (7.5 g, 19 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 12.0 ml, 19 mmol) was added and the mixture was stirred for 30 min. Methanesulphinyl chloride (1.9 g, 19 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 3 h. Filtration, evaporation and

trituration with ethyl acetate gave crystals of triphenylphosphine oxide and triphenylphosphine.

vii Attempted preparation of [(ethanesulphinyl)-4-methoxybenzylidene] triphenylphosphorane

A solution of n-butyl lithium (2.5M, 9.6 ml, 24 mmol) was added to a solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. Ethanesulphinyl chloride (1.3 g, 12 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a solid which contained triphenylphosphine sulphide, the phosphonium salt and two unidentified compounds, δ_P +20.6 and +18.0.

viii Attempted preparation of [(2-propanesulphinyl)-4-methoxy benzylidene]triphenylphosphorane

A solution of n-butyl lithium (1.6M, 13.5 ml, 22 mmol) was added to a solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. A solution of 2-propanesulphinyl chloride (1.4 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration and evaporation gave a product which contained triphenylphosphine oxide, triphenylphosphine sulphide, triphenyl

phosphine, and at least 3 other products, including a minor one at δ_P +18.0 which may have been the desired product.

ix Attempted preparation of [(phenylmethanesulphinyl)-4-methoxy benzylidene]triphenylphosphorane

A solution of n-butyl lithium (2.5M, 8.6 ml, 22 mmol) was added to a solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. Phenylmethanesulphinyl chloride (1.9 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a yellow powder which was mostly triphenylphosphine oxide and an unknown compound that contained the 4-methoxyphenyl group together with smaller amounts of triphenylphosphine and the phosphonium salt.

x Attempted preparation of [(ethanesulphinyl)-4-nitrobenzylidene] triphenylphosphorane

A solution of n-butyl lithium (2.5M, 4.6 ml, 11 mmol) was added to a solution of (4-nitrobenzyl)triphenylphosphonium bromide (5.0 g, 10 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. Ethanesulphinyl chloride (0.7 g, 6 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave triphenylphosphine oxide with a small amount of triphenylphosphine.

xi Attempted preparation of [(2-propanesulphinyl)-4-nitrobenzylidene] triphenylphosphorane

A solution of n-butyl lithium (2.5M, 4.6 ml, 11 mmol) was added to a solution of (4-nitrobenzyl)triphenylphosphonium bromide (5.0 g, 10 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. A solution of 2-propanesulphinyl chloride (0.7 g, 6 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a solid which contained triphenylphosphine oxide, triphenylphosphine sulphide and triphenylphosphine together with a purely aliphatic compound.

xii Attempted preparation of [(phenylmethanesulphinyl)-4-nitro benzylidene]triphenylphosphorane

A solution of n-butyl lithium (2.5M, 8.4 ml, 21 mmol) was added to a solution of (4-nitrobenzyl)triphenylphosphonium bromide (5.0 g, 10 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. Phenylmethanesulphinyl chloride (1.8 g, 10 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave an oil which contained triphenylphosphine sulphide, triphenylphosphine oxide, triphenyl phosphine, two different phosphonium salts and an unknown compound, δ_P +10.5.

2 FVP of [(alkanesulphinyl)benzylidene]triphenyl phosphoranes

a FVP of [(ethanesulphinyl)benzylidene]triphenylphosphorane 355

FVP of the title compound (0.1106g) [500°C, 5 x 10^{-3} torr, 50°C] gave yellow droplets in the cold trap [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{13}C (75 MHz) and ^{13}P NMR indicated the presence of

PhCOSEt, (53% yield) R_T 6.40, m/z 166 (4%), 105 (100), 77 (98) and 51 (85); δ_H 8.1–7.9 (2H, m), 7.5–7.3 (3H, m), 3.08 (2H, q, J = 7 Hz) and 1.35 (3H, t, J = 8 Hz); δ_C 192.1 (C=O), 133.2, 131.9, 128.6 (2C), 127.1 (2C), 23.4 and 14.8.

Ph_3P, R_T 11.45, peak height 60 units, m/z 262 (10%), 183 (59), 152 (19) and 108 (100); δ_H 7.3 (m); δ_C 137.1 (3C, d, J = 10 Hz), 133.7 (6C, d, J = 19 Hz), 128.6 (6C, d, J = 11 Hz) and 128.5 (3C).

$Ph_3P{=}O$, R_T 14.41, peak height 11 units, m/z 277 (8%), 199 (7), 183 (8) and 112 (11); δ_C 132.4 (3C, d, J = 104 Hz), 132.1 (6C, d, J = 10 Hz), 131.9 (3C) and 128.5 (6C, d, J = 12 Hz).

$Ph_3P{=}S$, R_T 15.24, 5 units, m/z 294 (6%), 262 (5), 183 (53) and 107 (50).].

b FVP of [(2-propanesulphinyl)benzylidene]triphenyl phosphorane 227

FVP of the title compound (0.1088g) [500°C, 5 x 10^{-3} torr, 50°C] gave colourless droplets at the furnace exit and cold trap. These were collected together. [GCMS (60-20-300) and ^{1}H (200 MHz) indicated the presence of

PhCOS^{i}Pr, (37% yield) R_T = 6.17, m/z 180 (4%), 105 (100), 77 (82) and 51 (63); δ_H 7.4–8.1 (5H, m), 3.88 (1H, septet, J = 7 Hz) and 1.44 (6H, d, J = 7 Hz).

Ph_3P, R_T = 11.08, m/z 262 (42%), 183 (100), 152 (22) and 108 (88), peak height 84 units.

$Ph_3P=O$, R_T = 13.41, m/z 277 (36%), 199 (22), 183 (23) and 152 (26), peak height 9 units.

$Ph_3P=S$, R_T = 14.17, m/z 294 (22%), 262 (8), 215 (5) and 183 (100), peak height 7 units.]

c FVP of [(phenylmethanesulphinyl)benzylidene]triphenyl phosphorane 356

i FVP of [(phenylmethanesulphinyl)benzylidene]triphenylphosphorane

FVP of the title compound (0.0643g) [500°C, 8 x 10^{-2} torr, 50°C] gave a yellow solid at the furnace exit [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{31}P NMR indicated the presence of Ph_3P, $Ph_3P=O$ and $Ph_3P=S$ in the ratio 30:23:7

Ph_3P, δ_P = –5.4.

$Ph_3P=O$, δ_P = +28.8.

$Ph_3P=S$, δ_P = +43.1.

$PhCH_2SCOPh$, (30% yield) R_T = 10.17, m/z 228 (4%), 105 (100) and 77 (68); δ_H 4.35.

E-stilbene, (8% yield), R_T = 10.57, m/z 180 (98%), 179 (100), 165 (68) and 89 (48).

Z-stilbene, (2% yield), R_T = 9.40, m/z 180 (82%), 179 (100), 165 (62) and 89 (70).

$(PhCH_2)_2S$, (2% yield), R_T = 11.49, m/z 214 (7%), 123 (25), 91 (100) and 77 (10).].

ii Preparation of benzyl thiolobenzoate

Phenylmethanethiol (10.0 g, 81 mmol), and triethylamine (8.3 g, 82 mmol) were stirred in dry toluene (100 ml). Benzoyl chloride (11.3 g, 82 mmol) in dry toluene (10 ml) was added dropwise. Filtration, washing with water, drying, evaporation and kugelrohr distillation gave benzyl thiolobenzoate **358** (5.9 g, 32%). b.p. 110°C (oven temp.) at 2mmH g, m.p. 34–36°C (lit.,[212] m.p. 39.5°C); δ_H (80 MHz) 8.0–8.2 (2H, m), 7.2–7.6 (8H, m) and 4.35 (2H, s); GCMS showed one major component, M^+ 228, which was correct for the title compound.

G Preparation and pyrolysis of alkane- and arenesulphonyl aryl diazomethanes

1 Preparation of sulphides

These were not purified since they were oxidised straight away to sulphones and sulphides.

i Preparation of benzyl ethyl sulphide **361**

Sodium metal (2.0 g, 87 mmol) was dissolved in ethanol (100 ml) and ethanethiol (5.4 g, 87 mmol) was added. Benzyl chloride (11.0 g, 87

mmol) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying, evaporation and kugelrohr distillation gave benzyl ethyl sulphide **361** as a colourless liquid (7.3 g, 69%). b.p. 107°C (oven temp.) at 2 mmHg (lit.,[213] 222–3°C at 759 mmHg); δ_H (200 MHz) 7.2–7.4 (5H, m), 3.70 (2H, s), 2.42 (2H, q, J = 8 Hz) and 1.23 (3H, t, J = 8 Hz).

ii Preparation of benzyl 2-propyl sulphide **362**

Sodium metal (3.0 g, 130 mmol) was dissolved in ethanol (100 ml) and propane-2-thiol (10.0 g, 131 mmol) was added. Benzyl chloride (16.6 g, 131 mmol) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying, evaporation and kugelrohr distillation gave benzyl 2-propyl sulphide **362** as a colourless liquid (9.1 g, 42%). b.p. 110°C (oven temp.) at 2 mmHg (lit.,[214] 99–104°C at 14 mmHg); δ_H (200 MHz) 7.1–7.3 (5H, m), 3.60 (2H, s), 2.66 (1H, septet, J = 8 Hz) and 1.13 (6H, d, J = 8 Hz); δ_C (50 MHz) 139.6 (4ry), 129.5 (2C), 129.0 (2C), 127.4, 35.8, 34.7 and 23.9 (2 x CH_3).

iii Preparation of benzyl phenyl sulphide **363**

Sodium metal (6.3 g, 270 mmol) was dissolved in ethanol (100 ml) and thiophenol (30.0 g, 270 mmol) was added. Benzyl chloride (34.5 g, 270 mmol) was added dropwise and the mixture was stirred for for 12 h.

Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying, evaporation and recrystallisation from ethanol gave benzyl phenyl sulphide **363** as a white solid (33.1 g, 61%). m.p. 40–41°C (lit.,[215] 44.5°C); δ_H (200 MHz) 7.1–7.3 (10H, m) and 4.07 (2H, s); δ_C (50 MHz) 137.4 (4ry), 136.3 (4ry), 129.7 (2C), 128.8 (4C), 128.5 (2C), 127.1, 126.3 and 39.0.

iv Preparation of dibenzyl sulphide **364**

Sodium metal (1.9 g, 81 mmol) was dissolved in ethanol (100 ml) and phenylmethanethiol (10.0 g, 81 mmol) was added. Benzyl chloride (10.2 g, 81 mmol) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying and evaporation gave a yellow solid. This was kugelrohr sublimed (180°C (oven temp.) at 3 mmHg) to give dibenzyl sulphide **364** as a white solid (10.4 g, 60%). m.p. 44–47°C (lit.,[216] 44°C); δ_H (200 MHz) 7.1–7.4 (10H, m) and 3.56 (4H, s); δ_C (50 MHz) 138.1 (2C, 4ry), 128.9 (4C), 128.4 (4C), 126.9 (2C) and 35.4 (2C).

v Preparation of benzyl 4-methylphenyl sulphide **353**

Sodium metal (0.4 g, 17 mmol) was dissolved in ethanol (50 ml) and 4-methyl thiophenol (2.0 g, 16 mmol) was added. Benzyl chloride (2.0 g, 16 mmol) in ethanol (10 ml) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying and

evaporation gave benzyl 4-methylphenyl sulphide **353** as a colourless solid (1.0 g, 30%). m.p. 38–43°C (lit.,[217] 44°C); δ_H (200 MHz) 7.1–7.5 (9H, m), 4.20 (2H, s) and 2.42 (3H, s); δ_C (50 MHz) 138.4 (4ry), 137.1 (4ry), 133.2 (4ry), 131.2, (2C), 130.3 (2C), 129.5 (2C), 129.1 (2C), 127.7, 40.3 and 21.7.

vi Preparation of benzyl 4-chlorophenyl sulphide **352**

Sodium metal (0.4 g, 17 mmol) was dissolved in ethanol (50 ml) and 4-chloro thiophenol (2.0 g, 16 mmol) was added. Benzyl chloride (2.0 g, 16 mmol) in ethanol (10 ml) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying and evaporation gave benzyl 4-chlorophenyl sulphide **352** as a colourless solid (1.4 g, 38%). m.p. 45–49°C (lit.,[218] 52–53°C); δ_H (200 MHz) 7.1–7.3 (9H, m) and 4.05 (2H, s); δ_C (50 MHz) 137.6 (4ry), 135.3 (4ry), 133.0 (4ry), 131.9, (2C), 129.5 (2C), 129.3 (2C) 129.1 (2C), 127.9 and 39.8.

vii Preparation of 4-methoxybenzyl phenyl sulphide **365**

Sodium metal (0.5 g, 22 mmol) was dissolved in ethanol (100 ml) and thiophenol (2.2 g, 20 mmol) was added. A solution of 4-methoxybenzyl bromide (4.0 g, 20 mmol) in ethanol (50 ml) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying and evaporation gave 4-methoxybenzyl phenyl sulphide **365** as a colourless

solid (1.4 g, 28%). m.p. 85–86°C (lit.,[217] 85–86°C); δ_H (200 MHz) 7.1–7.4 (7H, m), 6.82 (2H, half of AB pattern, J = 8 Hz), 4.06 (2H, s) and 3.75 (3H, s); δ_C (50 MHz)159.3 (4ry), 137.1 (4ry), 130.5 (2C), 130.3 (2C), 129.9 (4ry), 129.3 (2C), 126.8, 114.4 (2C), 55.8 and 38.9.

viii Preparation of 4-nitrobenzyl phenyl sulphide **366**

Sodium metal (0.9 g, 39 mmol) was dissolved in ethanol (50 ml) and thiophenol (4.2 g, 38 mmol) was added. 4-Nitrobenzyl bromide (8.2 g, 38 mmol) in ethanol (50 ml) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (2 x 100 ml), drying and evaporation gave a yellow solid. Kugelrohr sublimation gave 4-nitrobenzyl phenyl sulphide **366** as a colorless solid (6.1 g, 65%). m.p. 73–5°C (lit.,[219] 72°C); δ_H (200 MHz) 8.07 and 7.35 (4H, AB pattern, J = 8 Hz), 7.2–7.3 (5H, m) and 4.13 (2H, s); δ_C 147.5 (4ry), 146.1 (4ry), 135.1 (4ry), 131.4 (2C), 130.1 (2C), 129.6 (2C), 127.8, 124.2 (2C) and 39.4.

2 Preparation of sulphoxides

i Preparation of benzyl ethyl sulphoxide **367**

Ethyl benzyl sulphide (2.0 g, 13 mmol) was stirred in methanol (20 ml) and a solution of sodium metaperiodate (3.2 g, 15 mmol) in water (20 ml) was added dropwise and the mixture was stirred for 12 h. Filtration followed by extraction of the product into dichloromethane, drying and evaporation gave benzyl ethyl sulphoxide **367** (0.8 g, 36%). m.p. 44–5°C

(lit.,[215] 49°C); δ_H (200 MHz) 7.2–7.4 (5H, m), 3.95 and 4.02 (AB pattern, J = 10 Hz), 2.62 (2H, m) and 1.32 (3H, t, J = 7 Hz)

ii Preparation of benzyl 2-propyl sulphoxide **368**

Benzyl 2-propyl sulphide (2.0 g, 12 mmol) was stirred in methanol (20 ml) and a solution of sodium metaperiodate (2.7 g, 13 mmol) in water (20 ml) was added dropwise and the mixture was stirred for 12 h. Filtration followed by extraction of the product into dichloromethane, drying and evaporation gave 2-propyl benzyl sulphoxide **368** (1.1 g, 56%). m.p. 24–5°C (lit.,[220] 25°C); δ_H (200 MHz) 7.2–7.4 (5H, m), 3.88 (2H, s), 2.63 (1H, septet, J = 7 Hz), 1.30 (3H, d, J = 7 Hz) and 1.25 (3H, d, J = 7 Hz).

iii Preparation of benzyl phenyl sulphoxide **369**

Benzyl phenyl sulphide (10.0 g, 50 mmol) was stirred in methanol (100 ml) and sodium metaperiodate (11.2 g, 52 mmol) in water (37 ml) was added dropwise and the mixture was stirred for 12 h. Filtration, extraction of the product into dichloromethane, drying and evaporation gave benzyl phenyl sulphoxide **369** (7.9 g, 73%). m.p. 123–5°C (lit.,[221] 125°C); δ_H (200 MHz) 6.9–7.5 (10H, m) and 4.09 and 3.97 (2H, AB pattern, J = 12.5 Hz); δ_C (50 MHz) 142.7 (4ry), 131.1, 130.3 (2C), 129.1 (4ry), 128.8 (2C), 128.4 (2C), 128.2, 124.4 (2C) and 63.5.

iv Preparation of dibenzyl sulphoxide **370**

A solution of dibenzyl sulphide (4.0 g, 19 mmol) in methanol (50 ml) was stirred and a solution of sodium metaperiodate (4.4 g, 20 mmol, 1.05eq) in methanol (150 ml) was added and the mixture was stirred for 36 h. The mixture was evaporated and the residue taken up into dichloromethane. Washing with water, drying and evaporation gave dibenzyl sulphoxide **370** (2.5 g, 58%). m.p. 134–6°C (lit.,[222] 134°C); δ_H (200 MHz) 7.3–7.5 (10H, m) and 3.95 and 3.87 (4H, AB pattern, J = 15 Hz); δ_C (50 MHz) 130.1 (4C + 2C, 4ry), 138.9 (4C), 128.3 (2C) and 57.2 ($2CH_2$).

v Preparation of benzyl 4-methylphenyl sulphoxide **371**

Benzyl 4-methylphenyl sulphide (5.0 g, 23 mmol) was stirred in methanol (20 ml) and sodium metaperiodate (5.3 g, 25 mmol) in water (20 ml) was added dropwise and the mixture was stirred for 12 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give benzyl 4-methylphenyl sulphoxide **371** (3.2 g, 59%). m.p. 135–7°C (lit.,[223] 139–40°C); δ_H (200 MHz) 6.9–7.4 (9H, m), 4.05 and 3.95 (2H, AB pattern, J = 12.5 Hz) and 2.38 (3H, s); δ_C (50 MHz) 141.6 (4ry), 139.5 (4ry), 130.3 (2C), 129.5 (2C), 129.3 (4ry), 128.4 (2C), 128.2, 124.4 (2C), 63.7 (CH_2) and 21.4.

vi Preparation of benzyl 4-chlorophenyl sulphoxide **372**

Benzyl 4-chlorophenyl sulphide (0.5 g, 2 mmol) was stirred in water (20 ml) and sodium metaperiodate (0.6 g, 2 mmol) in methanol (20 ml) was

added and the mixture was stirred for 12 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give benzyl 4-chlorophenyl sulphoxide **372** (0.3 g, 54%). m.p. 133–134°C (lit.,[224] 134); δ_H (200 MHz) 7.4–7.1 (7H, m), 7.0–6.8 (2H, m), 4.07 and 3.95 (2H, AB pattern, J = 12.5 Hz); δ_C (50 MHz) 141.2 (4ry), 137.3 (4ry), 130.3 (2C), 129.1 (2C), 128.6 (4ry), 128.5 (2C), 128.4, 125.8 (2C) and 63.4

vii Preparation of 4-methoxybenzyl phenyl sulphoxide **373**

4-Methoxybenzyl phenyl sulphide (1.0 g, 4.6 mmol) was stirred in methanol (200 ml) and sodium metaperiodate (1.0 g, 5 mmol) in water (20 ml) was added and the mixture was stirred for 12 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give 4-methoxybenzyl phenyl sulphoxide **373** (0.34 g, 32%). m.p. 138–9°C (Found: C, 68.4; H, 5.6; m/z 231.0823. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7%; $M^+ + H - O$, 231.0844); δ_H (200 MHz) 7.5–7.3 (5H, m), 6.90 and 6.78 (4H, AB pattern, J = 10 Hz), 4.02 and 3.95 (2H, AB pattern, J = 12.5 Hz) and 3.78 (3H, s); δ_C (50 MHz) 159.7 (4ry), 142.9 (4ry), 131.6 (2C), 131.1, 128.8 (2C), 124.5 (2C), 121.0 (4ry), 113.9 (2C), 62.9 (CH_2) and 55.3; ν_{max} 1600, 1500, 1295, 1245, 1165, 1100, 1025, 825, 750, 730 and 680 cm^{-1}; m/z 231 ($M^+ + H - O$, 5%), 121 (100), 106 (10), 91 (28), 77 (50), 65 (15) and 51 (32).

viii Preparation of 4-nitrobenzyl phenyl sulphoxide **374**

4-Nitrobenzyl phenyl sulphide (3.0 g, 12 mmol) was stirred in methanol (150 ml) and sodium metaperiodate (2.8 g, 12 mmol, 1.05eq) in water (150 ml) was added and the mixture was stirred for 36 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give a colourless solid which was recrystallised from ether/dichloromethane gave 4-nitrobenzyl phenyl sulphoxide **374** (1.0 g, 31%). m.p. 154–6°C (lit.,[225] 153–5°C); δ_H (200 MHz) 8.07 and 7.11 (4H, AB pattern, J = 8 Hz), 7.5-7.3 (5H, m) and 4.20 and 4.04 (2H, AB pattern, J = 16 Hz).

3 Preparation of sulphones

i Preparation of benzyl ethyl sulphone **375**

This was prepared by the method discovered by Mesher[226]. Benzyl ethyl sulphide (2.0 g, 13 mmol), benzoic acid (1.6 g, 13 mmol) and benzyl triethylammonium chloride (0.48 g, 2.2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (4.2 g, 26 mmol) in water (100 ml) was added and the mixture was stirred for 3 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 200 ml), aqueous sodium hydroxide (2M, 200 ml) and saturated brine (200 ml), drying, evaporation and recrystallisation of the residue from ethanol gave benzyl ethyl sulphone **375** (1.6 g, 66%). m.p. 83°C (lit.,[213] 84°C); δ_H (200

MHz) 7.38 (5H, s), 4.22 (2H, s), 2.86 (2H, q, J = 8 Hz) and 1.35 (3H, t, J = 8 Hz); δ_C (50 MHz) 130.5 (2C), 129.0 (2C), 129.0, 128.1 (4ry), 58.7, 45.5 and 6.4.

ii Preparation of benzyl 2-propyl sulphone **376**

Benzyl 2-propyl sulphide (3.0 g, 18 mmol), benzoic acid (2.2 g, 18 mmol) and benzyl triethylammonium chloride (0.7 g, 3 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (5.7 g, 36 mmol, 2 equivs) in water (100 ml) was added and the mixture was stirred for 3 days. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 200 ml), aqueous sodium hydroxide (2M, 200 ml) and saturated brine (200 ml), drying, evaporation of the dichloromethane and recrystallisation from ethanol gave benzyl 2-propyl sulphone **376** (1.2 g, 34%). m.p. 65–7°C (lit.,[227] 65°C); δ_H (200 MHz) 7.3–7.5 (5H, m), 4.20 (2H, s), 3.00 (1H, septet, J = 8 Hz) and 1.37 (6H, d, J = 8 Hz); δ_C (50 MHz) 130.6 (2C), 129.0 (2C), 128.8, 127.9 (4C), 56.1 (Ph$\underline{C}H_2$), 51.1 and 15.2 (2C).

iii Preparation of dibenzyl sulphone **377**

Dibenzyl sulphide (3.0 g, 15 mmol), benzoic acid (1.7 g, 14 mmol) and benzyl triethylammonium chloride (0.5 g, 2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (4.4 g, 28 mmol) in water (100 ml) was added and the mixture was stirred for 12 h.

Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and recrystallisation from ethanol gave dibenzyl sulphone **377** (2.7 g, 78%). m.p. 150°C (lit.,[228] 150°C); δ_H (200 MHz) 7.38 (10H, s) and 4.12 (4H, s); δ_C (50 MHz) 130.9 (4C), 128.93 (2C), 128.90 (4C), 127.5 (2C, 4ry) and 58.0 (2C).

iv Preparation of benzyl 4-chlorophenyl sulphone **378**

Benzyl 4-chlorophenyl sulphide (1.0 g, 4 mmol), benzoic acid (0.5 g, 4 mmol) and benzyl triethylammonium chloride (0.2 g, 1 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (1.4 g, 9 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and recrystallisation from ethanol gave benzyl 4-chlorophenyl sulphone **378** (0.7 g, 63%). m.p. 157–8°C (lit.,[229] 157–8°C); δ_H (200 MHz) 7.0–7.6 (9H, m) and 4.30 (2H, s); δ_C (50 MHz) 140.5 (4ry), 136.3 (4ry), 130.8 (2C), 130.1 (2C), 129.2 (2C), 128.9, 128.7 (2C), 127.9 (4ry) and 62.9.

v Preparation of 4-nitrobenzyl phenyl sulphone **379**

Benzoic acid (1.0 g, 8 mmol), 4-nitrobenzyl phenyl sulphide (2.0 g, 8 mmol) and benzyl triethylammonium chloride (0.3 g, 1 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (2.6 g, 16 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and recrystallisation from ethanol gave 4-nitrobenzyl phenyl sulphone **379** (1.6 g, 69%). m.p. 212–24°C (lit.,[230] 209.5–210.5°C); δ_H (200 MHz) 8.15 and 7.32 (4H, AB pattern, J = 14 Hz), 7.7–7.8 (3H, m), 7.5–7.6 (2H, m) and 4.42 (2H, s).

vi Preparation of methyl (ethanesulphonyl)acetate **380**

Methyl (ethanesulphenyl)acetate (4.0 g, 30 mmol), benzoic acid (3.6 g, 30 mmol) and benzyltriethylammonium chloride (1.1 g, 5 mmol,) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (9.2 g, 58 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr

distillation gave methyl (ethanesulphonyl)acetate **380** (3.9 g, 79%). m.p. 40°C (lit.,[231] 42–4°C); δ_H (200 MHz) 4.02 (2H, s), 3.83 (3H, s), 3.28 (2H, q, J = 7 Hz) and 1.43 (3H, t, J = 7 Hz); δ_C (50 MHz) 163.6 (C=O), 56.4, 53.3, 48.1 and 6.5.

vii Preparation of ethyl (ethanesulphonyl)acetate **382**

Ethyl (ethanesulphenyl)acetate (2.0 g, 14 mmol), benzoic acid (1.7 g, 14 mmol) and benzyl triethylammonium chloride (0.5 g, 2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (4.4 g, 28 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr distillation gave ethyl (ethanesulphonyl)acetate **382** (1.6 g, 66%). b.p. 161°C (oven temp.) at 0.7 mmHg (lit.,[232] 110°C at 0.3 mmHg °C); δ_H (200 MHz) 4.30 (2H, q, J = 7 Hz), 4.02 (2H, s), 3.30 (2H, q, J = 7 Hz), 1.43 (3H, t, J = 7 Hz) and 1.35 (3H, t, J = 7 Hz); δ_C (50 MHz) 162.7 (C=O), 62.1 (OCH_2), 56.2 ($SCH_2C{=}O$), 47.6 (SCH_2), 13.5 ($OCH_2\underline{C}H_3$) and 6.1 ($SCH_2\underline{C}H_3$).

viii Preparation of methyl (benzenesulphonyl)acetate **381**

Methyl (benzenesulphinyl)acetate (2.0 g, 11 mmol), benzoic acid (1.3 g, 11 mmol) and benzyl triethylammonium chloride (0.4 g, 2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (3.5 g, 22 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr distillation gave methyl (benzenesulphonyl)acetate **381** (1.4 g, 60%). b.p. 160°C (oven temp.) at 0.3 mmHg (lit.,[233]145°C at 0.01 mmHg); δ_H (200 MHz) 7.9–8.0 (2H, m), 7.5–7.8 (3H, m), 4.17 (2H, s) and 3.65 (3H, s); δ_C (50 MHz) 162.9 (C=O), 138.7 (4ry), 134.4, 129.3 (2C), 128.4 (2C), 60.7 (CH_2) and 53.0.

ix Preparation of ethyl (benzenesulphonyl)acetate **383**

Ethyl (benzenesulphinyl)acetate (2.0 g, 10 mmol), benzoic acid (1.1 g, 9 mmol) and benzyl triethylammonium chloride (0.3 g, 1 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (2.8 g, 18 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine

dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr distillation gave ethyl (benzenesulphonyl)acetate **383** (1.3 g, 52%). b.p. 155°C (oven temp.) at 0.3 mmHg (lit.,[234] 134–5°C at 0.01 mmHg); δ_H (200 MHz) 7.9–8.0 (2H, m), 7.5-7.8 (3H, m), 4.18 (2H, s), 4.11 (2H, q, J = 8 Hz) and 1.13 (3H, t, J = 8 Hz); δ_C (50 MHz) 161.9 (C=O), 138.3 (4ry), 133.8 , 128.8 (2C), 128.0 (2C), 61.7 (OCH_2), 60.4 (SCH_2) and 13.3 (CH_3).

4 Preparation of diazosulphones

a Preparation of methyl (ethanesulphonyl) diazoacetate 385

i via tosyl azide

This was performed according to the method of Regitz and Bartz.[235] Methyl (ethanesulphonyl)acetate (1.0 g, 6 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (0.6 g, 6 mmol) was added, followed by tosyl azide (1.2 g, 6 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2 x 100 ml) and the ether solution was dried and evaporated to give a viscous yellow oil which contained tosyl amide and may have contained the desired product. Dissolution of the oil in ether (200 ml) and further washing with sodium hydroxide (6 x 75 ml, 2M) hydolysed the ester.

ii via 4-(N-acetylamino)benzenesulphonyl azide

Methyl (ethanesulphonyl)acetate (4.7 g, 28 mmol) and 4-(N-acetylamino) benzenesulphonyl azide (6.7 g, 28 mmol) were stirred in acetonitrile (100 ml) at 0°C and triethylamine (8.6 g, 85 mmol) was added. The mixture was stirred for 12 h and the solvent was then evaporated. Trituration of the residue with 1:1 ether:petroleum (3 ml) and column chromatography (silica, ether) gave methyl (ethanesulphonyl)diazoacetate **385** (0.9 g, 17%). m.p. 41–45°C (Found: m/z = 192.0196. $C_5H_8N_2O_4S$ requires 192.0205 [pure by TLC (silica, Et_2O)]); δ_H (300 MHz) 3.86 (3H, s), 3.42 (2H, q, J = 7 Hz) and 1.42 (3H, t, J = 7 Hz); δ_C (75 MHz) 159.9 (C=O), 71.6 (CN_2), 52.5, 50.5, 6.7; ν_{max} 2110, 1700, 1595, 1430, 1270, 1205, 1140, 1080, 905, 795, 740, 710 and 605 cm^{-1}; m/z 192 (M^+, 28%), 161 (11), 153 (5), 135 (5), 100 (70) and 59 (100).

b Preparation of ethyl (ethanesulphonyl)diazoacetate 386

i via tosyl azide

Ethyl (ethanesulphonyl)acetate (2.0 g, 11 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (1.1 g, 11 mmol) was added, followed by tosyl azide (1.5 g, 11 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2 x 100 ml) and the ether solution was dried and evaporated to give a viscous yellow oil which contained tosyl amide and triethylamine. δ_H (200 MHz) 4.45 (2H, q, J = 7 Hz), 3.52 (2H, q, J = 7 Hz), 2.47 (4H, s), 1.5–1.3 (6H, 2 x t)

ii via 4-(N-acetylamino) benzenesulphonyl azide

Ethyl (ethanesulphonyl)acetate (1.0 g, 6 mmol) and 4-(N-acetylamino) benzenesulphonyl azide (1.3 g, 6 mmol) were stirred in acetonitrile (20 ml) at 0°C and and triethylamine (1.6 g, 16.5 mmol) was added. The mixture was stirred for 12 h and the solvent was evaporated. Trituration of the residue with 1:1 ether:petroleum (3 ml) and column chromatography (silica, ether) gave ethyl (ethanesulphonyl)diazoacetate **386** (0.58 g, 50%). m.p. 37°C (Found: C, 35.4; H, 4.9; N, 13.3; m/z = 206.0363. $C_6H_{10}N_2O_4S$ requires C, 34.9; H, 4.9; N, 13.6%, 206.0361 [pure by TLC (silica, Et_2O)]; δ_H (200 MHz) 4.37 (2H, q, J = 7 Hz), 3.43 (2H, q, J = 7 Hz), 1.44 (3H, t, J = 7 Hz) and 1.36 (3H, t, J = 7 Hz); δ_C (75 MHz) 159.5 (C=O), 71.6 (CN_2), 62.0, 50.5, 13.7 and 6.8; ν_{max} 2100, 1700, 1440, 1365, 1330, 1280, 1210, 1140, 1070, 1000, 850, 775, 740, 710 and 600 cm^{-1}; m/z 206 (M^+, 73%), 180 (7), 161 (24), 153 (16), 135 (13), 114 (100), 94 (39), 78 (24) and 66 (80).

c Preparation of methyl (benzenesulphonyl)diazoacetate 387

i via tosyl azide

Methyl (benzenesulphonyl)acetate (1.0 g, 5 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (0.5 g, 5 mmol) was added, followed by tosyl azide (1.0 g, 5 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2 x 100 ml) and the ether solution was dried and evaporated to give crude

methyl (benzenesulphonyl) diazoacetate **387** δ_H (200 MHz) 8.0–8.1 (2H, m), 7.5–7.7 (3H, m), 3.75 (3H, s) plus tosyl amide; ν_{max} 2120 cm^{-1}.

ii via 4-(N-acetylamino)benzenesulphonyl azide

Methyl (benzenesulphonyl)acetate (1.5 g, 8 mmol) and 4-(N-acetylamino) benzenesulphonylazide (1.7 g, 7 mmol) were stirred in acetonitrile (30 ml) at 0°C and triethylamine (2.1 g, 21 mmol) was added. The mixture was stirred for 12 h and the solvent was evaporated. Trituration of the residue with 1:1 ether:petroleum (30 ml) and column chromatography (silica, ether) gave methyl (benzenesulphonyl) diazoacetate **387** (0.9 g, 54%). m.p. 48–51°C (Found: m/z = 240.0201. $C_9H_8N_2O_4S$ requires 240.0205 [pure by TLC (silica, Et_2O)]); δ_H (200 MHz) 8.0–8.1 (2H, m), 7.5–7.7 (3H, m) and 3.75 (3H, s); δ_C (75 MHz) 159.7 (C=O), 141.4 (4ry), 134.0, 129.0 (2C), 127.6 (2C), 75.6 (CN_2) and 52.7; ν_{max} 2100, 1700, 1575, 1500, 1430, 1380, 1150, 1085, 720, 675 and 600 cm^{-1}; m/z 240 (M^+, 33%), 180 (7), 141 (28), 125 (72), 105 (74), 97 (35) and 77 (100).

d Preparation of ethyl (benzenesulphonyl)diazoacetate 388

i via tosyl azide

Ethyl (benzenesulphonyl)acetate (1.0 g, 4 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (0.4 g, 4 mmol) was added, followed by tosyl azide (1.0 g, 4 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2

x 100 ml) and the ether solution was dried and evaporated to give crude ethyl (benzenesulphonyl) diazoacetate **388** (0.9 g, 81%). δ_H (200 MHz) 8.0–8.1 (2H, m), 7.5–7.7 (3H, m), 4.20 (2H, q, J = 7 Hz) and 1.23 (3H, t, J = 7 Hz) plus $TsNH_2$.

ii via 4-(N-acetylamino) benzenesulphonyl azide

Ethyl (benzenesulphonyl)acetate (1.0 g, 4 mmol) and 4-(N-acetylamino) benzenesulphonyl azide (1.1 g, 4 mmol) were stirred in acetonitrile (20 ml) at 0°C and and triethylamine (1.3 g, 13 mmol) was added. The mixture was stirred for 12 h and the solvent was then evaporated. Trituration of the residue with 1:1 ether:petroleum (3 ml) and column chromatography (silica, ether) gave ethyl (benzenesulphonyl) diazoacetate **388** (0.5 g, 47%). m.p. 41–45°C (Found: m/z = 254.0352. $C_{10}H_{10}N_2O_4S$ requires 254.0361 [pure by TLC (silica, Et_2O)]); δ_H (200 MHz) 8.0–8.1 (2H, m), 7.5–7.7 (3H, m), 4.20 (2H, q, J = 7 Hz) and 1.24 (3H, t, J = 7 Hz); δ_C (75 MHz) 158.9(C=O), 141.0 (4ry), 133.6, 128.6 (2C), 127.2 (2C), 75.3 (CN_2), 61.8 and 13.5; ν_{max} 2100, 1700, 1440, 1270, 1200, 1150, 1090, 1060, 1000, 730, 710, 670 and 590 cm^{-1}; m/z 254 (M^+, 12%), 209 (7), 180 (3), 141 (24), 134 (26), 105 (29), 89 (9) and 77 (100).

e Attempted preparation of phenylmethanesulphonyl phenyl diazomethane

i via tosyl azide

Dibenzyl sulphone (0.5 g, 2 mmol), tosyl azide (0.4 g, 2 mmol) and triethylamine (0.2 g, 2 mmol) were stirred in dichloromethane for 4 days and the solvent was then evaporated. The residue was added to aqueous sodium hydroxide (2 x 100 ml). Extraction with ether, drying and evaporation gave just the starting materials.

ii via 4-(N-acetylamino)benzenesulphonyl azide

Dibenzyl sulphone (1.0 g, 4 mmol) was stirred in extra dry THF (20 ml) under nitrogen. n-Butyl lithium (1.6 ml, 2.5M, 4 mmol) was added, followed by 4-(N-acetylamino) benzenesulphonyl azide (1.0 g, 4 mmol). This was stirred for 3 days then triturated with 1:1 ether:petroleum (30 ml). Filtration and evaporation gave a product whose mass spectrum showed stilbene and whose ^{1}H NMR spectrum showed mostly starting materials.

f Attempted preparation of benzenesulphonyl-4-nitrophenyl diazomethane

A solution of 4-nitrobenzyl phenyl sulphone (0.5 g, 2 mmol), tosyl azide (0.3 g, 2 mmol) and triethylamine (0.2 g, 2 mmol, 0.2 ml) in acetonitrile was stirred for 4 days and the solvent was then evaporated. The residue

was added to aqueous sodium hydroxide (2 x 100 ml). Extraction with ether, drying and evaporation gave just the starting materials.

5 FVP of alkane- and arenesulphonyldiazoacetates

a FVP of methyl (ethanesulphonyl)diazoacetate 385

FVP of the title compound (0.2006 g) [600°C, 8.0 x 10^{-2} torr, 80°C] gave a colourless oil in the cold trap [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{13}C (75 MHz) indicated the presence of

unknown, R_T = 4.11, m/z 140 (27%), 112 (7), 64 (28), 45 (62) and 29 (100).

unknown, R_T = 4.46, m/z 154 (18%), 93 (8), 61 (40) and 29 (100).

unknown, R_T = 6.44, m/z 218 (1%), 170 (22), 141 (10) and 109 (22).

unknown (possibly $EtSO_2CH_2CO_2H$), R_T = 4.59, m/z 152 (1%), 77 (10), 66 (13), 43 (38) and 29 (68).

unknown, R_T = 6.53, m/z 182 (3%), 138 (3), 123 (10) and 110 (35).

unknown, R_T = 6.13, m/z 156 (92%), 141 (75), 109 (89) and 77 (65).

$EtSO_2CH{=}CH_2$, (30% yield) R_T = 3.14, m/z 120 (2%), 78 (53), 63 (100) and 45 (65); δ_H 6.63 (1H, dd, J = 10 Hz, 16 Hz), 6.45 (1H, d, J = 16 Hz), 6.19 (1H, d, J = 10 Hz), 3.00 (2H, q, J = 7 Hz) and 1.35 (3H, t, J = 7 Hz); δ_C 135.5, 130.8, 48.6 and 7.0.

MeSSMe, R_T = 3.36, m/z 126 (6%), 111 (13), 79 (60) and 45 (100).].

b FVP of ethyl (ethanesulphonyl)diazoacetate 386

i FVP of the title compound (0.2045g) [600°C, 6.1 x 10^{-2} torr, 80°C] gave an oil in the cold trap [^{1}H (300 MHz) and ^{13}C (75 MHz) indicated the presence of

ethyl E-propenyl sulphone **392**, (6.4% yield) δ_H 6.92 (1H, half of AB pattern of q, J_{AB} = 16 Hz, J = 8 Hz), 6.30 (1H, half of AB pattern of q, J_{AB} = 16 Hz, J = 2 Hz), 3.02 (2H, q, J = 8 Hz), 2.00 (3H, dd, J = 8 Hz, 2 Hz) and 1.3 (3H, t, J = 8 Hz); δ_C 144.5, 128.5, 48.9, 17.5 and 7.1.

ethyl Z-propenyl sulphone **393**, (3.6% yield) δ_H 6.57 (1H, half of AB pattern of q, J_{AB} = 13 Hz, J = 8 Hz), 6.22 (1H, half of AB pattern of q, J_{AB} = 13 Hz, J = 2 Hz), 3.03 (2H, q, J = 8 Hz), 2.19 (3H, dd, J = 8 Hz, 2 Hz) and 1.3 (3H, t, J = 8 Hz); δ_C 144.6, 128.1, 49.8, 14.3 and 6.9.

CH_3CHO, (2.7% yield) δ_H 9.73 (1H, q, J = 2 Hz) and 2.18 (3H, d, J = 2 Hz).].

ii FVP of the title compound (0.0844 g) [400°C, 4 x 10^{-2} torr, 50°C] gave a yellow oil in the cold trap and furnace exit. This was collected as one fraction [GCMS (60-20-300) and ^{1}H (200 MHz) and ^{13}C (75 MHz) NMR indicated the presence of

$EtSSO_2Et$, (17% yield) R_T = 5.32, m/z 154 (8%), 125 (1), 105 (4) and 95 (18); δ_H 3.35 (2H, q, J = 7 Hz), 3.13 (2H, q, J = 7 Hz), 1.3–1.5 (2 x t, J = 7 Hz); δ_C 56.8, 30.4, 14.9, and 8.1.

E- and Z-$EtSO_2CH{=}CHMe$, (E- 6.7% yield, Z- 4.6% yield) R_T = 5.15, m/z 134 (13%), 105 (8), 89 (17) and 39 (100); δ_H as **bi**.

$EtSO_2CH_2CO_2Et$, R_T = 6.44, m/z 153 (17%), 135 (18), 78 (22) and 60 (48); δ_H 4.25 (2H, q, J = 7 Hz), 4.02 (2H, s), 3.30 (2H, q, J = 7 Hz), triplets hidden under $EtSSO_2Et$ peaks; δ_C (C=O not observed), 62.7, 48.1, 14.0, 6.2.].

c FVP of methyl (benzenesulphonyl)diazoacetate 387

i FVP of the title compound (0.2749 g) [600°C, 8 x 10^{-3} torr, 80°C] gave a colourless oil in the cold trap [^{1}H (200 MHz) NMR and TLC (silica, 1:1 ether:60–80 petroleum ether) indicated the presence of biphenyl, δ_H 7.35 (s).].

ii FVP of the title compound (0.50g) [400°C, 2.0 x 10^{-2} torr, 80°C] gave brown droplets at the furnace exit [GCMS (60-20-300) indicated the presence of

$PhSCO_2Me$, R_T = 6.27, m/z 168 (1%), 136 (2), 124 (1), 105 (89) and 77 (100).

PhSOMe, R_T = 7.09, m/z 140 (30%), 125 (45), 97 (55) and 77 (60).

$PhSO_2CH=CH_2$, R_T = 8.05, m/z 168 (5%), 156 (1), 141 (2) and 125 (55).

$PhSO_2Me$, R_T = 7.45, m/z 156 (9%), 141 (9), 125 (1) and 94 (31).

PhSPh, R_T = 8.25, m/z 186 (42%), 152 (8) and 77 (38).

$PhSO_2Ph$, R_T = 10.43, m/z 218 (18%), 202 (312), 154 (17) and 109 (42).

$PhSCOCO_2H$, R_T = 9.03, m/z 182 (5%), 165 (1), 157 (1) and 125 (68).

PhCOPh, R_T = 6.53, m/z 182 (1%), 154 (12), 105 (100) and 77 (74).]

and brown droplets at the cold trap products [GCMS (60-20-300) indicated the presence of

PhCOEt, R_T = 6.00, m/z 134 (1%), 105 (8) and 77 (12).

MeO_2CSPh, R_T = 6.28, m/z 168 (2%), 136 (2), 124 (2), 105 (100) and 77 (82).

PhSOMe, R_T = 7.12, m/z 140 (35%), 125 (55), 97 (52) and 77 (82).

MeO_2CPh, R_T = 4.36, m/z 136 (70%), 105 (96) and 77 (100).].

d FVP of ethyl (benzenesulphonyl)diazoacetate 388

FVP of the title compound (1.00 g) [400°C, 8.0 x 10^{-2} torr, 140°C] gave a dark oil in the cold trap [GCMS (60-20-300) and ^1H (300 MHz) NMR indicated the presence of

$HCOCO_2Et$, R_T = 4.29, m/z 102 (1%), 74 (3), 45 (5) and 29 (100).

EtO_2CCO_2Et, R_T = 3.41, m/z 146 (1%), 117 (2), 101 (1), 74 (5) and 29 (100).

unknown, R_T = 6.51, m/z 182 (1)%, 151 (1), 138 (1) and 133 (3).

an aldehyde, δ_H 10.02 (s).]

and a dark oil in the furnace exit [GCMS (60-20-300) indicated the presence of

$PhSO_2Ph$, R_T = 10.04, m/z 218 (8%), 109 (20) and 77 (100).

EtO_2CCO_2Et, R_T = 3.41, m/z 146 (1%), 117 (2), 74 (5) and 29 (100).

unknown (possibly $PhCOCO_2Et$), R_T = 6.51, m/z 178 (1%), 150 (2), 105 (100) and 77 (90).

PhSPh, R_T = 8.22, m/z 186 (42%), 152 (9), 77 (40) and 51 (100).

$PhSO_2OEt$, R_T = 7.39, m/z 186 (3%), 158 (4), 141 (18), 94 (16) and 77 (100).

PhSOCOEt, R_T = 9.04, m/z 182 (5%), 153 (1), 125 (65) and 77 (70).

$PhSCOCO_2Et$, R_T = 8.50, m/z 210 (2%), 166 (1), 138 (2) and 110 (22).].

e Preparation of alkyl alkanethiolosulphonates

i methyl methanethiolosulphonate

Dimethyl disulphide (2.0 g, 21 mmol) was stirred in dichloromethane (50 ml). A solution of peracetic acid in dilute acetic acid (8.5 g, 38% by weight, 42 mmol)was added and the mixture was stirred for 12 h. Evaporation and kugelrohr distillation gave methyl methanethiolo sulphonate as a colourless liquid (0.57 g, 21%). b.p. 100°C (oven temp.) at 8 mmHg (lit.,[236] 90–91°C at 0.8 mmHg); δ_H (200 MHz) 3.35 (3H, s) and 2.71 (3H, s); δ_C (50 MHz) 48.8 and 18.3.

ii ethyl ethanethiolosulphonate **396**

The same method as above but starting from diethyl disulphide failed to give the correct product. Instead, the starting material was left unreacted.

6 attempted conversion of diazoester to the phosphorus ylide

i preparation of bis-(2,4-pentanedionato)-copper(II)

A solution of pentan-2,4-dione in methanol (10 ml) was added dropwise, with stirring to a solution of copper(II) dichloride dihydrate (4.0 g, 23 mmol) in distilled water (25 ml), followed by dropwise addition of a

solution of sodium acetate (6.8 ml, 83 mmol) in distilled water (15 ml). The mixture was heated to 80°C for 20 min, then cooled to 0°C. Filtration gave bis-(2,4-pentanedionato)-copper(II) as a steely-blue blue powder. (4.1 g, 67%). m.p. 225°C (lit.,[237] 230°C).

ii attempted preparation of [(ethanesulphonyl)ethoxycarbonylmethylene] triphenylphosphorane **409**

A solution of ethyl (ethanesulphonyl)diazoacetate **386** (0.5 g, 2 mmol), triphenylphosphine (1.3 g, 5 mmol) and bis-(2,4-pentanedionato)-copper(II) (0.1 g, 0.5 mmol) in toluene was heated under reflux for two hours then allowed to cool for 12 h. Evaporation of the solvent, trituration with ether (5 ml) and filtration gave a brown oil which rapidly deposited a yellow powder. This powder had spectra δ_H 7.4–7.8 (10H, m), 7.30 (3H, m), 4.32 (2H, q, J = 7 Hz), 3.15 (2H, q, J = 7 Hz) and 1.45 (3H, m, J = 7 Hz); δ_P +28.7 (60, $Ph_3P{=}O$?), +22.8 (16, possibly $Ph_3P^+CHR_2$), +18.7(7, $Ph_3P{=}CR_2$?) and –5.3 (7, Ph_3P); δ_C 133.9, 133.7, 132.2, 132.1, 131.9, 131.2, 129.0, 128.6, 128.5, 128.4, 62.0 ($O\underline{C}H_2CH_3$?), 48.9, 48.1 (d for $SO_2\underline{C}H_2CH_3$?), 14.2 ($OCH_2\underline{C}H_3$?), 7.5 and 7.3 (d for $SO_2CH_2\underline{C}H_3$?). TLC (silica, 1:1 ether: hexane) showed that the powder was almost entirely triphenylphosphine oxide.

iii FVP of the product of 4(ii)

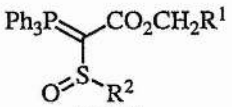
The product from the above reaction was pyrolysed at (400°C, 8 x 10^{-3} torr, 100°C) to give a range of products similar to that from the pyrolysis of the corresponding diazoacetate. This seemed to confirm that the yellow powder was just a mixture of triphenylphosphine oxide and the diazoacetate.

DISCUSSION

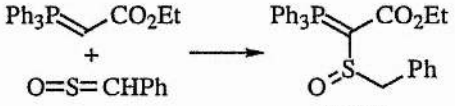
A Preparation and pyrolysis of alkane- and arenesulphinyl alkoxycarbonylmethylenetriphenylphosphoranes

1 Preparation

The first literature preparation of ylides **222** was by Hamid and Trippett.[238] Addition of an ester-stabilised ylide to phenylsulphine (prepared *in situ* from Et_3N and $PhCH_2SOCl$) gave **229** in 73% yield.

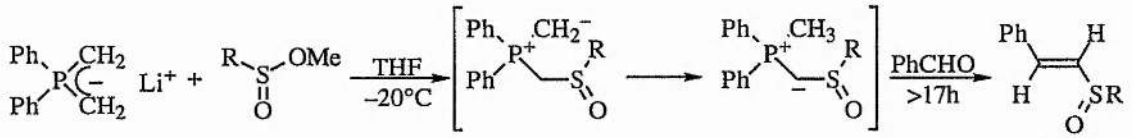


222



229

A more recent paper reported the synthesis of α,β-unsaturated sulphoxides **230**. These were prepared by reacting the lithium phosphonium di-ylide **231** with sulphinates **232** to obtain the sulphinyl ylides **233**. Wittig reaction with benzaldehyde, performed at 66°C over a number of hours, gave the desired sulphoxides **230** in 48–78% yield.[239]

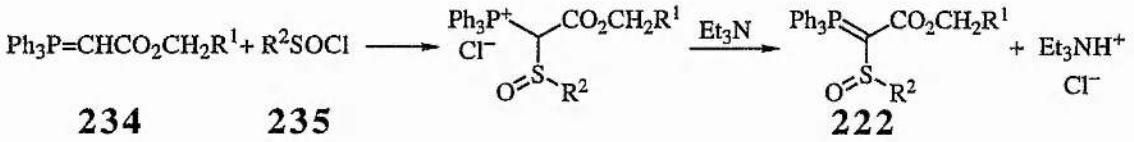


231 **232** **233** **230**

The sulphoxides **230** were all obtained with an E:Z ratio in excess of 10:1. The authors also attempted to obtain a chiral sulphoxide but this failed at the Wittig reaction stage.

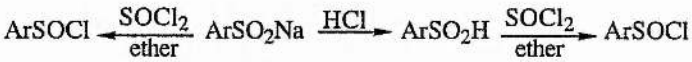
The method of preparation of **222** used in this work was based on a patent by Josey.[240] His procedure was analogous to that used to prepare acyl ylides which involved reaction of an acyl chloride with a stabilised

ylide **234** to give a phosphonium salt. *In situ* reaction of the phosphonium salt with Et_3N gave the acyl ylides. Sulphinyl chlorides **235** were used to provide the "acyl" unit in the preparation of the ylides **222** for this work.

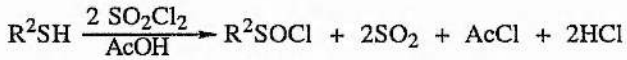


234 **235** **222**

Sulphinyl chlorides **235** are notoriously unstable and unpleasant compounds. Literature methods of preparation include treatment of sodium sulphinates with dilute HCl to generate the free sulphinic acids, which are then reacted with thionyl chloride.[241] Alternatively, direct treatment of the sulphinate with thionyl chloride has been used to generate **235**.[242]



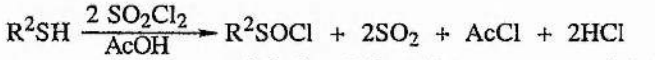
However the method of choice is one published by Youn and Hermann.[192] A mixture of the thiol and AcOH is stirred at –40°C and sulphuryl chloride is added cautiously. After the mixture has warmed to RT, cautious evaporation removes the by-products.



235

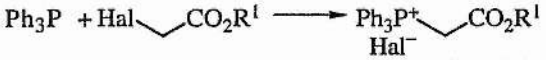
The aliphatic compounds could be distilled (this was a useful feature since some decomposition ocurred if the compounds were stored longer than about 5 days, even at –20°C) and this was the only check on the purity of the products. However, attempts to distil the aromatic chlorides usually

caused the products to polymerise. Hence there was no real check on the purity of these compounds. Attempts were made to characterise the compunds by MS but this led to further confusion since the spectra indicated that only sulphenyl and sulphonyl species reached the detector. In the end, it was assumed that if a presumed sulphinyl chloride gave the desired ylide on reaction with **234**, this would imply it had been a true sulphinyl chloride. The best results for the preparation of the sulphinyl chlorides are given below;



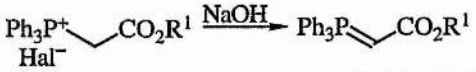
236	$R^2 = Et$	85%
237	$R^2 = Pr^i$	95%
238	$R^2 = CH_2Ph$	23%
239	$R^2 = Ph$	29%
240	$R^2 = p\text{-Me-}C_6H_4$	93%
241	$R^2 = p\text{-Cl-}C_6H_4$	76%

The stabilised ylides **234** were prepared by reaction of triphenylphosphine with alkyl haloacetates to give the phosphonium salts **242–244**;



242	$R^1 = Et$, Hal = Br	98%
243	$R^1 = Bu^t$, Hal = Cl	83%
244	$R^1 = CH_2Ph$, Hal = I	51%

followed by reaction of **242–244** with aqueous NaOH to give **245–247**.

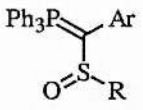


245 $R^1 = Et$ 85%

246 $R^1 = Bu^t$ 51%

247 $R^1 = CH_2Ph$ 50%

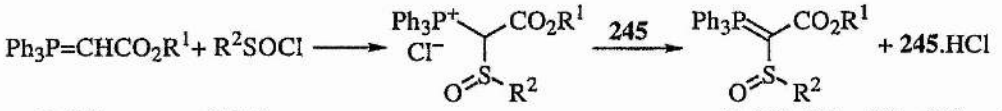
The sulphinyl ylides **222** were prepared in poor to moderate yield by either the method from Josey's patent or by an adaptation in which a second equivalent of stabilised ylide **234** was used as the base in the transylidation step. This adaptation was based on the method used in the preparation of alkanesulphinylbenzylidenetriphenylphosphoranes **226**.



226

Use of Et_3N seemed to give slightly better results, as can be seen from the yield data given below. The acyl ylides previously mentioned can be worked up using an aqueous extraction but this was avoided here since it was known that sulphinyl ylides were extremely likely to hydrolyse.[185] Instead, the reactions were performed in dry toluene and the reaction mixtures were filtered to remove the byproduct phosphonium or triethylammonium salts. Evaporation of the solvent and trituration with dry ethyl acetate gave the desired ylides. It was assumed that where no ylide was formed and the starting phosphonium salt was detected that either the sulphinyl chlorides had been poor or the product had been formed but

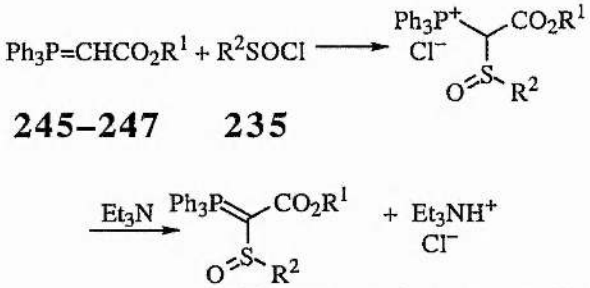
had hydrolysed before it could crystallise. The results for the preparation are given:



245 **235** **248** R^1 =Et, R^2 = Et 16%

249 R^1 =Et, R^2 = Ph 25%

As detailed in the experimental chapter, six variants on this reaction gave no product and one variant gave an impure product. The latter was prepared in a pure form by the triethylamine route. The results of these experiments are given below:



245–247 **235**

250 R^1 = Et, R^2 = $PhCH_2$ 8%

251 R^1 = But, R^2 = *p*-Me-C_6H_4 19%

252 R^1 = But, R^2 = *p*-Cl-C_6H_4 21%

253 R^1 = $PhCH_2$, R^2 = Et 17%

254 R^1 = $PhCH_2$, R^2 = Pri 10%

255 R^1 = $PhCH_2$, R^2 = Ph 6%

256 R^1 = $PhCH_2$, R^2 = *p*-Me-C_6H_4 24%

257 R^1 = $PhCH_2$, R^2 = *p*-Cl-C_6H_4 68%

The 8% yield quoted for **250** is the crude product. All attempts to recrystallise or otherwise purify the ylides resulted in their hydrolysis. Of the others, only **252, 253** and **257** were obtained in an analytically pure state. The impurites were usually solvents (CH_2Cl_2, toluene and/or ethyl acetate). The elemental analyses differed from the theoretical values by at most 2% in carbon and in each case where the elemental analysis was not satisfactory, accurate mass measurements were taken. Each of these also showed the $[M^+ - O]$ ion, not the M^+ ion. However, since **252, 253** and **257** also gave $[M^+ - O]$ as the heaviest ion in their normal mass spectra, it was assumed that the others were also the desired products.

The ylides are stable, colourless solids, although **249** was observed to become faintly pink over a couple of months. The ^{13}C NMR spectra were straightforward, apart from the ylide doublets which were quite small and difficult to identify. Similarly, the ^{31}P NMR spectra show good consistency. However, since the products have δ_P ~+28·0, which almost coincides with the peak for $Ph_3P{=}O$, the preparations of **251** and **252** were assumed to have failed until near the end of the work. A table of the signals is given on page 158 (J_{P-C} in brackets);

Ylide	δ_P	δ_C							
		P=C	C=O	P-Phenyl				R^2	R^2
				C-1	C-2	C-3	C-4		
248	27·5	37·0 (120)	172·2 (br)	130·8 (58)	133·8 (10)	128·3 (12)	131·7 (2)	58·6 (br) 13·9 (br)	33·1 13·4
249	28·1	36·0 (120)	172·4 (br)	124·8 (104)	133·7 (10)	128·3 (12)	131·9 (2)	59·0 (br) 14·6 (br)	144.4 128·0 (4C) 124.1
251	28·5	36·7 (118)	171·8 (br)	127.7 (89)	133·8 (10)	128·2 (12)	131·8 (2)	78·2 28·4 (3C)	141.3 133.6 128·7 (2C) 126·0 (2C) 20·9
252	28·2	36·3 (118)	170·6 (br)	127·5 (66)	133·8 (9)	128·3 (12)	132·0 (0)	78·6 28·4 (3C)	132·1 128·6 128·0 (4C)
253	27.5	37·0 (120)	172·0 (br)	127·8 (83)	133·8 (10)	128·3 (12)	131·8 (2)	132·0 127·9 (2C) 127·8 (2C) 127·0 64·7 (br)	33·2 (br) 13·4
254	24·1	55.2 (119)	166.4 (11)	125.0 (93)	133.8 (10)	128.8 (13)	132.4 (2)	132.0 128.1 (2C) 128.0 (2C) 127.3 64.8	49.8 (9) 18.8 18.4
255	28·3	36·7 (120)	172·0 (br)	127·5 (75)	133·8 (9)	128·4 (12)	132·0 (0)	131.9 128.6 128.0 (2C) 127.9 (2C) 65·0	144·3 132.1 (2C) 125.6 (2C) 124.2
256	28·5	36·8 (122)	172.0 (br)	126.7 (91)	133·7 (9)	128·3 (12)	131.8 (2)	128·8 (2C) 128.5 127.9 (2C) 127·8 64·8	140·7 133.7 (2C) 127.0 (2C) 125.8 20·9
257	28·2	36·4 (121)	172·0 (br)	127·4 (59)	133·7 (9)	128·4 (12)	132·1 (2)	133.8 132·0 128·0 (2C) 127·9 (2C) 65·0	135·1 128.4 127·2 (2C) 126·8 (2C)

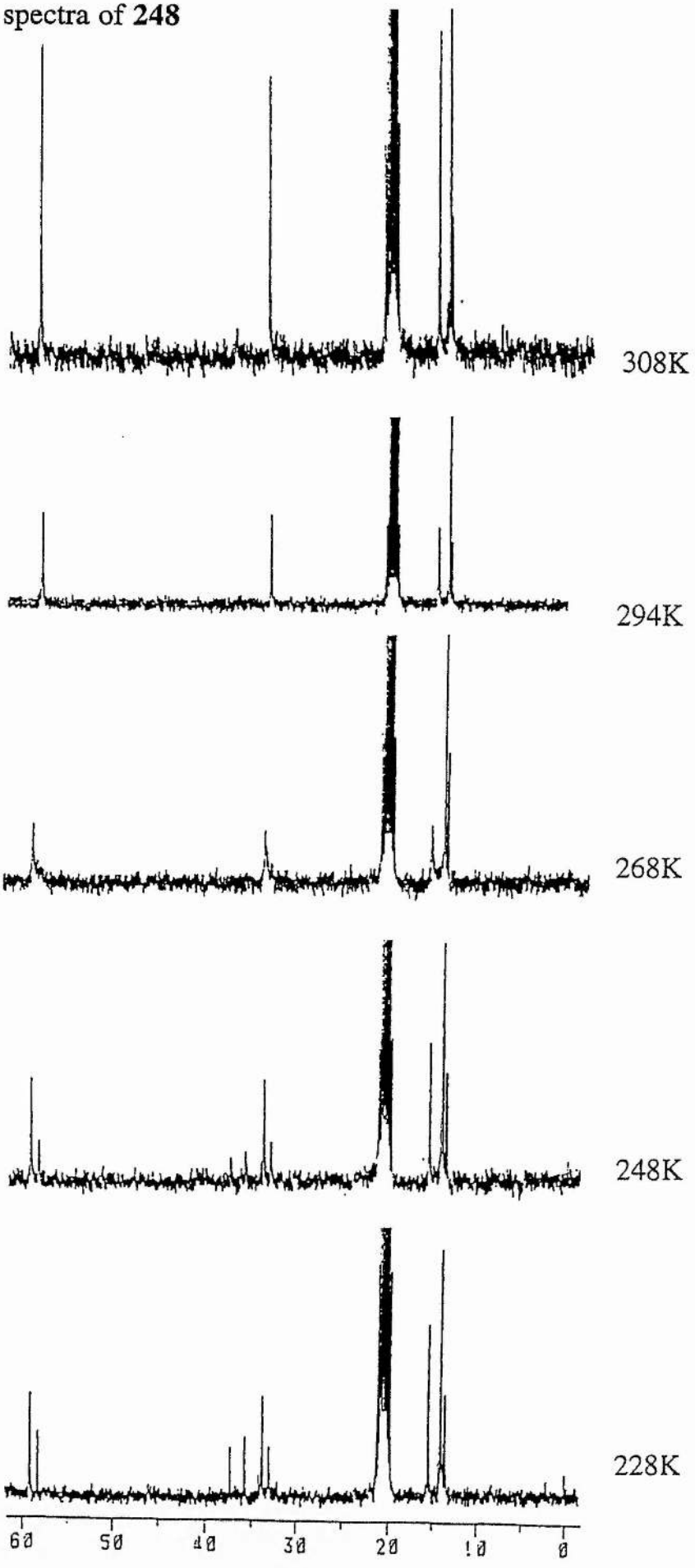
It was noticed that the ^1H spectra often showed broadened peaks for the CO_2R^1 protons. Such peak broadening is indicative of restricted rotation in the molecule. When this occurs, the molecule in question has two or more conformers. An equilibrium exists between the conformers; at higher temperatures, the conformers interconvert too quickly to be observed and an "average" signal is recorded. At lower temperatures, spectra due to the individual conformers are recorded. As with all equilibria, thermodynamic equations can be used to describe the situation. The relevant equations are

$$\frac{\Delta G^*}{RT_c} = 22.96 + \ln\left(\frac{T_c}{\delta_v}\right) \text{ and } \frac{n_a}{n_b} = \exp\left(\frac{\Delta G}{RT}\right)$$

where δ_v is the separation of the signals of the two conformers, T_c is the temperature at which the signals merge and ΔG^*, ΔG, T and R have their usual thermodynamic meanings.

In a variable temperature NMR (VTNMR) experiment, firstly a spectrum is recorded at a temperature high enough to allow only the "average" signal to be recorded. The temperature is then lowered in steps of 10K and a spectrum recorded at each temperature until all the signals for the conformers are seen. It is possible to find the various sets of T_c and measure n_a and n_b by integrating the signals at the lowest temperature. This was attempted for ylide **248**. The first set of spectra were taken in $CDCl_3$. It was found that this solvent became viscous at too high a temperature for the spectra of the conformers to be obtained. The experiment was repeated using d_8-toluene, which has a higher boiling point and lower melting point than $CDCl_3$. The spectra are shown on p160–1.

Figure 1: ^{13}C NMR spectra of **248**



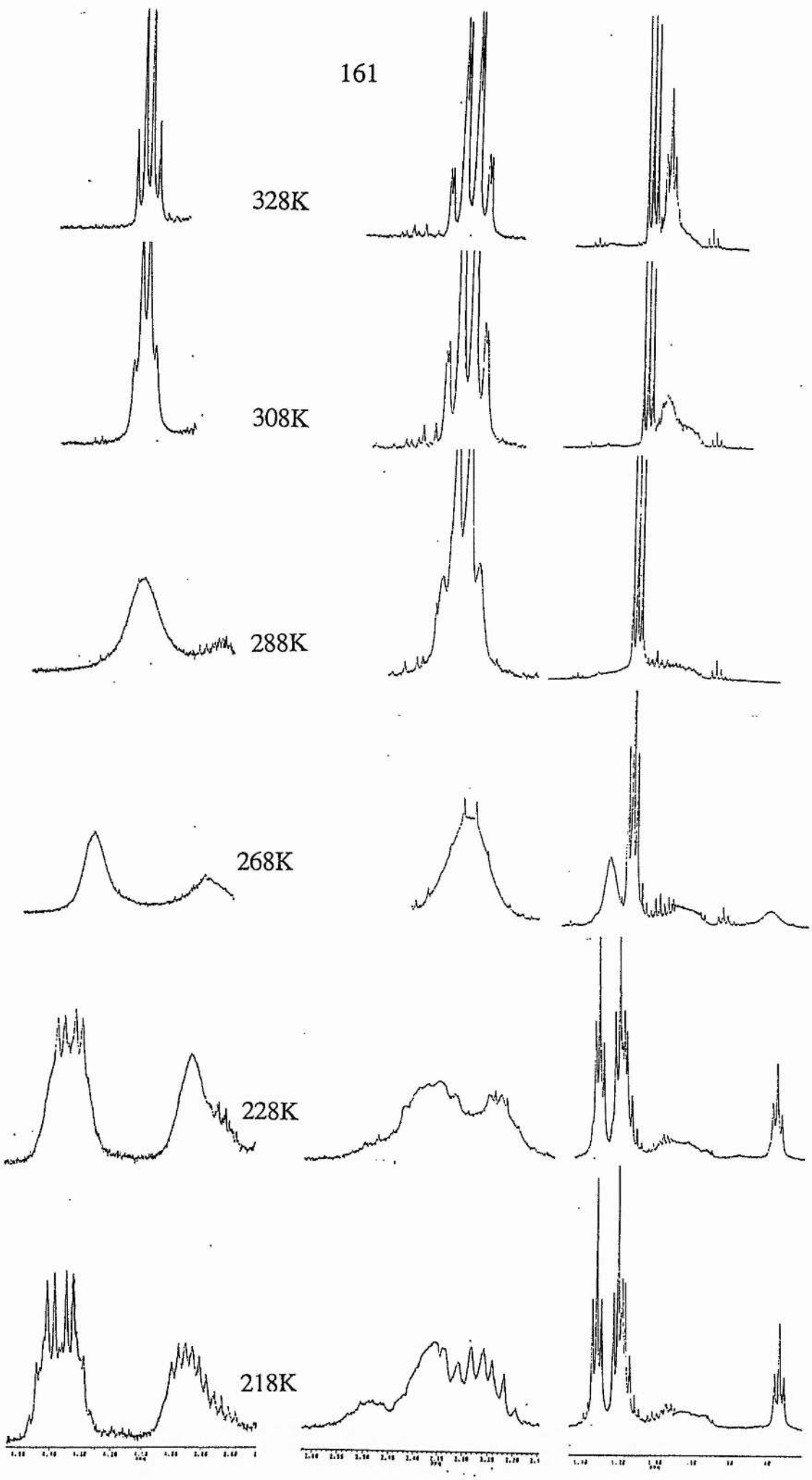


Figure 2: ^{1}H NMR spectra of **248**

^{13}C NMR spectra

The ^{13}C spectrum at 308K shows single peaks for each of the alkyl carbons ($O\text{-}\mathbf{C}H_2\text{-}CH_3$, $O\text{-}CH_2\text{-}\mathbf{C}H_3$, $S\text{-}\mathbf{C}H_2\text{-}CH_3$ and $S\text{-}CH_2\text{-}\mathbf{C}H_3$). (There are also spurious peaks at 14 p.p.m. on this spectrum and the spectra taken at 294K and 268K.) By 268K, the signal for the $O\text{-}\mathbf{C}H_2\text{-}CH_3$ carbon (58 p.p.m.) has begun to broaden and by 248K it has split into two well-defined singlets.

Similarly, the signal for the $O\text{-}CH_2\text{-}\mathbf{C}H_3$ carbon (13 p.p.m.) shows its coalescence at 268K. By 248K, it too shows a doublet. In contrast to this, the $S\text{-}CH_2\text{-}\mathbf{C}H_3$ stays a sharp singlet all through the range of temperatures.

The $S\text{-}\mathbf{C}H_2\text{-}CH_3$ carbon shows the most interesting pattern of all. In the spectra taken at 308 and 294K, the signal is a singlet (33 p.p.m.). The signal is a broad peak at 268K yet by 248K it appears as four peaks. This would imply that there may be four conformers "observable" at this temperature. This notion was supported by the evidence of the ^{1}H spectra.

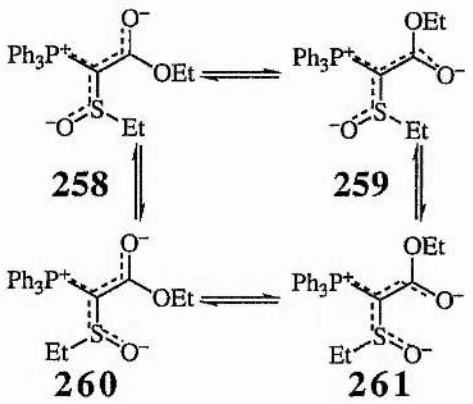
^{1}H NMR spectra

Considering first the $O\text{-}\mathbf{C}H_2\text{-}CH_3$ signals (4.1 p.p.m.); at 328K, the signal is a quartet for the "averaged" behaviour of the molecules. This is broadening by 308K and has split into two by 268K. The high frequency signal begins to be resolved by 228K and at 218K, both sets of signals are showing fine structure. It appears at this temperature that the high frequency portion is about to resolve into two quartets. This provides further evidence for the involvement of four separate conformers, consistent with the ^{13}C signals of SCH_2.

The S-CH_2-CH_3 signal (2.3 p.p.m.) at 328K is a quartet of doublets showing coupling to phosphorus ($^4J_{P-H}$ 1.8Hz). By 288K this quartet is becoming broad and ill-defined. It shows its coalescence temperature at 268K and has split into two by 228K. At 218K, the low-frequency portion shows some fine structure

The S-CH_2-CH_3 signal (1.1 p.p.m.) is a sharp triplet at 328K and remains so down to 268K. By 228K it has split into a multiplet which appears to be two superimposed triplets. The O-CH_2-CH_3 signal (1.0 p.p.m.) appears as a slightly broadened triplet at 328K. By 288K the signal has broadened so far it is almost invisible. By 268K, it appears as two widely spaced humps. These have become well-defined triplets by 228K.

This somewhat complex pattern indicates the involvement of four conformers **258–261** from rotation of both the ylide C–SOEt and the ylide C–COOEt bonds.



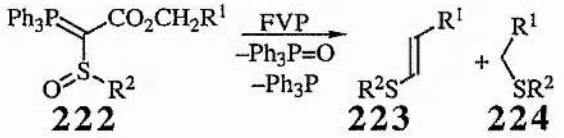
The occurrence of up to four separate signals at the lowest temperature is consistent with these each giving separate signals at least for some of the atoms present. Careful consideration of the data leads to the

conclusion that the rotation of the sulphoxide group has a low activation energy and so still occurs rapidly at temperatures where the ester rotation has been "frozen out". Attempts to quantify the conclusions by calculating energy barriers were complicated by the ambiguity over which signal in the low temperature spectra corresponded to each of the four conformers. Similarly, rough calculations based on the observed coalescence temperatures gave values of ΔG^* in the range 10–15kcal mol^{-1} for most of the processes involved but these could not be assigned to specific interconversion processes. These values do correspond well with that of 13·8kcal mol^{-1} previously obtained by Drysdale[185] for [(4-methylbenzene sulphinyl)ethoxycarbonylmethylene]triphenylphosphorane, where the larger S-Ar group prevents rotation of the sulphoxide (or possibly the rotations are always too fast to observe). Clearly, further detailed study of this problem would be required to fully understand and quantify the processes occurring.

2 FVP

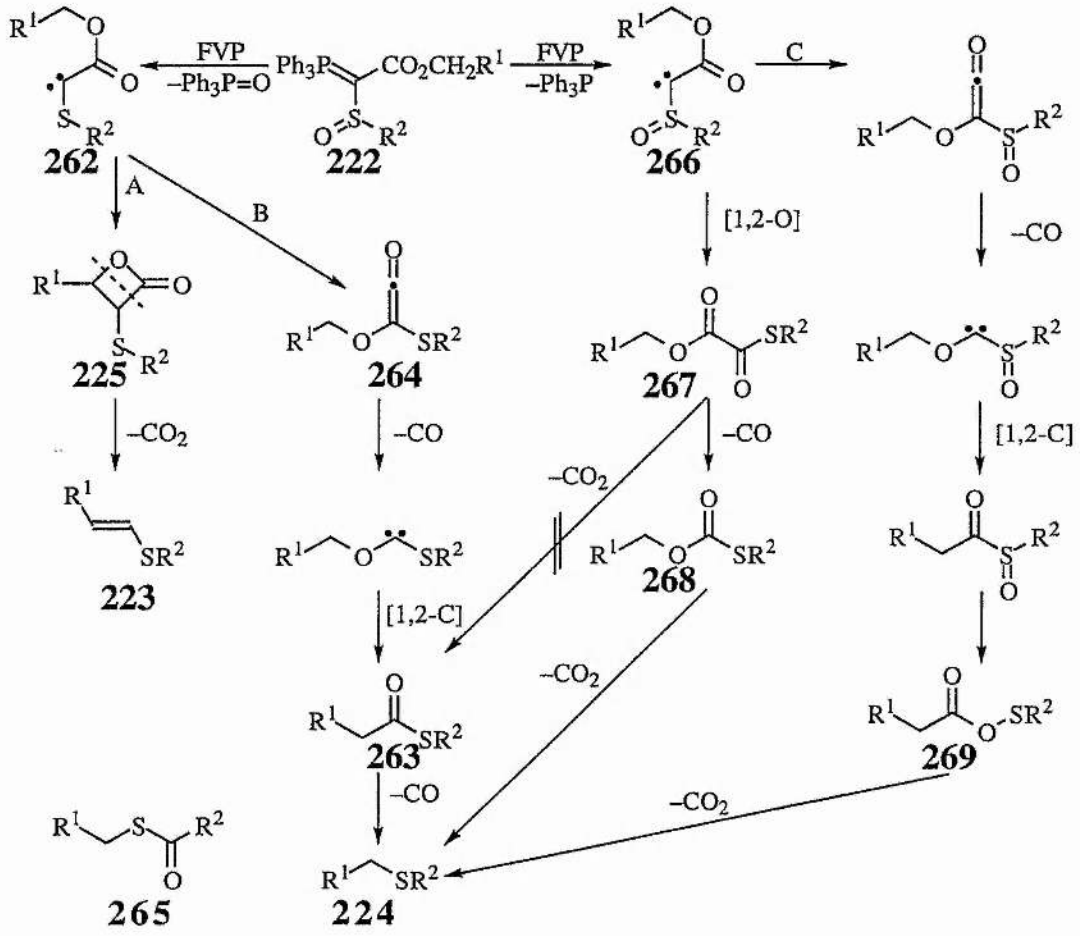
a FVP of ylides of type 222

As already noted, previous pyrolyses[185] of ylides **222** (R^1 = H, Me and Et) gave, for aromatic R^2, $Ph_3P{=}O$, vinyl sulphides **223** and sulphides **224**. For aliphatic R^2, the products were Ph_3P and **224**.



222 **223** **224**

Formation of the vinyl sulphide **223** had been rationalised by assuming extrusion of $Ph_3P{=}O$ to give carbene **262**, followed by intramolecular C–H insertion to give β-lactone **225** (route A). It was already known that such β-lactones can extrude CO_2 to give alkenes[243]. However, a variety of routes were envisaged for the formation of **224**.

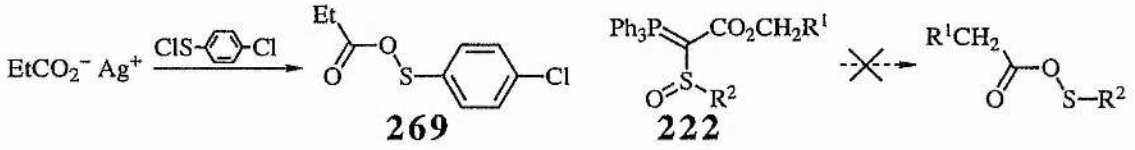


Comparison with authentic samples had shown that aryl thiopropionate **263** was not present in the pyrolysate of ylide **222** (R^1 = Me, R^2 = *p*-Cl-C_6H_4). This seems to rule out the potential alternative reaction shown for carbene **262**, (route B) which would have given the ketene **264**, since aryl thioesters **263** have been shown to pass unchanged through the FVP apparatus at 550°C (*vide infra*). Similarly the isomeric thiobenzoate **265**

was also not present in the pyrolysate of ylide **222** (R^1 = Me, R^2 = *p*-Cl-C_6H_4) and so it too cannot be formed by pyrolysis of **222**; otherwise at least a trace of **265** would be in the pyrolysate.

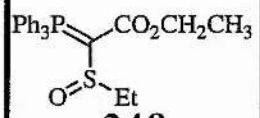
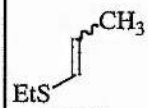
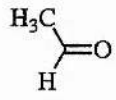
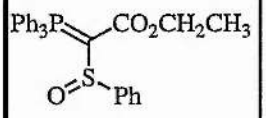
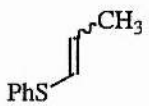
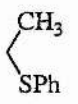
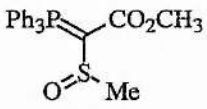
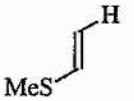
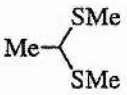
An alternative route to **224** was extrusion of Ph_3P from **222** to give carbene **266**, which might rearrange to alkyl arylthiooxalate **267**. This could then successively lose CO and CO_2 to give sulphide **224**. FVP of alkyl arylthiooxalate **267** (R^1 = Me, R^2 = Ph, *p*-Me-C_6H_4) at 600°C had given alkyl arylthiocarbonate **268** and at 750°C had given **268** and sulphide **224** (R^1 = Me, R^2 = Ph, *p*-Me-C_6H_4). Similarly, FVP of **267** (R^1 = Me, R^2 = *p*-Cl-C_6H_4 and R^1 = H, R^2 = Ph) at both 600°C and 750°C had given **224**. The final mechanism to check in this potential route was whether **266** itself would actually give **267**. Attempts were made to generate examples of **266** via the corresponding diazo precursors but these were not successful (*vide infra*).

The problem remained that unidentified carbonyl compounds had been detected in the pyrolysates. The masses of these compounds corresponded with the masses of the isomeric thioesters **263** and **265**, yet as stated previously, these would have been detected if they were formed. Early in the course of this work, a crude sample of **269** was prepared. Its ^{13}C NMR spectrum was obtained but the carbonyl signal was different to that of the unknown carbonyl compound in the pyrolysate of **222** (R^1 = Me, R^2 = *p*-Cl-C_6H_4).



This is some slight evidence against the route C. However the only way of disproving this route would have been to prepare **266** and prove (i) that **266** was formed by FVP of **222** and (ii) that **266** was the source of **224**. Further useful evidence would have been obtained from the pyrolysis of **269** and its presumed precursor on route C. Hence a fresh attempt to discover the identity of these mystery carbonyl compounds was needed.

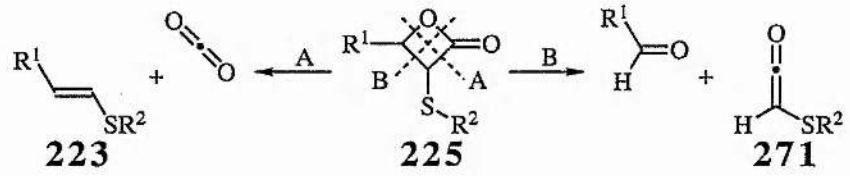
The results obtained for pyrolysis of ylides **222** at 600°C in this work are as follows;

ylide	ratio of Ph_3P: $Ph_3P{=}O$:$Ph_3P{=}S$	% yields of other products
 **248**	84:9:7	 36%  7%
 **249**	1:1:0	PhSSPh 10%  10%  5% two unknowns: m/z = 166, m/z = 260.
 **270***	80:14:6	 20% MeSSMe trace  trace

* A sample of **270** for pyrolysis was available from previous work[185]

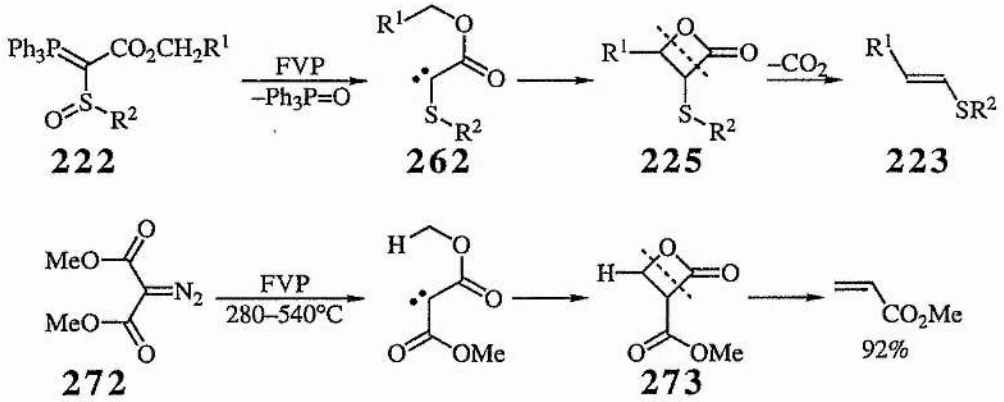
These correlate somewhat with previous work. However, the absence of sulphides **224** in two cases does not agree with the previous work. It is possible to argue that **224** might formed in these cases but have evaporated (MeSMe, b.p. 38°C) before the analyses were made. Formation of acetaldehyde, which was not recognised previously, was explained by

proposing an alternative disintegration of β-lactone **225** to give the ketene **271**. Also, re-examination of the spectra from the previous work showed the presence of acetaldehyde and propionaldehyde in the pyrolysates of **222** (R^1 = Me, Et).

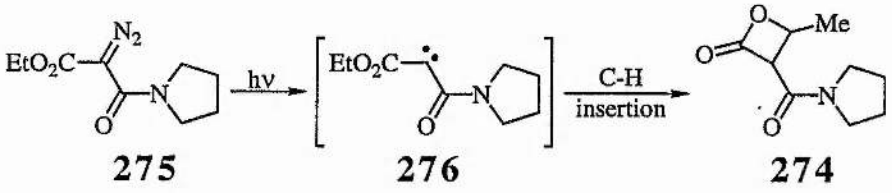


Reaction of **271** with water would give $R^2SCH_2CO_2H$ but this was never detected. An attempt was made to trap any labile double bond-containing compounds by putting methanol in the cold trap but no new products were identified. It is in fact probable that **271** would lose CO under the conditions involved to give the thiocarbene which might end up as R^2SMe but this was not observed either. Thus although several aspects of the thermal decomposition of **222** remain unclear, the main processes appear to involve loss of of Ph_3P and/or $Ph_3P{=}O$ and subsequent intramolecular reactions of the resulting carbenes.

Support for the proposed route to vinyl sulphides **223** comes from FVP of the diazomalonate **272**. This gave methyl acrylate by the mechanism shown below, which involves formation and decarboxylation of the β-lactone **273**.[244]

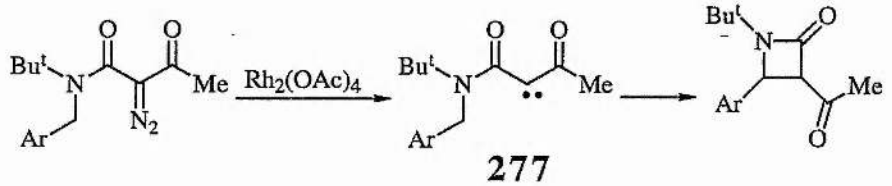


The stable β-lactone **274** was produced by photolysis of diazoester **275**: intermediacy of carbene **276** was assumed.[245]

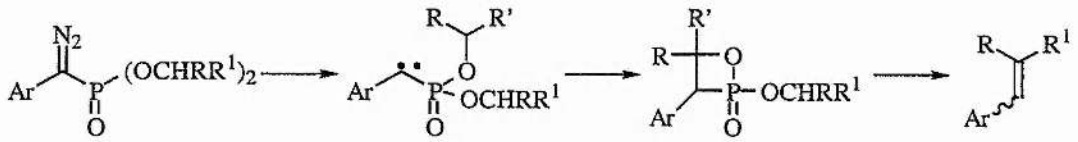


275 **276** **274**

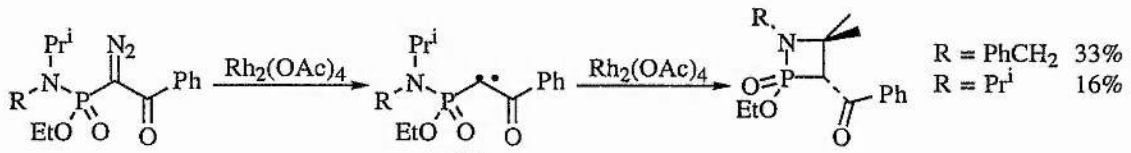
The formation of β-lactams by intramolecular C–H insertion of carbenes such as **277** is also known.[246] Similar 4-membered rings can be obtained from carbenes **278**[247] and **279**.[248] The metaphosphate extrusion product from one example of **278** has been observed.



277



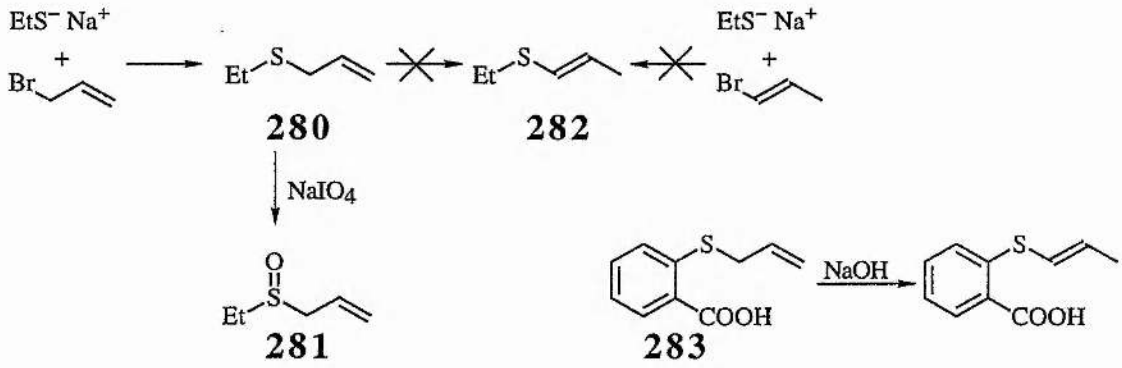
278



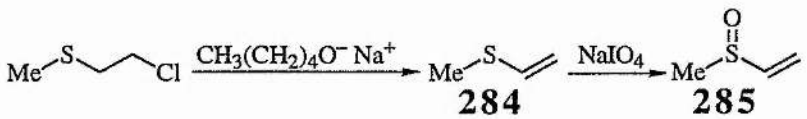
279

In order to confirm the identity of the FVP products from **248** and **270** authentic samples of vinyl sulphides and sulphoxides were prepared. Reaction of allyl bromide and sodium ethanethiolate gave ethyl allyl sulphide **280** in 51% yield. Sodium metaperiodate oxidation of this then gave ethyl allyl sulphoxide **281** in 34% yield. However ethyl propenyl

sulphide **282** could not be prepared: attempted base-catalysed migration of the double bond of **280** gave no reaction (even though this is possible for the aromatic species **283**[249]) and reaction of sodium ethanethiolate with 1-bromo-1-propene gave no unsaturated compounds. Although the desired ethyl propenyl sulphide could not be prepared, the spectra of **280** and **281** did provide model data from which it was clear that **282**, not its sulphoxide, was the product formed in the FVP of **248**. Thus, the methylene group next to a sulphoxide has a more complex ^{1}H NMR spectrum because the S=O group makes the two hydrogens magnetically non-equivalent and the ethyl group of **280** showed a normal quartet and triplet, while **281** showed two superimposed quartets and a triplet.



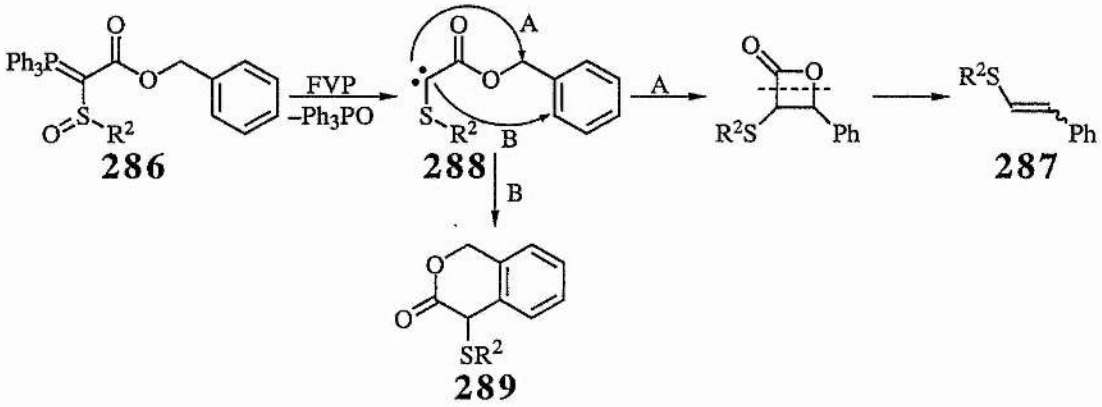
Methyl vinyl sulphide **284** was prepared by dehydrochlorination of 2-chloroethyl methyl sulphide and periodate oxidation of **284** gave the sulphoxide **285**.



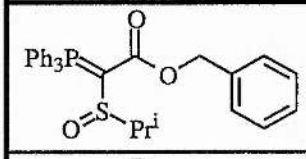
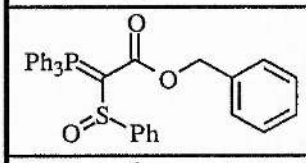
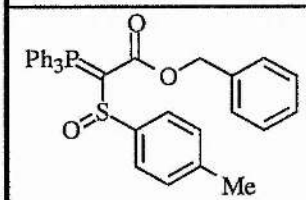
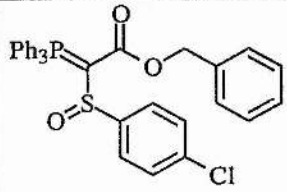
Comparison of the S(=O)CH_3 signals of **285** and **284** with the pyrolysate from **270** confirmed that the pyrolysis product was the sulphide.

b FVP of ylides of type 286

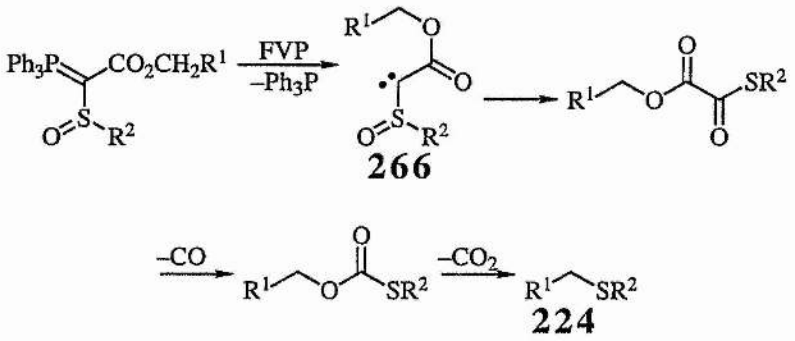
These ylides were of interest since, if the carbene insertion pattern seen for previous examples of **222** held, the alkyl styryl sulphides **287** would be obtained. Alternatively, it was possible that the carbene **288** might insert into an aromatic C–H to give the six-membered lactones **289**.



The results of the pyrolyses at 500°C of ylides of type **286** are given below;

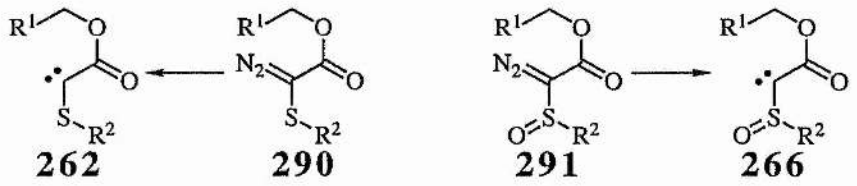
ylide	Ph_3P:Ph_3P=O:Ph_3P=S	other products
 **254**	0:40:7	$PhCH_2OH$
 **255**	0:1:0	$PhCH_2OH$
 **256**	0:1:0	$PhCH_2OH$
 **257**	0:1:0	$PhCH_2OH$ $PhCH_2SC_6H_4Cl$ ClC_6H_4Me unknown, m/z = 156 $PhCH_3$ $PhCH_2CH_2Ph$ $(ClC_6H_4S)_2$

The compounds appear to have mostly just disintegrated. A trace of sulphide **224** was observed in one case but no proven vinyl sulphides **223** were seen. The major phosphorus-containing product observed was $Ph_3P{=}O$, which is again inconsistent with the proposed route to **224**, which is:

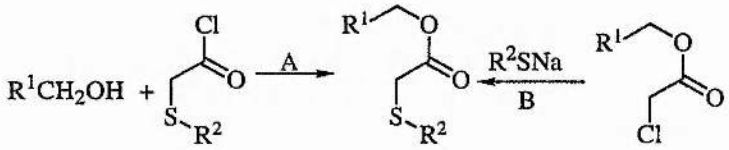


It is possible that air oxidation of Ph_3P gave $Ph_3P{=}O$, but this is unlikely to have converted all the Ph_3P to $Ph_3P{=}O$. This discrepancy added further weight to the need to investigate alkyloxycarbonyl sulphinyl carbenes **266**.

The above discrepancies made it desirable to have more evidence about the behaviour of carbenes **262** and **266** (whatever the nature of R^1) and so it was hoped that the diazo compounds **290** and **291** could be prepared. Pyrolysis of these compounds would then have given the carbenes **262** and **266**.



The required sulphenyl acetates **292–5** were prepared by either (method A) reacting benzenesulphenylacetyl chloride with methanol and ethanol or (method B) by reacting alkyl chloroacetates with alkylthiolates.



292 $R^1 = H$, $R^2 = Et$ 52%[b]

293 $R^1 = H$, $R^2 = Ph$ 63%[a], 74%[b]

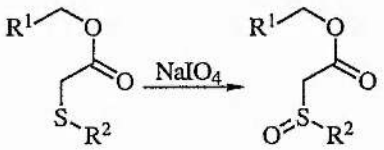
294 $R^1 = Me$, $R^2 = Et$ 42%[b]

295 $R^1 = Me$, $R^2 = Ph$ 58%[a], 72%[b]

a = method A, b = method B

Attempts to carry out diazo exchange on the sulphenyl acetates were not successful. Treatment of **293** and **294** with Et_3N and tosyl azide **296** in acetonitrile gave no reaction. Increasing the strength of the base to NaH and even Bu^nLi gave no better results.

The sulphinyl acetates **297–300** were prepared by oxidation of **292–295** with sodium metaperiodate in methanol and water.[194] (**297–300** gave poor elemental analyses, but accurate mass measurements showed that they were the major components present in the samples obtained.)



297 $R^1 = H$, $R^2 = Et$ 36%

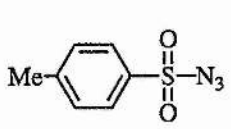
298 $R^1 = H$, $R^2 = Ph$ 32%

299 $R^1 = Me$, $R^2 = Et$ 85%

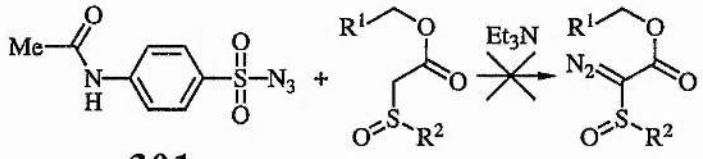
300 $R^1 = Me$, $R^2 = Ph$ 45%

Again, no reaction was obtained when sulphinyl acetates were treated

with either tosyl azide **296** or 4-(N-acetylamino)benzenesulphonyl azide **301**.



296

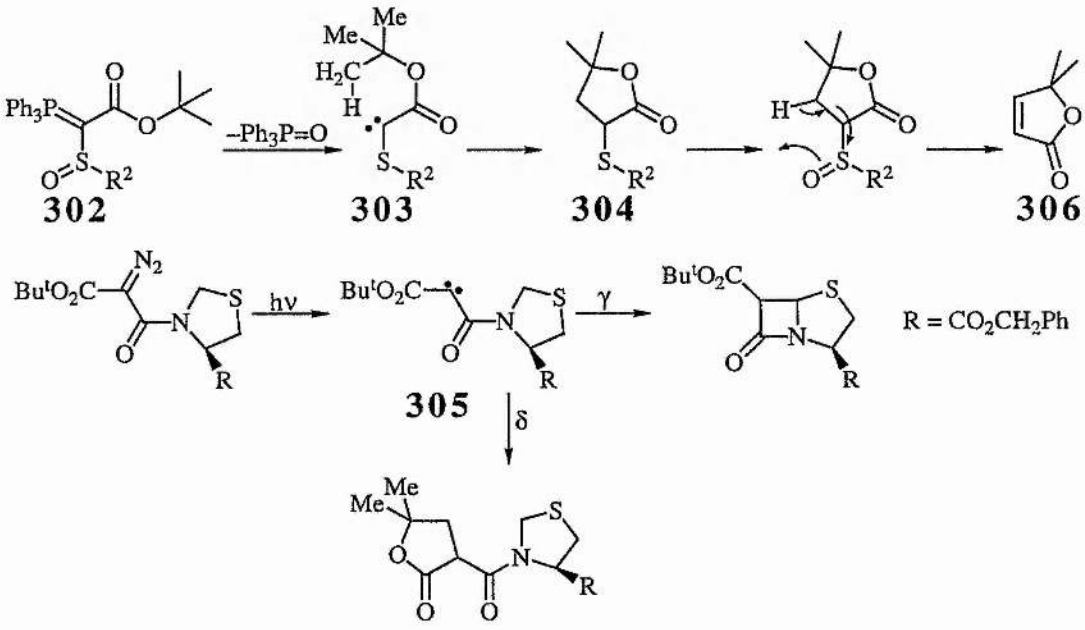


301

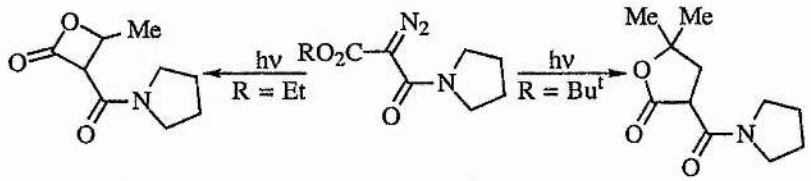
Diazo exchange of β-keto-sulphoxides appears not to have been achieved, the sole related example being the formation of the cephalosporin compound mentioned in the Introduction (page 33) which is stabilised by a vinylogous ester group.[135] The failure of these reactions is surprising in view of the successful diazo exchange of the sulphonyl ester described later in section **D1**, page 193.

c FVP of ylides of type 302

The study of FVP of t-butoxycarbonyl ylides of type **302** was prompted by the idea that δ C–H insertion of carbene **303** would give γ-lactone **304** since it was known that carbene **305** showed both γ and δ insertion.[245] Oxidation of **304** would give the sulphoxide which would lose R^2SOH to give the synthetically useful γ-lactone **306**.

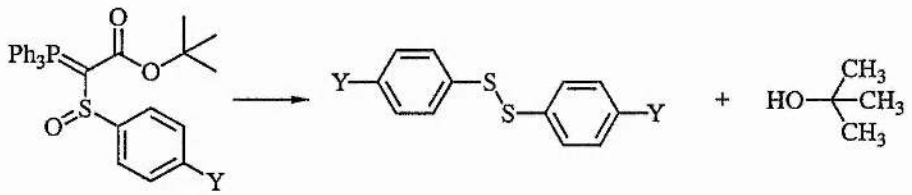


It should be noted that for the pyrrolidine compound, **307**, when R was ethyl, only β-lactone **274** was formed and when R was t-butyl, only γ-lactone **308** was formed.[245]



274 **307** **308**

In the event, FVP of **251** and **252** at 500°C gave only Bu^tOH and R^2SSR^2.



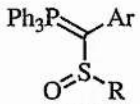
The yields are given below;

ylide	FVP fraction	Ph_3P:Ph_3P=O:Ph_3P=S	other products
251 (Y=Me)	cold trap	--	$(MeC_6H_4S)_2$
	furnace exit	7:30:0	
	furnace exit, after 17 days	0:12:1	
252 (Y=Cl)	cold trap	—	$(ClC_6H_4S)_2$ t-BuOH
	furnace exit	0:60:7	$(ClC_6H_4S)_2$

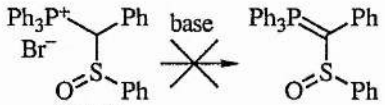
B Preparation and pyrolysis of arenesulphinylbenzylidene triphenylphosphoranes

1 Preparation

Previous attempts to prepare ylides **226** were not at all successful.[185] Reaction of benzyl phenyl sulphoxide with triphenylphosphine dibromide and Et_3N in dry toluene gave only $Ph_3P{=}O$. Various attempts were made to dehydrohalogenate [(α-benzenesulphinyl)benzyl]triphenylphosphonium bromide **309**.

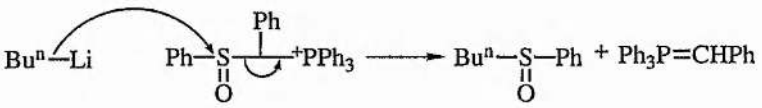


226



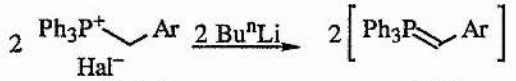
309

Reaction with NaOH in water and $KOBu^t$ in both t-butanol and THF gave only $Ph_3P{=}O$ and benzyl phenyl sulphoxide. Reaction with LDA in THF gave $Ph_3P{=}O$, benzyl phenyl sulphoxide and some Ph_3P, while reaction with Bu^nLi in THF gave $Ph_3P{=}O$ and benzyl phenyl sulphoxide and a product tentatively identified as n-butyl phenyl sulphoxide.

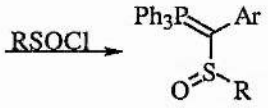


The method of choice turned out to be reaction of two equivalents of non-stabilised ylide **310** (prepared *in situ* by the action of Bu^nLi on phosphonium salts **311**) with one equivalent of sulphinyl chloride **235** in dry toluene. Filtration removed the byproduct phosphonium salt and the products were isolated by evaporation and trituration with dry ethyl acetate. It is both interesting and disappointing to note that no ylides

apart from where Ar was Ph were obtained.



311 **310**



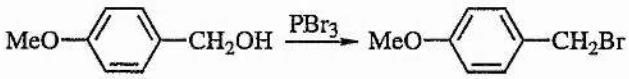
235

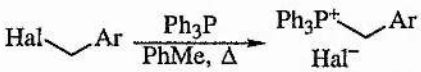
312 Ar = Ph, R = Ph 29%

313 Ar = Ph, R = *p*-Me-C_6H_4 45%

314 Ar = Ph, R = *p*-Cl-C_6H_4 31%

The phosphonium salts **315–317** had been obtained by reaction of Ph_3P with the appropriate benzyl halides. One benzyl halide had to be prepared from the corresponding alcohol.





315 Ar = Ph Hal = Cl^- 48%

316 Ar = *p*-O_2N-C_6H_4 Hal = Br^- 83%

317 Ar = *p*-MeO-C_6H_4 Hal = Br^- 90%

Apart from **313**, these compounds were not obtained in an analytically pure state. However, their identities were confirmed by ^{13}C spectra and accurate mass measurements. The ^{31}P and ^{13}C NMR spectra of the ylides **312–314**, a previously unknown class of compounds, are tabulated overleaf (J_{P-C} in brackets);

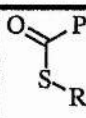
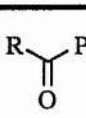
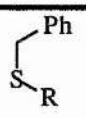
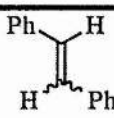
ylide	δP	δC								
		P-Phenyl					P–C–Ph		R	
		P=C	C–1	C–2	C–3	C–4				
312	+20·4	52·2 (122)	126·8 (89)	134·3 (10)	128·8 (12)	132·4 (2)	137·2 (12)	129·7 (2C), (6)	147·7 (16)	128.6
							127·3 (2C)	122·7	127·8 (2C)	126·3 (2C)
313	+20·2	52·1 (125)	128·0 (78)	134·3 (10)	128·8 (12)	132·3 (<2)	137·4 (12)	132·0 (2C), (7)	144·6 (16)	137·7
							127·3 (2C)	122·6	128·7 (2C)	126·3 (2C)
									21·1	
314	+19·7	*	127·9 (88)	133·9 (9)	128·5 (12)	131·9	*	132·1 (10)	146·3 (21)	145·1
							127·9 (2C)	122·7	127·6 (2C)	125·3 (2C)

* ylide C and 2C not apparent

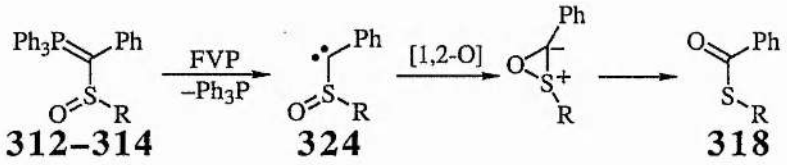
Again, there is reasonable consistency between the spectra; this was fortunate in the cases of **312** and **314**, where apart from the ylide doublets, only aromatic signals were expected.

2 FVP

FVP of ylides **312–314** at 500°C gave a mixture of Ph_3P, $Ph_3P{=}O$ and $Ph_3P{=}S$ at the furnace exit. A brilliant blue liquid collected further along the trap. This liquid became colourless within a few minutes of opening the trap and attempts to isolate it under N_2 were not very successful. In the few cases when the blue colour was still present and the products had been transferred to an NMR tube or cuvette, the colour had faded by the time the spectrum had been obtained. However, ^{1}H, ^{13}C and ^{31}P NMR and GCMS showed that the pyrolysate contained thiobenzoates **318**, ketones **319**, sulphides **320**, stilbene **321**, thiols **322** and disulphides **323**. The yields are given overleaf.

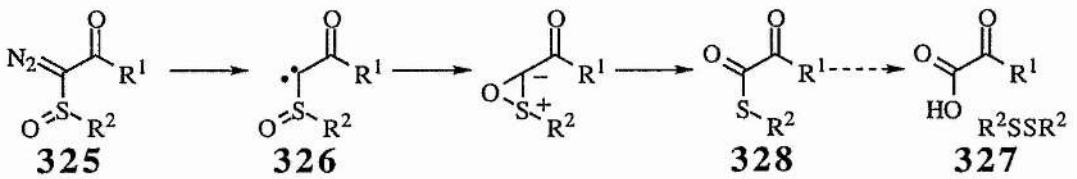
Ylide	Ph_3P:Ph_3P=O: Ph_3P=S	 **318**	 **319**	 **320**	 **321**	RSH **322**	RSSR **323**
312	12:6:1	20	0	4	10	8	10
313	82:15:3	25	5	0	0	20	6
314	9:24:2	9	18	7	7	25	17

The formation of thiobenzoates **318** is rationalised by assuming S–C transfer of oxygen in the carbene **324**, formed by loss of Ph_3P from **312–314**. This process is the predominant one for (alkanesulphinyl)benzylidene triphenylphosphoranes.



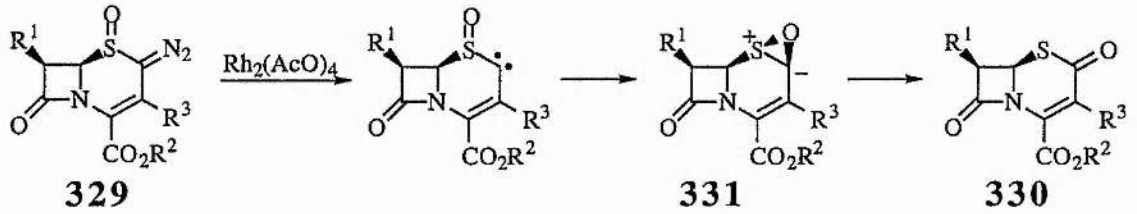
312–314 **324** **318**

A similar S–C transfer of oxygen has been reported in two cases. In the first, reaction of tosyl azide with β-keto-sulphoxides is presumed to have given the diazo-keto-sulphoxide **325**. S–C transfer of oxygen in carbene **326** is invoked to explain the observed reaction products, the α-keto-acids **327** and disulphides, which are presumed to be formed by solvolysis of the α-ketothioesters **328**.[134]



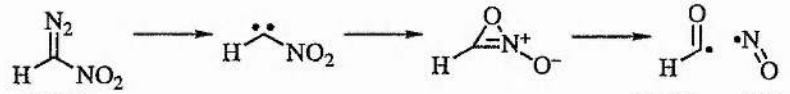
325 **326** **328** **327**

In the second example, diazocephalosporin S-oxides **329** were treated with di-rhodium tetra-acetate. The 2-oxocephalosporins **330** were produced and the authors favour the intermediate ylide **331**.[135]



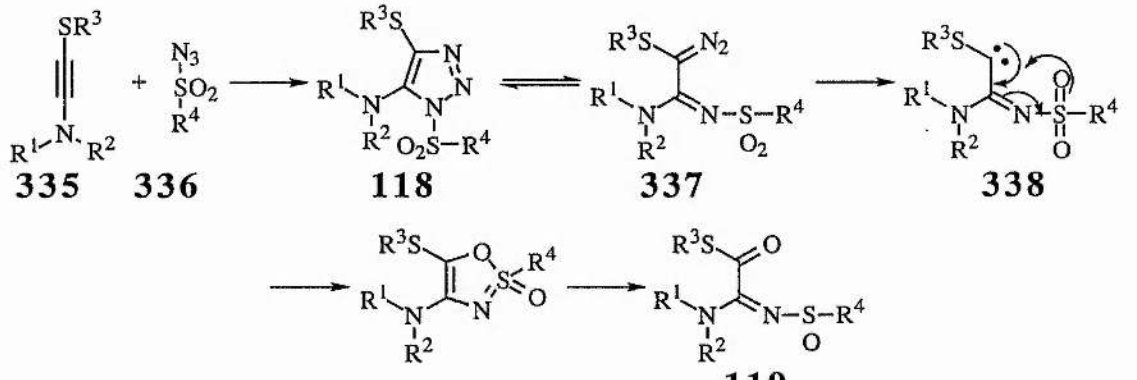
329 **331** **330**

Similar heteroatom to carbon transfers of oxygen have also been noted in other cases. Nitrodiazomethane **332** gives formyl radical **333** and nitric oxide **334** on photolysis.[250]



332 **333** **334**

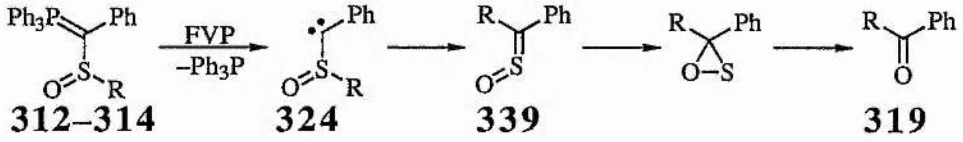
As seen in the section on carbenes in the Introduction, S-C transfer of oxygen can also happen in sulphonyl species. In the example quoted, reaction of aminoalkynes **335** with sulphonylazides **336** in ether gave the sulphinylimines **119**. This reaction was presumed to go by cycloaddition of **335** to **336** to give the triazole **118**. Cycloreversion to diazoimine **337**, followed by loss of nitrogen and S–C transfer of oxygen in carbene **338** was invoked to explain the final reaction product.[115]



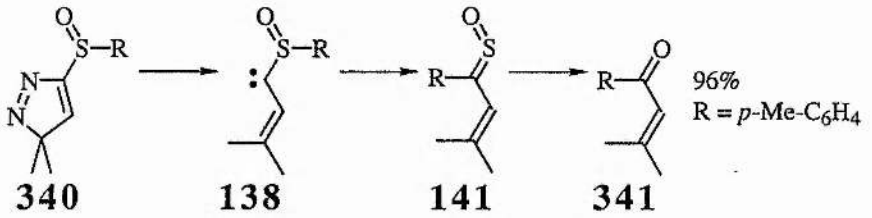
335 **336** **118** **337** **338**

119

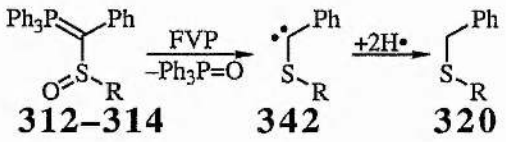
Other major products in the pyrolysis of ylides **312–314** were the ketones **319**. Rearrangement of carbenes **324** is likely to give sulphines **339**, which could lose sulphur as shown to give ketones **319**.



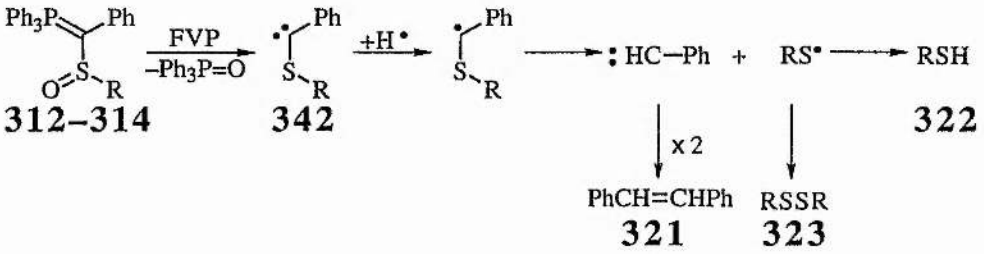
Support for this idea comes from the photolysis of pyrazolines **340**: Wolff-type rearrangment of carbene **138** leads via sulphine **141** to the formation of ketone **341** in high yield.[137]



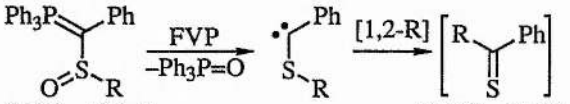
Sulphides **320** are presumed to be formed by abstraction of 2 × H• by carbene **342**, which is formed by extrusion of $Ph_3P{=}O$ from **312–314**.



It is also attractive to assume that **342** is the precursor of **321**, **322** and **323**, by means of α-elimination of the arylthiobenzyl radical as shown, although **322** and **323** could come from other radical processes.



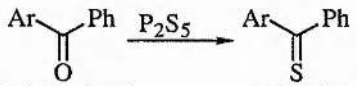
It was believed that the blue colour of the pyrolysates of **312–314** may have come from the thioketones **343–345**.



312–314 **343–345**

Attempts were made to obtain the UV spectra of the pyrolysates but the pyrolysates had always become colourless by the time such spectra had been recorded.

It was thought that if thioketones were being formed, then they were being consumed very quickly once the FVP system was opened. Otherwise the colour would not last when the apparatus was left untouched after all the starting material had passed through the furnace. It was therefore thought that the addition of the $CDCl_3$ solvent may have had something to do with the loss of colour. Hence authentic samples of thioketones were made. Thiobenzophenones **343–345** were prepared by reaction of the corresponding benzophenones **346–348** with P_2S_5 in boiling xylene.



346–348

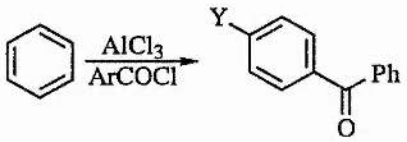
343 R = Ph 69%

344 R = *p*-Me-C_6H_4 37%

345 R = *p*-Cl-C_6H_4 Ph 20%

The benzophenones **347** and **348** were prepared by acylation of benzene with the relevant acid chlorides. Since **346–348** were also

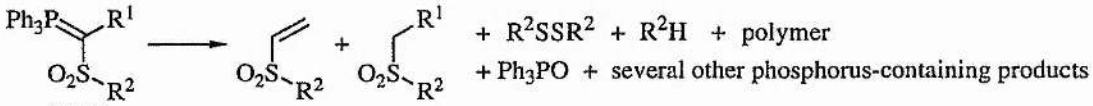
detected in the pyrolysates of **312–314**, they too were subjected to FVP at 500°C. This left them completely unchanged.



346 Y = H
347 Y = Cl 84%
348 Y = Me 52%

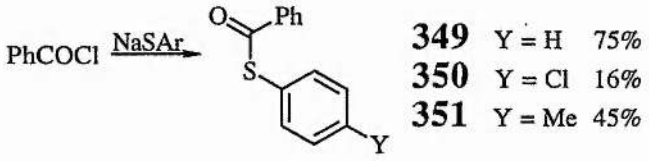
No spectral evidence could be found for the presence of thioketones **343–345** in the pyrolysates of **312–314**. However it was thought worthwhile to check on the reactions of thioketones with Ph_3P, since it was thought that the addition of the $CDCl_3$ might provide a reaction medium for the Ph_3P to desulphurise the thioketones. An NMR tube was prepared, containing Ph_3P and thiobenzophenone. The blue colour of thioketone persisted, despite several additions of Ph_3P and ^{31}P NMR showed that the Ph_3P had been converted to $Ph_3P{=}S$.

It is also possible that sulphinyl ylides may disproportionate in the inlet tube – this would lead to products from pyrolysis of sulphonyl and sulphenyl ylides. However the relevant sulphonyl ylides **219** had been prepared and pyrolysed in previous work in this laboratory.[185] They give a white polymer as the major component of a complex pyrolysate. No sulphonyl species were detected in the pyrolysates of **312–314** in this work, so it is not believed that disproportionation is a major factor in these pyrolyses.



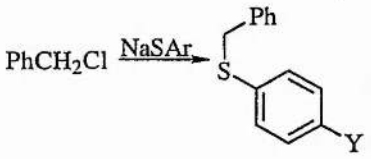
219

Other authentic samples prepared to check the pyrolyses of **312–314** were the thiolobenzoates **349–351**. These were prepared by reaction of sodium thiophenols with benzoyl chloride. FVP of **350** and **351** at 500°C gave the unchanged starting materials.



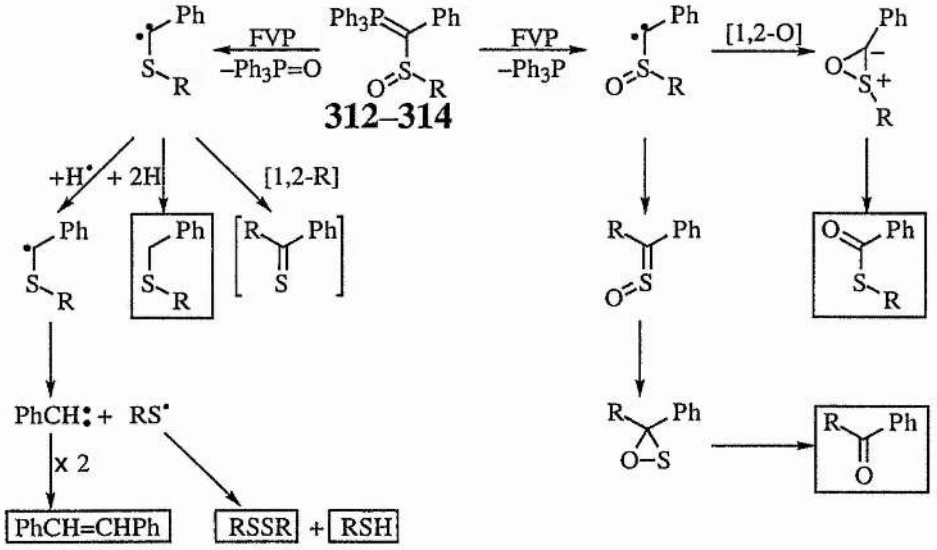
349 Y = H 75%
350 Y = Cl 16%
351 Y = Me 45%

Similarly, the sulphides **352** and **353** were prepared and pyrolysed. There was no change to these compounds on pyrolysis, so, as with the thiobenzoates and the ketones, formation of these compounds is believed to be one of the final steps in the pyrolysis mechanism.



352 Y = Cl 38%
353 Y = Me 30%

So the pyrolysis of ylides **312–314** can be summarised by the following scheme. The final products are outlined.



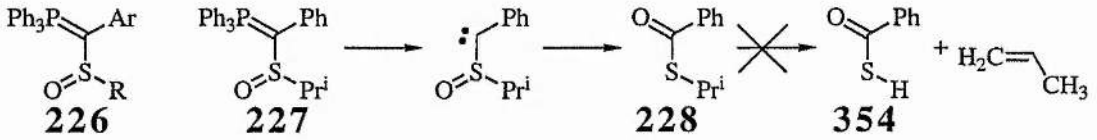
Referring back to the yield data on page 179, for **312** and **313**, where the yield ratio of Ph_3P:Ph_3P=O is greater than 1, the yield ratio of **318**:**320** (the major products associated with Ph_3P and $Ph_3P=O$ respectively) is also greater than 1. However, for **314**, the yield ratio of Ph_3P:Ph_3P=O is less than 1 but the yield ratio of **318**:**320** is slightly greater than 1, possibly implying some change of mechanism. However, in each case, there is enough of the relevant phosphorus compound formed (assuming that 100% of the phosphorus compounds were isolated) to allow the mechanisms outlined above to be plausible.

No rationalisation can yet be offered as to why the relative amounts of products changed.

C Preparation and pyrolysis of alkanesulphinylbenzylidene triphenylphosphoranes

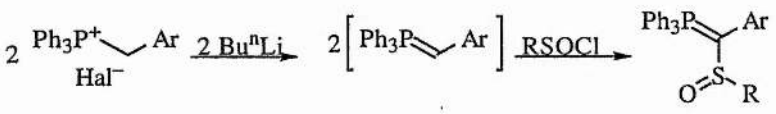
1 Preparation

The only previous example of these ylides **226** to be prepared was 2-propanesulphinylbenzylidenetriphenylphosphorane **227**. This was a beautiful yellow compound, whose pyrolysis was straightforward.[185] FVP at 500°C caused extrusion of Ph_3P only, in contrast to the aromatic compounds, where varying proportions of Ph_3P and $Ph_3P{=}O$ were extruded. The only other product was the thiobenzoate **228**, although at first it was thought (on the evidence of a ^1H NMR spectrum) that the thiobenzoate might have lost propene to give the thiobenzoic acid **354**.



226 **227** **228** **354**

The method of preparation of these ylides was identical to the preparation of the aromatic compounds. Here again, only examples of **226** with Ar = phenyl were ever obtained.



355 Ar = Ph, R = Et 23%

227 Ar = Ph, R = Pr^i 19%

356 Ar = Ph, R = $PhCH_2$ 4%

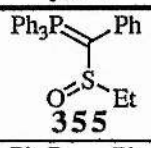
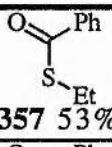
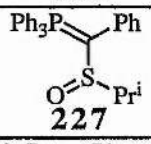
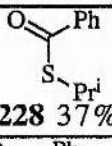
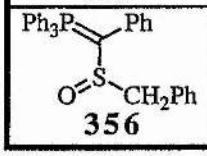
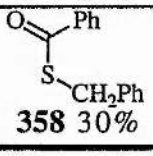
The spectra of **227**, **355** and **356** were similar to those of **312–314**. In fact, the absence of aromatic signals from R was of considerable help in

assigning the peaks for the Ph groups in **312–314** and hence the R groups in these compounds. A table of the ^{31}P and ^{13}C NMR data is given below. Compound **356** was not obtained in an analytically pure form but the spectra showed that the sample obtained did consist largely of the desired compound.

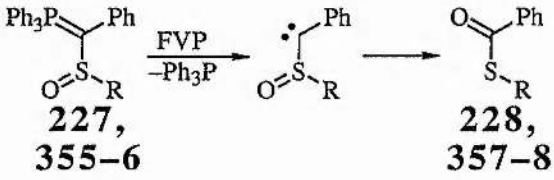
ylide	δ_P	δ_C								
		P=C	P–Phenyl				P=C–Ph		R	
			C–1	C–2	C–3	C–4				
355	+19.7	47.9 (126)	127.7 (86)	134.2 (10)	128.6 (12)	131.9 (2)	137.1 (14) 127.8 (2C)	131.5 (2C) (6) 124.0	45.2 (12)	10.1
227	+20.2	47.2 (123)	127.5 (89)	134.3 (10)	128.6 (12)	132.0 (2)	137.3 (11) 127.7 (2C)	131.9 (2C) (5) 124.1	49.6 (12) 18.7	19.0
356	+18.7	47.1 (128)	127.0 (90)	134.0 (10)	128.6 (12)	132.1 (<2)	138.3 (12) 127.9 (2C)	131.9 (2C) (5) 123.5	133.2 128.4 (2C) 56.3 (12)	130.5 (2C) 127.0

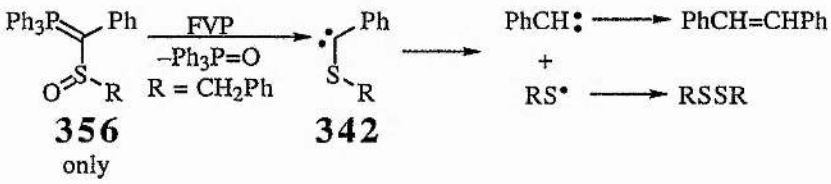
2 Pyrolysis

The pyrolysis of these compounds was also straightforward, except that some $Ph_3P{=}S$ and $Ph_3P{=}O$ were also detected The major non phosphorus-containing compounds obtained were the corresponding thiolobenzoates **228**, **357** and **358**. The yields of the products are given overleaf;

ylide	Ph_3P:Ph_3P=O:Ph_3P=S	other products
 **355**	80:13:7	 **357** 53%
 **227**	84:9:7	 **228** 37%
 **356**	50:40:10	 **358** 30% E + Z $PhCH=CHPh$ 10% $(PhCH_2)_2S$ 2%

It is proposed that similar mechanisms to those described for the aryl compounds **312–314** account for the formation of the thiolobenzoates and for the stilbene formed in the pyrolysis of **356**.

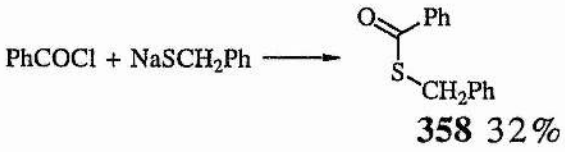




The absence of the range of products formed in the FVP of the aryl compounds **312–314** may be explained by recalling that formation of ketones requires migration of R. Alkyl groups have poorer migratory aptitude than aryl groups[251] as is borne out by this work. The small amount of dibenzyl sulphide in the pyrolysate of **356** is assumed to arise as for **312–314** by hydrogen atom abstraction by carbene **342**.

An authentic sample of benzyl thiolobenzoate **358** for comparison was prepared by reaction of sodium phenylmethanethiolate and benzoyl

chloride, and showed identical spectroscopic properties to that produced in the pyrolysis of **356**.

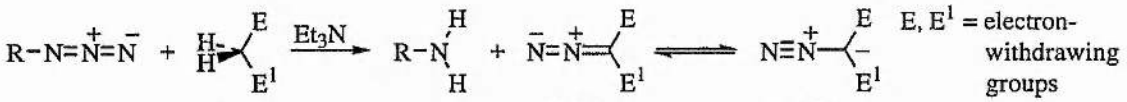


358 32%

D Preparation and pyrolysis of alkane- and arenesulphonylaryl diazomethanes

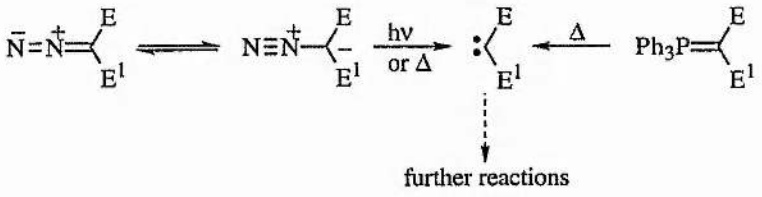
1 Preparation

Diazo compounds **359** are the molecules of choice for any study of carbenes. The diazo moiety easily loses N_2, which is an unreactive molecule and so is unlikely to undergo any secondary reactions with the other products of the carbene reaction. The diazo moiety is also easy to form; reaction of an "activated methylene" **360** with a variety of agents containing the $-N_3$ group gives the diazo compound and the amine byproduct.



360 **359a** **359b**

Diazo compounds are easily pyrolysed or photolysed to give carbenes. Thus, in the course of this work, it was thought that it would be beneficial to have direct comparison between the pyrolysates from ylides and those from diazo compounds which would almost certainly give the carbenes under study.



Attempts to prepare some diazosulphinyl and sulphenyl compounds have been reported elsewhere in this thesis. However, the sulphonyl species seemed worthy of attention, since an amount of work on the pyrolysis of

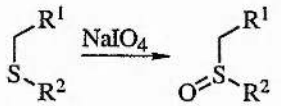
sulphonyl ylides had been performed in this laboratory.[185, 186]

The required sulphones were also worthy of attention in themselves, since an improved route to these compounds had been discovered in this laboratory.[226] The required sulphides **292–295, 361–368** were prepared by reaction of sodium alkanethiolates with alkyl halides.

$R^1CH_2Cl + R^2SNa \longrightarrow R^1CH_2SR^2$

361	R^1 = Ph	R^2 = Et	69%
362	R^1 = Ph	R^2 = Pr^i	42%
363	R^1 = Ph	R^2 = Ph	61%
364	R^1 = Ph	R^2 = $PhCH_2$	60%
353	R^1 = Ph	R^2 = *p*-Me-C_6H_4	30%
352	R^1 = Ph	R^2 = *p*-Cl-C_6H_4	38%
365	R^1 = *p*-MeO-C_6H_4	R^2 = Ph	28%
366	R^1 = *p*-O_2N-C_6H_4	R^2 = Ph	65%
292	R^1 = CO_2Me	R^2 = Et	52%
293	R^1 = CO_2Me	R^2 = Ph	74%
294	R^1 = CO_2Et	R^2 = Et	42%
295	R^1 = CO_2Et	R^2 = Ph	72%

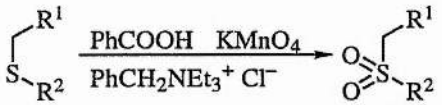
The corresponding sulphoxides were also prepared by periodate oxidation of the sulphides. This was done before it was found that neither these, nor the sulphides, nor the sulphones mentioned overleaf, unless stabilised by ester groups, would give diazocompounds (see section A2).



367	R^1 = Ph	R^2 = Et	36%
368	R^1 = Ph	R^2 = Pr^i	56%

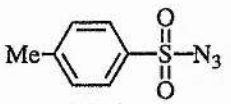
369	R^1 = Ph	R^2 = Ph	73%
370	R^1 = Ph	R^2 = $PhCH_2$	58%
371	R^1 = Ph	R^2 = *p*-Me-C_6H_4	59%
372	R^1 = Ph	R^2 = *p*-Cl-C_6H_4	54%
373	R^1 = *p*-MeO-C_6H_4	R^2 = Ph	32%
374	R^1 = *p*-O_2N-C_6H_4	R^2 = Ph	31%
297	R^1 = CO_2Me	R^2 = Et	36%
298	R^1 = CO_2Me	R^2 = Ph	32%
299	R^1 = CO_2Et	R^2 = Et	85%
300	R^1 = CO_2Et	R^2 = Ph	45%

Permanganate oxidation of the sulphides in the presence of benzoic acid and a phase-transfer catalyst gave the sulphones **377–385**.[226]

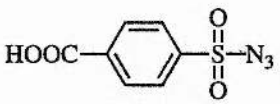


375	R^1 = Ph	R^2 = Et	66%
376	R^1 = Ph	R^2 = Pr^i	34%
377	R^1 = Ph	R^2 = $PhCH_2$	78%
378	R^1 = Ph	R^2 = *p*-Cl-C_6H_4	63%
379	R^1 = *p*-O_2N-C_6H_4	R^2 = Ph	69%
380	R^1 = CO_2Me	R^2 = Et	79%
381	R^1 = CO_2Me	R^2 = Ph	60%
382	R^1 = CO_2Et	R^2 = Et	66%
383	R^1 = CO_2Et	R^2 = Ph	52%

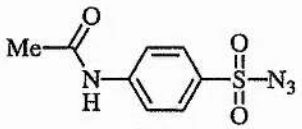
The next stage was to synthesise the diazo compounds. There are a number of diazo exchange reagents in common use. The most well-known is tosyl azide **296**.[202] 4-Carboxybenzenesulphonyl azide **384** is also in use, but the reagent most suitable for this work was 4-(N-acetylamino)benzene sulphonyl azide **301**.[198]



296

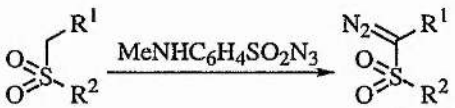


384



301

The diazo exchange reaction was attempted first with tosyl azide and Et_3N in dry CH_2Cl_2. The resulting oils contained mostly tosyl amide, but dibenzyl sulphone and 4-nitrobenzyl phenyl sulphone gave no reaction at all. Some attempts to remove the tosyl amide by washing with NaOH caused any ester-containing groups to hydrolyse. Fortunately, the ester-containing sulphones could be cleanly reacted with 4-(N-acetylamino) benzenesulphonyl azide in reasonable yield. This was reported to have a byproduct amide that was not soluble in the mixture of ether and petroleum in which the diazo exchange reaction was performed.[198] In practice, some amide byproduct was found but the reaction mixture was easily separated by simple column chromatography through silica with ether. Even better, the product was the first compound to elute! The results of the successful syntheses are given below;



385 $R^1 = CO_2Me$ $R^2 = Et$ 17%

386 $R^1 = CO_2Et$ $R^2 = Et$ 50%

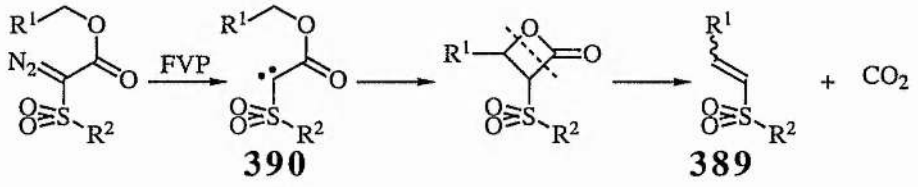
387 $R^1 = CO_2Me$ $R^2 = Ph$ 54%

388 $R^1 = CO_2Et$ $R^2 = Ph$ 47%

The four diazosulphones **385–388** are previously unknown and gave the expected spectroscopic data, including a distinctive signal at δ_C 71–76 for the diazo carbon. Due to their thermal instability, satisfactory elemental analyses could not be obtained but correct high resolution mass spectral measurements were made in each case. The compounds appeared to be pure since they gave a single spot in TLC tests.

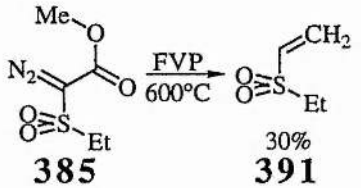
2 FVP

FVP of these compounds gave some unexpected results. Most significantly, the vinyl sulphones **389** were formed in three of the four cases, almost certainly by intramolecular insertion of carbenes **390**, a result in excellent agreement with the pattern observed for ylides **222** discussed in section A. The products from each diazosulphone and some suggestions as to their mechanism of formation are discussed in detail below.



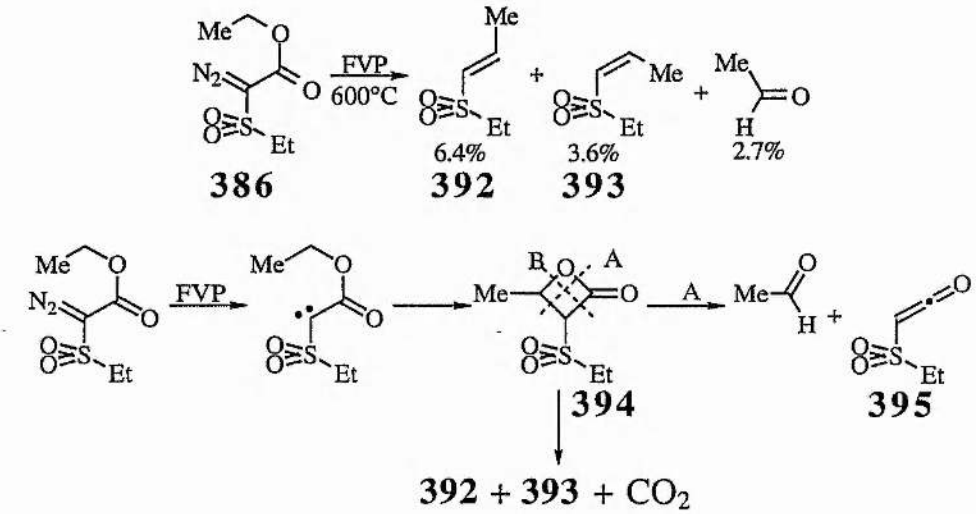
390 **389**

Methyl ethanesulphonyldiazoacetate **385** was the only one of these compounds to give a reasonable yield of the expected vinyl sulphone, **391**, at 600°C.



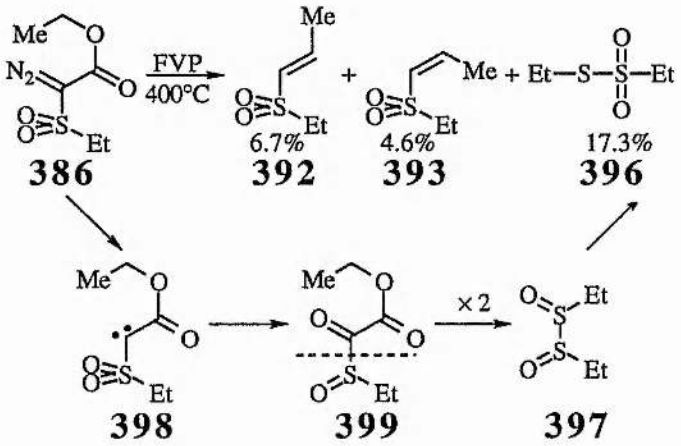
385 **391**

At 600°C, ethyl ethanesulphonyldiazoacetate **386** gave poor yields of the two isomers of the expected E- and Z-propenyl sulphones, **392** and **393**. Also detected was a small amount of acetaldehyde, which was assumed to come from the alternative splitting of β-lactone **394**, as already observed for ylides **222**. As with the ylides, no products derived from ketene **395** were detected.

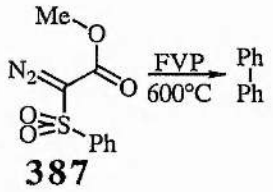


At 400°C, **386** also gave the expected ethyl propenyl sulphones but the major product was now ethyl ethanethiolosulphonate **396**. This was the first sign of oxygen transfer, in that **396** could have been formed by combination of two ethanesulphinyl radicals followed by internal disproportionation of the gem-disulphoxide **397**. The ethanesulphinyl radicals could, in turn, have been formed by transfer of oxygen from sulphone to carbene in **398**, followed by rupture of the keto sulphoxide **399**. In order to confirm the identity of **396**, an attempt was made to prepare an authentic sample by oxidation of diethyldisulphide.

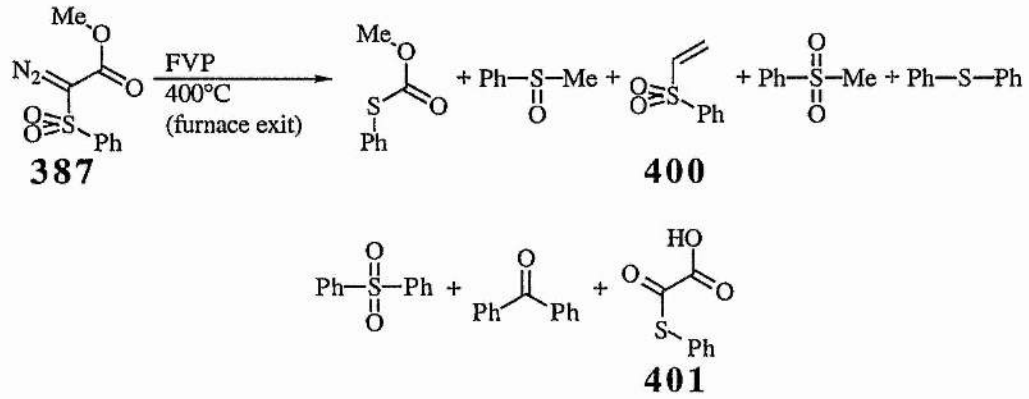
Unfortunately, this was not successful, even though the corresponding reaction of MeSSMe to give $MeSSO_2Me$ did work.

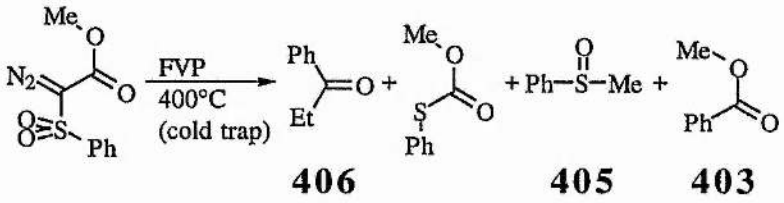


FVP of methyl benzenesulphonyldiazoacetate **387** at 600°C gave only biphenyl. It was this result that prompted the pyrolyses of these diazocompounds at a lower temperature.



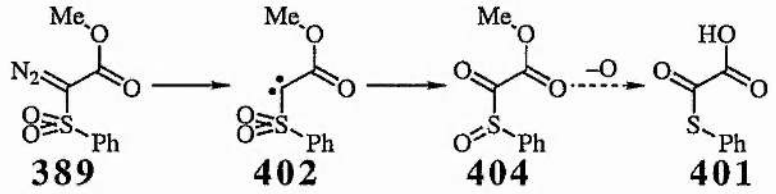
FVP of **387** at 400°C gave a mixture of products which included the expected phenyl vinyl sulphone **400**. The products are shown (in order of decreasing abundance) in the diagrams below:





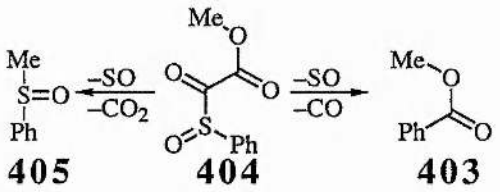
406 **405** **403**

Phenyl thiooxalate **401** is possibly produced by oxygen transfer in carbene **402.**



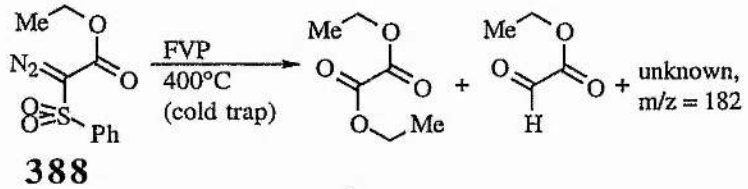
389 **402** **404** **401**

Methyl benzoate **403** could also be from this route by loss of SO and CO from the keto sulphoxide **404**. An alternative breakdown of **404** leads to methyl phenyl sulphoxide **405**. The route to ethyl phenyl ketone **406** is completely unknown, as are the routes to the remaining products.

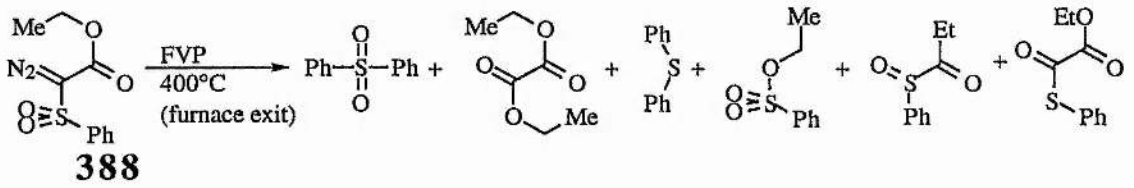


405 **404** **403**

The pyrolysis of ethyl (benzenesulphonyl)diazoacetate **388** follows a somewhat different pattern.

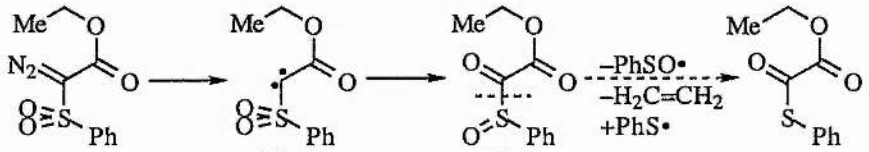


388



388

Again, oxygen transfer within **407**, followed by break-down of the resulting ketosulphoxide **408** is presumed to be the source of some of the products but the overall pattern is clearly complex and requires further study to elucidate the mechanisms involved.



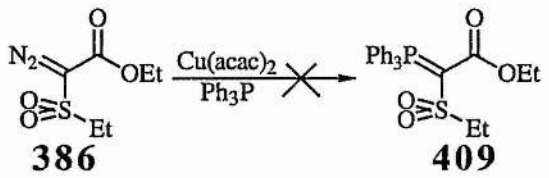
407 **408**

3 Attempted conversion of diazocompound to ylide

It was hoped, since the actual ylides corresponding to **385–388** had not yet been prepared, that reaction of these diazocompounds with Ph_3P would lead to a Staudinger-like reaction. The decomposition of diazocompounds has been catalysed by copper $(acac)_2$ [bis-(2,4-pentandionato)-copper (II)] in a number of investigations and it was thought that such a catalytic decomposition of **386**, in the presence of Ph_3P would lead to ylides such as **409**.

Hence ethyl (ethanesulphonyl)diazoacetete **386** was heated with triphenylphosphine and copper $(acac)_2$ in toluene. This gave a yellow powder whose phosphorus spectrum showed a large peak at δ_P +28.7. This was close to the values for alkoxycarbonyl sulphinyl ylides, but also to $Ph_3P{=}O$. TLC showed that the powder was almost entirely

triphenylphosphine oxide. FVP at 400°C gave a range of products similar to that from the original diazoacetate, so it was concluded that the reaction had not occurred.



386 **409**

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APPENDIX: PUBLICATIONS

i "Pyrolysis of stabilised phosphorus ylides as a route to hetero carbenes", R. A. Aitken, M. J. Drysdale, A. Ford, P. E. Y. Milne, D. W. Russell, B. M. Ryan and M. Whittaker, *Phosphorus, Sulfur and Silicon*, 1993, **75**, 31.

ii "Flash Vacuum Pyrolysis of Sulphinyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulphinylcarbenes", R. A. Aitken, M. J. Drysdale and B. M. Ryan, *J. Chem. Soc., Chem. Commun.*, 1993, 1699.

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Flash Vacuum Pyrolysis of Sulfinyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulfinylcarbenes

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Flash Vacuum Pyrolysis of Sulfinyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulfinylcarbenes

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Flash vacuum pyrolysis of α-alkanesulfinyl phosphorus ylides results mainly in extrusion of Ph_3P to give thioesters, presumably by 1,2-oxygen transfer in the initially formed sulfinyl carbenes; for α-arenesulfinyl ylides loss of Ph_3PO to give additional products is also observed.

Although the thermal extrusion of Ph_3PO from α-acylphosphonium ylides **1** to give alkynes is well established,[1] the corresponding reaction of ylides bearing other oxygen containing functional groups on the α-position has been little investigated. Sulfonyl cyanides have been prepared by spontaneous extrusion from α-nitroso ylides **2** at −40 °C,[2] and there is evidence for extrusion of Ph_3PO from α-nitro ylides **3** to give nitrile oxides,[3] but we recently reported that sulfonyl ylides **4** undergo loss of Ph_3P rather than Ph_3PO upon flash vacuum pyrolysis (FVP) to give products derived from sulfonylcarbenes.[4] We now report the preparation and pyrolytic behaviour of representative α-sulfinyl ylides **5**.

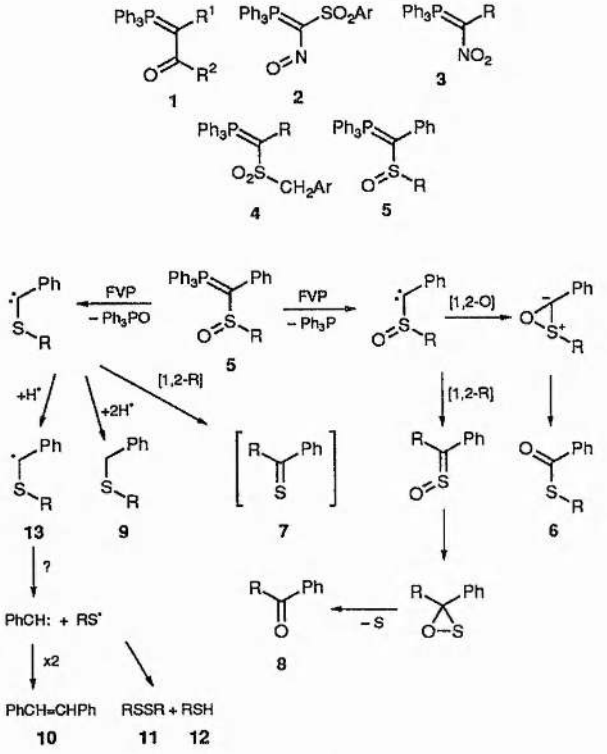
The sulfinyl ylides are little known and there were only two reports,[5] both involving additional stabilisation by an ester group, until the (sulfinylmethylene)diphenylmethylphosphoranes were recently described,[6] formed by reaction of a lithium phosphonium diylide with sulfinate esters. The required ylides **5** were readily formed in low to moderate yield (Table 1) in analogy to the acyl ylides **1**, by reaction of $Ph_3P{=}CHPh$ (2 equiv.) with sulfinyl chlorides RS(O)Cl. The sulfinyl chlorides, which are notoriously unstable and difficult to purify, were used directly as obtained from the improved method recently reported[7] involving treatment of RSH with 2 equiv. SO_2Cl_2 and 1 equiv. AcOH. The ylides were recognised easily from the characteristic doublet ($^1J_{P-C}$ 122–128 Hz) due to the ylide carbon in their ^{13}C NMR spectra (see Table 1).

For the alkanesulfinyl ylides **5a–c**, FVP at 500 °C and 10^{-2} Torr (contact time *ca.* 10^{-2} s) resulted mainly in extrusion of Ph_3P to give the thioesters **6** (Table 1). This can be explained by a 1,2-O-transfer in the initially formed sulfinylcarbenes *via* the zwitterionic oxathirane intermediate shown. Sulfinylcarbenes are a little known class of reactive intermediates,[8] but this type of oxygen transfer has been observed before in two cases.[9] The analogous rearrangement of nitrocarbenes to acynitroso compounds has been described,[10] as has 1,4-O-transfer from sulfur in an *N*-sulfonylimidoylcarbene to give the sulfinylimidoyl ketone.[11]

For **5a–c** there was also some loss of Ph_3PO to give unknown

Table 1 Formation of ylides **5** and results of their pyrolysis at 500 °C

R	Yield of **5** (%)	δ_P	δ_C (ylide)	Products from FVP of **5** (%)							
				Ph_3P	Ph_3PO	**6**	**8**	**9**	**10**	**11**	**12**
a Et	24	+19.7	47.9	80	13	53	—	—	—	—	—
b Pr^i	33	+20.2	47.2	84	9	37	—	—	—	—	—
c CH_2Ph	4	+18.7	47.1	50	40	30	—	2	10	—	—
d Ph	29	+20.4	52.2	64	32	20	—	4	10	10	8
e *p*-Me-C_6H_4	45	+20.2	52.1	82	15	25	5	—	—	6	20
f *p*-Cl-C_6H_4	31	+19.7		27	67	9	18	7	7	17	25



Scheme 1

products, and for the arenesulfinyl ylides **5d–f** competing processes were more important, although **6** was still formed in each case.† The most obvious feature in these cases was the production of an intense dark-blue colour in the cold trap that faded rapidly upon warming. This is attributed to the thioketone **7** although it was only present in trace quantities and could not be detected spectroscopically. The formation of this product may be due to rearrangement of the thiocarbene resulting from Ph_3PO extrusion. A major product for **5e,f** was the ketone **8** (Scheme 1) which most likely results from rearrangement of the sulfinylcarbene to a sulfine followed by loss of sulfur. A closely related example, dimethylvinyl(*p*-toluenesulfinyl)carbene, has been reported to give the ketone in excellent yield in an analogous way,[12] and the absence of this process for **5a–c** reflects the poorer migratory aptitude of alkyl *vs.* aryl groups. The remaining products can be accounted for by alternative reactions of the thiocarbene resulting from extrusion of Ph_3PO. The benzyl sulfide **9** (Scheme 1) is clearly formed by hydrogen atom abstraction, but the formation of stilbene **10** is more difficult to explain. Although the disulfide **11** and thiol **12** may be formed by a variety of radical processes which generate RS•, it is attractive to speculate that all three products may result as shown from an α-elimination process of radical **13** formed by abstraction of single hydrogen atom by the thiocarbene, although we are not aware of any precendent for this process. A further complication is the possibility of disproportionation of **5** in the inlet tube which has been observed for other sulfinyl ylides,[13] and would lead to further products from pyrolysis of sulfenyl and sulfonyl ylides.

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† In Table 1 the balance of the phosphorus products is accounted for in each case by Ph_3PS, presumably formed by interaction of Ph_3P with sulfur contining products.

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PYROLYSIS OF STABILISED PHOSPHORUS YLIDES AS A ROUTE TO NEW HETERO CARBENES

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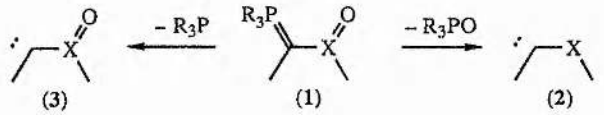
Abstract: Flash vacuum pyrolysis of sulphonyl- and sulphinyl-stabilised phosphorus ylides results in loss of either phosphine or phosphine oxide to generate thio-, sulphinyl- and sulphonyl-carbenes which undergo a variety of rearrangement and insertion processes to give stable products. The first case of phosphine extrusion from a ß-oxo ylide is reported, giving access to benzotriazolyl acetyl carbene which rearranges to an acetyl benzotriazine and 2-cyanoacetophenone.

Thermal extrusion of Ph_3PO from both phosphorus ylides[1] and phosphinimines[2] stabilised by an α-acyl group is well known to lead to alkynes and nitriles, respectively, and in the former case the use of flash vacuum pyrolysis (FVP) gives improved yields in many cases.[3] We have carried out a detailed study of the pyrolytic behaviour of a variety of phosphorus ylides stabilised by other oxygen-containing functional groups, notably sulphoxide and sulphone. As described below, this has revealed processes involving loss of both phosphine and phoshine oxide, so that in general (**1**) may give either (**2**) or (**3**) depending both on the nature of X and the substituents present.

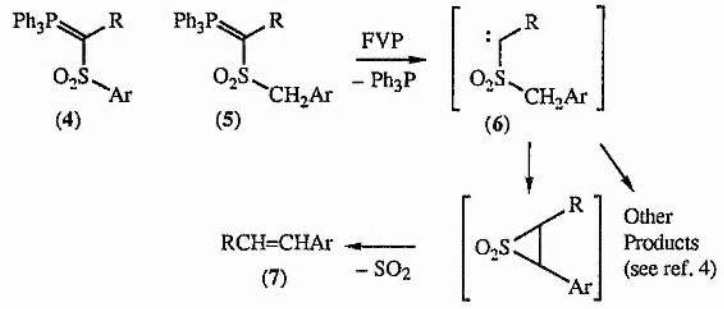


(3) (1) (2)

SULPHONYL YLIDES

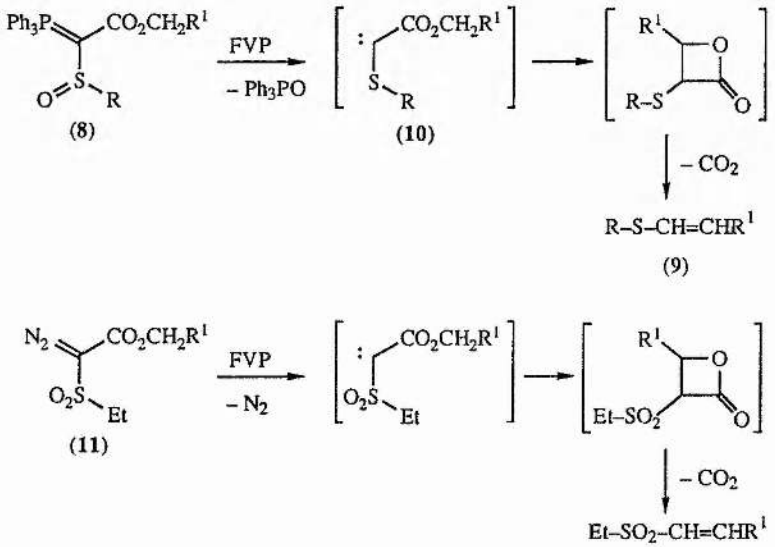
The results for sulphonyl stabilised ylides have already been described briefly.[4] Compounds of type (**4**) lost Ph_3PO to give a complex mixture of products which could not be fully identified and the process was of no preparative value. In contrast the phenylmethanesulphonyl ylides (**5**) underwent exclusive loss of Ph_3P to give products which could be accounted for by intramolecular insertion and rearrangement of the

sulphonylcarbenes (**6**). In all cases the alkene products (**7**) were formed as shown, accompanied in some cases by other products depending on the nature of R.[4]



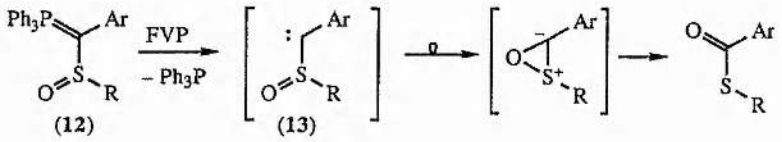
SULPHINYL YLIDES

A range of sulphinyl ylides have also been prepared by acylation of the appropriate starting ylides with sulphinyl chlorides. For the compounds of type (**8**) stabilised both by a sulphinyl and an ester group, Ph_3PO is lost and the final product is a vinyl sulphide (**9**)[5]. We believe that these reactions proceed by intramolecular insertion of the carbene (**10**) to give a β-lactone which loses CO_2 to afford the observed product. Support for this idea is provided by the pyrolysis of α-sulphonyl-α-diazoesters (**11**) which gives the expected vinyl sulphones presumably by a similar mechanism. Since (**8**) is prepared in two steps from RSH and the pyrolysis proceeds in good yield, this represents a viable if

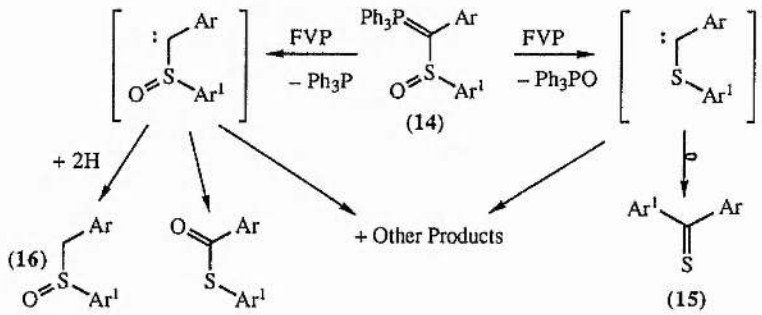


unusual route to convert thiols into vinyl sulphides.

The simpler ylides (**12**) stabilised only by the alkanesulphinyl group undergo a different process. Loss of Ph_3P is followed by rapid rearrangement of the sulphinylcarbene (**13**) by 1,2-oxygen transfer to give the thioesters.

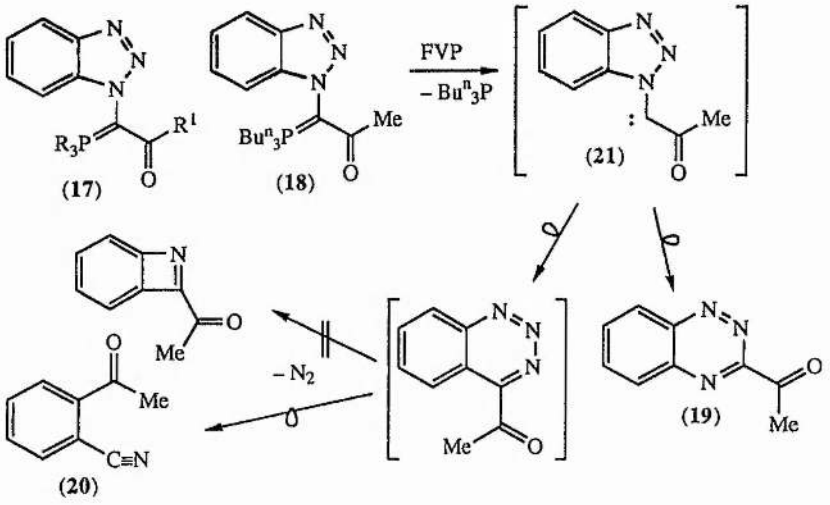


The pyrolytic behaviour of the arenesulphinyl ylides (**14**) is more complex and is not yet fully understood. Both Ph_3P and Ph_3PO are eliminated and both the resulting carbenes lead to products. The bright blue colour produced is almost certainly due to the thioketones (**15**) but these are only there in trace amounts and the colour quickly fades due to reaction with some of the other products present. These include the sulphoxide (**16**) resulting from hydrogen abstraction by one carbene, the thioester from its rearrangement, and products of radical decomposition such as diaryl sulphides.



EXTRUSION OF PHOSPHINE FROM A β-OXO YLIDE

A wide range of benzotriazolyl ylides (**17**) have been prepared and pyrolysed. They generally lose Bu^n_3PO and N_2 to give complex products. In contrast, compound (**18**) loses Bu^n_3P to give two heterocyclic products. After detailed studies these have been confirmed to be 3-acetyl-1,2,4-benzotriazine (**19**) and 2-cyanoacetophenone (**20**).[6] As shown these products can be explained by a series of rearrangements and loss of N_2 from the new carbene (**21**). The reason for (**18**) losing Bu^n_3P and not Bu^n_3PO, an apparently unprecedented process, is not yet clear.



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