FLASH VACUUM PYROLYSIS OF SOME SULPHONYL AND SULPHINYL STABILISED PHOSPHOROUS YLIDES

Martin James Drysdale

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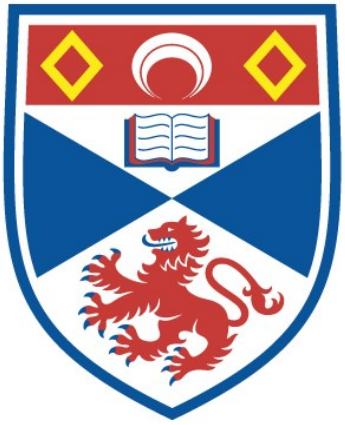
at the
University of St Andrews



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FLASH VACUUM PYROLYSIS OF SOME SULPHONYL AND SULPHINYL STABILISED PHOSPHORUS YLIDES

by

MARTIN JAMES DRYSDALE, B.Sc.

Thesis presented for the degree of

DOCTOR OF PHILOSOPHY

University of St. Andrews

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Dedication

To Mum and Dad – Mere words cannot say Thank You enough.

To Elaine – Finished at last!

Carbon

It was caught by the wind, flung down on the earth, lifted ten kilometers high. It was breathed in by a falcon, descending into its precipitous lungs, but did not penetrate its rich blood and was expelled. It dissolved three times in the water of the sea, once in the water of a cascading torrent, and again was expelled. It travelled with the wind for eight years: now high, now low, on the sea and among the clouds, over forests, deserts, and limitless expanses of ice; then it stumbled into capture and the organic adventure.

Primo Levi

I Martin James Drysdale 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 of professional qualification.

Signed ... Date..19/.10/.89.....

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on October 1st 1986 and as a candidate for the degree of Ph. D. on October 1st 1987.

Signed . Date..19/.10/.89.....

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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Lecture Courses

The following is a statement of the courses attended during the period of research ; Organic Research Seminars (3 years attendance) ; Solar Energy Conversion, Dr.J.A. Crayston (8 lectures) ; Naturally occurring organo-sulphur compounds, Dr. R.A. Aitken (3 lectures) ; Pharmaceutical Chemistry, Dr. A. R. Butler and Dr. R.A. Aitken (8 lectures) ; Naphthalenes, Anthracenes and other Polycyclic Compounds, Dr. D.M.G. Lloyd (3 lectures) ; Heavy-atom multiply bonded compounds, Dr. R.A. Aitken (3 lectures) ; New synthetic methods using sulphur, selenium and phosphorus, Dr.R.K. Mackie (3 lectures).

Acknowledgements

I would like to thank Dr. Alan Aitken for his excellent supervision over the past three years.

My thanks also go to all past and present colleagues in Labs 414 and 434 for all their help and friendship, to the technical staff of the St. Andrews University Chemistry Department for the provision of various services and to Sheila Wilson for the excellent typing.

Thanks are also due to B.P. International for their financial support.

ABSTRACT

The reaction between alkylidene or arylmethylene triphenyl phosphoranes and sulphonyl fluorides or sulphonic anhydrides has been used to give a variety of α-sulphonyl stabilised phosphorus ylides. Flash Vacuum Pyrolysis (FVP) of alkyl- and arylsulphonyl alkylidene triphenyl phosphoranes leads to two fractions. The first fraction is made up of up to 20 phosphorus containing products, the major one being Ph_3PO. The second fraction is a liquid at low temperature which forms a white, insoluble polymeric material on warming to room temperature. Trapping reactions of the liquid with Diels-Alder dienes or chlorine gives unknown and unstable compounds except with anthracene where an unidentified complex is formed.

FVP of benzyl- and substituted-benzylsulphonyl alkylidene and phenylmethylene triphenyl phosphoranes proceeds by loss of Ph_3P followed by intramolecular insertion of the resulting carbene to form episulphones which lose SO_2 to give stilbene or styrene derivatives. In the cases where the phosphorane is an α-sulphonyl ethylidene triphenyl phosphorane, a 1,2-H shift of the carbene can occur to form a vinyl sulphone, which decomposes to vinyl and benzyl radicals and SO_2 with formation of bibenzyl products. Where the phosphorane is an α-sulphonyl ortho-substituted-benzylidene triphenyl phosphorane, a second carbene insertion pathway occurs to give eventually benzofuran or benzothiophene

and bibenzyl. The Ph_3P group reacts with the liberated SO_2 to give some conversion to a 2:1 mixture of Ph_3PO and Ph_3PS, a previously unrecognised reaction. The initially formed stilbene or styrene products can react to a certain extent to form cross over products under the reaction conditions used.

A number of α-sulphinyl alkoxycarbonylmethylene triphenyl phosphoranes have been made from alkoxycarbonylmethylene triphenyl phosphoranes, sulphinyl chlorides and Et_3N. These ylides exhibit broadening in their ^1H and ^{13}C NMR spectra, variable temperature NMR studies indicating the presence of cis and trans rotamers. FVP of these compounds gave Ph_3P, Ph_3PO, vinyl or substituted vinyl sulphides, alkyl sulphides and an as yet unidentified carbonyl compound. The vinyl or substituted vinyl sulphides are obtained via loss of Ph_3PO from the starting ylide followed by insertion of the carbene form of the initially formed thia-acetylene and loss of CO_2 from the resulting β-lactone. The other products are obtained from a variety of insertion, rearrangement and elimination reactions of the initially formed carbenes some of which have been elucidated with the help of ^{13}C labelling.

Isopropylsulphinyl benzylidene triphenyl phosphorane was synthesised and upon FVP gave Ph_3P, isopropyl thiobenzoate and thiobenzoic acid. The formation of isopropyl thiobenzoate is rationalised via an S to C oxygen transfer mechanism of the initially formed carbene, involving the

intermediacy of the previously unknown λ^4-oxathiirene ring system.

A β-keto tri-n-butyl phosphorane, benzoyl butylidene tri-n-butyl phosphorane was synthesised and its FVP performed at room temperature, 300°C and 500°C. The almost complete extrusion of Bu^n_3PO from the ylide at 300°C indicates that much lower temperatures are required for loss of Bu^n_3PO as compared to loss of Ph_3PO.

CONTENTS

E Preparation of Sulphinyl Stabilised Phosphorus Ylides

INTRODUCTION

A Extrusion and Elimination Reactions by Flash Vacuum Pyrolysis

Dating to the days when destructive distillation was one of the few preparative methods available to alchemists and the first chemists, the process of decomposition by heat is as old as experimental chemistry itself.

Hurd's[1] classic monograph from 1929, "The Pyrolysis of Carbon Compounds", reviewed all the pyrolytic processes examined up to that time. The scope of this review was extensive, with the term "pyrolysis" covering everything from decomposition of solids at their melting points, to the decomposition of gases at temperatures above 1000°C.

Flash Vacuum Pyrolysis (FVP), subject of a recent review by Brown[2], uses conditions of high temperature and low pressure[3] to provide a mild and elegant alternative to the sledgehammer approach of conventional pyrolysis*. These conditions are ideal for promoting extrusion and elimination reactions where a small stable molecule is expelled from a parent compound. When such a reaction takes place the remaining component may rearrange to generate ring structures or

---

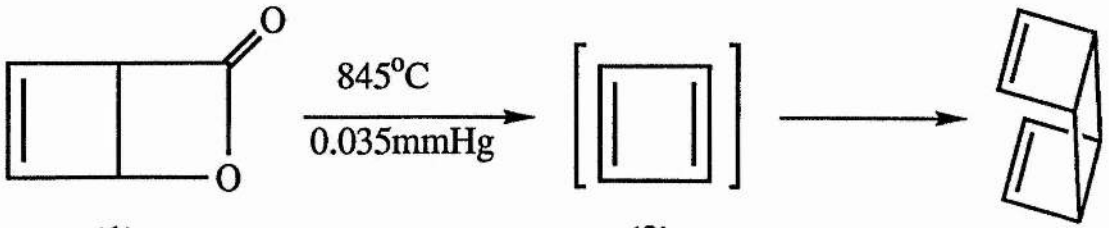
* The terms "pyrolysis" and "conventional pyrolysis" are taken to mean reactions which involve heating neat or in solution, usually at ambient pressures. In the present discussion, Flash Vacuum Pyrolysis (FVP) involves temperatures usually above 350°C with an externally applied high vacuum.

undergo further reactions to give acyclic products. Typical common fragments which can be extruded include nitrogen, carbon monoxide and carbon dioxide, sulphur monoxide and sulphur dioxide, acetone, ethylene, hydrogen chloride and even more unlikely groups, such as tellurium[4] and arsenic[5].

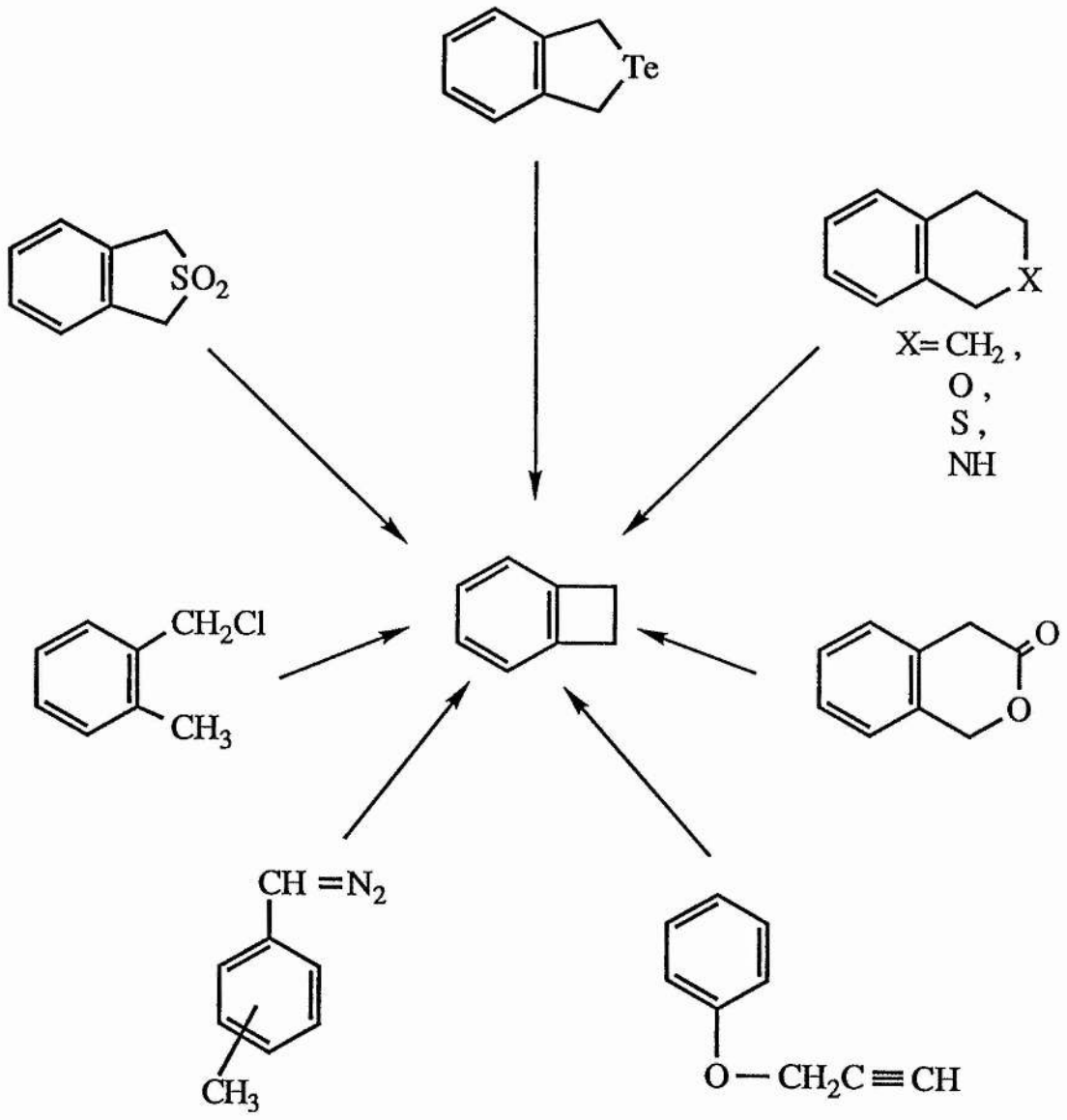
The diversity of possible fragmentation processes can be seen in Schemes 1 and 2. The breakdown of a variety of different substrates with the loss of one, two or three fragments, gives benzocyclobutene and biphenylene respectively.

The examples which follow serve to illustrate the wide range of extrusion and elimination reactions found in flash vacuum pyrolysis to produce interesting and novel species, as well as showing some typical reaction conditions.

The conditions of low pressure and short contact times involved with FVP have proved ideal for observing reactive species formed from primary molecular processes. Free cyclobutadiene (2) is produced in good yield by the FVP of photo-α-pyrone (1)[6] and can be observed spectroscopically by trapping in an Argon matrix, or by the isolation of



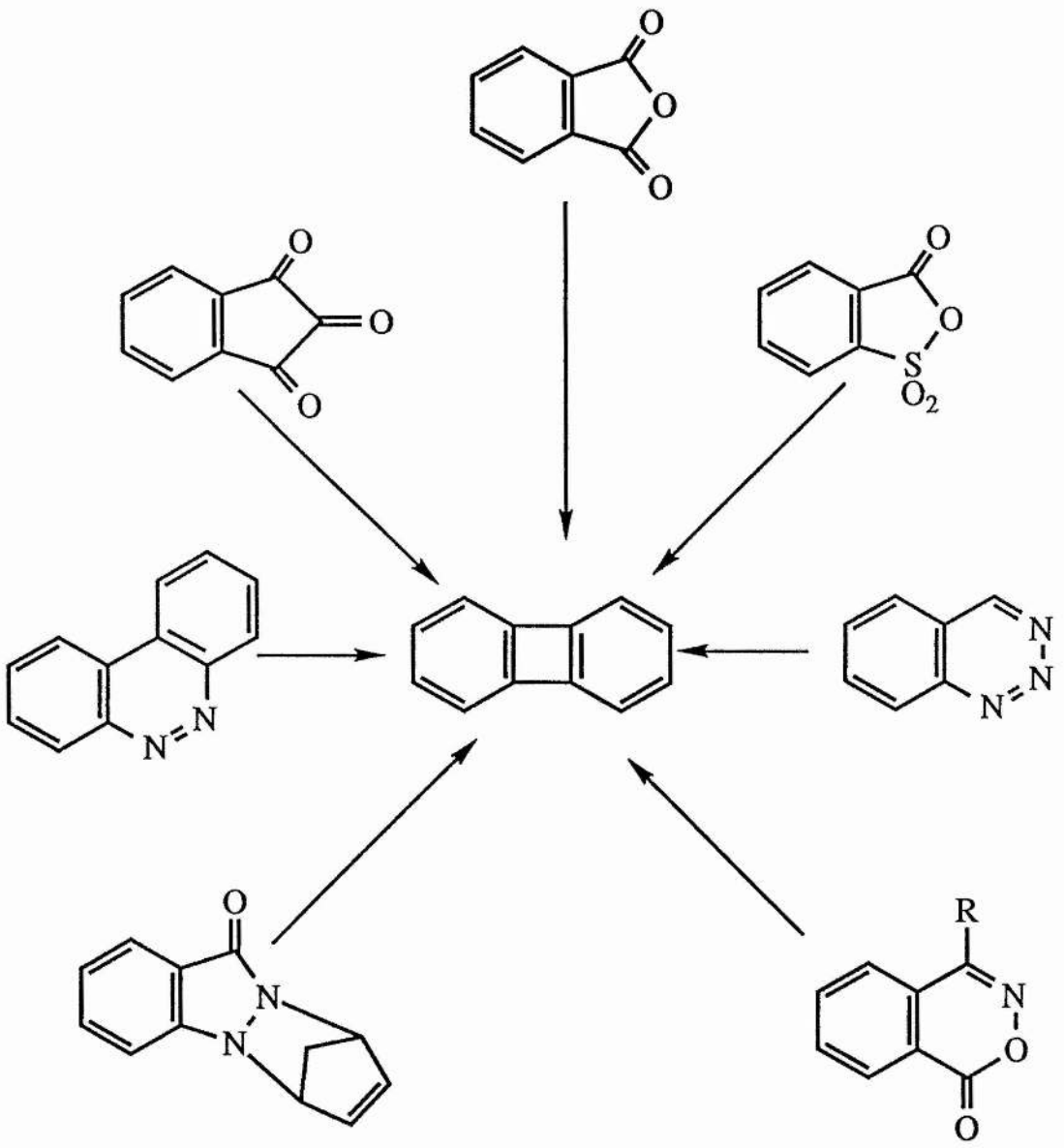
(1) (2) (3)



SCHEME 1

the syn-dimer (3) from the pyrolysate.

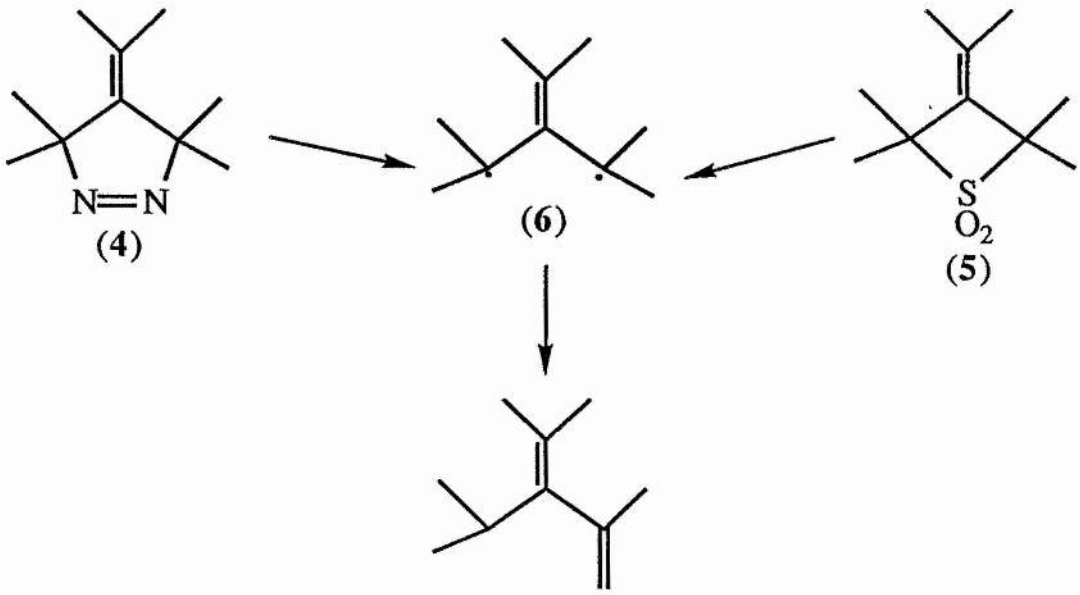
Radical species are also readily generated under FVP conditions. The generation of the trimethylene methane diradical (6) is achieved equally well from the azo compound 4-isopropylidene-3,3,5,5-tetra-



SCHEME 2

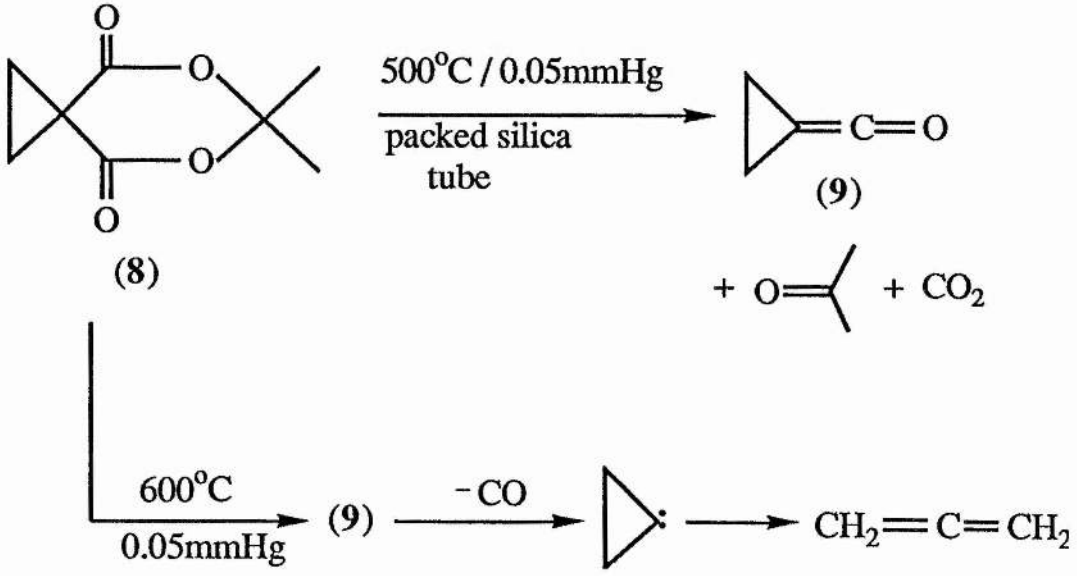
methyl-Δ^1-pyrazoline (4)[7] or the sulphone 3-isopropylidene-2,2,4,4-tetramethylthietan-1,1-dioxide (5)[8]. Bushby and Pollard[7,8] found that each gave the diene 3-isopropyl-2,4-dimethylpenta-1,3-diene (7).

Derivatives of 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's Acid) over the temperature range 400-600°C have been used to generate a variety of substituted ketenes, some of which undergo decarbonylation



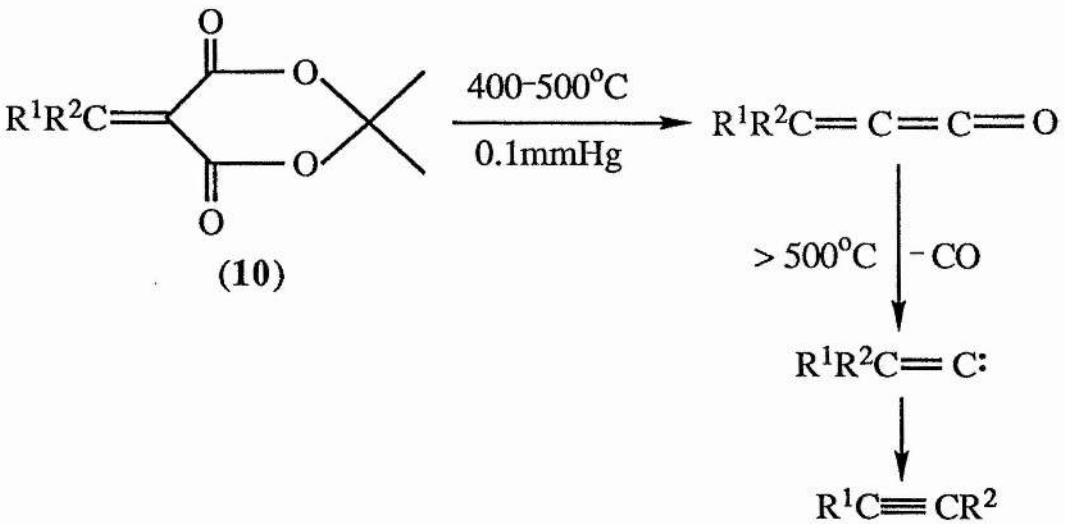
with great ease giving products derived only from the corresponding carbenes.

For example the FVP of 2,2-dimethyl-1,3-dioxan-4,6-dione-5-spirocyclopropane (8)[9] at 500°C gives the corresponding ketene, carbonylcyclopropane (9), whereas at 600°C decarbonylation of the ketene



to the carbene, followed by ring opening to allene is the only observed process.

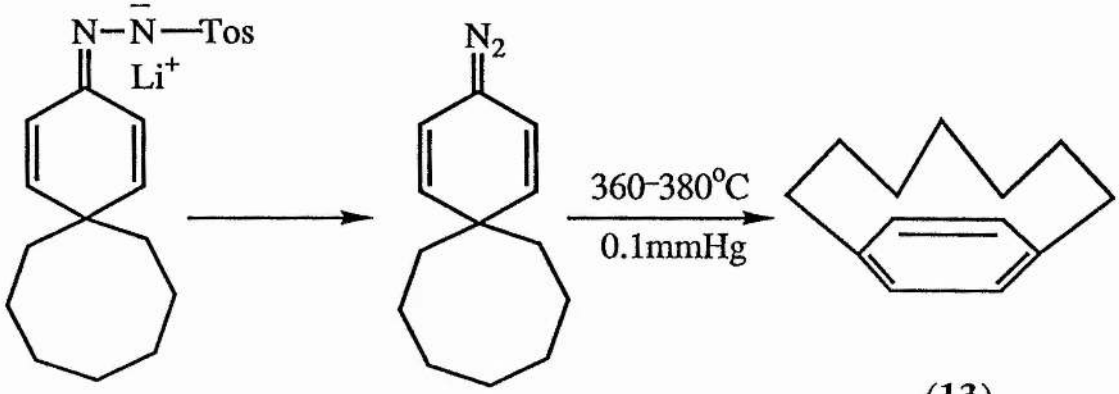
Methylene ketenes can be formed by the FVP of methylene or substituted methylene derivatives of Meldrum's Acid (10)[10,11]. At higher temperatures (500-650°C) the substituted methylene ketenes[12]



(10)

decarbonylate to the methylene carbenes $R^1R^2C = C:$, which in the absence of alternative pathways rearrange to acetylenes. When R^1 = substituted phenyl and R^2 = H this provides a convenient synthesis of substituted phenyl acetylenes[12].

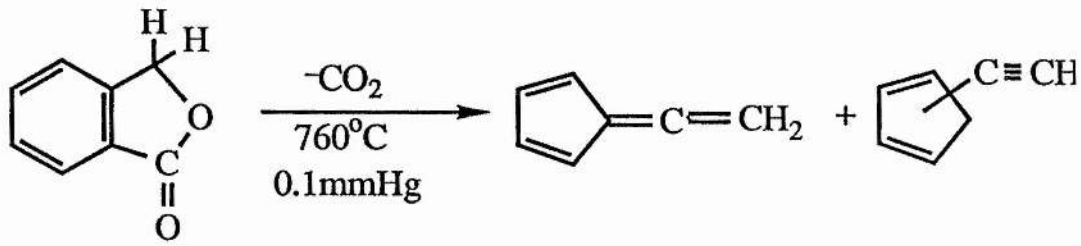
A further well used route for the generation of carbenes is the FVP of diazo compounds[13]. For example the FVP of phenyldiazomethane has been studied exhaustively[14]. More spectacularly however, the lithium salt of spiro-[5,7]-trideca-1,4-dien-3-tosylhydrazone (11) affords the diazo compound (12)[15] which decomposes with loss of N_2 to [7]-paracyclophane (13)[13].



(11) (12) (13)

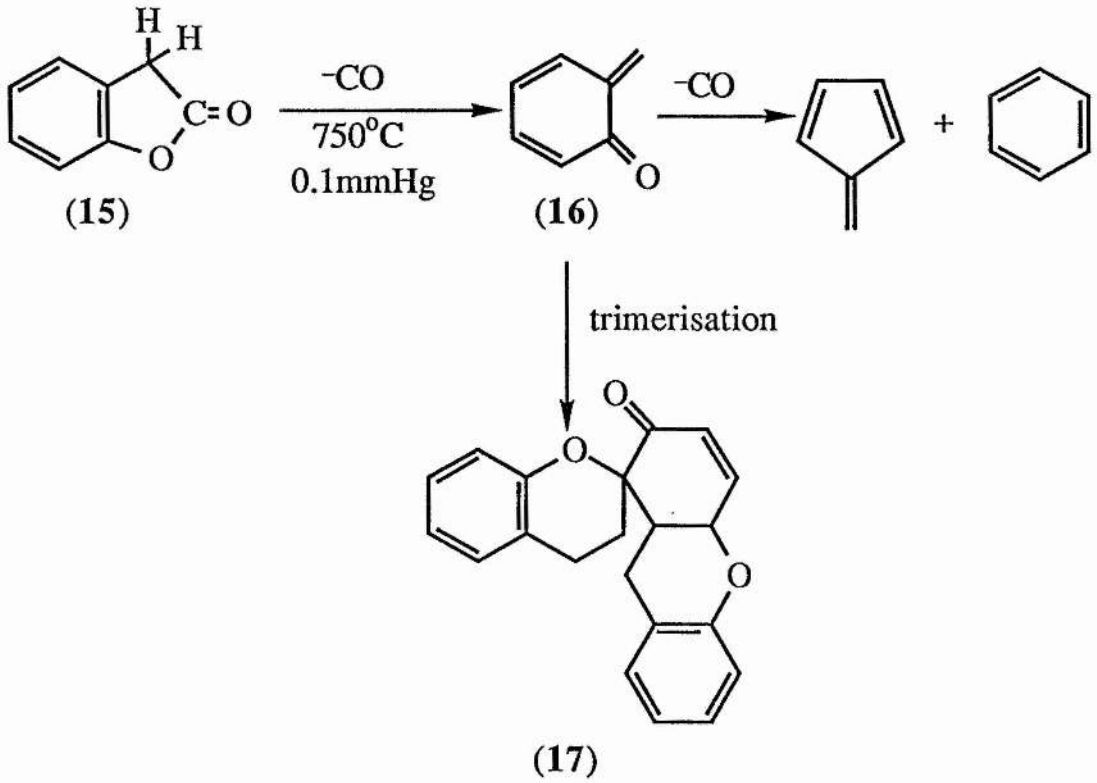
Though many extrusion reactions are expected and can be predicted, an almost equal number of less predictable and/or unexpected reactions occur.

Comparison of the FVP products of phthalide (14) and its isomer α-coumaranone (15) show this[17,18]. Phthalide (14) loses CO_2 to give

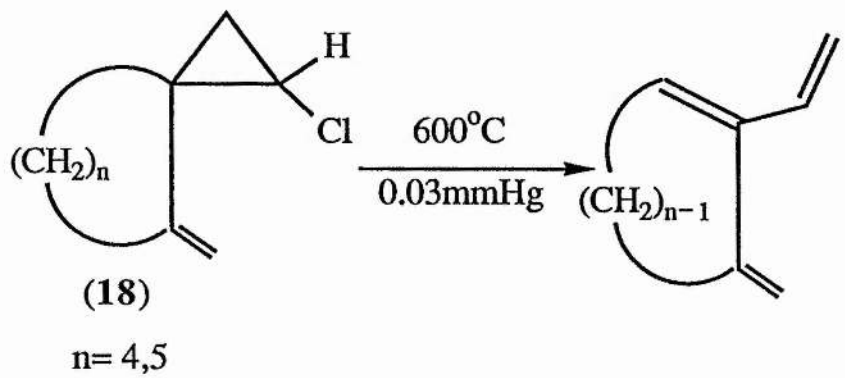


(14)

fulvenallene and ethynylcyclopentadiene, whereas α-coumaranone (15) loses only one mole of CO to give the trimer (17)[19] derived from o-quinonemethide (16) or two moles of CO to give fulvene and benzene.



Another of these unexpected reactions was reported recently by Bickelhaupt *et al.*[20]. The FVP of 1-chloro-4-methylenespiro [2.m] alkenes (18) gave the halogen-free trienes by HCl-elimination, rather than the



expected vinylcyclopropane rearrangement[21,22] to chlorocyclopentenes.

B Phosphorus Yides Stabilised by an adjacent Sulphonyl, Sulphinyl or Selenenyl Group

1. Sulphonyl Stabilised Phosphorus Ylides

a) Bis-sulphonyl Ylides

The first preparation of a bis-sulphonyl ylide was by Horner and Oediger in 1958[23]. They synthesised [bis(phenylsulphonyl)methylene] triphenylphosphorane (19) from the condensation of triphenylphosphine dichloride and bis(phenylsulphonyl)methane in the presence of

$$Ph_3PCl_2 + H_2C(SO_2Ph)_2 \xrightarrow{Et_3N} Ph_3P{=}C(SO_2Ph)_2$$

(19)

triethylamine in 67% yield.

The same methodology was employed by Difenbach *et al.*[24], who prepared (phenylsulphonyl)vinylsulphonyl methylene triphenyl phosphorane (20) in 12% yield for use in co-polymerisation studies with

$$Ph_3P{=}C(SO_2Ph)(SO_2{-}CH{=}CH_2)$$

(20)

styrene[24].

Hoffmann and Förster[25] prepared the ylide (19) from both bromo- and dibromo[bis(phenylsulphonyl)]methane. This is probably explained by

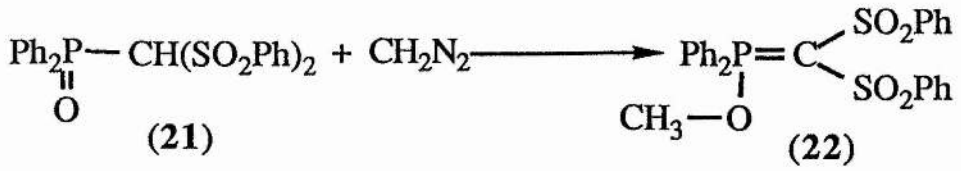
$$(PhSO_2)_2CHBr + Ph_3P \xrightarrow[\text{solvent}]{\text{Aprotic}} \underset{(19)}{Ph_3P{=}C(SO_2Ph)_2} + (PhSO_2)_2CH_2 + Ph_3PBr_2$$

the spontaneous loss of HBr from the initially formed phosphonium salt. The HBr then reacts with the two starting materials to give bis(phenylsulphonyl)methane and triphenylphosphinedibromide. In the presence of excess triphenyl phosphine, dibromo[bis(phenylsulphonyl)]-methane gave the ylide (19) and triphenylphosphine dibromide.

The remaining literature up to this point consists of a series of papers by Russian workers[26-30]. These are primarily concerned with P-substitution reactions.

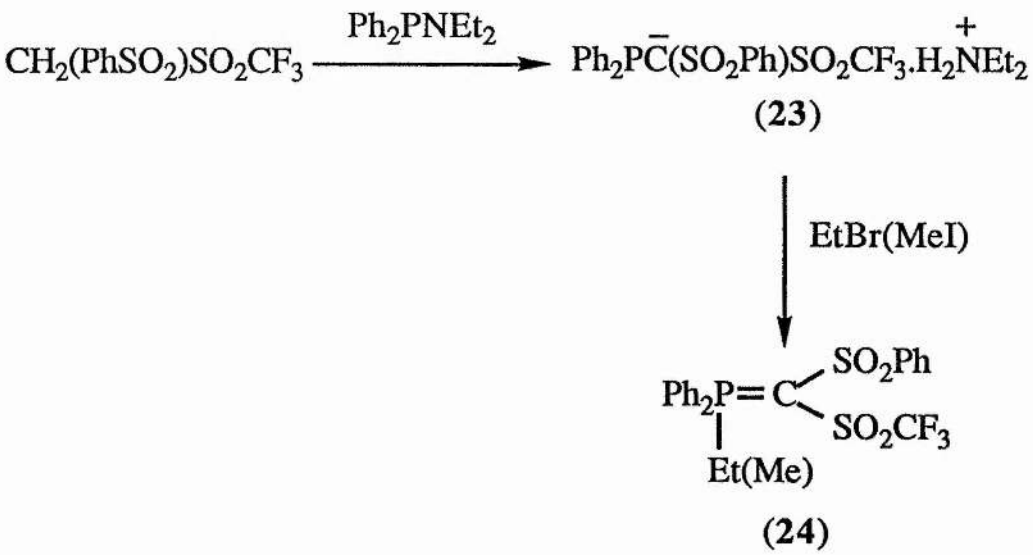
Kolodyazhnyi[26] found that the strong acidity of [bis(phenylsulphonyl)methyl] diphenylphosphine oxide (21), due to the powerful inductive effect of the substituents, means that the proton is highly mobile. Thus the equilibrium of O = P-C-H and O = P - C^- + H^+ leads to reactions with participation of the phosphoryl oxygen becoming characteristic

Thus, with diazomethane the phosphine oxide (21) forms the O-methylated product [bis(phenylsulphonyl)methylene] methoxydiphenyl-phosphorane (22) in high yield[26].



(21) (22)

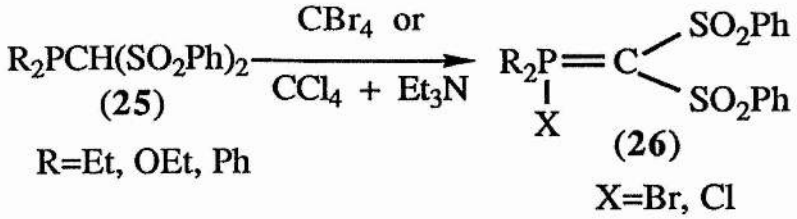
The reaction of phenylsulphonyl(trifluoromethylsulphonyl)methane with diethylaminodiphenylphosphine gives the diethyl-ammonium salt of diphenyl[phenylsulphonyl(trifluoromethylsulphonyl)methyl] phosphine (23)[27].



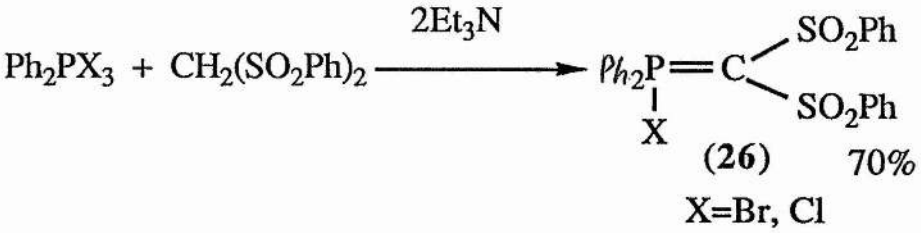
(23) (24)

With alkyl halides the ammonium salt (23) reacts with migration of reaction centre (the P atom, and not the negatively charged C atom) with the formation of the ylide (24) in 50% yield[27].

The synthesis of P-halo ylides can be accomplished in two ways. Firstly[28], the phosphines (25) are reacted with carbon tetrabromide or with carbon tetrachloride and triethylamine to give the P-halo ylides (26).



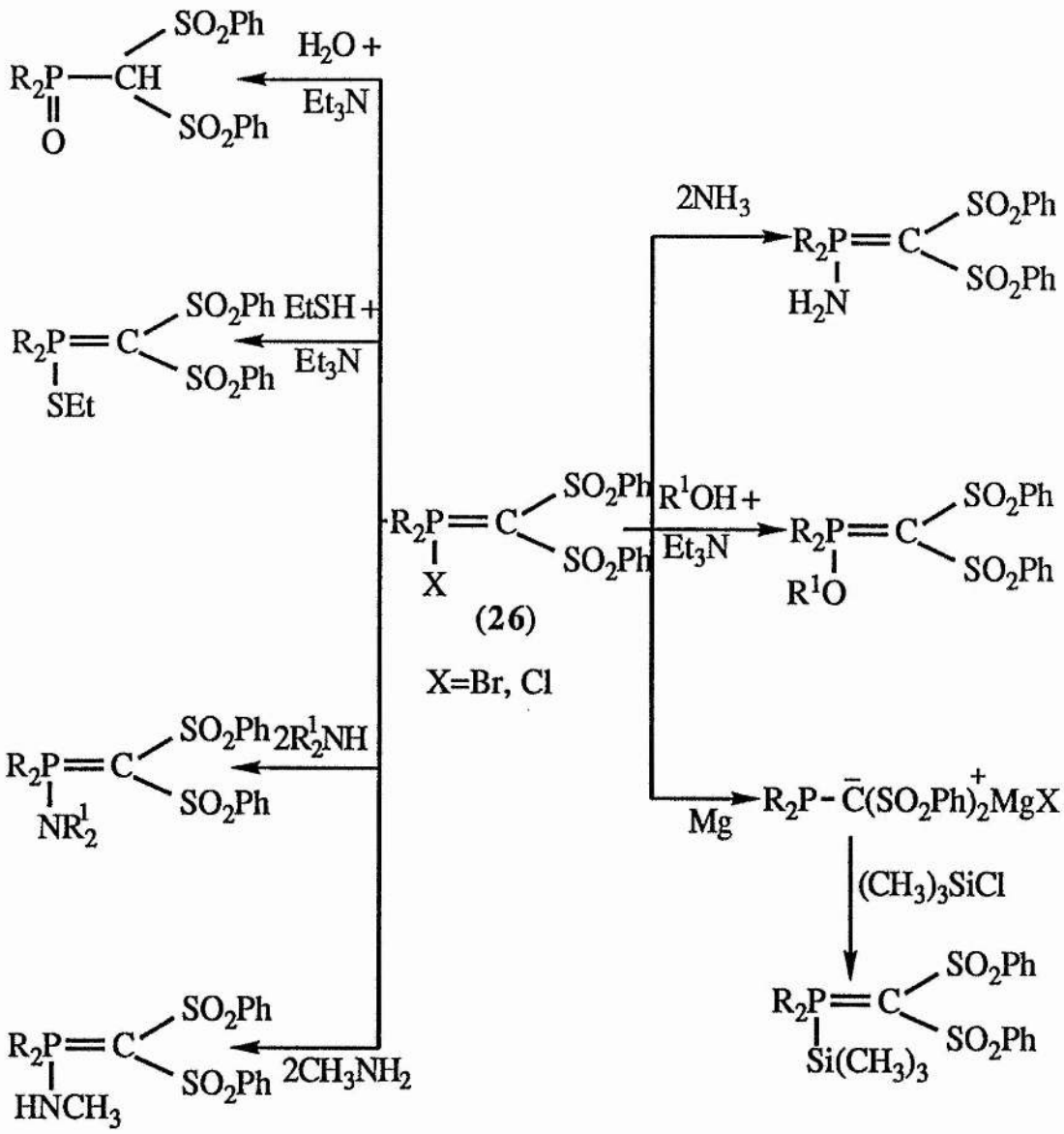
Secondly[29], the ylides (26) are made from diphenyltrihalophosphines,



bis(phenylsulphonyl)methane and triethylamine in higher yields than before[28].

By varying the number of phenyl groups to halogens, a number of other P-halo ylides can be prepared[29].

These P-halo ylides (26) are extremely useful since substitution of the halogen with a variety of substituents gives many novel P-functionalized ylides[30]. Scheme 3 shows the examples of reactions with amines, alcohols, thiols, ammonia and even with magnesium to form a Grignard reagent, followed by its reaction with trimethylsilyl chloride.

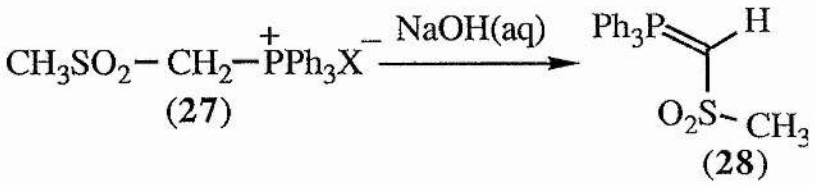


SCHEME 3

b) Mono-sulphonyl Ylides

The first preparation of a mono-sulphonyl stabilised phosphorus ylide was by Hellmann and Bader in 1961[31]. They prepared

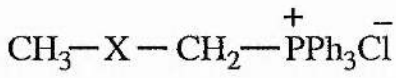
methylsulphonylmethylene triphenylphosphorane (28) in 65% yield by



(27) (28)

the action of aqueous sodium hydroxide on the phosphonium salt (27).

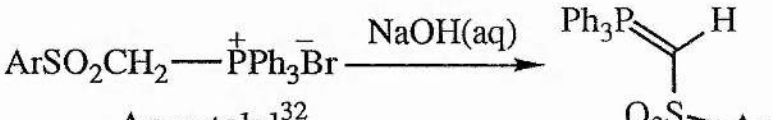
Speziale and Ratts[32] made the same compound (28) in very low yield (3.4%) by oxidation of the salt (29, X=S) to the corresponding sulphone



(29)

(29, $X=SO_2$) followed by sodium hydroxide degradation. The low yield was due to oxidative cleavage of the CH_2-P bond in competition with the sulphone formation.

Speziale and Ratts[32] did however synthesise the first arylsulphonyl-methylene phosphorane (30) by the reaction of tosylmethyltriphenyl-phosphonium bromide with aqueous sodium hydroxide.

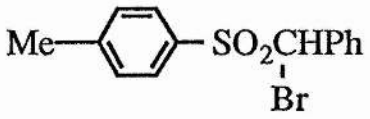


Ar=*p*-tolyl[32]
Ar=Ph[33], *p*- chlorophenyl[33]

(30)

This was seen as a potentially general method to produce compounds of type (30) and a few more examples were reported by Van Leusen *et al*[33].

The earliest attempts to make arylsulphonylbenzylidenephosphoranes were by Hoffman and Förster[25]. Starting from the α-bromosulphones (31 and 32), they found that (31) gave no phosphonium salt with triphenyl-



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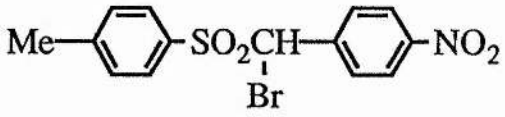
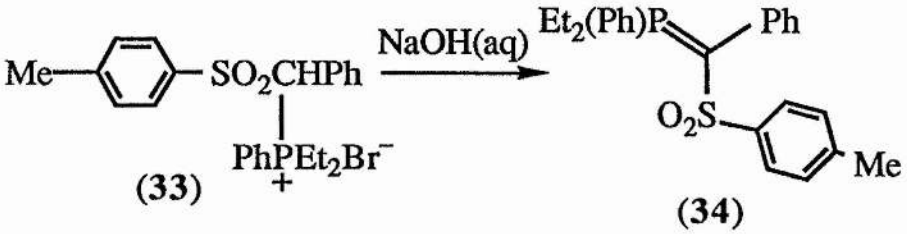


(32)

phosphine and, though the triphenylphosphonium salt of (32) could be made, it was stable to alkali, as well as boiling methanol and acetic acid. However the phosphonium salt of (31) with diethylphenylphosphine (33) could be made and converted to the ylide (34) by treatment with alkali[25].

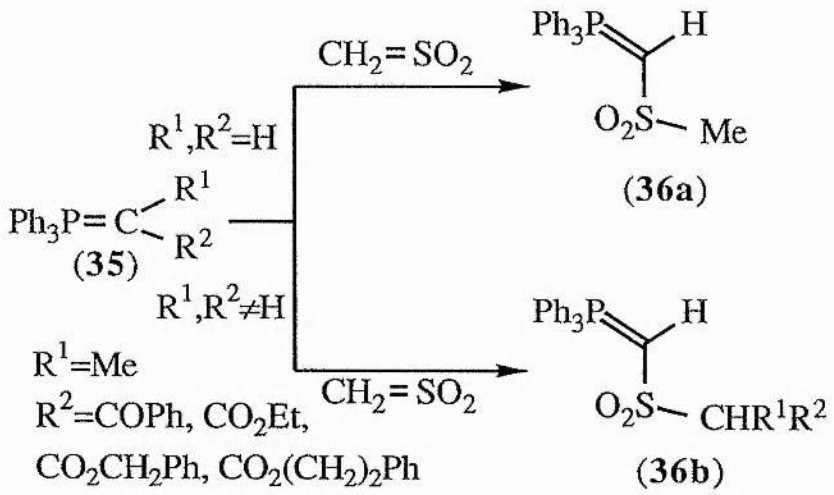


(33) **(34)**

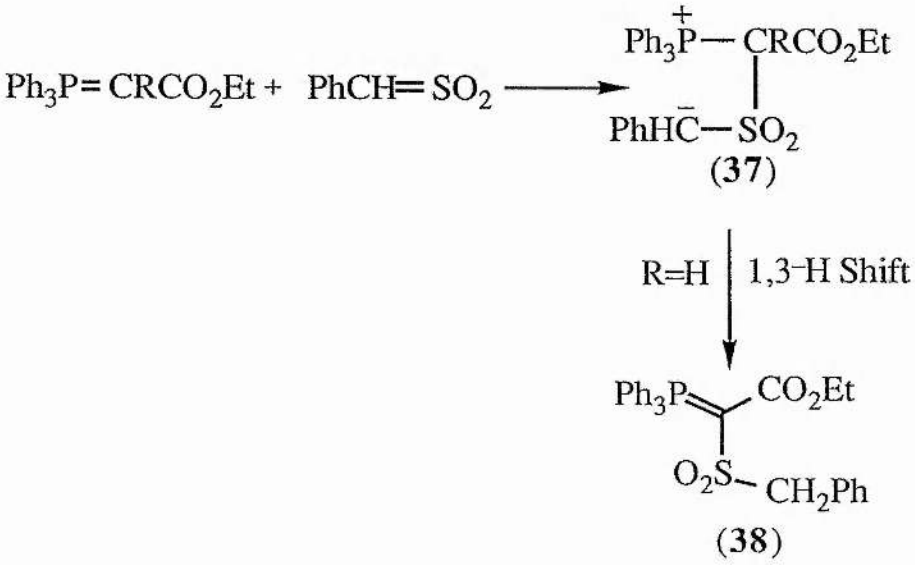
The most successful synthetic methods have been those which use

precursor P-ylides which react with an "RSO_2" moiety to give the desired sulphonylphosphorane.

Ito, Okano and Oda[34] developed a synthesis, whereby a stabilised phosphorus ylide (35) reacted with sulphene, a species generated by dehydrochlorination of methane sulphonyl chloride by triethylamine[35], to give sulphonyl phosphoranes (36a) and (36b) in 10-86% yields.



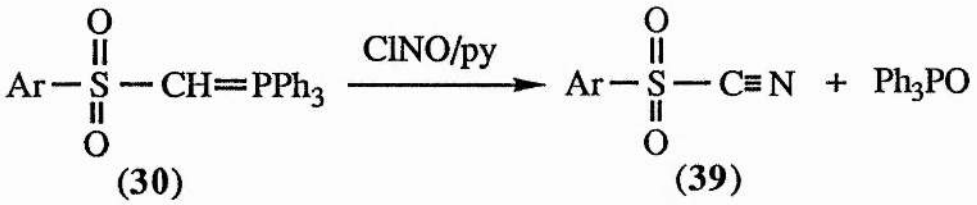
Using the same methodology, Hamid and Trippett[36] reacted an aromatic sulphene, phenylsulphene, with ethoxycarbonylmethylene triphenyl



phosphorane to give the ylide (38), via a 1,3-H-shift in the initially formed betaine (37).

Not surprisingly the ethoxycarbonyl ylide with R = Me, gave no product of type (38).

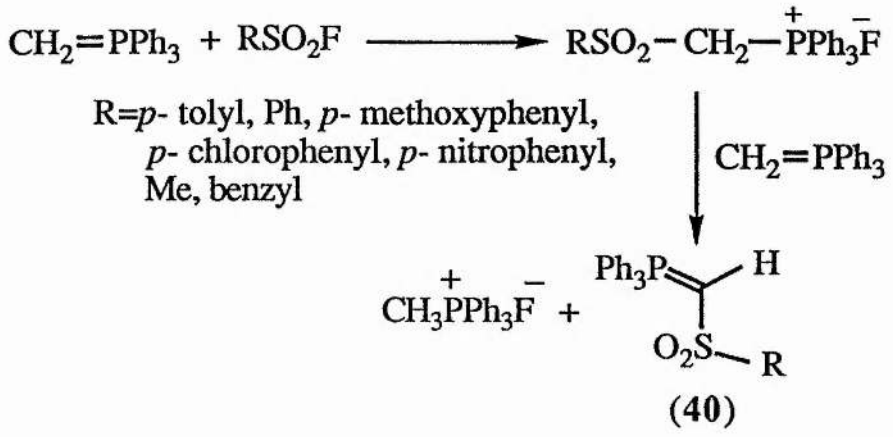
Van Leusen *et al* in developing the first successful synthesis of sulphonyl cyanides $RSO_2C \equiv N$ (39)[37], concurrently developed methods to



(30) **(39)**

synthesise arylsulphonyl phosphoranes (30)[33].

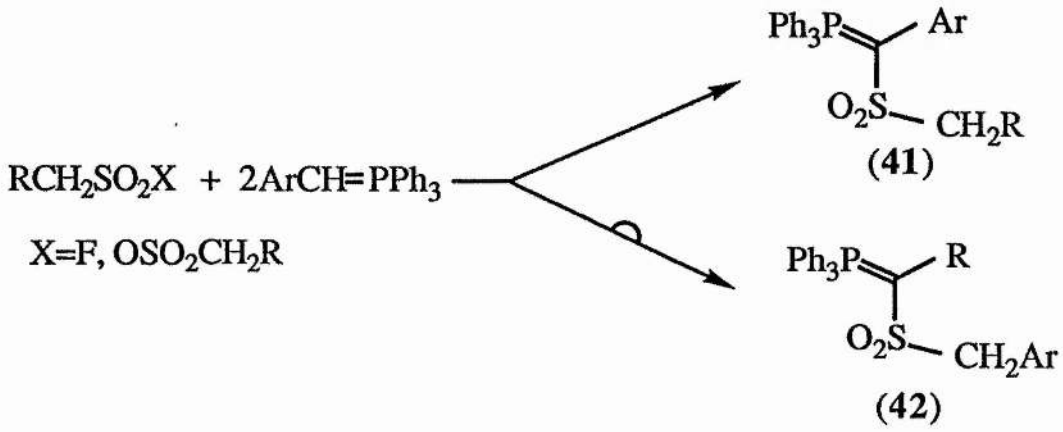
The first, previously mentioned, involved the action of aqueous sodium hydroxide on α-bromomethyl arylsulphones. The second involved using sulphonyl fluorides as the source of the "RSO_2" moiety. They found that sulphonyl fluorides reacted with methylene triphenylphosphorane in a 1:2 ratio to give sulphonylphosphoranes (40) in 29% (R = p-nitrophenyl) and 63-78% yields.



(40)

The same workers extended this work to a variety of alkylidene- and benzylidene phosphoranes, encountering an unexpected but useful rearrangement[38].

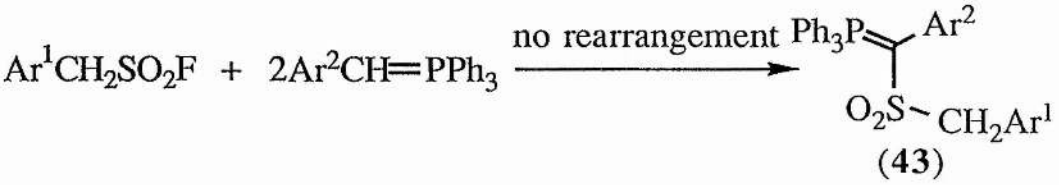
First of all they found that the reaction between benzylidenephosphoranes and alkylsulphonyl fluorides or anhydrides gave the rearranged ylide (42) rather than the expected ylide (41). This was true except in the case where R = Bu^t. For steric reasons the betaine type intermediate of these reactions, similar to the intermediate (37), is unable to rearrange, thus the compound of type (41) is obtained for R=Bu^t.



(41)

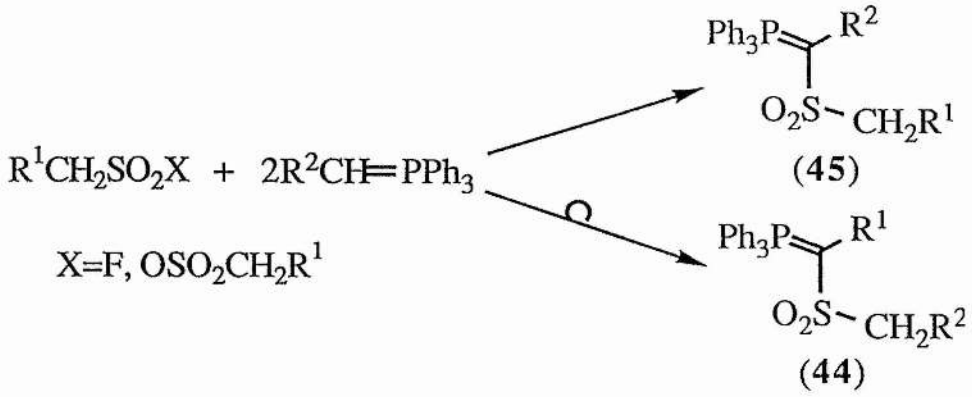
(42)

Secondly the reaction of benzylidenephosphoranes and arylsulphonyl fluorides gives the unrearranged product (43).



(43)

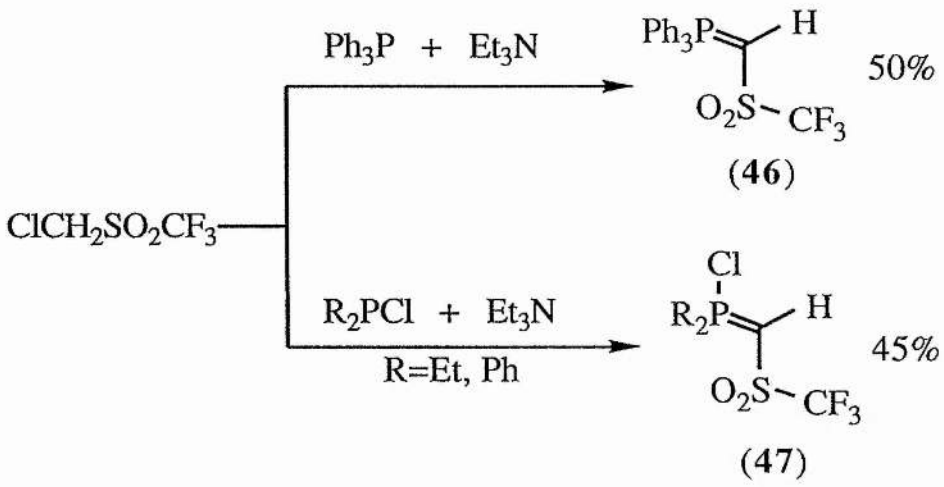
Thirdly, alkylidenephosphoranes react with alkylsulphonyl fluorides and anhydrides to give the rearranged product (44), except, not surprisingly, in the case where R^1 or R^2 = Bu^t, when product (45) is obtained.



(45)

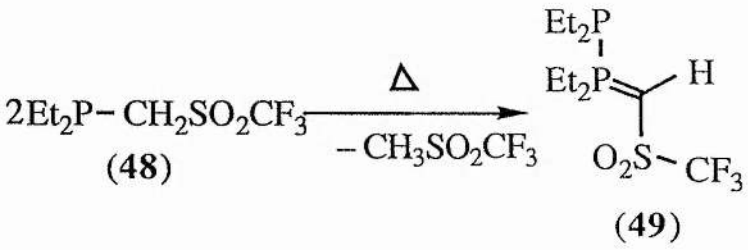
(44)

Kolodyazhnyi *et al*[28,30,39,40] synthesised the novel ylides (46)[39] and (47)[28,30,39] starting from chloromethyl trifluoromethyl sulphone and reacting it with triphenylphosphine and triethylamine and a chlorophosphine and triethylamine respectively.



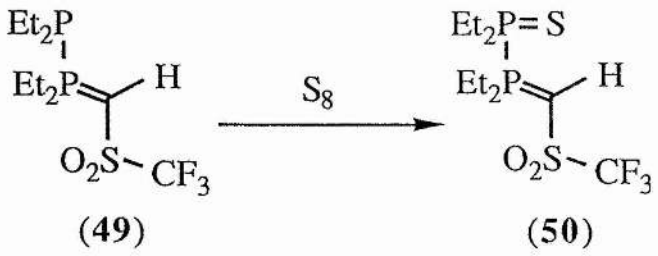
The P-chloro ylides (47) can undergo the same type of P-substitution reactions[30] as described for the bis-sulphonyl ylide (26) in Scheme 3.

A further unusual type of ylide is reported[30], derived from heating of the phosphine (48). On heating (48) disproportionates into methyl



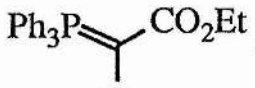
trifluoromethylsulphone and (trifluoromethylsulphonyl) methylene-(diethylphosphinyl)diethylphosphorane (49) in 50% yield.

The phosphinyl-phosphorane (49) can react with elemental sulphur to give a further phosphinyl-phosphorane (50).



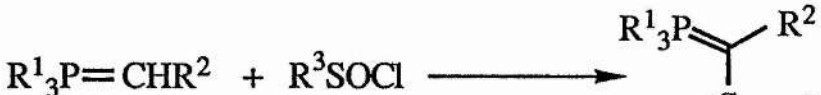
2. Sulphinyl Stabilised Phosphor us Ylides

The first of only two mentions of sulphinyl ylides was by Hamid and Trippett in 1968[36]. The reaction of phenyl sulphine, generated from the dehydrochlorination of phenylmethanesulphinyl chloride by triethylamine[41], with ethoxycarbonylmethylene triphenyl phosphorane gave the ylide (51).



(51)

The second mention of sulphinyl ylides is in a U.S. Patent, by Alden on behalf of the Du Pont company[42]. This describes the preparation of the ylides (54) from a precursor ylide (52), where R^2 is an electron withdrawing group, and a sulphinyl chloride (53). The reported yields of (54) are > 90%.



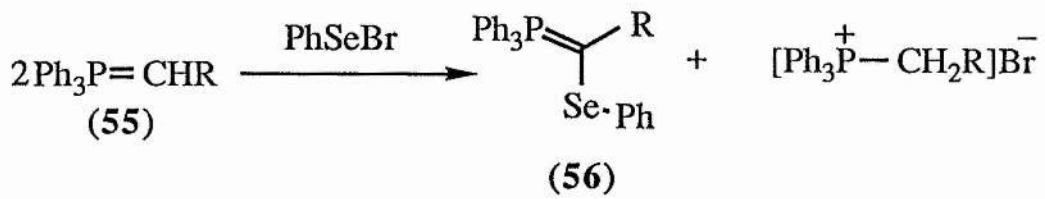
(52) **(53)** **(54)**

3. Selenenyl Stabilised Phosphorus Ylides

The examples of selenenyl stabilised phosphorus ylides are restricted to

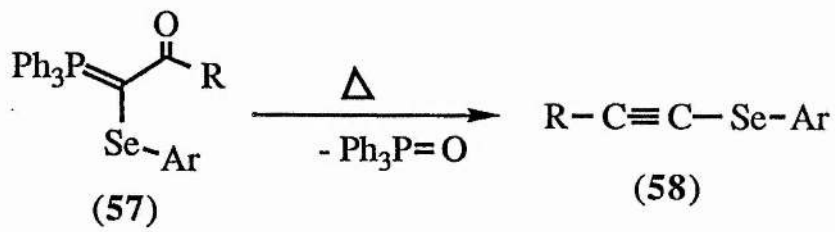
those stabilised by a phenylselenyl group [43,44].

Either a stabilised ylide such as ethoxycarbonylmethylenetriphenylphosphorane (55, R = CO_2Et)[43] or a nonstabilised ylide (55, R = H,Me)[44] can react with phenyl selenenyl bromide to give the phenylselenylalkylidene triphenylphosphoranes (56).



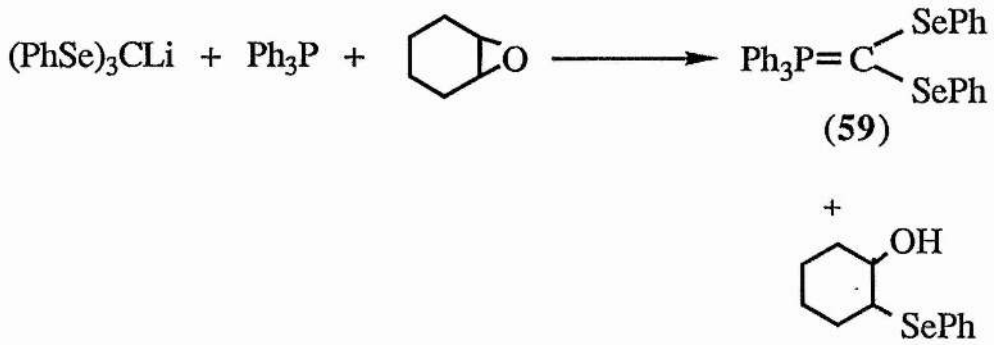
The ylides (56) have found use in the Wittig reaction to prepare vinylic selenides[44] and 1,3-bis(seleno)-propenes[45].

A similar type of ylide, the α-acyl-α-(arylseleno)phosphoranes (57), were made by Petragnani *et al*[46] from acylphosphoranes and arylselenenyl bromides.



When the ylides (57) are heated at 230°C at 0.005 mmHg for 1h, the arylselenoacetylenes (58) are obtained in moderate to good yields[46].

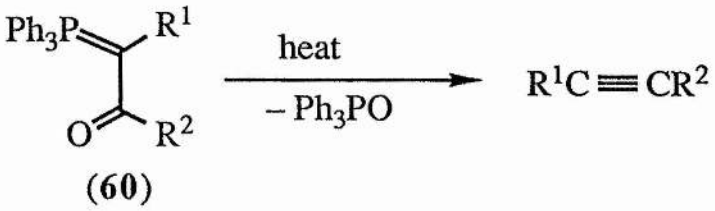
An example of a bis(phenylseleno) phosphorane has been reported by Seebach and Peleties[47]. They describe the preparation of bis(phenyl



seleno) methylene triphenylphosphorane (59) in 65% yield from tris(phenylseleno)methyl lithium, triphenylphosphine and cyclohexene oxide.

C Programme of Research

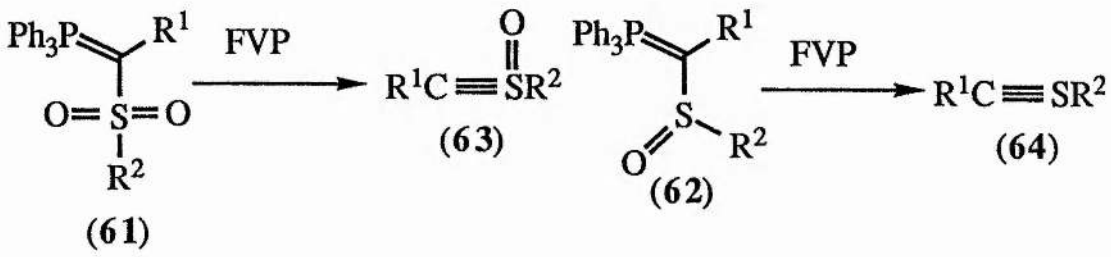
The thermal elimination of triphenylphosphine oxide from β-keto ylides (60) to produce substituted acetylenes was first reported 30 years ago[48]. This route has since proved useful for the synthesis of a wide range



(60)

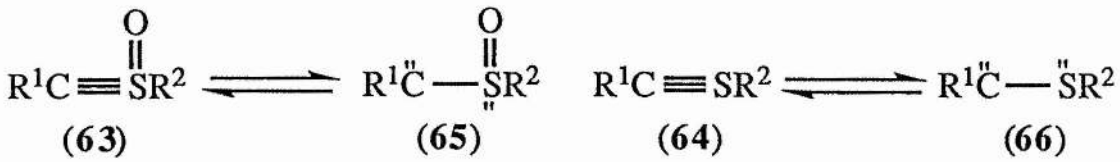
of acetylenic compounds for a variety of R^1 and R^2[46,49-55]. Recently the use of flash vacuum pyrolysis has extended the scope of this reaction for R^1 = H or alkyl, producing aliphatic and terminal acetylenes in good yield[56].

The sulphonyl ylides (61) have been prepared, most generally from triphenylphosphoranes and sulphonylfluorides or sulphonic anhydrides, by the method of Van Leusen *et al*[33,38]. The sulphinyl analogues (62) have been described by Alden[42] where R^1 is an electron withdrawing group. However no studies of the thermal reactions of (61) and (62) have been carried out. The aim of this work was to perform the first study of the flash vacuum pyrolysis behaviour of ylides (61) and (62).



(61) (63) (62) (64)

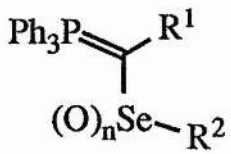
Just as the β-keto ylides (60) eliminate triphenyl phosphine oxide to give a C ≡ C triple bond, it was envisaged that (61) and (62) could similarly eliminate triphenyl phosphine oxide to give, at least initially, the novel compounds (63) and (64). These could of course be drawn alternatively as the carbenes (65) and (66) but recent reports of RC ≡ SF_3[57], RS ≡ N[58],



(63) **(65)** **(64)** **(66)**

RS(0) ≡ N[59] and R_2P ≡ N[60] suggest that there might be some genuine C ≡ S triple bond character for certain groups R^1 and R^2.

The novelty of (63) and (64) make their behaviour of great interest and if this protocol is successful a similar route to the C ≡ Se moiety might be achieved via the synthesis and FVP of ylides (67).



(67) n=1, 2

EXPERIMENTAL

A Symbols and Abbreviations

mmol	millimoles
M	mol dm^{-3}
h,min	hours, minutes
G.C.M.S.	gas chromatography-mass spectrometry
T.L.C.	thin layer chromatography
N.M.R.	nuclear magnetic resonance
δ	chemical shift
J	spin-spin coupling constant
s,d,t,q,m	singlet, doublet, triplet, quartet, multiplet
M.S.	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

B Instrumentation and General Techniques

1. N.M.R. Spectroscopy

a) ^{1}H N.M.R.

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 WP 80. High resolution and variable temperature spectra were obtained at 300 MHz on a Bruker AM-300 spectrometer both operated by Mrs M Smith and Mr I W Harvey.

b. ^{13}C N.M.R.

All spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith and Mr I W Harvey.

c. ^{31}P N.M.R.

Spectra were obtained at 32 MHz on a Varian CFT-20 spectrometer or at 121 MHz on a Bruker AM-300 spectrometer, both operated by Mrs M Smith and Mr I W Harvey.

All spectra were obtained from solutions in deuteriochloroform, except variable temperature studies where dideuteriomethylene chloride was used, and chemical shifts are expressed in parts per million to high frequency of tetramethylsilane.

2. Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrophotometer. Solution spectra were run in chloroform using

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

3. Mass Spectroscopy

Earlier mass spectra and accurate mass measurements were obtained on an A.E.I. M.S.-902 instrument and later mass spectra obtained on a Finnigan Incos 50 mass spectrometer, both operated by Mr C Millar.

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.

5. Elemental Analysis

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

6. Melting points

Routine melting points were determined using an Electrothermal melting point apparatus while melting points of new compounds were determined on a Reichert hot-stage microscope.

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 3h.

9. Column Chromatography

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

10. Drying and Evaporation of Organic Solutions

Organic solutionswere dried by standing over anhydrous magnesium sulphate or anhydrous calcium chloride and were evaporated under reduced pressure on a rotary evaporator.

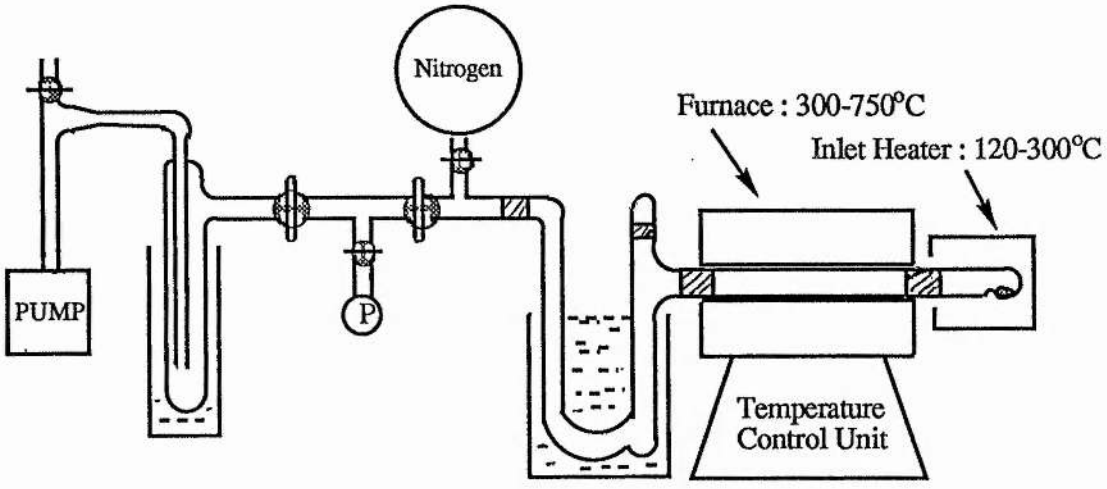
11. Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise indicated. Where pure acetone or carbon tetrachloride were required the commerical Analytical Reagent (A.R.) grade solvents were used. Dry acetonitrile was prepared by storing over freshly activated molecular sieves. Dry ether and dry toluene were prepared by the addition of sodium wire. Extra dry tetrahydrofuran 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. Pyridine and triethylamine were dried by heating under reflux with potassium hydroxide for 2h then distilling onto molecular sieves. Dry N,N-dimethylformamide was prepared by heating under reflux with calcium hydride under a nitrogen atmosphere for 2h then distilling onto molecular sieves. "Petroleum ether" refers to light petroleum, the redistilled 40-60°C boiling fraction being used for chromatography.

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[1].

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 × 2.5 cm silica tube. This was heated at temperatures in the range of 350-750°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}-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.

The pyrolysis conditions are quoted as follows: "(weight of material volatilised, furnace temperature, average pressure during the pyrolysis, inlet temperature)".

Pyrolyses were generally carried out using 200-500 mg of material. After the pyrolysis the system was isolated from the pump and filled with nitrogen gas. The products were then dissolved out of the trap in deuteriochloroform, unless otherwise stated, and analysed directly by N.M.R. Yields were estimated by adding a known amount of dichloromethane or 1,2-dichloroethane and comparing the N.M.R. signals.

C Preparation of Sulphonyl Stabilised Phosphorus Ylides

1. Preparation of Phosphonium Salts

(i) Ethyl triphenyl phosphonium bromide

This was prepared by the most common phosphonium salt procedure[61]. Ethyl bromide (41.54g, 381.3 mmol, 2 equiv), triphenyl phosphine (50g, 190.6 mmol) and toluene (250 ml) were heated under reflux for 19h. The resulting precipitate was filtered, washed with ether and after drying gave ethyl triphenyl phosphonium bromide (53.9g, 76%) as a white powder, m.p. 203-205°C (lit[62] 205-206°C).

The following phosphonium salts were similarly prepared, varying only in the reaction times and equivalents of halide:phosphine used.

(ii) n-Propyl triphenyl phosphonium bromide

This was prepared from bromopropane:phosphine 1.1:1, after heating for 20h, in 46% yield as a white powder, m.p. 232-234°C (lit[63] 229°C).

(iii) Benzyl triphenyl phosphonium chloride

This was prepared from benzyl chloride:phosphine 1.05:1, after heating for 24h, in 80% yield as a white powder, m.p. 312-318°C (lit[64] 325-328°C).

(iv) p-Methyl benzyl triphenyl phosphonium bromide

This was prepared from p-methyl benzyl bromide:phosphine 1:1, after heating for 18h, in 60% yield as a white powder, m.p. 272-277°C (lit[65]

276-277°C).

(v) p-Methoxy benzyl triphenyl phosphonium bromide

This was prepared from p-methoxy benzyl bromide:phosphine 1:1, after heating for 18h, in 80% yield as a white powder, m.p. 230-234°C (lit[66] 236-238°C).

(vi) o-Methyl benzyl triphenyl phosphonium bromide

This was prepared from o-methyl benzyl bromide:phosphine 1:1, after heating for 17h, in 72% yield as a white powder, m.p. 250-254°C (dec) (lit[67] 253-255°C (dec)).

(vii) o-Methoxybenzyl triphenyl phosphonium bromide

This was prepared from o-methoxybenzyl bromide:phosphine 1:1, after heating for 17h, in 68% yield as a white powder. o-Methoxybenzyl-triphenylphosphonium bromide, m.p. 219.5-220°C. (Found: C, 67.1; H, 5.2. $C_{26}H_{24}BrOP$ requires C, 67.4; H, 5.2%.)

(viii) o-Methylthio benzyl triphenyl phosphonium chloride

This was prepared from o-methylthiobenzylchloride:phosphine 1:1, after heating for 17h, in 62% yield as a white power. o-Methylthio benzyltriphenylphosphonium chloride, m.p. 230-234°C dec. (Found: C, 71.6; H, 5.3. $C_{26}H_{24}ClPS$ requires C, 71.8; H, 5.6%.)

2. Preparation of Sulphonyl Fluorides and Sulphonic Anhydrides

(i) Methane sulphonyl fluoride

This was prepared by the patent method described in Houben-Weyl, "Methoden der Organischen Chemie"[68]. Methane sulphonyl chloride (8.7g, 75.9 mmol) was added over 10min, to a vigorously stirring solution of potassium hydrogen difluoride (6.5g, 83.2 mmol) in water (5 ml). The temperature rose to 33°C over 35min and was then raised to 50°C for 5min. The resulting mixture was steam distilled, the lower layer of distillate separated and dried over $CaCl_2$. This clear oil was distilled to afford methane sulphonyl fluoride (3.29g, 44%), b.p. 120-123°C (lit[68] 122-123°C). M.S. showed an M^+ peak at m/z = 98, with no sign of any chlorinated material.

(ii) Ethane sulphonyl fluoride

This was prepared by the method of Davies and Dick[69]. Ethane sulphonyl chloride (10g, 78 mmol) and neutral potassium fluoride solution (70%, 73g in 100 ml H_2O, 10 ml) were stirred and heated nearly to boiling for 1h. On cooling the mixture was diluted with water and extracted with ether (3 × 75 ml). The combined ether layers were dried ($MgSO_4$), filtered, solvent removed under vacuum and the residue distilled to give ethane sulphonyl fluoride (5.2g, 60%), b.p. 133-134°C (lit[69] 134-135°C) as a colourless liquid.

(iii) Benzene sulphonyl fluoride

This was prepared by a modification of the method of Davies and Dick[70]. A mixture of benzene sulphonyl chloride (20g, 113.2 mmol) and neutral potassium fluoride solution (70%, 73g in 100 ml H_2O, 25 ml) was heated under reflux for 3h. The mixture was diluted with water and extracted with ether (4 × 25 ml). The combined ether layers were washed once with water, dried ($MgSO_4$), filtered and evaporated. Distillation gave benzene sulphonyl fluoride (9.48g, 53%) as a clear oil, b.p. 62-63°C at 6 mm Hg (lit[70] 207°C at 760 mm Hg).

(iv) p-Toluene sulphonyl fluoride

An adaptation of the method of Davies and Dick[70] was used. p-Toluene sulphonyl chloride (20g, 104.9 mmol) and neutral potassium fluoride solution (70%, 73g in 100 ml H_2O, 25 ml) was heated under reflux for 1h. The mixture was diluted with water, extracted with ether (4 × 25 ml) and the combined ether extracts washed once with water. Drying ($MgSO_4$), evaporation and distillation gave p-toluene sulphonyl fluoride (16.5g, 90%) as a colourless solid on cooling, b.p. 92-93°C at 9 mmHg, m.p. 41-42°C (lit[70] 41-42°C).

(v) α-Toluene sulphonyl fluoride (Phenylmethanesulphonyl fluoride)

An adaptation of the method of Davies and Dick[69] was used. α-Toluene

sulphonyl chloride (9.8g, 51.4 mmol), xylene (10 ml) and neutral potassium fluoride solution (70%, 73g in 100 ml water, 20 ml) were heated under reflux for 1.5 h. The mixture was diluted with water and extracted with ether (3 × 25 ml). Drying ($MgSO_4$), filtration and evaporation gave on cooling an off white solid. Recrystallisation from 60/80 petroleum ether gave α-toluene sulphonyl fluoride (4.8g, 54%) as a colourless solid, m.p. 89-90°C (lit[69] 90-91°C).

(vi) Methane sulphonic anhydride

This was prepared by a modification of the method of Field and Settlage[71]. One half of a mixture of phosphorus pentoxide (30g, 211 mmol) and celite (9g) was added, with manual stirring, to methane sulphonic acid (30.5g, 318 mmol). When the reaction had largely subsided, the mixture was heated to 80°C for 2.5h while the remainder of the phosphorus pentoxide/ celite mixture was added in 5 portions and mixed in as well as possible. Heating was continued for 3h and the mixture was now a black, nodule like solid. This was extracted with 1,2-dichloroethane (5 × 30 ml) with gentle heating followed by decantation. Evaporation gave a dirty black/white flecked solid which on recrystallisation from ether/benzene (2:1) using charcoal gave methane sulphonic anhydride (5.74g, 21%) as beautiful colourless crystals, m.p. 65-67°C (lit[71] 65.5-67°C).

3. Preparation of Alkyl- and Arylsulphonyl alkylidene triphenyl phosphoranes

(i) Preparation of p-Toluenesulphonylethylidene triphenyl phosphorane

This compound and the succeeding ones have been prepared using modifications of the method of Van Leusen *et al*[33,38]. An example of the procedure is given here.

The phosphonium salt (ethyltriphenylphosphonium bromide (9.65g, 26 mmol)) was stirred at R.T., under N_2, in extra dry tetrahydrofuran (150 ml) while n-butyl lithium (2.5M in hexane, 26 mmol) was added via a syringe. If excessive heat is evolved, ice-cooling is employed. This was allowed to stir for 30min, when p-toluenesulphonyl fluoride (2.26g, 13 mmol) in extra dry tetrahydrofuran (10 ml) was added slowly. A precipitate was seen to form immediately and the mixture was allowed to stir at R.T. for 2 - 3h. The precipitate was filtered off, the filtrate evaporated and the residue dissolved in chloroform or dichloromethane (250 ml). The solution was washed with water (3 × 200 ml), dried ($MgSO_4$), and evaporated. The residue was triturated with 15-30 ml of ether to give the desired product (4.56g, 79%) as a light yellow solid. Two recrystallisations from ethyl acetate/hexane gave p-toluenesulphonylethylidene triphenylphosphorane, m.p. 150-153°C; (Found: C, 73.0; H, 5.7. $C_{27}H_{25}O_2PS$ requires C, 72.9; H, 5.7%); δ_P + 19.63(s); δ_H 6.9-7.9 (m, 19H), 2.35 (s, 3H) and 1.7 (d, 3H, J_{P-H} = 13 Hz); m/z 444 (M^+, 33%), 379(7), 294(16), 289(100), 282(22), 277(56), 262(22)

and 183(82).

(ii) Preparation of benzenesulphonylethylidenetriphenylphosphorane

Preparation as above gave after recrystallisation from ethyl acetate/hexane benzenesulphonylethylidenetriphenylphosphorane (3.97g, 71%), m.p. 138-140°C. (Found: C, 72.6; H, 5.4. $C_{26}H_{23}O_2PS$ requires C, 72.5; H, 5.4%); δ_P + 19.79(s); δ_H 7.0-7.85 (m, 20H) and 1.72 (d, 3H, J_{P-H} = 13 Hz); m/z 430 (M^+, 57%), 415(2), 365(4), 294(9), 289(100), 277(36), 262(25) and 183(85).

(iii) Preparation of p-toluenesulphonylpropylidenetriphenylphosphorane

Preparation as above and recrystallisation from ethyl acetate/hexane gave p-toluenesulphonylpropylidenetriphenylphosphorane (1.53g, 26%), m.p. 161-163°C. (Found: C, 73.0; H, 6.15. $C_{28}H_{27}O_2PS$ requires C, 73.3; H, 5.9%); δ_P + 19.78(s); δ_H 6.95-7.9 (m, 19H), 2.33 (s, 3H), 1.7-2.21 (m, 2H) and 1.8 (t, 3H, J = 7 Hz); m/z 458 (M^+, 56%), 443(100), 423(8), 409(20), 391(3), 377(2), 363(3), 328(3), 310(49), 294(100), 284(17) and 269(26).

(iv) Preparation of benzenesulphonylpropylidenetriphenylphosphorane

The method as above with recrystallisation from ethyl acetate/hexane gave benzenesulphonylpropylidenetriphenylphosphorane (4.5g, 78%) as colourless translucent crystals, m.p. 136-139°C. (Found: C, 72.9; H, 5.6.

$C_{27}H_{25}O_2PS$ requires C, 72.9; H, 5.7%); δ_P + 19.99(s); δ_H 7.25-7.9 (m, 20H), 1.84-2.4 (m, 2H) and 0.84 (t, 3H, J = 6 Hz); δ_C 134.8, 134.67, 132.45, 132.42, 130.39, 129.17, 129.01, 128.56, 126.42, 42.02 (d, ylide C, J_{P-C} = 122.5 Hz), 22.24 (d, methylene C, J_{P-C} = 10.4 Hz), 18.93 (methyl C); m/z 444 (M^+, 12%), 430(29), 429(100), 414(1), 303(10), 287(43), 279(2), 262(5), 183(19).

(v) Preparation of p-toluenesulphonylbutylidenetriphenylphosphorane

The method as above with recrystallisation from ethyl acetate/hexane gave p-toluenesulphonylbutylidenetriphenylphosphorane (4.11g, 67%) as a light yellow solid, m.p. 184-186°C. (Found: C, 73.5; H, 6.2. $C_{29}H_{29}O_2PS$ requires C, 73.7; H, 6.2%); δ_P + 19.79(s); δ_H 7.0-8.0 (m, 19H), 2.37 (s,3H), 0.7-2.3 (m, 4H) and 0.55 (t, 3H, J = 7 Hz); m/z 472 (M^+, 11%), 443(100), 423(25), 317(6), 287(81) and 262(13).

(vi) Preparation of p-toluenesulphonylmethylenetriphenyl phosphorane

This was prepared directly by the method of Van Leusen *et al*[33] in 79% yield. The crystals had m.p. 182-185°C (lit[33] 182-184°C); δ_P + 14.03.

(vii) Preparation of benzenesulphonylmethylenetriphenylphosphorane

This was prepared directly by the method of Van Leusen *et al*[33] in 60% yield. The crystals had m.p. 143-146°C (lit[33] 144-147°C); δ_P + 14.15.

(viii) Preparation of methanesulphonylethylidenetriphenylphosphorane

This was prepared by reaction between the appropriate ylide, ethylidenetriphenylphosphorane, and methane sulphonyl fluoride (46% yield) or methane sulphonic anhydride (60% yield). However even after repeated recrystallisations from ethyl acetate/hexane, a by-product, ethanesulphonylmethylenetriphenylphosphorane, formed *via* a rearrangement during the reaction, was still observed. This was seen as two peaks in the ^{31}P N.M.R. at δ + 20.46 (desired product) and + 15.58 (rearranged product) and was also confirmed by ^{1}H N.M.R. The reverse of this rearrangement was used by Van Leusen *et al*[38], and in this instance by us to obtained the desired product. Thus ethane sulphonyl fluoride was reacted with methylenetriphenylphosphorane to give the desired methane-sulphonylethylidenetriphenylphosphorane free from unwanted byproducts after only one recrystallisation in 52% yield, m.p. 198-200°C, (lit[38] 200-201°C); δ_P + 20.46.

4. Preparation of arylmethanesulphonyl alkylidene triphenyl phosphoranes

The first four compounds in this section were prepared by the method of Van Leusen *et al*[38] and a representative description is given.

(i) Preparation of Phenylmethanesulphonylbenzylidenetriphenyl phosphorane

The phosphonium salt (benzyltriphenylphosphonium chloride) (10g, 25.7 mmol) was stirred at R.T. under N_2 in extra dry THF (250 ml) while n-butyl lithium (25.7 mmol) was added. After stirring for 30min at R.T., α-toluene sulphonyl fluoride (2.26g, 13 mmol) in dry THF (20 ml) was added. A precipitate was immediately observed to form and the mixture stirred for a further 30min. The precipitate was filtered off and the filtrate evaporated. The residue was dissolved in chlorobenzene or chloroform (250 ml) and washed with water (3 × 100 ml). Drying ($MgSO_4$), evaporation, and trituration with ether or hexane (60 ml) gave phenylmethanesulphonylbenzylidenetriphenylphosphorane (5.3g, 82%) as a light yellow solid, m.p. 210-211°C (lit[38] 210-211°C). (Found: C, 75.9; H, 5.1. $C_{32}H_{27}O_2PS$ requires C, 75.9; H, 5.4%); δ_P + 18.17; δ_H 6.95-7.6 (m, 25H) and 3.96 (s, 2H); δ_C 135.49, 135.45, 134.89, 134.78, 133.87, 133.74, 131.51, 131.42, 131.22, 128.37, 128.21, 128.09, 127.68, 127.46, 126.98, 125.41, 61.40 (methylene C), 47.05 (d, ylide C, J_{P-C} = 129.71). m/z 506 (M^+), 415, 367 and 351 [Characteristic M.S. breakdown, i.e. M^+, M^+–(CH_2Ar), M^+–($SOCH_2Ar$) and M^+–(SO_2CH_2Ar)];

(ii) Preparation of phenylmethanesulphonyl-p-methylbenzylidene triphenyl phosphorane

Preparation as before gave phenylmethanesulphonyl-p-methyl benzylidenetriphenyl phosphorane (4g, 72%) as a light yellow solid, m.p. 188.5-189°C. (Found: C, 75.8; H, 5.8. $C_{33}H_{29}O_2PS$ requires C, 76.1; H, 5.6%) ; δ_P + 18.11; δ_H 6.8-7.8 (m, 24H), 3.98 (s, 2H) and 2.21 (s, 3H); m/z 520 (M^+), 429 (M^+–CH_2Ph), 381 (M^+–$SOCH_2Ph$), 365 (M^+–SO_2CH_2Ph).

(iii) Preparation of phenylmethanesulphonyl-o-methoxy benzylidene triphenyl phosphorane

Preparation as above gave, after recrystallisation from dichloromethane / hexane, phenylmethanesulphonyl-o-methoxy benzylidenetriphenylphosphorane (2.27g, 40%) as a white powder, m.p. 210-213°C. (Found: C, 73.5; H, 5.4. $C_{33}H_{29}O_3PS$ requires C, 73.9; H, 5.5%); δ_P + 17.88; δ_H 6.8-8.0 (m; 24H), 4.03 (s; 2H) and 3.35 (s; 3H).

(iv) Preparation of phenylmethanesulphonyl-o-methylthiobenzylidene triphenyl phosphorane

Preparation as above gave after recrystallisation from dichloromethane / hexane phenylmethanesulphonyl-o-methylthio benzylidene triphenyl phosphorane (4.33g, 67%) as a white powder, m.p. 248-251°C. (Found: C, 71.3, 71.2; H, 5.0, 5.2, $C_{33}H_{29}O_2PS_2$ requires C, 71.7; H, 5.3); δ_P +17.54(s); d_H 6.8-8.0 (m, 24H), 4.25(s, 2H) and 2.15(s, 3H).

The method of preparation for the remaining 4 compounds is the same as described above. However, here use is made of the rearrangement mentioned previously[38] to obtain the desired compound as the sole or major product.

(v) Preparation of o-methoxyphenylmethanesulphonylethylidene triphenylphosphorane

In this case the appropriate phosphonium ylide, o-methoxybenzylidene triphenylphosphorane (10.74g, 23.2 mmol) was reacted with ethane sulphonyl fluoride (1.3g, 11.6 mmol) to give after recrystallisation from dichloromethane/hexane o-methoxyphenylmethanesulphonylethylidene triphenylphosphorane (3.2g, 58%) as white crystals, m.p. 193-194.5°C. (Found: C, 70.75; H, 5.9, $C_{28}H_{27}O_3PS$ requires C, 70.9; H, 5.7%); δ_P + 20.78(s); δ_H 6.7-7.75 (m, 19H), 4.25 (s, 2H), 3.77 (s, 3H) and 1.6 (d, 3H, J_{P-H} = 13 Hz).

(vi) Preparation of phenylmethanesulphonylethylidenetriphenyl phosphorane

The preparation was carried out as above to give after recrystallisation from dichloromethane/hexane, phenylmethanesulphonyl ethylidenetriphenylphosphorane (3.6g, 62%), m.p. 170-172°C (lit[38] 171.5-172.5°C); δ_P + 21.35.

(vii) Preparation of o-methylphenylmethanesulphonyl ethylidenetriphenyl phosphorane

The reaction was carried out as described above to give o-methylphenylmethanesulphonyl ethylidene triphenylphosphorane (1.19g, 66%) as a white powder, m.p. 150-153°C. (Found: M^+ 458.146054. $C_{28}H_{27}O_3PS$ requires 458.146930); δ_P +21.67(s); δ_H 7.0-7.9(m, 19H), 4.35(broad s, 2H), 2.25(s, 3H) and 2.74(d, 3H, J=14Hz); m/z 458(M^+, 18%), 353(100), 305(15), 289(77), 263(48) and 183(47).

(viii) Preparation of p-methoxyphenylmethanesulphonylmethylene triphenyl phosphorane

The reaction between p-methoxybenzylidene triphenylphosphorane (20.4 mmol) and methane sulphonyl fluoride (0.7g, 7.1 mmol) gave the rearranged product p-methoxyphenylmethanesulphonylmethylene triphenylphosphorane (3.2g, 87%) as light yellow crystals, m.p. 214-215°C (lit[38] 214-215°C).

5. Attempted Preparation of benzenesulphonylbenzylidene-triphenyl phosphorane

(a) From triphenylphosphine dihalides

(i) Benzyl phenyl sulphone

Peracetic acid (35% wt/wt in acetic acid, 27.2g, 125.3 mmol) was added slowly to benzyl phenyl sulphide (5g, 25 mmol) and the mixture kept at

10°C for 2h before being stirred at R.T. for 24h. The mixture was diluted with water, the white solid filtered off and washed with more water. Recrystallisation from ethanol and drying over phosphorus pentoxide in a vacuum desiccator gave benzyl phenyl sulphone (5.41g, 93%) as a white solid, m.p. 146-147°C (lit[72], 146-146.5°C).

(ii) Reaction of sulphone with triphenyl phosphine dibromide

Triphenyl phosphine dibromide (5.28g, 12.5 mmol) and triethylamine (3.04g, 30 mmol) in dry toluene (35 ml) were stirred at R.T. while benzyl phenyl sulphone (2.9g, 12.5 mmol) in dry toluene (10 ml) was added slowly. The mixture was stirred at R.T. for 17h then heated under reflux for 15min. The resulting solid was filtered off and the filtrate evaporated. The resulting brown solid was insoluble in all N.M.R. solvents. The solid filtered off was washed exhaustively with water to remove triethylamine hydrobromide. The remaining solid gave a signal at δ_p + 28.53 suggesting triphenylphosphine oxide with the ^{1}H N.M.R. showing the starting sulphone plus extra aromatic signals confirming the phosphine oxide.

(iii) Reaction of sulphone with triphenylphosphine dichloride

The procedure was similar to that used for the preparation of bis(phenylsulphonyl)methylenetriphenyl phosphorane by Horner and Oediger[23]. To a solution of triphenyl phosphine (6.55g, 25 mmol) in dry benzene (70 ml) stirred at 0°C was added carbon tetrachloride (3 × 10 ml)

saturated with chlorine gas. After stirring for 15min, triethylamine (6.07g, 60 mmol) in dry benzene (20 ml) followed by solid benzyl phenyl sulphone (5.8g, 25 mmol) was added. The mixture was heated under reflux for 15min, cooled, the precipitate filtered off and the filtrate evaporated leaving a red oil which on trituration with ether gave a red solid (11.7g). This solid went dark on standing and gave off a very unpleasant odour. Its ^{31}P N.M.R. showed a high intensity signal at +40.88 and a minor peak at +40.61. The ^{1}H N.M.R. shows some starting sulphone with extra peaks in the aromatic region.

(b) From phosphonium salts of α-halosulphones

(i) α-Chlorobenzyl phenyl sulphone

This was prepared using the procedure of Tuleen and Marcum[73]. To a solution of benzylphenyl sulphide (5g, 25 mmol) in carbon tetrachloride (60 ml) was added N-chlorosuccinimide (6.68g, 50 ml) and the mixture stirred for 17h. The solid present was filtered off and an N.M.R. of the mother liquor showed the disappearance of the methylene signal of the starting sulphone (δ_H 4.0) and the appearance of a singlet at δ_H 6.2 of the methine proton of the α-chlorosulphide. The solvent was removed under vacuum and the crude α-chlorosulphide dissolved in chloroform (125 ml), cooled to 0°C and m-chloroperbenzoic acid (85%, 12.18g, 60 mmol) was added portionwise. After stirring at R.T. for 18h the mixture was filtered, and the filtrate washed with saturated sodium bicarbonate solution and

water. Drying over $MgSO_4$ and evaporation produced α-chlorobenzylphenyl sulphone (1.1g, 17%) as a white solid, m.p. 183-185°C (lit[73] 184-185°C).

(ii) Reaction of α-chlorosulphone with triphenylphosphine

A mixture of α-chlorobenzyl phenyl sulphone (1.1g, 4.1 mmol), triphenylphosphine (1.08g, 4.1 mmol) and toluene (50 ml) was heated under reflux for 20h. The solvent was removed under vacuum and the residue triturated with ethyl acetate to give 0.22g of white solid. ^{31}P and ^{1}H N.M.R. showed only phosphine oxide and the parent benzyl phenyl sulphone.

(iii) Preparation of α-bromobenzyl phenyl sulphone

The procedure is an adaption of the procedure of Jarvis and Saukaitis[74]. Benzyl phenyl sulphide (10g, 50 mmol) in carbon tetrachloride (200 ml) was brought to the boil and N-bromosuccinimide (10.68g, 60 mmol) and a few milligrammes of benzoyl peroxide were added all at once. The mixture was heated under reflux for a further 1.5h, cooled and the succinimide filtered off under a stream of dry nitrogen. The sulphide was oxidised to the sulphone by the dropwise addition of m-chloroperbenzoic acid (85%, 22.35g, 110 mmol) in dry methylene chloride (250 ml) over 30min. After stirring at R.T. for 70h the solution was washed successively with saturated sodium carbonate, aqueous sodium thiosulphate, saturated sodium

bicarbonate and water. The organic layer was dried ($MgSO_4$), filtered, evaporated and the resulting solid recrystallised from methylene chloride to give α-bromobenzylphenyl sulphone (2.7g, 17%) as white crystals, m.p. 192-194°C (lit[74] 193-194°C).

(iv) Attempted preparation of the triphenyl phosphonium salt

α-Bromobenzyl phenyl sulphone (0.5g, 1.6 mmol), triphenyl phosphine (0.42g, 1.6 mmol) and dry toluene (60 ml) were refluxed for 48h. The solid present (0.5g) was filtered and its ^{31}P N.M.R. showed δ_P–5.97, triphenylphosphine as the major product plus two smaller peaks at δ_P+23.96 and δ_P+26.53. The ^1H showed a singlet at δ_H 6.83, possibly the desired product. Recrystallisation from dichloromethane/ethyl acetate gave 0.32g white crystals which gave no phosphorus signal.

Repeating the procedure in sulpholane (25 ml) and heating at 150°C under N_2 for 48h gave a brown solid which showed no signal in its ^{31}P N.M.R.

D Flash Vacuum Pyrolysis of Sulphonyl Stabilised Phosphorus Ylides

1. Flash Vacuum Pyrolysis of Alkyl- and arylsulphonyl alkylidene triphenyl phosphoranes

a) FVP of p-methylbenzenesulphonyl ethylidene triphenylphosphorane

FVP of the title compound (0.2g, 600°C, 2.2×10^{-2} mmHg, inlet 200-240°C) gave two fractions. At the furnace exit, a dark oil collected which shown seven peaks in the ^{31}P N.M.R. of which those for triphenyl phosphine oxide and unreacted starting material (30%) were significant. The ^{1}H N.M.R. confirmed the presence of starting material with extra peaks in the aromatic region for triphenyl phosphine oxide. The liquid in the cold trap was dissolved out and its ^{1}H N.M.R. obtained. Peaks could be identified for p-tolyl vinyl sulphone, ethyl p-tolyl sulphone and di-p-tolyldisulphide. These products were confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}), though they were all present in very low yields. The major component of the cold trap was a white polymeric material which could not be dissolved out and identified.

FVP of the title compound (0.5g, 700°C, 8.0×10^{-2} mmHg, inlet 200-240°C) showed that all the material had reacted, with no starting material observed in the product. The products identified were the same as in the FVP at 600°C, with the major constituent of the cold trap once again being white, insoluble polymeric material.

FVP of the title compound (0.2g, 750°C, 2.2×10^{-2} mmHg, inlet 200-240°C) gave two fractions. The dark oil at the furnace exit showed eight peaks in the ^{31}P N.M.R., with the major one corresponding to triphenyl phosphine oxide. The light green liquid in the cold trap consisted mainly of toluene and a small amount of p-tolyl vinyl sulphone, as seen on the ^{1}H N.M.R. and GCMS (S.E. 54, 50-200°C, 10°C min^{-1}). Once more the majority of the product in the cold trap was a white, insoluble polymeric material.

b) FVP of p-methylbenzenesulphonyl ethylidene triphenyl phosphorane and attempted trapping of products

(i) With Anthracene

FVP of the title compound (1g, 750°C, 8.0×10^{-2} mmHg, inlet 200-240°C) was carried out as before. Anthracene (2 equivalents) was added to the cold trap before the pyrolysis. Once all the material had undergone FVP the cold trap was allowed to warm to 0°C and washed out with ether. The ether solution was then warmed to R.T. and stirred at R.T. for 36h. The solvent was evaporated and the residue chromatographed on silica (benzene/ether, 1:1) to give a light brown oily solid (0.2g). δ_H 7.0-8.0 (m, aromatic H's), 5.90 (finely split d, J_{Major} = 11 Hz, J_{Minor} = 0.5 Hz), 5.25 (finely split d, J_{Major} = 4 Hz, J_{Minor} = 0.5 Hz), 2.45 (broad s), 2.4 (broad s); m/z, 344 (M^+). This could correspond to a product-anthracene

cycloadduct, the product being derived from loss of Ph_3PO from the starting ylide.

(ii) With 2,3-dimethylbuta-1,3-diene

FVP of the title compound (3g, 750°C, 9.5×10^{-2} mmHg, inlet 200-240°C) was carried out as before with 2,3-dimethylbuta-1,3-diene (5 equivalents) predeposited in the cold trap. After the pyrolysis was completed the cold trap was warmed to R.T. and washed out with a further small quantity of 2,3-dimethylbuta-1,3-diene. This mixture was heated on a water bath (40°C) for 3h, then R.T. for 17h. Evaporation of the excess butadiene gave a green oil which gave three fractions on preparative TLC (silica, ether/40-60 pet. ether, 1:1). No meaningful information was obtained from the ^1H N.M.R. of these fractions. It should be noted that after washing out the cold trap, there remained a considerable amount of insoluble polymeric material.

(iii) With Cyclopentadiene

FVP of the title ylide (3g, 750°C, 9.0×10^{-2} mmHg, inlet 200-240°C) was carried out as before with cyclopentadiene (2 equivalents), freshly prepared by the cracking of the cyclopentadiene dimer, predeposited in the cold trap. After pyrolysis the cold trap was washed with hexane, and the hexane solution stirred at 0°C for 2h, then R.T. for 17h. Removal of solvent gave a green oil which gave three fractions on chromatography on silica (ether). The ^1H N.M.R. of these fractions gave no meaningful

information. Once again a white, insoluble polymeric material was left in the cold trap.

c) FVP of p-methylbenzenesulphonyl propylidene triphenyl phosphorane

FVP of the title compound (0.2g, 750°C, 3.2×10^{-2} mmHg, inlet 200°C) gave two fractions. The dark oil at the furnace exit gave fourteen peaks in the ^{31}P N.M.R. of which the only significant peak was triphenyl phosphine oxide. This was confirmed by GCMS (S.E. 54, 50-300°C, 15°C min^{-1}) and ^{1}H N.M.R. In the cold trap a colourless liquid collected as well as an insoluble polymeric material. ^{1}H N.M.R. and GCMS (S.E. 54, 50-200°C, 10°C min^{-1}) showed toluene and ethyl benzene as the major constituents of the colourless liquid.

d) FVP of benzenesulphonyl propylidene triphenylphosphorane

FVP of the title compound (0.5g, 500°C, 9.5×10^{-2} mmHg, inlet 200-240°C) gave two fractions. The dark oil at the furnace exit gave five peaks in the ^{31}P N.M.R. of which only triphenyl phosphine and triphenyl phosphine oxide could be identified. The cold trap contained a light green oil, δ_H 7.15-8.1 (m, aromatic H's) and 1.0-3.05 (many peaks), which decomposed on standing. Some insoluble polymeric material was left behind in the cold trap.

FVP of the title compound (0.5g, 550°C, 7.0×10^{-2} mmHg, inlet 200-240°C) gave similar products to the FVP at 500°C.

e) FVP of benzenesulphonyl propylidene triphenyl phosphorane and attempted trapping of products

(i) With Cyclopentadiene

FVP of the title compound (3g, 750°C, 6.0×10^{-2} mmHg, inlet 200-240°C) was carried out as before, with freshly prepared cyclopentadiene (2 equivalents) predeposited in the cold trap. The cold trap contents were washed out with hexane and the hexane solution stirred at 0°C for 3h, then R.T. for 17h. Evaporation of the solvent left a green oil whose ^{1}H N.M.R. gave no meaningful information, containing only peaks at δ_H 7.0-8.0 (aromatic H's) and a series of small peak at δ_H 1.0-3.5. Most of the cold trap contents remained behind as a white, insoluble polymeric material.

(ii) With Chlorine

FVP of the title compound (3g, 750°C, 2×10^{-1} mmHg, inlet 200-240°C) was carried out. The contents of the cold trap were kept cold and washed out with hexane. This hexane was kept cold at -40°C in a cardice/acetone bath before being added to a well stirred mixture of ether (10 ml) and hexane (20 ml) previously saturated with Cl_2 and cooled to -195°C. After the addition the mixture was warmed to -30°C, stirred for 1h, then allowed to come to R.T. over 2h. Evaporation of the solvent gave a yellow liquid which decomposed rapidly upon attempted Kugelrohr distillation at 65°C

(oven temperature) and 0.5 mmHg. It should be noted that a considerable amount of white polymeric material was left in the cold trap after washing with hexane.

f) FVP of methanesulphonyl ethylidene triphenyl phosphorane

FVP of the title compound (0.5g, 500°C, 5.0×10^{-2} mmHg, inlet 160-200°C) gave two fractions. The dark solid at the furnace exit contained unreacted starting material and triphenyl phosphine oxide in the ratio 10:1 as seen in ^{31}P and ^{1}H N.M.R. The cold trap had $CDCl_3$ added and the ^{1}H N.M.R. obtained: However no peaks were seen in the N.M.R. even after several thousand scans, with the only cold trap product being a little insoluble polymeric material.

FVP of the title compound (0.3g, 750°C, 7.4×10^{-2} mmHg, inlet 160-200°C) gave two fractions. The combined fractions were examined together. The ^{31}P N.M.R. showed ten peaks of which triphenyl phosphine oxide was by far the largest. The ^{1}H N.M.R. had δ_H 7.0-8.0 (large aromatic peaks, consistent with $Ph_3P=0$), 5.0-6.0 (vinylic proton peaks) and 0.9-4.0 (mass of peaks). No information could be gleamed from the forest of peaks in the region δ_H 0.9-4.0 or the vinylic protons. Again a considerable quantity of the cold trap product remained behind as a white, insoluble polymeric solid.

2. Flash Vacuum Pyrolysis of phenylmethane- and substituted phenylmethanesulphonyl alkylidene triphenyl phosphoranes

a) FVP of the ylides

(i) FVP of phenylmethanesulphonyl benzylidene triphenyl phosphorane

FVP of the title compound (1g, 600°C, 1.7×10^{-1} mmHg, inlet 160-200°C) gave a dark oil at the furnace exit. Chromatography on silica ($CHCl_3$) gave trans-stilbene (0.2g, 56%) and a mixture of phosphorus containing products (0.42g, 66%). The trans-stilbene was identical to an authentic sample by ^1H N.M.R. (300 MHz), ^{13}C N.M.R. (75 MHz), M.S., analysis and T.L.C. (silica, $CHCl_3$). The phosphorus products were triphenyl phosphine, triphenyl phosphine oxide and triphenyl phosphine sulphide confirmed by ^{31}P N.M.R., in the proportions 6%:44%:16%.

(ii) FVP of phenylmethanesulphonyl p-methylbenzylidene triphenyl phosphorane

FVP of the title compound (2g, 600°C, 1.8×10^{-1} mmHg, inlet 160°C) gave a dark oil at the furnace exit. ^1H N.M.R. and GCMS (Methylsilane, 60-220°C, 10°C/min) showed the products to be p-methyl stilbene (0.35g, 47%), stilbene (0.04g, 6%), p,p'-dimethylstilbene (0.07g, 9%) and bibenzyl (0.02g, 3%) by comparison with authentic samples. The ^{31}P N.M.R. also showed the presence of triphenyl phosphine oxide and triphenyl phosphine sulphide in the ratio 35%:13%.

(iii) FVP of phenylmethanesulphonyl ethylidene triphenyl phosphorane

FVP of the title compound (0.2g, 600°C, 1.0×10^{-2} mmHg, inlet 160-200°C) gave two fractions. At the furnace exit the dark oil, on ^{31}P N.M.R. and GCMS (S.E. 54, 60-300°C, 10°C min^{-1}), proved to be a mixture of Ph_3P, $Ph_3P=O$ and $Ph_3P=S$ in the ratio 5%:24%:11%. In the cold trap the ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C m^{-1}) allowed identification of the products as β-methyl styrene (cis and trans, 24%), trans-stilbene (7%) and bibenzyl (49%) by comparison with authentic samples.

(iv) FVP of o-methoxyphenylmethanesulphonyl ethylidene triphenyl phosphorane

FVP of the title compound (0.2g, 600°C, 9.5×10^{-2} mmHg, inlet 160-200°C) gave two fractions. At the furnace exit the dark oil, on ^{31}P N.M.R. and GCMS (S.E. 54, 70-300°C, 15°C min^{-1}), proved to be $Ph_3P=O$ and $Ph_3P=S$ in the ratio 25%:4%. The clear liquid in the cold trap contained 2-methoxy-1-propenylbenzene (cis and trans, 6%), 2,2'-dimethoxylstilbene (cis and trans, 5%) and o-tolualdehyde (22%) by ^{1}H N.M.R. and GCMS (S.E. 54, 50-250°C, 10°C min^{-1}) comparison with authentic samples.

(v) FVP of o-methylphenylmethanesulphonyl ethylidene triphenylphosphorane

FVP of the title compound (0.2g, 600°C, 1.5×10^{-2} mmHg, inlet 160-200°C) gave two fractions. At the furnace exit the dark oil, on ^{31}P N.M.R. and GCMS (S.E. 54, 70-300°C, 10°C min^{-1}), proved to be a mixture of Ph_3P, $Ph_3P=0$ and $Ph_3P=S$ in the ratio 4%:23%:16%. The clear liquid in the cold trap contained o-propenyltoluene (cis and trans, 7%), 2,2'-dimethylstilbene (9%) and 2,2'-dimethylbibenzyl (34%) by ^1H N.M.R. and GCMS (S.E. 54, 60-250°C, 10°C min^{-1}) comparison with authentic samples.

(vi) FVP of phenylmethanesulphonyl o-methoxybenzylidene triphenyl phosphorane

FVP of the title compound (0.2g, 600°C, 5×10^{-2} mmHg, inlet 160-200°C) gave two fractions. The dark oil at the furnace exit was shown to contain Ph_3P,$Ph_3P=0$ and $Ph_3P=S$ in the ratio 37%:46%:17% by ^{31}P N.M.R. and GCMS (S.E. 54, 70-300°C, 10°C min^{-1}). The clear liquid in the cold trap was seen to be bibenzyl (11%), o-tolualdehyde (7%), benzofuran (14%) and 2-methoxystilbene (cis and trans, 39%) by ^1H N.M.R. and GCMS (S.E. 54, 60-250°C, 10°C min^{-1}) comparison with authentic samples.

(vii) FVP of phenylmethanesulphonyl o-methylthiobenzylidene triphenyl phosphorane

FVP of the title compound (0.2g, 600°C, 6×10^{-2} mmHg, inlet 160-200°C) gave two fractions. The dark oil at the furnace exit was shown to contain Ph_3P,$Ph_3P=0$ and $Ph_3P=S$ in the ratio 56%:31%:19% and 2-methylthio-stilbene (5%) by ^1H, ^{31}P N.M.R. and GCMS (S.E. 54, 70-300°C, 10°C min^{-1}). The clear liquid in the cold trap was seen to be bibenzyl (29%) and benzothiophene (58%) by ^1H N.M.R. and GCMS (S.E. 54, 60-250°C, 10°C min^{-1}) comparison with authentic samples.

b) Preparation of Authentic Stilbene and Styrene Derivatives

(i) p-Methylstilbene

This was made by close analogy to the original Wittig reaction procedure[75]. Benzyl triphenyl phosphonium chloride (5g, 13 mmol) was stirred at R.T. under N_2 in dry THF (100 ml) while Bu^nLi (13 mmol, 2.5 M in hexane) was added. After stirring for 45min p-tolualdehyde (1.56g, 13 mmol) in dry THF (10 ml) was added and the mxiture stirred at R.T. for 17h. The mixture was diluted with water and extracted with ether (3×100 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated and chromatography on silica (40/60 pet. ether) gave a mixture of cis and trans p-methylstilbene, m.p. 115-120°C (lit[76] m.p. 120°C) in the ratio 1:4 by ^1H N.M.R. and GCMS (Methyl Silane, 60-300°C, 15°C min^{-1}).

(ii) 4,4'-Dimethylstilbene

The same procedure as above from p-methylbenzyltriphenyl phosphonium bromide (2.23g, 5 mmol) and p-tolualdehyde (0.6g, 5 mmol) gave cis and trans 4,4'-dimethylstilbene, m.p. 176-179°C (lit[76] m.p. 179-180°C) in the ratio 1:3 by ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C min^{-1}).

(iii) β-Methylstyrene

The procedure was as above from ethyl triphenyl phosphonium bromide (1.37g, 3.7 mmol) and benzaldehyde (0.39g, 3.7 mmol). Kugelrohr distillation, b.p. 80-85°C (oven temp) at 15 mmHg, gave β-methyl styrene (lit[77] 74°C at 13 mmHg) in the ratio 43:57 (cis:trans), by ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C min^{-1}).

(iv) 2-Methoxy-1-propenylbenzene

The procedure was as above from ethyl triphenyl phosphonium bromide (1.37g, 3.7 mmol) and o-methoxybenzaldehyde (0.5g, 3.7 mmol). Kugelrohr distillation gave 2-methoxy-1-propenyl benzene, b.p. 130°C (oven temp) at 15 mmHg (lit[78] b.p. 104°C at 13 mmHg) as a colourless liquid being a mixture of cis and trans isomers in the ratio 58:42 by ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C min^{-1}).

(v) 2,2'-Dimethoxystilbene

Procedure as above from o-methoxybenzyl triphenyl phosphonium bromide (1.71g, 3.7 mmol) and o-methoxybenzaldehyde (0.5g, 3.7 mmol). Chromatography on silica (ether/pet. ether, 1:9) gave 2,2'-dimethyl stilbene, m.p. 130-134°C (lit[79] m.p. 136°C), as the cis and trans isomers in the ratio 42:58 by ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C min^{-1}).

(vi) o-Propenyltoluene

Procedure as above from ethyl triphenyl phosphonium bromide (1.19g, 3.2 mmol) and o-tolualdehyde (0.38g, 3.2 mmol). Kugelrohr distillation gave o-propenyltoluene, b.p. 80-100°C (oven temp) at 15 mmHg (lit[80] b.p. 68-71°C at 5 mmHg for a 23:77, cis:trans ratio) as a colourless liquid as the cis and trans isomers in the ratio 48.5:51.5 by ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C min^{-1}).

(vii) 2,2'-Dimethylstilbene

Procedure as above from 2-methylbenzyl triphenyl phosphonium bromide (3.71g, 8.3 mmol) and o-tolualdehyde (1g, 8.3 mmol). Chromatography on silica (ether/pet. ether, 1:9) gave 2,2'-dimethyl stilbene, m.p. 79-82°C (lit[76] m.p. 82-83°C) as a white solid as the cis and trans isomers in the ratio 51:49 by ^{1}H N.M.R. and GCMS (S.E. 54, 60-200°C, 10°C min^{-1}).

(c) FVP of Authentic Samples

(i) FVP of p-Methylstilbene

FVP of the title compound (0.5g, 750°C, 1.0×10^{-1} mmHg, inlet 160-220°C) gave a mixture of unreacted starting material, trans-stilbene and 4,4'-dimethyl stilbene by comparison of ^{1}H N.M.R. and GCMS (S.E. 54, 70-300°C, 15°C min^{-1}) with authentic samples.

(ii) FVP of β-Methylstyrene

FVP of the title compound (0.5g, 750°C, 5×10^{-1} mmHg, inlet 160-200°C) gave unreacted starting material and trans-stilbene by comparison of ^{1}H N.M.R. and GCMS (S.E. 54, 70-300°C, 15°C min^{-1}) with authentic samples.

(iii) FVP of $Ph_3P + SO_2(g)$

FVP of Ph_3P in a stream of sulphur dioxide (100 mg, 750°C, 5×10^{-2} - 1.0×10^{0} mmHg, inlet 160-200°C) gave a solid product which showed 22 peaks in the ^{31}P N.M.R. spectrum. These were all very minor except for those of Ph_3P (δ_P –5.27), $Ph_3P=O$ (δ_P +29.4) and $Ph_3P=S$ (δ_P +43.09). GCMS (S.E. 54, 70-300°C, 15°C min^{-1}) and integration confirmed these products with the $Ph_3P=O$: $Ph_3P=S$ ratio being the expected 2:1.

E Preparation of Sulphinyl Stabilised Phosphorus Ylides

1. Attempted Preparation of benzene sulphinyl benzylidene triphenyl phosphorane

(i) Preparation of benzyl phenyl sulphoxide

The method of Shriner *et al*[72] was used. Benzyl phenyl sulphide (13g, 64.9 mmol) was dissolved in A.R. acetone (65 ml), filtered and 30% H_2O_2 (10g, 88.2 mmol) added. The mixture was shaken and allowed to stand at R.T. for 72h. The resulting solid was filtered off and after recrystallisation from 60% ethanol gave benzyl phenyl sulphoxide (12.13g, 88%), m.p. 121-122°C, (lit[72] 122-123°C) as colourless needles.

(ii) Preparation of α-bromobenzyl phenyl sulphoxide

The preparation was a modification of the procedure of Cinquini and Colonna[81]. Benzyl phenyl sulphoxide (10.8g, 50 mmol) in anhydrous pyridine/acetonitrile (125 ml, 1:4 v/v) was stirred and cooled to -40°C while Br_2 (16g, 100 mmol) in anhydrous acetonitrile (50 ml) was added dropwise. The mixture was kept at -40°C for 1h then at R.T. for 76h. The solvent was evaporated under reduced pressure, the residue dissolved in chloroform (200 ml) and washed successively with aqueous sodium thiosulphate, aqueous sulphuric acid and water. Drying ($MgSO_4$), evaporation and chromatography of the resulting brown solid on silica (ether/40/60 pet. ether 1:1) gave α-bromobenzyl phenyl sulphoxide (4.5g,

31%), m.p. 193-194°C (lit[81] m.p. 193-194°C) as a white solid.

(iii) Reaction between Ph_3PBr_2 and benzyl phenyl sulphoxide

Triphenyl phosphine dibromide (5.28g, 12.5 mmol) was stirred at R.T. in dry toluene (35 ml) while Et_3N (3.04g, 30 mmol) in dry toluene (10 ml) and solid benzyl phenyl sulphoxide (2.7g, 12.5 mmol) were added. The mixture was heated under reflux for 30min then stirred at R.T. for 1.5h. The resulting solid was filtered and the solvent evaporated to leave a dark brown solid on cooling. ^{31}P and ^{1}H N.M.R. showed only the presence of $Ph_3P{=}0$ and the starting sulphoxide.

(iv) Preparation of benzylphenyl sulphoxide-α-triphenyl phosphonium bromide

α-Bromobenzylphenyl sulphoxide (2g, 6.8 mmol), Ph_3P (1.78g, 6.8 mmol) and sulpholane (25 ml) were stirred and heated to 120°C under N_2 for 18h then stirred at R.T. for 12h. The sulpholane was evaporated under reduced pressure and the residual black oil triturated with ethyl acetate to give benzylphenylsulphoxide-α-triphenyl phosphonium bromide (0.82g, 22%) as a light brown solid. ^{31}P N.M.R., δ_P +22.92(s); δ_H 7.0-8.0 (m, 25H), 5.36 (d, 1H, J_{P-H} = 15 Hz).

(v) Attempted dehydrohalogenation of phosphonium salt with various base/solvent systems

(v.i) With NaOH/water

The phosphonium salt (0.1g, 0.21 mmol) was stirred in water (15 ml). Though complete dissolution was not observed, NaOH (9.7 mg, 0.24 mmol) in water (5 ml) was added dropwise. The observed yellow precipitate (0.07g) was filtered and sucked dry. ^{31}P and ^{1}H N.M.R. showed only $Ph_3P=0$ and benzyl phenyl sulphoxide.

(v.ii) With Bu^nLi/THF

The phosphonium salt (0.09g, 0.19 mmol) was stirred under N_2, in dry THF (10 ml), while Bu^nLi (0.2 mmol, 2.5 M in hexane) was added. After stirring for 30min the solvent was evaporated. ^{31}P and ^{1}H N.M.R. showed $Ph_3P=0$, starting salt and Ph_3P as well as a product containing an n-butyl group, tentatively assigned as n-butyl phenyl sulphoxide[44].

(v.iii) With potassium t-butoxide/t-butanol

The phosphonium salt (0.1g, 0.21 mmol) was stirred in t-butanol (10 ml) while $KOBu^t$ (0.03g, 0.26 mmol) was added. After stirring for 30min the solvent was evaporated. ^{31}P and ^{1}H N.M.R. of the residue showed only $Ph_3P=0$ and benzyl phenyl sulphoxide as the major identifiable products.

(v.iv) With KOBu^t/THF

The salt (0.1g, 0.21 mmol) was stirred in dry THF (10 ml) while KOBu^t (0.03g, 0.26 mmol) was added. After stirring at R.T. for 30min the solvent was evaporated. ^{31}P and ^1H N.M.R. showed only $Ph_3P=0$, unreacted starting material and Ph_3P as the products.

(v.v) With LDA/THF

Diisopropyl amine (0.03g, 0.3 mmol) was stirred in dry THF (10 ml) under N_2 and Bu^{n}Li (0.25 mmol, 2.5 M in hexane) was added to generate L.D.A. To this solution was added the phosphonium salt (0.1g, 0.21 mmol) and the mixture stirred at R.T. for 30min. The solvent was evaporated under reduced pressure and the residue showed only $Ph_3P=0$ and benzyl phenyl sulphoxide as recognisable products from ^{31}P and ^1H N.M.R.

2. Attempted Preparation of arylsulphinyl alkylidene triphenyl phosphoranes

a) Preparation of sulphinyl chlorides from sodium sulphinates

(i) p-Toluenesulphinyl chloride

Sodium p-toluenesulphinate (2.8g, 13 mmol) was added to 5 M HCl (5 ml) and the resulting solid filtered, sucked dry, then heated with thionyl chloride (3.26g, 27 mmol) in ether (10 ml) for 30min. Evaporation of solvent gave a dark yellow oil.

(ii) Benzene Sulphinyl Chloride

The procedure as above from sodium benzene sulphinate (2.13g, 13 mmol) gave a yellow oil.

b) Attempted reaction of Sulphinyl Chlorides with Nonstabilised Ylides

(i) p-Toluene sulphinyl chloride and benzylidene triphenyl phosphorane

Benzyl triphenyl phosphonium chloride (10g, 25.7 mmol) was stirred at R.T. under N_2 in extra dry THF (100 ml) while Bu^nLi (26 mmol, 2.5 M in hexane) was added. After stirring at R.T. for 30min the crude p-toluene sulphinyl chloride (13 mmol), described above, in extra dry THF (20 ml) was added at 0°C. The mixture was refluxed for 18h then water (150 ml) and ether (50 ml) added. Further extraction with ether (2 × 75 ml), drying of the combined organic extracts ($MgSO_4$), and evaporation gave 5.68g of a brown solid whose ^{31}P and ^1H N.M.R. showed only $Ph_3P=0$ to be present.

(ii) p-Toluene sulphinyl chloride and ethylidene triphenyl phosphorane

With ethyl triphenyl phosphonium bromide (9.65g, 26 mmol) as the phosphonium salt, using the same procedure as above gave 3.5g of brown solid whose ^{31}P and ^1H N.M.R. showed only $Ph_3P=0$ present.

(iii) Benzene sulphinyl chloride and benzylidene triphenyl phosphorane

The above procedure was repeated with benzyl triphenyl phosphonium chloride (10g, 25.7 mmol) and benzene sulphinyl chloride (13 mmol) which gave 7.29g of a brown solid whose ^{31}P and ^{1}H N.M.R. show only $Ph_3P=0$ present.

(iv) Benzene sulphinyl chloride and ethylidene triphenyl phosphorane

The same procedure as above with ethyl triphenyl phosphonium bromide (9.65g, 26 mmol) gave 4g of dark brown crystals whose ^{31}P and ^{1}H N.M.R. showed only $Ph_3P=0$.

c) p-Toluene Sulphinyl Chloride (Literature Method)[82]

The procedure of Kurzer in Organic Synthesis[82] was used to prepare p-toluene sulphinyl chloride (5.2g, 71%) as a yellow oil, which was used without further purification.

A repeat of procedure (b).(ii) above with this genuine sulphinyl chloride again gave only $Ph_3P=0$ as observed on ^{31}P and ^{1}H N.M.R.

3. Preparation of α-sulphinyl alkoxycarbonylmethylene triphenyl phosphoranes

a) Preparation of Sulphinyl Chlorides

There were prepared by the procedure of Youn and Hermann[83].

(i) Benzene Sulphinyl Chloride

Thiophenol (5.45g, 50 mmol) and glacial acetic acid (3g, 50 mmol) were stirred well then cooled to -40°C. Sulphuryl chloride (14.18g, 105 mmol) was added dropwise over 30min. The temperature was kept at -40°C for a further 30min, allowed to come to R.T. over 2h, then stirred at approximately 30°C for 4h. The acetyl chloride byproduct was removed under vacuum on a rotary evaporator and finally by direct attachment to an oil pump. This left benzene sulphinyl chloride (7.58g, 95%) as a light green oil, δ_H 7.0-8.0 (m). All aromatic sulphinyl chlorides remained undistilled due to the danger of explosions and were pure enough to be used directly for further reactions.

(ii) p-Toluene Sulphinyl Chloride

The procedure as above from p-thiocresol (6.21g, 50 mmol) gave p-toluene sulphinyl chloride (8.37g, 96%) as a dark yellow oil, δ_H 7.63 (AB pattern, 4H, J = 8 Hz) and 2.47 (s, 3H).

(iii) p-Bromobenzene Sulphinyl chloride

The procedure as above from p-bromothiophenol (3.49g, 18.5 mmol)

gave after cooling, p-bromobenzene sulphinyl chloride (4.2g, 97%) as a yellow solid, δ_H 7.2-8.0 (m).

(iv) p-Chlorobenzene Sulphinyl chloride

The procedure as above from p-chlorothiophenol (7g, 48.4 mmol) gave p-chlorobenzene sulphinyl chloride (8.04g, 85%) as a dark red oil, δ_H 7.1-8.1 (m).

(v) Ethane Sulphinyl Chloride

The procedure as above from ethane thiol (7g, 112.7 mmol) gave after distillation ethane sulphinyl chloride (10.18g, 80%), b.p. 60°C (Kugelrohr oven temp) at 19 mmHg (lit[83] 67°C at 26 mmHg) as a clear yellow liquid, δ_H 3.5 (q, 2H, J = 7 Hz) and 1.55 (t, 3H, J = 7 Hz).

b) Preparation of Phosphonium Salts and Stabilised Ylides

(i) Methoxycarbonylmethyl triphenyl phosphonium bromide

Methyl bromoacetate (29.2g, 191 mmol), Ph_3P (50g, 191 mmol) and toluene (250 ml) were stirred and heated at 80°C for 2h. Filtration of the resulting precipitate and washing with ether gave methoxycarbonyl methyl triphenyl phosphonium bromide (74.6g, 94%), m.p. 225-227°C (lit[84] 227°C).

(ii) Methoxycarbonylmethylene triphenyl phosphorane

Methoxycarbonylmethyl triphenyl phosphonium bromide (50g, 120 mmol) was dissolved in water (500 ml) and NaOH (4.81g, 120 mmol) in water (5 ml) added dropwise. After stirring for 30min the supernatant liquid was poured off and the sticky solid dissolved in CH_2Cl_2. After washing with water, drying ($MgSO_4$), and removal of solvent methoxycarbonylmethylene triphenyl phosphorane (36.1g, 90%), m.p. 167-169°C (lit[85] 169-169.5°C) was obtained as a light yellow solid.

(iii) Ethoxycarbonylmethyl triphenyl phosphonium bromide

The method as in (b)(i) above from ethyl bromoacetate (31.9g, 191 mmol) gave ethoxycarbonylmethyl triphenyl phosphonium bromide (75.44g, 92%), m.p. 154-156°C (lit[84] 155-156°C).

(iv) Ethoxycarbonylmethylene triphenyl phosphorane

The procedure as in (b)(ii) above gave ethoxycarbonylmethylene triphenyl phosphorane (36.33g, 87%) as a light yellow solid, m.p. 116-117°C (lit[86] 116-117°C).

(v) n-Propyl Chloroacetate

A variation on the method of Whitesides *et al*[87] was used. Chloroacetyl chloride (5.65g, 50 mmol) in CCl_4 (20 ml) was stirred at R.T. while n-propanol (3.05g, 50 mmol) was added slowly. The mixture was stirred at

R.T. for 2h, 60°C for 3h, then R.T. for a further 6h. Removal of solvent and Kugelrohr distillation gave n-propyl chloroacetate (6.33g, 93%) b.p. 180-210°C (oven temp), (lit[87] b.p. 75°C at 22 mmHg).

(vi) n-Propyl Iodoacetate

n-Propyl chloroacetate (34.1g, 250 mmol) was added to NaI (37.47g, 250 mmol) in A.R. acetone (150 ml). The mixture was stirred at R.T. for 2h. The solvent was removed and the residue partitioned between toluene and water. The toluene layer was dried and filtered and used without further purification for the next reaction.

(v) Propoxycarbonylmethyl triphenyl phosphonium iodide

To the toluene layer from the previous experiment was added Ph_3P (65.57g, 250 mmol). Stirring was continued for 14h at R.T., then the precipate formed filtered off, washed with ether and sucked dry in a vacuum oven to give propoxycarbonylmethyl triphenyl phosphonium iodide (95.41g, 78%). Recrystallisation from dichloromethane/toluene gave colourless needles, m.p. 147.5-148°C. (Found: C, 56.6; H,4.8. $C_{23}H_{24}IO_2P$ requires C, 56.3; H, 4.8); δ_P +20.29(s); δ_H 7.5-8.2(m, 15H), 5.3(d, 2H, J=14Hz), 4.04(t, 2H, J=6.5Hz), 1.52(sextet, 2H, J=6.5Hz) and 0.8(t, 3H, J=6.5Hz).

c) Preparation of α-sulphinyl alkoxycarbonylmethylene triphenyl phosphoranes

The procedure of Alden[42] was used to prepare these sulphinyl ylides. An illustrative example is given.

(i) Benzenesulphinyl methoxycarbonylmethylene triphenyl phosphorane

Methoxycarbonylmethylene triphenyl phosphorane (4g, 12 mmol), dry, redistilled triethylamine (1.21g, 1.69 ml, 12 mmol) and dry toluene (100 ml) werestirred at 0°C. Benzene sulphinyl chloride (1.92g, 12 mmol) in dry toluene (15 ml) was added over 30min. The mixture was stirred at 0°C for 2h then allowed to come to R.T. over 1h. The precipitate of $Et_3N.HCl$ was filtered off, the solvent removed and the residual oil triturated with ethyl acetate (10 ml) to give benzenesulphinyl methoxycarbonylmethylene triphenyl phosphorane (3.5g, 64%), m.p. 212-218°C dec., as a white solid. (Found: M^+–Me, 443.121401. $C_{26}H_{20}O_3PS$ requires 443.087071); δ_P +28.18; δ_H 7.4-8.0 (m, 15H), 7.0-7.38 (m, 5H) and 3.63 (s, 3H); δ_C 172.78 (C=0, broadened), 144.34, 133.82, 133.69, 131.95, 131.93, 128.46, 128.30, 128.09, 127.43, 126.22, 125.26, 124.16, 50.96 (methyl C, broadened), 35.70 (ylide C, J_{P-C} 123.3 Hz); M.S. (No M^+ peak at 458), m/z 443 (5%), 442(19), 365(5), 278(18), 277(42), 263(14), 262(74), 201(11), 183(42), 86(100).

(ii) Benzenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

The procedure as above from ethoxycarbonylmethylene triphenyl phosphorane (4g, 11 mmol), Et_3N (1.53 ml, 11 mmol) and benzene sulphinyl chloride (1.76g, 11 mmol) was used. After prolonged pumping of the residual oil at an oil pump benzenesulphinyl ethoxycarbonyl methylene triphenyl phosphorane (3.68g, 71%) was obtained as a white powder, whose ^1H N.M.R. showed it to contain residual solvent even after a further 12h under an oil pump vacuum. m.p. 73-103°C; (Found: M^+–Me, 457.105817. $C_{27}H_{22}O_3PS$ requires 457.102721); δ_P +23.46(s); δ_H 7.3-7.9(m, 20H), 2.13(broad s, 2H) and 0.65(t, 3H); M.S. (No M^+ peak at 472), m/z 457(17%), 395(10), 278(20), 277(43), 262(100) and 183(81).

(iii) p-Toluene sulphinyl methoxycarbonylmethylenetriphenyl phosphorane

The procedure as above from methoxycarbonylmethylene triphenyl phosphorane (3.79g, 11.5 mmol), Et_3N (1.6 ml, 11.5 mmol) and p-toluene sulphinyl chloride (2g, 11.5 mmol) gave p-toluenesulphinyl methoxy-carbonylmethylene triphenyl phosphorane (1.63g, 30%), m.p. 215-215.5°C as glistening colourless crystals; (Found: M^+–Me, 457.138523. $C_{27}H_{22}O_3PS$ requires 457.102721); δ_P +28.91; δ_H 7.2-8.0 (m, 15H), 6.95-7.2 (m, 4H), 3.62 (s, 3H) and 2.27 (s, 3H); δ_C 172.89 (C=0, broadened), 140.88, 133.86, 133.73, 131.90, 131.87, 128.90, 128.43,

128.27, 127.60, 126.40, 125.55, 50.88 (methyl C, broadened), 36.15 (ylide C, J_{P-C} = 122.7 Hz), 20.89 (p-methyl C); M.S. (No M^+ peak at 472), m/z 457 (9%), 456(30), 365(4), 277(5), 262(100), 183(45), 165(10), 152(10), 135(18), 108(28) and 107(36).

(iv) p-Toluenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

The procedure as above from ethoxycarbonylmethylene triphenyl phosphorane (4g, 11.5 mmol), Et_3N (1.6 ml) and p-toluenesulphinyl chloride (2g, 11.5 mmol) gave p-toluenesulphinyl ethoxycarbonyl methylene triphenyl phosphorane (2.28g, 41%), m.p. 199.5-202°C as glistening colourless crystals; (Found: M^+–Me, 471.152931. $C_{28}H_{24}O_3PS$ requires 471.118370); δ_P +28.35; δ_H 7.32-7.9 (m, 15H), 6.9-7.3 (m, 4H), 4.08 (q, 2H, J = 7Hz), 2.27 (s, 3H) and 0.97 (broad t, 3H, J = 7 Hz); δ_C 172.23 (C=0, broadened), 141.02, 133.82, 133.69, 131.80, 131.78, 128.78, 128.34, 128.18, 127.81, 126.60, 125.85, 58.91 (methylene C, broadened), 36.95 (ylide C, J_{P-C} = 120.8 Hz), 20.88 (p-methyl C), 14.62 (methyl C, broadened). M.S. (no M^+ peak at 486), m/z 471(4), 470(13), 263(13), 262(100), 185(11), 183(37), 165(8), 135(17), 108(20) and 107(14).

(v) p-Bromobenzenesulphinyl methoxycarbonylmethylene triphenyl phosphorane

The procedure as above from methoxycarbonylmethylene triphenyl phosphorane (2.75g, 8.35 mmol), Et_3N (1.16 ml, 8.35 mmol) and p-bromobenzenesulphinyl chloride (2g, 8.35 mmol) gave p-bromobenzenesulphinyl methoxycarbonylmethylene triphenyl phosphorane (2.39, 53%), m.p. 171.5-172.5°C; δ_P+ 28.82; δ_H 7.5-8.0 (m, 15H), 7.1-7.48 (m, 4H) and 3.63 (s, 3H).

(vi) p-Bromobenzenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

The procedure as above from ethoxycarbonylmethylene triphenyl phosphorane (2.91g, 8.35 mmol). Et_3N (1.16 ml, 8.35 mmol) and p-bromobenzenesulphinyl chloride (2g, 8.35 mmol) gave p-bromobenzene sulphinyl ethoxycarbonylmethylene triphenyl phosphorane (2.75g, 60%), m.p. 190-192°C dec; δ_P +28.90; δ_H 7.45-8.95 (m, 15H), 7.0-7.45 (m, 4H), 4.07 (q, 2H, J = 7 Hz) and 0.92 (broad s, 3H).

(vii) Ethanesulphinyl methoxycarbonylmethylene triphenyl phosphorane

The procedure as above from methoxycarbonylmethylene triphenyl phosphorane (5.95, 17.8 mmol), Et_3N (2.4 ml, 17.8 mmol) and ethane

sulphinyl chloride (2g, 17.8 mmol) gave ethanesulphinyl methoxycarbonyl methylene triphenylphosphorane (2.54g, 35%), m.p. 134-136°C as a yellow powder; (Found: M^+–Me, 395.085031. $C_{22}H_{20}O_3PS$ requires 395.087071); δ_P +27.98; δ_H 7.45-8.0 (m, 15H), 3.53 (s, 3H), 2.2 (q, 2H, J = 7 Hz) and 1.0 (t, 3H, J = 7 Hz).

(viii) Ethanesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

The procedure was as above from ethoxycarbonylmethylene triphenyl phosphorane (6.2g, 17.8 mmol), Et_3N (2.4 ml, 17.8 mmol) and and ethane sulphinyl chloride (2g, 17.8 mmol), giving ethanesulphinyl ethoxycarbonylmethylene triphenyl phosphorane (3.33g, 44%), m.p. 140-143°C, as a yellow powder; (Found: M^+–Me, 409.106856. $C_{23}H_{22}O_3PS$ requires 409.102721); δ_P +28.15; δ_H 7.4-8.0 (m, 15H), 4.0 (q, 2H, J = 7 Hz), 2.22 (q, 2H, J = 7 Hz) and 1.0 (2 superimposed t's, 6H).

(ix) p-Chlorobenzenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

The procedure as above from ethoxycarbonylmethylene triphenyl phosphorane (3.58g, 10.3 mmol), Et_3N (1.39, 10.3 mmol) and p-chlorobenzenesulphinyl chloride (2g, 10.3 mmol) gave p-chlorobenzene sulphinyl ethoxycarbonylmethylene triphenyl phosphorane (3.75g, 72%),

m.p. 191-194°C dec; (Found: M^+–Me, 491.075049 for ^{35}Cl. $C_{27}H_{21}ClO_3PS$ requires 491.063749); δ_P +28.93; δ_H 7.35-8.0 (m, 15H), 7.22 (s, 4H), 4.7 (q, 2H, J = 7Hz) and 0.93 (broad t, 3H, J = 7Hz); δ_C 172.23(C=O), 143.41, 133.79, 133.66, 132.02, 131.99, 129.71, 128.48, 128.32, 128.07, 127.51, 126.80, 126.30, 59.11, 36.00 (ylide C,J_{P-C} 121.12Hz) and 14.65.

(x) p-Toluenesulphinyl propoxycarbonylmethylene triphenyl phosphorane

The procedure to generate the title ylide was an adaptation of a procedure for formation of keto ylides by Hamper[88]. Propoxycarbonylmethyl triphenyl phosphonium iodide (6.66g, 13.6 mmol) in dry toluene (100 ml) was stirred at R.T. and dry Et_3N (1.9 ml, 13.6 mmol) added. After stirring at R.T. for a further 30min the precipitate was filtered off, more dry Et_3N (1.9 ml, 13.6 mmol) added, the mixture cooled to 0°C and p-toluenesulphinyl chloride (2.37g, 13.6 mmol) added over 30min. The rest of the procedure was as described above to give p-toluenesulphinyl propoxycarbonylmethylene triphenyl phosphorane (0.2g, 3%), δ_P+28.23; δ_H 7.25-7.7 (m, 15H), 6.85-7.1 (m, 4H), 3.88 (broad, undefined peak, 2H), 2.23 (s, 3H), 0.5-1.5 (very broad, undefined peaks, 5H); M.S. (no M^+ peak at 500), m/e 485(2%), 262(46), 196(5), 183(57), 165(17), 152(10), 135(25), 121(21), 108(38), 91(23), 77(22),

51(25) and 43(100).

4. Attempted Ylide preparation from nonstabilised precursor ylides

(i) Attempted preparation of benzenesulphinyl benzylidene triphenyl phosphorane

The ylide generated from benzyl triphenyl phosphonium chloride (4.86g, 12.5 mmol) in dry toluene (100 ml) under N_2 and Bu^nLi (12.5 mmol, 2.5 M in hexane) reacted with benzene sulphinyl chloride (2g, 12.5 mmol) and worked up as in Section 3.(c) above gave 0.3g of a white solid, δ_P+22.97; δ_H 7.5-8.3 (m, 15H), 7.1-7.5 (m, 5H) and 5.5 (d, 2H, J = 14 Hz) which was identical to the authentic starting salt.

(ii) Attempted preparation of benzenesulphinyl-p-nitrobenzylidene triphenyl phosphorane

The ylide generated from p-nitrobenzyl triphenyl phosphonium bromide (1g, 2.1 mmol) under N_2 reacted as above gave a white solid δ_P+22.97; δ_H 7.4-8.2 (m, 19H) and 6.12 (d, 2H, J = 16 Hz) identical to an authentic sample of the starting salt.

5. Preparation of isopropylsulphinyl benzylidene triphenyl phosphorane

(i) Preparation of isopropylsulphinyl chloride

This was prepared by the method of Youn and Herrmann[83] in 95% yield, b.p. 75°C (Kugelrohr oven) at 32 mmHg (lit[83] b.p. 49°C at 12 mmHg).

(ii) Preparation of isopropylsulphinyl benzylidene triphenyl phosphorane

Benzyl triphenyl phosphonium chloride (10.1g, 26 mmol) was stirred at R.T. under N_2 in dry toluene (100 ml) and Bu^nLi (26 mmol, 2.5 M in hexane) was added. After stirring for 30min, the mixture was cooled to 0°C and isopropylsulphinyl chloride (1.64g, 13 mmol) in dry toluene (10 ml) was added slowly. The mixture was stirred at 0°C for 2h then allowed to warm to R.T. over 1h. Filtration of the precipitate, evaporation of the filtrate and trituration with ethyl acetate immediately gave a white powdery solid, which was filtered off and turned out to be identical to the starting phosphonium salt. The mother liquid was allowed to stand at R.T. for 48h and yielded isopropylsulphinyl benzylidene triphenyl phosphorane (1.91g, 33%) as yellow cubes. (Found: M^+–Pr^i, 399.095617. $C_{25}H_{20}OPS$ requires 399.097243); δ_P +20.17; δ_H 7.0-8.0 (m, 20H), 3.27 (P split septet, 1H, J = 7 Hz, J_{P-H} = 2 Hz), 1.28 (d, 3H, J = 7 Hz), 1.09 (d, 3H, J = 7 Hz); M.S.(No M^+ peak at 442) m/z 426(1%), 400(12), 399(41), 263(43), 262(71), 183(78), 121(76) and 105(100).

F Flash Vacuum Pyrolysis of Sulphinyl Ylides

1. FVP of α-sulphinyl alkoxycarbonyl triphenyl phosphoranes

(i) FVP of benzenesulphinyl methoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 4.7×10^{-2} mmHg, Inlet 200-240°C) gave two fractions. The dark solid at the furnace exit was shown to be mainly $Ph_3P=0$ and Ph_3P by ^{31}P and ^{1}H N.M.R. The cold trap contained a colourless foul smelling liquid. Calibration of the ^{1}H N.M.R. with dichloroethane showed the products to be phenyl vinyl sulphide (14%), thioanisole (22%) and an unknown compound, m/z 152 (M^+ ,15%). These products were confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}), which also showed the presence of diphenyl disulphide as a further product in low yield.

(ii) FVP of benzenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 2.7×10^{-2} mmHg, Inlet 200°C) showed only starting material at the furnace exit.

FVP of the title compound (0.2g, 600°C, 2.8×10^{-2} mmHg, Inlet 200-240°C) gave two fractions. The dark oil at the furnace exit was shown to be $Ph_3P=0$ by ^{31}P and ^{1}H N.M.R. The colourless liquid in the cold trap was examined by ^{1}H N.M.R. and GCMS. The only identifiable product by NMR was phenyl propenyl sulphide (10%) by calibration with

dichloroethane. GCMS (S.E. 54, 50-200°C, 10°C min^{-1}) confirmed the presence of this compound and also indicated the presence of ethyl phenyl sulphide (5%), an unknown compound, m/z 166 (M^+,7%), diphenyldisulphide (19%) and an unidentified peak of m/z 260 (M^+,39%).

(iii) FVP of p-toluenesulphinyl methoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 4.2×10^{-2} mmHg, Inlet 200-240°C) gave two fractions. The dark oil at the furnace exit was shown to contain $Ph_3P=0$, Ph_3P and some unreacted starting material by ^{31}P and ^1H N.M.R. The colourless liquid in the cold trap gave, by calibration of the N.M.R. with dichloroethane, p-tolyl vinyl sulphide (11%), p-methyl thioanisole (25%) and an unknown compound, m/z 166 (M^+ ,21%). These were confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}).

(iv) FVP of p-toluenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 4.2×10^{-2} mmHg, Inlet 200-240°C) gave two fractions. The dark oil at the furnace exit was shown to contain $Ph_3P=0$, Ph_3P and between 40 and 50% unreacted starting material. Calibration of the N.M.R. of the colourless liquid in the cold trap with dichloroethane indicated propenyl p-tolyl sulphide (20%) and an unknown compound, m/z 180 (M^+,7%). Both compounds were confirmed

by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}).

FVP of the title compound (0.2g, 600°C, 2.3×10^{-2} mmHg, Inlet 200°C) gave two fractions. The dark oil at the furnace exit contained only $Ph_3P=0$ and Ph_3P by ^{31}P and ^{1}H N.M.R. The colourless liquid in the cold trap was examined by ^{1}H N.M.R. and on calibration with dichloroethane, only propenyl p-tolyl sulphide (51%) could be identified.

GCMS (S.E. 54, 50-200°C, 10°C m^{-1}) confirmed this product and also indicated the presence of an unknown compound, m/z 180 (M^+,6%) and ethyl p-tolyl sulphide (1%).

(v) FVP of p-bromobenzenesulphinyl methoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 2.4×10^{-2} mmHg, Inlet 200-240°C) gave two fractions. The dark oil at the furnace exit was shown to be $Ph_3P=0$ and unreacted starting material (25%). Calibration of the N.M.R. of the colourless liquid in the cold trap with dichloroethane indicated only p-bromothioanisole (11%), confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}).

(vi) FVP of p-bromobenzenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 3.2×10^{-2} mmHg, Inlet 200-240°C) gave only unreacted starting material.

FVP of the title compound (0.2g, 600°C, 3.1×10^{-2} mmHg, Inlet 200-240°C) gave two fractions. The dark oil at the furnace exit was seen to be $Ph_3P=0$ from ^{31}P and ^{1}H N.M.R. Calibration with dichloroethane of the ^{1}H N.M.R. of the colourless liquid in the cold trap indicated only p-bromophenyl propenyl sulphide (53%).

The GCMS (S.E. 54, 50-200°C, 10°C min^{-1}) confirmed this as well as indicating the presence of p-bromophenyl ethyl sulphide (11%) and an unknown compound, M^+=m/z 244 and 246 (9%).

(vii) FVP of ethanesulphinyl methoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 1.4×10^{-2} mmHg, Inlet 180-200°C) gave two fractions. The dark oil at the furnace exit was seen to contain $Ph_3P=S$, $Ph_3P=0$ and Ph_3P by ^{31}P and ^{1}H N.M.R. A further peak at δ_P+17.52 corresponding to a peak at δ_H 3.57 (s; CO_2Me type) was not identified. In the cold trap, a colourless, evil smelling, liquid was collected. Calibration of its ^{1}H N.M.R. with dichloroethane indicated ethyl vinyl sulphide (10%) and an unknown compound, m/z 104 (M^+,< 1%) as the only products, both confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}).

(viii) FVP of ethanesulphinyl ethoxycarbonylmethylene triphenyl phosphorane

FVP of the title compound (0.2g, 500°C, 1.6×10^{-2} mmHg, Inlet

160-200°C) gave two fractions. The dark oil at the furnace exit contained $Ph_3P=0$, $Ph_3P=S$ and Ph_3P by ^{31}P and ^1H N.M.R. A further component with peaks at δ_P+17.75 and δ_H 4.1 (q) and 1.05 (t) was not identified. The cold trap contained a colourless, foul smelling, liquid. Calibration of its ^1H N.M.R. with dichloroethane indicated the presence of ethyl propenyl sulphide (34%) and an unknown compound, m/z 118 (M^+,< 1%), both confirmed by GCMS (50-200°C, 10°C min^{-1}).

FVP of the title compound (0.2g, 600°C, 5.2×10^{-2} mmHg, Inlet 170-200°C) gave $Ph_3P=S$, $Ph_3P=0$ and Ph_3P at the furnace exit, by ^{31}P and ^1H N.M.R. Calibration of the ^1H N.M.R. of the cold trap colourless liquid indicated only ethyl propenyl sulphide (20%). This was confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}) which also indicated the presence of a small amount of diethyl sulphide (< 1%).

(ix) <u>FVP of p-chlorobenzenesulphinyl ethoxycarbonylmethylene triphenyl phosphorane</u>

FVP of the title compound (0.2g, 500°C, 2.1×10^{-2} mmHg, Inlet 200-240°C) gave $Ph_3P=0$, Ph_3P and unreacted starting material (60%) at the furnace exit as seen by ^{31}P and ^1H N.M.R. The cold trap contained a colourless liquid. Calibration of its ^1H N.M.R. with dichloroethane showed only p-chlorophenyl propenyl sulphide (9%), confirmed by GCMS (S.E. 54, 50-200°C, 10°C min^{-1}).

FVP of the title compound (0.2g, 600°C, 2.2×10^{-2} mmHg, Inlet 200°C) gave $Ph_3P=0$ and Ph_3P at the furnace exit as seen by ^{31}P and ^{1}H N.M.R. Calibration of the ^{1}H N.M.R. of the colourless liquid in the cold trap indicated p-chlorophenyl propenyl sulphide (17%).

The GCMS (S.E> 54, 50-200°C, 10°C min^{-1}) confirmed this and also indicated the presence of p-chlorophenyl ethyl sulphide (1%) and an unknown compound, m/z 200 and 202 (M^+,2%).

The ^{13}C N.M.R. of the cold trap products was taken as part of some mechanistic investigations(see section **F.** 2. below). This contained the correct peaks for both p-chlorophenyl propenyl sulphide and p-chlorophenyl ethyl sulphide by comparison with authentic samples, but also contained sufficient other peaks to indicate the presence of two other products, one of which was not seen in the GCMS.

(x) <u>FVP of p-toluenesulphinyl propoxycarbonylmethylene triphenyl phosphorane</u>

FVP of the title compound (0.18g, 600°C, 2.9×10^{-2} mmHg, Inlet 200-240°C) gave a dark oil at the furnace exit. ^{31}P and ^{1}H N.M.R. showed this to contain $Ph_3P=0$ and Ph_3P. The cold trap contained a colourless liquid. Calibration of its ^{1}H N.M.R. with CH_2Cl_2 indicated 1-butenyl p-tolyl sulphide (34%).

This was confirmed by GCMS (S.E> 54, 50-200°C, 10°C min^{-1}) as well as showing the presence of an unknown compound, m/z 194 (M^+,2.5%)

and di-p-tolyldisulphide (2%).

2. Mechanistic Studies

(a) Preparation of allyl p-chlorophenyl sulphide

This was prepared by the method of Hurd and Greengard[89] in 81% yield from allyl bromide and p-chlorobenzenethiol, b.p. 145-155°C (Kugelrohr oven) at 16 mmHg. (Found: m/z 184.012457 and 186.008928. C_9H_9ClS requires 184.011347 and 186.008397); δ_H 7.38 (s, 4H), 5.7-6.25 (m, 1H), 5.0-5.35 (m, 2H) and 3.56 (split d, 2H, major J = 6.5 Hz); δ_C 135.02, 133.88, 132.90, 131.93, 129.52, 118.54 and 38.04.

(b) Preparation of p-chlorophenyl propenyl sulphide

This was prepared by the method of Tarbell and McCall[90] in 85% yield by refluxing allyl p-chloropropenyl sulphide in ethanolic sodium ethoxide for 16h, b.p. 110-120°C (Kugelrohr oven) at 3 mmHg. (Found: m/z 184.010697 and 186.008048. C_9H_9ClS requires 184.011347 and 186.008397); δ_H 7.2-7.5 (m, 4H), 5.75-6.4 (m, 2H) and 1.83 (split d, 3H, J = 5 Hz); δ_C 135.22, 134.92, 133.39, 131.95, 131.62, 129.78, 129.42, 128.95, 128.92, 128.86, 122.87, 121.06, 18.46 and 14.63 (cis and trans isomeric mixture).

(c) Preparation of p-chlorophenyl ethyl sulphide

This was prepared by the method of Tuleen and Marcum[73] in 70% yield, b.p. 75-85°C (Kugelrohr oven) at 25 mmHg (lit[91] 123°C at 18mmHg). δ_H 7.24 (s, 4H), 2.9 (q, 2H, J = 7 Hz) and 1.3 (t, 3H, J = 7 Hz); δ_C 135.20, 131.70, 130.34, 128.93, 27.90 and 14.27.

(d) Preparation of S-p-chlorophenyl thiopropionate

This was prepared by a method similar to that described by Meyers and Walkup[92] from p-chlorobenzenethiol and propion yl chloride in 81% yield, b.p. 80-90°C (Kugelrohr oven) at 25 mmHg. (Found: m/z 200.005496 and 202.003432. C_9H_9ClOS requires 200.006261 and 202.003311); δ_H 7.3-7.45 (m, 4H), 2.69 (q, 2H, J = 7.5 Hz) and 1.24 (t, 3H, J = 7.5 Hz); δ_C 197.53 (C=0), 135.71, 130.72, 129.36, 126.31, 37.15 and 9.56.

(e) Preparation of S-ethyl p-chlorothiobenzoate

This was prepared similarly to a method described by Meyers and Walkup[92] from p-chlorobenzoyl chloride and ethanethiol in 82% yield, b.p. 120-130°C (Kugelrohr oven) at 3 mmHg. (Found: m/z 200.007802 and 202.002688. C_9H_9ClOS requires 200.006261 and 202.003311); δ_H 7.64 (AB pattern, 4H, J = 6.5 Hz), 3.06 (q, 2H, J = 7.5 Hz) and 1.34 (t, 3H, J = 7.5 Hz); δ_C 190.78 (C=0), 139.56, 135.51, 128.83, 128.49, 23.60 and

14.70.

(f) Preparation of p-chlorobenzenesulphinyl ethoxycarbonyl-^{13}C-methylene triphenyl phosphorane

This was prepared starting from 5% ^{13}C-enriched ethyl bromo-acetate-1-^{13}C, via the phosphonium salt and ethoxycarbonyl-^{13}C-methylene triphenyl phosphorane in a similar manner to the unlabelled compound (section E3c(ix). The title compound was obtained in 21% overall yield based on starting ethyl bromoacetate. ^{13}C Data were identical to the unlabelled compound, with enhanced carbonyl carbon.

(g) Preparation of p-chlorobenzenesulphinyl ethoxycarbonylmethylene-^{13}C -triphenyl phosphorane

This was prepared in 3 steps in 22% overall yield starting from 5% ^{13}C enriched ethyl bromoacetate-2-^{13}C. The ^{13}C N.M.R. data were consistent with the unlabelled compound(E.3.c(ix)), with enhanced ylidic carbon.

(h) FVP of p-chlorobenzenesulphinyl ethoxycarbonyl-^{13}C-methylene triphenyl phosphorane

FVP of the title compound (0.2g, 600°C, 1.0×10^{-2} mmHg, 200°C) gave two fractions. The yellow solid at the furnace exit contained triphenyl phosphine and triphenyl phosphine oxide. The colourless liquid in the cold

trap by ^{13}C N.M.R. was found to contain p-chlorophenyl propenyl sulphide and p-chlorophenyl ethyl sulphide identified by comparison with authentic samples. As with the unlabelled sample, a third, carbonyl containing product was seen by ^{13}C, I.R. spectroscopy and GCMS. The ^{13}C N.M.R. contained extra peaks in the region δ_C 10-45ppm indicating the possible presence of a 4th product not seen in the GCMS.

(i) FVP of p-chlorobenzenesulphinyl ethoxycarbonylmethylene-^{13}C -triphenylphosphorane

FVP of the title compound (0.2g, 600°C, 1.1×10^{-2} mmHg, 200°C) gave a product distribution identical to the previous compound.

3. FVP of isopropylsulphinyl benzylidene triphenylphosphorane

FVP of the title compound (0.2g, 600°C, 2.4×10^{-2} mmHg, 160°C) gave two fractions. The yellow solid at the furnace exit was seen to contain almost exclusively triphenyl phosphine from the ^{31}P N.M.R., δ_P –5.46. Very small traces of triphenyl phosphine oxide and sulphide were also observed by ^{31}P N.M.R. The ^{1}H N.M.R. showed only aromatic proton signals. In the cold trap, the colourless liquid on GCMS (S.E. 54, 50-200°C, 10°C min^{-1}) analysis showed only one peak, $M^+ = 180$; δ_H 7.3-8.25 (m, aromatic protons), 3.93 (septet, J = 7 Hz), 2.67 (broad s) and 1.44 (d, J = 7 Hz); δ_C 192.08 (C=0), 137.39, 133.16, 128.51, 127.11, 34.90

and 23.13, plus small aromatic carbon signals below printing threshold of the spectrometer. From this evidence the product seen on GCMS analysis is assigned as S-isopropyl thiobenzoate. TLC (silica, ether/light petroleum, 1:1) showed three components. Two of these were assigned to thiobenzoic acid after comparative TLC (silica, ether/light petroleum, 1:1) with an authentic sample. This is in agreement with the presence of the broad singlet at δ_H=2.67 for the S–H proton and the extra, small peaks in the aromatic region of the ^{13}C N.M.R.

G Ylides Containing Bu^n_3P instead of Ph_3P

1. Preparation of α-benzoyl butylidene tri-n-butylphosphorane

(i) Tetra-n-butyl phosphonium bromide

Tri-n-butylphosphine (17.8g, 88 mmol), butyl bromide (12.06g, 88 mmol) and toluene (250 ml) were heated under reflux for 16h. Filtration and washing with ether gave tetra-n-butyl phosphonium bromide (23.86g, 80%), m.p. 100-103°C (lit[93] 102-104°C).

(ii) α-Benzoyl butylidene tri-n-butyl phosphorane

An analogous procedure to that of Bestmann and Arnason[94] was used. Tetra-n-butyl phosphonium bromide (10g, 32.4 mmol) was stirred in extra dry THF (100 ml) at R.T. under N_2, while Bu^nLi (32.4 mmol, 2.5 M in hexane) was added. After stirring for 30min, benzoyl chloride (2.28g, 16.2 mmol) in extra dry THF (10 ml) was added. The mixture was stirred for 21h at R.T. then water and ether (75 ml of each) added. Further extractions with ether (2 × 75 ml) followed by drying ($MgSO_4$), and evaporation of the combined ether extracts gave an orange oil. This solidified when triturated with a little ethyl acetate and ether and then stored at -20°C for 4 weeks. δ_H 7.15-7.6 (m, 5H), 3.95-4.5 (sextet, 2H), 3.5-3.8 (m, impurity), 0.5-2.5 (complex multiplet); δ_P+48.39 (Bu^n_3P=0), +32.60 (starting salt), +20.41 (product). Due to the low temperature required to induce crystallisation and the nature of the next experiment, no

further purification was undertaken.

2. FVP of α-Benzoyl butylidene tri-n-butyl phosphorane

The starting material contained a small amount of $Bu^n_3P=0$, δ_P+48.39 and starting material δ_P+32.60. The FVP was examined at various temperatures with ^{31}P N.M.R. being used to determine the extent of reaction.

FVP of the title compound (0.22g, 500°C, 4×10^{-2} mmHg, Inlet 120-160°C) showed complete reaction, δ_P+48.56($Bu^n_3P=0$) as the only peak.

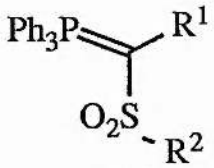
FVP of the title compound (0.22g, 300°C, 3.8×10^{-2} mmHg, Inlet 120-160°C) showed almost complete reaction, δ_P+48.56($Bu^n_3P=0$) (60%), increased in proportion cf. δ_P+20.41 (4%), starting material.

FVP of the title compound (0.22g, R.T., 3.9×10^{-2} mmHg, Inlet 120-160°C) showed the starting material subliming unchanged.

DISCUSSION

A Preparation of Sulphonyl Stabilised Phosphorus Ylides

The preparation of the sulphonyl stabilised phosphorus ylides (61) was achieved by the method of Van Leusen *et al*[33,38].

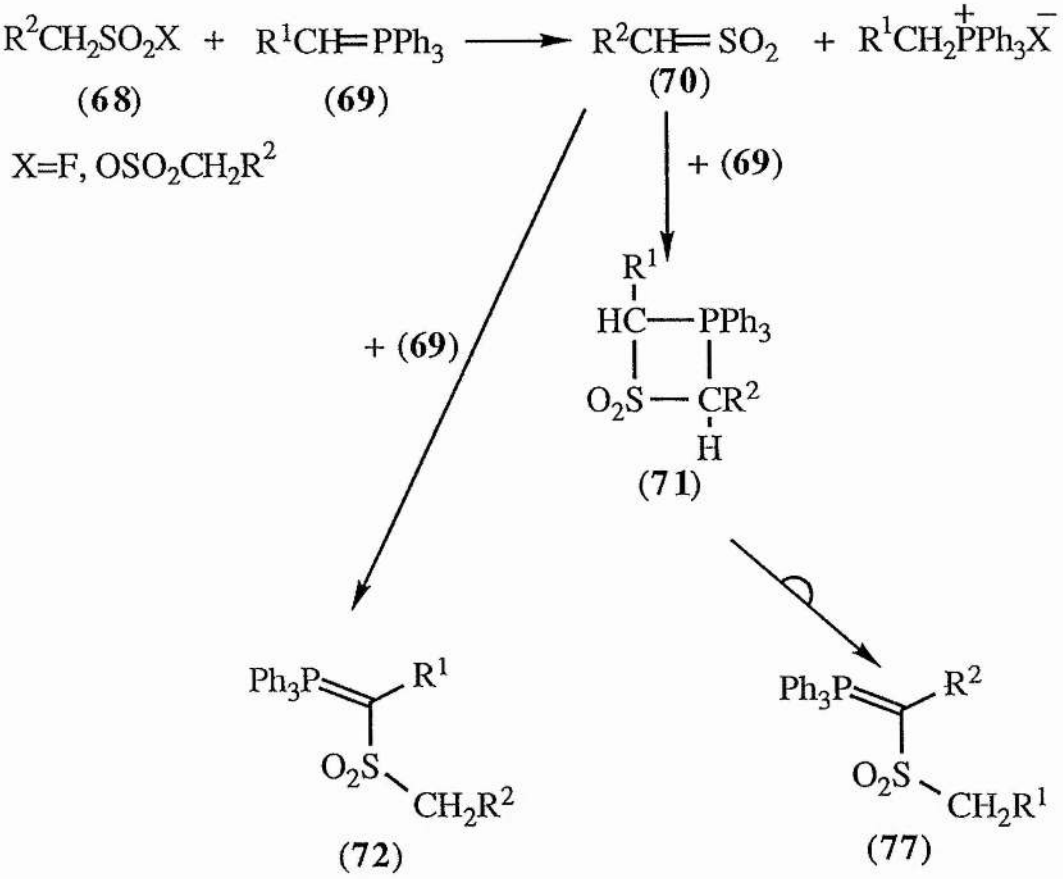


(61)

R^1=alkyl, R^2=Ar
R^1=Ar, R^2=CH_2Ar
R^1=alkyl, R^2=CH_2Ar

The reaction was accomplished using two equivalents of a precursor ylide (69), generated from the action of n-butyl lithium on a phosphonium salt, with one equivalent of sulphonyl fluoride or sulphonic anhydride (68). When the sulphonyl moiety (68) has a H α-to the sulphonyl group, the first mole of ylide (69) generates an in-situ sulphene (70). The sulphene then reacts with a second mole of ylide (69) to give the four membered ring intermediate (71). This can then ring open in two directions, and following 1,3-H migration, give the product (72), as seen by compounds (73)-(76), or the rearranged product (77), indicated by (78)-(82). The direction of ring opening is controlled by steric and electronic factors[38] relating to the groups R^1 and R^2.

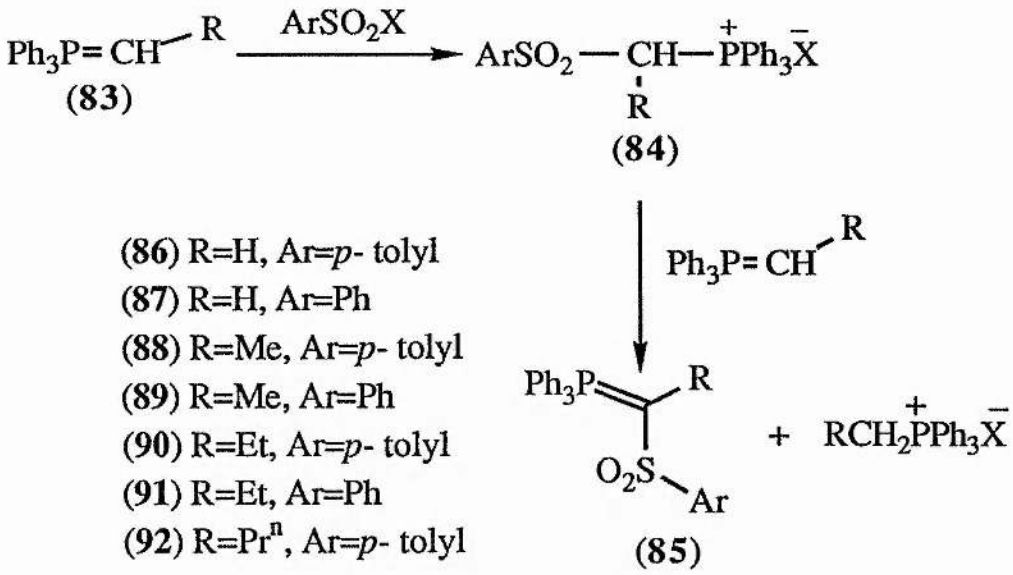
The generation of the in-situ sulphene by abtraction of HX from a sulphonic acid derivative with base, is a well documented reaction[95].



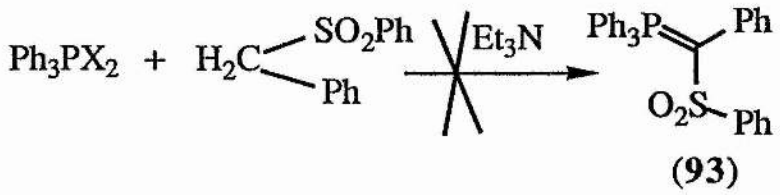
(73) R^1=R^2=Ph
(74) R^1=*p*- tolyl, R^2=Ph
(75) R^1=*o*- $MeOC_6H_4$, R^2=Ph
(76) R^1=*o*- $MeSC_6H_4$, R^2=Ph

(78) R^1=H, R^2=Me
(79) R^1=*p*- $MeOC_6H_4$, R^2=H
(80) R^1=Ph, R^2=Me
(81) R^1=*o*- MeC_6H_4, R^2=Me
(82) R^1=*o*- $MeOC_6H_4$, R^2=Me

In the case of aromatic sulphonyl fluorides and sulphonic anhydrides, sulphonylation occurs analogously to the well documented acylation[96] of phosphorus ylides. Sulphonylation of the phosphorane (83) affords the intermediate phosphonium salt (84), which, via transylidation, reacts with another molecule of phosphorane (83) to give the desired ylide (85) , illustrated by compounds (86)-(92), and a phosphonium salt.



The attempts to produce arylsulphonyl benzylidene phosphoranes were somewhat less successful. Using the method of Horner and Oediger[23], the reaction of triphenyl phosphine dihalide with benzyl phenyl sulphone in the



presence of base did not give the desired ylide (93). Only triphenyl phosphine oxide, starting sulphone and two unidentified phosphorus containing products were obtained. It would appear that the combination of a phenyl sulphonyl group and a phenyl group is not sufficiently electron withdrawing to make the methylene protons acidic enough to allow the above reaction. Indeed Horner and Oediger[23] only made ylides of the type (94) where X and Y were both highly electron withdrawing.

$Ph_3P{=}C(X)(Y)$ (94)

X=Y=CO_2Et
X=Y=CN
X=Y=SO_2Ph

The strategy to prepare ylide (93) from the phosphonium salt of α-bromobenzyl phenyl sulphone originally seemed a promising one. The synthesis of sulphonyl methylene phosphoranes from such salts had been described[32,33], and though the attempts by Hoffmann and Förster[25] to obtain the phosphonium salt of α-bromobenzyl-p-tolyl sulphone were unsuccessful, their paper contained little experimental detail, so some further attempt was warranted.

It was found that α-chlorobenzyl phenyl sulphone and triphenyl phosphine in refluxing toluene gave triphenyl phosphine oxide and benzyl phenyl sulphone. Under these reaction conditions, without the exclusion of air, this is not surprising in view of the report by Jarvis and Saukaitis[74]. They reported that triphenyl phosphine reacted with a variety of α-halobenzyl phenyl sulphones (95) in 90% aqueous DMF (v/v) to give the parent sulphone (96) and triphenyl phosphine oxide, via nucleophilic

$$Ph_3P + ArCHSO_2Ph \longrightarrow ArCH_2SO_2Ph + Ph_3PO + HX$$

(95) (96)

displacement on the halogen atom.

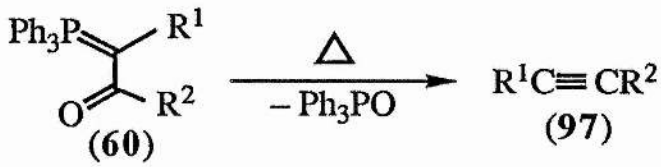
Discouragingly for us, α-bromobenzyl phenyl sulphone with triphenyl phosphine gave none of the desired phosphonium salt when heated under reflux in dry toluene or heated at 140°C in sulpholane with the exclusion of air.

B Flash Vacuum Pyrolysis of Sulphonyl Stabilised Phosphorus Ylides

1. General Background

In contrast to β-ketophosphoranes, the pyrolysis of sulphonyl ylides is effectively unknown. Only one report by Ito, Okano and Oda[34] refers to the effects of heating sulphonyl stabilised phosphorus ylides (this will be dealt with later).

As mentioned earlier the pyrolysis of β-ketoalkylidene triphenyl phosphoranes (60) has been known for 30 years[48]. The alkyne (97) is produced by the thermal elimination of triphenyl phosphine oxide from the ylide (60).

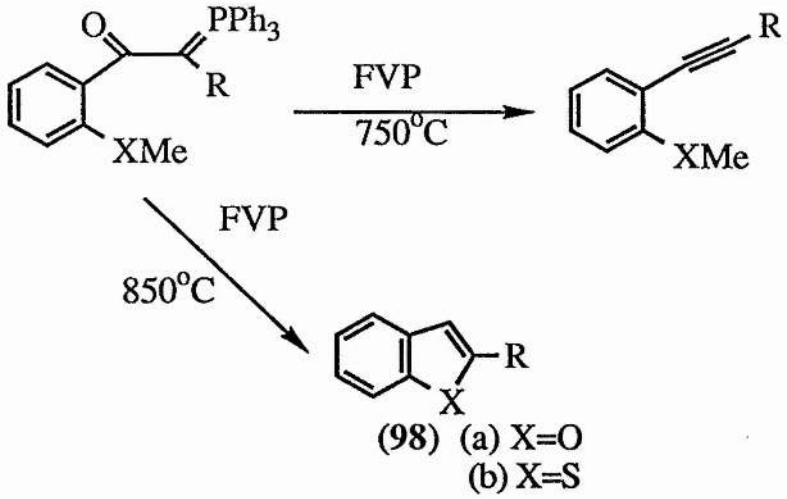


Using conventional pyrolysis techniques this process has been successful for cases in which R^1 is an electron withdrawing group. Thus ylides (60) in which R^1 = Ar[48-51,97,98], COR[52a,99], CO_2R[49,50,53], CN[49,50,54], SR[46], SeAr[46], OAr[100], CHO[52b] and $PO(OPh)_2$[101] have all been converted into (97).

Work in this laboratory on the flash vacuum pyrolysis of ylides (60)[56] extended the scope of the reaction to cases where R^1 = alkyl or H, which

failed on conventional pyrolysis[49,50,102]. The nature of the FVP apparatus gave the acetylenes (97) in the cold trap in pure form, high yields and free from solvents, reagents or by-products.

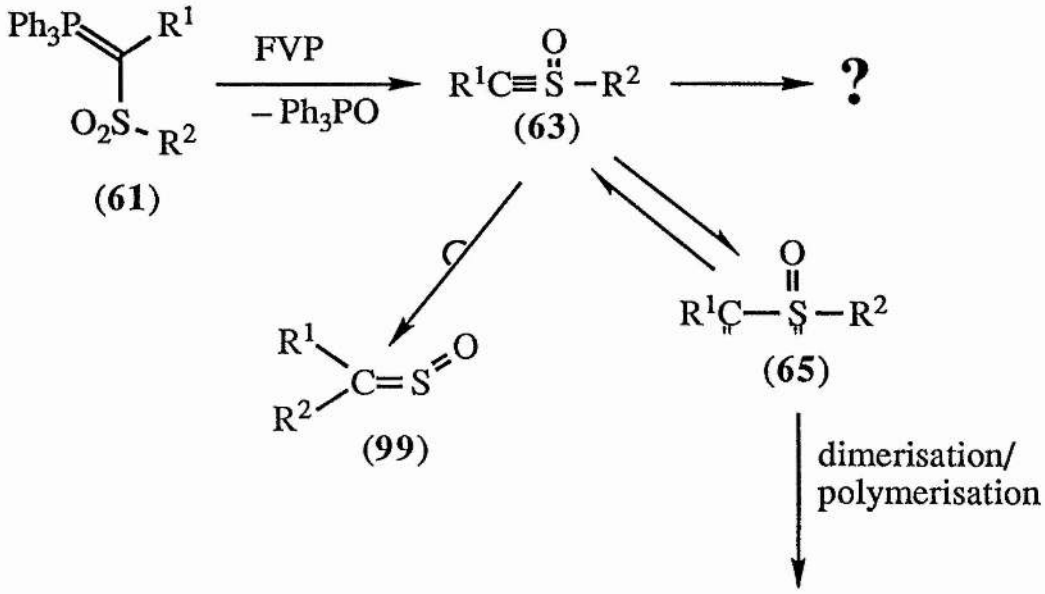
The FVP work was extended by Aitken and Burns[103], who described a new synthesis of 2-substituted benzofurans (98a) and benzothiophenes (98b).



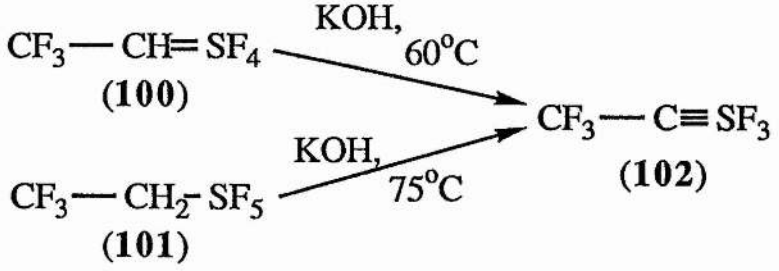
(98) (a) X=O
(b) X=S

We were interested to see how the analogous sulphonyl and sulphinyl (see later) stabilised phosphorus ylides would behave under flash vacuum pyrolysis conditions. Our hope was that extrusion of triphenyl phosphine oxide from the ylide (61) would give the λ^6-oxythiacetylene (63). This would then have the possibility to react as the carbon-sulphur triple bond species directly or to rearrange in some way, possibly direct to the sulphine (99) via a Wölff-type rearrangement, or via the carbene form (65), leading

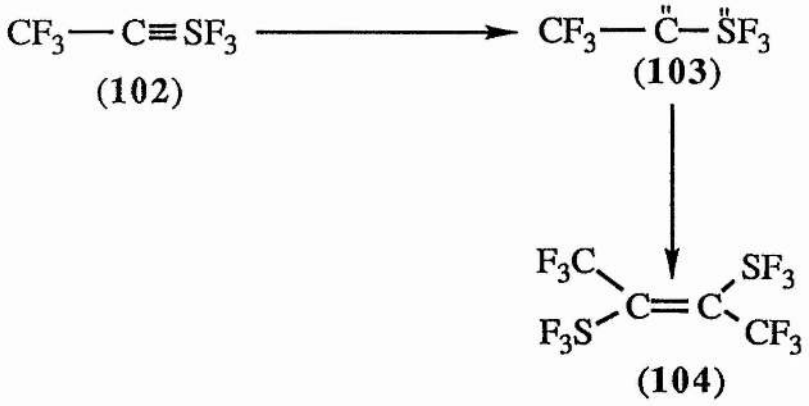
to dimerisation/polymerisation.



Recently Seppelt and Potter[57a] and Seppelt *et al*[57b] have reported the preparation and low temperature X-ray structure of the first carbon-sulphur triple bond species (102). They made trifluoroethylidyne sulphur trifluoride (102) by pumping either (2,2,2-trifluoroethylidene)sulphur tetrafluoride (100), or 2,2,2-trifluoroethyl sulphur pentafluoride (101) through a 60cm pyrex or quartz tube, packed with powdered potassium



hydroxide, at 60°C or 75°C respectively. The product (102) was trapped at -196°C and characterised by low temperature I.R. gas spectra, ^{19}F N.M.R., high resolution mass spectroscopy and low temperature X-ray crystallography. On warming to -30°C, the dimer (104), was seen to form.

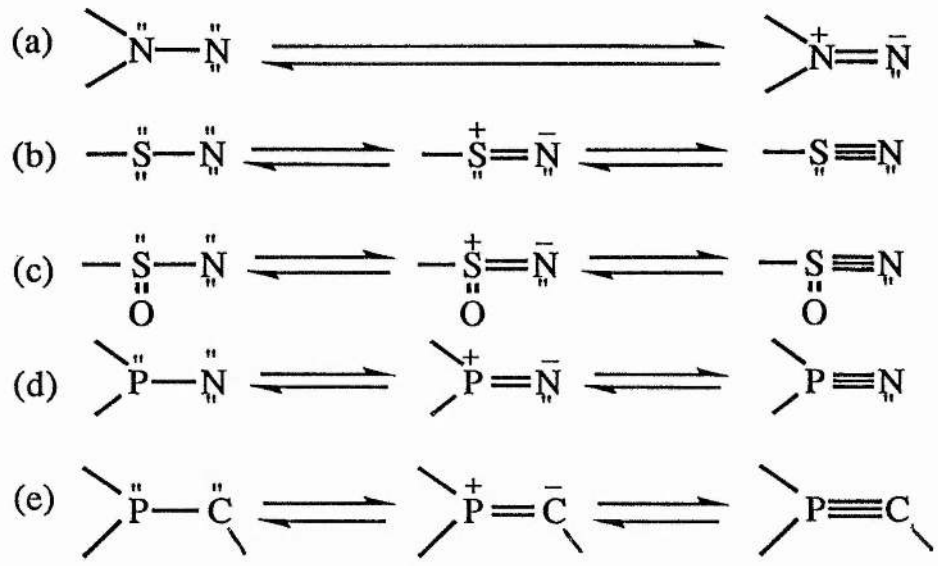


This is proposed to go through the carbene type intermediate (103).

Extensive theoretical studies on the carbon-sulphur triple bond moiety have recently been carried out[104] and interest in this species is considerable.

In nitrene chemistry it is well established that aminonitrene[105], sulphenylnitrene[58], sulphinylnitrene[59] and phosphinonitrene[60] can behave as diazene, thiazene, oxathiazene and phosphanitrile (Scheme 4, (a)-(d)).

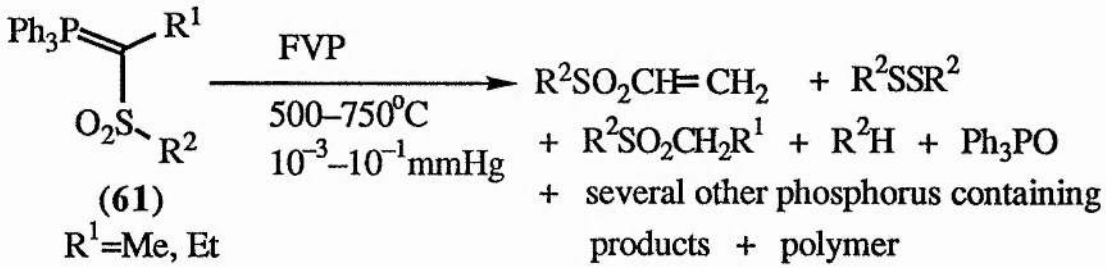
More recently it was reported that λ^3-phosphinocarbenes (Scheme 4(e)) can behave either as "normal" carbenes or the λ^5-phospha- acetylenes[106].



SCHEME 4

2. FVP of alkyl- and arylsulphonyl alkylidene triphenyl phosphoranes

The original FVP of the ylides of type (61) was carried out in the



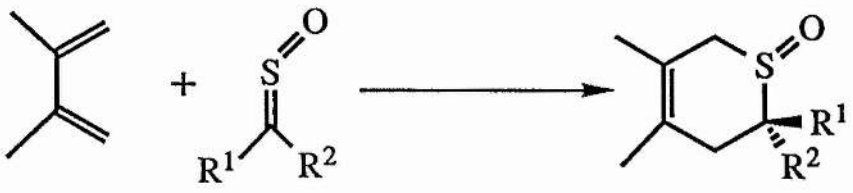
temperature range 500-750°C at 10^{-3}-10^{-1} mmHg. This gave a product distribution consisting of some or all of vinyl sulphones, disulphides, sulphones and hydrocarbons, as well as triphenyl phosphine oxide and as many as fifteen other phosphorus containing products. Triphenyl phosphine oxide was by far the largest constituent of the phosphorus containing components collected at the furnace exit. While the yields of the phosphorus containing components were practically quantitative, the

amounts of soluble cold trap products collected were comparatively insignificant. In all these cases however, the cold trap contained considerable quantities of a white, insoluble polymeric material which coated the inside of the trap.

In an effort to identify the composition of this polymeric material, a series of trapping experiments were carried out to attempt to trap the monomer via a chemical reaction.

As stated previously it was thought that the loss of triphenyl phosphine oxide from an ylide of type (61), might result in the formation of the oxythiacetylene (63) or sulphine (99). The use of 1,3-dienes to try to trap these species via a Diels-Alder type 4+2-cycloaddition on the multiply bonded species was attempted.

In the case of sulphines, a rich variety of cycloaddition reactions exist[41]. The Diels-Alder type 1,4-cycloadditions are particularly good examples of this. For example a variety of sulphines are known to react readily



(105)

R^1=*p*- tolyl, R^2=SMe, SO_2Ph
R^1=SPh, R^2=*p*- tolyl, Cl
R^1=R^2=SPh, Cl

with 2,3-dimethyl-1,3-butadiene to give the adducts (105) in good yield. The dienophilicity of sulphines in the above reaction, is dependent on their substituents. As expected, electron withdrawing substituents, e.g. Cl, enhance reactivity, while sterically demanding groups have a strong retarding effect.

We thus set up our FVP apparatus, with a diene component added to the cold trap, cooled to -196°C, before the sample was pyrolysed. This meant that the reactive component would mix with the diene on the walls of the cold trap and these would hopefully react together as the temperature was raised upon completion of the FVP.

In the case of the ylides (61) with R^1 = Me, R^2 = p-tolyl and R^1 = Et, R^2 = Ph, the pyrolysis products with 2,3-dimethyl-1,3-butadiene or cyclopentadiene as the diene in the cold trap, were green oils. These were treated by either chromatography on silica (ether) or by preparative TLC on silica (ether/40/60 petroleum ether). The fractions obtained had complex ^{1}H N.M.R. spectra, with many peaks in the region δ_H 0.5-3.5, suggesting mixtures of products which were not identified. In these experiments most of the cold trap product remained behind as a white, insoluble polymeric material.

With the ylide (61), R^1 = Me, R^2 = p-tolyl and anthracene as the diene, a light brown oily solid was obtained from the chromatography of the reaction product on silica (benzene/ether, 1:1). This had approximately the correct ^{1}H N.M.R. for a 1:1 adduct of anthracene with either the sulphine

or oxythiacetylene derived from ylide (61). The compound had the correct mass spectrum, with an M^+ peak at m/z = 344, but attempts to purify the sample by recrystallisation failed.

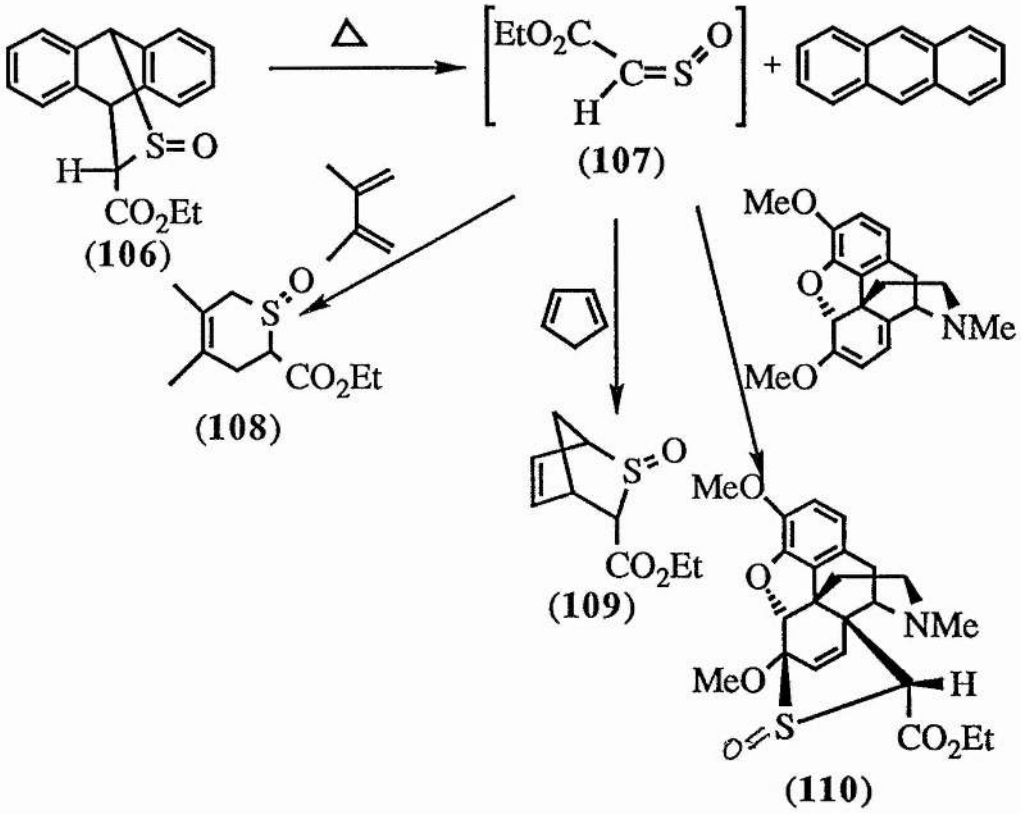
Thus, in terms of the unknown component of the cold trap being sulphine derived, these trapping experiments were very disheartening.

Sauer in his review of the reaction mechanism of the Diels-Alder reaction[107] gives kinetic data which shows that cyclopentadiene is a more reactive diene than 2,3-dimethyl-1,3-butadiene, with anthracene being much less reactive.

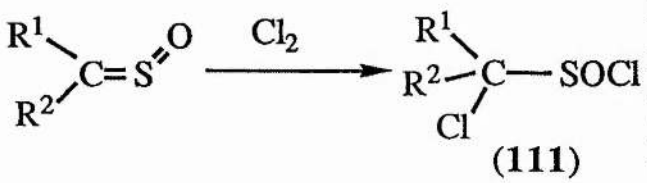
Zwanenburg *et al*[108] found that sulphines reacted readily with cyclopentadiene and 2,3-dimethyl-1,3-butadiene and only sulphines with electron withdrawing groups, such as dichlorosulphine, reacted with anthracene.

Similarly, Kirby *et al*[109] used the adduct (106), obtained from the m-chloroperbenzoic acid oxidation of the ethylthioxoacetate adduct of anthracene, to generate the sulphine (107) in a retro Diels-Alder reaction. This then reacts in the presence of 2,3-dimethyl-1,3-butadiene, cyclopentadiene and thebaine to give the adducts (108), (109) and (110) respectively.

Therefore, if the brown oily solid obtained from the reaction of anthracene with the cold trap products of the FVP of ylide (61), R^1 = Me, R^2 = p-tolyl, was a sulphine-anthracene adduct, we would have expected to have obtained some signs of the corresponding sulphine adduct with 2,3-dimethyl-1,3-butadiene and cyclopentadiene.



It is known that some unstable sulphines do not undergo cycloaddition reactions. Sheppard and Diekmann[110] found that dimethyl sulphine could not be trapped with reactive alkenes or dienes. In this case however, as in others[111,112], the sulphines were trapped with chlorine to give the chlorosulphinylchlorides (111). These are relatively stable compounds which can be distilled if low pressures are used.

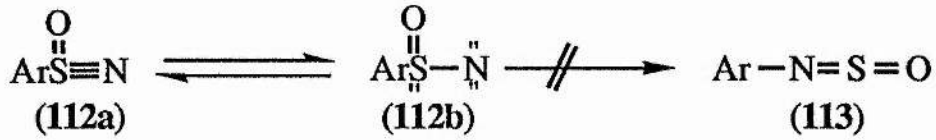


R^1=R^2=Me[110]
R^1=H, R^2=Ph,
2–methoxy–1–naphthyl[111]
R^1=Me, R^2=Cl

An attempt was made to trap the FVP product of ylide (61), R^1 = Et, R^2 = Ph, with chlorine which gave a yellow oil after the reaction. This oil however decomposed on Kugelröhr distillation at only 65°C (oven temperature) and 0.5 mmHg. Again in this case some of the pyrolysis product remained as an insoluble white solid in the cold trap.

On the basis of all the above evidence, the probability of the unknown component being a sulphine is low.

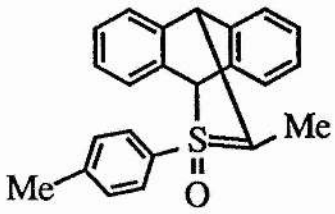
One further piece of evidence against the presence of a sulphine, is that in the case of the nitrene analogue, the oxythiazyne/sulphinylnitrene compound (112) does not undergo a Curtius-type rearrangement to the N-sulphinyl aniline derivatives (113)[59,113]. Therefore it is possible that the



oxythiacetylene/sulphinyl carbene would not undergo the corresponding Wolff-type rearrangement required to form the sulphine.

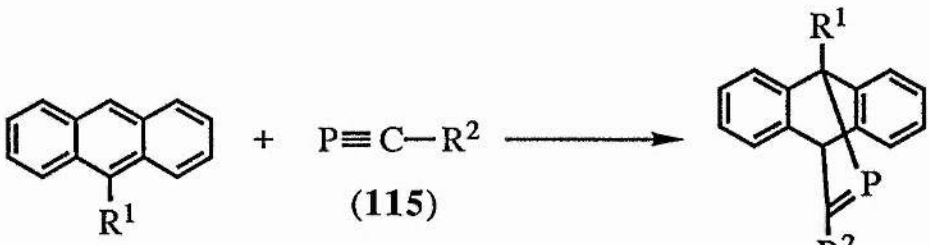
An explanation for the compound formed from the reaction with anthracene could be that it is in fact the adduct between the oxythiacetylene itself and anthracene to give the compound (114).

It has been observed that carbon-heteroatom triple bond species can undergo Diels-Alder cycloadditions. In the case of the phosphaalkynes



(114)

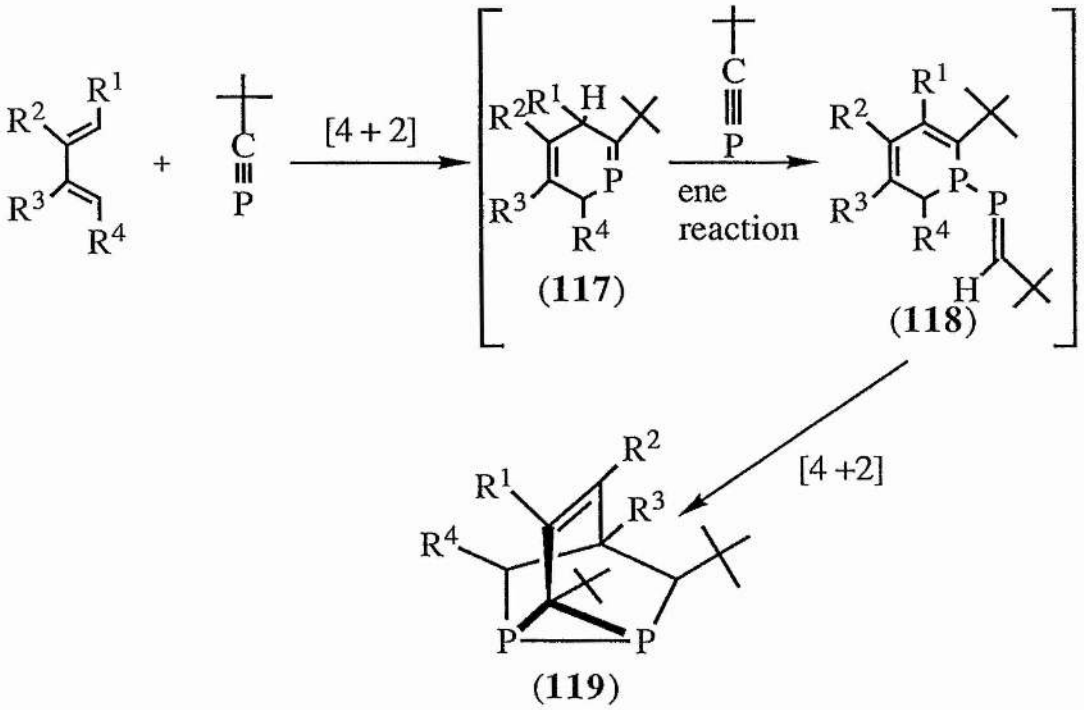
(115), these have been reacted with anthracene and substituted anthracenes, to give the stable 2-phosphabarrelenes (116)[114].



(116)

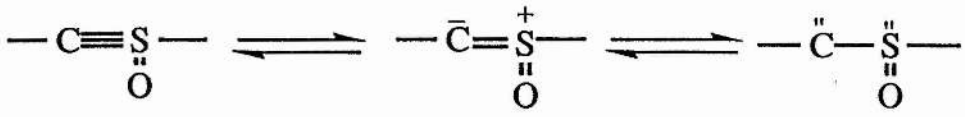
Similar phosphaalkynes have been reacted with substituted butadienes[115]. In these cases the products obtained are much more complex than expected. This is due to the initially formed Diels-Alder adduct (117) undergoing an ene reaction with a second equivalent of phosphaalkyne to give (118), which in turn undergoes an intramolecular [4+2] cycloaddition to give the final product (119).

The possibility of the carbon-sulphur triply bonded species giving a more "normal" Diels-Alder cycloaddition with anthracene rather than with



2,3-dimethyl-1,3-butadiene or cyclopentadiene could be explained by invoking the idea of the Diels-Alder reaction with inverse electron demand. The "normal" Diels-Alder reaction involves an electron rich diene, like cyclopentadiene, reacting with an electron poor dienophile such as tetracyanoethylene. In the case of inverse electron demand there is an eloquent description by Sauer[107] for systems whereby an electron rich dienophile reacts preferentially with an electron poor diene. This may well be the case for a carbon-sulphur triple bond species.

There does therefore exist the possibility that the species of interest, i.e. the oxythiacetylene may well be formed in the FVP experiments. This species could well exist somewhere between a true carbon-sulphur triple bond and a carbene form (Scheme 5). The polymer seen to be

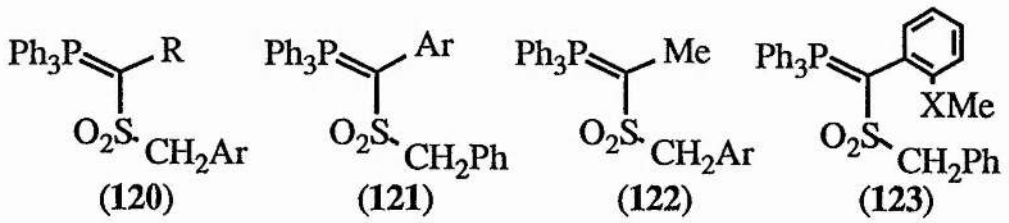


SCHEME 5

formed in most of the reactions attempted is not surprising in the absence of suitable trapping agents. In all cases, further experimentation, with the aid of a recently installed GCMS instrument, would be desirable.

3. FVP of benzyl- and substituted-benzyl sulphonyl alkylidene- and benzylidene phosphoranes

The pyrolysis behaviour of this particular class of α-sulphonyl ylides is completely different to that of the previously described alkyl- and arylsulphonyl alkylidene phosphoranes (61). The compounds studied are all of type (120), but it turns out that the sub-classes (121-123) each behave differently on pyrolysis.

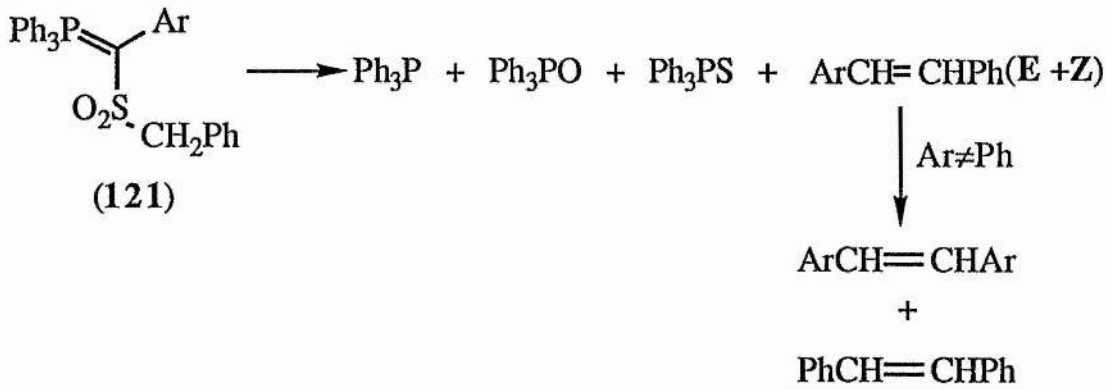


(120) **(121)** **(122)** **(123)**

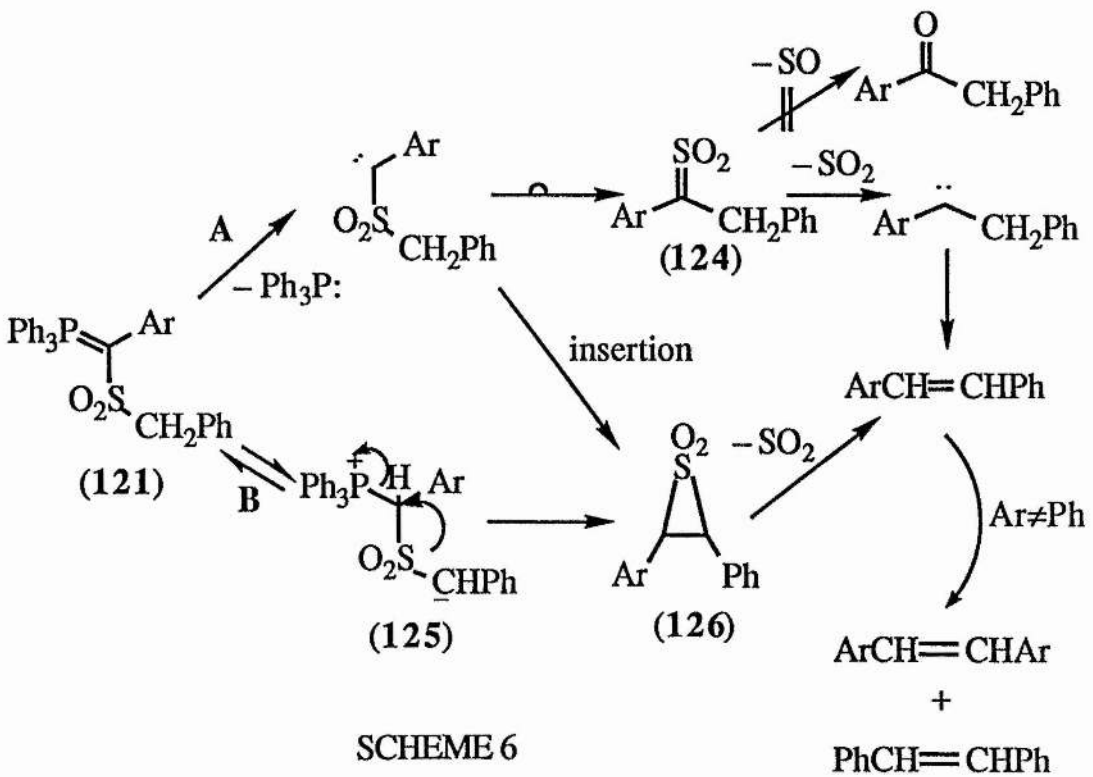
All the pyrolyses were carried out at 600°C and the product distributions are shown in Table 1.

(a) Compounds of type (121)

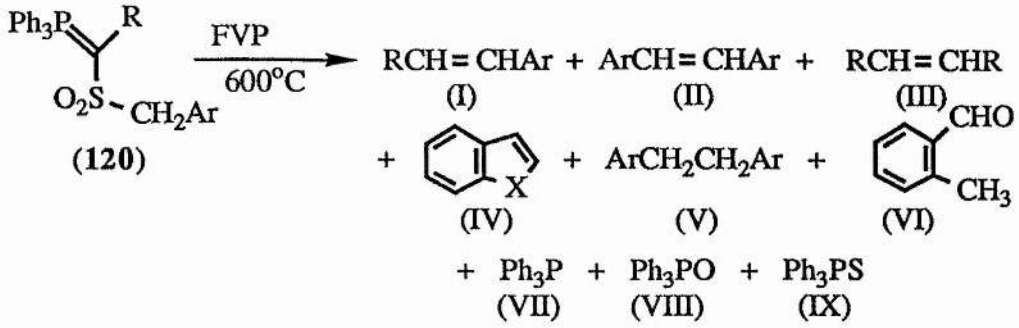
The pyrolyses of these compounds give good yields of stilbenes together with triphenylphosphine, triphenyl phosphine oxide and triphenyl phosphine sulphide. For Ar ≠ Ph there is in addition some cross-over in the stilbenes.



The possible mechanisms which could explain these results are shown in Scheme 6.



SCHEME 6

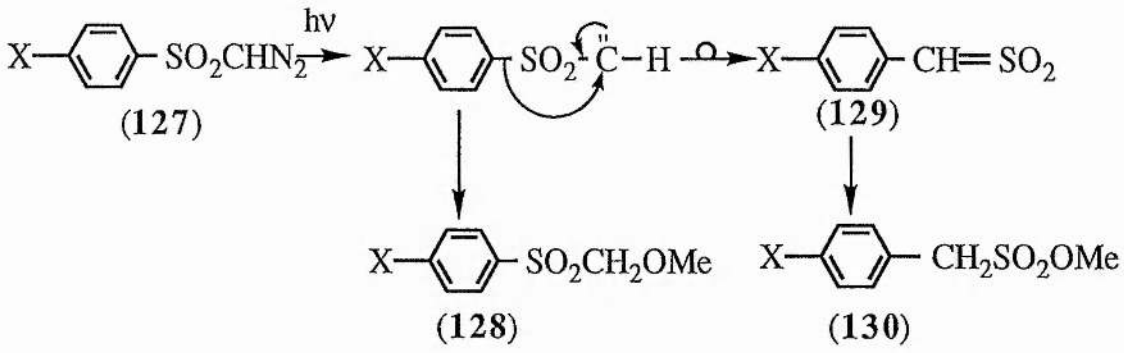


FVP of Ylides (120)

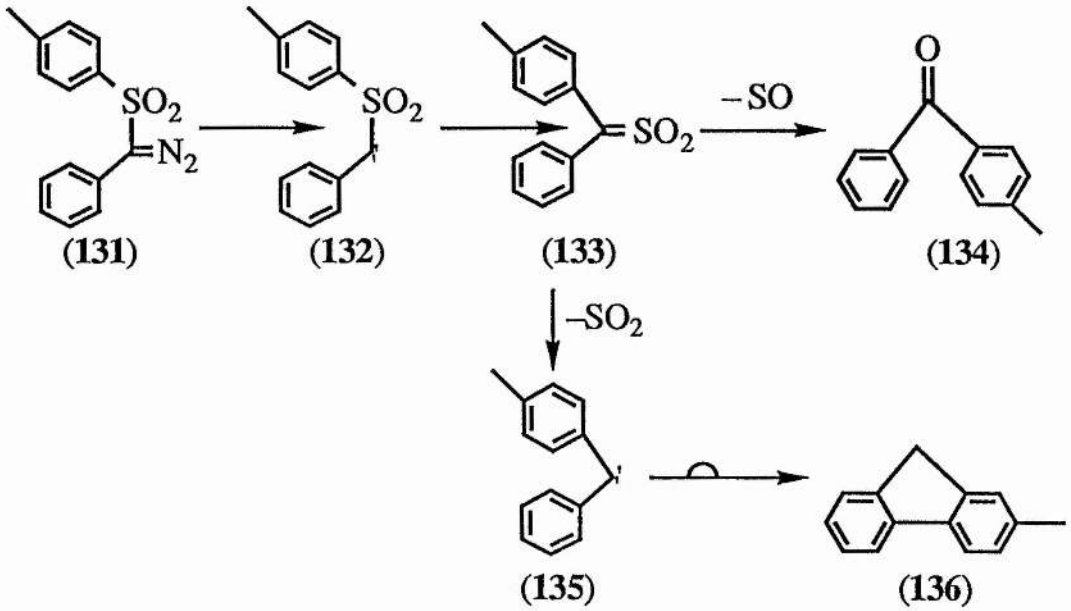
	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
R=C_6H_5 Ar=C_6H_5	77	–	–	–	–	–	6	44	16
R=p-tolyl Ar=C_6H_5	47	6	9	–	3	–	0	35	13
R=Me Ar=C_6H_5	24	7	–	–	49	–	5	24	11
R=Me Ar=o-$MeOC_6H_4$	6	5	–	–	–	22	0	25	4
R=Me Ar=o-MeC_6H_4	7	9	–	–	34	–	4	23	16
R=o-$MeOC_6H_4$ Ar=C_6H_5	39	–	–	14	11	7	37	46	17
R=o-$MeSC_6H_4$ Ar=C_6H_5	5	–	–	58	29	–	56	31	9

Table 1

In route A the loss of triphenyl phosphine generates a sulphonyl carbene which can react in two ways. It could firstly undergo a Wolff-type rearrangement to give the sulphene (124). This type of behaviour was first observed in solution photochemistry by Van Leusen *et al*[116]. They found that the irradiation of α-diazosulphones (127) in methanol gave, as well as the aryl methoxymethyl sulphones (128), the products (130) in about 10% yield which are rationalised via the sulphene (129).



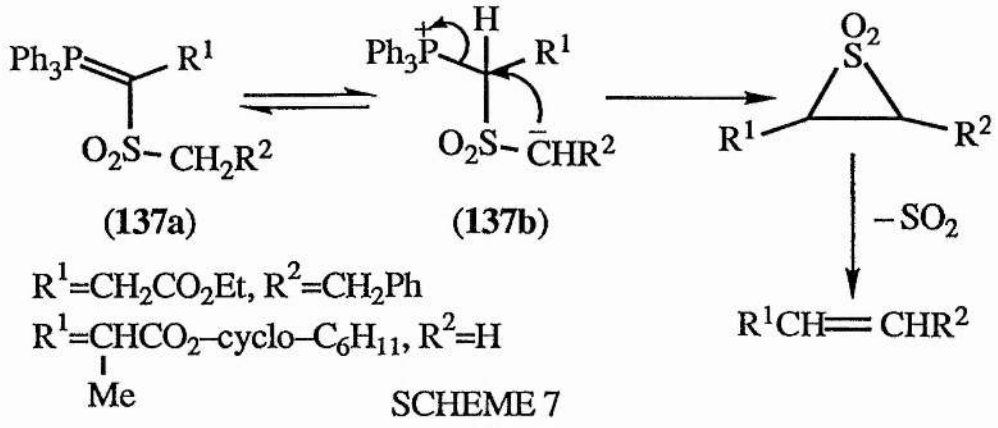
In the gas phase such a rearrangement has been observed once before by Sarver *et al*[117]. They found that the flash pyrolysis of α-(p-tolylsulphonyl) phenyl diazomethane (131) generated the sulphonyl carbene (132). This rearranges to the sulphene (133), which forms 4-methylbenzophenone (134) by the loss of sulphur monoxide, and 2-methylfluorene (136), the characteristic product of rearrangement of p-tolylphenyl carbene (135), formed by loss of sulphur dioxide from (132). Sulphenes are known to lose sulphur monoxide on FVP to leave the residual carbonyl compounds[94] but no carbonyl compounds are observed in our FVP experiments. The second possibility is for the carbene to insert into the



benzylic methylene group to directly form the episulphone (126). Episulphones are well known precursors of alkenes by loss of sulphur dioxide, a reaction first reported by Staudinger and Pfenninger in 1916[118] and the subject of several reviews[94,119,120].

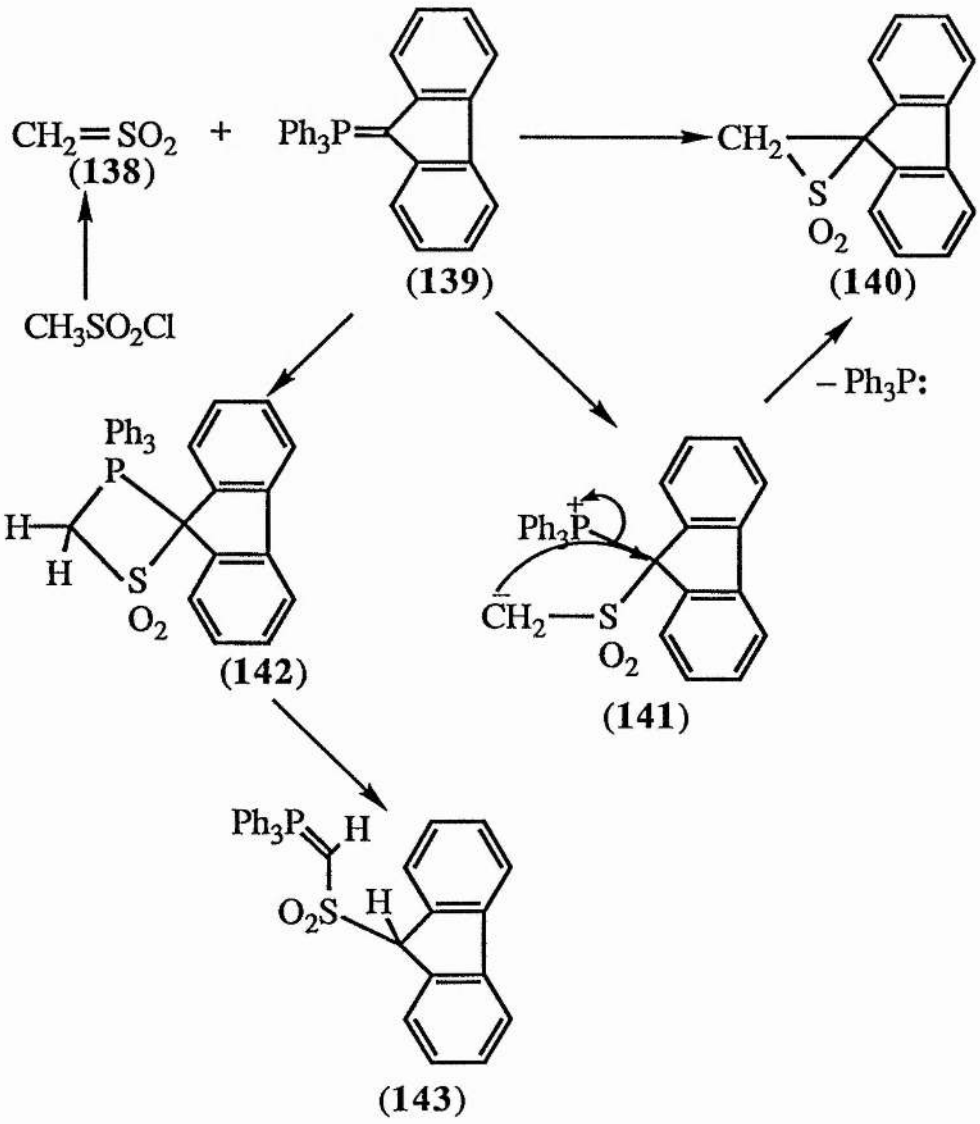
In route B we first postulate intramolecular proton transfer from the benzylic position to give an intermediate (125) which will readily expel phosphine to form the episulphone (126). As mentioned above, expulsion of SO_2 from episulphones to give alkenes is a well documented process.

Ito, Oda and Okano[34] claim that this overall reaction on a similar system (Scheme 7) goes via a route B type path. They base their evidence for the episulphone intermediate, via (137b), on the fact that in the reaction between the sulphene (138) and fluorenylidene triphenyl phosphorane (139), they can isolate the stable episulphone (140) as well as the ylide (141). They also imply that the formation of the alkene products occurs spontaneously in the reaction without doing anything extra to the ylide



SCHEME 7

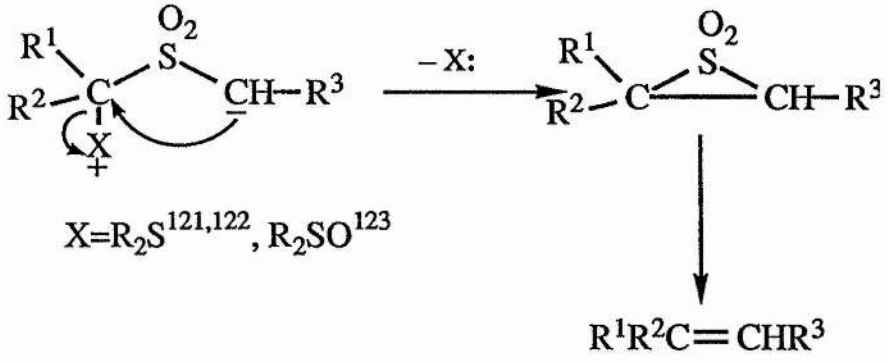
(137a) or (143). In fact in the cases where alkenes were obtained these workers firstly split the crude product (137a), recrystallised one half to



confirm the product as the ylide, then heated the remaining half at over

100°C under vacuum to obtain the alkenes. It thus seems likely that this reaction to the alkene proceeds in a similar manner to path A(Scheme 6), and that the formation of the ylides (137a) and (143) proceeds via the four membered ring intermediate (142) followed by proton transfer and ring opening in the same manner described by Van Leusen et al[38] and seen in intermediate (71). The formation of the stable episulphone (140) is via a different mechanism possibly through the intermediacy of (141).

The proton transfer mechanism has been observed for sulphonium[121,122] and sulphoxonium[123] ylides to give olefinic products

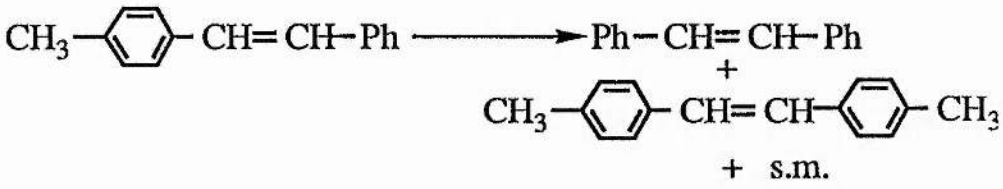


but these are solution mechanisms similar to the episulphone (140) formation above.

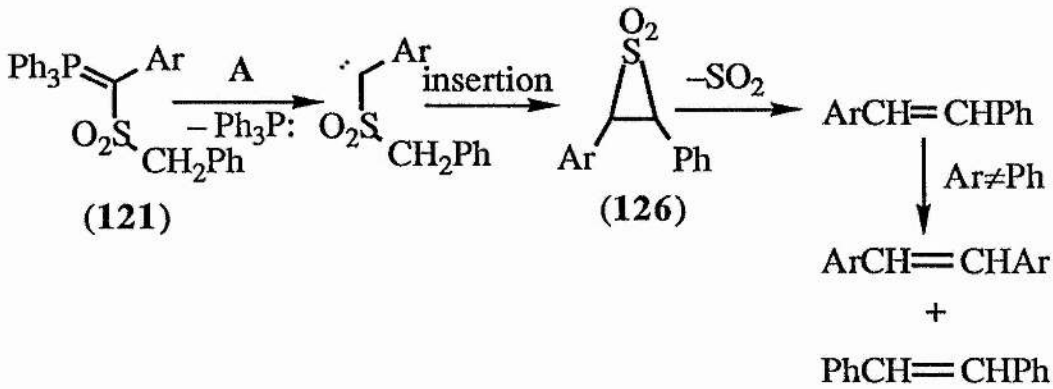
In either route A or route B, the phosphorus products are readily explained by the interaction of triphenyl phosphine and sulphur dioxide in the gas phase. This was demonstrated by pyrolysis of triphenyl phosphine in a stream of sulphur dioxide gas, which gave some conversion to a 2:1 mixture of triphenyl phosphine oxide and triphenyl phosphine sulphide.

$$Ph_3P + SO_2 \xrightarrow[750^{\circ}C,\ 1mmHg]{FVP} 2Ph_3PO + Ph_3PS + s.m.$$

The cross-over products are explained as a secondary process after the initial formation of ArCH = CHPh. This was checked by the pyrolysis of an authentic sample of p-methylstilbene which gave some conversion to a mixture of stilbene and 4,4'-dimethylstilbene as seen by ^1H N.M.R. and GCMS.

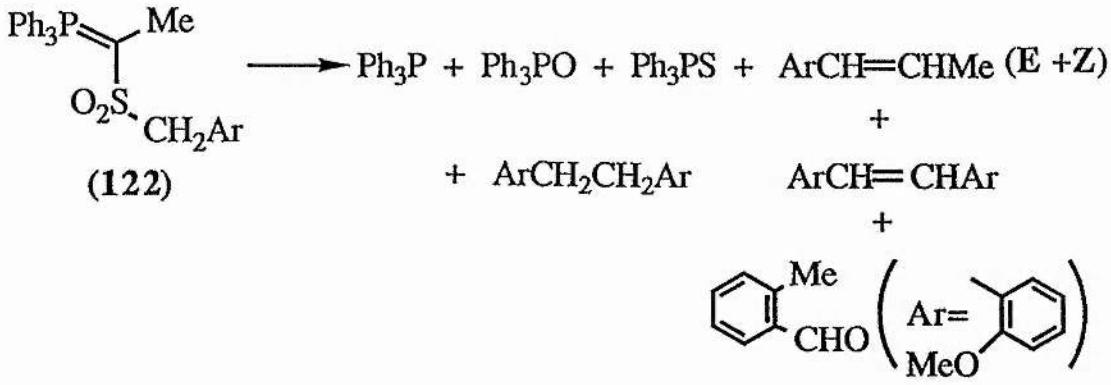


We tend to favour path A as a more likely gas phase mechanism, with the carbene insertion to the episulphone (126) being preferred over the sulphene formation since in none of our experiments were carbonyl compounds, the usual products of sulphene FVP experiments, observed.



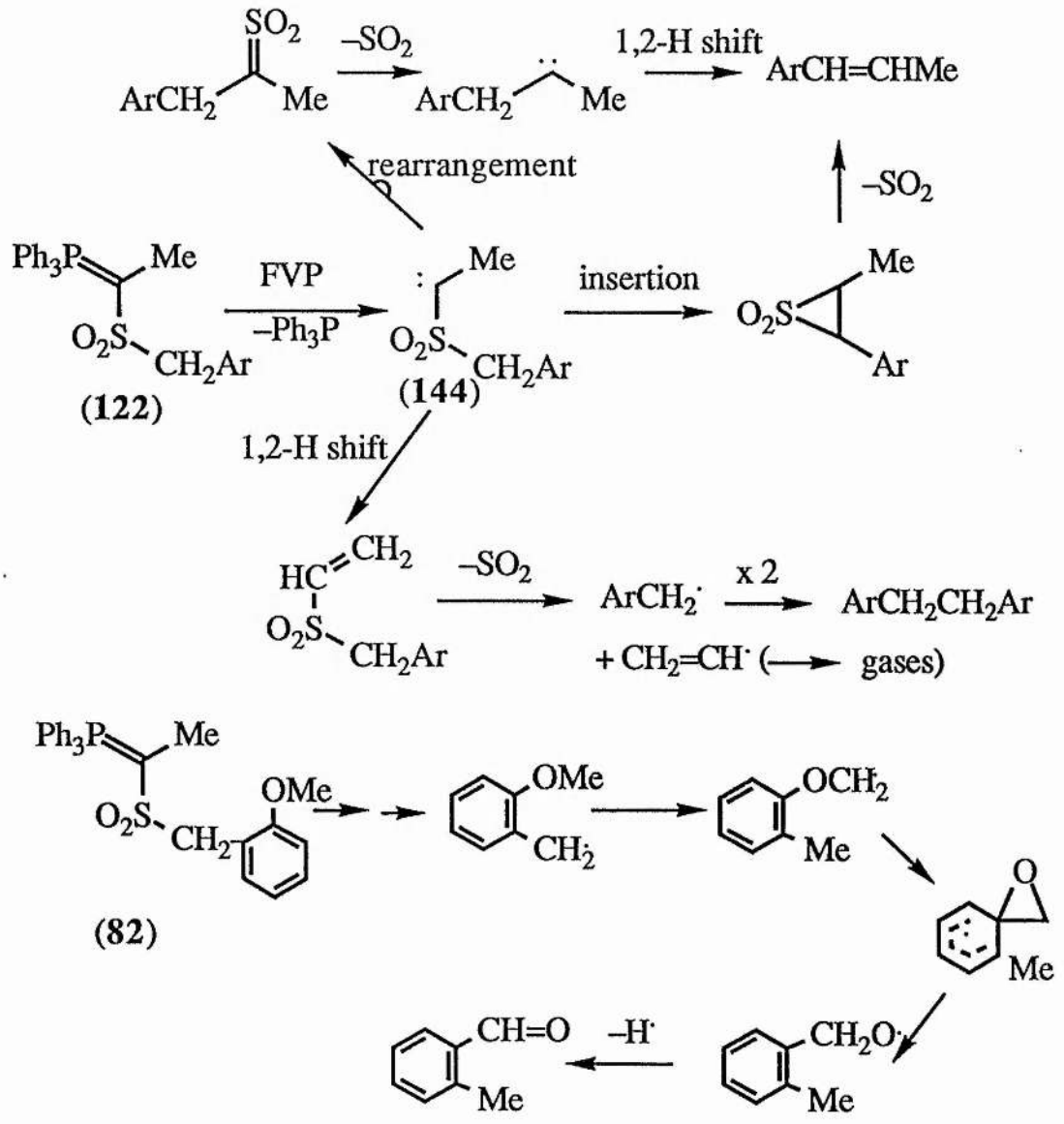
(b) Compounds of type (122)

The compounds of type (122) upon FVP give some formation of β-methylstyrenes, ArCH = CH-Me, together with cross-over products ArCH = CHAr, but the major products are now those derived from the radical $ArCH_2$·. In the case of Ar = Ph or o-MeC_6H_4 the product is a bibenzyl derivative $ArCH_2$-CH_2Ar but for Ar = o-$MeOC_6H_4$, o-tolualdehyde predominates.



The mechanistic scheme is shown in Scheme 8. The minor pathway giving the styrene products ArCH = CH-Me can be explained as before by formation of the carbene (144) followed by rearrangement to the sulphene or insertion to the episulphone. The formation of the benzyl radical can be explained by envisaging a 1,2-H shift in the carbene (144) to form a vinyl sulphone. The thermal decomposition of sulphones[124] is known to proceed with loss of sulphur dioxide and production of radicals and so the benzyl vinyl sulphones will readily break down to give benzyl radical and

subsequent products and the vinyl radical which presumably ends up as gaseous products and is undetected in our set up. The mechanism for the formation of o-tolualdehyde from the o-methoxybenzyl radical is included. This is an almost identical process to the one described by Marty and de Mayo[125] for the formation of aromatic aldehydes from



SCHEME 8

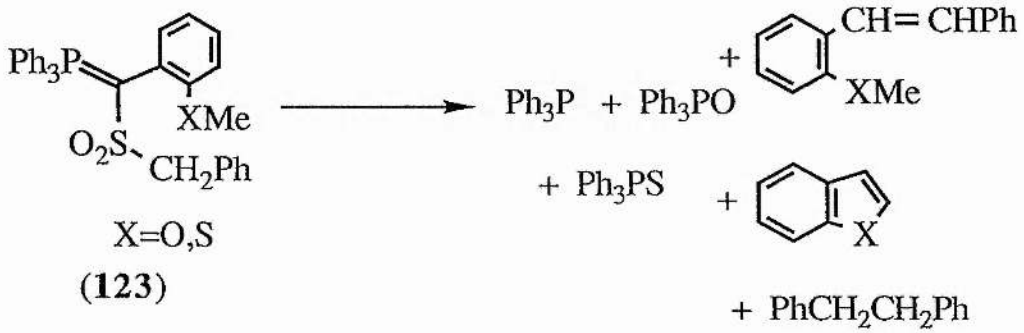
o-methoxy phenyl radicals.

The cross-over products were again seen to be formed by a secondary process. This was confirmed by the pyrolysis of an authentic sample of β-methyl styrene which gave some conversion to trans-stilbene as seen by ^{1}H N.M.R. and GCMS.

The case of type (122) therefore seems to strongly favour the formation of the carbene (144) since this can readily account for the formation of benzyl radical products. The insertion of the carbene to form the episulphone is also favoured over sulphene formation due to the absence of any carbonyl compounds which would be anticipated if the reaction went through a sulphene intermediate.

(c) Compounds of type (123) (X = O,S)

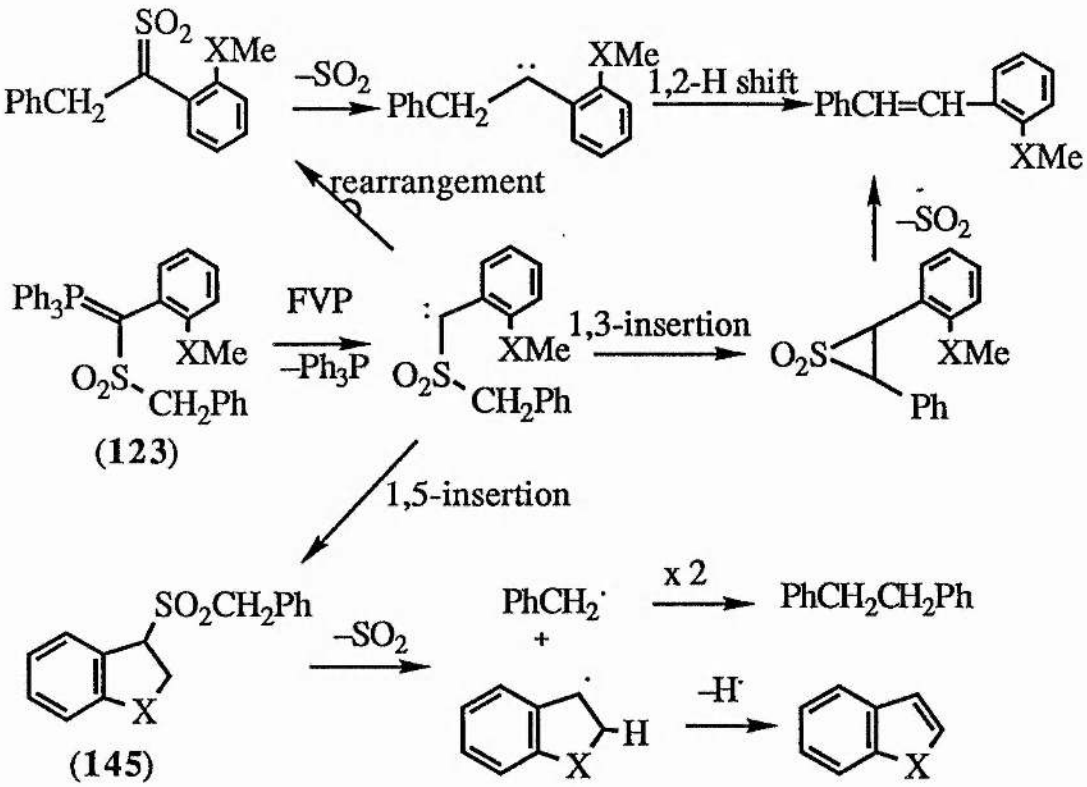
In the pyrolysis of these ylides, stilbene products are still formed, but now benzofuran/benzothiophene and bibenzyl emerge as new products.



The stilbene is still the major product for X=0, but for X=S, we get mainly benzothiophene and bibenzyl. The proposed mechanism is shown in

Scheme 9.

The stilbene formation could again be by either rearrangement of the carbene to the sulphene followed by loss of SO_2 and a 1,2-H shift or by, in this case, 1,3-insertion of the carbene to form an episulphone followed by loss of SO_2. The other products could arise from a 1,5-insertion of the carbene into the XMe group to give the sulphone (145). The sulphone (145) will break down[124] as indicated to give eventually benzofuran or



SCHEME 9

benzothiophene and bibenzyl.

Again in this case we favour the 1,3-insertion of the carbene over the rearrangement to the sulphene, since again no carbonyl products were detected in these reactions.

In all these cases the products were conclusively identified by ^{1}H N.M.R. and GCMS comparison with authentic samples prepared by literature methods.

The conclusion from these studies is that while the products can be explained by several routes in each case, the weight of evidence points to the carbene mechanism followed by carbene insertion in all cases, although the others cannot be totally ruled out.

C Preparation of Sulphinyl Stabilised Phosphorus Ylides

1. Attempted Preparation of benzenesulphinyl benzylidene triphenyl phosphorane

Our initial efforts in the attempted preparation of α-sulphinyl phosphoranes were guided by what we knew about the synthesis of α-keto ylides and α-sulphonyl ylides.

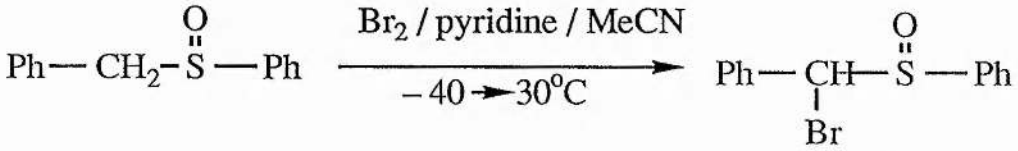
(a) From Ph_3PX_2 and benzylphenyl sulphoxide

The method of Horner and Oediger[23] which reacted triphenyl phosphine dihalides with activated methylene compounds in the presence of triethylamine was used with sulphoxides. Many benzylic sulphoxides can be bought or synthesised by oxidation of the corresponding sulphides and so their ease of availability as starting materials made an investigation of this reaction worthwhile.

Thus benzyl phenyl sulphide was treated with 30% hydrogen peroxide in A.R. acetone and after standing at R.T. for 72h, gave benzyl phenyl sulphoxide[72] in 95% yield. The sulphoxide was stirred in dry toluene with triphenyl phosphine dibromide and triethylamine which after filtration of the white precipitate and evaporation of the solvent, gave a brown solid, whose ^{31}P and ^{1}H N.M.R. showed it to be triphenyl phosphine oxide. As mentioned before in connection with the preparation of α-sulphonyl ylides, the groups adjacent to the methylene function must be highly electron withdrawing to enable this reaction to work[23].

(b) From benzylphenyl sulphoxide-α-triphenyl phosphonium bromide

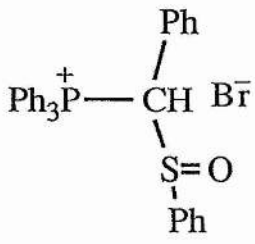
The next process attempted was to synthesise the phosphonium salt of an α-halosulphoxide and to dehydrohalogenate the salt with base to obtain the desired ylides. α-Bromobenzyl phenyl sulphoxide (146) was prepared by the method of Cinquinni and Colonna[81] by the careful addition of bromine in anhydrous acetonitrile to a mixture of benzylphenyl sulphoxide and anhydrous pyridine/acetonitrile (1:4, v/v) at -40°C.



(146)

After work up and chromatography on silica (ether/light petroleum, 1:1), the α-bromobenzyl phenyl sulphoxide (146) was obtained in 31% yield.

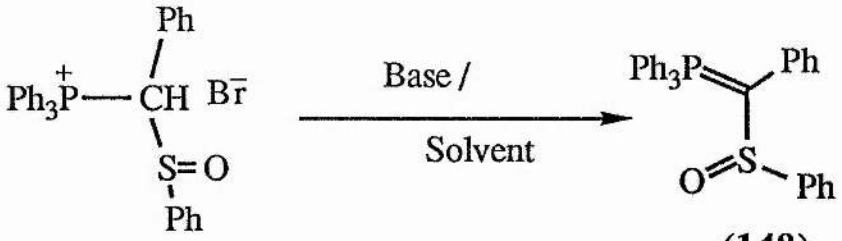
The α-bromosulphoxide (146) and triphenyl phosphine were stirred under a nitrogen atmosphere in boiling toluene or sulpholane at 120°C for 18h then at R.T. for 12h to give benzylphenyl sulphoxide-α-triphenyl phosphonium bromide (147) in 22% yield. The salt was characterised on



(147)

the basis of a single peak in the ^{31}P N.M.R. at δ_P+22.92 and the ^{1}H N.M.R. which has a characteristic doublet at δ_H 5.36 (J_{P-H} = 15 Hz) as well as aromatic signals at δ_H 7.0-8.0.

We next attempted to find a suitable base/solvent system in order to dehydrobrominate the salt (147) to the desired benzenesulphinyl-benzylidene triphenyl phosphorane (148).



(147) **(148)**

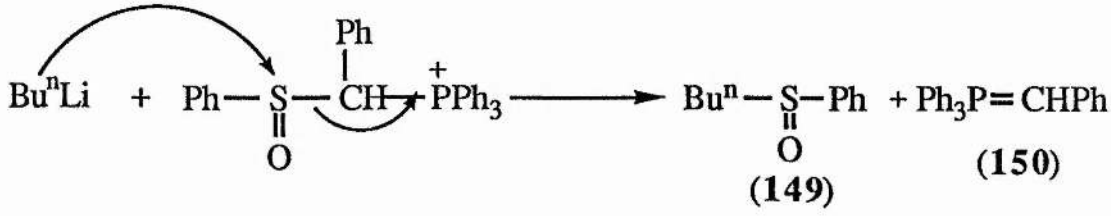
A variety of base/solvent systems were employed and are listed in Table 2. In each case the salt (147)

	Base	Solvent
(i)	NaOH	water
(ii)	$KOBu^t$	t-butanol
(iii)	$KOBu^t$	THF
(iv)	LDA	THF
(v)	Bu^nLi	THF

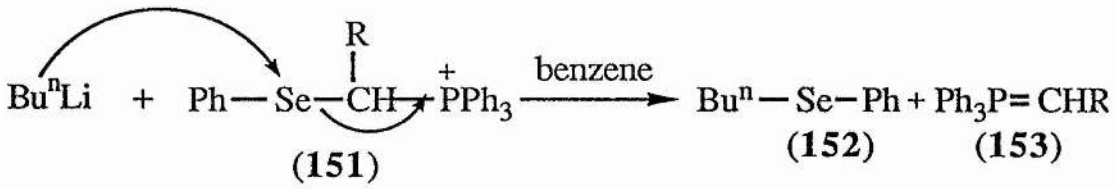
Table 2

was stirred in the appropriate solvent and the base, dissolved in the same solvent where appropriate, was added. In entry (iv), the lithium di-isopropylamine (LDA) was generated in situ by the addition of n-butyl lithium to di-isopropylamine in dry THF under N_2 and the salt (147) was added to this mixture in one portion.

In the case of systems (i)-(iii) in Table 2, triphenyl phosphine oxide and benzylphenyl sulphoxide were the major identifiable products, with in entry (iii), some triphenylphosphine and unreacted starting material also being observed. In the course of what we have learnt during this project, the ease with which a "PPh_3" moiety can be hydrolysed to triphenyl phosphine oxide is astonishing. Thus with water as solvent in the presence of a base in (i) and with no attempt to exclude moisture from entries (ii) and (iii), the formation of phosphine oxide is not surprising. In the case of LDA and THF, even with the exclusion of moisture and the use of a non-nucleophilic base, we could only identify triphenylphosphine oxide and benzylphenyl sulphoxide in the product mixture. In entry (v) of Table 2, the products obtained include a compound containing an n-butyl group. We suggest that this product may be n-butyl phenyl sulphoxide (149),



formed by the nucleophilic attack of the n-butyl lithium on the sulphur atom, with the expulsion of the ylide (150). n-Butyl lithium is a well known powerfully nucleophilic base and a similar reaction was observed by Petragnani *et al*[44] in their preparation of α-selenophosphoranes. In the treatment of the selenophosphonium salt (151) with n-butyl lithium in

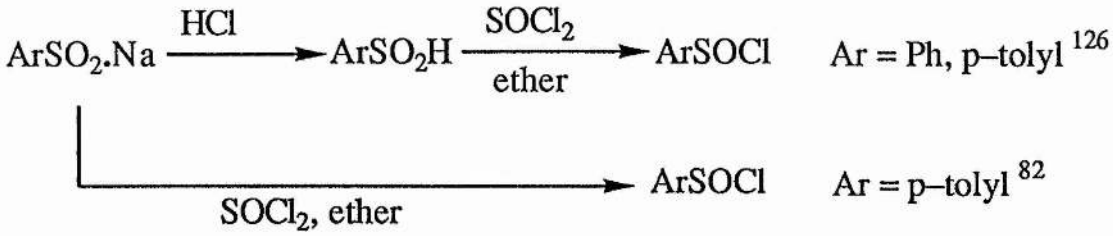


benzene they observed an indiscriminate attack on the selenium atom which by elimination of the ylide (153) gave n-butylphenyl selenide (152) in 30% yield.

2. Attempted Preparation of arylsulphinyl alkylidene and benzylidene triphenyl phosphoranes

With α-keto ylides the most successful preparative method is the acylation of phosphoranes with acid chlorides described by Bestmann and Arnason[94]. Thus we attempted the directly analogous reaction to obtain sulphinyl ylides via sulphinylation of phosphoranes with sulphinyl chlorides. The sulphinyl chlorides used in these attempts were synthesised in two ways. Firstly sodium-p-toluene sulphinate or sodium benzene

sulphinate were carefully treated with dilute HCl to liberate the free sulphinic acid. The acid was immediately heated with thionyl chloride in ether, which after removing excess reagents and solvents gave the crude sulphinyl chlorides which were considered pure enough for further use as described by Raiford and Hazlet[126]. Alternatively, the sodium salts were

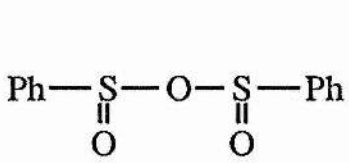


treated directly with thionyl chloride in ether as described by Kurzer[82]. The sulphinyl chlorides in dry THF, were added to either benzylidene - or ethylidene triphenyl phosphorane at 0°C in dry THF under a nitrogen atmosphere. After heating for 18h, water and ether were added and after further ether washings the organic layer yielded only triphenyl phosphine oxide in all cases.

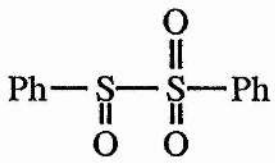
It was thought that the sulphinylation might be better achieved using either sulphinyl fluorides or sulphinic anhydrides as the source of the sulphinyl moiety in an analogous manner to the preparation of sulphonyl ylides described by Van Leusen *et al*[33,38].

In the case of sulphinic anhydrides a claim by Knoevenagel and Polack[127] to have synthesised benzene sulphinic anhydride (154) by the dehydration of benzene sulphinic acid with acetic acid and acetic anhydride

was proved to be erroneous. Though this would appear to have potential as a general method for the production of sulphinic anhydrides, work by Bredereck *et al*[128,129] showed that the compound claimed by Knoevenagel and Polack[127] to be the anhydride (154) was in fact the

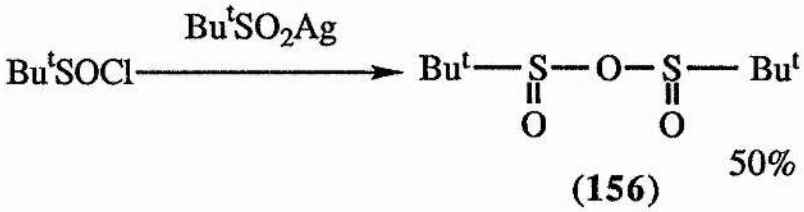


(154)



(155)

sulphinylsulphone (155). A genuine sulphinic anhydride, t-butylsulphinic anhydride (156), was prepared by Kice and Ikura[130] by the reaction of t-butyl sulphinyl chloride and silver-t-butyl sulphinate. Since this is an



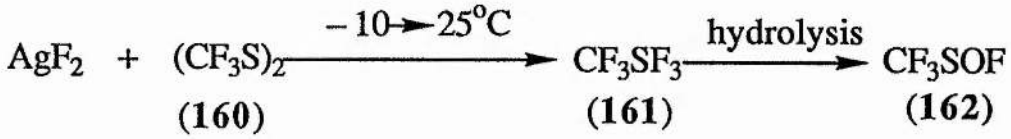
(156) 50%

isolated example, further work to assess the potential as a general method would require considerable investment in a selection of silver salts and was considered to be too costly.

Sulphinyl fluorides are also relatively scarce in the chemical literature. Sheppard[131] synthesised benzene sulphinyl fluoride (158) in his

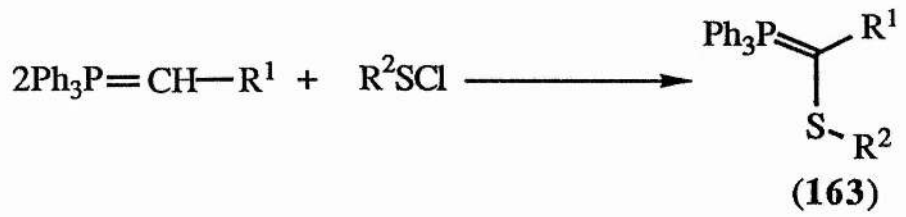
investigations into the reactions of trifluorinated sulphur compounds. He found that in the reaction of benzene sulphur trifluoride (157) with benzaldehyde, α,α-difluorotoluene (159) and benzene sulphinyl fluoride

(158) were produced in 71-80% and 82-89% yields respectively. However this was found not to be a general reaction. A second sulphinyl fluoride, trifluoromethyl sulphinyl fluoride (162)[132] was prepared by the slow hydrolysis of trifluoromethyl sulphur trifluoride (161). The trifluoride (161)[132] was itself prepared by the action of silver difluoride on bis(trifluoromethyl)disulphide (160). All these reactions, described by



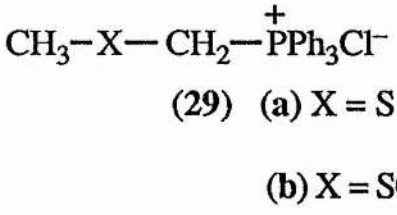
Lawless and Harmann[132], were carried out in vacuum lines which makes the procedure more complex than convenient.

Another seemingly rewarding approach worth consideration was the oxidation of α-thiophosphoranes (163). These compounds are readily



(163)

available from the reaction of two equivalents of phosphorane with one of sulphenyl chloride to give the α-thiophosphoranes (163)[133-137] via a transylidation reaction. The oxidation however was thought unlikely to produce the corresponding sulphinyl ylide in good yield by comparison to work carried out by Speziale and Ratts[32]. As mentioned earlier these workers attempted to oxidise the phosphonium salt (29a, X=S) into the sulphone salt (29b, $X=SO_2$). They found that yields were very low (3.4%),



(29) (a) X = S

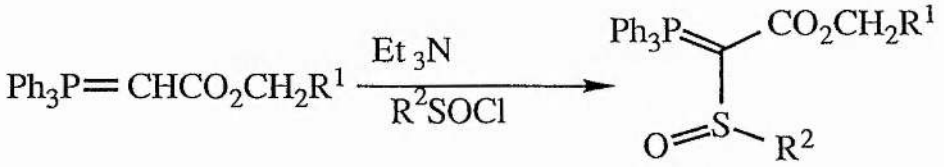
(b) $X = SO_2$

due to oxidative cleavage at the P-C bond to give triphenyl phosphine oxide. It was anticipated that a similar problem would arise in any attempted oxidation of the α-thiophosphoranes (163).

3. Preparation of α-sulphinyl alkoxycarbonylmethylene triphenyl phosphoranes

A successful method for the synthesis of a class of α-sulphinyl ylides

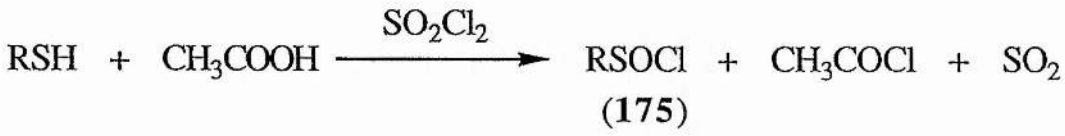
(164) was described in a U.S. Patent by Alden[42]. The reaction of a sulphinyl chloride with a stabilised phosphorane in the presence of triethyl-amine, gave the ylides (164), exemplified by compounds (165)-(174).



(**164**)

(**165**) R^1=H, R^2=Ph
(**166**) R^1=H, R^2=*p*- tolyl
(**167**) R^1=H, R^2=*p*- BrC_6H_4
(**168**) R^1=H, R^2=Et
(**169**) R^1=Me, R^2=Ph
(**170**) R^1=Me, R^2=*p*- tolyl
(**171**) R^1=Me, R^2=*p*- BrC_6H_4
(**172**) R^1=Me, R^2=*p*- ClC_6H_4
(**173**) R^1=Me, R^2=Et
(**174**) R^1=Et, R^2=*p*- tolyl

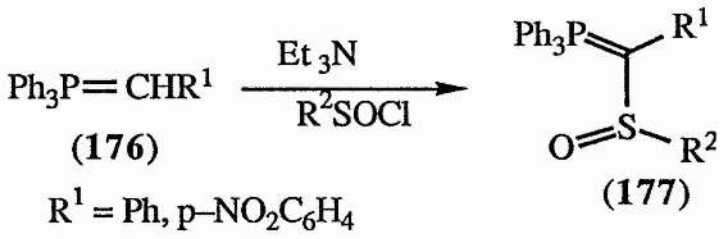
A recent report by Youn and Hermann[83] gave a convenient synthesis of sulphinyl chlorides which avoided the use of chlorine[138,139] or the production of excessive quantities of HCl gas as a by-product[138]. In this method a mixture of thiol and acetic acid is stirred at -40°C and sulphuryl chloride is added slowly. After the reaction the only by-product is the



(**175**)

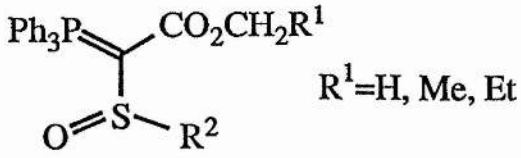
extremely volatile acetyl chloride which can be easily removed under vacuum to leave the sulphinyl chlorides (175) which were sufficiently pure for further use. When the sulphinyl chlorides are added to a stabilised

phosphorane and triethylamine in dry toluene at 0°C, an immediate precipitate of triethylamine hydrochloride is observed. After the reaction, the precipitate is filtered off, the solvent removed and the residue triturated with ethyl acetate to give the α- sulphinyl phosphoranes (144) in 30-72% yield. The patent[42] claims that any starting ylide with an electron withdrawing group, R^1 (176), could be used to form an ylide of the type (177), including cases where R^1 = Ph, p-$NO_2C_6H_4$. In our attempts, the benzylidene- and p-nitrobenzylidene triphenyl phosphoranes generated from their respective phosphonium salts with n-butyl lithium, gave only the starting phosphonium salts. It would appear that since these phosphoranes are themselves strongly basic, triethylamine is unable to



abstract the α-hydrogen from the phosphorane as it can from alkoxycarbonylmethylene phosphoranes, and so some other reaction occurs, eventually regenerating the phosphonium salts.

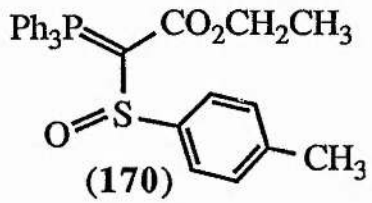
In the course of the analysis of the α-sulphinyl alkoxycarbonyl ylides (164) a broadening of peaks in the N.M.R. spectra was noticed. In



(164)

the ^{1}H N.M.R., broadening of the CH_2R^1 signals was considerable and in the ^{13}C N.M.R. broadening of both the CH_2R^1 and carbonyl signals was seen.

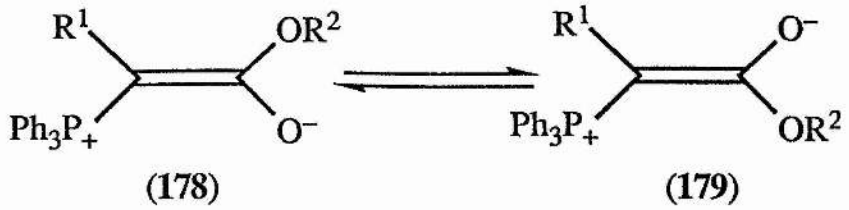
The presence of broad lines in the spectra is indicative of an equilibration process and so it was decided to investigate one of the ylides, p-methylbenzene sulphinyl ethoxycarbonylmethylene triphenyl phosphorane (170), by variable temperature ^{1}H and ^{13}C N.M.R. Variable temperature N.M.R. is a convenient technique to study hindered rotation in molecular systems and a variety of rate parameters can be deduced from simple N.M.R. measurements.



(170)

Selected sections of the ^{1}H and ^{13}C data at temperatures from 233K-303K are shown in Schemes 10-12.

Previously, alkoxycarbonyl ylides have been seen to exhibit hindered internal rotation about the ylidic carbon-carbonyl bond[140-143]. This results in a cis/trans equilibrium between the rotamers (178) and (179).



(178) (179)

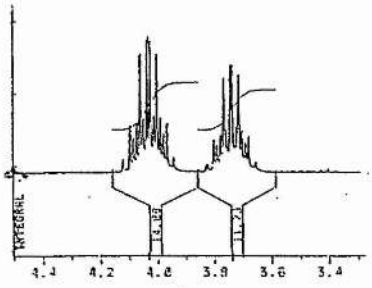
In the ^1H N.M.R. (Scheme 10), at 333K two rotamers can be seen with two well separated triplets for the methyl groups and two phosphorus- split quartets of the methylene groups. By analogy with others[140,142,143] we assign the downfield signals at $\delta = 4.03$ and 1.22 to the cis rotamer and the signals at $\delta = 3.74$ and 0.38 to the trans rotamer.

As the temperature increases the signals begin to broaden until at 273K the signals are undefined humps. As the temperature rises further the signals for each rotamer converge and finally merge into one at T_c, the coalescence temperature. This temperature is different for the methylene and methyl groups and we are able to assign these with varying degrees of accuracy. (Table 3)

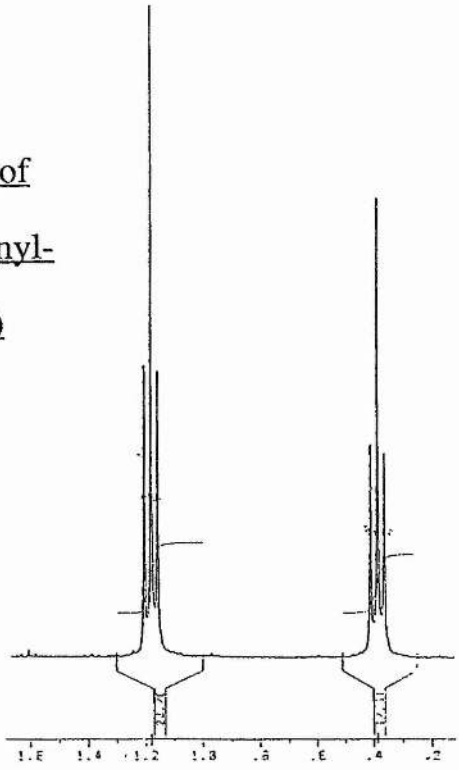
From the separation of the rotamer signals at low temperature and the coalescence temperature, using simple equations[144] we can derive the free energy of activation, $\Delta G^{\ddagger}$, for this system, in this case $\Delta G^{\ddagger} = 13.8$k cal mol^{-1} ($\pm$ 0.2k cal mol^{-1}). This is in good agreement with values quoted for the nearest comparable cases[140,142].

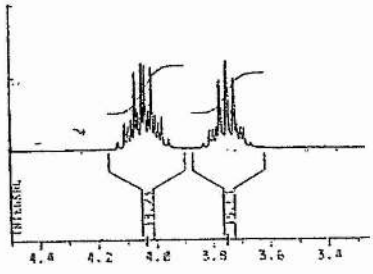
Integration at 333K gives us the cis:trans rotamer ratio which in this case is 54:46. Again a simple thermodynamic equation, using this ratio and

Variable Temperature ^{1}H NMR Spectra of p-methylbenzene sulphinyl ethoxycarbonyl-methylene triphenyl phosphorane (170)

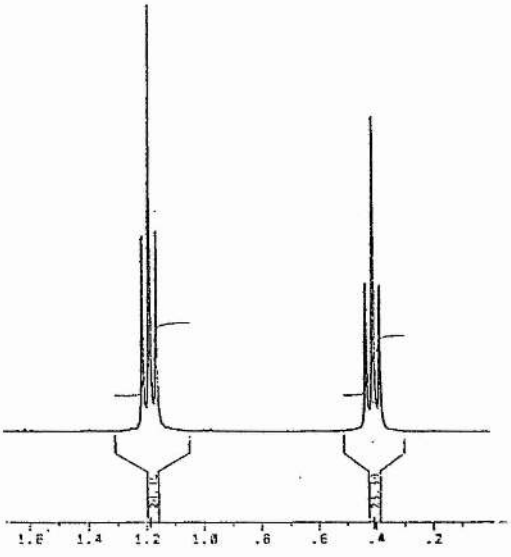


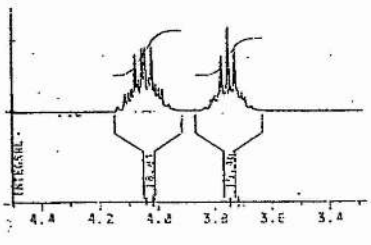
233K



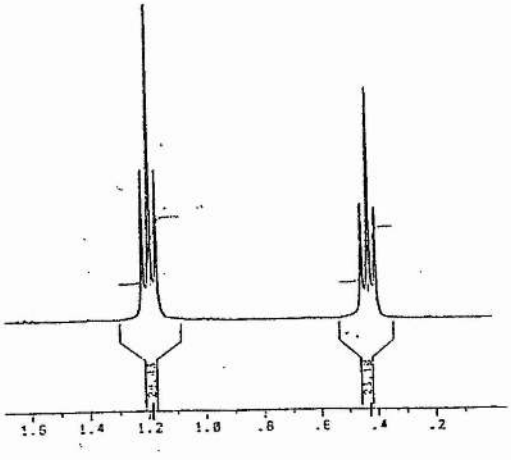


243K

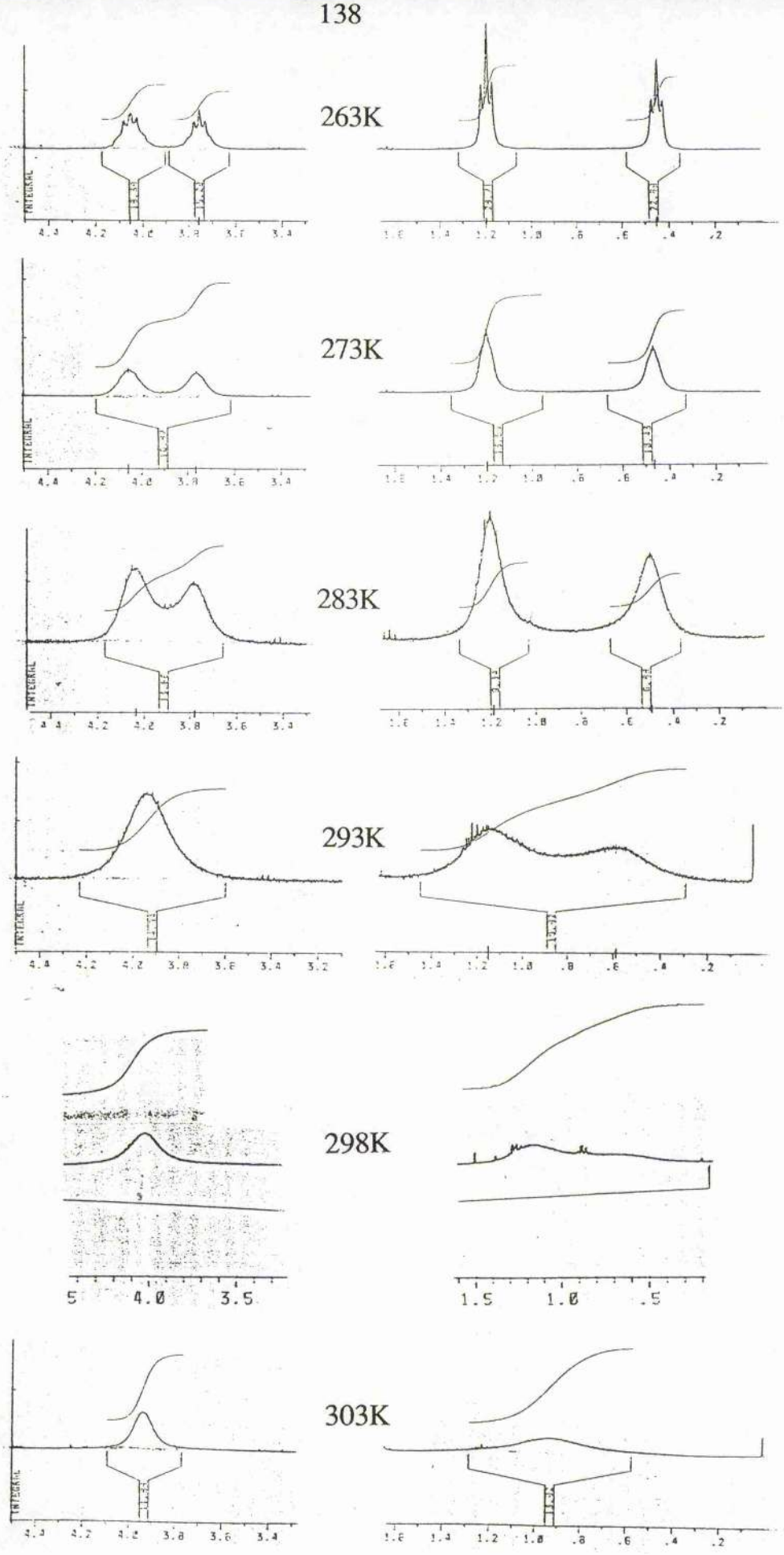




253K



SCHEME 10



SCHEME 10 continued

T_c, the coalescence temperature, gives us a value of -0.091k cal mol^{-1} (± 0.003k cal mol^{-1}) for ΔG, the free energy barrier to rotation.

Variable Temperature ^1H N.M.R. Spectra of p-methylbenzenesulphinyl ethoxycarbonyl-methylene triphenyl phosphorane

	Coalescence Temperature T_c (K)	Low Temperature rotamer ratio cis:trans	$\Delta G^{\ddagger}$ (±0.2 kcal mol^{-1})	ΔG (±0.003 kcal mol^{-1})
CH_2	288 (±4)	54:46	13.8	-0.091
CH_3	301 (±2)	54:46	13.8	

Table 3

In the ^{13}C N.M.R. (Schemes 11 & 12) different chemical shifts can be found for the ylide carbon and carbonyl carbon of each rotamer as well as the methyl and methylene carbons. If as in the ^1H N.M.R. we assign the downfield signals to the cis rotamer we find that the phosphorus-carbon coupling in each rotamer is different. In the cis rotamer the relevant coupling constants are 126.376 Hz for the ylidic carbon and 27.298 for the carbonyl carbon. For the trans rotamer these values are 117.283 Hz and 22.561 Hz respectively (Scheme 11).

Table 4 shows the coalescence temperature for the methylene and methyl

carbons. From these values and the chemical shift difference of the rotamers at low temperature, we can work out $\Delta G^{\ddagger}$ values as before. As expected these values shown in Table 4 are in excellent agreement with the values obtained from the ^{1}H N.M.R. data.

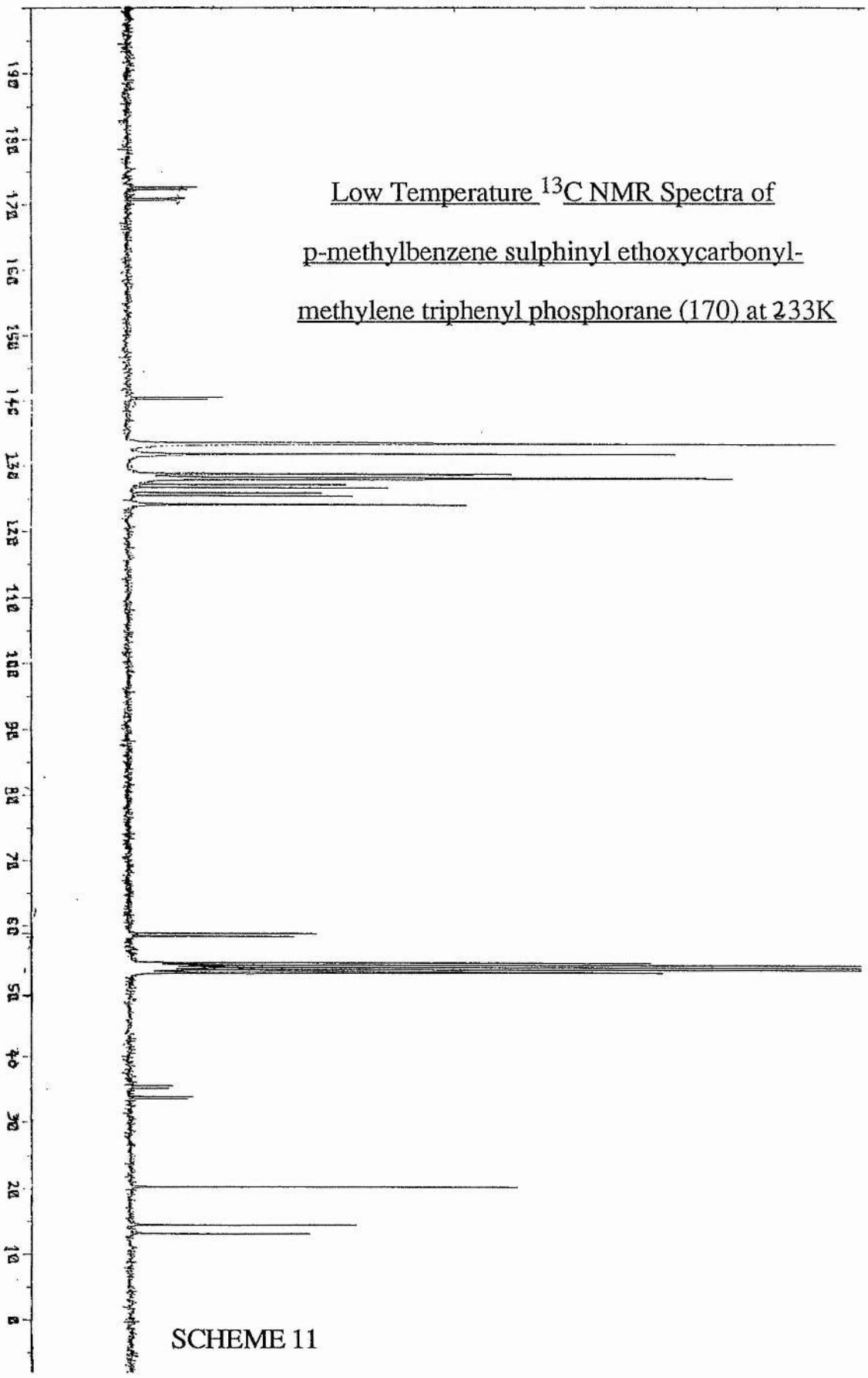
Variable Temperature ^{13}C N.M.R. Spectra of

p-methylbenzenesulphinyl ethoxycarbonylmethylene

triphenyl phosphorane

	CH_2	CH_3
Coalescence Temperature ($T_c \pm 4K$)	278	288
Free energy of activation ($\Delta G^{\ddagger} \pm 0.2$ kcal mol^{-1})	13.8	13.7

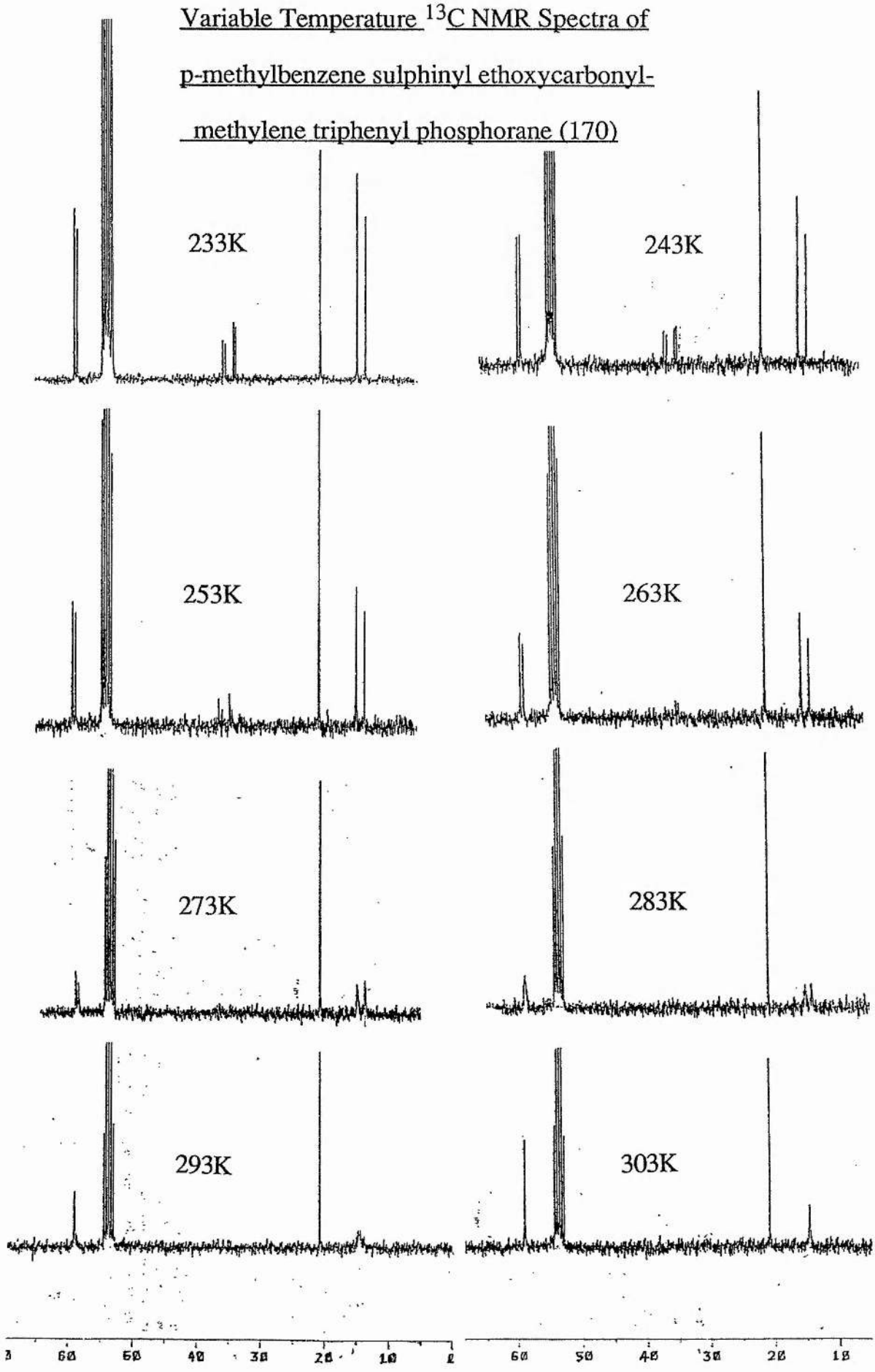
Table 4



Low Temperature ^{13}C NMR Spectra of p-methylbenzene sulphinyl ethoxycarbonyl-methylene triphenyl phosphorane (170) at 233K

SCHEME 11

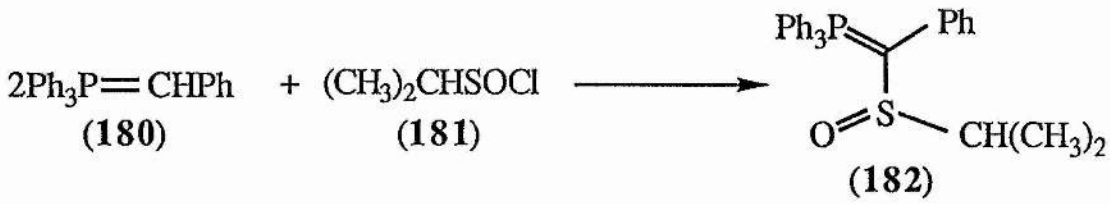
Variable Temperature ^{13}C NMR Spectra of p-methylbenzene sulphinyl ethoxycarbonyl-methylene triphenyl phosphorane (170)



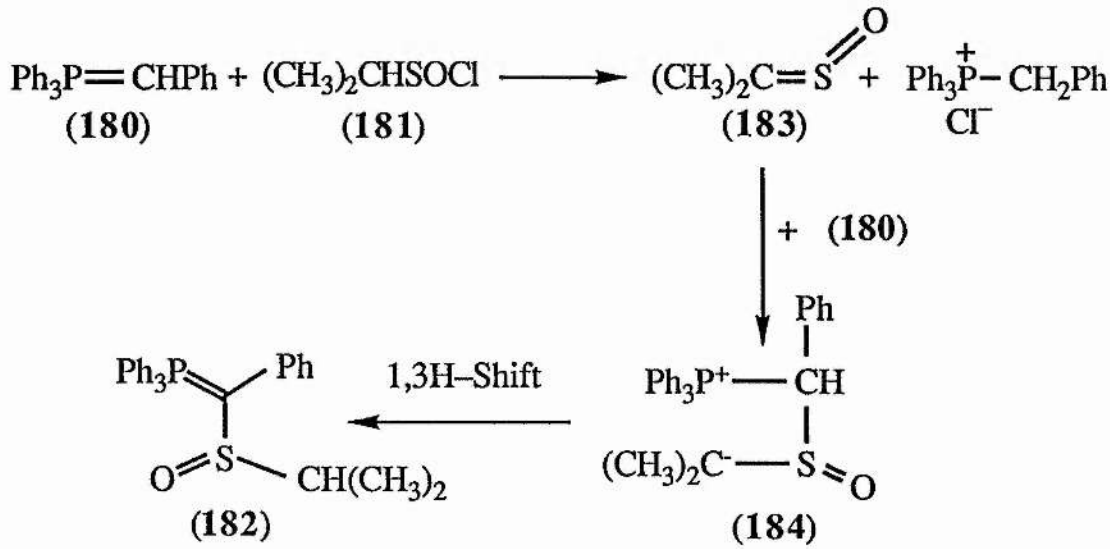
SCHEME 12

4. Preparation of isopropylsulphinyl benzylidene triphenyl phosphorane

The preparation of isopropylsulphinyl benzylidene triphenyl phosphorane (182) was achieved by the reaction of 2 equivalents of benzylidene triphenyl phosphorane (180) with one equivalent of isopropylsulphinyl chloride (181).

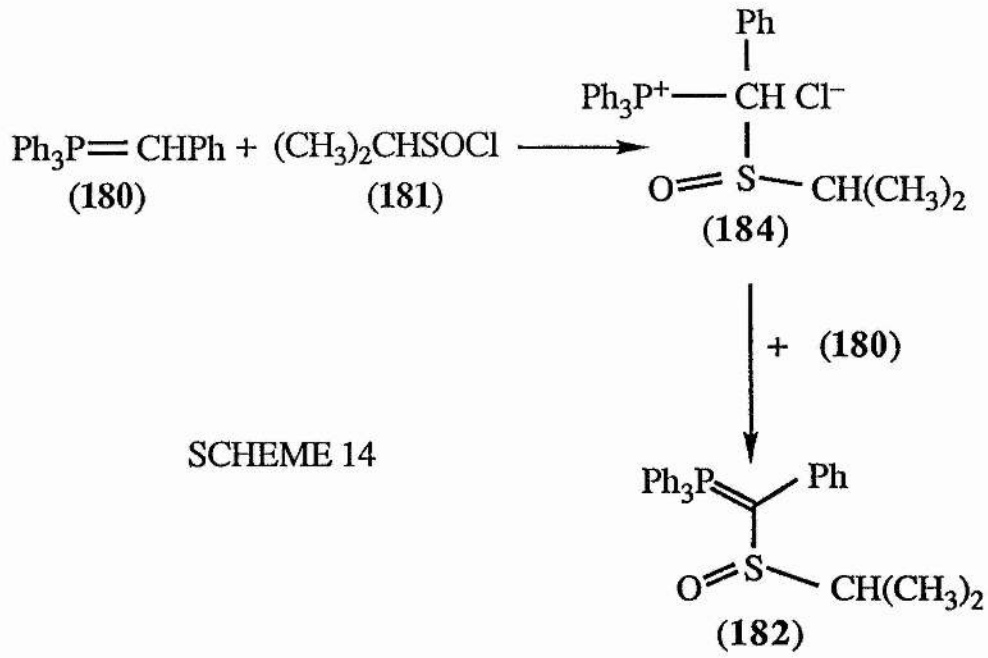


The reaction pathway in this case could conceivably be explained by two different routes. Firstly, Scheme 13, the first equivalent of ylide (180) generates a sulphine (183) by extraction of HCl from (181). The sulphine (183) then reacts with the second equivalent of (180) and via the betaine (184) and a 1,3-H shift, forms the product (182). The same type of



SCHEME 13

mechanism was proposed by Hamid and Trippett[36] to explain the reaction of a sulphine with the stabilised ylide, ethoxycarbonylmethylene triphenyl phosphorane. An alternative mechanism is the transylidation reaction (Scheme 14). The initially formed salt (184) reacts with the second



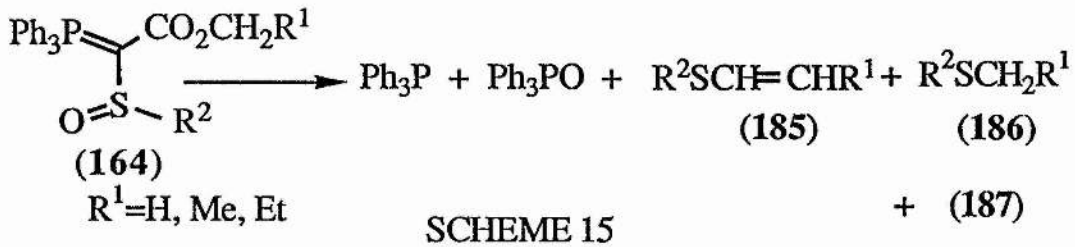
SCHEME 14

equivalent of (180) to form the ylide (182) and regenerate $Ph_3P^+–CH_2Ph\ Cl^-$.

D Flash Vacuum Pyrolysis of Sulphinyl Stabilised Phosphorus Ylides

1. Flash Vacuum Pyrolysis of α-Sulphinyl alkoxycarbonylmethylene triphenyl phosphoranes

In the flash vacuum pyrolysis of the α-sulphinyl alkoxycarbonyl ylides (164), Scheme 15, the phosphorus containing products collected at the furnace exit, are triphenyl phosphine and triphenyl phosphine oxide. The non-phosphorus containing products still contain the sulphur atom and so the triphenyl phosphine oxide can be claimed to be a genuine extrusion product. This fraction collected in the cold trap of the FVP apparatus in the form of a colourless liquid, consists of three major components. These



(164)

R^1=H, Me, Et

SCHEME 15

are the vinyl sulphide derivative (185), the sulphide (186) and a carbonyl compound (187). At 500°C the product distribution is as shown in Table 5. At this temperature some of the starting ylide (164) sublimes over unchanged, and in some cases no reaction occurs at all. At a furnace temperature of 600°C, no such problem occurs(Table 6). The phosphorus and non-phosphorus containing fractions are well separated after the reaction and are generally obtained with higher rates of conversion.

FVP of Ylides (164) at 500°C

	(185)	(186)	(187)	Ph_3P[a]	Ph_3PO[a]	S.M.[a]
R^1=H R^2=						
Ph[b]	14	22	15	3	40	0
p-tolyl	11	25	21	5	40	1
p-BrC_6H_4	0	11	0	0	100	16
Et	10	0	<1	40	12	0
R^1=Me R^2=						
Ph[c]	–	–	–			
p-tolyl	20	0	<1	11	29	40
p-BrC_6H_4[c]	–	–	–	0	40	18
p-ClC_6H_4	9	<1	<1	2	14	40
Et	34	0	<1	40	6	

a Ratio of Ph_3P:Ph_3PO:S.M., not percentage yield.

b Some PhSSPh seen in GCMS.

c No volatile products observed.

Table 5

FVP of Ylides (164) at 600°C

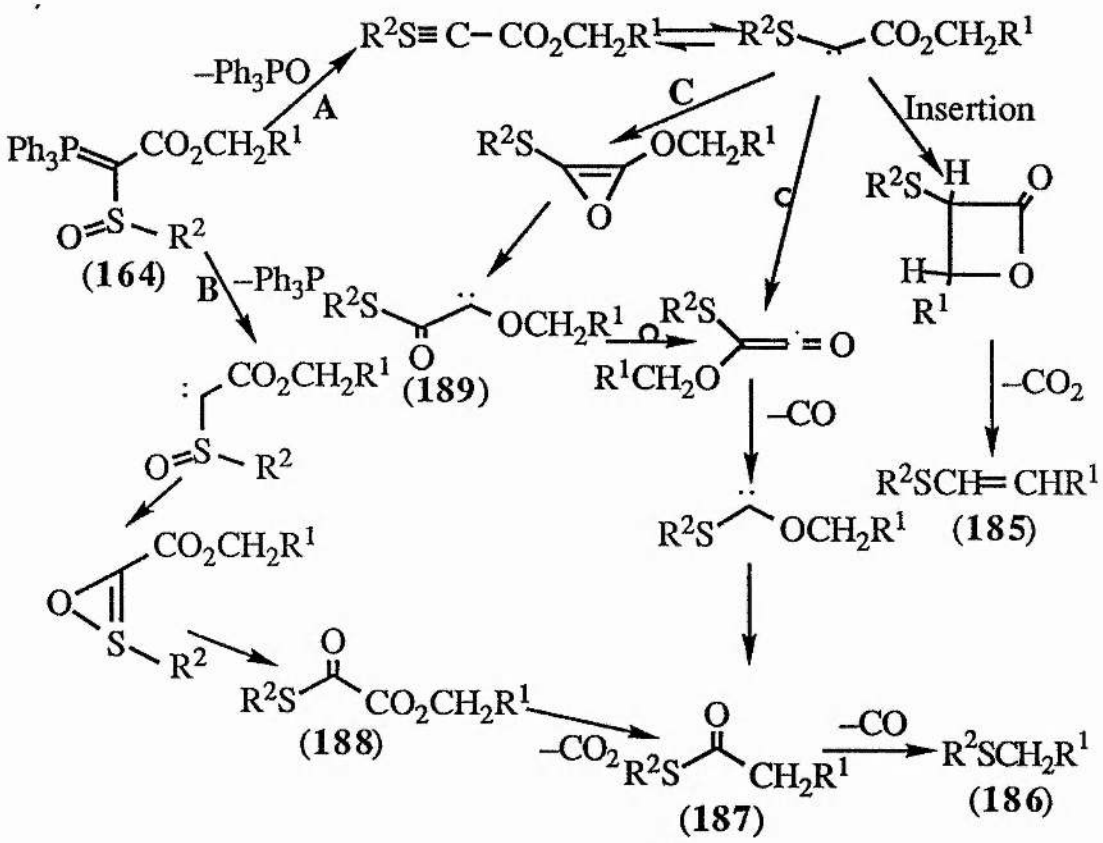
	(185)	(186)	(187)	Ph_3P[a]	Ph_3PO[a]
R^1=Me R^2=					
Ph[b]	10	7	5	0	100
p-tolyl	51	1	6	24	10
p-BrC_6H_4	53	11	9	0	100
p-ClC_6H_4	17	1	2	40	26
Et[c]	20	<1	0	60	31
R^1=Et R^2=					
p-tolyl[d]	34	0	3	8	5

a Ratio of Ph_3P:Ph_3PO, not percentage yield.
b 19% PhSSPh and 39% unidentified product seen in GCMS.
c <1% EtSSEt seen in GCMS.
d 2% $MeC_6H_4SSC_6H_4Me$ seen in GCMS.

Table 6

At this stage a tentative mechanism was proposed on the basis of GCMS and ^1H and ^{31}P N.M.R. of the product mixture (Scheme 16).

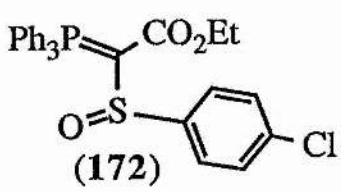
The original assignment of the structure of the carbonyl compound (187) as in Scheme 16 was based on ^1H N.M.R. and, mainly, GCMS analysis. A correct M^+ peak assignment and fragmentation process, loss of



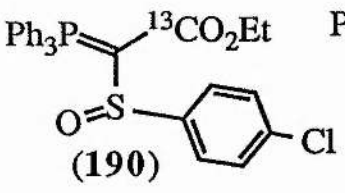
SCHEME 16

CH_2R^1 followed by loss of C=O, indicated such a structure. Further evidence however was sought from ^{13}C N.M.R. analysis. p-Chlorobenzene sulphinyl ethoxycarbonylmethylene triphenyl phosphorane (172) was chosen for a ^{13}C N.M.R. study of the cold trap product mixture. The ^{13}C labelled compounds (190) and (191) were also synthesised in three stages starting from 5% ^{13}C enriched ethylbromoacetate-1- and 2-^{13}C respectively. It was anticipated that by observing which peaks in the ^{13}C spectra of the pyrolysate of (190) and (191) were enhanced by ^{13}C enrichment, we could confirm or amend our proposed mechanism (Scheme 16).

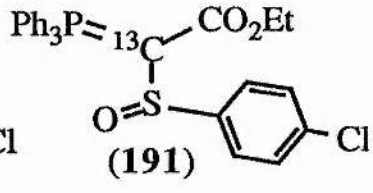
Once obtained, the ^{13}C N.M.R. of the cold trap products of (172) was



(172)

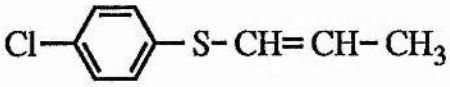


(190)

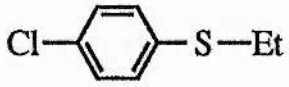


(191)

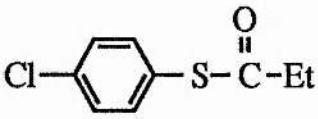
much more complex than expected for a relatively simple three component mixture of (185)-(187). In order to confirm the presence of the components (185)-(187) ($R^1 = CH_3$, $R^2 = p\text{-}ClC_6H_4$), the authentic p-chlorophenyl vinyl sulphide (192), p-chlorophenyl ethyl sulphide (193) and S-p-chlorophenyl thiopropionate (194) were synthesised by other means. On obtaining their ^{13}C N.M.R. data, comparison with that obtained



(192)



(193)



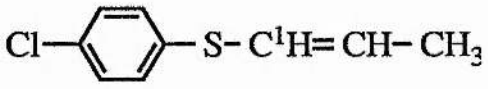
(194)

from the pyrolysate of (172) confirmed the presence (192) and (193) but no peak matchup for (194) was observed. Synthesis of the isomer of (194), S-ethyl p-chlorothiobenzoate, which would also fit the mass spectral data, and comparison of it's ^{13}C spectra indicated it was not the carbonyl compound present in the mixture either.

To double check these observations two courses of action were taken. Firstly, some authentic (194) was added to the pyrolysate of (172) and the ^{13}C N.M.R. of this mixture obtained. This showed new peaks for compound (194) as well as all the previous peaks, thus eliminating the possibility that (194) was in the original pyrolysate of (172) but its peaks

were shifted by the presence of (192) and (193), effectively a solvent effect. Secondly a series of compounds of type (188) were synthesised and their FVP studied*. Their pyrolysis products indicated no loss of carbon dioxide to give products of type (187). Thus a new reaction pathway following the loss of triphenyl phosphine must be found, as well as investigating other possible routes to products of type (186).

The pyrolysate of the ^{13}C enriched ylide (190) showed no relative peak enhancements in the ^{13}C spectra. This implies that the carbonyl carbon is not incorporated in any of the products of pyrolysis. On the other hand, the ^{13}C N.M.R. of the pyrolysate of ylide (191) shows considerable peak enhancement. The ^{13}C signals at δ_c 121.1 and 122.91 corresponding to C^1 in the cis and trans isomers of the p-chlorophenyl



(192)

propenylsulphide (192),were enhanced by five times relative to the methyl signal. This is in good agreement with the proposed route A (Scheme 16), with insertion, followed by loss of carbon dioxide.

This type of insertion of a carbene followed by loss of carbon dioxide was observed by Richardson *et al* in the FVP of dimethyl diazomalonate

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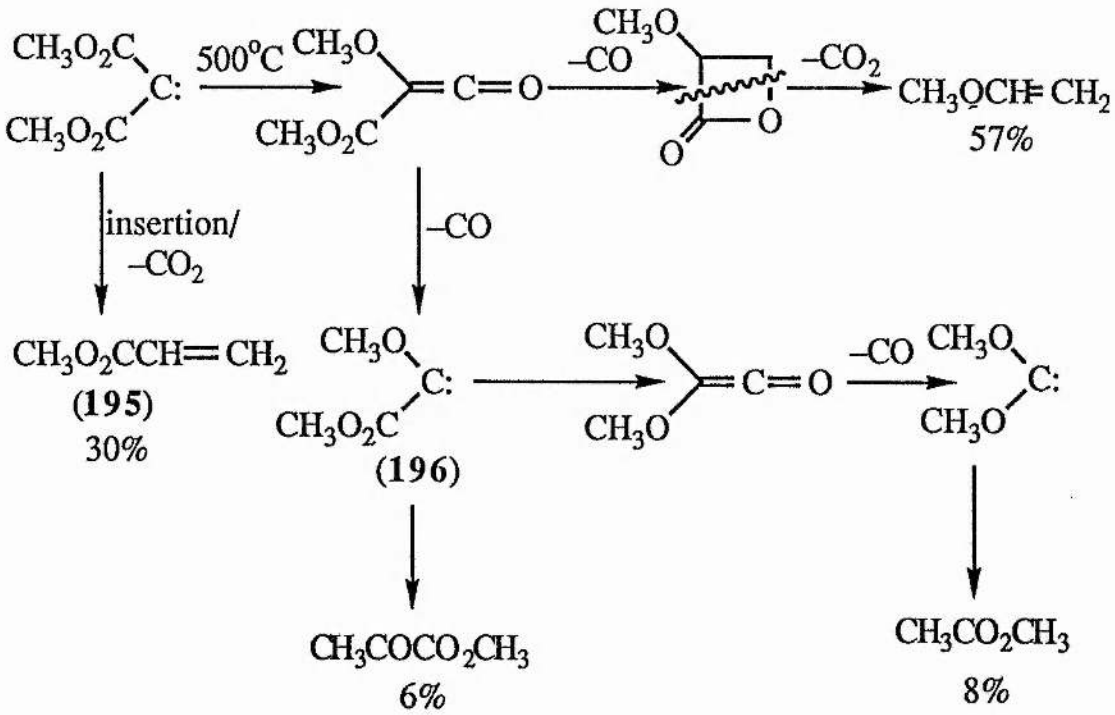
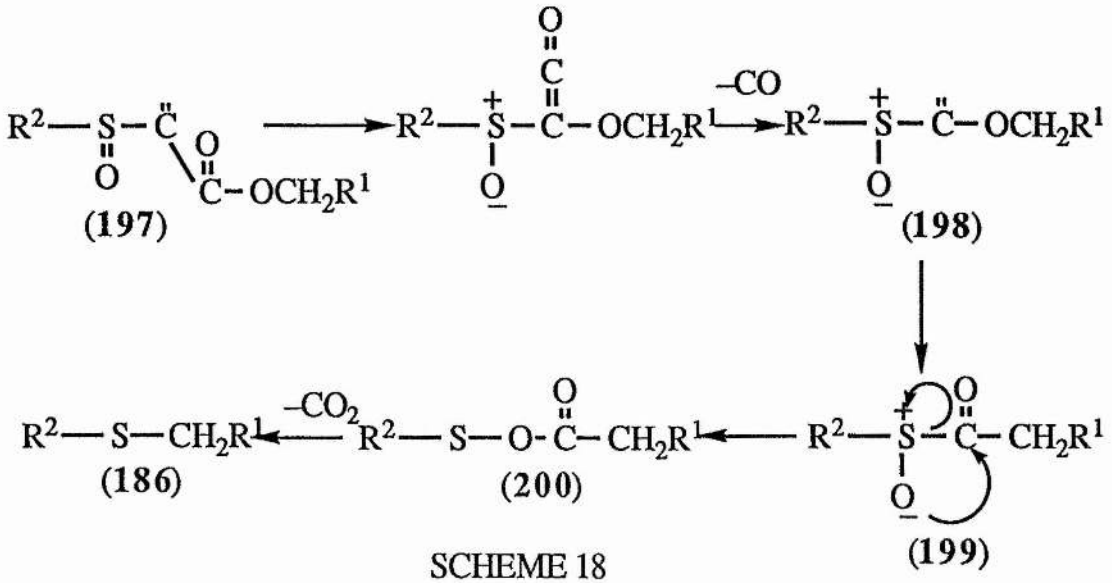
* Work carried out by J M Armstrong (Summer Project 1989)

280°C[145], which gave methyl acrylate (195) in 92% yield. At higher temperatures a similar process was observed, but was accompanied by a series of Wolff-rearrangements and decarbonylations as



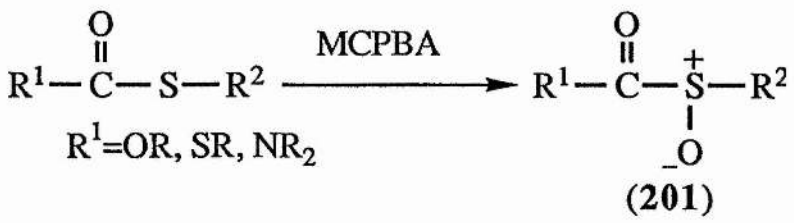
SCHEME 17

shown in Scheme 17. Thus in our case, Scheme 16 may be an over-simplification. For example alternative pathways for loss of triphenyl phosphine (Path B, Scheme 16) might be envisaged (Scheme 18). In this route to the alkyl sulphides (186), a Wolff rearrangement of the initially formed carbene (197) followed by loss of carbon monoxide gives the secondary carbene (198). This may rearrange to the α-ketosulphoxide (199), which via an S → O acyl migration, followed by loss of carbon dioxide, gives (186).



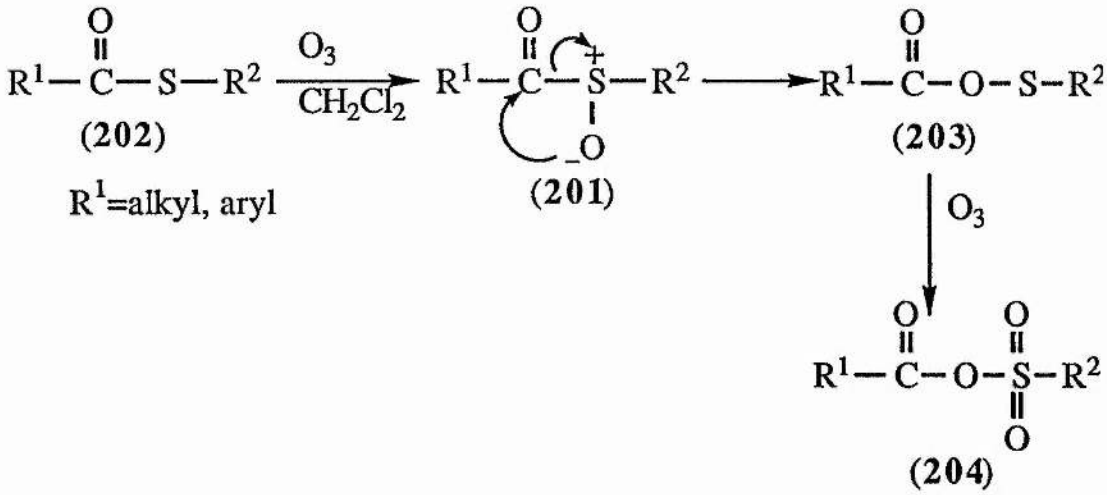
SCHEME 18

The α-ketosulphoxides (201) were first postulated as intermediates in thiol ester oxidation with either N-bromosuccinimide or iodosobenzene[146]. Stable representatives were prepared by Barton *et al*[147] by MCPBA oxidation of thiocarbonate O,S-diesters, dithiocarbonate S,S-diesters and N,N-disubstituted thiocarbamate S-esters, the stability of compounds (201) relying on the fact that R^1 is an electron donating substituent.



More interesting from our point of view is the rearrangement

observed by das Neves *et al*[148,149] in their attempted preparation of α-ketosulphoxides (201) by ozone oxidation of the thiolesters (202). They obtained the mixed sulphonic acid carboxylic acid anhydride (204) most probably arising from further oxidation of an intermediate acylsulphenate (203), itself originating from an S → O acyl shift of the



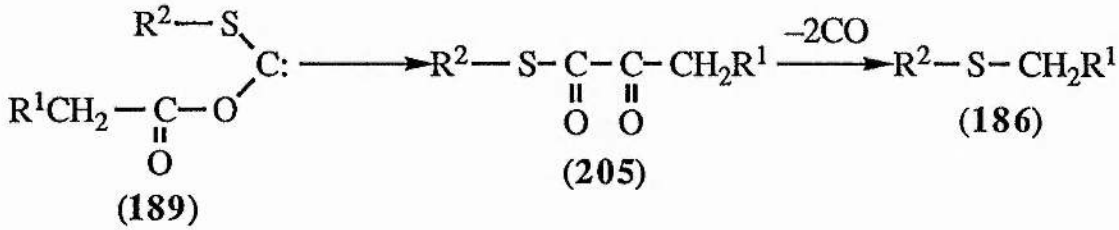
acyl group in the S-acyl sulphoxide (201).

Thus if as in Scheme 18, the S-acyl sulphoxide (199) is formed, rearrangement to an acylsulphenate (200) is possible. Then the loss of carbon dioxide under our reaction conditions can give the alkyl sulphide (186).

Though the rearrangements (199) to (200) and (201) to (203) have not to our knowledge been observed in the gas phase, high temperature FVP is an excellent medium for the observation of unusual and novel intramolecular processes. For example, the first observed gas phase Wolff

rearrangement mentioned above[145] required high temperature FVP. This was proved by the fact that other workers had observed no Wolff rearrangement of (196) at 140°C[150].

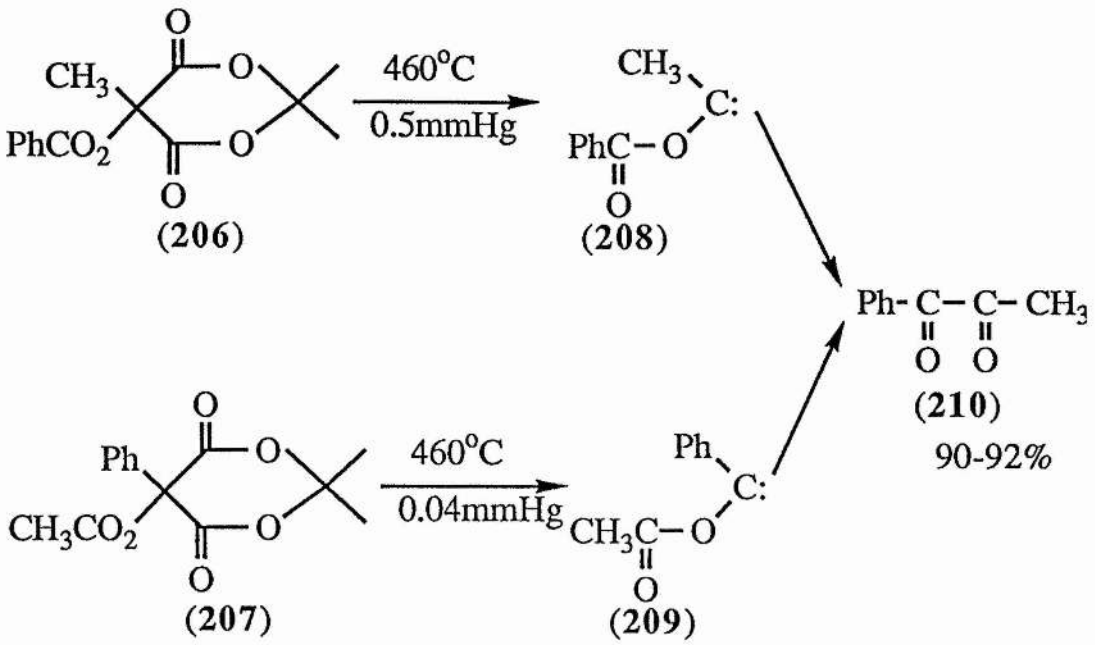
Another pathway to compounds (186) can be drawn in Scheme 19. The carbene (189) formed through path A (Scheme 16) and via an oxirene intermediate could rearrange to the diketone (205) which under the reaction conditions could lose two moles of carbon monoxide to give



SCHEME 19

the sulphide (186). The rearrangement (189) to (205) which is analogous to the rearrangement in Scheme 18 of (198) to (199) has literature precedent in the studies of Brown and co-workers[151]. They found that in the FVP of 5-acyloxy derivatives of Meldrums acid (206) and (207) the initially formed carbenes (208) and (209) undergo an acyl shift to give the diketone (210) in high yield.

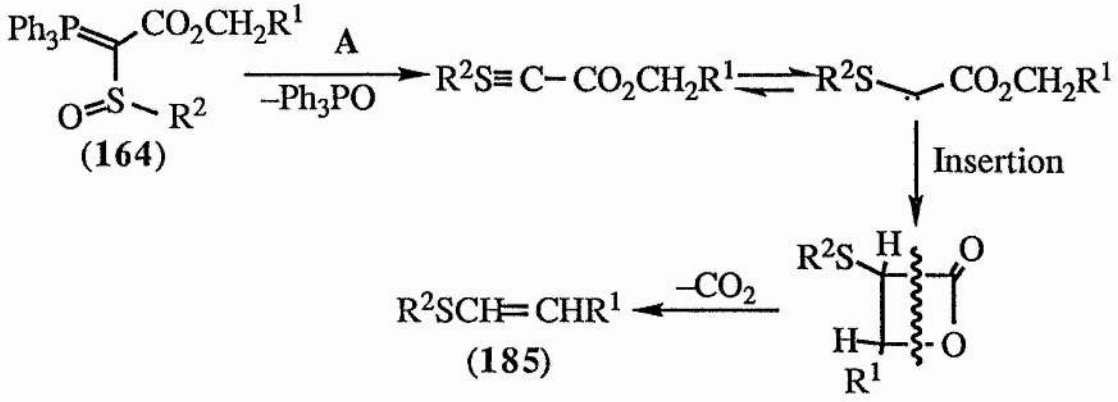
Importantly, Schemes 18 and 19 satisfy the criteria for ^{13}C N.M.R. enhancement in the FVP of ylides (190) and (191).



Two other peaks are enhanced in the ^{13}C N.M.R. of (190). The first is the carbonyl peak which implies that at some stage we obtain a stable compound by oxygen transfer from an adjacent carbonyl or sulphinyl group. The second is at δ_C 41.0, but the compound or compounds giving rise to these peaks remain unidentified.

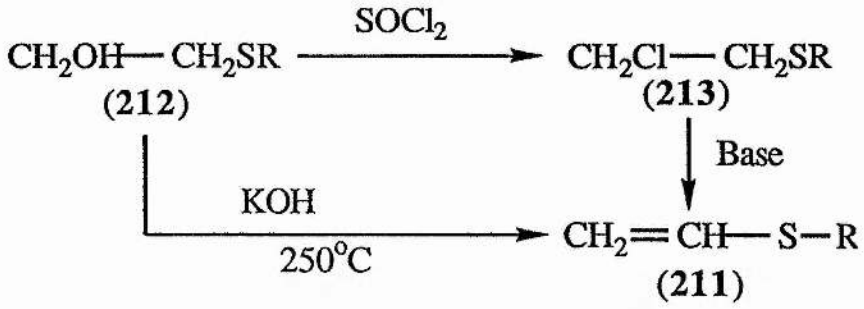
Thus from the above information our original proposed mechanism Scheme 16, has been superseded to a large degree by the mechanisms in Schemes 18 and 19, though as mentioned the carbonyl containing compound remains unknown. However from Scheme 16 the route to the vinyl and substituted vinyl sulphides still holds. This is particularly encouraging since as seen in Scheme 16 and below, the carbene, in which the insertion occurs, is in fact the carbene form of the C ≡ S thia-acetylene,

one of our original target groups.



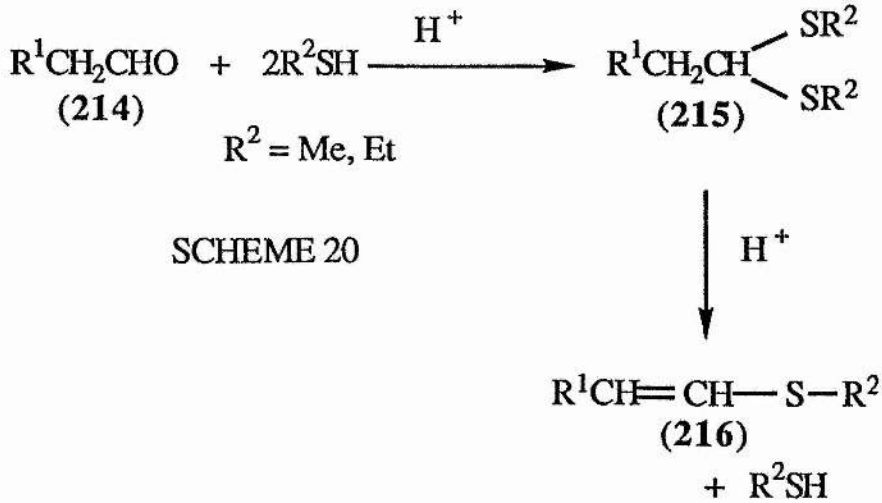
Over the years, a variety of methods have been developed for the synthesis of vinyl and substituted vinyl sulphides. In the case of the parent vinyl sulphides (211) one of the most used methods involves the condensation of vinyl bromide with the sodium salt of a thiol in a sealed

tube experiment[152,153]. The necessity of using vinyl bromide is avoided in preparing vinyl sulphides (211) via the β-hydroxyethyl sulphides (212)[154-157]. Heating (212) at 250°C in the presence of potassium hydroxide[154,155], or converting (212) into the β-chloroethyl sulphide (213) with thionylchloride followed by base induced elimination of HCl[156,157] gives the sulphides (211).



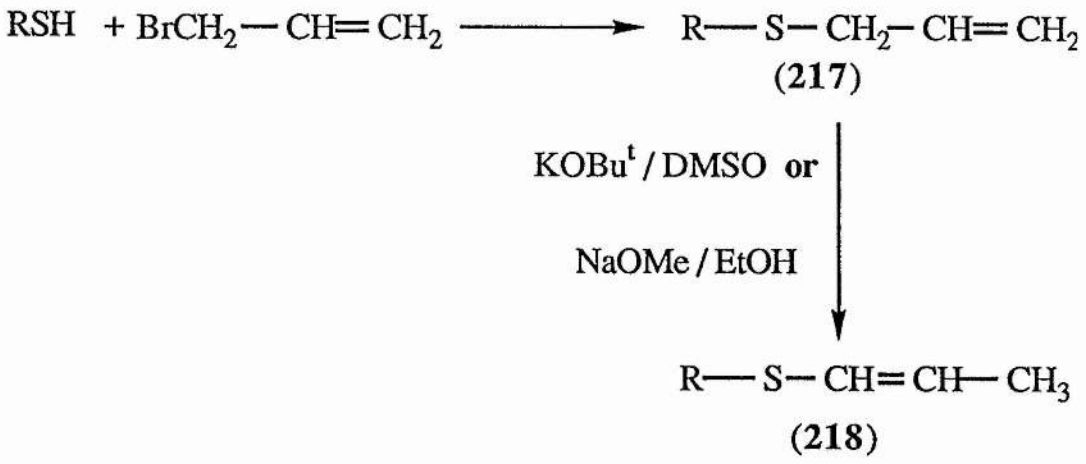
Boonstra *et al*[158] describes the preparation of methyl and ethyl vinyl sulphides from the reaction of acetaldehyde (214, R'=H) with two equivalents of thiol to give the dithioacetal (215, R'=H), which in the presence of acid, loses one equivalent of thiol to give the vinyl sulphide (216, R'=H) [Scheme 20]. This method was also employed with propionaldehyde (214, R'=CH_3) to give methyl- and ethyl propenyl sulphides in 28% and 41% yields respectively based on the starting aldehyde.

Propenyl sulphides have been prepared by similar methods to vinyl sulphides. Propenyl bromide with sodium salts of thiols give the

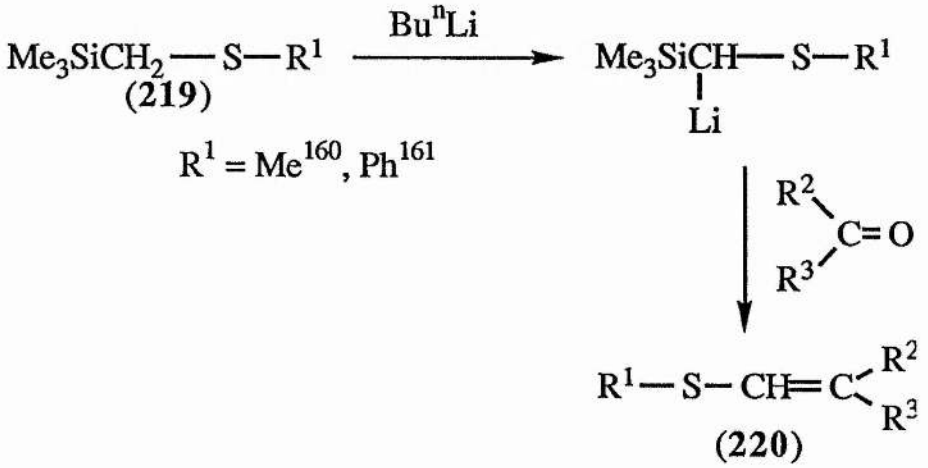


SCHEME 20

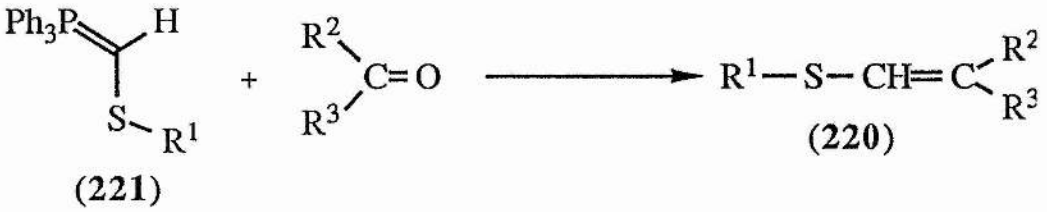
corresponding sulphides[152,153]. Similarly the isomerisation of allylsulphides (217), prepared from allyl bromide and sodium thiols, with potassium t-butoxide in DMSO or preferably sodium ethoxide in ethanol gives the propenyl sulphides (218).[90]



Trimethyl silyl substituted methyl sulphides (219)[159] can be readily lithiated with n-butyl lithium and subsequent reaction with aldehydes or ketones gives the vinyl sulphides (220)[160,161].

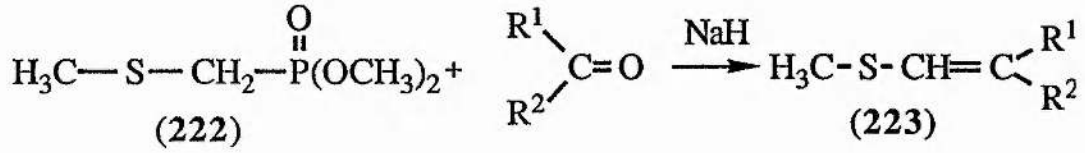


The reaction of carbonyl compounds with other reagents to produce double bonded species brings to mind the Wittig reaction. This has been used to produce vinyl sulphides. α-Sulphenyl triphenyl phosphoranes (221) are reacted with carbonyl compounds to give the vinyl sulphides



(221) (220)

(220)[94,133b,137]. Similarly the Wittig-Horner reaction has been employed by Shahak and Almog[162] to prepare methylvinyl sulphides (223). The reagent (222), prepared by the Arbusov reaction of chloromethyl methyl sulphide and trimethylphosphite, is reacted with aldehydes or ketones in the presence of sodium hydride to give the

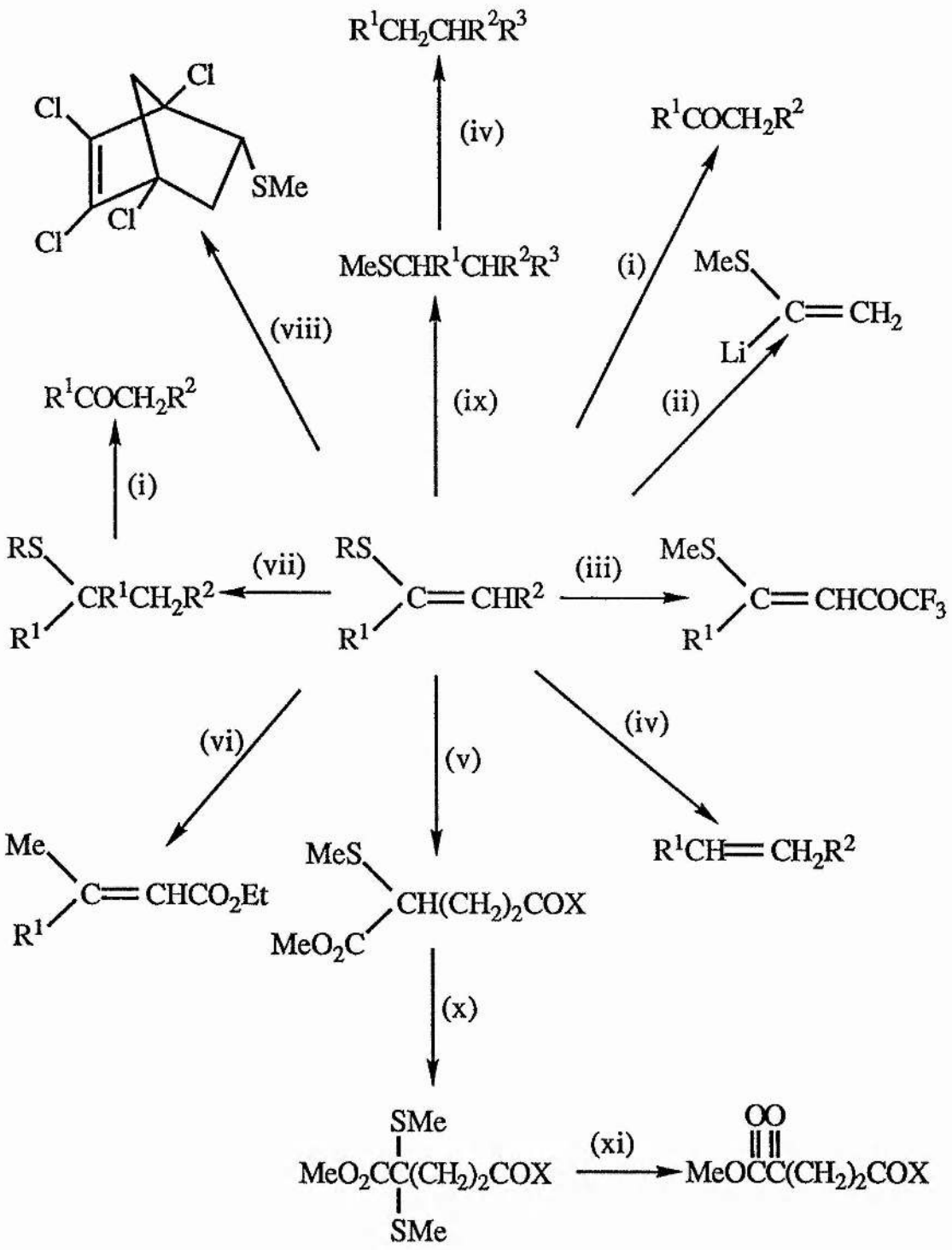


(222) (223)

sulphides (223).

The uses of vinyl sulphides are widespread and are especially important in a number of areas. Scheme 21 illustrates a number of reactions of these compounds[163]. A more detailed examination of some of these areas is warranted.

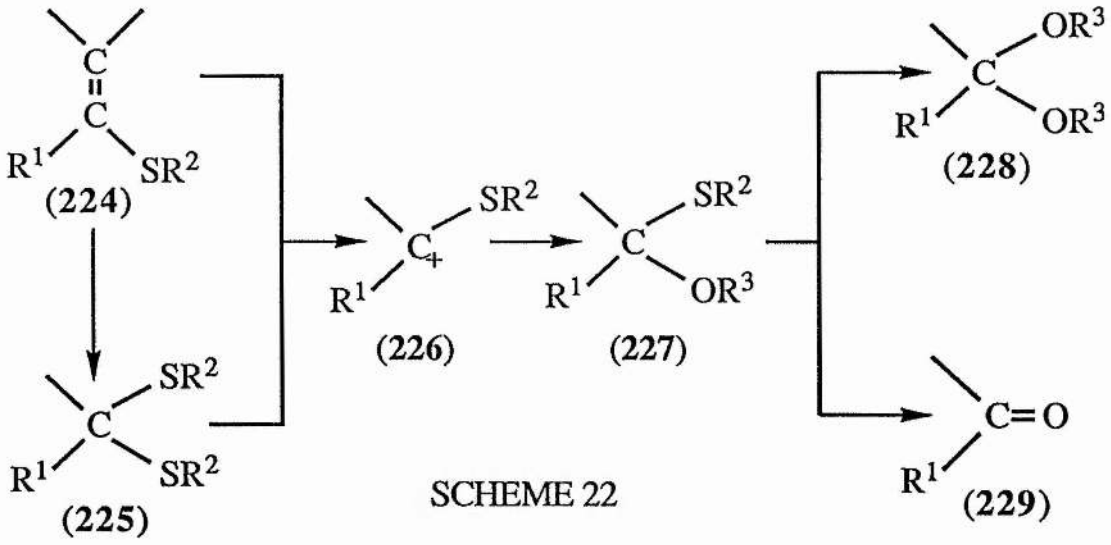
One of the most fruitful is in the umpolung of the reactivity of carbonyl



(i) $HgCl_2$, H_2O, MeCN or $TiCl_4$; HgO, H_2O, MeCN (R^1=H); (ii) Bu^sLi, –78°C, THF, HMPT (R^1=R^2=H); (iii) $(CF_3CO)_2O$ (R^2=H); (iv) Raney Ni; (v) Michael addition of $\bar{C}H_2COX$ (R^1=MeO_2C, R^2=H); (vi) Me_2CuLi (R= Ph, R^1=Me, R^2=CO_2Et); (vii) R^3SH, HCl; (viii) tetrachlorocyclopentadiene (R^1=R^2=H, R=Me); (ix) $R^3{}_2Cu$ (R=Me); (x) $LiNPr^i{}_2$, $TolSO_2SMe$; (xi) NBS, H_2O, MeCN.

SCHEME 21

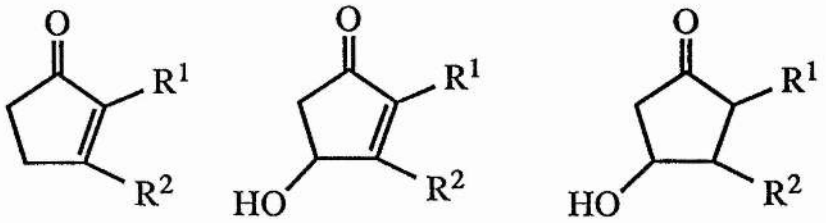
compounds[164]. The sulphides (224) themselves are used in many cases but these are also readily converted into the dithioacetals (225) which are extensively employed in such reactions. These reagents employed for



SCHEME 22

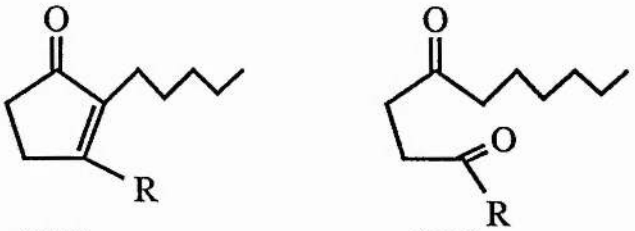
carbonyl umpolung must be hydrolysed, (Scheme 22), proceeding through the carbenium ion (226) to the monothioacetal (227) and finally to the products, acetals (228) or carbonyl compounds (229) depending on the reaction conditions. In umpolung reactions the reactivity of the acyl and adjacent carbon atoms is reversed compared to the normal carbonyl compound by the use of sulphur containing reagents.

The vinyl sulphides have found application in natural product synthesis. They can be used in the synthesis of 1,4-diketones which are important precursors to the jasmanoids (230), retrolonoids (231) and



(230) (231) (232)

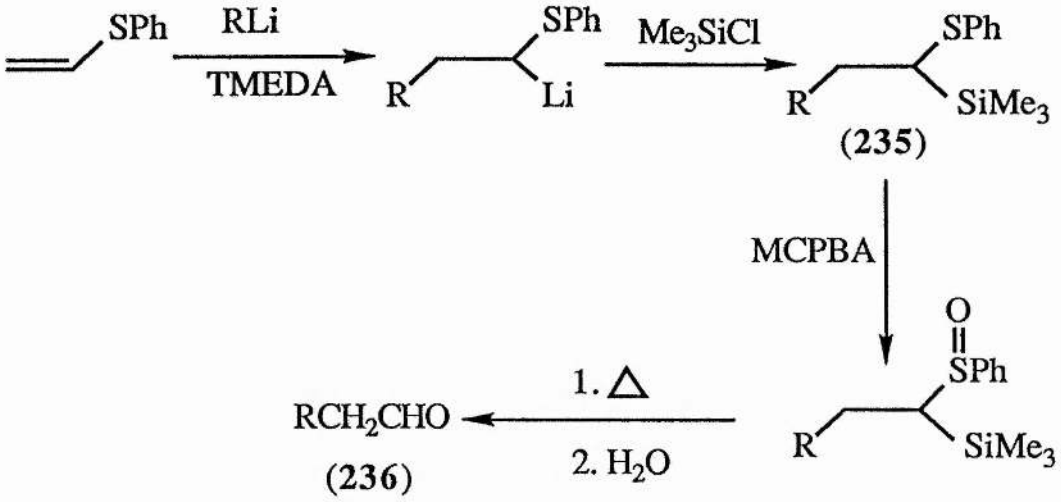
prostanoids (232). Cookson and Parsons[165] have synthesised the derivatives (233) in good yield, starting from phenyl vinyl sulphide and proceeding through the 1,4-diketone (234).



(233) (234)

The only drawback to the carbonyl umpolung reaction is that the hydrolysis step (Scheme 22) is often difficult. In the search for alternatives the synthesis of the 1-phenylthiotrimethylsilyl alkanes (235) has been developed[166] starting from phenyl vinyl sulphide. The alkanes (235) are readily oxidised to the sulphoxide and after thermal rearrangement, readily hydrolyse to the aldehydes (236)[167,168].

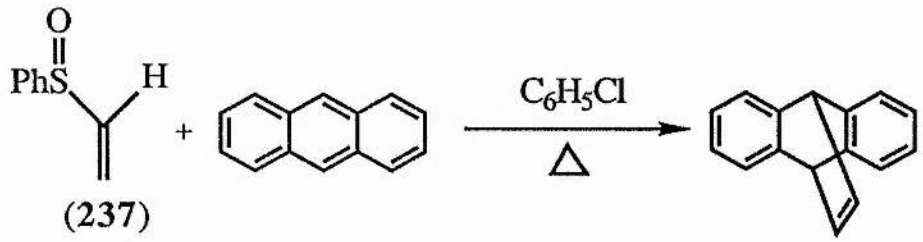
Another area of use for vinyl sulphides is via their oxidation to vinyl sulphoxides and sulphones and subsequent use as synthons for acetylene[169]



and ethylene[170,171] in Diels-Alder cycloadditions.

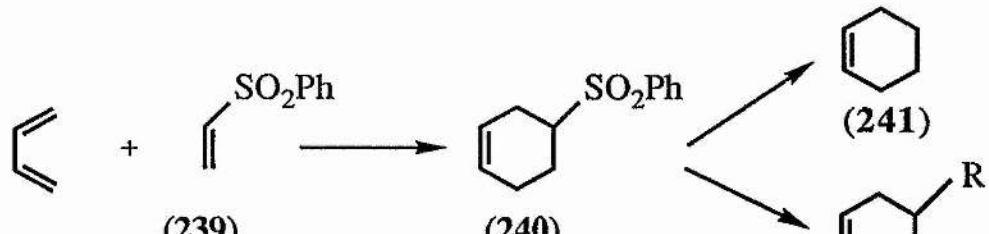
The search for an acetylene equivalent in Diels-Alder reactions has cast a wide net over the chemical literature. Over the years a wide variety of specialised and limited procedures have been reported. These have included; (a) dehydrobromination of vinyl bromide adducts[172], (b) sodium and zinc induced dechlorination of cis-1,2-dichloroethylene derived substrates[173], (c) thermal extrusion of cyclopentadiene from norbornadiene adducts[174], (d) cycloaddition of 2-substituted-1,3-dioxol-4- enes with reactive dienes followed by treatment with n-butyl lithium or trimethyl phosphite[175], (e) diene addition to dimethylacetylene dicarboxylate, hydrolysis and decarboxylation[173c], and (f) copper (I) promoted oxidative decarboxylation of vicinal dicarboxylic acids derived from cycloadducts of maleic anhydride[176]. All the methods (a)-(f) suffer the disadvantage of being multi-step processes requiring the isolation of intermediates followed by functional group manipulations as

well as proceeding in modest overall yields. In the case of phenyl vinyl sulphoxide the reaction is a single step procedure with high yields of adducts obtained. For example dibenzobarrelene (238) is obtained in 83% yield by heating phenyl vinyl sulphoxide (237) with anthracene in chlorobenzene at 130°C for 120h[169].



(237) (238)

Phenyl vinyl sulphone (239) can be employed as both an ethylene or 1-alkene synthon[170,171].

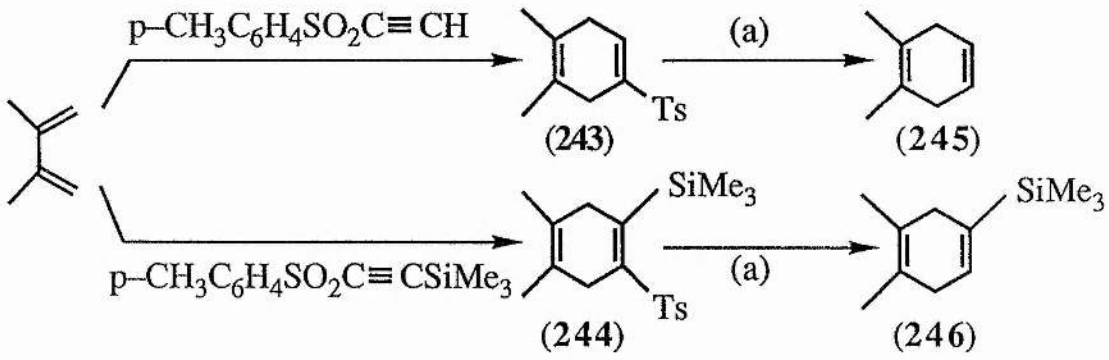


(239) (240) (241) (242)

The cycloadduct (240) can be subjected to reductive desulphonylation as a means of achieving ethylene equivalency to give (241), or since α-sulphonylcarbanions are readily formed, prior alkylation followed by reductive desulphonylation gives the adducts (242), formally a 1-alkene cycloadduct.

Other sulphonyl groups have been similarly reductively removed to provide an acetylene equivalent in Diels-Alder reactions. Davis and

Whitham[177] used ethynyl p-tolyl sulphone and p-tolyl 2-(trimethylsilyl)-ethynyl sulphone to give Diels-Alder adducts (243) and (244), which



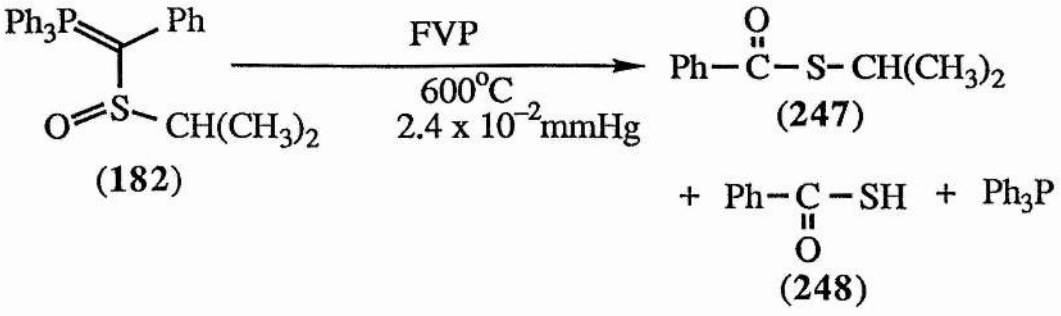
(a) Na–Hg, NaH_2PO_4, MeOH

after loss of p-toluenesulphinic acid give the derivatives (245) and (246) respectively.

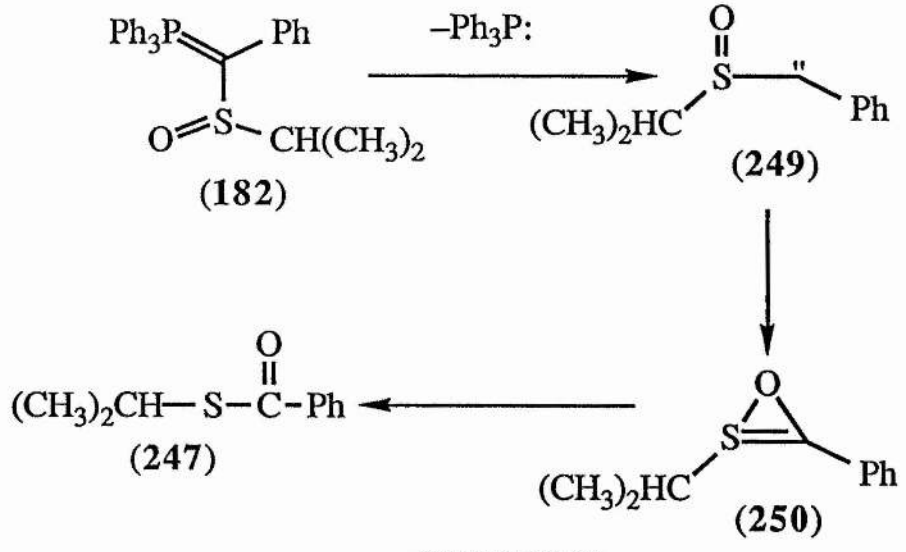
Thus substituted vinyl sulphides (185) after oxidation to sulphoxides or sulphones have the potential to be used as 1,2-substituted alkene or alkyne synthetic equivalents in Diels-Alder cycloadditions.

2. FVP of isopropylsulphinyl benzylidene triphenylphosphorane

The FVP of isopropylsulphinyl benzylidene triphenyl phosphorane (182) gave a 4:1 mixture of isopropylthiobenzoate (247) and thiobenzoic acid (248), plus triphenyl phosphine. This combination of products throws up a novel reaction mechanism.



The loss of triphenyl phosphine generates the carbene (249), and the transformation of (249) to the thioester (247) is rationalised via



SCHEME 23

the oxathiirene intermediate (250). The alternative charge transfer mechanism to explain loss of phosphine, as described for sulphonyl ylides, is discounted since an entirely different product mixture would be expected.

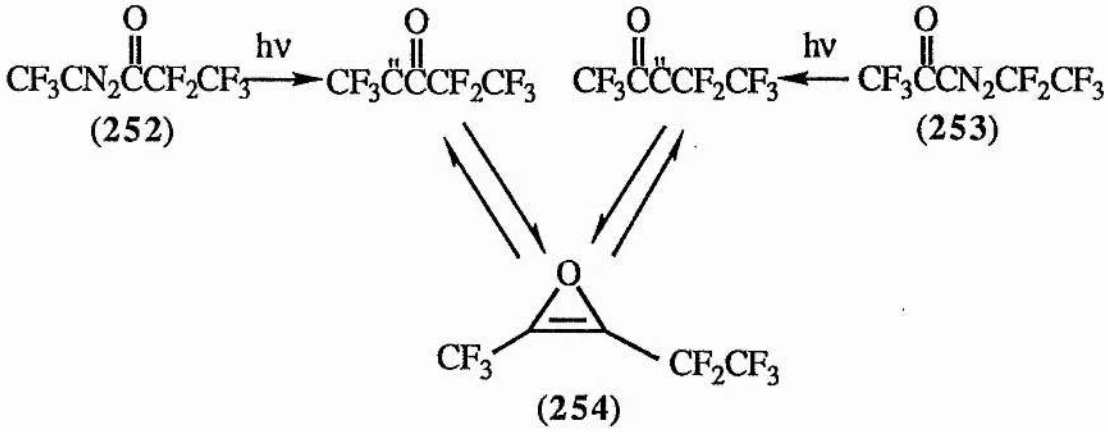
The suggested oxygen transfer mechanism in Scheme 23 via the

oxathiirene (250), is comparable to two related transient ring systems reported in the literature.

The first was observed in photochemical studies of α-diazoketones[178], where oxygen transfer occurs from intermediate

(251)

ketocarbenes, presumably via the 4-π-electron oxirenes (251). A similar

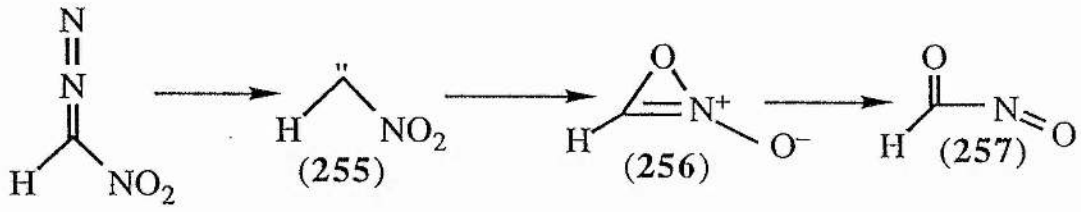


(252) (253) (254)

mechanism involving the oxirene (254) is proposed by Strausz *et al*[179] to explain the product distribution in their gas-phase photolysis studies of perfluoro α-diazoketones (252) and (253).

Secondly, experimental evidence exists to show that nitrocarbene (255) spontaneously rearranges into nitrosoformaldehyde (257) via an oxygen transfer mechanism which proceeds through the oxazirine-N-oxide

(256)[180,181].



Other 4-π-electron heterocyclic species such as thiirenes[182], 1-H germirenes[183], 1-H borirene[184] and selenirenes[182a,185] have been proposed as intermediates in a variety of thermal and photochemical processes. Other related species such as selenadiphosphirenes[186], thiadiphosphirenes[186] and triphosphirenes[187] are known in organometallic complexes. However to our knowledge this is the first observation of an oxathiirene 4-π-electron species *.

The formation of the thiobenzoic acid (248) is rationalised by loss of propene and hydrogen transfer from (247).

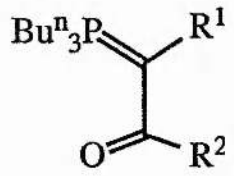
* Note : Since the original preparation of this manuscript two published examples of S to C oxygen transfer in sulphinyl carbenes have come to our attention[a,b]. In the second of these the authors postulate a dipolar λ^4-oxathiirane with + on S and – on C as the intermediate.

a. D. Dodson and G. Holt, *J. Chem. Soc.*,1968, 1602.

b. C.F. Ebbinghaus, P. Morrissey, and R.L. Rosati, *J. Org. Chem.*, 1979, **44**, 4697; D.H. Bremner and M.M. Campbell, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2298.

E Comparison of the Reactivity of Tri-n-butyl with Triphenyl Phosphonium Ylides

In the course of other studies in this lab[188] the furnace temperatures required to extrude triphenyl phosphine oxide during FVP, caused problems with the stability of the desired products. It is well known that in carrying out FVP reactions, the lower the furnace temperature at which the desired transformation occurs, the cleaner the reaction. Thus it was thought that by making the tri-n-butylphosphoranes (258) from the corresponding tri-n-butyl phosphonium salts, their pyrolysis, with



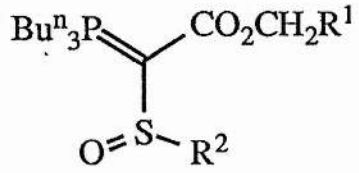
(258)

extrusion of tri-n-butyl phosphine oxide, could be achieved at lower temperatures than the corresponding triphenyl phosphoranes.

On FVP of (258), $R^1 = Pr^n$, R^2 =Ph at 500°C, only tri-n-butylphosphine oxide was observed at δ_p+48.56 At 300°C there was almost complete reaction, with the ratio of Bu^n_3PO:starting material being 15:1. Only when the FVP was carried out with the inlet tube attached directly to the cold trap did the ylide sublime across unchanged.

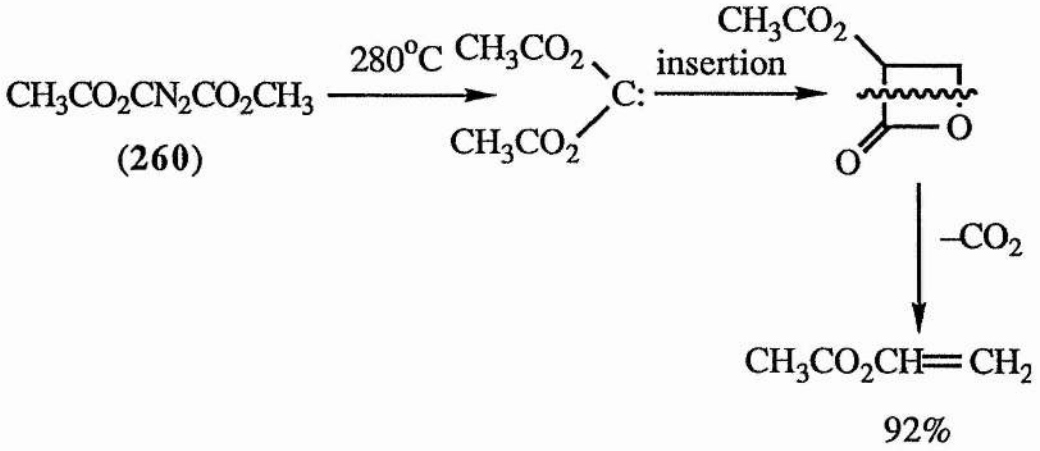
As a result of subsequent work by others in our lab[189], the synthesis of tri-n-butyl ylides, and in particular obtaining them in crystalline form, is

now an easier proposition than before. Thus it would be attractive to produce, for example, α-sulphinyl alkoxycarbonylmethylene tri-n-butyl phosphoranes (259) and investigate their FVP. From the results of



(259)

Richardson *et al*[145] on the FVP of dimethyldiazomalonate (260), lower temperatures favour the carbene insertion. Only at higher temperatures



(Scheme 17) was the Wolff rearrangement and decarbonylation observed. Analogously one might expect preferential formation of vinyl and substituted vinyl sulphides from the FVP of ylides (259) at lower furnace temperatures, greatly simplifying the mechanistic deductions, and making this a potentially useful route to these compounds.

Similarly for all the ylides used during this research the lower temperature required for extrusion of tri-n-butyl phosphine oxide would make for cleaner reactions a possible area for future investigation.

REFERENCES

1. C.D. Hurd, "The Pyrolysis of Carbon Compounds", Chem. Catalogue Co., New York, 1929.
2. R.F.C. Brown, "Pyrolytic Methods in Organic Chemistry", Academic Press, New York, 1980.
3. Reference 2, p.21.
4. E. Cuthbertson, and D.D. MacNicol, *Tetrahedron Lett.*, 1975, 1893.
5. J.C. Tou, C.S. Wang and E.G. Alley, *Org. Mass Spectrom.*, 1970, **3**, 747.
6. E. Hedaya, R.D. Miller, D.W. McNeil P.F. D'Angelo and P. Schissel, *J. Am. Chem. Soc.*, 1969, **91**, 1875.
7. R.J. Bushby and M.D. Pollard, *Tetrahedron Lett.*, 1977, 3671.
8. R.J. Bushby, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2513.
9. G.J. Baxter, R.F.C. Brown, F.W. Eastwood and K.J. Harrington, *Tetrahedron Lett.*, 1975, 4283.
10. R.F.C. Brown, F.W. Eastwood and G.L. McMullen, *Aust. J. Chem.*, 1977, **30**, 179.
11. R.F.C. Brown, F.W. Eastwood and K.J. Harrington, *Aust. J. Chem.*, 1974, **27**, 2373.
12. R.F.C. Brown, F.W. Eastwood, K.J.Harrington and G.L. McMullen, *Aust. J. Chem.*, 1974, **27**, 2393.
13. Reference 2, Ch. 5.
14. G. Seybold, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 365 and references cited therein.

15. G.M. Kaufman, J.A. Smith, G.G. Van der Stouw and H. Schechter, *J. Am. Chem. Soc.*, 1965, **87**, 935.

16. A.D. Wolf, V.V. Kane, R.H. Levin and M. Jones, *J. Am. Chem. Soc.*, 1973, **95**, 1680.

17. C. Wentrup, *Tetrahedron Lett.*, 1973, 2919.

18. C. Wentrup and P. Müller, *Tetrahedron Lett.*, 1973, 2915.

19. S.B. Cavitt, R. Sarrafizadeh and P.D. Gardner, *J. Org. Chem.*, 1962, **27**, 1211.

20. L.W. Jenneskens, W.H. de Wolf and F. Bickelhaupt, *Chem. Ber.*, 1986, **119**, 754.

21. L.W. Jenneskens, L.A.M. Turkenburg, W.H. de Wolf and F. Bickelhaupt, *Rec. Trav. Chim. Pays-Bas*, 1985, **104**, 184.

22. Reference 2, p.309-310 and references cited therein.

23. L. Horner and H. Oediger, *Chem. Ber.*, 1958, **91**, 437.

24. H. Diefenbach, H. Ringsdorf and R.E. Wilhelms, *J. Polymer Sci. B.*, 1967, **5**, 1039.

25. H. Hoffmann and H. Förster, *Tetrahedron Lett.*, 1963, 1547.

26. O.I. Kolodyazhnyi, *Zh. Obshch. Khim.*, 1976, **46** (10), 2386 [English translation, p.2285].

27. O.I. Kolodyazhnyi, *Zh. Obshch. Khim.*, 1977, **47** (4), 957 [English translation, p.872].

28. O.I. Kolodyazhnyi, *Zh. Obshch. Khim.*, 1977, **47** (9), 2159 [English translation, p.1971].

29. O.I. Kolodyazhnyi, *Zh. Obshch. Khim.*, 1977 **47** (10), 2390

[English translation, p.2185].

30. O.I. Kolodyazhnyi, *Zh. Obshch. Khim.*, 1979, **49** (1), 104 [English translation, p.88].

31. H. Hellmann and J. Bader, *Tetrahedron Lett.*, 1961, 724.

32. A.J. Speziale and K.W. Ratts, *J. Am. Chem. Soc.*, 1965, **87**, 5603.

33. A.M. Van Leusen, B.A. Reith, A.J.W. Iedema and J.Strating, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 37.

34. Y. Ito, M. Okono and R. Oda, *Tetrahedron* , 1967, **23**, 2137.

35. (a) W.E. Truce, R.W. Campbell and J.R. Norell, *J. Am. Chem. Soc.*, 1964, **86**, 288; (b) W.E. Truce and R.W. Campbell, *J. Am. Chem. Soc.*, 1966, **88**, 3599.

36. A.M. Hamid and S. Trippett, *J. Chem. Soc. C.*, 1968, 1612.

37. (a) A.M. Van Leusen, A.J.W. Iedema and J. Strating, *J. Chem. Soc. Chem. Commun.*, 1968, 440; (b) A.M. Van Leusen and J.C. Jagt, *Tetrahedron Lett.*, 1970, **967**, 971.

38. B.A. Reith, J. Strating and A.M. Van Leusen, *J. Org. Chem.*, 1974, **39**, 2728.

39. O.I.Kolodyazhnyi, L.I. Shevchuk and V.P. Kurkhar, *Zh. Obshch. Khim.*, 1977, **47** (3), 723 [English translation, p.658].

40. O.I. Kolodyazhnyi, *Zh. Obshch. Khim.*, 1982, **52** (7), 1538 [English translation, p.1358].

41. B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas.*, 1982, **101**, 1.

42. D.J. Alden, U.S. Pat. No.3 647 856, 1972.

43. N. Petragnani and M. de Moura Campos, *Chem. and Ind. (London)* ,

1964, 1461.

44. N. Petragnani, R. Rodrigues and J.V. Comasseto, *J. Organomet. Chem.*, 1976, **114**, 281.

45. M. Renard and L. Hevesi, *Tetrahedron*, 1985, **41**, 5939.

46. A.L. Braga, J.V. Comasseto and N. Petragnani, *Synthesis*, 1984, 240.

47. D. Seebach and N. Peleties, *Chem. Ber.*, 1972, **105**, 511.

48. S. Trippett and D.M. Walker, *J. Chem. Soc.*, 1959, 3874.

49. S.T.D. Gough and S. Trippett, *J. Chem. Soc.*, 1962, 2333.

50. S.T.D. Gough and S. Trippett, *J. Chem. Soc.*, 1964, 543.

51. (a) S. Akiyama, K. Nakasuji and Makagawa, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2231; (b) Y. Kobayashi, T. Yamashita, K. Takahashi, H. Kuroda and I. Kumadaki, *Tetrahedron Lett.*, 1982, 343; (c) A.D. Abell, G.W. Heinicke and R.A. Massy-Westropp, *Synthesis*, 1985, 764.

52. (a) P.A. Chopard, R.J.G. Searle and F.H. Devitt, *J. Org. Chem.*, 1965, **30**, 1015; (b) Y. Shen, W. Cen and Y. Huang, *Synthesis*, 1985, 159.

53. (a) G. Märkl, *Chem. Ber.*, 1961, **94**, 3005; (b) H.J. Bestmann and C. Geismann, *Liebigs Ann. Chem.*, 1977, 282.

54. Y.Z. Huang, Y. Shen, W. Ding and J. Zheng, *Tetrahedron Lett.*, 1984, 5283.

55. A.L. Braga, J.V. Comasseto and N. Petragnani, *Tetrahedron Lett.*, 1984, 1111.

56. R.A. Aitken and J.I. Atherton, *J. Chem. Soc., Chem. Commun.*, 1985, 1140.

57. (a) B. Pötter and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 150; (b) B. Pötter, K. Seppelt, A. Simon, E.M. Peters and B. Hettich, *J. Am. Chem. Soc.*, 1985, **107**, 980.

58. (a) O. Glemser and R. Mews, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 883 and references cited therein; (b) R.S. Atkinson and B.D. Judkins, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2615.

59. T.J. Maricich and V.L. Hoffmann, *J. Am. Chem. Soc.*, 1974, **96**, 7770.

60. (a) A. Baceiredo, G. Bertrand, J.P. Majoral, G. Sicard, J. Jaud and J. Galy, *J. Am. Chem. Soc.*, 1984, **106**, 6088; (b) A. Baceiredo, G. Bertrand, J.P. Majoral, F. El-Anba and G. Manuel, *J. Am. Chem. Soc.*, 1985, **107**, 3948; (c) J. Boske, E. Niecke, E. Ocando, E., J.P. Majoral andG. Bertrand, *Inorg. Chem.*, 1986, **25**, 2695.

61. G.M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds", Wiley-Interscience, New York, 1972, Vol. 2, p.190.

62. L. Horner. and A. Mentrup, *Liebigs Ann. Chem.*, 1961 , **646**, 65.

63. L. Bergel'son, V. Vaver, L. Barsukov and M. Shemyakin, *Izv. Akad. Nauk. SSR Otd. Khim. Nauk*, 1963, 1053.

64. G. Wittig and M. Schlosser, *Tetrahedron*, 1962, **18**, 1023.

65. R. McDonald and T. Campbell,, *J. Org. Chem.*, 1959, **24**, 1969.

66. A. Johnson and V. Kyllingstad, *J. Org. Chem.*, 1966, **31**, 334.

67. C. Griffen and M. Gorden, *J. Organomet. Chem.*, 1965, **3**, 414.

68. D.W. Pound and B.C. Saunders, British Pat. No. 628 796, 1949; *Chem.Abs.* 1950, **44**, 3224[b].

69. W. Davies and J.H. Dick, *J. Chem. Soc.*, 1932, 483.

70. W. Davies and J.H. Dick, *J. Chem. Soc.*, 1931, 2104.

71. L. Field and P.H. Settlage, *J. Am. Chem. Soc.*, 1954, **76**, 1222.

72. R.L. Shriner, H.C. Struck and W.J. Jorison, *J. Am. Chem. Soc.*, 1930, **52**, 2060.

73. D.L. Tuleen and V.C. Marcum, *J. Org. Chem.*, 1967, **32**, 204.

74. B.B. Jarvis and J.C. Saukaitis, *J. Am. Chem. Soc.*, 1973, **95**, 7708.

75. G. Wittig and U. Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.

76. E. Späth, *Monatsh..Chem.* 1914, **35**, 463.

77. A.Klages, *Chem. Ber.*, 1902, **35**, 2245.

78. T.R. Govindachari and B.R. Pai, *J. Org. Chem.*, 1953, **18**, 1253.

79. K. Kopp, *Chem. Ber.*, 1892, **25**, 600.

80. S. Cabiddu, A. Maccioni and M. Secci, *Ann. Chim. (Rome)*, 1964, **54**, 1153: *Chem. Abs.*, **63**, 4190f.

81. M. Cinquini and S. Colonna, *J. Chem. Soc. Perkin 1*, 1972, 1883.

82. F. Kurzer, *Org. Synth.*, 1954, **34**, 93.

83. J-H. Youn and R. Hermann, *Synthesis*, 1987, 72.

84. G. Aksnes andJ. Songstad, *Acta. Chem. Scand.*, 1964, **18**, 655.

85. H.J. Bestmann and P.J. Snyder, *J. Am. Chem. Soc.*, 1967, **89**, 3936.

86. O, Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser and P. Zeller, *Helv. Chim. Acta.*, 1957, **40**, 1242.

87. L.S. Trzupek, E.R. Stedronsky and G.M. Whitesides, *J. Org.*

Chem., 1972, **37**, 3300.

88. B.C. Hamper, *J. Org. Chem.*, 1988, **53**, 5558.

89. C.D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, 1930, **52**, 3356.

90. D.S. Tarbell and M.A. McCall, *J. Am. Chem. Soc.*, 1952, **74**, 48.

91. M. Kulka, *Can. J. Chem.*, 1958, **36**, 750.

92. A.I. Meyers and R.D. Walkup, *Tetrahedron*, 1982, **41**, 5089.

93. A. Speziale andL. Smith, *J. Am. Chem. Soc.*, 1962, **84**, 1868.

94. H.J. Bestmann, and B. Arnason, *Chem. Ber.*, 1962, **95**, 1513.

95. J.F. King, *Acc. Chem. Res.*, 1975, **8**, 10 and references therein.

96. A.W. Johnson, "Ylide Chemistry", Academic Press, New York, 1966, p.45.

97. Y. Kobayashi, T. Yamashita, K. Takahashi, H. Kuroda and I. Kumadaki, *Chem. Pharm. Bull.*, 1984, **32**, 4402.

98. Y. Shen and W. Qiu, *Synthesis*, 1987, 42.

99. (a)Y. Shen, Y. Xin, W. Cen and Y. Huang, *Synthesis*, 1984, 35; (b) Y. Shen, W. Qiu, Y. Xin and Y. Huang, *Synthesis*, 1984, 924.

100. Y. Shen, W. Cen and Y. Huang, *Synthesis*, 1987, 626.

101. Y. Shen, Y. Lin and Y. Xin, *Tetrahedron Lett.*, 1985, **26**, 5137.

102. H.J. Bestmann, *Angew. Chem. Int. Ed. Engl.*, 1965, **4**, 645.

103. R.A. Aitken and G. Burns, *Tetrahedron Lett.*, 1987, **28**, 3717.

104. (a) D.A. Dixon and B.E. Smart, *J. Am. Chem. Soc.*, 1986, **108**, 2688; (b) T. Grelbig, B. Pötter and K. Seppelt, *Chem. Ber.*, 1987, **120**, 815; (c) D. Christen, H-G. Mack, C.J. Marsden, H. Oberhammer, G. Schatte, K. Seppelt and H. Willner, *J. Am. Chem.*

Soc., 1987, **109**, 4009.

105. (a) W.D. Hinsberg, P.G. Schultz and P.B. Dervan, *J. Am. Chem. Soc.*, 1982, **104**, 766 and references therein; (b) A.P. Sylwester and P.B. Derivan, *J. Am. Chem. Soc.*, 1984, **106**, 4648.

106. A. Igau, H. Grutzmacher, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1988, **110**, 6463.

107. J. Sauer, *Angew. Chem. Int. Ed. Engl.*, 1967, **6**, 16.

108. B. Zwanenburg, L. Thijs, J.B. Broens and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 443.

109. A.A.Freer, G.W. Kirby and R.A. Lewis, *J. Chem. Soc., Chem. Commun.*, 1987, 718.

110. W.A. Sheppard and J. Diekmann, *J. Am. Chem. Soc.*, 1964, **86**, 1891.

111. J. Strating, L. Thijs and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 641.

112. L.A. Carpino and J.R. Williams, *J. Org. Chem.*, 1979, **44**, 1177.

113. M. Kobayashi and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2733.

114. U. Annen and M. Regitz, *Tetrahedron Lett.*, 1987, 5141.

115. E.P.O. Fuchs, W. Rösch and M. Regitz, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 1011.

116. R.J. Mulder, A.M. Van Leusen and J. Strating, *Tetrahedron Lett.*, 1967, 3057.

117. B.E. Sarver, M. Jones Jr. and A.M. Van Leusen, *J. Am. Chem. Soc.*,

1975, **97**, 4771.

118. H. Staudinger and F. Pfenninger, *Chem. Ber.*, 1916, **49**, 1941.

119. T. Nagai and N. Tokura, *Int. J. Sulfur Chem. B.*, 1972, **7**, 207.

120. N.H. Fischer, *Synthesis,* 1970, 393.

121. H. Nozaki, M. Takaku and Y. Hayasi, *Tetrahedron Lett.*, 1967, 2303.

122. H. Nozaki, M. Takaku, Y. Hayashi and K. Kondo, *Tetrahedron*, 1968, **24**, 6536.

123. J. Ide and Y. Yura, *Tetrahedron Lett.*, 1968, 3491.

124. W.K. Bushfield and K.H. Ivin, *Trans. Faraday Soc.*, 1961, **57**, 1044.

125. R.A. Marty and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 1971, 127.

126. L.C. Raifordand S.E. Hazlet, *J. Am. Chem. Soc.*, 1935, **57**, 2172.

127. E. Knoevenagel and L. Polack, *Chem. Ber.*, 1908, **41**, 3323.

128. H. Bredereck, A. Wagner, E.H. Beck, H. Herlinger and K-G. Kottenhahn, *Angew. Chem.*, 1958, **70**, 268.

129. H. Bredereck, A. Wagner, E.H. Beck and R.J. Klein, *Chem. Ber.*, 1960, **93**, 2736.

130. J.L. Kice and K. Ikura, *J. Am. Chem. Soc.*, 1968, **90**, 7378.

131. W.A. Sheppard, *J. Am. Chem. Soc.*, 1962, **84**, 3058.

132. E.W. Lawless and L.D. Harman, *Inorg. Chem.*, 1968, **7**, 391.

133. (a) G. Wittig and M. Schlosser, *Angew Chem.*, 1960, **72**, 324; (b) G. Wittig and M. Schlosser, *Chem. Ber.*, 1961, **94**, 1373.

134. A.A. Grigorenko, M.I. Shevchuk and A.V. Dombrovsky, *Zh. Obshch. Khim.*, 1966, **36** (6), 1121; *Chem.Abs.* , 1966, **65**, 12230.

135. E. Zbiral and E. Werner, *Angew Chem.*, 1967, **79**, 89.

136. H. Saikachi and S. Nakamura, *Yakugaku Zasshi*, 1968, **88** (6), 715; *Chem.Abs.*, 1968, **69**, 106824m.

137. T. Mukaiyama, S. Fukuyama and T. Kumamoto, *Tetrahedron Lett.*, 1968, 3787.

138. I.B. Douglass and B.S. Farah, *J. Org. Chem.*, 1958, **23**, 330; *Org. Synth.*, 1961, **40**, 62.

139. I.B. Douglass and R.V. Norton, *J. Org. Chem.*, 1968, **33**, 2104.

140. H.J. Bestmann, G. Joachim, I. Lengyel, J.F.M. Oth, R. Merényi and H. Weitkamp, *Tetrahedron Lett.*, 1966, 3355.

141. D.M. Crouse, A.T. Wehman and E.E. Schweizer, *J. Chem. Soc., Chem. Commun.*, 1968, 866.

142. H.I. Zeliger, J.P. Snyderand H.J. Bestmann, *Tetrahedron Lett.*, 1969, 2199.

143. J.P. Snyder, *Tetrahedron Lett.*, 1971, 215.

144. R.J. Abraham, J. Fisher and P. Loftus, "Introduction to N.M.R. Spectroscopy", John Wiley and Sons Ltd., 1988, p.194-197

145. D.C. Richardson, M.E. Hendrick and M. Jones Jr., *J. Am. Chem. Soc.*, 1971, **93**, 3790.

146. T. Kumanoto and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2111.

147. D.H.R. Barton, D.P. Manley and D.A. Widdowson, *J. Chem. Soc.*,

Perkin Trans. 1, 1975, 1568.

148. H.J.C. das Neves and M.F. Machete, *Tetrahedron Lett.*, 1977, 187.

149. M.J. Sousa Lobo and H.J.C. das Neves, *Tetrahedron Lett.*, 1978, 2171.

150. J. Gelhaus and R.W. Hoffmann, *Tetrahedron*, 1970, **26**, 5901.

151. R.F.C. Brown, F.W. Eastwood, S.T. Lim and G.L. McMullen, *Aust. J. Chem.*, 1976, **29**, 1705.

152. J. Loevenich, J. Losen and A. Dierichs, *Chem. Ber.*, 1927, **60**, 950.

153. W.E. Truce, H.E. Hill and M.M. Boudakian, *J. Am. Chem. Soc.*, 1956, **78**, 2760.

154. J.F. Arens, H.C. Volger, T. Doornbos, J. Bonnema, J.W. Greidanus and J.H. van den Hende, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 1459.

155. T.F. Douman, U.S. Patent 2 402 878; *Chem.Abs.*, 1946, **40**, 649b^{6}.

156. C.C. Price and H. Morita, *J. Am. Chem. Soc.*, 1953, **75**, 4747.

157. C.C. Price and R.G. Gilles, *J. Am. Chem. Soc.*, 1953, **75**, 4750.

158. H.H. Boonstra, L. Brondsma, A.M. Wiegman and J.F. Arens, *Recl. Trav. Chim. Pays-Bas*, 1959, **78**, 252.

159. D.J. Peterson, *J. Org. Chem.*, 1967, **32**, 1717.

160. D.J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.

161. F.A. Carey and A.S. Court, *J. Org. Chem.*, 1972, **37**, 939.

162. I. Shahak and J. Almog, *Synthesis*, 1969, 170.

163. D.H.R. Barton and W.D. Ollis, "Comprehensive Organic Chemistry", Vol.3, p.82

164. D. Seebach and B-T. Gröbel, *Synthesis*, 1977, 357 and references cited therein.

165. R.C. Cookson and P.J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1976, 990.

166. D.J. Ager, *Tetrahedron Lett.*, 1981, 587.

167. P.J. Kocienski, *Tetrahedron Lett.*, 1980, 1559.

168. D.J. Ager and R.C. Cookson, *Tetrahedron Lett.*, 1980, 1677.

169. L.A. Paquette, R.E. Moerck, B. Harirchian and P.D. Magnus, *J. Am. Chem. Soc.*, 1978, **100**, 1597.

170. R.V.C. Carr and L.A. Paquette, *J. Am. Chem. Soc.*, 1980, **102**, 853.

171. R.V.C. Carr, R.V. Williams and L.A. Paquette, *J. Org. Chem.*, 1983, **48**, 4976.

172. J. Sauer, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 211.

173. (a) S.J. Cristol and N.L. Hause, *J. Am. Chem. Soc.*, 1952, **74**, 2193; (b) S.J. Cristol and R.K. Bly, ibid., 1960, **82**, 6155; (c) H.P. Figeys and A. Dralants, *Tetrahedron*, 1972, **28**, 3031.

174. K.J. MacKenzie, *J. Chem. Soc.*, 1960, 473.

175. W.K. Anderson and R.J. Dewey, *J. Am. Chem. Soc.*, 1973, **95**, 7161.

176. R.A. Snow, C.R. Degenhardt and L.A. Paquette, *Tetrahedron Lett.*, 1976, 4447.

177. A.P. Davis and G.H. Whitham, *J. Chem. Soc., Chem. Commun.*, 1980, 639.

178. (a) I.G. Csizmadia, J. Fontand O.P. Strausz, *J. Am. Chem. Soc.*,

1968, **90**, 7360; (b) J. Fenwick, G. Frater, K. Ogi and O.P. Strausz, *ibid.*, 1973, **95**, 124.

179. Mahaffy, P.G., Visser, D., Torres, M., Bourdelande, J.L. and Strausz, O.P., *J. Org. Chem.*, 1987, **52**, 2680.

180. P.E. O'Bannon and W.P. Dailey, *Tetrahedron Lett.*, 1988, 987.

181. P.E. O'Bannon and W.P. Dailey, *Tetrahedron Lett.*, 1988, 5719.

182. (a) A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, 1977, **99**, 4842; (b) A. Krantz and J. Laureni, *ibid.*, 1981, **103**, 486.

183. E.B. Norsoph, B. Coleman and M. Jones Jr., *J. Am. Chem. Soc.*, 1978, **100**, 994.

184. J.J. Eisch, *Govt. Rep. Announce. (U.S.)*, 1972, **72**, 59; *Chem.Abs.*, 1973, **78**: 96987m.

185. M. Harrit, S. Rosenkilde, B.D. Larsen and A. Holme, *J. Chem. Soc., Perkin Trans. 1*, 1985, 907.

186. M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Chem. Soc. ,Dalton Trans.*, 1984, 359.

187. M. Peruzzini and P. Stoppioni, *J. Organomet. Chem.*, 1985, **288**, 44.

188. S. Seth and R.A. Aitken, unpublished observations.

189. H.R. Cooper and R.A. Aitken, unpublished results.