PREPARATION AND PYROLYSIS OF SOME SULPHINYL-STABILISED PHOSPHOROUS YLIDES

Bruce Martin Ryan

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

1996

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PREPARATION AND PYROLYSIS OF SOME SULPHINYL-STABILISED PHOSPHORUS YLIDES

by

BRUCE MARTIN RYAN, B. Sc.

Thesis presented for the degree of Doctor of Philosophy

University of St. Andrews May, 1995
DECLARATIONS

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

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

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

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

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

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TO ALYSSA, HANNAH AND EWAN

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

ACKNOWLEDGEMENTS

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

I am very grateful for the help of members of the technical staff of the department, particularly Melanja Smith and Colin Millar.

I also want to record my sincere gratitude to Craig, Dave, Elly, Jack, Jane, Janice, Julian, Kathy, Lena, the Mariannes, Matt, Matthew, Mhairi, Ro, Rosie, the Sandras, Trina, Yvonne and Zena who have been deeply entwined in the kinks in my learning curve and to the people who lent me lecture notes in undergraduate days (Derek, Ros, Sharon, Pamela).

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

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

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

The results of further investigation into the pyrolytic behaviour of alkane- and arenesulphinyl alkoxy carbonyltriphosphoranes are reported. Flash vacuum pyrolysis (FVP) of these ylides at 600°C gives vinyl sulphides, sulphides and aldehydes. The vinyl sulphides and aldehydes are explained by assuming extrusion of Ph₃P=O, followed by C–H insertion in the resulting carbene to give a β-lactone. This can either lose CO₂ to give the vinyl sulphides or fragment in the opposite sense to give the aldehydes together with unknown products. The sulphides are explained by assuming extrusion of Ph₃P, followed by successive loss of CO and CO₂. A variable temperature study of Ph₃P=C(CO₂Et)SOEt has revealed a complex pattern of interdependent restricted rotation of both ester and sulphinyl groups.

FVP of the alkanesulphinylbenzylidenetriphenylphosphoranes at 500°C gives the alkyl thiolobenzoates by oxygen transfer in the carbene formed by extrusion of Ph₃P. The first three examples of arenesulphinyl benzylidenetriphenylphosphoranes have been prepared. FVP of these at 500°C gives a mixture containing aryl thiolobenzoates formed as above together with ketones, sulphides, thiols, disulphides and stilbene. Mechanisms are suggested for the formation of these products.

Four new alkyl sulphonyldiazoacetates have been prepared. FVP of these at 600°C gives vinyl sulphones, while at lower temperatures, products resulting from transfer of oxygen in the carbenes formed by extrusion of N₂ predominate.
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xix R¹ = But, R² = p-Me-C₆H₄ (phosphorane as base) 78
2 FVP of

\[
\begin{array}{c}
\text{Ph}_3\text{P} \text{CO}_{2}\text{R}^1 \\
\text{O} \text{S} \text{R}^2
\end{array}
\]

\[
\begin{array}{ll}
i & R^1 = \text{Et}, R^2 = \text{Et} \\
ii & R^1 = \text{Et}, R^2 = \text{Ph} \\
iii & R^1 = \text{Me}, R^2 = \text{Me} \\
iv & R^1 = \text{PhCH}_2, R^2 = \text{Pr}^1 \\
v & R^1 = \text{PhCH}_2, R^2 = \text{Ph} \\
vi & R^1 = \text{PhCH}_2, R^2 = p-\text{Cl-C}_6\text{H}_4 \\
vii & R^1 = \text{PhCH}_2, R^2 = p-\text{Me-C}_6\text{H}_4 \\
viii & R^1 = \text{Bu}^t, R^2 = p-\text{Me-C}_6\text{H}_4 \\
ix & R^1 = \text{Bu}^t, R^2 = p-\text{Cl-C}_6\text{H}_4
\end{array}
\]

3 Preparation of authentic samples of FVP products

\[
\begin{array}{ll}
i & \text{ethyl prop-2-enyl sulphide} \\
ii & \text{ethyl prop-1-enyl sulphide} \\
iii & \text{ethyl prop-2-enyl sulphone}
\end{array}
\]

D Attempted preparation of alkane and arene-
sulphinyl and sulphenyl diazoacetates

1 Preparation of diazo-transfer reagents

\[
\begin{array}{ll}
i & p-\text{toluenesulphonyl azide} \\
ii & 4-(\text{N-acetylamino})\text{benzenesulphonyl azide}
\end{array}
\]
2 Preparation of sulphenyl acetates

\[
\text{Ar} + \text{CO}_2\text{R}^1 \rightarrow \text{CO}_2\text{R}^1\text{Ar}
\]

a (ethanesulphenyl)acetyl chloride

b \(R^1 = \text{CO}_2\text{Me}, R^2 = \text{Et}\)

c \(R^1 = \text{CO}_2\text{Et}, R^2 = \text{Et}\)

d \(R^1 = \text{CO}_2\text{Me}, R^2 = \text{Ph}\)

e \(R^1 = \text{CO}_2\text{Et}, R^2 = \text{Ph}\)

3 Preparation of alkane- and arenesulphinylacetates

\[
\text{CO}_2\text{R}^1\text{S}\]

i \(R^1 = \text{CO}_2\text{Me}, R^2 = \text{Et}\)

ii \(R^1 = \text{CO}_2\text{Et}, R^2 = \text{Et}\)

iii \(R^1 = \text{CO}_2\text{Me}, R^2 = \text{Ph}\)

iv \(R^1 = \text{CO}_2\text{Et}, R^2 = \text{Ph}\)

4 Attempted preparation of alkane- and arenesulphinyl diazoacetates

\[
\text{N}_2\text{CO}_2\text{R}^1\text{S}\]

a \(R^1 = \text{Et}, R^2 = \text{Et}\)

b \(R^1 = \text{Me}, R^2 = \text{Ph}\)

c \(R^1 = \text{Et}, R^2 = \text{Ph}\)

i via TsN₃

ii via p-MeCONH-C₆H₄SO₂TsNa

5 Attempted preparation of benzenesulphinyl(phenyl)diazomethane

\[
\text{PhS}\]

i triethylamine as base

ii n-butyl lithium as base
6 Attempted preparation of alkyl benzenesulphonyldiazoacetates

a $R^1 = \text{Me}$

b $R^1 = \text{Et}$

i $\text{Et}_3\text{N}$ as base

ii NaH as base

iii LDA as base

E Preparation and pyrolysis of arenesulphinyl-benzyldiene triphenylphosphoranes

1 Preparation

a Phosphonium salts $\text{Ph}_3\text{P}^+\text{CH}_2\text{Ar} \text{Hal}^-$

i $\text{Ar} = \text{Ph}$

ii $\text{Ar} = p\text{-NO}_2\text{C}_6\text{H}_4$

iii $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$

b Preparation of $\text{Ph}_3\text{P}^+\text{Ar} \text{O}^\ominus\text{S}^-\text{R}$

i $\text{Ar} = \text{Ph}$, $R = \text{Ph}$

ii $\text{Ar} = \text{Ph}$, $R = p\text{-Me-C}_6\text{H}_4$

iii $\text{Ar} = \text{Ph}$, $R = p\text{-Cl-C}_6\text{H}_4$

iv $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$, $R = \text{Ph}$

v $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$, $R = p\text{-Me-C}_6\text{H}_4$

vi $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$, $R = p\text{-Cl-C}_6\text{H}_4$

vii $\text{Ar} = p\text{-NO}_2\text{C}_6\text{H}_4$, $R = p\text{-Me-C}_6\text{H}_4$

viii $\text{Ar} = p\text{-NO}_2\text{C}_6\text{H}_4$, $R = p\text{-Cl-C}_6\text{H}_4$
2 FVP of

\[ \text{FVP of } \begin{array}{c}
\text{Ar} \\
\text{R}
\end{array} \begin{array}{c}
\text{Ar} \\
\text{R}
\end{array} \begin{array}{c}
\text{Ar} \\
\text{R}
\end{array} \begin{array}{c}
\text{Ar} \\
\text{R}
\end{array} \]

a \quad \text{Ar} = \text{Ph}, \text{R} = \text{Ph} 

b \quad \text{Ar} = \text{Ph}, \text{R} = p-\text{Me-C}_6\text{H}_4 

c \quad \text{Ar} = \text{Ph}, \text{R} = p-\text{Cl-C}_6\text{H}_4 

3 Preparation and pyrolysis of authentic samples of FVP products

a Preparation of benzophenones 

i \quad p-\text{Cl-C}_6\text{H}_4\text{COPh} 

ii \quad p-\text{Me-C}_6\text{H}_4\text{COPh} 

b FVP of benzophenones 

i \quad p-\text{Cl-C}_6\text{H}_4\text{COPh} 

ii \quad p-\text{Me-C}_6\text{H}_4\text{COPh} 

c Preparation of thiobenzophenones \text{RCSPh} 

i \quad \text{R} = \text{Ph} 

ii \quad \text{R} = p-\text{Cl-C}_6\text{H}_4 

iii \quad \text{R} = p-\text{Me-C}_6\text{H}_4 

d Preparation of thiolobenzoates \text{PhCOSR} 

i \quad \text{R} = \text{Ph} 

ii \quad \text{R'} = p-\text{Cl-C}_6\text{H}_4 

iii \quad \text{R'} = p-\text{Me-C}_6\text{H}_4 

e FVP of thiolobenzoates 

i \quad \text{R'} = p-\text{Cl-C}_6\text{H}_4 

ii \quad \text{R'} = p-\text{Me-C}_6\text{H}_4 


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xi. R₁ = p-NO₂-C₆H₄, R₂ = Pri 122
xii. R₁ = p-NO₂-C₆H₄, R₂ = CH₂Ph 122
2 FVP of \[ \begin{align*} & \text{R}^1 & \text{R}^2 \\
& Ph & Ph \\
& Ph & Et \\
& Ph & Pr \\
& Ph & CH_2Ph \\
\end{align*} \]

a \( R^1 = Ph, R^2 = Et \) 123
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v \( R^1 = Ph, R^2 = p-Me-C_6H_4 \) 127
vi \( R^1 = Ph, R^2 = p-Cl-C_6H_4 \) 128
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iv $R^1 = Ph, R^2 = p-Cl-C_6H_4$ 135

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viii $R^1 = CO_2Me, R^2 = Ph$ 138

ix $R^1 = CO_2Et, R^2 = Ph$ 138

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i via TsN$_3$ 139

ii via $p$-MeCONHC$_6$H$_4$SO$_2$N$_3$ 140

b $R^1 = CO_2Et, R^2 = Et$ 140

i via TsN$_3$ 140

ii via $p$-MeCONHC$_6$H$_4$SO$_2$N$_3$ 141

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\[
\begin{array}{c}
\text{N}_2\text{CO}_2\text{Et} \\
\text{O}_2\text{S}\text{Et}
\end{array} \xrightarrow{\text{Ph}_3\text{P}}
\begin{array}{c}
\text{PhP}\text{CO}_2\text{Et} \\
\text{O}_2\text{S}\text{Et}
\end{array}
\]
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1 Preparation of \[ \text{Ph}_3\text{P}^\ominus \text{Ar} \]
2 FVP of \[ \text{Ph}_3\text{P}^\ominus \text{Ar} \]

C Preparation and pyrolysis of alkanesulphinylarylidene triphenylphosphoranes
1 Preparation of \[ \text{Ph}_3\text{P}^\ominus \text{Ar} \]
2 FVP of \[ \text{Ph}_3\text{P}^\ominus \text{Ar} \]

D Preparation and pyrolysis of alkane- and arenesulphonylaryl diazomethanes
1 Preparation of \[ \text{N}_2=\text{R}^1 \]
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INTRODUCTION
A Flash Vacuum Pyrolysis

1 Techniques and apparatus

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

What was needed was for the pyrolytic reaction to take place away from the bulk of substrate and for the products to be collected elsewhere. A step
towards this was made with Hurd's apparatus for the generation of ketene in which acetone is vapourised by immersing the pyrolysis vessel in boiling water. The vapour is led through a hot tube containing broken porcelain where the decomposition takes place and excess acetone is condensed from the gas stream by passage through a vertical water condenser.

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

\[
\text{Spangler introduced the idea of sweeping the substrate along on a stream of nitrogen to prevent products from condensing around the hot zone.} \\
\text{Brown and Solly pyrolysed indanetrione in a stream of benzene through a vertical furnace to give biphenylene, naphthalene and acetylene.} \\
\text{These products were assumed to be formed via benzyne. Similarly, Cava and co-workers found that phthalic anhydride gave biphenylene on low pressure pyrolysis.}
\]
Finally, the desire to probe short-lived intermediates led several groups to the idea of flash vacuum pyrolysis (FVP). The idea is very similar to the acetone $\Rightarrow$ ketene apparatus, except the pressure in the apparatus is kept very low ($10^{-3}$ to $10^{-4}$ torr), and the substrate is sublimed through the hot zone under the influence of this vacuum and gentle heating of the substrate container. In all cases the idea is to supply a dilute stream of substrate into a hot zone where (unimolecular) reactions can occur. Products can be fed directly into analytical equipment or trapped on liquid nitrogen cold fingers, rare gas matrices, or collected for further work.

One of the first reports was from Hedaya and McNeil. They investigated the FVP of phenyl allyl ether 3 and found this produced hexa-1,5-diene 4 (13% at 954°C), cyclopentadiene (3%), allylcyclopentadiene 5 (36%), naphthalene (1%), phenol (7%) and benzene (1%). It is interesting to note that there was no sign of any Claisen-rearranged product.

$$\begin{align*}
&\text{3} \\
\rightarrow & \text{4} + \text{5} + \text{CH}_2\text{CH}=	ext{CH}_2 \\
& + \text{C}_\text{6} \text{H}_{\text{5}} \text{C}_\text{6} \text{H}_{\text{5}} + \text{C}_\text{6} \text{H}_6 + \text{C}_\text{6} \text{H}_6
\end{align*}$$
Crow and Solly used a similar system to pyrolyse phenyl hydrazones. These gave aniline and phenylisocyanide. The apparatus was essentially similar to that shown at the beginning of the experimental section.

\[
\begin{array}{c}
\text{Ph—NH}_2 \quad \text{Ph—NH} \quad \text{Ph—N—Ph} \quad \text{Ph—CN} + \text{Ph—NHR}
\end{array}
\]

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

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

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

2 **FVP Reactions**

Reactions can be classified in several ways, depending on whether the important point is the product, the mechanism or the intermediates. The following is a necessarily brief outline of the major sorts of reaction that have been performed under FVP conditions.
a Extrusion of small molecules
i SO₂ extrusion

Probably the best known work in this area is Vogtle’s work on the preparation of cyclophanes.¹⁵ However SO₂ loss can happen in many ways and has recently been reviewed.¹⁶ A few examples are given.

The thiazolidin-2-one-1,1-dioxide 6 loses SO₂ in an electrocyclic reaction to give benzyl isocyanate, allyl benzene and bibenzyl.¹⁷

\[
\begin{align*}
\text{Ph} & \quad \text{PhCH}_2^* \quad \text{Ph} \\
\text{Ph} & \quad \text{PhCH}_2^* \\
\text{6} & \quad \text{PhN} = \text{C} = \text{O} + \text{Ph} \\
& \quad + \text{SO}_2
\end{align*}
\]

Similarly, the sulphate 7 gave hydroxydibenzofuran 8 whereas the related sulphite 9 gave dibenzofuran 10, xanthone 11 and 3,4-benzocoumarin 12.¹⁸
The benzothiazepine dioxide 13 gave the tetrahydroquinoline\(^1\), and loss of \(\text{SO}_2\) from the simple bicyclic system 14 gave 1,5-hexadiene.\(^2\)

![Diagram of the reaction between 13 and 14](image)

**ii  \(\text{H}_2\) and alkane extrusion**

There is a great contrast in ease of loss of \(\text{H}_2\) from 1,3- and 1,4-cyclohexadiene. The former gives benzene via a radical mechanism; the latter goes by 1,4-elimination.\(^2\) Similar effects occur with benzo-fused systems.\(^2\)

![Diagram of the dehydrogenation of cyclohexadiene](image)

The dehydrogenation of triquinacene 15 to give azulene 16 involves an interesting series of rearrangements.\(^2\)

![Diagram of the dehydrogenation of triquinacene](image)
A striking reaction occurs in the pyrolysis of 4-ethyltoluene. The carbene "jumps" into the ring and styrene is given by an "aryl carbene walk" mechanism.\textsuperscript{24}

![Chemical diagram]

iii  \(\alpha\)-Elimination from esters

This has been observed in cases when \(\beta\)-elimination is not possible, such as the example noted by Brown.\textsuperscript{25}

![Chemical diagram]

FVP of dioxole 17 gives the acetylene in 24\% yield.\textsuperscript{26} This is related to the conventional pyrolysis of dioxolanes 18 derived from 1,2-diols to give the corresponding alkenes.\textsuperscript{27}
iv  β-Elimination from esters and similar species

This is seen in systems that can give appropriate 6-membered transition states such as S-alkyl xanthates\(^{19}\) 19, thiono-\(^{20}\) 20 and thioloacetates\(^{29}\) 21, dialkylcarbonates\(^{30}\) 22, alkyl carbamates\(^{31}\) 23 and imidates\(^{32}\) 24.

![Chemical structures]

There is some argument over the amount of ion pair character in the TS, especially when the reaction is carried out in conditions where the reactor surface would stabilise such a pair.\(^{33}\)

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

![Chemical reactions]
v  **γ-Eliminations from esters**

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

\[
\begin{align*}
\text{Me} & \quad \rightarrow \quad \text{Me} \\
\text{Me} & \quad \rightarrow \quad \text{Me}
\end{align*}
\]

vi  **H-Hal elimination**

A notable example is the synthesis of phospha-acetylene by FVP of MePCl₂.

\[
\text{MePCl}_2 \xrightarrow{1000^\circ C} 2\text{HCl} + \text{HC≡P}
\]

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

b Formation of reactive intermediates

i Ketenes

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

\[
\text{CH}_3\text{CO}_2\text{H} \xrightarrow{\text{750°C}} \text{H}_2\text{C}=\text{C}=\text{O} \xrightarrow{(\text{MeCO})_2\text{O}} \text{H}_2\text{O}
\]

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

Recently, Wentrup and co-workers have shown that pyrolysis of 5-cyclopentylidene Meldrum’s acid does not entirely follow this scheme. In addition to the formation of benzene via cyclopentylidene carbene, the ketenes 31, 32 and 33 were observed by low temperature IR.44
Variations on the methyleneketene cyclisation (dubbed "the McMullen reaction") outlined below have been used to prepare substituted dibenzofurans such as $34^{45}$ and pyrrolones $35^{46}$ and $36^{47}$.

This approach has also been used to prepare bicyclic hydroxypyrazoles.$^{48}$

Decarbonylation of ketenes to give carbenes is quite common$^{49}$ and ketenes can also be formed by 1,2- and 1,4-elimination of ROH from esters. Leyendecker used these ideas to prepare a fused cyclopentanone via a keto-carbene.$^{50}$
An example of a 1,4-elimination that serves to point towards some of the other types of reaction encountered in FVP work is the pyrolysis of 2-(methoxycarbonyl)phenol 37. The ketene formed can be trapped with alcohol or left to undergo further reactions.\textsuperscript{51}

\begin{equation}
\begin{aligned}
\text{OMe} &\rightarrow \text{MeOH} \\
\text{37} &\rightarrow \text{\textbullet \text{CO}} \\
&\rightarrow \text{+2H} \\
&\rightarrow \text{OH} \\
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\text{Cyclobutadiene} \\
\text{The history of the search for cyclobutadiene has been chronicled by Cava and Mitchell.}^\text{52} \text{Although cyclobutadiene was first obtained by oxidation of the iron complex Fe(CO)}_3(\text{C}_4\text{H}_4)\text{38}\text{, FVP syntheses are known. FVP of 38 gave acetylene, vinylacetylene, butadiene, benzene, cyclooctatetraene and styrene, and this product mixture is indicative, if not conclusive proof, that cyclobutadiene has been formed.}^\text{54}
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\text{Fe(CO)}_3 &\rightarrow \text{450-700°C} \\
&\rightarrow 0.001\text{mmHg} \\
\text{38} &\rightarrow \text{Hedaya pyrolysed photo-α-pyrone 39 and analysed the gas phase products directly by MS.}^\text{55} \text{Cyclobutadiene was detected at m/z=52. Subsequently the pyrolysis was repeated in a normal FVP apparatus: the}
\end{aligned}
\end{equation}
product mixture, especially syn-tricyclo[4.2.0.02.5]octa-3,7-diene 40, left little doubt that cyclobutadiene had been formed.

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

Kobayashi has “conventionally” pyrolysed 41 to get the syn dimer 43 of tetrakis(trifluoromethyl)cyclobutadiene 42⁵⁷, whereas Warrener found that FVP at 700°C of the same substrate gave the anti dimer of 42, tetrakis(trifluoromethyl)butatriene and bis(trifluoromethyl) acetylene.⁵⁸
FVP of the complex 44 gives the isomer 45. It was suggested that the two acetylene units undergo metathesis to give a transient tricyclo species. The CoCp unit then hops along the π-cloud and the now vacant cyclobutadiene opens up to form two acetylenes.59

iii Cyclopentadienone and similar molecules
FVP of p-benzoquinone gives vinyl acetylene.60 Dewar-cyclopentadienone has been postulated as an intermediate but no cyclopentadienone dimer was observed.

A synthetically useful process is decarbonylation of the quinone 46. This presumably goes by the path shown and is thus able to lead to reliably labelled naphthalenes.61
Similar decarbonylation processes are known for o-phenylene sulphite\textsuperscript{18} and carbonate.\textsuperscript{62} The sulphite reaction was discovered in an attempt to prepare cyclobutadiene.

\[ \text{Sulphite reaction} \]

iv Carbenes

A major feature in FVP studies is the formation of carbenes. Some examples have been seen above but it is worthwhile considering some specific examples. A reaction that is pertinent to the present work is the intra-molecular insertion of bis(methoxycarbonyl)carbene. Extrusion of CO\textsubscript{2} from the resulting \( \beta \)-lactone then leads to the acrylate ester.\textsuperscript{63}

\[ \text{Carbene reaction} \]

The most fascinating examples of carbene rearrangements are the reversible acetylene-carbene rearrangements (recently reviewed by Brown\textsuperscript{64}) and the related "aryl carbene walk" and benzyne-cyclopentadienylidene process. The former has recently been used by Scott to prepare corannulene \textsuperscript{47}.\textsuperscript{65}
The transient existence of cyclopentadienylidene car bene 50 has been deduced from the formation of benzene and biphenylene by pyrolysis of norbornenylidene Meldrum's acid 48 over hydrogen-donating bitumen.\(^{66}\) 50 had been postulated as an intermediate in the pyrolysis of benzocyclo butenedione.\(^{67}\)

![Diagrams of chemical reactions](attachment:diagrams.png)

Brown has performed some elegant hydrocarbon syntheses by fragmentation of substituted phthalic anhydrides. One such is triphenylbenzopentalene 51.\(^{68}\)

![Fragmentation of cyclic molecules](attachment:fragmentation.png)

c **Fragmentation of cyclic molecules**

i **Three and four-membered rings**

Halocyclopropenes were observed to open cleanly on pyrolysis to the corresponding allenes.\(^{69}\)
FVP comes into its own with the preparation of very unstable molecules in the gas phase. Thus silaethene 52 has been prepared and characterised by Barton and McIntosh by FVP of 53 and trapping the products at -196°C.70

\[
\begin{align*}
\text{Me}_2\text{Si} & \longrightarrow \text{Me}_2\text{Si} = \text{CH}_2 + \text{H}_2\text{C} = \text{CH}_2 \\
53 & \quad 52
\end{align*}
\]

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

\[
\begin{align*}
\text{H}_3\text{C} - & + \xi = + \text{O} \\
54 & \rightarrow 55
\end{align*}
\]

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

\[
\begin{align*}
\text{Me}_2\text{C} = = \text{O} & \rightarrow \text{Me}_2\text{C} = \text{C} \rightarrow \text{Me}_2\text{C} = \text{O} \\
\text{H}_3\text{C} - & + \text{H}_2\text{C} = \text{CH}_2
\end{align*}
\]

Pyrolytic preparation of alkyl ketenes was achieved by Brown and Baxter.73
FVP of azetidine 56 was used to produce methanimine 57 and thietane and dithietane oxides 58 – 60 have been pyrolysed to produce the relevant sulphines.

\[ \text{HN} \xrightarrow{\geq 400^\circ} \text{HN}=\text{CH}_2 + \text{H}_2\text{C}=\text{CH}_2 \]

\[ \text{O} \xrightarrow{\geq 600^\circ} 2\text{H}_2\text{C}=\text{S}=\text{O} + \text{H}_2\text{C}=\text{CH}_2 \]

\[ \text{N=S} \xrightarrow{500^\circ} \text{H}_2\text{C}=\text{S}=\text{O} + \text{H}_2\text{C}=\text{S} \]

\[ \text{O} \xrightarrow{400^\circ} 2\text{Me}_2\text{C}=\text{S} + \text{Me}_2\text{C}=\text{S}=\text{O} \]

Wentrup has investigated the valence isomerism between 61 and 62.

\[ \xrightarrow{X=O,S} \]

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

A number of interesting alkenes have been prepared by pyrolysis of substituted norbornenes. These include 71\textsuperscript{77} and 72\textsuperscript{78}. Pyrolysis of the related formal furan adducts 73 (obtained by alkaline peroxide oxidation of the corresponding enones) gave the relevant cyclopentadienone-epoxides 74\textsuperscript{79}.

Roth and co-workers attempted to synthesise butatriene 75 from substituted norbornadienes and related compounds 76 a–d. 76 a and b gave the desired product in 80 and 100\% yields respectively\textsuperscript{80}.
Bourdon, Ripoll and Vallée obtained 77 by FVP of 78. The isopropyl compound mostly tautomerises to 79 while the parent compound stays as the ketone-thioketone tautomer.\textsuperscript{81}

\[
\begin{align*}
\text{R} = \text{H, Me} & \quad \overset{\text{O}}{\text{C}} \quad \text{S} \\
\text{R}_2\text{HC} & \quad \rightarrow \quad \overset{\text{O}}{\text{C}} \quad \text{R}_2\text{HC} \\
\text{S} & \quad \rightarrow \quad \overset{\text{O}}{\text{C}} \quad \text{R}_2\text{C} \quad \text{SH}
\end{align*}
\]

Benzocyclobutanedione was prepared from 80 via the intermediate azocarbonyl compound 81.\textsuperscript{82}

\[
\begin{align*}
\text{80} & \quad \rightarrow \quad \text{81} \\
\text{81} & \quad \rightarrow \quad \text{82}
\end{align*}
\]

1-methylpentalene 82 was obtained by pyrolysing 83, which was prepared by base-catalysed cyclisation of 84. The dimer 85 can also be dissociated by FVP.\textsuperscript{83}

\[
\begin{align*}
\text{84} \quad \overset{\text{MeNH}}{\text{MeOH}} & \quad \rightarrow \quad \text{83} \\
\text{83} & \quad \overset{650^\circ\text{C}}{0.005\text{mm}} \quad \rightarrow \quad \text{82} \\
\text{82} & \quad \overset{>150^\circ\text{C}}{\text{FVP}} \quad \overset{700^\circ\text{C}}{700^\circ\text{C}} \quad \rightarrow \quad \text{85}
\end{align*}
\]
iii Elimination of aromatic residues

Another attempted route to carbonylcyclopropane was the pyrolytic cycloreversion of 86. Again, the temperature needed to achieve the cycloreversion was too high and the products were vinyl ketene, methyl acetylene and allene.\(^{84}\)

\[
\begin{array}{ccc}
\text{O} & \text{C} = \text{C} & \text{H} \\
\text{86} & 750^\circ\text{C} & 0.001\text{mm} \\
\end{array}
\]

\[
\text{C}_{10} \text{H}_{10} \text{O} + \text{CH}_{2} = = = \text{O} + \text{CH} = \text{C} + \text{C} = \text{C} \\
35\% \quad 52\% \quad 13\%
\]

Rippoll and Thuillier were more successful in their preparation of pentatetraene.\(^{85}\) Pentatetraene is unstable, with a half-life of 20min in solution. Nevertheless, they recorded a 70% yield with the balance being pentadiyne.

\[
\begin{array}{ccc}
\text{H} & \text{C} = \text{C} & \text{H} \\
\text{H} & 700^\circ\text{C} & 0.001\text{mm} \\
\end{array}
\]

\[
\text{CH}_{2} = = = \text{C} + \text{H}_{2} \text{C} = = = \text{CH} + \text{H}_{2} \text{C} = = = \text{C} 
\]

Similarly, doubly labelled acetylene was produced by pyrolysis of the tetrafluorobenzyne-1-methoxynapthalene adduct.\(^{86}\)

\[
\begin{array}{ccc}
\text{O} & \text{C} = \text{C} & \text{H} \\
\text{86} & \text{C}_{6}\text{F}_{4} & \text{C}_{6}\text{F}_{4} \\
\end{array}
\]

\[
\text{C}_{10} \text{H}_{8} \text{O} + \text{CH}_{2} = = = \text{D} + \text{C}_{10} \text{H}_{8} \text{O} \\
\text{600}^\circ\text{C} \quad 0.05\text{mm} \\
^* = 13\text{C}
\]
Pyrolysis of [2,2]paracyclophane gives p-xylylene \( 87 \). A strong coat of polymerised \( 87 \) ("Parylene") can be deposited directly onto substrates from a gaseous stream of \( 87 \).

\[
\begin{align*}
\text{Pyrolysis} & \quad \begin{array}{c}
\text{[2,2]paracyclophane} \\
\xrightarrow{600^\circ C, 0.1 \text{mm}}
\end{array} \\
& \quad \begin{array}{c}
p-\text{xylylene } 87
\end{array}
\end{align*}
\]

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

\[
\begin{align*}
\text{Pyrolysis} & \quad \begin{array}{c}
\text{anthracene adduct} \\
\xrightarrow{650^\circ C, 10^{-6} \text{torr}}
\end{array} \\
& \quad \begin{array}{c}
\text{vinyl phosphine } 88
\end{array}
\end{align*}
\]

iv Retro-ene reactions

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

Similarly, de Mayo has produced cyclohexanethione and other delicate thiocarbonyl compounds by pyrolysis of allylic sulfides and Block and Reveille have prepared silacyclobutenes such as \( 92 \).
d Rearrangement without loss

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

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

Butadiene-2,3-dicarboxylic acid 94 has been formed by FVP of the cyclobutene diester 95 followed by ester hydrolysis.94
In a similar manner, ring opening reactions (which retain all the atoms), followed by decarbonylation or rearrangement have given tropone\textsuperscript{95} and hydroxyacenaphthalenone \textsuperscript{96,96}.

The following heterocyclic example of ring closure gives oxazete \textsuperscript{97}. Pyrolysis at a slightly higher temperature leads to acyclic products.\textsuperscript{97}

\[
\text{OAc} \quad \text{I} \quad \text{I} \quad \text{I}
\]

Formation of some relatively inaccessible heterocycles has been pioneered by Weber.\textsuperscript{98} Arylbutadienes are formed by pyrolytic extrusion of acetic acid from 4-aryl-4-acetylbut-1-enes. Spontaneous rearrangement and loss of H\textsubscript{2} leads to the dihydrobicyclic and aromatised products.
The pyrolysis of the 3-pyridyl species is interesting since the product mix includes a small amount of quinoline. The rearrangement shown below, starting from the intermediate 98, is postulated to account for this.

Examples of internal Diels-Alder reactions include Nomura's work on bicyclo[4.2.1]nona-trienes. Similarly, in Claisen rearrangement of allyl and propargyl aryl ethers, the resulting dienones can react intramolecularly. The authors suggested that the minor product, 1,2-dihydrocyclobutene, was formed via a carbene.

An elegant example of the ene reaction was reported by Bloch and Bortolussi. The various isomers interconverted via diradicals but the endo, endo isomer underwent an ene reaction to give the compound 99.
Another example of ring rearrangement occurs in the tricyclooctene 100.\textsuperscript{103}

A case where an \(\alpha\)-dicarbonyl compound does not decarbonylate is the pyrolysis of 7-isopropylidene-bicyclo[2.2.1]heptane-2,3-dione 101.\textsuperscript{104}

Temporary loss of aromaticity occurs in the formation of methylene-benzocyclobutene 102 from 2-ethynyltoluene.\textsuperscript{105}

Brown and co-workers have investigated the interconversion of 2- and 3-substituted indenes and assume the intermediacy of isoindenes.\textsuperscript{106}
Similarly, 1,5- shifts of spiro allyl groups have been noted.\textsuperscript{107}

\[
\text{Similar reaction diagram}
\]

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

\[
\text{Cope rearrangement diagram}
\]

Trahanovsky and co-workers have studied the FVP of aryl propynoates and have come across an unexpected ring expansion.\textsuperscript{109}

\[
\text{Rearrangement of aryl propynoates}
\]

\[
\text{Final product with different R values}
\]
B Thio-, Sulphinyl- and Sulphonylcarbenes

1 Thiocarbenes

The most obvious desire for thiocarbenes is in the production of “organic metals” such as tetrathiafulvalene (TTF) \(104^{110}\). TTF is the formal dimer of \(105\) and the related species \(106\) has been detected at \(-50^\circ\text{C}\).\(^{111}\)

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

\[
\begin{align*}
\text{105} & \quad \xrightarrow{\times 2} \quad \text{104} \\
\text{106} & \quad \xrightarrow{13\text{CS}_2} \quad \ast = 13\text{C}
\end{align*}
\]
Phenylthiocarbene 111 has been produced by photolysis of the sulphonium ylide 112\(^\text{113}\) and FVP of the Meldrum's acid derivative 113 gives the thiocarbene 114. This then undergoes a 1,2-H shift to give vinyl sulphide 115. (The ketene can be isolated as a stable product from FVP at lower temperatures.\(^\text{11}\))

\[
\text{PhS}^\text{Me}_2 \xrightarrow{\text{hv}} \text{[PhS}^\text{Me}_2\text{H]} \xrightarrow{} \text{PhS}^\text{Me}_2 \xrightarrow{} \text{Me}_2\text{C} = \text{CM}_2
\]

Photolysis of the pyrazole 116 gives the carbene 117. This is detected by trapping with styrene.\(^\text{114}\)

The triazole 118 also loses N\(_2\) but the resulting carbene can extract oxygen from a neighbouring sulphonyl group to give the sulphonyliminothioester 119.\(^\text{115}\)
Bis-lithiated alcohols such as 120 can eliminate thiophenolate to give the ketones 121. This approach has been used to expand some small ring systems.

![Chemical reaction diagram]

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

- abstraction of O:
- abstraction of S:
- abstraction of Se:
- elimination of "C≡S":
- elimination of "RSSR":
- elimination of RH:
- elimination of MX:

CS₂ + "alkene/yne":
Carbenes have been used to dehydrogenate ketones such as 122.\textsuperscript{126}

\[
\begin{array}{c}
\text{122} \\
\text{\begin{tikzpicture}
  \node[draw,shape=circle] (a) at (0,0) {	extbf{122}};
  \node[draw,shape=circle] (b) at (0.5,0) {	extbf{122}};
  \draw (a) -- (b);
\end{tikzpicture}}
\end{array}
\]

Bis(phenylthio)carbene undergoes a Wolff rearrangement to give the thioester 123\textsuperscript{125} and a nearly quantitative 2,3-sigmatropic rearrangement has been reported for 124.\textsuperscript{127}

\[
\begin{array}{c}
\text{123} \\
\text{\begin{tikzpicture}
  \node[draw,shape=circle] (a) at (0,0) {	extbf{PhS}};
  \node[draw,shape=circle] (b) at (0.5,0) {	extbf{PhS}};
  \draw (a) -- (b);
\end{tikzpicture}}
\end{array}
\]

In the absence of trapping agents, 125 gives a mixture of the dimer and 126.\textsuperscript{128}

\[
\begin{array}{c}
\text{125} \\
\text{\begin{tikzpicture}
  \node[draw,shape=circle] (a) at (0,0) {	extbf{MeS}^+\textbf{NMe}_2};
  \node[draw,shape=circle] (b) at (0.5,0) {	extbf{MeS}^+\textbf{NMe}_2};
  \draw (a) -- (b);
\end{tikzpicture}}
\end{array}
\]

\[
\text{125} \overset{\text{NaH}}{\rightarrow} \text{MeS}^+\textbf{NMe}_2 \times 2 \rightarrow \text{Me}_2\text{N}(\text{MeS})=\text{C}=\text{C}(\text{Me})\text{NMe}_2 + \text{Me}_2\text{N}-\text{CH}=(\text{SMe})_2
\]

\[
20\% \\
52\% 126
\]

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

\[
\begin{array}{c}
\text{127} \\
\text{\begin{tikzpicture}
  \node[draw,shape=circle] (a) at (0,0) {	extbf{MeOSO}_3^+\textbf{Me}};
  \node[draw,shape=circle] (b) at (0.5,0) {	extbf{MeOSO}_3^+\textbf{Me}};
  \draw (a) -- (b);
\end{tikzpicture}}
\end{array}
\]

\[
\begin{array}{c}
\text{127} \\
\text{\begin{tikzpicture}
  \node[draw,shape=circle] (a) at (0,0) {	extbf{Ph} \textbf{S} \textbf{N} \textbf{C}};
  \node[draw,shape=circle] (b) at (0.5,0) {	extbf{Ph} \textbf{S} \textbf{N} \textbf{C}};
  \draw (a) -- (b);
\end{tikzpicture}}
\end{array}
\]

\[
\begin{array}{c}
\text{128} \\
\text{\begin{tikzpicture}
  \node[draw,shape=circle] (a) at (0,0) {	extbf{Ph} \textbf{S} \textbf{N} \textbf{C}};
  \node[draw,shape=circle] (b) at (0.5,0) {	extbf{Ph} \textbf{S} \textbf{N} \textbf{C}};
  \draw (a) -- (b);
\end{tikzpicture}}
\end{array}
\]

\[
75\% \\
100\%
\]
The carbenes 129 are formed by elimination of nitrogen from the azido-imines 130. Diazo-coupling of the parent compound with 131 gives the azo-compound 132. Addition of the nitro-variant of 129 to methanol followed by thermal re-elimination of methanol gives the dimer 133.\textsuperscript{130}

\begin{align*}
\text{R} = \text{H, Cl, OMe, NO} _2, \text{CO}_2\text{Et} \\
\text{Ph} & : \text{N} - \text{N} : \\
\text{Me} & \text{Et}
\end{align*}

2 Sulphinylcarbenes
Thermolysis of phenylsulphinyl-diazomethane in the presence of alkenes gives the corresponding cyclopropanes, predominantly the anti-isomer.\textsuperscript{131} Sulphinyl carbenes are also implicated in a reaction of chloromethyl phenyl sulphoxide.\textsuperscript{132}
Phenylsulphinylcarbene reacts with alkynes in an unexpected manner. The expected adduct, 134, ionises to 135. Addition of 135 to a further mole of phenylsulphinylidiazomethane and loss of N\textsubscript{2} gives the 2:1 adduct, 136.\textsuperscript{133}

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

This sort of reaction has been used in the cephalosporin ring system.\textsuperscript{135}

Addition of alkenylsulphinyl carbenes 138 to alkenes has been observed by Frank-Neumann and Lohmann.\textsuperscript{136}
When no other alkene is available, 138 can react intramolecurally to give cyclopropane 139. This may then add to excess 2-diazopropane (one of the components of the original diazene) to give the diazabicyclohexene 140 or rearrange to the sulphine 141. Loss of sulphur gives the ketone and addition of a further molecule of 2-diazopropane to 141 gives the thia diazoline-1-oxide 142.137

A synthesis of 2-amino-4-sulphinyl furans 143 was developed by Kossack and Himbert. They started from the yne-amine 144 and sulphonyl acetylene 145 which undergo cycloaddition to give 146. This then undergoes an electrocyclic process to generate the sulphinyl carbene which goes on to form 143.138
3 Sulphonyl carbenes

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

\[
\begin{align*}
R^1\text{SO}_2\overset{\text{hv}, \Delta}{\rightleftharpoons} R^1\text{SO}_2\overset{\text{or cat.}}{\text{SO}_2R} R, R^1 &= \text{alkyl, aryl} \\
X &= N_2, 1-\text{Ph}
\end{align*}
\]

Thermolysis of bis(phenylsulphonyl) diazomethane in the presence of bis(hexafluoroacetoacetonyl)copper gives the carbenes \textsuperscript{147}.\textsuperscript{140}

\[
\text{PhSO}_2\overset{\text{Cu(hfa)}_2}{\rightarrow} \text{PhSO}_2 \\
\text{PhSO}_2\overset{\text{hfa}}{\rightarrow} \text{PhSO}_2
\]

\textbf{147}

Loss of \(N_2\) from diazomethane can also be catalysed by \(BF_3\)\textsuperscript{141} or rhodium acetate, as shown below.\textsuperscript{142}

\[
\begin{align*}
\text{SO}_2\overset{\text{BF}_3}{\rightarrow} \text{SO}_2\overset{\text{Me}}{\rightarrow} \text{SO}_2\overset{\text{Rh(OAc)}_4}{\rightarrow} \text{SO}_2\overset{\text{Me}}{\rightarrow} \text{SO}_2
\end{align*}
\]

The reactions of sulphonyl carbenes can be grouped as follows;

\textbf{a dimerisation}

This gives 1,2-sulphonylethenes, such as \textsuperscript{148}.\textsuperscript{143}

\[
\begin{align*}
\text{PhSO}_2\overset{\Delta}{\rightarrow} \text{PhSO}_2\overset{\text{Ph-H}}{\rightarrow} \text{PhSO}_2\overset{\text{CH=CHSO}_2\text{Ph}}{\rightarrow} \text{PhSO}_2\overset{\text{CH}_2\text{OSO}_2\text{Ph}}{\rightarrow} \\
(2\%) \quad \textbf{148} \quad (28\%) \quad \textbf{148} \quad (23\%)
\end{align*}
\]
b Wolff-type rearrangements

This leads to sulphenes, such as 149\textsuperscript{144} and 150\textsuperscript{145}. Trapping the original carbene with methanol gives the sulphone ether, while loss of SO from the sulphene 150 gives the ketone and loss of SO\textsubscript{2} gives the methylene carbene, which undergoes further reactions.

\[
\text{PhSO}_2\text{CH}=\text{N}_2 \xrightarrow{\text{hv}} \text{PhSO}_2\text{CH}^* \xrightarrow{\text{Wolff}} \text{PhCH}=\text{=SO}_2
\]

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

\[
\text{ArSO}_2\text{CO}_2\text{Et} \xrightarrow{\text{hv}} \text{ArSO}_2\text{CO}^* \xrightarrow{\text{EtOH}} \text{Me-PhSO}_2\text{CO}_2\text{Et}
\]

c addition to multiple bonds

Examples of trapping carbenes by addition to alkenes\textsuperscript{144} and alkynes\textsuperscript{147} have been reported, and typical examples are shown below.
Under forcing conditions, $\alpha$-metallated dichlorosulphones such as 153 eliminate metal halide to give carbenes which can be trapped by addition.\cite{148}

\[
\begin{align*}
\text{PhSO}_2\text{ClCl} & \xrightarrow{140^\circ\text{C}} \text{PhSO}_2\text{Cl} + \text{Me}_3\text{SiCH}_2\text{CH} = \text{C} = \text{PhSO}_2 \quad \text{A} \rightarrow \text{C} \quad \text{CH}_2\text{SiMe}_3 \\
153
\end{align*}
\]

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

\[
\begin{align*}
\text{Ar} \quad \text{SO}_2 \quad \text{Ar} & \quad \times 3 \quad \text{Ar} \quad \text{SO}_2 \quad \text{Ar} \\
155 \quad (23\%) & \quad 154 \quad (17\%) & \quad 156 \quad (23\%)
\end{align*}
\]

e insertion into OH
This reaction, giving ethers, is a “classical” method of detecting carbenes.\cite{144}

\[
\begin{align*}
\text{Me} \quad \text{SO}_2 \quad \text{N}_2 \xrightarrow{80^\circ\text{C}} \text{Me} \quad \text{SO}_2 \quad \text{CH} + \text{MeOH} \rightarrow \text{Me} \quad \text{SO}_2 \quad \text{OME} \quad (76\%)
\end{align*}
\]
reaction with nucleophiles

Intramolecular reaction of the carbene derived from 157 with the ether oxygen gives the oxonium species, 158. Hydrolysis of 158, leading to loss of benzyl cation, gives the sulphonyl ether, 159.143

\[
\begin{align*}
157 & \xrightarrow{BF_3} 158 \xrightarrow{H_2O} 159 (56\%)
\end{align*}
\]

Bis-sulphonyl carbene 147 was reacted electrophilically with Ph₃Sb to give the ylide 160.142

\[
\begin{align*}
\text{PhSO}_2 & \xrightarrow{\text{Cu(hfa)}} \text{PhSO}_2 \\
\text{PhSCN} & \xrightarrow{\text{Ph}_3\text{Sb}} \text{PhSO}_2 \xrightarrow{\text{SbPh}_3}
\end{align*}
\]

insertion into C–H

This is another classic carbene reaction. Rhodium acetate has been used to catalyse the elimination of N₂ from diazo compound 161 to give the carbene 162. C–H insertion of the carbene then gives 163.144

\[
\begin{align*}
\text{PhSO}_2 & \xrightarrow{\text{Rh(OAc)}_4} \text{PhSO}_2 \\
\text{N} & \xrightarrow{\text{Me}} \text{Me} \xrightarrow{\text{Me}} \text{Me} \xrightarrow{\text{Me}} \text{Me}
\end{align*}
\]

In the absence of any trapping agent, bis(mesitylsulphonyl)carbene can insert into one of the ortho-methyls to give 164. This carbene also undergoes a Wolff rearrangement to give 165, which loses SO₂ to generate
a second sulphonyl carbene 166. This undergoes 1,2 oxygen transfer to give α-ketosulphoxide 167 which immediately hydrolyses to the corresponding benzoic acid and disulphide,\textsuperscript{150}

\[
\begin{align*}
\text{ArSO}_2 &= \text{Ar} = \text{SO}_2 \\
\Delta &\rightarrow \text{ArSO}_2 + \text{ArSO}_2 \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ar} &= \text{H} \\
\text{Ar} &= \text{H} \\
\text{Ar} &= \text{H} \\
\text{Ar} &= \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{ArSO}_2 &\rightarrow \text{ArSO}_2 \\
\text{Ar} &\text{SO}_2 \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ar} &= \text{H} \\
\text{Ar} &= \text{H} \\
\text{Ar} &= \text{H} \\
\text{Ar} &= \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} &\rightarrow \text{ArCOOH} + \text{ArSSAr} (22\%) \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\end{align*}
\]
C Pyrolysis of phosphorus ylides

Modern interest in this area began in 1959 with Trippett and Walker’s attempts to produce 168. An aqueous solution of nitromethyl triphenylphosphonium bromide immediately gave a quantitative precipitate of $\text{Ph}_3\text{P}=\text{O}$ on addition of alkali. Fulminate ion was detected in the solution and the authors hypothesised an internal Wittig reaction.

$$\text{Ph}_3\text{P} + \text{BrNO}_2 \xrightarrow{\Delta} \text{Ph}_3\text{P}^+\text{Br}^- \quad \xrightarrow{\text{alkali}} \quad \text{Ph}_3\text{P}=\text{O} \quad \text{nomic}$$

This was in line with Staudinger and Hauser’s 1921 report that benzoyl iminotriphenylphosphorane 169 decomposed at 220°C to $\text{Ph}_3\text{P}=\text{O}$ and benzonitrile and Horner and Oediger’s 1958 finding that dichloro triphenylphosphorane reacted with phenylnitromethane to give benzonitrile oxide.

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

\[ \text{Ph}_3\text{P}^+\text{Br}^- \quad \xrightarrow{\text{alkali}} \quad \text{Ph}_3\text{P}=\text{O} \]

a. $R^1 = H, R^2 = \text{OMe}; \text{no alkyne}$

b. $R^1 = H, R^2 = \text{OEt}; \text{no alkyne}$

c. $R^1 = \text{Ph}, R^2 = \text{Ph}; \sim 100\%$
Trippett extended his work to other ylides in the hope of generalising production of alkenes.\textsuperscript{154} He found that ylides 170d-f pyrolysed at 280°C to give alkenes in 60–90% yield. Similarly, the phosphine oxides 171 gave alkenes in moderate yield but the phosphonate 172 gave only a trace of alkyne.

\[
\begin{align*}
\text{Ph}_3\text{P} & \xrightarrow{280^\circ\text{C}/0.4\text{mmHg}} \text{Ph}^1 \xrightarrow{280^\circ\text{C}/0.3\text{mmHg}} \text{Ph}^2 \\
\text{Ph}^1 & \xrightarrow{280^\circ\text{C}/0.3\text{mmHg}} \text{Ph}^2 \\
\text{Ph}^1 & \xrightarrow{280^\circ\text{C}/0.3\text{mmHg}} \text{Ph}^2
\end{align*}
\]

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

The next paper by Trippett saw the extension of this work to the production of diacetylenes, albeit in less satisfactory yield.\textsuperscript{156}
He also found that 173 did not give any diacetylene on pyrolysis; neither did phosphoranes 170 with $R^1 = H$. Instead, the acyl phosphoranes eliminated $\text{Ph}_3\text{P}$ which distilled over, leaving an intractable black residue.

Later, the pyrolysis was used to prepare a diacid 174\textsuperscript{157}, some diarylacetylenes 175\textsuperscript{158} and acetylenic ketones 176\textsuperscript{159}. For the non-symmetrical phosphorane 177c, the product was a mixture of 1-phenylbut-1-yn-3-one and 4-phenylbut-3-yn-2-one (major component).

The bis-alkynyl benzenes 178 and 179 were produced by Henry as part of his research into polymer-forming Diels-Alder reactions. His
attempts to produce the 1,3- equivalent of 178 and bis(alkynyl)hexafluoro propanes were unsuccessful.\cite{160}

\[
\begin{align*}
\text{Ph}_3\text{P} & \text{CO}_2\text{Et} + \text{H} + \text{Cl}_2 \rightarrow \text{Ph}_3\text{P} & \text{CO}_2\text{Et} + \text{Cl} \quad \text{275°C} \quad 1-2\text{mmHg} \\
\text{Ph}_3\text{P} \text{CN} & \text{CN} \quad \text{178} \\
\text{Ph}_3\text{P} & \text{CN} \text{CN} \quad \text{275°C} \quad 1-2\text{mmHg} \\
\text{CN} & \text{179}
\end{align*}
\]

Bestmann and Geismann used the readily available methoxycarbonyl methylenetriphenylphosphorane and various acid chlorides to produce acetylenic esters 180.\cite{161} Reaction of these esters with piperidine, followed by hydrolysis, was used to prepare the $\beta$-ketoesters 181.

\[
\begin{align*}
\text{Ph}_3\text{P} & \text{CO}_2\text{Me} + \text{R}^2\text{COCl} \quad \text{C}_6\text{H}_6 \rightarrow \text{Ph}_3\text{P} & \text{CO}_2\text{Me} + \text{R}^2 \quad \text{220°} \\
\text{R}^2 & \text{CO}_2\text{Me} \quad \text{180} \\
\text{R}^2 & \text{CO}_2\text{Me} \quad \text{H}_2\text{O} \rightarrow \text{R}^2 & \text{CO}_2\text{Me} \\
\text{181}
\end{align*}
\]

A chinese research group has had a long-standing interest in fluorine-containing organics as potential dipolarophiles and dienophiles. Pyrolysis
of cyano-stabilised ylides 182 gave perfluorinated acetylenic nitriles.\textsuperscript{162} The ylides were synthesised from cyanomethylenetriphenylphosphorane and perfluoroalkyl chlorides and the pyrolyses were performed under nitrogen.

\[
\begin{align*}
2 \text{Ph}_3\text{P}=&\text{CHCN} + \text{R}_f\text{COCI} & \xrightarrow{\text{C}_6\text{H}_6, \text{RT-80°C}} & \text{Ph}_3\text{P} R'\text{CN} + \text{Ph}_3\text{P}^+\text{-CH}_2\text{CN Cl}^- \\
182
\end{align*}
\]

182 \xrightarrow{220-260°C, 10-15\text{mmHg}} \text{Ph}_3\text{P}^+\text{-}

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

\[
\begin{align*}
\text{Ph}_3\text{P} + \text{Br}\text{-SMe} & \xrightarrow{\text{C}_6\text{H}_6, \text{RT}} \text{Ph}_3\text{P} R'\text{O-SMe} \\
& \xrightarrow{(i) \text{NaOH}} \xrightarrow{(ii) \text{R}_f\text{COCI/} \text{C}_6\text{H}_6/\text{RT}} \text{Ph}_3\text{P} R'\text{O-SMe} \\
& \xrightarrow{\text{N}_2, \text{Imm} \xrightarrow{190-220°C}} \text{Ph}_3\text{P} R'\text{O-SMe} \\
183
\end{align*}
\]

R\textsubscript{F} = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_7\text{F}_{15}, (\text{CF}_2)_3\text{Cl}, (\text{CF}_2)_5\text{Cl}, \text{CF(CF}_3)_2\text{O(CF}_2)_2\text{CF}_3

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

\[
\begin{align*}
\text{Ph}_3\text{P}=&\text{CHCN} + \text{R}_f\text{COCI} & \xrightarrow{\text{C}_6\text{H}_6/20°C} & \text{Ph}_3\text{P} R'\text{CN} + \text{Ph}_3\text{P}^+\text{-CH}_2\text{CN Cl}^- \\
& \xrightarrow{\text{pumice stone/}\text{N}_2, 10\text{mm/280°C}} & \xrightarrow{\text{N}_2} & \text{Ph}_3\text{P} R'\text{CN} \\
& \xrightarrow{\text{R}_f} & \xrightarrow{\text{R}_f} & \text{R}_f = \text{CCl}_3, \text{CF}_3\text{Cl, (CF}_2)_2\text{Cl, (CF}_2)_3\text{Cl, CF(CF}_3)_2\text{O(CF}_2)_2\text{CF}_3
\end{align*}
\]
The work on perfluoro compounds was continued with the pyrolysis of perfluoroacetyl(diphenylphosphinylmethylenetriphenylphosphoranes 184 to provide perfluoroalkynylphosphonates 185.165

A publication in 1987 reported the production of aryloxy perfluoroalkynes 186.166 Pyrolysis of ylides 187, which were obtained by the action of strong base on the phosphonium salts, at 250–270°C from powdered pumice stone gave 186 in 30–40% yield.

The thienyl ylides 188 were produced in 1988. The corresponding acetylenes 189 were obtained in good yield by pyrolysis from powdered pumice stone.167
In 1982, Kobayashi and co-workers synthesised aryl-trifluoromethyl alkynes, starting from phosphonium salts and trifluoracetic anhydride.\textsuperscript{168}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {$\text{Ph}_3\text{P}$};
\node (b) at (1,0) {$\text{Ph}$};
\node (c) at (0,-1) {$\text{Ph}_3\text{P}$};
\node (d) at (1,-1) {$\text{Ph}$};
\node (e) at (2,0) {$\text{CF}_3$};
\node (f) at (2,-1) {$\text{CF}_3$};
\node (g) at (3,0) {$\text{Ph}$};
\node (h) at (3,-1) {$\text{Ph}$};
\node (i) at (4,0) {$\text{CF}_3$};
\node (j) at (4,-1) {$\text{CF}_3$};
\node (k) at (5,0) {$\text{Ph}$};
\node (l) at (5,-1) {$\text{Ph}$};
\node (m) at (6,0) {$\text{CF}_3$};
\node (n) at (6,-1) {$\text{CF}_3$};
\node (o) at (7,0) {$\text{Ph}$};
\node (p) at (7,-1) {$\text{Ph}$};
\node (q) at (8,0) {$\text{CF}_3$};
\node (r) at (8,-1) {$\text{CF}_3$};
\node (s) at (9,0) {$\text{Ph}$};
\node (t) at (9,-1) {$\text{Ph}$};
\node (u) at (10,0) {$\text{CF}_3$};
\node (v) at (10,-1) {$\text{CF}_3$};
\node (w) at (11,0) {$\text{Ph}$};
\node (x) at (11,-1) {$\text{Ph}$};
\node (y) at (12,0) {$\text{CF}_3$};
\node (z) at (12,-1) {$\text{CF}_3$};
\node (aa) at (13,0) {$\text{Ph}$};
\node (bb) at (13,-1) {$\text{Ph}$};\end{tikzpicture}
\end{center}

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

Recently, the 1-phenyl-2-heteroarylethynes 192 were produced in ~90% yield by pyrolysis of the corresponding ylides at 300°C in the presence of silica. Similar procedures gave the diheteroarylethynes 193 and mixtures of the isomeric aroylethynes 194 and 195.\textsuperscript{169}
In 1984, Petragnani extended the range of alkynes accessible from ylides still further.\(^{170}\) All successful pyrolyses of ylides 170 so far had had an electron-withdrawing group at \(R^1\). Alkylthio groups, \(-\text{SR}\), are known to stabilise carbanions and so the thioacetylenes 196 were prepared in yields of 40% for \(R^2 = \text{alkyl}\) and 70–80% for \(R^2 = \text{CF}_3\), aryl.

\[
\begin{align*}
2 \text{Ph}_3\text{P} &= \text{CHR}^1 + \text{R}^2\text{COX} \\
\text{C}_6\text{H}_6/\text{RT}>\text{60\%} &\rightarrow \text{Ph}_3\text{P} = \text{CHR}^1 \\
&\rightarrow \text{X = Cl, COCl}_3 \\
\text{170} &\rightarrow 230^\circ\text{C}/5\times10^{-3}\text{mmHg} \\
&\rightarrow \text{R}^1 \\
&\rightarrow \text{R}^2
\end{align*}
\]

\[R^1 = \text{SR}^3; \ R^2 = \text{Ph}, \ p-\text{MeC}_6\text{H}_4, \ \text{Me}, \ ^9\text{Bu}, \ ^6\text{C}_5\text{H}_11; \ R^3 = \text{Me}, \ \text{Ph}\]

Petragnani also published a method of producing acetylenes which were otherwise inaccessible from phosphoranes 170 (i.e. where \(R^1 = \text{alkyl}\)).\(^{171}\) This involved transylidation of acylphosphoranes with arylseleno bromides, followed by pyrolysis of the resulting \(\alpha\)-acyl-\(\alpha\)-(arylseleno) methylenetriphenylphosphoranes 197 to give arylselenoacetylenes 198. Lithiation, followed by addition of electrophiles, gave the desired alkynes. Alternatively, borane reduction of 198 gave the Z-arylselenoalkenes and \(\text{LiAlH}_4\) reduction gave the E-arylselenoalkenes.

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{COR} + \text{Ph-Se-Br} \\
&\rightarrow \text{Ph}_3\text{P} \searrow \text{SePh} \\
&\rightarrow \text{230^\circ C}/5\times10^{-3}\text{mmHg} \\
&\rightarrow \text{1 hour, 40–80\%} \\
&\rightarrow \text{197} \\
&\rightarrow \text{R} \\
&\rightarrow \text{R}^2
\end{align*}
\]

\[\text{R} = \text{Ph}, \ p-\text{MeC}_6\text{H}_4, \ p-\text{Me-OC}_6\text{H}_4, \ p-\text{Cl-C}_6\text{H}_4, \ p-\text{O}_2\text{N-C}_6\text{H}_4, \ \text{CF}_3, \ 2\text{-thienyl}\]

\[\text{"El\textsuperscript{\textright}} = \text{H}_2\text{O}, \ \text{Me}, \ \text{MeCO}_2\text{Me}, \ \text{Ac}\]

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{COR} \\
&\rightarrow \text{Ph}_3\text{P} \searrow \text{SePh} \\
&\rightarrow \text{230^\circ C}/5\times10^{-3}\text{mmHg} \\
&\rightarrow \text{1 hour, 60\%} \\
&\rightarrow \text{198} \\
&\rightarrow \text{H}_2\text{SePh} \\
&\rightarrow \text{60\%} \\
&\rightarrow \text{E-arylselenoalkenes}
\end{align*}
\]
Braga and Comassetto extended their work on hetero-substituted ylides to α-halophosphoranes. These were produced by reacting the acylphosphoranes with halogen in CCl₄, followed by sodium carbonate work-up. FVP at 800°C gave the haloalkynes in moderate yield.

A long-standing limit to this “ylide → alkyne” route was that terminal and aliphatic alkynes were not directly accessible from phosphoranes. Bestmann had described two indirect routes to aliphatic alkynes. One involved O-triflation of the ylide followed by sodium amalgam reduction. The other used the adduct of triphenylphosphite and ozone to give the diketone. This was then reacted with hydrazine to give the dihydrazone. Copper (I) chloride catalysed oxidation gave the acetylene.
In earlier work in this laboratory, it was found that FVP of the ylides 170 gave aliphatic alkynes cleanly, separate from the phosphine oxide and in 60–85% yield.  

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{FVP} \quad 750^\circ \text{C} \\
\text{R}_1 & \quad \text{R}_2
\end{align*}
\]

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

FVP at 850°C gave the cyclised products; 2-phenylbenzofuran was produced in 80% yield and 2-phenylbenzothiophene in 53% yield. However, for the species with aliphatic R, the cyclised products were obtained in moderate yield but R was found to have fragmented to methyl, ethyl and vinyl. In the case where R was Me, a radical mechanism, based on ideas from Barton was proposed to explain the incorporation the methoxy carbon atom in the final product.
The route to terminal alkynes was improved in 1990. Instead of pyrolysing \( \text{203} \) to get the alkyne \( \text{204} \), so wasting one mole of starting material \( \text{205} \), pyrolysis of the ethoxycarbonyl ylide \( \text{206} \) gave the ester \( \text{207} \) at \( 500^\circ C \) and gave the terminal alkyne \( \text{204} \) directly upon simply raising the pyrolysis temperature to \( 750^\circ C \).

Hydrolysis of the acetylenic esters \( \text{207} \), reaction with thionyl chloride and use of the resulting acid chloride \( \text{208} \) to acylate ylide \( \text{209} \) gave ylides \( \text{210} \). \( \text{FVP} \) of these gave the diynes in moderate yield and the sequence was continued to the tri-yne in one case.
D Programme of Research

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

\[
\begin{align*}
\text{Ph}_3\text{P} & \overset{\text{FVP}}{\rightleftharpoons} \text{Ph}_3\text{PO} \\
211 & \rightarrow 212 & 213 & \rightarrow 214 & \rightarrow 215 \\
216 & \rightarrow 217 & \rightarrow 218
\end{align*}
\]

With this in mind, an earlier investigation in this laboratory\textsuperscript{185} was concerned with the pyrolysis of sulphonyl ylides. The first system to be investigated was the arenesulphonyl ylides 219. FVP of 219 at 500–750°C
a complex mixture of products, of which the major component was an intractable polymer.

![Chemical reaction diagram](image1)

More interesting results were obtained for the arylmethanesulphonyl ylides 220. They showed loss of triphenylphosphine to give products derived from the carbenes 221.\(^{186}\)

![Chemical reaction diagram](image2)

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

![Chemical reaction diagram](image3)
Similarly, formation of 224 was explained by assuming loss of Ph$_3$P, CO$_2$ and CO. However this route could not be confirmed and further investigation was needed.

$$\text{Ph}_3\text{P} - \text{CO}_2\text{CH}_2\text{R}^1 - \text{Ph}_3\text{P} \xrightarrow{\text{Ph}_3\text{P}} \text{CO}_2\text{CH}_2\text{R}^1 \xrightarrow{\text{CO}_2} \text{S}_2\text{R}^2$$

Finally, one representative of 226 had been synthesised. FVP of 227 gave Ph$_3$P and the thiolobenzoate 228.

$$\text{Ph}_3\text{P} - \text{Ar} - \text{S}_2\text{R} \xrightarrow{\text{FVP}} \text{Ph}_3\text{P} - \text{Ph} - \text{Ph} - \text{S}_2\text{Pr}^i$$

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

mmol millimoles

M mol dm$^{-3}$

h, min hours, minutes

GCMS gas chromatography-mass spectrometry

$R_T$ retention time (quoted in minutes)

TLC thin layer chromatography

NMR nuclear magnetic resonance

$\delta$ chemical shift in parts per million

$J$ spin-spin coupling constant in Hz

4ry quaternary

br, s, d, t, q, m broad, singlet, doublet, triplet, quartet, multiplet

$V_{\text{max}}$ infra-red absorption frequency in cm$^{-1}$

MS mass spectroscopy

m/z mass to charge ratio

$M^+$ mass of molecular ion

FVP flash vacuum pyrolysis

m.p. melting point

b.p. boiling point

ether diethyl ether

THF tetrahydrofuran
B Instrumentation and General Techniques

1 N.M.R. Spectroscopy

All spectra were obtained from solutions in CDCl₃, except variable temperature studies where CD₂Cl₂ and C₆D₅CD₃ were used, and chemical shifts are expressed in parts per million to high frequency of internal TMS for ¹H and ¹³C or 85% external H₃PO₄ for ³¹P. Relative peak areas are given for multi-component mixtures and unidentified compounds thus: “δp = +28.1 (8) and -5.4 (12)” where (8) and (12) are the spectrometer’s arbitrary units of peak height.

a ¹H NMR

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

b ¹³C NMR

Spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by Mrs M. Smith or Mr P. Pogorzelec and at 50 MHz on a Varian Gemini 200 spectrometer. Spectra were ¹H decoupled. Ylide spectra were assigned with reference to published values for analogues and DEPT spectra were taken where necessary to complete the assignment.
31P NMR
Spectra were obtained at 32 MHz on a Varian CFT-20 or at 121 MHz on a Bruker AM-300 operated by Mrs M. Smith or Mr P. Pogorzelec.

2 Infrared Spectroscopy
Spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrophotometer or on a Perkin-Elmer 1710 fourier transform spectrophotometer. Spectra of solids were run as nujol mulls and solution spectra were run in CDCl3 using matched sodium chloride cells of path length 0.1 mm. Spectra were calibrated with the polystyrene peak at 1603 cm⁻¹.

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

4 Gas Chromatography-Mass Spectrometry
Gas chromatography-mass spectrometry studies were carried out on a Hewlett-Packard 5890A gas chromatograph coupled to a Finnigan Incos mass spectrometer operated by Mr C. Miller. The column in the GC was a 25 m capillary column (HR17 – stationary phase phenyl methyl silicone). The components are given in order of decreasing signal on the gas
chromatogram and the temperature ramp quoted as [initial temp. (°C) - rise per minute (°C) - final temp. (°C)]

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

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

7 Thin Layer Chromatography
This was carried out using 0.2 mm layers of silica (Merck, Kieselgel 60F254) on aluminium sheets. The components were observed under ultraviolet light.

8 Preparative Thin Layer Chromatography
This was carried out using 1.0 mm layers of silica (Merck, Kieselgel 60-80 mesh), containing 0.5% Woelm fluorescent green indicator, on glass plates. After locating the components with ultraviolet light, the bands were scraped off and the products removed from the support by soaking in dichloromethane for 30 min.
9 **Column Chromatography**
This was carried out using Fisons silica gel for chromatography (60–120 mesh).

10 **Drying and Evaporation of Organic Solutions**
Organic solutions were dried by standing over anhydrous magnesium sulphate and were evaporated under reduced pressure on a rotary evaporator.

11 **Drying and Purification of Solvents**
Commercially available solvents were used without further purification unless otherwise indicated. Where pure acetone or carbon tetrachloride were required the commercial Analytical Reagent (A.R.) grade solvents were used. Dry acetonitrile, ethanol and ethyl acetate were prepared by storing over molecular sieves. Dry ether and dry toluene were prepared by the addition of sodium wire. Extra dry ether was prepared by preliminary drying with sodium wire and then distilling from sodium benzophenone ketyl. Extra dry THF was prepared by preliminary drying with sodium wire and then distilling from potassium benzophenone ketyl. Dry dichloromethane was distilled from phosphorus pentoxide and stored over molecular sieves. Triethylamine was dried by heating under reflux with potassium hydroxide for 2 h then distilling onto molecular sieves. Commercial solutions of n-butyl lithium in hexanes were used. Where necessary, the strength of these solutions was checked by titration with diphenylacetic acid under nitrogen.
12 **Flash Vacuum Pyrolysis**

The apparatus used was based on the design of W. D. Crow, Australian National University. A similar set up is illustrated in a recent monograph by Brown.\(^{187}\) The essential features of the apparatus are shown below. The sample was volatilised from a horizontal inlet tube, heated via an external heat source, through a 30 x 2.5 cm silica tube. This was heated at temperatures in the range of 400–600°C by a Carbolite Eurotherm Tube Furnace MTF-12/38A, the temperature being measured by a Pt/Pt-13% Rh thermocouple situated at the centre of the furnace. The non-volatile products were collected at the furnace exit and the volatile products collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10\(^{-2}\) to 10\(^{-3}\) mmHg by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured on a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1–10 ms.

![Diagram of Flash Vacuum Pyrolysis apparatus](image)
After the pyrolysis the system was isolated from the pump. The products were then dissolved out of the trap in deuteriochloroform, unless otherwise stated and analysed directly by NMR. Yields were estimated by adding a known amount of dichloromethane and comparing the NMR signals.

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

1 Preparation

a Phosphonium salts

i Preparation of (ethoxycarbonylmethyl)triphenylphosphonium bromide 242

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

ii Preparation of (t-butoxycarbonylmethyl)triphenylphosphonium chloride 243

A solution of t-butyl chloroacetate (10.0 g, 66 mmol) and triphenylphosphine (17.4 g, 66 mmol) in dry toluene (175 ml) was stirred and heated under reflux for 3 days. The resulting precipitate was filtered off and washed with ether to give (t-butoxycarbonylmethyl)triphenylphosphonium chloride 243 (22.8 g, 83%) as colourless crystals. m.p. 189°C (lit., 189 185°C) (Found: C, 70.5; H, 6.3. C24H26ClO2P requires C, 69.8; H, 6.3%); δp +20.6; δH (80 MHz) 7.8–8.2 (15H, m), 5.53 (2H, d, J = 14 Hz) and 1.22 (9H, s); δC (75 MHz) 163.1 (d, J = 4 Hz, C=O), 135.1
(3C, d, 4J_P = 3 Hz), 133.9 (6C, d, 2J_P = 11 Hz), 130.2 (6C, d, 3J_P = 13 Hz),
118.2 (3C, d, 1J_P = 89 Hz), 84.5 (CMe_3), 33.7 (d, 1J_P = 54 Hz, CH_2) and
27.5; m/z 376 (M^+ - HCl, 8%), 319 (53), 301 (100), 275 (25), 262 (12),
183 (76) and 165 (48).

iii  Preparation of (benzyloxy carbonylmethyl)triphenylphosphonium
    iodide 244

A solution of chloroacetyl chloride (27.0 g, 240 mmol) in carbon
tetrachloride (100 ml) was stirred while benzyl alcohol (28.2 g, 250 mmol)
was added slowly and the reaction mixture was stirred for 1 h at room
temperature, heated under reflux for 3 h, then left to cool for 12 h. The
solvent was evaporated and the residue added to a solution of sodium iodide
(37.5 g, 250 mmol) in AR acetone (150 ml). This mixture was stirred for
2 h then the solvent was evaporated and the residue partitioned between
toluene and water. The toluene layer was dried, then triphenylphosphine
(65.6 g, 250 mmol) was added and the solution stirred for one hour. The
yellow precipitate was filtered off, washed with ether and recrystallised
from toluene to give (benzyloxy carbonylmethyl)triphenylphosphonium
iodide 244 (67.5 g, 51%) as yellow crystals. m.p. 129–30°C (Found: C,
60.2; H, 4.7. C_{27}H_{24}O_2P requires C, 60.2; H, 4.5%); δ_P +20.0; δ_H (200
MHz) 7.5–7.9 (15H, m), 7.0–7.3 (5H, m), 5.21 (2H, d, J =14 Hz) and 4.98
(2H, s); δ_C (75 MHz) 162.8 (d, J = 4 Hz, C=O), 134.6 (3C, d, 4J_P = 2 Hz),
133.2 (6C, d, 2J_P = 11 Hz), 129.6 (6C, d, 3J_P = 13 Hz), 127.9 (3C), 127.8
(2C), 127.3 (4ry), 116.4 (3C, 4ry, d, 1J_P = 89 Hz), 67.7 and 32.6 (d, J = 55
\( \nu_{\text{max}} 2940, 1726, 1437, 1303, 1159, 1110, 737 \) and 692 cm\(^{-1} \); m/z 411 (M+ – I, 0.2%), 410 (0.5), 301 (8), 277 (100), 262 (23), 183 (26), 152 (8), 108 (13) and 91 (57).

**b Phosphoranes**

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

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

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

The procedure as above but using (t-butoxycarbonylmethyl)triphenylphosphonium chloride (10.0 g, 23 mmol) and sodium hydroxide (11.7 ml, 2M, 23 mmol) gave (t-butoxycarbonylmethylene)triphenylphosphorane 246 (3.7 g, 51%) as colourless crystals. m.p. 150°C (lit., \(^{191} 154–5°C \)); \( \delta_p +16.9; \) \( \delta_H (80 \text{ MHz}) 7.6–7.7 (6\text{H, m}), 7.35–7.5 (9\text{H, m}), 2.75 (1\text{H, br s}) \)
and 1.20 (9H, s); δC 171.0 (d, J = 9 Hz, C=O), 132.9 (6C, d, 2Jp = 10 Hz),
131.7 (3C), 128.5 (6C, d, 3Jp = 12 Hz), 128.3 (3C, 4ry, d, 1Jp = 91 Hz), 76.3
(CMe₃), 31.3 (d, J = 121 Hz) and 28.7 (3C).

iii Preparation of (benzyloxycarbonylmethylene)triphenylphosphorane

247

The procedure as above but using (benzyloxycarbonylmethyl)triphenyl
phosphonium iodide (30.0 g, 55 mmol) and sodium hydroxide (27.9 ml,
2M, 56 mmol), followed by recrystallisation from ethyl acetate gave
(benzyloxycarbonylmethylene)triphenylphosphorane 247 as colourless
crystals (11.3 g, 50%). m.p. 115–20°C; (Found: C, 77.3; H, 5.4; m/z =
410.1471. C₂₇H₂₃O₂P requires C, 79.0; H, 5.6%; 410.1430); δp +17.4; δH
(200 MHz) 7.0–7.7 (20H, m), 5.02 (2H, br s), 3.03 (1H, br s) [impurity
ethyl acetate]; δC (50 MHz) 170.6 (d, J = 12 Hz, C=O), 138.5 (4ry), 132.7
(6C, d, 2Jp = 10 Hz), 131.8 (3C, d, 4Jp = 1 Hz), 128.6 (6C, d, 3Jp = 12 Hz),
127.9 (2C), 127.6 (3C, d, 1Jp = 93 Hz), 127.5 (2C), 126.9, 63.8 and 30.3
(d, J = 125 Hz); νmax 1615, 1430, 1340, 1110, 1060, 872 and 690 cm⁻¹;
m/z 410 (M+, 0.1%), 379 (0.1), 301 (5), 277 (100), 262 (3), 201 (18), 183
(15), 152 (8), 108 (28), 91 (26) and 77 (18).

c Preparation of sulphinyl chlorides

These were prepared by the method of Youn and Herrmann.¹⁹² Aromatic
sulphinyl chlorides were usually not distilled due to danger of explosion or
loss of the compound by polymerisation.
i  Preparation of ethanesulphinyl chloride 236
A mixture of ethanethiol (15.5 g, 250 mmol) and acetic acid (15.0 g, 250 mmol) was stirred below −45°C while sulphuryl chloride (68.8 g, 510 mmol) was added dropwise. The mixture was kept below −45°C for 30 min then left to warm up for 12 h. The mixture was then heated to 35°C and stirred at that temperature for 2 h, then allowed to cool to RT. Evaporation followed by kugelrohr distillation gave ethanesulphinyl chloride 236 (23.9 g, 85%), as a yellow, fuming oil. b.p. 60°C (oven temp.) at 3 mmHg (lit.,192 67°C at 26 mmHg); δ_H (200 MHz) 3.41 (2H, q, J = 7 Hz) and 1.47 (3H, t, J = 7 Hz); δ_C (50 MHz) 57.9 and 5.8.

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

iii  Preparation of phenylmethanesulphinyl chloride 238
The method as above, using phenylmethanethiol (31.1 g, 250 mmol), gave phenylmethanesulphinyl chloride 238 (10.1 g, 23%) as a yellow oil. b.p. 128°C (oven temp.) at 20 mmHg (lit.,192 claimed not distillable); δ_H (200 MHz) 7.3–7.5 (5H, m) and 4.62 (2H, s).
iv **Preparation of benzenesulphinyl chloride 239**
The method as above, using thiophenol (27.5 g, 250 mmol), gave benzenesulphinyl chloride 239 as an orange oil (11.7 g, 29%). b.p. 138°C (oven temp.) at 20 mmHg (lit., 192 65°C at 0.012 mmHg); δ_H (200 MHz) 7.8–7.9 (2H, m) and 7.5–7.7 (3H, m); δ_C (50 MHz) 148.5, 133.7, 129.5 (2C) and 123.7 (2C).

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

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

d **Preparation of ylides**
i **Preparation of [(ethanesulphinyl)ethoxycarbonylmethylene]triphenylphosphorane 248**
(Ethoxycarbonylmethylene)triphenylphosphorane 245 (12.4 g, 35 mmol) was stirred in dry toluene (100 ml) at 0°C under nitrogen. Ethanesulphinyl
chloride (1.9 g, 17 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. The mixture was filtered and evaporation and trituration with ethyl acetate (5 ml) gave yellow cubes of slightly impure [(ethanesulphonyl)ethoxycarbonylmethylene]triphenylphosphorane 248 (1.2 g, 16%). m.p. 141–2°C (Found: C, 69.4; H, 5.9; m/z = 408.1307. C_{24}H_{25}O_3PS requires C, 67.9; H, 5.9%; M^+ - O, 408.1313); \( \delta_p +27.5 \) (120) [impurities +22.1 (7) and 18.7 (3)]; \( \delta_H \) (80 MHz) 7.4–8.0 (15H, m), 4.05 (2H, q, J = 7 Hz, OCH_2), 2.25 (2H, q of d, J = 7 Hz, J_p = 2 Hz, SCH_2), 0.95 (3H, t, J = 7 Hz, OCH_2CH_3) and 0.9–1.0 (3H, br s, SCH_2CH_3) [minor impurities 4.0–4.4 (m) and 1.2–1.4 (m)]; \( \delta_C \) (75 MHz) 172.2 (C=O), 133.8 (6C, d, \( ^2J_p = 10 \) Hz), 131.7 (3C, d, \( ^4J_p = 2 \) Hz), 130.8 (3C, 4ry, \( ^1J_p = 58 \) Hz), 128.3 (6C, d, \( ^3J_p = 12 \) Hz), 58.6 (OCH_2), 37.0 (d, J = 120 Hz), 33:1 (SCH_2), 13.9 (OCH_2CH_3) and 13.4; \( \nu_{\text{max}} \) 3040, 2970, 2920, 1640, 1595, 1482, 1436, 1365, 1230, 1190, 1170, 1100, 1070 and 865 cm\(^{-1}\); m/z 408 (M^+ - O, 45%), 379 (100), 301 (7), 277 (8), 262 (37), 183 (38), 152 (5), 108 (14) and 77(4).

**ii  Preparation of [(benzenesulphonyl)ethoxycarbonylmethylene]triphenylphosphorane 249**

(Ethoxycarbonylmethylene)triphenylphosphorane (3.0 g, 8.6 mmol) was stirred in dry toluene (100 ml) at 0°C under nitrogen. Benzenesulphonyl chloride (0.69 g, 4.3 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. The byproduct phosphonium salt was filtered off, then evaporation and trituration with ethyl acetate (5 ml) gave
colourless crystals of slightly impure [(benzenesulphonyl)ethoxycarbonylmethylene]triphenylphosphorane 249 (0.50 g, 25%). m.p. 167–70°C (Found: C, 72.8; H, 5.3; m/z, 456.1319. C$_{28}$H$_{25}$O$_3$PS requires C, 71.2; H, 5.3%; M$^+$ – O, 456.1313); $\delta$$_p$ +28.1; $\delta$$_H$ (80 MHz) 7.0–7.9 (20H, m), 4.06 (2H, q, J = 7 Hz) and 0.95 (3H, br t, J = 7 Hz) [and a trace of toluene]; $\delta$$_C$ (75 MHz) 172.4 (C=O), 144.4, 133.7 (6C, d, $^3$J$$_P$ = 10 Hz), 131.9 (3C, d, $^4$J$$_P$ = 2 Hz), 128.3 (6C, d, $^3$J$$_P$ = 12 Hz), 128.0 (4C, s), 124.8 (3C, 4ry, d, $^1$J$$_P$ = 104 Hz), 124.1, 59.0 (OCH$_2$), 36.0 (d, J = 120 Hz), and 14.6 (br, OCH$_2$CH$_3$) [and additional minor Ar-C peaks]; v$_{\text{max}}$ 1600, 1440, 1370, 1270, 1110, 1080, 740 and 690 cm$^{-1}$; m/z 456 (M$^+$ – O, 25%), 411 (3), 379 (4), 302 (7), 277 (100), 262 (78), 218 (7), 201 (20), 183 (42), 152 (13), 108 (15) and 77 (38).

iii Preparation of [(phenylmethanesulphonyl)ethoxycarbonylmethylene]triphenylphosphorane 250

(Ethoxycarbonylmethylene)triphenylphosphorane (10.0 g, 29 mmol) and triethylamine (2.9 g, 29 mmol) were stirred in dry toluene (100 ml) at 0°C under nitrogen. Phenylmethanesulphinyl chloride (5.0 g, 29 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. The byproduct triethylammonium salt was filtered off, then evaporation and trituration with ethyl acetate (5 ml) gave a yellow powder of crude [(phenylmethanesulphonyl)ethoxycarbonylmethylene]triphenylphosphorane 250 (1.2 g, 8%). $\delta$$_p$ +23.1; $\delta$$_H$ (80 MHz) 7.0–7.6 (20H, m), 5.47 and 4.17 (2H, AB pattern, J = 14 Hz), 3.98 (2H, m), 0.91 (3H, m); $\delta$$_C$ (75 MHz)
134.0, 133.8 (6C, d), 132.3 (3C, d), 130.5 (2C), 128.7 (2C), 128.5 (6C, d), 124.9 (3C, 4ry, \( \text{J}_P = 93 \text{ Hz} \)), 58.8, 56.6 (d, 3\( \text{J}_P = 10 \text{ Hz} \)) and 14.3 (4ry, C=O and ylide C not apparent). Recrystallisation from di-isopropyl ether/dichloromethane gave just triphenylphosphine oxide so no further characterisation was made.

iv Preparation of [(4-methylbenzenesulphinyl)-t-butoxycarbonylmethylene]triphenylphosphorane 251

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane 246 (4.0 g, 11 mmol) and triethylamine (1.1 g, 11 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. 4-Methylbenzenesulphinyl chloride (1.9 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 3 h. Filtration, evaporation and trituration with ethyl acetate gave slightly impure [(4-methylbenzenesulphinyl)-t-butoxycarbonylmethylene]triphenylphosphorane 251 as yellow crystals (1.02 g, 19%). m.p. 140°C (Found: C, 74.2; H, 5.8; m/z = 498.1815. \( \text{C}_{31}\text{H}_{31}\text{O}_3\text{PS} \) requires C, 72.4; H, 6.1%; \( \text{M}^+ - \text{O} \), 498.1782); \( \delta_P +28.5; \delta_H \) (80 MHz) 6.9–8.0 (19H, m), 2.25 (3H, m) and 1.15 (9H, s) [impurity toluene]; \( \delta_C \) (75 MHz) 171.8 (C=O), 141.3, 133.8 (6C, d, 2\( \text{J}_P = 10 \text{ Hz} \)), 133.6, 131.8 (3C, d, 4\( \text{J}_P = 2 \text{ Hz} \)), 128.7 (2C), 128.2 (6C, d, 3\( \text{J}_P = 12 \text{ Hz} \)), 127.7 (3C, 4ry, d, 1\( \text{J}_P = 89\text{ Hz} \)), 126.0 (2C), 78.2 (OCMe\(_3\)), 36.7 (d, J = 118 Hz), 28.4 (3C) and 20.9 [small signals in the aromatic region due to Ph\(_3\)P=O & toluene]; \( v_{\text{max}} \) 1610, 1304, 1252, 1170, 1112, 1070, 815, 730 and 700 cm\(^{-1}\); m/z 498 (M\(^+\) - O, 0.1%).
427 (0.2), 303 (0.1), 301 (0.2), 277 (100), 246 (8), 201 (22), 199 (20) and 183 (18).

v Preparation of [(4-chlorobenzenesulphonyl)-t-butoxycarbonylmethylene]triphenylphosphorane 252

A solution of t-butoxycarbonylmethylene-triphenylphosphorane (1.5 g, 4 mmol) and triethylamine (0.4 g, 4 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. 4-Chlorobenzenesulphonyl chloride (0.8 g, 4 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 3 h. Filtration, evaporation and trituration with ethyl acetate gave [(4-chlorobenzenesulphonyl)-t-butoxycarbonylmethylene]triphenylphosphorane 252 (0.45 g, 21%). m.p. 153°C (Found: C, 66.7; H, 5.0; m/z = 518.1204. C$_{30}$H$_{28}$ClO$_3$PS requires C, 67.3; H, 5.3%; M$^+$ – O, 518.1236); $\delta$$_{F}$ +28.2; $\delta$$_{H}$ (80 MHz) 7.4–7.9 (15H, m), 7.22 (4H, s) and 1.13 (9H, s); $\delta$$_{C}$ (75 MHz) 170.6 (C=O), 133.8 (6C, d, $^2$$J$$_P$ = 9 Hz), 132.1 (4ry), 132.0 (3C), 128.6 (4ry), 128.3 (6C, d, $^3$$J$$_P$ = 12 Hz), 128.0 (4C), 127.5 (3C, 4ry, d, $^1$$J$$_P$ = 66 Hz), 78.6 (OCMe$_3$), 36.3 (d, J = 118 Hz) and 28.4 (3C, OC(CH$_3$)$_3$); $\nu$$_{max}$ 1645, 1246, 1161, 1106, 1064, 820, 760, 722 and 697 cm$^{-1}$; m/z 518 ($^{35}$Cl-M$^+$ – O, 5%), 462 (2), 445 (2), 318 (1), 301 (8), 277 (68), 262 (100), 183 (54), 144 (36) and 108 (50).
vi Preparation of [(ethanesulphonyl)benzylxocarbonylmethylene]triphenylphosphorane 253

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

vii Preparation of [(2-propanesulphonyl)benzylxocarbonylmethylene]triphenylphosphorane 254

A solution of (benzlyoxycarbonylmethylene)triphenylphosphorane (2.7 g, 6.6 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.7 g, 7 mmol) was added, followed by 2-propanesulphonyl chloride (0.83 g, 6.6 mmol) and the mixture was stirred for 12 h.
Filtration, evaporation and trituration with ethyl acetate (1 ml) gave slightly impure [(2-propanesulphonyl)benzylloxycarbonylmethylene]triphenylphosphorane 254 (0.33 g, 10%). m.p. 122–5°C (Found: C, 72.5; H, 6.1; m/z = 484.1616. C_{30}H_{29}O_{3}PS requires C, 72.0; H, 5.8%; M+ - O, 484.1626); δ_p +24.1(60) [impurities +28.8 (8) and +27.2 (6)]; δ_H (20 MHz) 6.9–7.7 (20H, m), 5.02 and 4.88 (2H, AB pattern, J = 12 Hz), 4.35 (1H, m), 1.28 (3H, d, J = 8 Hz) and 1.02 (3H, d, J = 8 Hz) [impurities 3.08 (q), 2.35 (s) and 1.40 (t)]; δ_C (75 MHz) 166.4 (d, J = 11 Hz, C=O), 133.8 (6C, d, J = 10 Hz); 132.4 (3C, d, J = 2 Hz), 132.0 (4ry), 128.8 (6C, d, J = 13 Hz), 128.1 (2C), 128.0 (2C), 127.3, 125.0 (3C, 4ry, d, J = 93 Hz), 64.8 (OCH₂), 55.2 (d, J = 119 Hz), 49.8 (d, J = 9 Hz, SCHMe₂), 18.8 and 18.4 [impurities 136.9, 134.0, 133.5, 133.4, 132.1, 45.8 and 8.7]; ν_max 1620, 1320, 1275, 1112, 1063, 1012, 752, 730 and 700 cm⁻¹; m/z 484 (M+ - O, 0.1%), 441 (0.3), 294 (0.5), 277 (35), 201 (7), 199 (5), 108 (18) and 91 (100).

viii Preparation of [(benzenesulphonyl)benzylloxycarbonylmethylene]triphenylphosphorane 255

A solution of (benzylloxycarbonylmethylene)triphenylphosphorane (1.5 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.4 g, 3.65 mmol) was added, followed by benzenesulphonyl chloride (0.59 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave [(benzenesulphonyl)benzylloxycarbonylmethylene]triphenylphosphorane
255 (0.12 g, 6%). m.p. 145–7°C (Found: m/z = 518.1462. C$_{33}$H$_{27}$O$_3$PS
requires [M$^+ - $O], 518.1469); $\delta_p$ +28.3; $\delta_H$ (200 MHz) 6.95–7.55 (25H, m)
and 5.06 (2H, br s) [impurities CH$_2$Cl$_2$, 2.37 (s), 2.06 (s), 1.77 (br s) and
1.2–1.4 (m)]; $\delta_C$ (75 MHz) 172.0 (C=O), 144.3 (br, 4r), 133.8 (6C, d, $^3J_p$
= 9 Hz), 132.1 (2C), 132.0 (3C), 131.9, 128.6, 128.4 (6C, d, $^3J_p = 12$ Hz),
128.0 (2C), 127.9 (2C), 127.5 (3C, d, $^1J_p = 75$ Hz), 125.6 (2C), 124.2,
65.0 and 36.7 (d, J = 120 Hz); $\nu_{\max}$ 1603, 1440, 1260, 1105, 1050, 902,
752, 720 and 696 cm$^{-1}$; m/z 518 (M$^+ - $ O, 1%), 441 (5), 427 (1), 411 (9),
383 (18), 339 (5), 303 (63), 273 (58), 262 (100) and 183 (84).

ix Preparation of [(4-methylbenzenesulphinyl)benzyloxy carbonyl
methylenetriphenylphosphorane 256
A solution of (benzyloxy carbonylmethylene)triphenyl phosphorane (1.5 g,
3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen.
Triethylamine (0.37 g, 3.65 mmol) was added, followed by 4-methyl
tenzenesulphynyl chloride (0.64 g, 3.65 mmol) and the mixture was stirred
for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml)
gave slightly impure [(4-methylbenzenesulphinyl)benzyloxy carbonyl
methylenetriphenylphosphorane 256 (0.48 g, 24%). m.p. 160–2°C
(Found: m/z = 532.1619. C$_{34}$H$_{29}$O$_4$PS requires M$^+ - $O, 532.1626); $\delta_p$
+28.5; $\delta_H$ (200 MHz) 7.1–7.55 (20H, m), 7.05 and 6.88 (4H, AB pattern, J
= 8 Hz), 5.07 (2H, br s) and 2.23 (3H, s) [impurities 1.2–1.3 (m)]; $\delta_C$ (75
MHz) 172.0 (C=O), 140.7, 133.7 (2C), 133.7 (6C, d, $^2J_p = 9$ Hz), 131.8
(3C, d, $^4J_p = 2$ Hz), 128.8 (2C), 128.5, 128.3 (6C, d, $^3J_p = 12$ Hz), 127.9
(2C), 127.8, 127.0 (2C), 126.7 (3C, 4ry, d, \( ^1J_P = 91 \) Hz), 125.8, 64.8 (OCH\(_2\)), 36.8 (d, \( J = 122 \) Hz) and 20.9; \( \nu_{\text{max}} \) 1605, 1268, 1110, 1052, 906, 757, 725 and 698 cm\(^{-1}\); m/z 532 (M\(^+\) – O, 97%), 441 (3), 425 (5), 397 (3), 303 (20), 262 (100) and 183 (22).

**x** Preparation of \([4\text{-chlorobenzenesulphinyl}benzyl\text{oxycarbonylmethylene}triphenylphosphorane 257

A solution of (benzyl\text{oxycarbonylmethylene})triphenylphosphorane (1.5 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.37 g, 3.65 mmol) was added, followed by 4-chlorobenzenesulphinyl chloride (0.71 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave \([4\text{-chlorobenzenesulphinyl}benzyl\text{oxycarbonylmethylene}triphenylphosphorane 257 (1.42 g, 68%). m.p. 133–5°C (Found: C, 70.2; H, 4.7; m/z = 552.1084. C\(_{33}\)H\(_{26}\)ClO\(_3\)PS requires C, 69.7; H, 4.6%; \( ^{35}\)Cl-M\(^+\) – O, 552.1080); \( \delta_p \) +28.2; \( \delta_H \) (200MHz) 7.15–7.6 (20H, m), 7.08 and 7.02 (4H, AB pattern, \( J = 9 \) Hz) and 5.05 (2H, br s); \( \delta_C \) (75 MHz) 172.0 (C=O), 135.1, 133.8 (4ry), 133.7 (6C, d, \( ^2J_P = 9 \) Hz), 132.1 (3C, d, \( ^4J_P = 2 \) Hz), 132.0, 128.4 (6C, d, \( ^3J_P = 12 \) Hz), 128.4, 128.0 (2C), 127.9 (2C), 127.4 (3C, 4ry, d, \( ^1J_P = 59 \) Hz), 127.2 (2C), 126.8 (2C), 65.0 (OCH\(_2\)) and 36.4 (d, \( J = 121 \) Hz); \( \nu_{\text{max}} \) 1604, 1266, 1106, 1086, 1010, 819, 750, 723 and 696 cm\(^{-1}\); m/z 554 (\( ^{37}\)Cl-M\(^+\) – O, 7%), 552 (\( ^{35}\)Cl-M\(^+\) – O, 20%), 303 (13), 301 (16), 262 (95), 183 (40), 108 (82) and 91 (100).
xi  Attempted preparation of ((benzenesulphonyl)-t-butoxycarbonylmethylene)triphenylphosphorane
A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (3.5 g, 9 mmol) was stirred in dry toluene (100 ml). Triethylamine (0.9 g, 9 mmol) and benzenesulphonyl chloride (1.6 g, 10 mmol) in dry toluene (10 ml) were added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a mixture which, in addition to the phosphonium salt, starting phosphorane and triphenylphosphine oxide, contained two major products, $\delta_p = +23.4$ and +28.2 but these could not be isolated.

xii  Attempted preparation of ((phenylmethanesulphonyl)benzyloxy carbonylmethylene)triphenylphosphorane
A solution of (benzyloxy carbonylmethyl)triphenylphosphorane (1.50 g, 3.65 mmol) in dry toluene (50 ml) was stirred at 0°C under nitrogen. Triethylamine (0.74 g, 7.3 mmol) was added, followed by phenylmethanesulphonyl chloride (0.64 g, 3.65 mmol) and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate (1 ml) gave an oil that had $\delta_p +28.9$ (Ph$_3$P=O), +28.5 (possibly the desired product) and +18.9 (starting phosphorane); $\delta_H$ 6.9–7.6 (25H, m) and 5.0 (br s).
xiii Attempted preparation of [(4-chlorobenzenesulphonyl)ethoxycarbonylmethylene]triphenylphosphorane

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

xiv Attempted preparation of [(ethanesulphonyl)-t-butoxycarbonylmethylene]triphenylphosphorane

A solution of freshly prepared (t-butoxycarbonylmethylene)triphenylphosphorane (9.1 g, 24 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. Ethanesulphonyl chloride (1.4 g, 12 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration and evaporation gave an oil whose mass spectrum showed evidence for the presence of the desired product (m/z = 436 [M+ - O], 407 [M+ - O, Et], 380 [M+ - O, H2C=CMMe2], 351, 319, 307, 277 and 262) but whose 31P NMR spectrum (+27.9, +27.7 to +25.0, +21.6, +21.4 and +20.7) appeared too complex to make further purification possible and whose 1H spectrum appeared very unpromising.

xv Attempted preparation of [(2-propanesulphonyl)-t-butoxycarbonylmethylene]triphenylphosphorane

A solution of freshly prepared (t-butoxycarbonylmethylene)triphenylphosphorane (9.14 g, 24 mmol) in dry toluene (100 ml) was stirred at 0°C
under nitrogen. 2-Propanesulphinyl chloride (1.5 g, 12 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave the starting phosphonium salt and in the residual oil a major component \( \delta_p = +26.2 \). Attempts to crystallise this failed.

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

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

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

A solution of (t-butoxycarbonylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol) in dry toluene (100 ml) was stirred at 0°C under nitrogen. Benzenesulphinyl chloride (0.4 g, 2.5 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave an oil containing triphenylphosphine oxide, the starting phosphorane, its conjugate phosphonium salt and what may have been the product (\( \delta_p = +24.3 \)). No crystals ever formed.
xviii Attempted preparation of (4-chlorobenzensulphinyl)-t-butoxycarbonylmethylene]triphenylphosphorane

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

xix Attempted preparation of (4-methylbenzencesulphinyl)-t-butoxycarbonylmethylene]triphenylphosphorane

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

2 FVP of alkane- and arenesulphinylalkoxycarbonylmethylene]triphenylphosphoranes

i FVP of (ethanesulphinyl)ethoxycarbonylmethylene]triphenylphosphorane 248

FVP of the title compound (0.2105 g) [600°C, 5 x 10⁻³ torr, 200°C] gave a colourless liquid in the cold trap [GCMS (40-20-300) and ¹H (300 MHz) and ¹³C (75 MHz) NMR indicated the presence of
ethyl 1-propenyl sulphide. (36% yield) \( R_T = 2.35, \text{m/z} \ 162 \ (61\%), \ 87 \ (9), \ 73 \ (53) \) and 45 \ (100\%); \( \delta_H \ 5.8-5.9 \ (1\text{H, m}), \ 5.4-5.9 \ (1\text{H, m}), \ 2.5-2.6 \ (2\text{H, m}), \ 1.6-1.7 \ (3\text{H, m}) \) and 1.1-1.3 \ (3\text{H, m}); \( \delta_C \) (major component, hence presumably E- isomer) 124.9, 122.2, 25.7, 17.4 and 13.6; (Z- isomer) 124.4, 122.8, 26.6, 14.5 and 13.5.

acetaldehyde. (7% yield) \( \delta_H \ 9.75 \ (1\text{H, q, } J = 4 \text{ Hz}) \) and 2.15 \ (3\text{H, d, } J = 4 \text{ Hz})]; \( \delta_C \ 198.9 \) and 29.9.;

and a yellow amorphous solid at the furnace exit \([^{31}P \text{ NMR indicated the presence of } \text{Ph}_3\text{P, Ph}_3\text{P}=\text{O and Ph}_3\text{P}=\text{S in the ratio } 84:9:7. \]

\( \text{Ph}_3\text{P}, \delta_p -5.0. \]

\( \text{Ph}_3\text{P}=\text{O}, \delta_p +28.5. \]

\( \text{Ph}_3\text{P}=\text{S}, \delta_p +43.5. \]

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

FVP of the title compound \((0.10g) \ [600^\circ C, 5 \times 10^{-3} \ \text{torr, } 80^\circ C] \) gave a colourless liquid in the cold trap \([\text{GCMS (40-20-300) and } ^1\text{H (80 MHz) and } ^{13}\text{C (75 MHz) NMR indicated the presence of } \text{PhSSPh. (10% yield) } R_T = 12.30, \text{m/z} \ 218 \ (42\%), \ 185 \ (15), \ 154 \ (29) \) and 109 \ (100). \]

phenyl E- and Z-propenyl sulphide. (10% yield) \( R_T = 7.54, \text{m/z} \ 150 \ (100\%), \ 135 \ (82), \ 121 \ (11), \ 109 \ (40) \) and 105 \ (58); \( \delta_H \ 7.2-7.7 \ (5\text{H, m}), \ 5.9-6.3 \ (2\text{H, m}) \) and 1.85 \ (3\text{H, d of m, } J = 5 \text{ Hz}); \( \delta_C \) many Ar-C, 123.6, 121.7 \ (\text{PhSCH=CHMe}), 18.5 and 14.7 \ (\text{PhSCH=CHMe})
ethyl phenyl sulphide, (5% yield) \( R_T = 7.01, \frac{m}{z} 138 (100\%), 123 (80) \) and 110 (70); \( \delta_H 2.95 (2H, q, J = 7 \text{ Hz}) \) and 1.30 (3H, \( t, J = 7 \text{ Hz} \)); \( \delta_C 27.7 \) and 14.4. unknown, \( R_T = 8.55, \frac{m}{z} 166 (15\%), 137 (100), 121 (2) \) and 109 (50).

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

an aldehyde, \( \delta_H 9.6 (\text{d, } J = 3 \text{ Hz}) \) and \( \delta_C 195.5. \)

and a yellow solid at the furnace exit \( [^{13}\text{C NMR indicated the presence of Ph}_3\text{P}=\text{O and Ph}_3\text{P in the ratio 1:1.} \]

\( \text{Ph}_3\text{P, } \delta_C 137.1 (3\text{C, d, } J_p = 10 \text{ Hz}), 133.7 (6\text{C, d, } J_p = 19 \text{ Hz}), 128.5 (6\text{C, d, } J_p = 15 \text{ Hz}) \) and 128.4 (3C).

\( \text{Ph}_3\text{P=O, } \delta_C 132.3 (3\text{C, d, } J_p = 104 \text{ Hz}), 132.1 (6\text{C, d, } J_p = 10 \text{ Hz}), 131.9 (3\text{C, d, } J_p = 2 \text{ Hz}) \) and 128.5 (6C, d, \( J_p = 12 \text{ Hz} \)).]

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

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

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

1,1-di(methylthio)ethane, \( R_T = 2.23, \frac{m}{z} 122 (33\%), 105 (2) \) and 75 (100); \( \delta_H 2.12 (6\text{H, s}), 2.09 (3\text{H, d, } J = 9 \text{ Hz}) \) and 1.23 (1H, q, \( J = 9 \text{ Hz} \)).
MeSSMe, $R_T = 1.38$, m/z 94 (58%), 79 (49), 61 (13), 47 (44) and 45 (100); $\delta_H 2.43.$

and brown droplets at the furnace exit [GCMS (60-20-300) and $^{31}$P NMR indicated the presence of Ph$_3$P, Ph$_3$P=O and Ph$_3$P=S in the ratio 80:14:6.

Ph$_3$P, $R_T = 9.58$, m/z 262 (69%), 183 (100), 152 (15) and 108 (59); $\delta_P -5.5.$

Ph$_3$P=O, $R_T = 11.32$, m/z 277 (65%), 199 (27), 103 (26), 152 (25) and 51 (100) [Most intense ion in molecular ion cluster at m/z 277 (M$^+$ - 1)]; $\delta_P +31.9.$

Ph$_3$P=S, $R_T = 11.56$, m/z 294 (35%), 201 (11), 215 (9) and 183 (100); $\delta_P +43.1.$

iv  FVP of [(2-propanesulphonyl)benzyloxy carbonylmethylene]triphenylphosphorane 254

FVP of the title compound (0.1103g) [500°C, 1.8 x $10^{-2}$ torr, 150°C] gave a colourless liquid in the cold trap [$^1$H NMR indicated the presence of benzyl alcohol, $\delta_H 7.4-7.1$ (5H, m), 4.65 (2H, s,) and 3.0 (1H, br s.); and brown droplets at the furnace exit [31P NMR indicated the presence of Ph$_3$P=O, $\delta_P +28.9$ (40).

Ph$_3$P=S, $\delta_P +43.1$ (7).]

v  FVP of [(benzenesulphonyl)benzyloxy carbonylmethylene]triphenylphosphorane 255

FVP of the title compound (0.0453g) [500°C, 1.8 x $10^{-2}$ torr, 150°C] gave a colourless liquid in the cold trap [$^1$H NMR indicated the presence of
and brown droplets at the furnace exit [$^3$P NMR indicated the presence of Ph$_3$P=O, $\delta_P$ +28.5].

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

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

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

4-Cl-C$_6$H$_4$SCH$_2$Ph, $R_T = 10.00$, m/z 234 (1%), 165 (1), 143 (3) and 91 (100); $\delta_H$ 4.1 (s).

4-Cl-C$_6$H$_4$Me, $R_T = 3.43$, m/z 130 (2%), 128 (5%), 126 (15) and 91 (100)
unknown, $R_T = 7.04$, m/z 156 (3%), 129 (46), 115 (6) and 91 (88)
toluene, $R_T = 1.50$, m/z 92 (54%), 91 (100), 74 (2) and 65(18)
PhCH$_2$CH$_2$Ph, $R_T = 7.34$, m/z 182 (3%), 91 (100), 77 (6) and 65 (20).]

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

(4-Cl-C$_6$H$_4$S)$_2$, $R_T = 11.41$, m/z 290 (0.5%), 288 (1), 286 (2), 145 (30)
and 143 (100); $\delta_H$ 7.41 and 7.30 (8H, AB pattern, $J = 9$ Hz).

Ph$_3$P=O, $R_T = 14.21$, m/z 277 (4%), 199 (5), 183 (5) and 77 (59)
vii FVP of [(4-methylbenzenesulphonyl)benzoxycarbonylmethylene] triphenylphosphorane 256

FVP of the title compound (0.1259g) [500°C, 3 x 10^-3 torr, 150°C] gave brown droplets at the furnace exit and a colourless liquid in the cold trap. These were collected together [^1H (200 MHz) and ^31P NMR indicated the presence of benzyl alcohol, δ_H 7.4-7.1 (5H, m) and 4.7 (2H, s).

Ph3P=O, δ_H 7.7-7.4 (m); δ_P +28.6.]

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

FVP of the title compound (0.0950g) [500°C, 1.6 x 10^-2 torr, 50°C] gave yellow droplets in the cold trap [GCMS (60-20-300) and ^1H (200 MHz) and ^13C (75 MHz) NMR indicated the presence of (4-Me-C6H4S)2, R_T = 10.25, m/z 246 (26%), 182 (8), 123 (100) and 77 (64); δ_H 7.19 and 7.04 (8H, AB pattern, J = 8 Hz) and 2.32 (6H, s); δ_C 135.7 (2C), 132.2 (2C), 129.8 (4C), 128.5 (4C) and 20.9 (2C).]

and yellow droplets at the furnace exit [^1H (200 MHz) and ^31P NMR indicated the presence of Ph3P and Ph3P=O in the ratio 7:30.

Ph3P, δ_H 7.3 (m); δ_P -5.4.

Ph3P=O, δ_H 7.8-7.4 (m); δ_P +29.3.

However, a GCMS taken 17 days later indicated the presence of Ph3P=O, R_T = 13.42, m/z 277 (18%), 199 (15), 186 (16) and 77 (100).

Ph3P=S, R_T = 14.11, m/z 294 (10%), 263 (15), 183 (100) and 139 (38).

in the ratio 12:1].
FVP of [(4-chlorobenzenesulphonyl)-t-butoxycarbonylmethylene]triphenylphosphorane 252

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

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

(4-Cl-C₆H₄S)₂, Rₜ = 11.13, m/z 290 (5%), 288 (25), 286 (30), 145 (23) and 143 (88); δₜ 7.20 (8H, s); δₗ 130.8 (4C) and 129.2 (4C).

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

(4-Cl-C₆H₄S)₂, Rₜ = 11.13, m/z 290 (4%), 288 (12), 286 (19), 222 (6), 145 (28), 143 (70) and 108 (100).

Ph₃P=O, Rₜ = 13.37, m/z 277 (28%), 199 (18), 183 (12) and 77 (100) (peak area 60 units); δₗ +29.2.

Ph₃P=S, Rₜ = 14.07, m/z 294 (33%), 278 (5), 203 (24) and 183 (100) (peak area 7 units).]
3 Preparation of authentic samples of FVP products

i Preparation of ethyl prop-2-enyl sulphide

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

ii Attempted preparation of ethyl prop-1-enyl sulphide

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

A repeat of this experiment, heating the reagents in a sealed tube at 120°C gave a clear liquid whose spectra showed no sign of the double bond.
Ethyl prop-2-enyl sulphide 280 (2.0 g, 20 mmol) and sodium hydroxide (5.0 g, 125 mmol) were stirred in water (50 ml) under nitrogen, while being heated under reflux for 12 h. Acidification with HCl (2M) and extraction with dichloromethane (2×100 ml) gave only the starting material.

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

iv Preparation of methyl vinyl sulphide 284
2-chloroethyl methyl sulphide (5.6 g, 51 mmol) was added to a solution of sodium (1.17 g, 51 mmol) in pentan-1-ol (100 ml) and heated at reflux for 30 min. Distillation, collecting all fractions boiling lower than 87°C, followed by kugelrohr distillation at 760 mmHg gave 1.5g clear liquid which was mostly pentanol but which did contain the desired product,
methyl vinyl sulphide 284 (0.4g by calculation from $^1$H NMR, 11%). $\delta_H$ (300 MHz) 6.42 (1H, dd, $J = 10$ Hz, 16 Hz), 5.18 (1H, d, $J = 10$ Hz), 4.95 (1H, d, $J = 16$ Hz) and 2.22 (3H, s); $\delta_C$ (75 MHz) 132.9, 108.5 and 13.5.

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

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

1 Diazo-transfer reagents

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

ii Preparation of 4-(N-acetylamino)benzenesulphonyl azide 301
This diazotransfer agent was supposed to have the distinction that the byproduct amide would be easily separated from the diazo-products.198 A solution of sodium azide (3.9 g, 60 mmol) in water (30 ml) was added to a solution of 4-(N-acetylamino)benzenesulphonyl chloride (11.7 g, 50 mmol) in acetone (100 ml). This mixture was stirred for 12 h, poured into water (1450 ml). These mixtures were stirred for 1 h, after which the product was filtered off. Recrystallisation from toluene gave 4-(N-acetylamino)benzenesulphonyl azide 301 as a white powder (9.1 g, 76%). m.p. 114°C
(lit.,\textsuperscript{198} 113–5°C); δ\textsubscript{H} (300 MHz) 8.32 (1H, s), 7.87 and 7.82 (4H, AB pattern, J = 10 Hz) and 2.25 (3H, s); δ\textsubscript{C} (50 MHz) 169.7 (C=O), 144.2 (4ry), 132.3 (4ry), 128.9 (2C), 119.7 (2C) and 24.7; ν\textsubscript{max} 3250, 3170, 2340, 2120, 1665 and 1580 cm\textsuperscript{-1}.

2 Alkane- and arenesulphenylacetates

a Preparation of (benzenesulphenyl)acetyl chloride

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

b Preparation of methyl (ethanesulphenyl)acetate \textit{292}

Sodium metal (2.1 g, 92 mmol) was dissolved in methanol (100 ml). Ethanethiol (4.8 g, 92 mmol) was added, followed by methyl chloroacetate (10.0 g, 77 mmol) and the mixture was stirred for 30 min. The mixture was evaporated and the residue taken up into dichloromethane. This solution was washed with water, dried, evaporated and kugelrohr distilled to give methyl (ethanesulphenyl)acetate \textit{292} as a colourless liquid (4.1 g, 52%). b.p. 60°C (oven temp.) at 6 mmHg (lit.,\textsuperscript{199} 106–8°C at 100 mmHg); δ\textsubscript{H} (200 MHz) 3.74 (3H, s), 3.25 (2H, s), 2.67 (2H, q, J = 8 Hz) and 1.29
(3H, t, J = 8 Hz); $\delta_C$ (50 MHz), 171.0 (C=O), 52.3 (OCH$_3$), 33.1 (CH$_2$CO), 26.6 (SCH$_2$Me) and 14.2.

c  Preparation of ethyl (ethanesulphenyl)acetate 294
Sodium metal (2.0 g, 87 mmol) was dissolved in ethanol (100 ml). Ethanethiol (5.1 g, 82 mmol) was added, followed by ethyl chloroacetate (10.0 g, 82 mmol) and the mixture was stirred for 30 min. The mixture was evaporated and the residue taken up in dichloromethane (200 ml). Washing with water (2 x 200 ml), drying, evaporation and kugelrohr distillation gave ethyl (ethanesulphenyl)acetate 294 as a colourless liquid (5.1 g, 42%). b.p. 100°C (oven temp.) at 4 mmHg (lit., 187–9°C at 759 mmHg); $\delta_H$ (200 MHz), 4.19 (2H, q, J = 8 Hz), 3.22 (2H, s), 2.65 (2H, q, J = 8 Hz, SCH$_2$Me), 1.28 (3H, t, J = 8 Hz) and 1.27 (3H, t, J = 8 Hz); $\delta_C$ (50 MHz), 170.5 (C=O), 61.2 (OCH$_2$), 33.3 (CH$_2$CO), 26.6 (SCH$_2$Me) and 14.2 (2 x CH$_3$).

d  Preparation of methyl (benzenesulphenyl)acetate 293
i  A solution of (benzenesulphenyl)acetyl chloride (4.0 g, 21 mmol) in methanol (60 ml) was stirred for 12 h. Evaporation and kugelrohr distillation gave methyl (benzenesulphenyl)acetate 293 as a golden yellow liquid (2.5 g, 63%). b.p. 170°C (oven temp.) at 3 mmHg (lit., 262–3°C at 759.4 mmHg); $\delta_H$ (200 MHz) 7.2–7.5 (5H, m), 3.69 (3H, s) and 3.62 (2H, s); $\delta_C$ (50 MHz), 170.1 (C=O), 135.0 (4ry), 129.8 (2C), 129.0 (2C), 126.9, 52.4 (OCH$_3$) and 36.4 (SCH$_2$).
Sodium metal (2.1 g, 92 mmol) was dissolved in ethanol (100 ml) and thiophenol (10.1 g, 92 mmol) was added. Methyl chloroacetate (10.0 g, 92 mmol) was added dropwise and the mixture was stirred for 12 h. The mixture was evaporated and the residue taken up into dichloromethane. This solution was washed with water, dried, evaporated and kugelrohr distilled to give methyl (benzenesulphenyl)acetate 293 (12.4 g, 74%) as a colourless liquid. Spectra identical to those of the product of di above.

e Preparation of ethyl (benzenesulphenyl)acetate
i Sodium metal (1.9 g, 82 mmol) was dissolved in ethanol (100 ml) and thiophenol (9.0 g, 82 mmol) was added. Ethyl chloroacetate (10.0 g, 82 mmol) was added dropwise and the mixture was stirred for 12 h. The mixture was evaporated and the residue taken up into dichloromethane. This solution was washed with water, dried, evaporated and kugelrohr distilled to give ethyl (benzenesulphenyl)acetate as a colourless liquid 295 (11.5 g, 72%). b.p. 130°C (oven temp.) at 2 mmHg (lit.,201 265°C at 759.4 mmHg); δH (200 MHz) 7.1–7.5 (5H, m), 4.12 (2H, q, J = 8 Hz), 3.62 (2H, s) and 1.20 (2H, t, J = 8 Hz); δC (50 MHz) 169.6 (C=O), 135.1 (4ry), 129.8 (2C), 129.0 (2C), 126.8, 61.4 (OCH2), 36.6 (SCH2) and 14.0.

ii A solution of (benzenesulphenyl)acetyl chloride (4.0 g, 21 mmol) in ethanol (100 ml) was stirred for 12 h. Evaporation and kugelrohr distillation gave ethyl (benzenesulphenyl)acetate 295 (2.44 g, 58%) as a
golden yellow liquid which had identical properties to the product of experiment ei above

3 Preparation of alkane- and arenesulphinylacetates

i Preparation of methyl (ethanesulphonyl)acetate 297

Sodium metaperiodate (1.6 g, 7 mmol) was stirred in 20 ml deionised water. Methyl (ethanesulphonyl)acetate (1.0 g, 7 mmol) in methanol was added dropwise and the mixture was stirred for 12 h. The product was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave methyl (ethanesulphonyl)acetate 297 as a colourless oil (0.4 g, 36%). b.p. 150°C (oven temp.) at 0.1 mmHg; (Found: 150.0349. C$_5$H$_{10}$O$_3$S requires 150.0351); δ$_H$ (200 MHz) 3.77 (3H, s), 3.78 and 3.68 (2H, AB pattern, J = 18 Hz), 2.89 (2H, m) and 1.35 (3H, t, J = 7 Hz); δ$_C$ (50 MHz) 166.2 (C=O), 55.2 and 53.0 (OCH$_3$ and CH$_2$CO), 46.2 (SCH$_2$CH$_3$) and 6.7 (SCH$_2$CH$_3$); ν$_{\text{max}}$ 1710, 1330, 1285, 1255, 1140 and 1086 cm$^{-1}$; m/z 150 (M$^+$, 3%), 134 (45), 122 (5), 105 (21), 89 (11), 75 (100), 61 (84), 59 (92) and 45 (61).

ii Preparation of ethyl (ethanesulphonyl)acetate 299

Sodium metaperiodate (4.8 g, 22 mmol) was stirred in 20 ml deionised water. Ethyl (ethanesulphonyl)acetate (4.0 g, 27 mmol) in methanol (20 ml) was added dropwise and mixture was stirred for 12 h. The reaction mixture was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave ethyl (ethanesulphonyl)acetate...
299 as a yellow oil (3.1 g, 85%). b.p. 105°C (oven temp.) at 0.3 mmHg; (Found: m/z \([M^+ - O]\) 148.0570. \(\text{C}_6\text{H}_{12}\text{O}_3\text{S}\) requires \([M^+ - O]\) 148.0558); \(\delta_H\) (200 MHz) 4.23 (2H, q, \(J = 8\) Hz), 3.73 and 3.66 (2H, AB pattern, \(J = 18\) Hz), 2.90 (2H, m), 1.36 (3H, t, \(J = 8\) Hz) and 1.32 (3H, t, \(J = 8\) Hz); \(\delta_C\) (50 MHz) 165.6 (C=O), 62.4 (OCH\(_2\)), 55.6 (CH\(_2\)CO), 46.5 (SCH\(_2\)CH\(_3\)), 14.5 (OCH\(_2\)CH\(_3\)) and 6.9 (SCH\(_2\)CH\(_3\)); \(\nu_{\max}\) 1720, 1440, 1370, 1295, 1090 and 855 cm\(^{-1}\); m/z = 148 (M+ - O, 3%), 135 (3), 88 (9), 75 (31), 61 (10), 47 (32) and 29 (100).

iii Preparation of methyl (benzenesulphinyl)acetate 298

Sodium metaperiodate (1.17 g, 5.5 mmol) was stirred in 20 ml deionised water. Methyl (benzenesulphenyl)acetate (1.0 g, 5.5 mmol) in methanol was added dropwise and mixture was stirred for 12 h. The reaction mixture was extracted with dichloromethane (200 ml). Drying, evaporation and kugelrohr distillation gave methyl (benzenesulphonyl) acetate 298 as a yellow oil (0.35 g, 32%). b.p. 200°C (oven temp.) at 1 mmHg; (Found: m/z = 198.0355. \(\text{C}_9\text{H}_{10}\text{O}_3\text{S}\) requires 198.0351); \(\delta_H\) (200 MHz) 7.70 (2H, m), 7.6–7.5 (3H, m), 3.86 and 3.74 (2H, AB pattern, \(J = 16\) Hz) and 3.69 (3H, s); \(\delta_C\) (50 MHz) 165.2 (C=O), 142.9 (4ry), 131.8, 129.4 (2C), 124.1 (2C), 61.3 (OCH\(_3\)) and 52.7; \(\nu_{\max}\) 1720, 1435, 1275, 1110, 1080, 1040, 900, 740 and 690 cm\(^{-1}\); m/z = 198 (M+, 22%), 182 (1), 167 (2), 138 (3), 125 (100), 109 (5), 97 (32) and 77 (38).
iv Preparation of ethyl (benzenesulphonyl)acetate 300

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

4 Attempted preparation of alkane- and arenesulphonyl diazoacetates

a Preparation of ethyl (ethanesulphonyl)diazoacetate

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

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

c **Preparation of ethyl (benzenesulphinyl)diazoacetate**

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

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

i **triethylamine as base**

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

ii **n-butyl lithium as base**

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

a Preparation of methyl (benzenesulphenyl)diazoacetate

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

b Preparation of ethyl (benzenesulphenyl)diazoacetate

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

ii Sodium hydride (60% dispersion in oil [0.2g = 0.1g sodium hydride] 5 mmol) was washed with 40–60 petroleum to remove the oil and then dispersed in extra dry THF (50 ml). To this was added ethyl (phenylthio) acetate (1.0 g, 5 mmol) in dry THF (50 ml) and tosyl azide (5 mmol) in dry THF (1.0 g, 50 ml). This mixture was stirred for 72 h, then the THF
was evaporated, the residue partitioned between ether (200 ml) and aqueous potassium hydroxide (200 ml, 0.2M). The ether layer was dried and evaporated to give just the starting materials.

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

E Preparation and pyrolysis of (arenesulphinyl)benzylidene triphenylphosphoranes

1 Preparation

a Preparation of phosphonium salts Ph₃P+CH₂Ar Hal⁻

i Preparation of benzyltriphenylphosphonium chloride 315

A solution of triphenylphosphine (25.0 g, 95 mmol) and benzyl chloride (13.1 g, 105 mmol) in toluene (250 ml) was heated under reflux for 24 h. The white precipitate was filtered off and washed with ether to give benzyltriphenyl phosphonium chloride 315 as a white powder (18.1 g,
48%). m.p. 282–3°C (lit.,203 287–8°C); δ\textsubscript{p} +23.0; δ\textsubscript{H} (80 MHz) 7.5–8.0 (15H, m), 7.1–7.4 (5H, m) and 5.55 (2H, d, J\textsubscript{P-H} = 16 Hz).

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

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

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

A solution of 4-methoxybenzyl alcohol (50.0 g, 362 mmol) in dichloromethane (100 ml) was stirred at 0°C while a solution of phosphorus tribromide (32.7 g, 121 mmol) in dichloromethane (50 ml) was added dropwise. The mixture was stirred for 90 min, added to water (100 ml) and the product extracted with ether. Drying and evaporation gave 4-methoxybenzyl bromide (68.0 g, 93%). δ\textsubscript{H} (60 MHz) 7.2 and 6.8 (4H, AB pattern, J = 8 Hz), 4.5 (2H, s) and 3.7 (3H, s). The product was not purified further because it is a severe irritant.
The product from the previous reaction, 4-methoxybenzyl bromide (68.0 g, 338 mmol) was added to a solution of triphenylphosphine (88.6 g, 338 mmol) in toluene (200 ml). This mixture was heated under reflux for 6 h, then the white precipitate was filtered off and washed with ether to give 4-methoxybenzyltriphenylphosphonium bromide 317 as a white powder (140.8 g, 90%). m.p. 230–2°C (lit., 205–217°C); δ_p +22.1; δ_H (200 MHz) 7.6–7.9 (15H, m), 7.00 and 6.65 (4H, AB pattern, J = 10 Hz), 5.15 (2H, d, J = 16 Hz) and 3.73 (3H, s); δ_C (200 MHz) 159.6 (d, J = 4 Hz), 135.1 (3C, d, 4J_P = 2 Hz), 134.3 (6C, d, 2J_P = 10 Hz), 132.6 (2C, d, J = 10 Hz), 130.2 (6C, d, 3J_P = 12 Hz), 118.4 (d, J = 4 Hz), 117.6 (3C, d, 1J_P = 85 Hz), 114.2 (2C, d, J = 2 Hz), 55.3 and 30.0 (d, J = 47 Hz).

b Preparation of ylides
i Preparation of [(benzenesulphinyl)benzylidene]triphenylphosphorane 312

Benzyltriphenylphosphonium chloride (10.2 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 11 ml, 28 mmol) was added and the mixture was stirred for 30 min. Benzenesulphinyl chloride (2.1 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of slightly impure [(benzenesulphinyl)benzylidene]triphenylphosphorane 312 (1.8 g, 29%). m.p. 172–4°C (Found: C, 76.8; H, 5.25, m/z = 460.1423. C_{31}H_{25}OPS requires C, 78.1; H, 5.3%; M+ – O, 460.1415); δ_p +20.4; δ_H (300 MHz)
7.4–7.8 (17H, m), 7.2–7.3 (2H, m), 7.1–7.2 (1H, m), 7.02 (2H, m), 6.75–
6.85 (2H, m) and 6.70 (1H, m); \( \delta_C \) (75 MHz) 147.7 (d, \( J = 16 \) Hz), 137.2
(d, \( J = 12 \) Hz), 134.3 (6C, d, \( J_P = 10 \) Hz), 132.4 (3C, d, \( J_P = 2 \) Hz), 129.7
(2C, d, \( J = 6 \) Hz), 128.8 (6C, d, \( J_P = 12 \) Hz), 128.6, 127.8 (2C), 127.3
(2C), 126.8 (3C, d, \( J_P = 89 \) Hz), 126.3 (2C), 122.7 and 52.2 (d, \( J = 122 \)
Hz); \( \nu_{max} \) 1735, 1590, 1485, 1440, 1245, 1100, 1000 and 930 cm\(^{-1}\); m/z
460 (M\(^+\) – O, 4%), 399 (1), 351 (1), 277 (13), 262 (24), 234 (2), 218 (42),
200 (42), 183 (13), 143 (15), 105 (50) and 91 (100).

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

Benzyltriphenylphosphonium chloride (6.4 g, 16 mmol) was stirred in dry
toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 10.2
ml, 16 mmol) was added and the mixture was stirred for 30 min. A
solution of 4-methyl benzenesulphinyl chloride (1.4 g, 8 mmol) in dry
toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration,
evaporation and trituration with ethyl acetate gave yellow crystals of
[(4-methylbenzenesulphinyl)benzylidene]triphenylphosphorane 313 (1.8 g,
45%). m.p. 168–73°C (Found: C, 78.6; H, 5.5. \( \text{C}_{32}\text{H}_{27}\text{OPS} \) requires C,
78.3; H, 5.6%); \( \delta_P +20.2; \delta_H \) (80 MHz) 6.8–8.0 (24H, m) and 2.27 (3H, s);
\( \delta_C \) (75 MHz) 144.6 (4ry, d, \( J = 16 \) Hz), 137.7, 137.4 (4ry, d, \( J = 12 \) Hz),
134.3 (6C, d, \( J_P = 10 \) Hz), 132.3 (3C), 132.0 (2C, d, \( J = 7 \) Hz), 128.8 (6C,
d, \( J_P = 12 \) Hz), 128.7 (2C), 128.0 (3C, 4ry, d, \( J_P = 78 \) Hz), 127.3 (2C),
126.3 (2C), 122.6, 52.1 (d, \( J = 125 \) Hz) and 21.1; \( \nu_{max} \) 1605, 1510, 1250,
1175, 1030, 835, 755 and 735 cm\(^{-1}\); m/z 474 (M\(^+\) - O, 0.2%), 394 (1), 379 (1), 277 (15), 262 (26), 241 (1), 228 (2), 183 (45), 105 (69), 91 (15) and 77 (100).

iii Preparation of [(4-chlorobenzenesulphonyl)benzylidene]triphenylphosphorane \textbf{314}

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

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

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

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

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

A solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 13.5 ml, 22 mmol) was added and the mixture was
stirred for 30 min. A solution of 4-chlorobenzenesulphinyl chloride (2.1 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave the starting phosphonium salt and 2 other products, δp +25.1 and 23.5.

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

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

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

A solution of (4-nitrobenzyl)triphenylphosphonium bromide (10.0 g, 21 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (1.6M, 13.1 ml, 21 mmol) was added and the mixture was stirred for 30 min. A solution of 4-chlorobenzenesulphinyl chloride (1.8 g, 10 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave triphenylphosphine oxide.
2 FVP of [(arenesulphonyl)benzylidene]triphenyl phosphoranes
a FVP of [(benzenesulphonyl)benzylidene]triphenylphosphorane 312

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

Ph3P, R_T = 11.47, m/z 261 (11%), 183 (47), 152 (12) and 108 (100); δ_P -5.0 (24).

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

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

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

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

Ph3P=O, R_T = 15.01, m/z 277 (19%), 199 (14), 183 (10) and 157 (17); δ_P +29.4 (12).

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

Ph3P=S, R_T = 15.41, m/z 294 (9%), 262 (4), 183 (55) and 139 (43); δ_P +43.7 (2).

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

Z-stilbene, (2% yield) R_T = 7.46, m/z 180 (39%), 179 (43), 165 (35), 152 (18) and 51 (100).
unknown, $R_T = 12.19$, m/z 215 (1%), 167 (100), 152 (28) and 109 (26).

In a separate run, stopped when half the substrate had been pyrolysed, the inlet tube was found to contain only a brown substance [GCMS (60-20-300) and $^1H$ (200 MHz) and $^{31}P$ NMR indicated the presence of $\text{Ph}_3\text{P}=\text{O}$, $R_T = 14.43$, m/z 277 (10%), 199 (12), 183 (13) and 157 (14); $\delta_p$ +28.6 (21).

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

$\text{Ph}_3\text{P}$, $R_T = 11.44$, m/z 262 (12%), 183 (45), 152 (16) and 108 (100); $\delta_p$ -5.4 (16).

$\text{Ph}_3\text{P}=\text{S}$, $R_T = 15.23$, m/z 294 (8%), 262 (15), 215 (8) and 183 (43).

b  FVP of [(4-methylbenzenesulphonyl)benzylidene]triphenylphosphorane

FVP of the title compound (0.21 g) [500°C, 3.8 x 10$^{-1}$ torr, 100°C] gave a small droplet of blue liquid in the cold trap [GCMS (60-20-300) and $^1H$ (200 MHz) and $^{31}P$ NMR indicated the presence of $\text{Ph}_3\text{P}$, $R_T = 11.46$, m/z 262 (16%), 183 (62), 152 (16) and 108 (100); $\delta_p$ -5.0 (140)

$\text{PhCOSC}_{6}\text{H}_4\text{Me}$, (25% yield) $R_T = 10.55$, m/z 228 (1%), 184 (1), 105 (100)

and 77 (89); $\delta_H$ and $\delta_C$ as for authentic material prepared in 3diii.

$\text{Ph}_3\text{P}=\text{O}$, $R_T = 14.44$, m/z 277 (18%), 199 (14), 183 (14) and 152 (12); $\delta_H$

7.4–7.8 (m); $\delta_p$ +28.8 (26).
4-MeC₆H₄SH, (20% yield) Rₜ = 4.15, m/z 124 (37%), 91 (100), 77 (15) and 45 (44) δ_H 2.26 (s).

(4-MeC₆H₄S)₂, (6% yield) Rₜ = 11.04, m/z 246 (8%), 214 (1), 182 (4) and 123 (74).

Ph₃P=S, Rₜ = 15.28, m/z 294 (13%), 262 (5), 215 (5) and 183 (62); δ_H 7.3 (m); δ_P +43.5 (5).

PhCOC₆H₄Me, (5% yield) Rₜ = 9.29, m/z 196 (12%), 181 (6), 165 (4), 152 (4), 119 (100) and 105 (38).

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

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

Ph₃P, Rₜ = 11.46, m/z 262 (16%), 183 (62), 152 (16) and 108 (100); δ_H 7.3 (m).

PhCOSC₆H₄Me, Rₜ = 10.55, m/z 228 (1%), 184 (1), 105 (100) and 77 (89).

Ph₃P=O, Rₜ = 14.44, m/z 277 (18%), 199 (14), 183 (14) and 152 (12).

Ph₃P=S, Rₜ = 15.28, m/z 294 (13%), 262 (5), 215 (5) and 183 (62).

(4-MeC₆H₄S)₂, Rₜ = 11.04, m/z 246 (8%), 214 (1), 182 (4) and 123 (74).

4-MeC₆H₄SH, Rₜ = 4.15, m/z 124 (37%), 91 (100), 77 (15) and 45 (44).

PhCOC₆H₄Me, Rₜ = 9.29, m/z 196 (12%), 181 (6), 165 (4), 152 (4), 119 (100) and 105 (38).]
FVP of the title compound (0.1812 g) [500°C, 1.0 x 10⁻³ torr, 100°C] gave a small droplet of blue liquid at the room temperature part of the trap and yellow droplets at the furnace exit. These were collected together [GCMS (60-20-300) and ¹H (200 MHz), ¹³C (50 MHz) and ³¹P NMR indicated the presence of

**Ph₃P=O, Rₜ = 17.46, m/z 277 (100%), 201 (28), 183 (27) and 152 (10); δₚ +29.4 (24).**

**Ph₃P, -5.1 (9).**

**Ph₃P=S, Rₜ = 19.28, m/z 294 (91%), 262 (15), 217 (15) and 183 (100); δₚ +43.6 (2).**

**4-ClC₆H₄SH, (25% yield) Rₜ = 6.19, m/z 146 (36%), 144 (100) and 109 (50); δH 3.47 (1H).**

**PhCOC₆H₄Cl, (18% yield) Rₜ = 10.59, m/z 218 (18%), 216 (70), 181 (20), 141 (88) and 105 (100).**

**(4-ClC₆H₄S)₂, (17% yield) Rₜ = 13.22, m/z 290 (3%), 288 (32), 175 (2) and 143 (100)**

**PhCOSC₆H₄Cl, (9% yield) Rₜ = 12.33, m/z 250 (2%), 248 (6), 197 (1), 184 (1) and 105 (100).**

**PhCH₂SC₆H₄Cl, (7% yield) Rₜ = 11.22, m/z 236 (8%), 234 (22), 165 (2), 143 (10) and 91 (100); δH 4.04 (2H).**

**E-stilbene, (7% yield) Rₜ = 10.07, m/z 180 (100%), 165 (48), 152 (16) and 89 (25).**
benzaldehyde, R_T = 4.31, m/z 106 (55%), 100 (100) and 77 (62)

3 Preparation and FVP of authentic samples of FVP products
a Preparation of benzophenones
i Preparation of 4-chlorobenzophenone 347
A solution of 4-chlorobenzoic acid (6.3 g, 40 mmol) in thionyl chloride (97.9 g, 823 mmol, 60 ml) was heated under reflux for 12 h. Evaporation and kugelrohr distillation gave 4-chlorobenzoyl chloride as a yellow oil which was used immediately for further experiments.

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

ii Preparation of 4-methylbenzophenone 348
A solution of 4-methylbenzoic acid (5.0 g, 37 mmol) in thionyl chloride (81.5 g, 684 mmol, 50 ml) was heated under reflux for 12 h. Evaporation
and kugelrohr distillation gave 4-methylbenzoyl chloride as a clear oil (5.0 g, 88%) $\delta_H$ (60 MHz) 8.1 and 7.4 (4H, AB pattern, J = 8 Hz) and 2.5 (3H, s). The oil was used immediately for further experiments and so was not distilled.

Aluminium trichloride (2.2 g, 9 mmol) was added slowly to a solution of 4-methylbenzoyl chloride (2.6 g, 17 mmol) in benzene (50 ml). The mixture was heated under reflux until HCl evolution had ceased then poured onto a mixture of concentrated HCl (100 ml) and ice (200 g). The ice was allowed to melt, then the benzene layer was separated off and washed with aqueous sodium hydroxide (2 M, 2 x 200 ml) and water (2 x 200 ml). Drying, evaporation and kugelrohr sublimation gave 4-methylbenzophenone 348 as a yellow solid (1.7 g, 52%). m.p. 49-50°C (lit., 207 50-51°C); $\delta_H$ (200 MHz) 7.7-7.9 (4H, m), 7.4-7.6 (3H, m), 7.2-7.3 (2H, m) and 2.43 (3H, s); $\delta_C$ (75 MHz) 196.3 (C=O), 143.2 (C-CH$_3$), 137.9 (4ry), 134.9 (4ry), 132.1, 130.2 (2C), 129.9 (2C), 128.9 (2C), 128.2 (2C) and 21.6.

b FVP of benzophenones
i FVP of 4-chlorobenzophenone 347
FVP of the title compound (0.5505 g) [500°C, 5 x 10$^{-3}$ torr, 100°C] gave only the unchanged starting material.

ii FVP of 4-methylbenzophenone 348
FVP of the title compound (0.3481 g) [500°C, 4 x 10$^{-3}$ torr, 100°C] gave only the unchanged starting material (100%).
c Preparation of thiobenzophenones

These were prepared according to the method of Gattermann.\textsuperscript{208}

i Preparation of thiobenzophenone

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

ii Preparation of 4-chlorothiobenzophenone 345

Phosphorus pentasulphide (4.2 g, 18 mmol) was stirred in xylene (10 ml). 4-chlorobenzophenone (2.0 g, 9 mmol) in xylene (20 ml) was added and the mixture was heated under reflux for for 12 h. Filtration and kugelrohr distillation gave 4-chlorothiobenzophenone 345 as a blue liquid (0.43 g, 20%). b.p. 170°C (oven temp.) at 0.1 mmHg (lit.,\textsuperscript{210} 145–6°C at 0.22 mmHg); (Found: m/z = 232.0102. C\textsubscript{13}H\textsubscript{9}\textsubscript{35}ClS requires 232.0113); δ\textsubscript{H} (200 MHz) 7.2–7.8 (m); δ\textsubscript{C} (50 MHz) 236.2 (C=S), 146.9 (4ry), 145.3 (4ry), 138.5 (4ry), 132.1, 130.8 (2C), 129.4 (2C), 128.2 (2C) and 128.0 (2C); λ\textsubscript{max} 592nm.
iii Preparation of 4-methylthiobenzophenone 344

Phosphorus pentasulphide (4.5 g, 20 mmol) was stirred in xylene (10 ml). 4-methylbenzophenone (1.0 g, 10 mmol) in xylene (20 ml) was added and the mixture heated under reflux for for 12 h. Filtration and kugelrohr distillation gave 4-methylthiobenzophenone 344 as a blue liquid (0.4 g, 37%). b.p. 170°C (oven temp.) at 0.1 mmHg (lit.,210 136–8°C at 0.3 mmHg); (Found: m/z = 212.0648. C14H12S requires 212.0660); δH (200 MHz) 7.1–7.8 (m, 9H) and 2.38 (3H, s); δC (50 MHz) 237.7 (C=S), 147.6 (4ry), 144.8 (4ry), 143.1 (4ry), 131.7, 129.9 (2C), 129.5 (2C), 128.7 (2C), 127.9 (2C) and 21.6; λmax 585nm

d Preparation of thiolobenzoates

i Preparation of phenyl thiolobenzoate 349

Sodium metal (1.0 g, 45 mmol) was dissolved in ethanol (100 ml) and thiophenol (5.0 g, 45 mmol) was added, followed by benzoyl chloride (6.4 g, 45 mmol). The mixture was stirred for 30 min, then the ethanol was evaporated and the residue taken up in dichloromethane. This solution was washed with water. Drying, evaporation and recrystallisation of the residue from ethanol gave phenyl thiolobenzoate 349 as colourless flakes (7.3 g, 75%). m.p. 50–1°C (lit.,211 56°C); δH (200 MHz) 8.0 (2H, m) and 7.3–7.6 (8H, m)
ii  Preparation of 4-chlorophenyl thiolobenzoate 350
A solution of benzoyl chloride (9.7 g, 69 mmol) in dry toluene (30 ml) was added dropwise to a solution of 4-chlorothiophenol (10.0 g, 69 mmol) and triethylamine (7.0 g, 9.6 ml, 69 mmol) in dry toluene (100 ml) and the mixture was stirred for 30 min. The byproduct amine salt was filtered off and the toluene solution was washed with water. Drying and evaporation gave 4-chlorophenyl thiolobenzoate 350 as colourless crystals (2.9 g, 16%). m.p. 57-9°C (Found: C, 62.2; H, 4.0; m/z = 248.0057. C_{13}H_{935}ClOS requires C, 62.8; H, 3.7%; 248.0063); δ_H (200 MHz) 8.0-8.15 (2H, m) and 7.2-7.7 (7H, m); δ_C (50 MHz) 190.0 (C=O), 136.9 (2C), 136.5 (C-Cl), 134.5, 130.1 (2C), 129.9 (4ry), 129.4 (2C), 128.1 (2C) and 126.4 (4ry); ν_{max} 1680, 1210, 1180, 1100, 1020, 900, 825, 780 and 690 cm\(^{-1}\); m/z 250 (^{37}Cl-M\(^{+}\), 3%), 248 (^{35}Cl-M\(^{+}\), 10), 226 (4), 198 (2), 176 (4), 145 (6, ^{37}ClC_{6}H_{4}S\(^{+}\)), 143 (18, ^{35}ClC_{6}H_{4}S\(^{+}\)), 122, (6), 105 (100), 91 (75) and 77 (92).

iii  Preparation of 4-methylphenyl thiolobenzoate 351
A solution of benzoyl chloride (11.3 g, 80 mmol) in dry toluene was added dropwise to a solution of 4-methylthiophenol (10.0 g, 81 mmol) and triethylamine (8.2 g, 11.3 ml, 81 mmol) in dry toluene (100 ml) and the mixture was stirred for thirty minutes. Filtration, washing with water, drying and evaporation gave 4-methylphenyl thiolobenzoate 351 (8.4 g, 45%) as colourless crystals. m.p. 65°C (Found: C, 73.7; H, 5.6; m/z = 228.0612. C_{14}H_{12}OS requires C, 73.7; H, 5.3%; 228.0609); δ_H (200 MHz)
8.02 and 7.18 (4H, AB pattern, J = 9 Hz), 7.35–7.55 (5H, m) and 2.34 (3H, s); δC (50 MHz) 191.0 (C=O), 140.3 (4ry), 137.3 (4ry), 135.7 (2C), 134.2, 130.7 (2C), 129.4 (2C), 128.1 (2C), 124.5 (4ry) and 22.0; νmax (CH2Cl2) 3030, 2920, 2870, 1670, 1605, 1590, 1500, 1460, 1410, 1310, 1210, 1185, 1105, 1030, 910 and 820 cm⁻¹; m/z 228 (M⁺, 15%), 123 (5), 105 (100), 91 (4) and 77 (65).

e  FVP of thiolobenzoates

i  FVP of 4-chlorophenyl thiolobenzoate 350
FVP of the title compound (1.81 g) [500°C, 2 × 10⁻³ torr, 100°C] gave a colourless solid which was shown by ¹H and ¹³C NMR to be the starting material (1.7 g, 96%) and toluene.

ii  FVP of 4-methylphenyl thiolobenzoate 351
FVP of the title compound (3.48 g) [500°C, 5 × 10⁻³ torr, 100°C] gave a pale yellow solid which was shown by ¹H and ¹³C NMR to be the unchanged starting material (3.0 g, 87%).

f  Reaction of triphenylphosphine and triphenylphosphine oxide with thiobenzophenones

i  Triphenylphosphine and thiobenzophenone
Triphenylphosphine (0.03 g, 0.1 mmol) was added to an NMR tube containing thiobenzophenone (0.2 g, 10 mmol) in CDCl₃. The blue colour of the thioketone persisted, even after 4 days, but the ³¹P NMR spectrum
showed that the phosphine had been almost entirely converted to triphenylphosphine sulphide ($\delta_p +42.8$).

**ii Triphenylphosphine oxide and 4-methylthiobenzophenone**

4-methylthiobenzophenone (0.72 g, 3 mmol) was stirred in chloroform and triphenylphosphine oxide (1.0 g, 3 mmol) was added. There appeared to be no colour diminution after 16 h so a further equivalent of triphenylphosphine oxide was added. After 16 days the colour had disappeared. The solvent was evaporated to give a waxy solid which was separated by column chromatography (silica, 2 Et$_2$O:1 40–60 petroleum ether) into two components, triphenylphosphine oxide ($\delta_p +28.9$) and 4-methylbenzophenone ($\delta_H$ identical to authentic sample spectra).

**g FVP of sulphides**

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

FVP of the title compound (0.2614 g) [500°C, 1.3 x 10$^{-2}$ torr, 20°C] gave a colourless band in the cold trap and a larger amount of colourless solid in the furnace exit. Both fractions were collected together and were shown by $^1$H and $^{13}$C NMR to be the unchanged starting compound (60% by calibration with CH$_2$Cl$_2$)

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

FVP of the title compound (0.3097 g) [500°C, 1.2 x 10$^{-2}$ torr, 40°C] to give a colourless band in the cold trap and a larger amount of colourless solid in
the furnace exit. Both fractions were collected together and were shown by \(^1\)H and \(^{13}\)C NMR to be the unchanged starting compound (85% by calibration with CH\(_2\)Cl\(_2\))

F  Preparation and pyrolysis of

\[\text{[(alkanesulphenyl)alkylidene]triphenyl phosphoranes}\]

1 Preparation

i  Preparation of \[\text{[(ethanesulphenyl)benzylidene]triphenylphosphorane}\]

355

Benzyltriphenylphosphonium chloride (10.0 g, 26 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 10.3 ml, 26 mmol) was added and the mixture was stirred for 30 min. Ethanesulphenyl chloride (1.5 g, 13 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of \[\text{[(ethanesulphenyl)benzylidene]triphenylphosphorane}\]

355 (1.3 g, 23%). m.p. 169-72°C (Found: C, 75.4; H, 5.9; m/z = 412.1436. \(\text{C}_{27}\text{H}_{25}\text{OPS}\) requires C, 75.7; H, 5.9%; \(\text{M}^+ - \text{O}\), 412.1415); \(\delta\)_P +19.7; \(\delta\)_H (200 MHz) 6.9-7.7 (20H, m), 2.85 (2H, q, J = 8 Hz) and 1.07 (3H, t, J = 8 Hz); \(\delta\)_C (75 MHz) 137.1 (d, J = 14 Hz), 134.2 (6C, d, \(^2\)J\(_P\) = 10 Hz), 131.9 (3C, d, \(^4\)J\(_P\) = 2 Hz), 131.5 (2C, d, J = 6 Hz), 128.6 (6C, d, \(^3\)J\(_P\) = 12 Hz), 127.7 (3C, d, \(^1\)J\(_P\) = 86 Hz), 127.8 (2C), 124.0, 47.9 (d, J = 126 Hz), 45.2 (d, J = 12 Hz) and 10.1; \(\nu\)\(_{\text{max}}\) 1591, 1489, 1436, 1255, 1240, 1101, 1093, 999, 977 and 754 cm\(^{-1}\); m/z 412 (\(\text{M}^+ - \text{O}\), 5%), 383 (10), 351 (1), 300 (277), 262 (12%), 183 (32), 121 (100).
ii Preparation of [(2-propanesulphonyl)benzylidene]triphenylphosphorane 227

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

iii Preparation of [(phenyl)methanesulphonyl]benzylidene]triphenylphosphorane 356

Benzyltriphenylphosphonium chloride (7.1 g, 18 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5 M, 7.3 ml, 18 mmol) was added and the mixture was stirred for 30 min.
Phenylmethanesulphinyl chloride (1.6 g, 9.1 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 2 h. Filtration, evaporation and trituration with ethyl acetate gave yellow crystals of slightly impure [(phenylmethanesulphinyl)benzylidene]triphenylphosphorane 356 (0.2 g, 4%). m.p. 159°C (Found: C, 75.1; H, 5.3. C$_{32}$H$_{27}$OPS requires C, 78.6; H, 5.6%); $\delta_p$ +18.7; $\delta_H$ (80 MHz) 7.0–8.0 (25H, m) and 4.60 (1H, half of AB pattern of d, J = 13 Hz, 2 Hz), 4.13 (1H, half of AB pattern, J = 13 Hz) [plus impurities of ethyl acetate and toluene]; $\delta_C$ (75 MHz) 138.3 (4ry, d, J = 12 Hz), 134.0 (6C, d, $^2$J$_P$ = 10 Hz), 133.2 (4ry), 132.1 (3C), 131.9 (2C, d, J = 5 Hz), 130.5 (2C), 128.6 (6C, d, $^3$J$_P$ = 12 Hz), 128.4 (2C), 127.9 (2C), 127.0 (3C, d, $^1$J$_P$ = 90 Hz), 127.0, 123.5, 56.3 (d, J = 12 Hz) and 47.1 (d, J = 128 Hz); $\nu_{max}$ 1580, 1430, 1300, 1250, 1180, 1100, 990, 925, 750, 710 and 685 cm$^{-1}$; m/z 455 (1%, impurity), 415 (3), 399 (M$^+$ – PhCH$_2$, 4), 398 (23), 382 (10), 366 (4), 351 (8), 303 (2), 294 (4), 277 (10), 262 (58), 183 (100), 152 (20), 105 (95) and 77 (98).

iv Attempted preparation of [(phenylmethanesulphinyl)ethylidene]triphenylphosphorane

Ethyltriphenylphosphonium bromide (10.0 g, 27 mmol) was stirred in dry toluene at 0°C under nitrogen. A solution of n-butyl lithium (2.5M, 10.3 ml, 26 mmol) was added and the mixture was stirred for 20 min. Phenylmethanesulphinyl chloride (2.4 g, 14 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave a few very small crystals $\delta_p$ +30.56.
Evaporation of the ethyl acetate gave a solid that was mostly triphenylphosphine oxide, $\delta_p 28.5$, and triphenylphosphine, $\delta_p -5.5$, with minor components $\delta_p 43.0$ (Ph$_3$P=S), 35.7, 33.6 and 30.7.

v Attempted preparation of [(ethanesulphinyl)ethylidene]triphenylphosphorane

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

vi Attempted preparation of [(methanesulphinyl)benzylidene]triphenylphosphorane

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

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

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

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

A solution of n-butyl lithium (1.6M, 13.5 ml, 22 mmol) was added to a solution of (4-methoxybenzyl)triphenylphosphonium bromide (10.0 g, 22 mmol) in dry toluene at 0°C under nitrogen. and the mixture was stirred for 30 min. A solution of 2-propanesulphinyl chloride (1.4 g, 11 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration and evaporation gave a product which contained triphenylphosphine oxide, triphenylphosphine sulphide, triphenyl
phosphine, and at least 3 other products, including a minor one at δP +18.0 which may have been the desired product.

ix Attempted preparation of [(phenylmethanesulphonyl)-4-methoxybenzylidene]triphenylphosphorane

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

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

A solution of n-butyl lithium (2.5M, 4.6 ml, 11 mmol) was added to a solution of (4-nitrobenzyl)triphenylphosphonium bromide (5.0 g, 10 mmol) in dry toluene at 0°C under nitrogen, and the mixture was stirred for 30 min. Ethanesulphonyl chloride (0.7 g, 6 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave triphenylphosphine oxide with a small amount of triphenylphosphine.
xi Attempted preparation of [(2-propanesulphinyl)-4-nitrobenzylidene] triphenylphosphorane

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

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

A solution of n-butyl lithium (2.5M, 8.4 ml, 21 mmol) was added to a solution of (4-nitrobenzyl)triphenylphosphonium bromide (5.0 g, 10 mmol) in dry toluene at 0°C under nitrogen and the mixture was stirred for 30 min. Phenylmethanesulphinyl chloride (1.8 g, 10 mmol) in dry toluene (10 ml) was added and the mixture was stirred for 12 h. Filtration, evaporation and trituration with ethyl acetate gave an oil which contained triphenylphosphine sulphide, triphenylphosphine oxide, triphenylphosphine, two different phosphonium salts and an unknown compound, δ_p +10.5.
2 FVP of [(alkanesulphinyi)benzylidenetriphenylphosphoranes
a FVP of [(ethanesulphinyi)benzylidene]triphenylphosphorane 355
FVP of the title compound (0.1106g) [500°C, 5 x 10^{-3} torr, 50°C] gave yellow droplets in the cold trap [GCMS (60-20-300) and $^1$H (200 MHz) and $^{13}$C (75 MHz) and $^{13}$P NMR indicated the presence of PhCOS$\text{Et}$, (53% yield) $R_T$ 6.40, m/z 166 (4%), 105 (100), 77 (98) and 51 (85); $\delta_H$ 8.1-7.9 (2H, m), 7.5-7.3 (3H, m), 3.08 (2H, q, $J$ = 7 Hz) and 1.35 (3H, t, $J$ = 8 Hz); $\delta_C$ 192.1 (C=O), 133.2, 131.9, 128.6 (2C), 127.1 (2C), 23.4 and 14.8.
Ph$_3$P, $R_T$ 11.45, peak height 60 units, m/z 262 (10%), 183 (59), 152 (19) and 108 (100); $\delta_H$ 7.3 (m); $\delta_C$ 137.1 (3C, d, $J$ = 10 Hz), 133.7 (6C, d, $J$ = 19 Hz), 128.6 (6C, d, $J$ = 11 Hz) and 128.5 (3C).
Ph$_3$P=O, $R_T$ 14.41, peak height 11 units, m/z 277 (8%), 199 (7), 183 (8) and 112 (11); $\delta_C$ 132.4 (3C, d, $J$ = 104 Hz), 132.1 (6C, d, $J$ = 10 Hz), 131.9 (3C) and 128.5 (6C, d, $J$ = 12 Hz).
Ph$_3$P=S, $R_T$ 15.24, 5 units, m/z 294 (6%), 262 (5), 183 (53) and 107 (50).]

b FVP of [(2-propanesulphinyi)benzylidene]triphenylphosphorane 227
FVP of the title compound (0.1088g) [500°C, 5 x 10^{-3} torr, 50°C] gave colourless droplets at the furnace exit and cold trap. These were collected together. [GCMS (60-20-300) and $^1$H (200 MHz) indicated the presence of
PhCOSiPr, (37% yield) $R_T = 6.17$, m/z 180 (4%), 105 (100), 77 (82) and 51 (63); $\delta_H$ 7.4–8.1 (5H, m), 3.88 (1H, septet, $J = 7$ Hz) and 1.44 (6H, d, $J = 7$ Hz).

Ph$_3$P, $R_T = 11.08$, m/z 262 (42%), 183 (100), 152 (22) and 108 (88), peak height 84 units.

Ph$_3$P=O, $R_T = 13.41$, m/z 277 (36%), 199 (22), 183 (23) and 152 (26), peak height 9 units.

Ph$_3$P=S, $R_T = 14.17$, m/z 294 (22%), 262 (8), 215 (5) and 183 (100), peak height 7 units.

c FVP of [(phenylmethanesulphinyl)benzylidene]triphenylphosphorane 356

d FVP of [(phenylmethanesulphinyl)benzylidene]triphenylphosphorane

FVP of the title compound (0.0643g) [500°C, 8 x 10$^{-2}$ torr, 50°C] gave a yellow solid at the furnace exit [GCMS (60-20-300) and $^1$H (200 MHz) and $^{31}$P NMR indicated the presence of Ph$_3$P, Ph$_3$P=O and Ph$_3$P=S in the ratio 30:23:7.

Ph$_3$P, $\delta_P = -5.4$.

Ph$_3$P=O, $\delta_P = +28.8$.

Ph$_3$P=S, $\delta_P = +43.1$.

PhCH$_2$SCOPh, (30% yield) $R_T = 10.17$, m/z 228 (4%), 105 (100) and 77 (68); $\delta_H$ 4.35.

E-stilbene, (8% yield), $R_T = 10.57$, m/z 180 (98%), 179 (100), 165 (68) and 89 (48).
Z-stilbene, (2% yield), \( R_T = 9.40, \frac{m}{z} \) 180 (82%), 179 (100), 165 (62) and 89 (70).

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

ii Preparation of benzyl thiolobenzoate

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

G Preparation and pyrolysis of alkane- and arenesulphonyl aryl diazomethanes

1 Preparation of sulphides

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

i Preparation of benzyl ethyl sulphide 361

Sodium metal (2.0 g, 87 mmol) was dissolved in ethanol (100 ml) and ethanethiol (5.4 g, 87 mmol) was added. Benzyl chloride (11.0 g, 87
mmol) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying, evaporation and kugelrohr distillation gave benzyl ethyl sulphide 361 as a colourless liquid (7.3 g, 69%). b.p. 107°C (oven temp.) at 2 mmHg (lit.,213 222–3°C at 759 mmHg); δH (200 MHz) 7.2–7.4 (5H, m), 3.70 (2H, s), 2.42 (2H, q, J = 8 Hz) and 1.23 (3H, t, J = 8 Hz).

ii Preparation of benzyl 2-propyl sulphide 362
Sodium metal (3.0 g, 130 mmol) was dissolved in ethanol (100 ml) and propane-2-thiol (10.0 g, 131 mmol) was added. Benzyl chloride (16.6 g, 131 mmol) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying, evaporation and kugelrohr distillation gave benzyl 2-propyl sulphide 362 as a colourless liquid (9.1 g, 42%). b.p. 110°C (oven temp.) at 2 mmHg (lit.,214 99–104°C at 14 mmHg); δH (200 MHz) 7.1–7.3 (5H, m), 3.60 (2H, s), 2.66 (1H, septet, J = 8 Hz) and 1.13 (6H, d, J = 8 Hz); δC (50 MHz) 139.6 (4ry), 129.5 (2C), 129.0 (2C), 127.4, 35.8, 34.7 and 23.9 (2 x CH3).

iii Preparation of benzyl phenyl sulphide 363
Sodium metal (6.3 g, 270 mmol) was dissolved in ethanol (100 ml) and thiophenol (30.0 g, 270 mmol) was added. Benzyl chloride (34.5 g, 270 mmol) was added dropwise and the mixture was stirred for 12 h.
Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying, evaporation and recrystallisation from ethanol gave benzyl phenyl sulphide 363 as a white solid (33.1 g, 61%). m.p. 40–41°C (lit.,215 44.5°C); δ_H (200 MHz) 7.1–7.3 (10H, m) and 4.07 (2H, s); δ_C (50 MHz) 137.4 (4ry), 136.3 (4ry), 129.7 (2C), 128.8 (4C), 128.5 (2C), 127.1, 126.3 and 39.0.

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

v Preparation of benzyl 4-methylphenyl sulphide 353
Sodium metal (0.4 g, 17 mmol) was dissolved in ethanol (50 ml) and 4-methyl thiophenol (2.0 g, 16 mmol) was added. Benzyl chloride (2.0 g, 16 mmol) in ethanol (10 ml) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying and
evaporation gave benzyl 4-methylphenyl sulphide 353 as a colourless solid (1.0 g, 30%). m.p. 38–43°C (lit., 217 44°C); δH (200 MHz) 7.1–7.5 (9H, m), 4.20 (2H, s) and 2.42 (3H, s); δC (50 MHz) 138.4 (4ry), 137.1 (4ry), 133.2 (4ry), 131.2, (2C), 130.3 (2C), 129.5 (2C), 129.1 (2C), 127.7, 40.3 and 21.7.

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

vii Preparation of 4-methoxybenzyl phenyl sulphide 365
Sodium metal (0.5 g, 22 mmol) was dissolved in ethanol (100 ml) and thiophenol (2.2 g, 20 mmol) was added. A solution of 4-methoxybenzyl bromide (4.0 g, 20 mmol) in ethanol (50 ml) was added dropwise and the mixture was stirred for 30 min. Evaporation, addition of the residue to dichloromethane (100 ml), washing with water (100 ml), drying and evaporation gave 4-methoxybenzyl phenyl sulphide 365 as a colourless
solid (1.4 g, 28%). m.p. 85–86°C (lit.,217 85–86°C); δ_H (200 MHz) 7.1–7.4
(7H, m), 6.82 (2H, half of AB pattern, J = 8 Hz), 4.06 (2H, s) and 3.75 (3H, 
s); δ_C (50 MHz) 159.3 (4ry), 137.1 (4ry), 130.5 (2C), 130.3 (2C), 129.9
(4ry), 129.3 (2C), 126.8, 114.4 (2C), 55.8 and 38.9.

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

2 Preparation of sulphoxides
i Preparation of benzyl ethyl sulfoxide 367
Ethyl benzyl sulphide (2.0 g, 13 mmol) was stirred in methanol (20 ml)
 and a solution of sodium metaperiodate (3.2 g, 15 mmol) in water (20 ml)
 was added dropwise and the mixture was stirred for 12 h. Filtration
 followed by extraction of the product into dichloromethane, drying and evaporation gave benzyl ethyl sulfoxide 367 (0.8 g, 36%). m.p. 44–5°C
(lit.,\textsuperscript{215} 49°C); $\delta_H$ (200 MHz) 7.2–7.4 (5H, m), 3.95 and 4.02 (AB pattern, $J = 10$ Hz), 2.62 (2H, m) and 1.32 (3H, t, $J = 7$ Hz)

ii  Preparation of benzyl 2-propyl sulphoxide 368

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

iii  Preparation of benzyl phenyl sulphoxide 369

Benzyl phenyl sulphide (10.0 g, 50 mmol) was stirred in methanol (100 ml) and sodium metaperiodate (11.2 g, 52 mmol) in water (37 ml) was added dropwise and the mixture was stirred for 12 h. Filtration, extraction of the product into dichloromethane, drying and evaporation gave benzyl phenyl sulphoxide 369 (7.9 g, 73%). m.p. 123–5°C (lit.,\textsuperscript{221} 125°C); $\delta_H$ (200 MHz) 6.9–7.5 (10H, m) and 4.09 and 3.97 (2H, AB pattern, $J = 12.5$ Hz); $\delta_C$ (50 MHz) 142.7 (4ry), 131.1, 130.3 (2C), 129.1 (4ry), 128.8 (2C), 128.4 (2C), 128.2, 124.4 (2C) and 63.5.
iv  Preparation of dibenzyl sulphoxide 370

A solution of dibenzyl sulphide (4.0 g, 19 mmol) in methanol (50 ml) was stirred and a solution of sodium metaperiodate (4.4 g, 20 mmol, 1.05eq) in methanol (150 ml) was added and the mixture was stirred for 36 h. The mixture was evaporated and the residue taken up into dichloromethane. Washing with water, drying and evaporation gave dibenzyl sulphoxide 370 (2.5 g, 58%). m.p. 134-6°C (lit.,222 134°C); δ_H (200 MHz) 7.3–7.5 (10H, m) and 3.95 and 3.87 (4H, AB pattern, J = 15 Hz); δ_C (50 MHz) 130.1 (4C + 2C, 4ry), 138.9 (4C), 128.3 (2C) and 57.2 (2CH₂).

v  Preparation of benzyl 4-methylphenyl sulphoxide 371

Benzyl 4-methylphenyl sulphide (5.0 g, 23 mmol) was stirred in methanol (20 ml) and sodium metaperiodate (5.3 g, 25 mmol) in water (20 ml) was added dropwise and the mixture was stirred for 12 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give benzyl 4-methylphenyl sulfoxide 371 (3.2 g, 59%). m.p. 135–7°C (lit.,223 139–40°C); δ_H (200 MHz) 6.9–7.4 (9H, m), 4.05 and 3.95 (2H, AB pattern, J = 12.5 Hz) and 2.38 (3H, s); δ_C (50 MHz) 141.6 (4ry), 139.5 (4ry), 130.3 (2C), 129.5 (2C), 129.3 (4ry), 128.4 (2C), 128.2, 124.4 (2C), 63.7 (CH₂) and 21.4.

vi  Preparation of benzyl 4-chlorophenyl sulfoxide 372

Benzyl 4-chlorophenyl sulphide (0.5 g, 2 mmol) was stirred in water (20 ml) and sodium metaperiodate (0.6 g, 2 mmol) in methanol (20 ml) was
added and the mixture was stirred for 12 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give benzyl 4-chlorophenyl sulfoxide 372 (0.3 g, 54%). m.p. 133–134°C (lit. 134); δₜ (200 MHz) 7.4–7.1 (7H, m), 7.0–6.8 (2H, m), 4.07 and 3.95 (2H, AB pattern, J = 12.5 Hz); δₓ (50 MHz) 141.2 (4ry), 137.3 (4ry), 130.3 (2C), 129.1 (2C), 128.6 (4ry), 128.5 (2C), 128.4, 125.8 (2C) and 63.4

vii Preparation of 4-methoxybenzyl phenyl sulfoxide 373

4-Methoxybenzyl phenyl sulphide (1.0 g, 4.6 mmol) was stirred in methanol (200 ml) and sodium metaperiodate (1.0 g, 5 mmol) in water (20 ml) was added and the mixture was stirred for 12 h. Evaporation gave a residue which was taken up into dichloromethane. This solution was washed with water, dried and evaporated to give 4-methoxybenzyl phenyl sulfoxide 373 (0.34 g, 32%). m.p. 138–9°C (Found: C, 68.4; H, 5.6; m/z 231.0823. C₁₄H₁₄O₂S requires C, 68.3; H, 5.7%; M⁺ + H – O, 231.0844); δₜ (200 MHz) 7.5–7.3 (5H, m), 6.90 and 6.78 (4H, AB pattern, J = 10 Hz), 4.02 and 3.95 (2H, AB pattern, J = 12.5 Hz) and 3.78 (3H, s); δₓ (50 MHz) 159.7 (4ry), 142.9 (4ry), 131.6 (2C), 131.1, 128.8 (2C), 124.5 (2C), 121.0 (4ry), 113.9 (2C), 62.9 (CH₂) and 55.3; νₘ₉ₐₓ 1600, 1500, 1295, 1245, 1165, 1100, 1025, 825, 750, 730 and 680 cm⁻¹; m/z 231 (M⁺ + H – O, 5%), 121 (100), 106 (10), 91 (28), 77 (50), 65 (15) and 51 (32).
viii Preparation of 4-nitrobenzyl phenyl sulfoxide 374

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

3 Preparation of sulphones

i Preparation of benzyl ethyl sulphone 375

This was prepared by the method discovered by Mesher226. Benzyl ethyl sulphide (2.0 g, 13 mmol), benzoic acid (1.6 g, 13 mmol) and benzyl triethylammonium chloride (0.48 g, 2.2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (4.2 g, 26 mmol) in water (100 ml) was added and the mixture was stirred for 3 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 200 ml), aqueous sodium hydroxide (2M, 200 ml) and saturated brine (200 ml), drying, evaporation and recrystallisation of the residue from ethanol gave benzyl ethyl sulphone 375 (1.6 g, 66%). m.p. 83°C (lit.,213 84°C); δH (200 MHz) 8.07 and 7.11 (4H, AB pattern, J = 8 Hz), 4.20 and 4.04 (2H, AB pattern, J = 16 Hz).
MHz) 7.38 (5H, s), 4.22 (2H, s), 2.86 (2H, q, J = 8 Hz) and 1.35 (3H, t, J = 8 Hz); δc (50 MHz) 130.5 (2C), 129.0 (2C), 129.0, 128.1 (4ry), 58.7, 45.5 and 6.4.

ii Preparation of benzyl 2-propyl sulphone 376

Benzyl 2-propyl sulphide (3.0 g, 18 mmol), benzoic acid (2.2 g, 18 mmol) and benzyl triethylammonium chloride (0.7 g, 3 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (5.7 g, 36 mmol, 2 equivs) in water (100 ml) was added and the mixture was stirred for 3 days. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 200 ml), aqueous sodium hydroxide (2M, 200 ml) and saturated brine (200 ml), drying, evaporation of the dichloromethane and recrystallisation from ethanol gave benzyl 2-propyl sulphone 376 (1.2 g, 34%). m.p. 65–7°C (lit., 227 65°C); δH (200 MHz) 7.3–7.5 (5H, m), 4.20 (2H, s), 3.00 (1H, septet, J = 8 Hz) and 1.37 (6H, d, J = 8 Hz); δc (50 MHz) 130.6 (2C), 129.0 (2C), 128.8, 127.9 (4C), 56.1 (PhCH2), 51.1 and 15.2 (2C).

iii Preparation of dibenzyl sulphone 377

Dibenzyl sulphide (3.0 g, 15 mmol), benzoic acid (1.7 g, 14 mmol) and benzyl triethylammonium chloride (0.5 g, 2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (4.4 g, 28 mmol) in water (100 ml) was added and the mixture was stirred for 12 h.
Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and recrystallisation from ethanol gave dibenzyl sulphone 377 (2.7 g, 78%). m.p. 150°C (lit., 228°C 150°C); $\delta_H$ (200 MHz) 7.38 (10H, s) and 4.12 (4H, s); $\delta_C$ (50 MHz) 130.9 (4C), 128.93 (2C), 128.90 (4C), 127.5 (2C, 4ry) and 58.0 (2C).

iv Preparation of benzyl 4-chlorophenyl sulphone 378

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

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

vi Preparation of methyl (ethanesulphonyl)acetate

Methyl (ethanesulphonyl)acetate (4.0 g, 30 mmol), benzoic acid (3.6 g, 30 mmol) and benzyltriethylammonium chloride (1.1 g, 5 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (9.2 g, 58 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr
distillation gave methyl (ethanesulphonyl)acetate 380 (3.9 g, 79%). m.p. 40°C (lit.,231 42–4°C); δ_H (200 MHz) 4.02 (2H, s), 3.83 (3H, s), 3.28 (2H, q, J = 7 Hz) and 1.43 (3H, t, J = 7 Hz); δ_C (50 MHz) 163.6 (C=O), 56.4, 53.3, 48.1 and 6.5.

vii Preparation of ethyl (ethanesulphonyl)acetate 382
Ethyl (ethanesulphenyl)acetate (2.0 g, 14 mmol), benzoic acid (1.7 g, 14 mmol) and benzyl triethylammonium chloride (0.5 g, 2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (4.4 g, 28 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr distillation gave ethyl (ethanesulphonyl)acetate 382 (1.6 g, 66%). b.p. 161°C (oven temp.) at 0.7 mmHg (lit.,232 110°C at 0.3 mmHg °C); δ_H (200 MHz) 4.30 (2H, q, J = 7 Hz), 4.02 (2H, s), 3.30 (2H, q, J = 7 Hz), 1.43 (3H, t, J = 7 Hz) and 1.35 (3H, t, J = 7 Hz); δ_C (50 MHz) 162.7 (C=O), 62.1 (OCH₂), 56.2 (SCH₂C=O), 47.6 (SCH₂), 13.5 (OCH₂CH₃) and 6.1 (SCH₂CH₃).
viii  Preparation of methyl (benzenesulphonyl)acetate 381

Methyl (benzenesulphonyl)acetate (2.0 g, 11 mmol), benzoic acid (1.3 g, 11 mmol) and benzyl triethylammonium chloride (0.4 g, 2 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (3.5 g, 22 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr distillation gave methyl (benzenesulphonyl)acetate 381 (1.4 g, 60%). b.p. 160°C (oven temp.) at 0.3 mmHg (lit., 233°C at 0.01 mmHg); δ_H (200 MHz) 7.9–8.0 (2H, m), 7.5–7.8 (3H, m), 4.17 (2H, s) and 3.65 (3H, s); δ_C (50 MHz) 162.9 (C=O), 138.7 (4ry), 134.4, 129.3 (2C), 128.4 (2C), 60.7 (CH₂) and 53.0.

ix  Preparation of ethyl (benzenesulphonyl)acetate 383

Ethyl (benzenesulphonyl)acetate (2.0 g, 10 mmol), benzoic acid (1.1 g, 9 mmol) and benzyl triethylammonium chloride (0.3 g, 1 mmol) were dissolved in dichloromethane (50 ml). A solution of potassium permanganate (2.8 g, 18 mmol) in water (100 ml) was added and the mixture was stirred for 12 h. Sodium metabisulphite was added until the mixture became clear. The mixture was then filtered through celite and the product was extracted into dichloromethane. Washing with hydrazine
dihydrochloride (1M, 100 ml), aqueous sodium hydroxide (2M, 100 ml) and saturated brine (100 ml), drying, evaporation and kugelrohr distillation gave ethyl (benzenesulphonyl)acetate 383 (1.3 g, 52%). b.p. 155°C (oven temp.) at 0.3 mmHg (lit.,234 134–5°C at 0.01 mmHg); \( \delta_H \) (200 MHz) 7.9–8.0 (2H, m), 7.5–7.8 (3H, m), 4.18 (2H, s), 4.11 (2H, q, \( J = 8 \) Hz) and 1.13 (3H, t, \( J = 8 \) Hz); \( \delta_C \) (50 MHz) 161.9 (C=O), 138.3 (4ry), 133.8, 128.8 (2C), 128.0 (2C), 61.7 (OCH\(_2\)), 60.4 (SCH\(_2\)) and 13.3 (CH\(_3\)).

4 Preparation of diazosulphones

a Preparation of methyl (ethanesulphonyl) diazoacetate 385

i via tosyl azide

This was performed according to the method of Regitz and Bartz.235 Methyl (ethanesulphonyl)acetate (1.0 g, 6 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (0.6 g, 6 mmol) was added, followed by tosyl azide (1.2 g, 6 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2 x 100 ml) and the ether solution was dried and evaporated to give a viscous yellow oil which contained tosyl amide and may have contained the desired product. Dissolution of the oil in ether (200 ml) and further washing with sodium hydroxide (6 x 75 ml, 2M) hydolysed the ester.
ii  via 4-(N-acetylamino)benzenesulphonyl azide

Methyl (ethanesulphonyl)acetate (4.7 g, 28 mmol) and 4-(N-acetylamino)benzenesulphonyl azide (6.7 g, 28 mmol) were stirred in acetonitrile (100 ml) at 0°C and triethylamine (8.6 g, 85 mmol) was added. The mixture was stirred for 12 h and the solvent was then evaporated. Trituration of the residue with 1:1 ether:petroleum (3 ml) and column chromatography (silica, ether) gave methyl (ethanesulphonyl)diazooacetate 385 (0.9 g, 17%). m.p. 41–45°C (Found: m/z = 192.0196. C$_7$H$_8$N$_2$O$_4$S requires 192.0205 [pure by TLC (silica, Et$_2$O)]); $\delta$$_H$ (300 MHz) 3.86 (3H, s), 3.42 (2H, q, J = 7 Hz) and 1.42 (3H, t, J = 7 Hz); $\delta$$_C$ (75 MHz) 159.9 (C=O), 71.6 (CN$_2$), 52.5, 50.5, 6.7; $\nu$$_{max}$ 2110, 1700, 1595, 1430, 1270, 1205, 1140, 1080, 905, 795, 740, 710 and 605 cm$^{-1}$; m/z 192 (M+, 28%), 161 (11), 153 (5), 135 (5), 100 (70) and 59 (100).

b  Preparation of ethyl (ethanesulphonyl)diazoacetate 386

i  via tosyl azide

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

Ethyl (ethanesulphonyl)acetate (1.0 g, 6 mmol) and 4-(N-acetylamino) benzenesulphonyl azide (1.3 g, 6 mmol) were stirred in acetonitrile (20 ml) at 0°C and and triethylamine (1.6 g, 16.5 mmol) was added. The mixture was stirred for 12 h and the solvent was evaporated. Trituration of the residue with 1:1 ether:petroleum (3 ml) and column chromatography (silica, ether) gave ethyl (ethanesulphonyl)diazoacetate 386 (0.58 g, 50%).

m.p. 37°C (Found: C, 35.4; H, 4.9; N, 13.3; m/z = 206.0363. C_{6}H_{10}N_{2}O_{4}S requires C, 34.9; H, 4.9; N, 13.6%, 206.0361 [pure by TLC (silica, Et_{2}O)];

\[ \delta_{H} \quad \text{(200 MHz)} \quad 4.37 \quad (2H, q, J = 7 \text{ Hz}), \quad 3.43 \quad (2H, q, J = 7 \text{ Hz}), \quad 1.44 \quad (3H, t, J = 7 \text{ Hz}) \text{ and } 1.36 \quad (3H, t, J = 7 \text{ Hz}); \delta_{C} \quad (75 \text{ MHz}) \quad 159.5 \quad (\text{C=O}), \quad 71.6 \quad (\text{CN}_{2}), \quad 62.0, \quad 50.5, \quad 13.7 \text{ and } 6.8; v_{\text{max}} \quad 2100, \quad 1700, \quad 1440, \quad 1365, \quad 1330, \quad 1280, \quad 1210, \quad 1140, \quad 1070, \quad 1000, \quad 850, \quad 775, \quad 740, \quad 710 \text{ and } 600 \text{ cm}^{-1}; \quad m/z \quad 206 \quad (M^{+}, \quad 73\%), \quad 180 \quad (7), \quad 161 \quad (24), \quad 153 \quad (16), \quad 135 \quad (13), \quad 114 \quad (100), \quad 94 \quad (39), \quad 78 \quad (24) \text{ and } 66 \quad (80).]

**c Preparation of methyl (benzenesulphonyl)diazoacetate 387**

**i via tosyl azide**

Methyl (benzenesulphonyl)acetate (1.0 g, 5 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (0.5 g, 5 mmol) was added, followed by tosyl azide (1.0 g, 5 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2 x 100 ml) and the ether solution was dried and evaporated to give crude
methyl (benzenesulphonyl) diazoacetate 387 $\delta_H$ (200 MHz) 8.0−8.1 (2H, m), 7.5−7.7 (3H, m), 3.75 (3H, s) plus tosyl amide; $\nu_{\text{max}}$ 2120 cm$^{-1}$.

**ii via 4-(N-acetylamino)benzenesulphonyl azide**

Methyl (benzenesulphonyl)acetate (1.5 g, 8 mmol) and 4-(N-acetylamino)benzenesulphonylazide (1.7 g, 7 mmol) were stirred in acetonitrile (30 ml) at 0°C and triethylamine (2.1 g, 21 mmol) was added. The mixture was stirred for 12 h and the solvent was evaporated. Trituration of the residue with 1:1 ether:petroleum (30 ml) and column chromatography (silica, ether) gave methyl (benzenesulphonyl) diazoacetate 387 (0.9 g, 54%). m.p. 48−51°C (Found: m/z = 240.0201. $C_9H_8N_2O_4S$ requires 240.0205 [pure by TLC (silica, Et$_2$O)]); $\delta_H$ (200 MHz) 8.0−8.1 (2H, m), 7.5−7.7 (3H, m) and 3.75 (3H, s); $\delta_C$ (75 MHz) 159.7 (C=O), 141.4 (4ry), 134.0, 129.0 (2C), 127.6 (2C), 75.6 ($CN_2$) and 52.7; $\nu_{\text{max}}$ 2100, 1700, 1575, 1500, 1430, 1380, 1150, 1085, 720, 675 and 600 cm$^{-1}$; m/z 240 (M+, 33%), 180 (7), 141 (28), 125 (72), 105 (74), 97 (35) and 77 (100).

**d Preparation of ethyl (benzenesulphonyl)diazoacetate 388**

**i via tosyl azide**

Ethyl (benzenesulphonyl)acetate (1.0 g, 4 mmol) was stirred in dry dichloromethane (100 ml). Triethylamine (0.4 g, 4 mmol) was added, followed by tosyl azide (1.0 g, 4 mmol). The mixture was stirred for 3 days, then the solvent was evaporated and the residue added to aqueous sodium hydroxide (200 ml, 2M). The product was extracted with ether (2
x 100 ml) and the ether solution was dried and evaporated to give crude ethyl (benzenesulphonyl) diazoacetate 388 (0.9 g, 81%). δ_H (200 MHz) 8.0–8.1 (2H, m), 7.5–7.7 (3H, m), 4.20 (2H, q, J = 7 Hz) and 1.23 (3H, t, J = 7 Hz) plus TsNH₂.

ii  via 4-(N-acetylamino) benzenesulphonyl azide

Ethyl (benzenesulphonyl)acetate (1.0 g, 4 mmol) and 4-(N-acetylamino) benzenesulphonyl azide (1.1 g, 4 mmol) were stirred in acetonitrile (20 ml) at 0°C and and triethylamine (1.3 g, 13 mmol) was added. The mixture was stirred for 12 h and the solvent was then evaporated. Trituration of the residue with 1:1 ether:petroleum (3 ml) and column chromatography (silica, ether) gave ethyl (benzenesulphonyl) diazoacetate 388 (0.5 g, 47%). m.p. 41–45°C (Found: m/z = 254.0352. C₁₀H₁₀N₂O₄S requires 254.0361 [pure by TLC (silica, Et₂O)]; δ_H (200 MHz) 8.0–8.1 (2H, m), 7.5–7.7 (3H, m), 4.20 (2H, q, J = 7 Hz) and 1.24 (3H, t, J = 7 Hz); δ_C (75 MHz) 158.9 (C=O), 141.0 (4ry), 133.6, 128.6 (2C), 127.2 (2C), 75.3 (CN₂), 61.8 and 13.5; ν_max 2100, 1700, 1440, 1270, 1200, 1150, 1090, 1060, 1000, 730, 710, 670 and 590 cm⁻¹; m/z 254 (M⁺, 12%), 209 (7), 180 (3), 141 (24), 134 (26), 105 (29), 89 (9) and 77 (100).
e Attempted preparation of phenylmethanesulphonyl phenyl diazomethane

i via tosyl azide

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

ii via 4-(N-acetylamino)benzenesulphonyl azide

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

f Attempted preparation of benzenesulphonyl-4-nitrophenyl diazomethane

A solution of 4-nitrobenzyl phenyl sulphone (0.5 g, 2 mmol), tosyl azide (0.3 g, 2 mmol) and triethylamine (0.2 g, 2 mmol, 0.2 ml) in acetonitrile was stirred for 4 days and the solvent was then evaporated. The residue
was added to aqueous sodium hydroxide (2 x 100 ml). Extraction with ether, drying and evaporation gave just the starting materials.

5 FVP of alkane- and arenesulphonyldiazoacetates

a FVP of methyl (ethanesulphonyl)diazoacetate 385

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

unknown, \( R_T = 4.11, \text{m/z} \ 140 \ (27\%), \ 112 \ (7), \ 64 \ (28), \ 45 \ (62) \) and 29 (100).
unknown, \( R_T = 4.46, \text{m/z} \ 154 \ (18\%), \ 93 \ (8), \ 61 \ (40) \) and 29 (100).
unknown, \( R_T = 6.44, \text{m/z} \ 218 \ (1\%), \ 170 \ (22), \ 141 \ (10) \) and 109 (22).

unknown (possibly EtSO\(_2\)CH\(_2\)CO\(_2\)H), \( R_T = 4.59, \text{m/z} \ 152 \ (1\%), \ 77 \ (10), \ 66 \ (13), \ 43 \ (38) \) and 29 (68).
unknown, \( R_T = 6.53, \text{m/z} \ 182 \ (3\%), \ 138 \ (3), \ 123 \ (10) \) and 110 (35).
unknown, \( R_T = 6.13, \text{m/z} \ 156 \ (92\%), \ 141 \ (75), \ 109 \ (89) \) and 77 (65).

EtSO\(_2\)CH=CH\(_2\), (30% yield) \( R_T = 3.14, \text{m/z} \ 120 \ (2\%), \ 78 \ (53), \ 63 \ (100) \) and 45 (65); \( \delta_H \ 6.63 \ (1\ H, \text{dd, } J = 10 \text{ Hz, } 16 \text{ Hz}), \ 6.45 \ (1\ H, \text{d, } J = 16 \text{ Hz}), \ 6.19 \ (1\ H, \text{d, } J = 10 \text{ Hz}), \ 3.00 \ (2\ H, \text{q, } J = 7 \text{ Hz}) \) and 1.35 (3H, t, J = 7 Hz); \( \delta_C \ 135.5, \ 130.8, \ 48.6 \) and 7.0.

MeSSMe, \( R_T = 3.36, \text{m/z} \ 126 \ (6\%), \ 111 \ (13), \ 79 \ (60) \) and 45 (100).]
b  FVP of ethyl (ethanesulphonyl)diazoacetate 386

i  FVP of the title compound (0.2045 g) [600°C, 6.1 x 10^{-2} torr, 80°C] gave an oil in the cold trap [^{1}H (300 MHz) and ^{13}C (75 MHz) indicated the presence of ethyl E-propenyl sulphone 392, (6.4% yield) \( \delta_{H} 6.92 \) (1H, half of AB pattern of q, \( J_{AB} = 16 \) Hz, \( J = 8 \) Hz), 6.30 (1H, half of AB pattern of q, \( J_{AB} = 16 \) Hz, \( J = 2 \) Hz), 3.02 (2H, q, \( J = 8 \) Hz), 2.00 (3H, dd, \( J = 8 \) Hz, 2 Hz) and 1.3 (3H, t, \( J = 8 \) Hz); \( \delta_{C} 144.5, 128.5, 48.9, 17.5 \) and 7.1.

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

CH₃CHO, (2.7% yield) \( \delta_{H} 9.73 \) (1H, q, \( J = 2 \) Hz) and 2.18 (3H, d, \( J = 2 \) Hz).

ii  FVP of the title compound (0.0844 g) [400°C, 4 x 10^{-2} torr, 50°C] gave a yellow oil in the cold trap and furnace exit. This was collected as one fraction [GCMS (60-20-300) and \(^{1}H (200 \text{ MHz}) \) and \(^{13}C (75 \text{ MHz}) \) NMR indicated the presence of EtSSO₂Et, (17% yield) \( R_{T} = 5.32 \), m/z 154 (8%), 125 (1), 105 (4) and 95 (18); \( \delta_{H} 3.35 \) (2H, q, \( J = 7 \) Hz), 3.13 (2H, q, \( J = 7 \) Hz), 1.3–1.5 (2 x t, \( J = 7 \) Hz); \( \delta_{C} 56.8, 30.4, 14.9, \) and 8.1.

E- and Z-EtSO₂CH=CHMe, (E- 6.7% yield, Z- 4.6% yield) \( R_{T} = 5.15 \), m/z 134 (13%), 105 (8), 89 (17) and 39 (100); \( \delta_{H} \) as bi.
EtSO₂CH₂CO₂Et, Rₜ = 6.44, m/z 153 (17%), 135 (18), 78 (22) and 60 (48); δH 4.25 (2H, q, J = 7 Hz), 4.02 (2H, s), 3.30 (2H, q, J = 7 Hz), triplets hidden under EtSSO₂Et peaks; δC (C=O not observed), 62.7, 48.1, 14.0, 6.2.]

c  FVP of methyl (benzenesulphonyl)diazoacetate 387
i  FVP of the title compound (0.2749 g) [600°C, 8 x 10⁻³ torr, 80°C] gave a colourless oil in the cold trap [¹H (200 MHz) NMR and TLC (silica, 1:1 ether:60–80 petroleum ether) indicated the presence of biphenyl, δH 7.35 (s).]

ii  FVP of the title compound (0.50g) [400°C, 2.0 x 10⁻² torr, 80°C] gave brown droplets at the furnace exit [GCMS (60-20-300) indicated the presence of PhSCO₂Me, Rₜ = 6.27, m/z 168 (1%), 136 (2), 124 (1), 105 (89) and 77 (100).
PhSOMe, Rₜ = 7.09, m/z 140 (30%), 125 (45), 97 (55) and 77 (60).
PhSO₂CH=CH₂, Rₜ = 8.05, m/z 168 (5%), 156 (1), 141 (2) and 125 (55).
PhSO₂Me, Rₜ = 7.45, m/z 156 (9%), 141 (9), 125 (1) and 94 (31).
PhSPh, Rₜ = 8.25, m/z 186 (42%), 152 (8) and 77 (38).
PhSO₂Ph, Rₜ = 10.43, m/z 218 (18%), 202 (312), 154 (17) and 109 (42).
PhSCOCO₂H, Rₜ = 9.03, m/z 182 (5%), 165 (1), 157 (1) and 125 (68).
PhCOPh, Rₜ = 6.53, m/z 182 (1%), 154 (12), 105 (100) and 77 (74).]
and brown droplets at the cold trap products [GCMS (60-20-300) indicated the presence of

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

MeO$_2$CSPh, $R_T = 6.28$, m/z 168 (2%), 136 (2), 124 (2), 105 (100) and 77 (82).

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

MeO$_2$CPh, $R_T = 4.36$, m/z 136 (70%), 105 (96) and 77 (100).

**d** FVP of ethyl (benzenesulphonyldiazoacetate 388

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

HCOCO$_2$Et, $R_T = 4.29$, m/z 102 (1%), 74 (3), 45 (5) and 29 (100).

EtO$_2$CCO$_2$Et, $R_T = 3.41$, m/z 146 (1%), 117 (2), 101 (1), 74 (5) and 29 (100).

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

an aldehyde, $\delta_H$ 10.02 (s).]

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

PhSO$_2$Ph, $R_T = 10.04$, m/z 218 (8%), 109 (20) and 77 (100).

EtO$_2$CCO$_2$Et, $R_T = 3.41$, m/z 146 (1%), 117 (2), 74 (5) and 29 (100).

unknown (possibly PhCOCO$_2$Et), $R_T = 6.51$, m/z 178 (1%), 150 (2), 105 (100) and 77 (90).

PhSPh, $R_T = 8.22$, m/z 186 (42%), 152 (9), 77 (40) and 51 (100).
PhSO₂OEt, Rₜ = 7.39, m/z 186 (3%), 158 (4), 141 (18), 94 (16) and 77 (100).

PhSO₂OEt, Rₜ = 9.04, m/z 182 (5%), 153 (1), 125 (65) and 77 (70).

PhSCOCO₂Et, Rₜ = 8.50, m/z 210 (2%), 166 (1), 138 (2) and 110 (22).

e Preparation of alkyl alkanethiolosulphonates

i methyl methanethiolosulphonate

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

ii ethyl ethanethiolosulphonate

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

6 attempted conversion of diazoester to the phosphorus ylide

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

A solution of pentan-2,4-dione in methanol (10 ml) was added dropwise, with stirring to a solution of copper(II) dichloride dihydrate (4.0 g, 23 mmol) in distilled water (25 ml), followed by dropwise addition of a
solution of sodium acetate (6.8 ml, 83 mmol) in distilled water (15 ml). The mixture was heated to 80°C for 20 min, then cooled to 0°C. Filtration gave bis-(2,4-pentanedionato)-copper(II) as a steely-blue blue powder. (4.1 g, 67%). m.p. 225°C (lit., 237–230°C).

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

A solution of ethyl (ethanesulphonyl)diazoacetate 386 (0.5 g, 2 mmol), triphenylphosphine (1.3 g, 5 mmol) and bis-(2,4-pentanedionato)-copper(II) (0.1 g, 0.5 mmol) in toluene was heated under reflux for two hours then allowed to cool for 12 h. Evaporation of the solvent, trituration with ether (5 ml) and filtration gave a brown oil which rapidly deposited a yellow powder. This powder had spectra $\delta_{\text{H}}$ 7.4–7.8 (10H, m), 7.30 (3H, m), 4.32 (2H, q, $J = 7$ Hz), 3.15 (2H, q, $J = 7$ Hz) and 1.45 (3H, m, $J = 7$ Hz); $\delta_{\text{P}}$ +28.7 (60, Ph$_3$P=O?), +22.8 (16, possibly Ph$_3$P=CHR$_2$), +18.7 (7, Ph$_3$P=CR$_2$?) and −5.3 (7, Ph$_3$P); $\delta_{\text{C}}$ 133.9, 133.7, 132.2, 132.1, 131.9, 131.2, 129.0, 128.6, 128.5, 128.4, 62.0 (OCH$_2$CH$_3$?), 48.9, 48.1 (d for SO$_2$CH$_2$CH$_3$?), 14.2 (OCH$_2$CH$_3$?), 7.5 and 7.3 (d for SO$_2$CH$_2$CH$_3$?). TLC (silica, 1:1 ether: hexane) showed that the powder was almost entirely triphenylphosphine oxide.
iii  **FVP of the product of 4(ii)**

The product from the above reaction was pyrolysed at \((400^\circ C, 8 \times 10^{-3} \text{ torr}, 100^\circ C)\) to give a range of products similar to that from the pyrolysis of the corresponding diazoacetate. This seemed to confirm that the yellow powder was just a mixture of triphenylphosphine oxide and the diazoacetate.
DISCUSSION
A Preparation and pyrolysis of alkane- and arenesulphinyl alkoxy carbonylmethylene triphenylphosphoranes

1 Preparation

The first literature preparation of ylides 222 was by Hamid and Trippett. Addition of an ester-stabilised ylide to phenylsulphine (prepared in situ from Et$_3$N and PhCH$_2$SOCl) gave 229 in 73% yield.

\[
\begin{align*}
\text{Ph}_2\text{P} &\rightarrow \text{CO}_2\text{Et} \\
\text{O} &\rightarrow \text{S} \rightarrow \text{CHPh} \\
222 &\rightarrow 229
\end{align*}
\]

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

\[
\begin{align*}
\text{Ph}_3\text{P} &\rightarrow \text{CO}_2\text{Et} \\
\text{O} &\rightarrow \text{S} \rightarrow \text{CHPh} \\
231 &\rightarrow 232 &\rightarrow 233 &\rightarrow 230
\end{align*}
\]

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

The method of preparation of 222 used in this work was based on a patent by Josey. His procedure was analogous to that used to prepare acyl ylides which involved reaction of an acyl chloride with a stabilised
ylide 234 to give a phosphonium salt. *In situ* reaction of the phosphonium salt with Et₃N gave the acyl ylides. Sulphinyl chlorides 235 were used to provide the “acyl” unit in the preparation of the ylides 222 for this work.

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{CHO}_2\text{CH}_2\text{R}^1 + R^2\text{SOCl} \\
\rightarrow & \quad \text{Ph}_3\text{P}^+\text{Cl}^- \quad \text{CO}_2\text{CH}_2\text{R}^1 + R^2\text{SO}^- \quad \text{Et}_3\text{N} \quad \text{Et}_3\text{NH}^+ \quad \text{Cl}^-
\end{align*}
\]

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

\[
\begin{align*}
\text{ArSOCl} & \xrightarrow{\text{SOCl}_2 \text{ether}} \text{ArSO}_2\text{Na} \xrightarrow{\text{HCl}} \text{ArSO}_2\text{H} \xrightarrow{\text{SOCl}_2 \text{ether}} \text{ArSOCl}
\end{align*}
\]

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

\[
\begin{align*}
\text{R}^2\text{SH} & \xrightarrow{\text{AcOH}} \text{R}^2\text{SOCl} + 2\text{SO}_2 + \text{AcCl} + 2\text{HCl}
\end{align*}
\]

The aliphatic compounds could be distilled (this was a useful feature since some decomposition occurred if the compounds were stored longer than about 5 days, even at -20°C) and this was the only check on the purity of the products. However, attempts to distil the aromatic chlorides usually
caused the products to polymerise. Hence there was no real check on the purity of these compounds. Attempts were made to characterise the compounds by MS but this led to further confusion since the spectra indicated that only sulphenyl and sulphonyl species reached the detector. In the end, it was assumed that if a presumed sulphinyl chloride gave the desired ylide on reaction with 234, this would imply it had been a true sulphinyl chloride. The best results for the preparation of the sulphinyl chlorides are given below;

$$R^2SH + \frac{2SO_2Cl_2}{AcOH} \rightarrow R^2SOCl + 2SO_2 + AcCl + 2HCl$$

236 $R^2 = Et$ 85%
237 $R^2 = Pri$ 95%
238 $R^2 = CH_2Ph$ 23%
239 $R^2 = Ph$ 29%
240 $R^2 = p-Me-C_6H_4$ 93%
241 $R^2 = p-Cl-C_6H_4$ 76%

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

$$Ph_3P + Hal\rightleftharpoons CO_2R^1 \rightarrow Ph_3P^+\rightleftharpoons CO_2R^1$$

242 $R^1 = Et, Hal = Br$ 98%
243 $R^1 = Bu^t, Hal = Cl$ 83%
244 $R^1 = CH_2Ph, Hal = I$ 51%
followed by reaction of 242–244 with aqueous NaOH to give 245–247.

\[
\text{Ph}_{3}\text{P}^+\text{CO}_2\text{R}^+ \xrightarrow{\text{NaOH}} \text{Ph}_{3}\text{P}^+\text{CO}_2\text{R}^+ \\
245 \quad R^+ = \text{Et} \quad 85\% \\
246 \quad R^+ = \text{Bu}^+ \quad 51\% \\
247 \quad R^+ = \text{CH}_2\text{Ph} \quad 50\%
\]

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

\[
\text{Ph}_{3}\text{P}^+\text{Ar} \\
226
\]

Use of Et\text{3}N seemed to give slightly better results, as can be seen from the yield data given below. The acyl ylides previously mentioned can be worked up using an aqueous extraction but this was avoided here since it was known that sulphinyl ylides were extremely likely to hydrolyse. Instead, the reactions were performed in dry toluene and the reaction mixtures were filtered to remove the byproduct phosphonium or triethylammonium salts. Evaporation of the solvent and trituration with dry ethyl acetate gave the desired ylides. It was assumed that where no ylide was formed and the starting phosphonium salt was detected that either the sulphinyl chlorides had been poor or the product had been formed but
had hydrolysed before it could crystallise. The results for the preparation are given:

\[
\text{Ph}_3\text{P} = \text{CHCO}_2\text{R}^1 + \text{R}^2\text{SOCl} \rightarrow \text{Ph}_3\text{P}^+ \text{CHO}_{2\text{R}^1} \text{Cl}^- \rightarrow \text{Ph}_3\text{P} = \text{CHCO}_2\text{R}^1 + \text{R}^2\text{SOCl} + 245.\text{HCl}
\]

245 235

248 \text{R}^1 = \text{Et}, \text{R}^2 = \text{Et} \quad 16\%

249 \text{R}^1 = \text{Et}, \text{R}^2 = \text{Ph} \quad 25\%

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

\[
\text{Ph}_3\text{P} = \text{CHCO}_2\text{R}^1 + \text{R}^2\text{SOCl} \rightarrow \text{Ph}_3\text{P}^+ \text{CHO}_{2\text{R}^1} \text{Cl}^- \rightarrow \text{Ph}_3\text{P} = \text{CHCO}_2\text{R}^1 + \text{R}^2\text{SOCl} + \text{Et}_3\text{NH}^+ \text{Cl}^-
\]

245-247 235

250 \text{R}^1 = \text{Et}, \text{R}^2 = \text{PhCH}_2 \quad 8\%

251 \text{R}^1 = \text{Bu}^t, \text{R}^2 = p\text{-Me-C}_6\text{H}_4 \quad 19\%

252 \text{R}^1 = \text{Bu}^t, \text{R}^2 = p\text{-Cl-C}_6\text{H}_4 \quad 21\%

253 \text{R}^1 = \text{PhCH}_2, \text{R}^2 = \text{Et} \quad 17\%

254 \text{R}^1 = \text{PhCH}_2, \text{R}^2 = \text{Pr}^i \quad 10\%

255 \text{R}^1 = \text{PhCH}_2, \text{R}^2 = \text{Ph} \quad 6\%

256 \text{R}^1 = \text{PhCH}_2, \text{R}^2 = p\text{-Me-C}_6\text{H}_4 \quad 24\%

257 \text{R}^1 = \text{PhCH}_2, \text{R}^2 = p\text{-Cl-C}_6\text{H}_4 \quad 68\%
The 8% yield quoted for 250 is the crude product. All attempts to recrystallise or otherwise purify the ylides resulted in their hydrolysis. Of the others, only 252, 253 and 257 were obtained in an analytically pure state. The impurities were usually solvents (CH₂Cl₂, toluene and/or ethyl acetate). The elemental analyses differed from the theoretical values by at most 2% in carbon and in each case where the elemental analysis was not satisfactory, accurate mass measurements were taken. Each of these also showed the [M⁺ - O] ion, not the M⁺ ion. However, since 252, 253 and 257 also gave [M⁺ - O] as the heaviest ion in their normal mass spectra, it was assumed that the others were also the desired products.

The ylides are stable, colourless solids, although 249 was observed to become faintly pink over a couple of months. The ¹³C NMR spectra were straightforward, apart from the ylide doublets which were quite small and difficult to identify. Similarly, the ³¹P NMR spectra show good consistency. However, since the products have δ₂ ~+28·0, which almost coincides with the peak for Ph₃P=O, the preparations of 251 and 252 were assumed to have failed until near the end of the work. A table of the signals is given on page 158 (J₃P-C in brackets);
<table>
<thead>
<tr>
<th>Ylide</th>
<th>$\delta_p$</th>
<th>$\delta_C$</th>
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<tbody>
<tr>
<td></td>
<td>P=C</td>
<td>C=O</td>
</tr>
<tr>
<td>248</td>
<td>27.5</td>
<td>37.0 (br)</td>
</tr>
<tr>
<td>249</td>
<td>28.1</td>
<td>36.0 (br)</td>
</tr>
<tr>
<td>251</td>
<td>28.5</td>
<td>36.7 (br)</td>
</tr>
<tr>
<td>252</td>
<td>28.2</td>
<td>36.3 (br)</td>
</tr>
<tr>
<td>253</td>
<td>27.5</td>
<td>37.0 (br)</td>
</tr>
<tr>
<td>254</td>
<td>24.1</td>
<td>55.2</td>
</tr>
<tr>
<td>255</td>
<td>28.3</td>
<td>36.7 (br)</td>
</tr>
<tr>
<td>256</td>
<td>28.5</td>
<td>35.8 (br)</td>
</tr>
<tr>
<td>257</td>
<td>28.2</td>
<td>36.4 (br)</td>
</tr>
</tbody>
</table>
It was noticed that the $^1$H spectra often showed broadened peaks for the \( \text{CO}_2\text{R}^{1} \) protons. Such peak broadening is indicative of restricted rotation in the molecule. When this occurs, the molecule in question has two or more conformers. An equilibrium exists between the conformers; at higher temperatures, the conformers interconvert too quickly to be observed and an "average" signal is recorded. At lower temperatures, spectra due to the individual conformers are recorded. As with all equilibria, thermodynamic equations can be used to describe the situation. The relevant equations are

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

where \( \delta_V \) is the separation of the signals of the two conformers, \( T_c \) is the temperature at which the signals merge and \( \Delta G^* \), \( \Delta G \), \( T \) and \( R \) have their usual thermodynamic meanings.

In a variable temperature NMR (VTNMR) experiment, firstly a spectrum is recorded at a temperature high enough to allow only the "average" signal to be recorded. The temperature is then lowered in steps of 10K and a spectrum recorded at each temperature until all the signals for the conformers are seen. It is possible to find the various sets of \( T_c \) and measure \( n_a \) and \( n_b \) by integrating the signals at the lowest temperature. This was attempted for ylide 248. The first set of spectra were taken in \( \text{CDCl}_3 \). It was found that this solvent became viscous at too high a temperature for the spectra of the conformers to be obtained. The experiment was repeated using \( \text{d}_5\)-toluene, which has a higher boiling point and lower melting point than \( \text{CDCl}_3 \). The spectra are shown on p160–1.
Figure 1: $^{13}$C NMR spectra of 248
Figure 2: $^1$H NMR spectra of 248
13C NMR spectra

The 13C spectrum at 308K shows single peaks for each of the alkyl carbons (O-CH₂-CH₃, O-CH₂-CH₃, S-CH₂-CH₃ and S-CH₂-CH₃). (There are also spurious peaks at 14 p.p.m. on this spectrum and the spectra taken at 294K and 268K.) By 268K, the signal for the O-CH₂-CH₃ carbon (58 p.p.m.) has begun to broaden and by 248K it has split into two well-defined singlets.

Similarly, the signal for the O-CH₂-CH₃ carbon (13 p.p.m.) shows its coalescence at 268K. By 248K, it too shows a doublet. In contrast to this, the S-CH₂-CH₃ stays a sharp singlet all through the range of temperatures.

The S-CH₂-CH₃ carbon shows the most interesting pattern of all. In the spectra taken at 308 and 294K, the signal is a singlet (33 p.p.m.). The signal is a broad peak at 268K yet by 248K it appears as four peaks. This would imply that there may be four conformers “observable” at this temperature. This notion was supported by the evidence of the 1H spectra.

1H NMR spectra

Considering first the O-CH₂-CH₃ signals (4.1 p.p.m.); at 328K, the signal is a quartet for the “averaged” behaviour of the molecules. This is broadening by 308K and has split into two by 268K. The high frequency signal begins to be resolved by 228K and at 218K, both sets of signals are showing fine structure. It appears at this temperature that the high frequency portion is about to resolve into two quartets. This provides further evidence for the involvement of four separate conformers, consistent with the 13C signals of SCH₂.
The S-CH$_2$-CH$_3$ signal (2.3 p.p.m.) at 328K is a quartet of doublets showing coupling to phosphorus (\(\text{^4}J_{P-H} 1.8\text{Hz}\)). By 288K this quartet is becoming broad and ill-defined. It shows its coalescence temperature at 268K and has split into two by 228K. At 218K, the low-frequency portion shows some fine structure.

The S-CH$_2$-CH$_3$ signal (1.1 p.p.m.) is a sharp triplet at 328K and remains so down to 268K. By 228K it has split into a multiplet which appears to be two superimposed triplets. The O-CH$_2$-CH$_3$ signal (1.0 p.p.m.) appears as a slightly broadened triplet at 328K. By 288K the signal has broadened so far it is almost invisible. By 268K, it appears as two widely spaced humps. These have become well-defined triplets by 228K.

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

\[
\begin{align*}
\text{258} & \quad \text{259} \\
\text{260} & \quad \text{261}
\end{align*}
\]

The occurrence of up to four separate signals at the lowest temperature is consistent with these each giving separate signals at least for some of the atoms present. Careful consideration of the data leads to the
conclusion that the rotation of the sulphoxide group has a low activation energy and so still occurs rapidly at temperatures where the ester rotation has been “frozen out”. Attempts to quantify the conclusions by calculating energy barriers were complicated by the ambiguity over which signal in the low temperature spectra corresponded to each of the four conformers. Similarly, rough calculations based on the observed coalescence temperatures gave values of $\Delta G^*$ in the range 10–15 kcal mol$^{-1}$ for most of the processes involved but these could not be assigned to specific interconversion processes. These values do correspond well with that of 13.8 kcal mol$^{-1}$ previously obtained by Drysdale$^{185}$ for [(4-methylbenzene sulphinyl)ethoxycarbonylmethylene]triphenylphosphorane, where the larger S-Ar group prevents rotation of the sulphoxide (or possibly the rotations are always too fast to observe). Clearly, further detailed study of this problem would be required to fully understand and quantify the processes occurring.

2 FVP

a FVP of ylides of type 222

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

\[
\begin{align*}
222 & \xrightarrow{\text{FVP}} 223 + 224 \\
\text{Ph}_3P & \xrightarrow{\text{CO}_2\text{CH}_2R^1} R^2S & R^1 & \xrightarrow{\text{Ph}_3P=O} R^2S & \xrightarrow{-\text{Ph}_3P} \text{SR}^2
\end{align*}
\]
Formation of the vinyl sulphide 223 had been rationalized by assuming extrusion of Ph$_3$P=O to give carbene 262, followed by intramolecular C–H insertion to give β-lactone 225 (route A). It was already known that such β-lactones can extrude CO$_2$ to give alkenes$^{243}$. However, a variety of routes were envisaged for the formation of 224.

Comparison with authentic samples had shown that aryl thiopropionate 263 was not present in the pyrolysate of ylide 222 ($R^1$ = Me, $R^2$ = $p$-Cl-C$_6$H$_4$). This seems to rule out the potential alternative reaction shown for carbene 262, (route B) which would have given the ketene 264, since aryl thioesters 263 have been shown to pass unchanged through the FVP apparatus at 550°C ($\textit{vide infra}$). Similarly the isomeric thiobenzoate 265
was also not present in the pyrolysate of ylide 222 (R\textsuperscript{1} = Me, R\textsuperscript{2} = p-Cl-C\textsubscript{6}H\textsubscript{4}) and so it too cannot be formed by pyrolysis of 222; otherwise at least a trace of 265 would be in the pyrolysate.

An alternative route to 224 was extrusion of Ph\textsubscript{3}P from 222 to give carbene 266, which might rearrange to alkyl arylthiooxalate 267. This could then successively lose CO and CO\textsubscript{2} to give sulphide 224. FVP of alkyl arylthiooxalate 267 (R\textsuperscript{1} = Me, R\textsuperscript{2} = Ph, p-Me-C\textsubscript{6}H\textsubscript{4}) at 600°C had given alkyl arylthiocarbonate 268 and at 750°C had given 268 and sulphide 224 (R\textsuperscript{1} = Me, R\textsuperscript{2} = Ph, p-Me-C\textsubscript{6}H\textsubscript{4}). Similarly, FVP of 267 (R\textsuperscript{1} = Me, R\textsuperscript{2} = p-Cl-C\textsubscript{6}H\textsubscript{4} and R\textsuperscript{1} = H, R\textsuperscript{2} = Ph) at both 600°C and 750°C had given 224. The final mechanism to check in this potential route was whether 266 itself would actually give 267. Attempts were made to generate examples of 266 via the corresponding diazo precursors but these were not successful (vide infra).

The problem remained that unidentified carbonyl compounds had been detected in the pyrolysates. The masses of these compounds corresponded with the masses of the isomeric thioesters 263 and 265, yet as stated previously, these would have been detected if they were formed. Early in the course of this work, a crude sample of 269 was prepared. Its $^{13}$C NMR spectrum was obtained but the carbonyl signal was different to that of the unknown carbonyl compound in the pyrolysate of 222 (R\textsuperscript{1} = Me, R\textsuperscript{2} = p-Cl-C\textsubscript{6}H\textsubscript{4}).
This is some slight evidence against the route C. However the only way of disproving this route would have been to prepare $266$ and prove (i) that $266$ was formed by FVP of $222$ and (ii) that $266$ was the source of $224$. Further useful evidence would have been obtained from the pyrolysis of $269$ and its presumed precursor on route C. Hence a fresh attempt to discover the identity of these mystery carbonyl compounds was needed.

The results obtained for pyrolysis of ylides $222$ at $600^\circ$C in this work are as follows;

<table>
<thead>
<tr>
<th>ylide</th>
<th>ratio of $\text{Ph}_3\text{P}:$</th>
<th>% yields of other products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Ph}_3\text{P}=\text{O}:\text{Ph}_3\text{P}=\text{S}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ph}_3\text{P} \overset{\text{CO}_2\text{C}_2\text{H}_3\text{CH}_3}{\text{O}} \text{S} \text{Et}$</td>
<td>84:9:7</td>
<td>$\text{EtS}$ 36% $\text{H}_3\text{C}$ 7%</td>
</tr>
<tr>
<td>$\text{Ph}_3\text{P} \overset{\text{CO}_2\text{C}_2\text{H}_3\text{CH}_3}{\text{O}} \text{S} \text{Ph}$</td>
<td>1:1:0</td>
<td>$\text{PhSSPh}$ 10% $\text{PhS}$ 10% 5%</td>
</tr>
<tr>
<td>$\text{Ph}_3\text{P} \overset{\text{CO}_2\text{C}_2\text{H}_3\text{CH}_3}{\text{O}} \text{S} \text{Me}$</td>
<td>80:14:6</td>
<td>$\text{MeS}$ 20% trace $\text{SMe}$ trace</td>
</tr>
</tbody>
</table>

* A sample of $270$ for pyrolysis was available from previous work$^{185}$

These correlate somewhat with previous work. However, the absence of sulphides $224$ in two cases does not agree with the previous work. It is possible to argue that $224$ might formed in these cases but have evaporated ($\text{MeSMe}$, b.p. $38^\circ$C) before the analyses were made. Formation of acetaldehyde, which was not recognised previously, was explained by
proposing an alternative disintegration of β-lactone 225 to give the ketene 271. Also, re-examination of the spectra from the previous work showed the presence of acetaldehyde and propionaldehyde in the pyrolysates of 222 (R¹ = Me, Et).

![Chemical reaction diagram]

Reaction of 271 with water would give R²SCH₂CO₂H but this was never detected. An attempt was made to trap any labile double bond-containing compounds by putting methanol in the cold trap but no new products were identified. It is in fact probable that 271 would lose CO under the conditions involved to give the thiocarbene which might end up as R²SMe but this was not observed either. Thus although several aspects of the thermal decomposition of 222 remain unclear, the main processes appear to involve loss of of Ph₃P and/or Ph₃P=O and subsequent intramolecular reactions of the resulting carbenes.

Support for the proposed route to vinyl sulphides 223 comes from FVP of the diazomalonate 272. This gave methyl acrylate by the mechanism shown below, which involves formation and decarboxylation of the β-lactone 273.²⁴⁴
The stable \( \beta \)-lactone 274 was produced by photolysis of diazoester 275: intermediacy of carbene 276 was assumed.\(^ {245} \)

\[
\begin{align*}
\text{EtO}_2\text{C} = \text{N}_2 & \xrightarrow{\text{hv}} \begin{array}{c}
\text{EtO}_2\text{C} - \text{N} \\
\text{Me} \end{array} \\
\text{275} & \xrightarrow{\text{C-H insertion}} \text{274}
\end{align*}
\]

The formation of \( \beta \)-lactams by intramolecular C–H insertion of carbenes such as 277 is also known.\(^ {246} \) Similar 4-membered rings can be obtained from carbenes 278\(^ {247} \) and 279.\(^ {248} \) The metaphosphate extrusion product from one example of 278 has been observed.

\[
\begin{align*}
\text{277}
\end{align*}
\]

In order to confirm the identity of the FVP products from 248 and 270 authentic samples of vinyl sulphides and sulfoxides were prepared. Reaction of allyl bromide and sodium ethanethiolate gave ethyl allyl sulphide 280 in 51% yield. Sodium metaperiodate oxidation of this then gave ethyl allyl sulfoxide 281 in 34% yield. However ethyl propenyl
sulphide 282 could not be prepared: attempted base-catalysed migration of the double bond of 280 gave no reaction (even though this is possible for the aromatic species 283\textsuperscript{249}) and reaction of sodium ethanethiolate with 1-bromo-1-propene gave no unsaturated compounds. Although the desired ethyl propenyl sulphide could not be prepared, the spectra of 280 and 281 did provide model data from which it was clear that 282, not its sulphoxide, was the product formed in the FVP of 248. Thus, the methylene group next to a sulphoxide has a more complex \(^1\)H NMR spectrum because the S=O group makes the two hydrogens magnetically non-equivalent and the ethyl group of 280 showed a normal quartet and triplet, while 281 showed two superimposed quartets and a triplet.

![Chemical structures](image)

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

![Chemical structures](image)

Comparison of the S(=O)CH\(_3\) signals of 285 and 284 with the pyrolysate from 270 confirmed that the pyrolysis product was the sulphide.
b FVP of ylides of type 286

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

![Chemical structure](image)

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

<table>
<thead>
<tr>
<th>ylide</th>
<th>Ph₃P:Ph₃P=O:Ph₃P=S</th>
<th>other products</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Image" /></td>
<td>0:40:7</td>
<td>PhCH₂OH</td>
</tr>
<tr>
<td><img src="image" alt="Image" /></td>
<td>0:1:0</td>
<td>PhCH₂OH</td>
</tr>
<tr>
<td><img src="image" alt="Image" /></td>
<td>0:1:0</td>
<td>PhCH₂OH</td>
</tr>
<tr>
<td><img src="image" alt="Image" /></td>
<td>0:1:0</td>
<td>PhCH₂OH, PhCH₂SC₆H₄Cl, ClC₆H₄Me, unknown, m/z = 156, PhCH₃, PhCH₂CH₃Ph, (ClC₆H₄S)₂</td>
</tr>
</tbody>
</table>
The compounds appear to have mostly just disintegrated. A trace of sulphide 224 was observed in one case but no proven vinyl sulphides 223 were seen. The major phosphorus-containing product observed was \( \text{Ph}_3\text{P}=\text{O} \), which is again inconsistent with the proposed route to 224, which is:

\[
\begin{align*}
\text{Ph}_3\text{P}=\text{CO}_2\text{CH}_3\text{R}^1 & \xrightarrow{\text{FVP}} \text{R}^1\cdot\text{O} \cdot \text{O} \rightarrow \text{R}^1\cdot\text{O} \cdot \text{O} \cdot \text{SR}^2 \\
\text{Ph}_3\text{P}=\text{O} & \xrightarrow{-\text{Ph}_3\text{P}} \text{R}^1\cdot\text{O} \cdot \text{O} \cdot \text{SR}^2
\end{align*}
\]

266

264

It is possible that air oxidation of \( \text{Ph}_3\text{P} \) gave \( \text{Ph}_3\text{P}=\text{O} \), but this is unlikely to have converted all the \( \text{Ph}_3\text{P} \) to \( \text{Ph}_3\text{P}=\text{O} \). This discrepancy added further weight to the need to investigate alkylloxycarbonyl sulphinyl carbenes 266.

The above discrepancies made it desirable to have more evidence about the behaviour of carbenes 262 and 266 (whatever the nature of \( \text{R}^1 \)) and so it was hoped that the diazo compounds 290 and 291 could be prepared. Pyrolysis of these compounds would then have given the carbenes 262 and 266.
The required sulphenyl acetates 292-5 were prepared by either (method A) reacting benzenesulphenylacetyl chloride with methanol and ethanol or (method B) by reacting alkyl chloroacetates with alkylthiolates.

\[
R'CH_2OH + \overset{\text{Cl}}{\overset{\text{A}}{\text{S}}} \rightarrow R'CH_2OH + \overset{\text{R'CH_2OH + \overset{\text{Cl}}{\text{S}}} \rightarrow R'CH_2OH + \overset{\text{R'SNa}}{\text{Cl}}}
\]

- **292**: \(R^1 = H, \ R^2 = Et\) 52\%\(^b\)
- **293**: \(R^1 = H, \ R^2 = Ph\) 63\%\(^a\), 74\%\(^b\)
- **294**: \(R^1 = Me, \ R^2 = Et\) 42\%\(^b\)
- **295**: \(R^1 = Me, \ R^2 = Ph\) 58\%\(^a\), 72\%\(^b\)

\(^a\) = method A, \(^b\) = method B

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

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

\[
\overset{\text{NaIO_4}}{\rightarrow}
\]

- **297**: \(R^1 = H, \ R^2 = Et\) 36\%
- **298**: \(R^1 = H, \ R^2 = Ph\) 32\%
- **299**: \(R^1 = Me, \ R^2 = Et\) 85\%
- **300**: \(R^1 = Me, \ R^2 = Ph\) 45\%

Again, no reaction was obtained when sulphinyl acetates were treated
with either tosyl azide 296 or 4-\((\text{N-acetylamino})\)benzenesulphonyl azide 301.

\[
\begin{align*}
\text{Me}_2\text{C}-&\text{O} - \text{N}_3 \\
\text{Me}-&\text{C}=\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me}-&\text{C}=\text{O} \\
\text{Et}_2\text{N} &= \text{O} \\
\text{Me}-&\text{C}=\text{O} \\
\end{align*}
\]

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

c  FVP of ylides of type 302
The study of FVP of t-butoxycarbonyl ylides of type 302 was prompted by the idea that \(\delta\ C-H\) insertion of carbene 303 would give \(\gamma\)-lactone 304 since it was known that carbene 305 showed both \(\gamma\) and \(\delta\) insertion.\textsuperscript{245} Oxidation of 304 would give the sulphoxide which would lose \(R^2\text{SOH}\) to give the synthetically useful \(\gamma\)-lactone 306.
It should be noted that for the pyrrolidine compound, 307, when \( R \) was ethyl, only \( \beta \)-lactone 274 was formed and when \( R \) was t-butyl, only \( \gamma \)-lactone 308 was formed.245

![Chemical structures of lactones 274, 307, and 308.]

In the event, FVP of 251 and 252 at 500°C gave only Bu\(^{t}\)OH and R\(^{2}\)SSR\(^{2}\).

![Chemical structure of products from thio Ketones.] (Y=Me)

The yields are given below:

<table>
<thead>
<tr>
<th>ylide</th>
<th>FVP fraction</th>
<th>Ph(_3)P:Ph(_3)P=O:Ph(_3)P=S</th>
<th>other products</th>
</tr>
</thead>
<tbody>
<tr>
<td>251</td>
<td>cold trap</td>
<td></td>
<td>(MeC(_6)H(_4)S(_2))(_2)</td>
</tr>
<tr>
<td></td>
<td>furnace exit</td>
<td>7:30:0</td>
<td>(MeC(_6)H(_4)S(_2))</td>
</tr>
<tr>
<td></td>
<td>furnace exit, after 17 days</td>
<td>0:12:1</td>
<td>(ClC(_6)H(_4)S(_2)) t-BuOH</td>
</tr>
<tr>
<td>252</td>
<td>cold trap</td>
<td></td>
<td>(ClC(_6)H(_4)S(_2))</td>
</tr>
<tr>
<td></td>
<td>furnace exit</td>
<td>0:60:7</td>
<td>(ClC(_6)H(_4)S(_2))</td>
</tr>
</tbody>
</table>
B Preparation and pyrolysis of arenesulphinylbenzylidene triphenylphosphoranes

1 Preparation

Previous attempts to prepare ylides 226 were not at all successful.\textsuperscript{185} Reaction of benzyl phenyl sulphonoxde with triphenylphosphine dibromide and Et\textsubscript{3}N in dry toluene gave only Ph\textsubscript{3}P=O. Various attempts were made to dehydrohalogenate [(α-benzenesulphinyl)benzyl]triphenylphosphonium bromide 309.

![Chemical structure of 226 and 309](image)

Reaction with NaOH in water and KOBu\textsubscript{t} in both t-butanol and THF gave only Ph\textsubscript{3}P=O and benzyl phenyl sulphonoxide. Reaction with LDA in THF gave Ph\textsubscript{3}P=O, benzyl phenyl sulphonoxide and some Ph\textsubscript{3}P, while reaction with Bu\textsuperscript{a}Li in THF gave Ph\textsubscript{3}P=O and benzyl phenyl sulphonoxide and a product tentatively identified as n-butyl phenyl sulphonoxide.

![Chemical structure of Bu\textsuperscript{a}Li reaction](image)

The method of choice turned out to be reaction of two equivalents of non-stabilised ylide 310 (prepared \textit{in situ} by the action of Bu\textsuperscript{a}Li on phosphonium salts 311) with one equivalent of sulphinyl chloride 235 in dry toluene. Filtration removed the byproduct phosphonium salt and the products were isolated by evaporation and trituration with dry ethyl acetate. It is both interesting and disappointing to note that no ylides
apart from where $\text{Ar}$ was $\text{Ph}$ were obtained.

\[
\begin{align*}
2 \text{Ph}_3\text{P}^+\text{Ar} \quad & 2 \text{Bu}^+\text{Li} \\
311 & \rightarrow 2 \left[ \text{Ph}_3\text{P}^+\text{Ar} \right] \\
310 & \\
\end{align*}
\]

\[
\begin{align*}
\text{RSOCl} & \rightarrow \\
235 & \text{312 Ar} = \text{Ph, R} = \text{Ph} \quad 29\% \\
313 & \text{Ar} = \text{Ph, R} = p-\text{Me-C}_6\text{H}_4 \quad 45\% \\
314 & \text{Ar} = \text{Ph, R} = p-\text{Cl-C}_6\text{H}_4 \quad 31\% \\
\end{align*}
\]

The phosphonium salts 315–317 had been obtained by reaction of $\text{Ph}_3\text{P}$ with the appropriate benzyl halides. One benzyl halide had to be prepared from the corresponding alcohol.

\[
\begin{align*}
\text{MeO-} & \quad \text{CH}_3\text{OH} \quad \text{PBr}_3 \quad \text{MeO-} \quad \text{CH}_2\text{Br} \\
\text{Hal-} & \quad \text{Ar} \quad \text{Ph}_3\text{P} \quad \text{PhMe, } \text{A} \\
315 & \text{Ar} = \text{Ph} \quad \text{Hal} = \text{Cl}^- \quad 48\% \\
316 & \text{Ar} = p-\text{O}_2\text{N-C}_6\text{H}_4 \quad \text{Hal} = \text{Br}^- \quad 83\% \\
317 & \text{Ar} = p-\text{MeO-C}_6\text{H}_4 \quad \text{Hal} = \text{Br}^- \quad 90\% \\
\end{align*}
\]

Apart from 313, these compounds were not obtained in an analytically pure state. However, their identities were confirmed by $^{13}\text{C}$ spectra and accurate mass measurements. The $^{31}\text{P}$ and $^{13}\text{C}$ NMR spectra of the ylides 312–314, a previously unknown class of compounds, are tabulated overleaf ($J_{\text{P-C}}$ in brackets);
Again, there is reasonable consistency between the spectra; this was fortunate in the cases of 312 and 314, where apart from the ylide doublets, only aromatic signals were expected.

2 FVP
FVP of ylides 312–314 at 500°C gave a mixture of Ph3P, Ph3P=O and Ph3P=S at the furnace exit. A brilliant blue liquid collected further along the trap. This liquid became colourless within a few minutes of opening the trap and attempts to isolate it under N2 were not very successful. In the few cases when the blue colour was still present and the products had been transferred to an NMR tube or cuvette, the colour had faded by the time the spectrum had been obtained. However, 1H, 13C and 31P NMR and GCMS showed that the pyrolysate contained thiobenzoates 318, ketones 319, sulphides 320, stilbene 321, thiols 322 and disulphides 323. The yields are given overleaf.
The formation of thiobenzoates 318 is rationalised by assuming S–C transfer of oxygen in the carbene 324, formed by loss of Ph₃P from 312–314. This process is the predominant one for (alkanesulphinyl)benzylidene triphenylphosphoranes.

A similar S–C transfer of oxygen has been reported in two cases. In the first, reaction of tosyl azide with β-keto-sulphoxides is presumed to have given the diazo-keto-sulphoxide 325. S–C transfer of oxygen in carbene 326 is invoked to explain the observed reaction products, the α-keto-acids 327 and disulphides, which are presumed to be formed by solvolysis of the α-ketothioesters 328.¹³⁴
In the second example, diazcephalosporin S-oxides 329 were treated with di-rhodium tetra-acetate. The 2-oxocephalosporins 330 were produced and the authors favour the intermediate ylide 331.135

\[
\begin{align*}
\text{329} & \quad \text{Rh}_2(\text{AcO})_4 \rightarrow \text{331} & \quad \text{330}
\end{align*}
\]

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

\[
\begin{align*}
\text{332} & \quad \rightarrow \quad \text{333} & \quad \rightarrow & \quad \text{334}
\end{align*}
\]

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

\[
\begin{align*}
\text{335} & \quad + \quad \text{336} & \quad \rightarrow & \quad \text{118} & \quad \rightarrow & \quad \text{337} & \quad \rightarrow & \quad \text{338} & \quad \rightarrow & \quad \text{119}
\end{align*}
\]
Other major products in the pyrolysis of ylides 312–314 were the ketones 319. Rearrangement of carbenes 324 is likely to give sulphines 339, which could lose sulphur as shown to give ketones 319.

![Reaction scheme](image)

Support for this idea comes from the photolysis of pyrazolines 340: Wolff-type rearrangement of carbene 138 leads via sulphine 141 to the formation of ketone 341 in high yield.\(^{137}\)

Sulphides 320 are presumed to be formed by abstraction of 2 × H* by carbene 342, which is formed by extrusion of Ph₃P=O from 312–314.

![Reaction scheme](image)

It is also attractive to assume that 342 is the precursor of 321, 322 and 323, by means of α-elimination of the arylthiobenzyl radical as shown, although 322 and 323 could come from other radical processes.
It was believed that the blue colour of the pyrolysates of 312-314 may have come from the thioketones 343-345.

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

It was thought that if thioketones were being formed, then they were being consumed very quickly once the FVP system was opened. Otherwise the colour would not last when the apparatus was left untouched after all the starting material had passed through the furnace. It was therefore thought that the addition of the CDCl$_3$ solvent may have had something to do with the loss of colour. Hence authentic samples of thioketones were made. Thiobenzophenones 343-345 were prepared by reaction of the corresponding benzophenones 346-348 with P$_2$S$_5$ in boiling xylene.

The benzophenones 347 and 348 were prepared by acylation of benzene with the relevant acid chlorides. Since 346-348 were also
detected in the pyrolysates of 312–314, they too were subjected to FVP at 500°C. This left them completely unchanged.

\[
\begin{align*}
\text{Ph} \quad \text{AlCl}_3 \quad & \quad \text{ArCOCl} \quad \rightarrow \quad \text{Y} \quad \text{Ph} \\
& \quad \begin{array}{c}
\text{Y = H} \\
\text{Y = Cl} \quad 84\% \\
\text{Y = Me} \quad 52\%
\end{array}
\end{align*}
\]

No spectral evidence could be found for the presence of thioketones 343–345 in the pyrolysates of 312–314. However it was thought worthwhile to check on the reactions of thioketones with Ph₃P, since it was thought that the addition of the CDCl₃ might provide a reaction medium for the Ph₃P to desulphurise the thioketones. An NMR tube was prepared, containing Ph₃P and thiobenzophenone. The blue colour of thioketone persisted, despite several additions of Ph₃P and ³¹P NMR showed that the Ph₃P had been converted to Ph₃P=S.

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

\[
\begin{align*}
\text{Ph₃P} & \quad \text{R}^1 \\
\text{O}_2\text{S} & \quad \text{R}^2
\end{align*}
\quad \rightarrow
\begin{align*}
\text{O}_2\text{S} & \quad \text{R}^1 + \text{R}^2\text{SSR}^2 + \text{R}^2\text{H} + \text{polymer} \\
& \quad + \text{Ph₃PO} + \text{several other phosphorus-containing products}
\end{align*}
\]

²¹⁹
Other authentic samples prepared to check the pyrolyses of 312–314 were the thiolobenzoates 349–351. These were prepared by reaction of sodium thiophenols with benzoyl chloride. FVP of 350 and 351 at 500°C gave the unchanged starting materials.

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

So the pyrolysis of ylides 312–314 can be summarised by the following scheme. The final products are outlined.
Referring back to the yield data on page 179, for \textbf{312} and \textbf{313}, where the yield ratio of \textit{Ph}_3\text{P}:\textit{Ph}_3\text{P}=:\text{O} is greater than 1, the yield ratio of \textbf{318:320} (the major products associated with \textit{Ph}_3\text{P} and \textit{Ph}_3\text{P}=:\text{O} respectively) is also greater than 1. However, for \textbf{314}, the yield ratio of \textit{Ph}_3\text{P}:\textit{Ph}_3\text{P}=:\text{O} is less than 1 but the yield ratio of \textbf{318:320} is slightly greater than 1, possibly implying some change of mechanism. However, in each case, there is enough of the relevant phosphorus compound formed (assuming that 100\% of the phosphorus compounds were isolated) to allow the mechanisms outlined above to be plausible.

No rationalisation can yet be offered as to why the relative amounts of products changed.
C  Preparation and pyrolysis of alkanesulphinylbenzylidene triphenylphosphoranes

1  Preparation

The only previous example of these ylides 226 to be prepared was 2-propanesulphinylbenzylidenetriphenylphosphorane 227. This was a beautiful yellow compound, whose pyrolysis was straightforward. FVP at 500°C caused extrusion of Ph₃P only, in contrast to the aromatic compounds, where varying proportions of Ph₃P and Ph₃P=O were extruded. The only other product was the thiobenzoate 228, although at first it was thought (on the evidence of a ¹H NMR spectrum) that the thiobenzoate might have lost propene to give the thiobenzoic acid 354.

\[
\begin{align*}
\text{Ph₃P} & \quad \text{Ar} \\
226 & \quad \rightarrow & \quad \text{Ph₃P} & \quad \text{Ph} \\
227 & \quad \rightarrow & \quad \text{Ph₃P} & \quad \text{Pr}^i \\
228 & \quad \rightarrow & \quad \text{Ph₃P} & \quad \text{Pr}^i \\
354 & \quad \rightarrow & \quad \text{H₃C} & \quad = \quad \text{CH₃}
\end{align*}
\]

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

\[
\begin{align*}
2 \text{Ph₃P}^+ & \quad \text{Ar} \\
\text{Bu}^+ \text{Li}^− & \quad \rightarrow & \quad 2 \left[ \text{Ph₃P}−\text{Ar} \right] \text{RSOCl} \\
355 & \quad \text{Ar} = \text{Ph}, \text{R} = \text{Et} & \quad 23\% \\
227 & \quad \text{Ar} = \text{Ph}, \text{R} = \text{Pr}^i & \quad 19\% \\
356 & \quad \text{Ar} = \text{Ph}, \text{R} = \text{PhCH₂} & \quad 4\%
\end{align*}
\]

The spectra of 227, 355 and 356 were similar to those of 312–314. In fact, the absence of aromatic signals from R was of considerable help in
assigning the peaks for the Ph groups in 312–314 and hence the R groups in these compounds. A table of the $^{31}$P and $^{13}$C NMR data is given below. Compound 356 was not obtained in an analytically pure form but the spectra showed that the sample obtained did consist largely of the desired compound.

<table>
<thead>
<tr>
<th>ylide</th>
<th>$\delta$P</th>
<th>$\delta$C</th>
<th>P-Phenylic</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>+19.7</td>
<td>47.9 (126)</td>
<td>127.7 (86)</td>
<td>134.2 (10)</td>
</tr>
<tr>
<td>227</td>
<td>+20.2</td>
<td>47.2 (123)</td>
<td>127.5 (89)</td>
<td>134.3 (10)</td>
</tr>
<tr>
<td>356</td>
<td>+18.7</td>
<td>47.1 (128)</td>
<td>127.0 (90)</td>
<td>134.0 (10)</td>
</tr>
</tbody>
</table>

2 Pyrolysis

The pyrolysis of these compounds was also straightforward, except that some Ph$_3$P=S and Ph$_3$P=O were also detected. The major non phosphorus-containing compounds obtained were the corresponding thiolobenzoates 228, 357 and 358. The yields of the products are given overleaf;
It is proposed that similar mechanisms to those described for the aryl compounds 312–314 account for the formation of the thiolobenzoates and for the stilbene formed in the pyrolysis of 356.

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

An authentic sample of benzyl thiolobenzoate 358 for comparison was prepared by reaction of sodium phenylmethanethiolate and benzoyl...
chloride, and showed identical spectroscopic properties to that produced in the pyrolysis of 356.
D Preparation and pyrolysis of alkane- and arenesulphonylaryl diazomethanes

1 Preparation

Diazo compounds 359 are the molecules of choice for any study of carbenes. The diazo moiety easily loses N₂, which is an unreactive molecule and so is unlikely to undergo any secondary reactions with the other products of the carbene reaction. The diazo moiety is also easy to form; reaction of an “activated methylene” 360 with a variety of agents containing the –N₃ group gives the diazo compound and the amine byproduct.

\[
\begin{align*}
R-N=N-N^+ + H_2 \text{Et}N &\rightarrow R-N^- + N=N^- + N=N^+ = N=N \quad \text{withdrawing groups}
\end{align*}
\]

Diazo compounds are easily pyrolysed or photolysed to give carbenes. Thus, in the course of this work, it was thought that it would be beneficial to have direct comparison between the pyrolysates from ylides and those from diazo compounds which would almost certainly give the carbenes under study.

Attempts to prepare some diazosulphinyl and sulphenyl compounds have been reported elsewhere in this thesis. However, the sulphonyl species seemed worthy of attention, since an amount of work on the pyrolysis of
sulphonyl ylides had been performed in this laboratory.\textsuperscript{185, 186}

The required sulphones were also worthy of attention in themselves, since an improved route to these compounds had been discovered in this laboratory.\textsuperscript{226} The required sulphides \textsuperscript{292–295, 361–368} were prepared by reaction of sodium alkanethiolates with alkyl halides.

\[
R^1\text{CH}_2\text{Cl} + R^2\text{SNa} \rightarrow R^1\text{CH}_2\text{SR}^2
\]

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Et</td>
<td>69%</td>
</tr>
<tr>
<td>Ph</td>
<td>Pri</td>
<td>42%</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>61%</td>
</tr>
<tr>
<td>Ph</td>
<td>PhCH(_2)</td>
<td>60%</td>
</tr>
<tr>
<td>Ph</td>
<td>p-Me-C(_6)H(_4)</td>
<td>30%</td>
</tr>
<tr>
<td>Ph</td>
<td>p-Cl-C(_6)H(_4)</td>
<td>38%</td>
</tr>
<tr>
<td>p-MeO-C(_6)H(_4)</td>
<td>Ph</td>
<td>28%</td>
</tr>
<tr>
<td>p-O(_2)N-C(_6)H(_4)</td>
<td>Ph</td>
<td>65%</td>
</tr>
<tr>
<td>CO(_2)Me</td>
<td>Et</td>
<td>52%</td>
</tr>
<tr>
<td>CO(_2)Me</td>
<td>Ph</td>
<td>74%</td>
</tr>
<tr>
<td>CO(_2)Et</td>
<td>Et</td>
<td>42%</td>
</tr>
<tr>
<td>CO(_2)Et</td>
<td>Ph</td>
<td>72%</td>
</tr>
</tbody>
</table>

The corresponding sulfoxides were also prepared by periodate oxidation of the sulphides. This was done before it was found that neither these, nor the sulphides, nor the sulphones mentioned overleaf, unless stabilised by ester groups, would give diazocompounds (see section A2).

\[
\text{S-R}^1 \text{NaO}_4 \rightarrow \text{O-S-R}^2
\]

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Et</td>
<td>36%</td>
</tr>
<tr>
<td>Ph</td>
<td>Pri</td>
<td>56%</td>
</tr>
</tbody>
</table>
Permanganate oxidation of the sulphides in the presence of benzoic acid and a phase-transfer catalyst gave the sulphones 377–385.226

![Reaction Scheme]

369 $R^1 = \text{Ph}$ $R^2 = \text{Ph}$ 73%
370 $R^1 = \text{Ph}$ $R^2 = \text{PhCH}_2$ 58%
371 $R^1 = \text{Ph}$ $R^2 = p\text{-Me-C}_6\text{H}_4$ 59%
372 $R^1 = \text{Ph}$ $R^2 = p\text{-Cl-C}_6\text{H}_4$ 54%
373 $R^1 = p\text{-MeO-C}_6\text{H}_4$ $R^2 = \text{Ph}$ 32%
374 $R^1 = p\text{-O}_2\text{N-C}_6\text{H}_4$ $R^2 = \text{Ph}$ 31%
297 $R^1 = \text{CO}_2\text{Me}$ $R^2 = \text{Et}$ 36%
298 $R^1 = \text{CO}_2\text{Me}$ $R^2 = \text{Ph}$ 32%
299 $R^1 = \text{CO}_2\text{Et}$ $R^2 = \text{Et}$ 85%
300 $R^1 = \text{CO}_2\text{Et}$ $R^2 = \text{Ph}$ 45%
375 $R^1 = \text{Ph}$ $R^2 = \text{Et}$ 66%
376 $R^1 = \text{Ph}$ $R^2 = \text{Pri}$ 34%
377 $R^1 = \text{Ph}$ $R^2 = \text{PhCH}_2$ 78%
378 $R^1 = \text{Ph}$ $R^2 = p\text{-Cl-C}_6\text{H}_4$ 63%
379 $R^1 = p\text{-O}_2\text{N-C}_6\text{H}_4$ $R^2 = \text{Ph}$ 69%
380 $R^1 = \text{CO}_2\text{Me}$ $R^2 = \text{Et}$ 79%
381 $R^1 = \text{CO}_2\text{Me}$ $R^2 = \text{Ph}$ 60%
382 $R^1 = \text{CO}_2\text{Et}$ $R^2 = \text{Et}$ 66%
383 $R^1 = \text{CO}_2\text{Et}$ $R^2 = \text{Ph}$ 52%
The next stage was to synthesise the diazo compounds. There are a number of diazo exchange reagents in common use. The most well-known is tosyl azide 296.\textsuperscript{202} 4-Carboxybenzenesulphonyl azide 384 is also in use, but the reagent most suitable for this work was 4-(N-acetylamino)benzene sulphonyl azide 301.\textsuperscript{198}

\[
\begin{align*}
296 & \quad \quad \quad 384 & \quad \quad \quad 301
\end{align*}
\]

The diazo exchange reaction was attempted first with tosyl azide and \( \text{Et}_3\text{N} \) in dry \( \text{CH}_2\text{Cl}_2 \). The resulting oils contained mostly tosyl amide, but dibenzyl sulphone and 4-nitrobenzyl phenyl sulphone gave no reaction at all. Some attempts to remove the tosyl amide by washing with \( \text{NaOH} \) caused any ester-containing groups to hydrolyse. Fortunately, the ester-containing sulphones could be cleanly reacted with 4-(N-acetylamino)benzenesulphonyl azide in reasonable yield. This was reported to have a byproduct amide that was not soluble in the mixture of ether and petroleum in which the diazo exchange reaction was performed.\textsuperscript{198} In practice, some amide byproduct was found but the reaction mixture was easily separated by simple column chromatography through silica with ether. Even better, the product was the first compound to elute! The results of the successful syntheses are given below;

\[
\begin{align*}
385 & \quad R^1 = \text{CO}_2\text{Me} \quad R^2 = \text{Et} \quad 17\% \\
386 & \quad R^1 = \text{CO}_2\text{Et} \quad R^2 = \text{Et} \quad 50\%
\end{align*}
\]
The four diazosulphones 385–388 are previously unknown and gave the expected spectroscopic data, including a distinctive signal at $\delta_c$ 71–76 for the diazo carbon. Due to their thermal instability, satisfactory elemental analyses could not be obtained but correct high resolution mass spectral measurements were made in each case. The compounds appeared to be pure since they gave a single spot in TLC tests.

2 FVP

FVP of these compounds gave some unexpected results. Most significantly, the vinyl sulphones 389 were formed in three of the four cases, almost certainly by intramolecular insertion of carbenes 390, a result in excellent agreement with the pattern observed for ylides 222 discussed in section A. The products from each diazosulphone and some suggestions as to their mechanism of formation are discussed in detail below.

Methyl ethanesulphonyldiazoacetate 385 was the only one of these compounds to give a reasonable yield of the expected vinyl sulphone, 391, at 600°C.
At 600°C, ethyl ethanesulphonyldiazoacetate 386 gave poor yields of the two isomers of the expected E- and Z-propienyl sulphones, 392 and 393. Also detected was a small amount of acetaldehyde, which was assumed to come from the alternative splitting of β-lactone 394, as already observed for ylides 222. As with the ylides, no products derived from ketene 395 were detected.

\[
\begin{align*}
\text{Me}^\text{O} & \quad \text{Me}^\text{O} \\
\text{Et} & \quad \text{Et} \\
\end{align*}
\]

At 400°C, 386 also gave the expected ethyl propenyl sulphones but the major product was now ethyl ethanethiolosulphonate 396. This was the first sign of oxygen transfer, in that 396 could have been formed by combination of two ethanesulphinyl radicals followed by internal disproportionation of the gem-disulphoxide 397. The ethanesulphinyl radicals could, in turn, have been formed by transfer of oxygen from sulphone to carbene in 398, followed by rupture of the keto sulphoxide 399. In order to confirm the identity of 396, an attempt was made to prepare an authentic sample by oxidation of diethyl disulphide.
Unfortunately, this was not successful, even though the corresponding reaction of MeSSMe to give MeSSO₂Me did work.

![Chemical reaction diagram](image)

FVP of methyl benzenesulphonyldiazoacetate 387 at 600°C gave only biphenyl. It was this result that prompted the pyrolyses of these diazocompounds at a lower temperature.

![Chemical reaction diagram](image)

FVP of 387 at 400°C gave a mixture of products which included the expected phenyl vinyl sulphone 400. The products are shown (in order of decreasing abundance) in the diagrams below:

![Chemical reaction diagram](image)

![Chemical reaction diagram](image)
Phenyl thiooxalate 401 is possibly produced by oxygen transfer in carbene 402.

Methyl benzoate 403 could also be from this route by loss of SO and CO from the keto sulfoxide 404. An alternative breakdown of 404 leads to methyl phenyl sulfoxide 405. The route to ethyl phenyl ketone 406 is completely unknown, as are the routes to the remaining products.

The pyrolysis of ethyl (benzenesulphonyl)diazoacetate 388 follows a somewhat different pattern.
Again, oxygen transfer within 407, followed by break-down of the resulting ketosulphoxide 408 is presumed to be the source of some of the products but the overall pattern is clearly complex and requires further study to elucidate the mechanisms involved.

3 Attempted conversion of diazocompound to ylide

It was hoped, since the actual ylides corresponding to 385-388 had not yet been prepared, that reaction of these diazocompounds with Ph₃P would lead to a Staudinger-like reaction. The decomposition of diazocompounds has been catalysed by copper (acac)₂ [bis-(2,4-pentandionato)-copper (II)] in a number of investigations and it was thought that such a catalytic decomposition of 386, in the presence of Ph₃P would lead to ylides such as 409.

Hence ethyl (ethanesulphonyl)diazoacetete 386 was heated with triphenylphosphine and copper (acac)₂ in toluene. This gave a yellow powder whose phosphorus spectrum showed a large peak at δₚ +28.7. This was close to the values for alkoxy carbonyl sulphinyl ylides, but also to Ph₃P=O. TLC showed that the powder was almost entirely
triphenylphosphine oxide. FVP at 400°C gave a range of products similar to that from the original diazoacetate, so it was concluded that the reaction had not occurred.

![Chemical structure diagram](image-url)
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APPENDIX: PUBLICATIONS


Flash Vacuum Pyrolysis of Sulfinyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulfinylcarbenes

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Flash Vacuum Pyrolysis of Sulfinyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulfinylcarbenes

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Flash vacuum pyrolysis of α-alkanesulfinyl phosphorus ylides results mainly in extrusion of Ph₃P to give thioesters, presumably by 1,2-oxygen transfer in the initially formed sulfinyl carbenes; for α-arenesulfinyl ylides loss of Ph₃PO to give additional products is also observed. Although the thermal extrusion of Ph₃PO from α-acylphosphonium ylides 1 to give alkynes is well established,¹ the corresponding reaction of ylides bearing other oxygen containing functional groups on the α-position has been little investigated. Sulfonyl cyanides have been prepared by spontaneous extrusion from α-nitroso ylides 2 at −40 °C,² and there is evidence for extrusion of Ph₃PO from α-nitro ylides 3 to give nitrile oxides,³ but we recently reported that sulfonyl ylides 4 undergo loss of Ph₃P rather than Ph₃PO upon flash vacuum pyrolysis (FVP) to give products derived from sulfinylcarbenes.⁴ We now report the preparation and pyrolytic behaviour of representative α-sulfinyl ylides 5.

The sulfinyl ylides are little known and there were only two reports, both involving additional stabilisation by an ester group, until the (sulfinylmethylene)diphenylmethylphosphoranes were recently described,⁵ formed by reaction of a lithium phosphonium diylide with sulfinate esters. The required ylides 5 were readily formed in low to moderate yield (Table 1) in analogy to the acyl ylides 1, by reaction of Ph₃P=CHPh (2 equiv.) with sulfinyl chlorides RS(O)Cl. The sulfinyl chlorides, which are notoriously unstable and difficult to purify, were used directly as obtained from the improved method recently reported involving treatment of RSH with 2 equiv. SO₂Cl₂ and 1 equiv. AcOH. The ylides were recognised easily from the characteristic doublet (Jₚ₋₆ 122–128 Hz) due to the ylide carbon in their ¹³C NMR spectra (see Table 1).

For the alkanesulfinyl ylides 5a–c, FVP at 500 °C and 10⁻² Torr (contact time ca. 10⁻² s) resulted mainly in extrusion of Ph₃P to give the thioesters 6 (Table 1). This can be explained by a 1,2-O-transfer in the initially formed sulfinylcarbenes via the zwitterionic oxathirane intermediate shown. Sulfinylcarbenes are a little known class of reactive intermediates,⁶ but this type of oxygen transfer has been observed before in two cases.⁷ The analogous rearrangement of nitrocarbenes to acynitroso compounds has been described,⁸ as has 1,4-O-transfer from sulfur in an N-sulfonylimidoylcarbene to give the sulfinylimidoyl ketone.⁹

For 5a–c there was also some loss of Ph₃PO to give unknown...
products, and for the arylsulfonyl ylides 5d-f competing processes were more important, although 6 was still formed in each case. The most obvious feature in these cases was the production of an intense dark-blue colour in the cold trap that faded rapidly upon warming. This is attributed to the thioaldehyde 7 although it was only present in trace quantities and could not be detected spectroscopically. The formation of this product may be due to rearrangement of the硫ofylcarbene resulting from PhSPO extrusion. A major product for Se,F was the ketone 8 (Scheme 1) which most likely results from rearrangement of the sulfenylcarbene to a sulfine followed by loss of sulfur. A closely related example, dimethyl vinyl(p-toluenesulfonyl)carbene, has been reported to give the ketone in excellent yield in an analogous way, and the absence of this process for Se,F reflects the poorer migratory aptitude of alkyl vs aryl groups. The remaining products can be accounted for by alternative reactions of the thioaldehyde resulting from extrusion of PhSPO. The benzyl sulfide 9 (Scheme 1) is clearly formed by hydrogen atom abstraction, but the formation of stilbene 10 is more difficult to explain. Although the disulfide 11 and thiol 12 may be formed by a variety of radical processes which generate RS⁻, it is attractive to speculate that all three products may result as shown from an α-elimination process of radical 13 formed by abstraction of single hydrogen atom by the thiocarbene, although we are not aware of any precedent for this process. A further complication is the possibility of disproportionation of 5 in the inlet tube which has been observed for other sulfinyl ylides.13 and would lead to further products from pyrolysis of sulfenyl and sulfonyl ylides.

We thank British Petroleum Research International Limited for Research Studentships (M. J. D. and B. M. R.) and the Royal Society for a Warren Research Fellowship (R. A. A.).

Received, 21st July 1993; Com. 310427D

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PYROLYSIS OF STABILISED PHOSPHORUS YLIDES AS A ROUTE TO NEW HETERO CARBENES

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Abstract: Flash vacuum pyrolysis of sulphonyl- and sulphinyl-stabilised phosphorus ylides results in loss of either phosphine or phosphine oxide to generate thion-, sulphinyl- and sulphonyl-carbenes which undergo a variety of rearrangement and insertion processes to give stable products. The first case of phosphine extrusion from a β-oxo ylide is reported, giving access to benzotriazolyl acetyl carbene which rearranges to an acetyl benzotriazine and 2-cyanoacetophenone.

Thermal extrusion of Ph₃PO from both phosphorus ylides¹ and phosphinimines² stabilised by an α-acyl group is well known to lead to alkenes and nitriles, respectively, and in the former case the use of flash vacuum pyrolysis (FVP) gives improved yields in many cases.³ We have carried out a detailed study of the pyrolytic behaviour of a variety of phosphorus ylides stabilised by other oxygen-containing functional groups, notably sulphoxide and sulphone. As described below, this has revealed processes involving loss of both phosphine and phosphine oxide, so that in general (1) may give either (2) or (3) depending both on the nature of X and the substituents present.

\[
\begin{align*}
(1) & \quad \rightarrow \quad (2) \\
\text{SULPHONYL YLIDES} & \\
(3) & \quad \rightarrow \quad (2)
\end{align*}
\]

The results for sulphonyl stabilised ylides have already been described briefly.⁴ Compounds of type (4) lost Ph₃PO to give a complex mixture of products which could not be fully identified and the process was of no preparative value. In contrast the phenylmethanesulphonyl ylides (5) underwent exclusive loss of Ph₃P to give products which could be accounted for by intramolecular insertion and rearrangement of the
sulphonylcarbenes (6). In all cases the alkene products (7) were formed as shown, accompanied in some cases by other products depending on the nature of R.\textsuperscript{4}

\[
\begin{align*}
\text{Ph}_3\text{P} \quad \text{R} & \quad \text{Ph}_3\text{P} \quad \text{R} \\
\text{O}_2\text{S} \quad \text{Ar} & \quad \text{O}_2\text{S} \quad \text{CH}_2\text{Ar} \\
(4) & \quad (5) \\
\end{align*}
\]

\[
\begin{align*}
\text{FVP} & \quad \text{Ph}_3\text{P} \\
\end{align*}
\]

\[
\begin{align*}
\text{RCH=CHAr} & \quad \text{R} \\
(6) & \quad (7) \\
\text{Other} & \quad \text{Products} \\
(\text{see ref. 4}) & \\
\end{align*}
\]

**SULPHINYL YLIDES**

A range of sulphinyl ylides have also been prepared by acylation of the appropriate starting ylides with sulphinyl chlorides. For the compounds of type (8) stabilised both by a sulphinyl and an ester group, \text{Ph}_3\text{PO} is lost and the final product is a vinyl sulphide (9).\textsuperscript{5} We believe that these reactions proceed by intramolecular insertion of the carbene (10) to give a \(\beta\)-lactone which loses \text{CO}_2 to afford the observed product. Support for this idea is provided by the pyrolysis of \(\alpha\)-sulphonyl-\(\alpha\)-diazoesters (11) which gives the expected vinyl sulphones presumably by a similar mechanism. Since (8) is prepared in two steps from \text{RSH} and the pyrolysis proceeds in good yield, this represents a viable if

\[
\begin{align*}
\text{Ph}_3\text{P} \quad \text{CO}_2\text{CH}_2\text{R}^1 & \quad \text{FVP} \\
\text{O} \quad \text{S} \quad \text{R} & \quad -\text{Ph}_3\text{PO} \\
(8) & \quad (10) \\
\end{align*}
\]

\[
\begin{align*}
\text{R-S-CH=CHR}^1 & \\
9 & \\
\end{align*}
\]

\[
\begin{align*}
\text{N}_2 \quad \text{CO}_2\text{CH}_2\text{R}^1 & \quad \text{FVP} \\
\text{O}_2\text{S} \quad \text{Et} & \quad -\text{N}_2 \\
(11) & \quad (11) \\
\end{align*}
\]

\[
\begin{align*}
\text{Et-SO}_2\text{-CH=CHR}^1 & \\
\end{align*}
\]
unusual route to convert thiols into vinyl sulphides.

The simpler ylides (12) stabilised only by the alkanesulphinyl group undergo a different process. Loss of Ph₃P is followed by rapid rearrangement of the sulphinylcarbene (13) by 1,2-oxygen transfer to give the thioesters.

The pyrolytic behaviour of the arenesulphinyl ylides (14) is more complex and is not yet fully understood. Both Ph₃P and Ph₃PO are eliminated and both the resulting carbenes lead to products. The bright blue colour produced is almost certainly due to the thioketones (15) but these are only there in trace amounts and the colour quickly fades due to reaction with some of the other products present. These include the sulphoxide (16) resulting from hydrogen abstraction by one carbene, the thioester from its rearrangement, and products of radical decomposition such as diaryl sulphones.

A wide range of benzotriazolyl ylides (17) have been prepared and pyrolysed. They generally lose Bu₃PO and N₂ to give complex products. In contrast, compound (18) loses Bu₃P to give two heterocyclic products. After detailed studies these have been confirmed to be 3-acetyl-1,2,4-benzotriazine (19) and 2-cyanoacetophenone (20). As shown these products can be explained by a series of rearrangements and loss of N₂ from the new carbene (21). The reason for (18) losing Bu₃P and not Bu₃PO, an apparently unprecedented process, is not yet clear.
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