

Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 15.¹ Generation of alkoxy-carbonyl(sulfenyl)carbenes and their intramolecular insertion to give alkenyl sulfides

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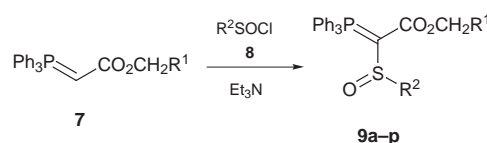
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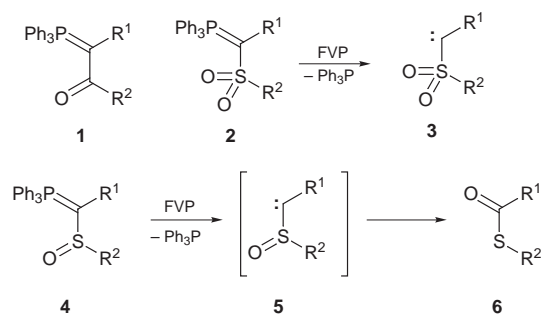
A range of 18 alkoxy-carbonyl sulfinyl phosphorus ylides **9** have been prepared and their behaviour upon flash vacuum pyrolysis (FVP) at 600 °C examined. For R¹ = H, Me and Et they lose Ph₃PO and in some cases Ph₃P to give mixtures of products including the alkenyl sulfides **10**, the sulfides **11**, the disulfides **12** and the thioesters **14**. The alkenyl sulfides **10** most likely arise from intramolecular insertion of the alkoxy-carbonyl sulfenyl carbenes resulting from loss of Ph₃PO to produce β-lactones which then lose CO₂ and this is supported by the results from ¹³C labelled ylides. Possible mechanisms for the formation of **11** and **14** are also presented and the feasibility of various steps has been examined by preparation and pyrolysis of the proposed intermediates. In contrast, pyrolysis of the ylides **9** where R¹ = Ph and the *tert*-butoxycarbonyl ylides **30** leads mainly to complete fragmentation with loss of Ph₃PO and benzyl alcohol or 2-methylpropan-2-ol and does not give any useful sulfur-containing products. Four alkoxy-carbonyl sulfonyl diazo compounds **33** have been prepared and in three cases they give the alkenyl sulfones **34** upon FVP at 400 °C, probably by an intramolecular insertion and decarboxylation process analogous to the formation of **10** from **9**. On the other hand the alkoxy-carbonyl carbenes produced by FVP of the amino acid-derived diazo compounds **35** undergo alternative processes with no sign of β-lactone formation. Fully assigned ¹³C NMR data are presented for 13 of the ylides.

In previous parts of this series we have described the thermal extrusion of triphenylphosphine oxide from a variety of β-oxo phosphorus ylides **1** using flash vacuum pyrolysis (FVP) to provide useful syntheses of a range of different functionalised alkynes. In contrast to this behaviour, the sulfonyl ylides **2** were found in most cases to undergo loss of triphenylphosphine to give products arising from secondary reactions of the sulfonyl carbenes **3** (Scheme 1).² In Part 13 of this work the sulfinyl

alkoxy-carbonyl ylides **7** with sulfinyl chlorides **8** in the presence of triethylamine (Scheme 2). The sulfinyl chlorides which are



Scheme 2



stabilised ylides **4** were also found to lose mainly Ph₃P under FVP conditions to give thioesters **6** formed by a 1,2-oxygen transfer in the sulfinyl carbenes **5**.³ We now describe the synthesis and pyrolytic behaviour of a range of ylides **9** with both alkoxy-carbonyl and sulfinyl stabilising groups in which many additional possibilities for thermal fragmentation arise.⁴

Results and discussion

The sulfinyl ylides **9** are a little known class of compounds and there are only two previous reports of their synthesis.⁵ A range of ylides **9a–k** were readily formed in low to moderate yield (Table 1) in analogy to the acyl ylides **1**, by reaction of the

notoriously unstable and difficult to purify were used directly as obtained from the improved method⁶ involving treatment of RSH with 2 equiv. SO₂Cl₂ and 1 equiv. AcOH. The ylides were easily recognised from the characteristic doublet (¹J_{P-C} 118–123 Hz) due to the ylide carbon in their ¹³C NMR spectra (see Table 2). As compared to the sulfinyl ylides **4** with R¹ = Ph, the compounds **9** show a significant increase in polarisation of the ylide bond which results in deshielding of the phosphorus (**4**, δ_p +18.7–20.4; **9**, δ_p +27.4–28.4) and shielding of the ylide carbon (**4**, δ_C 47–52; **9**, δ_C 35–37). Perhaps because of this polarisation, the compounds proved to be rather unstable and difficult to purify but correct HRMS values were obtained in each case except for **9h** where the low yield meant that full characterisation was not possible. The consistent pattern of ¹³C NMR data across the series leaves little doubt as to the identity of the compounds. As for the simpler sulfinyl ylides **4**, the majority of the compounds **9** showed a peak for M⁺ – O as the highest mass signal in the mass spectrum.

Most of the ylides **9** showed marked broadening of certain signals in the ¹H and ¹³C NMR spectra at room temperature, particularly those associated with the CO₂CH₂R¹ group. This is likely to be due to restricted rotation of this group, a phenomenon which is well established for ester-stabilised ylides. In the case of **9g** this was quantified by a variable temperature NMR study over the range 233–303 K which gave a value for the free

Table 1 Preparation of ylides **9** and results of their pyrolysis at 600 °C

	R ¹	R ²	Yield (%)	δ_p	Products from FVP (%)								other products	
					Ph ₃ PO	Ph ₃ P	Ph ₃ PS	10	11	12	13	14		
a	H	Me	13	27.6	14	80	6	20	—	—	—	—	—	MeCHO (5)
b	H	Et	35	27.4	20	67	13	10	—	2	—	—	—	—
c	Me	Et	44	27.5	30	60	10	36	—	—	—	—	—	MeCHO (2)
c^a					30	60	10	34	—	2	—	—	3	—
d^a	H	Ph	64	28.2	93	7	—	14	22	5	2	16	—	—
e	Me	Ph	71	28.1	100	0	—	10	5	10	15	6	—	—
f	H	4-MeC ₆ H ₄	30	28.3	90	10	—	11	25	3	—	5	—	—
g	Me	4-MeC ₆ H ₄	41	28.35	90	10	—	51	2	3	—	17	—	—
h	Et	4-MeC ₆ H ₄	3	28.2	40	60	—	34	—	2	—	3	—	—
i	Me	4-ClC ₆ H ₄	72	28.3	40	60	—	17	3	—	—	4	—	—
j^a	H	4-BrC ₆ H ₄	53	28.2	100	0	—	—	11	—	—	—	—	R ² SEt (2)
k	Me	4-BrC ₆ H ₄	60	28.3	100	0	—	53	11	—	—	10	—	—
l^a	Ph	Et	17	27.5	60	40	—	20	—	25	—	—	—	R ¹ CH ₂ OH (10)

^a Pyrolysis carried out at 500 °C

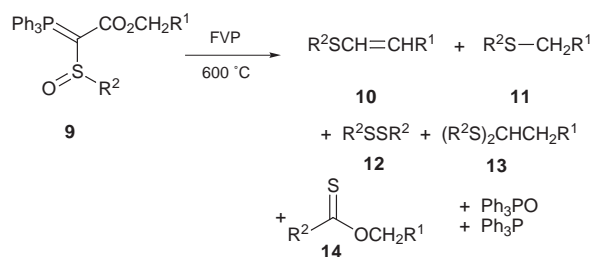
Table 2 ¹³C NMR Spectra of ylides **9** and **30**, δ_C (J_{P-C})

	R ¹	R ²	P=C	CO	P-Phenyl				CH ₂ R ¹ signals	R ² signals
					C-1	C-2	C-3	C-4		
9c	Me	Et	37.0 (120)	172.2 (br)	127.8 (88)	133.8 (10)	128.3 (12)	131.7 (2)	58.6 (br), 13.9 (br)	33.1, 13.4
9d	H	Ph	35.7 (123)	172.8 (br)	126.8 (91)	133.7 (10)	128.4 (12)	131.9 (2)	51.0 (br)	144.3, 128.1 (2C), 125.3 (2C, br), 124.2
9e	Me	Ph	36.0 (120)	172.4 (br)	124.8 (104)	133.7 (10)	128.3 (12)	131.9 (2)	59.0 (br), 14.6 (br)	144.4, 128.0 (4C), 124.1
9f	H	4-Me-C ₆ H ₄	36.2 (123)	172.9 (br)	127.0 (91)	133.8 (9)	128.4 (12)	131.9 (3)	50.9 (br)	140.9, 133.7, 128.9 (2C), 125.6 (2C, br), 20.9
9g	Me	4-Me-C ₆ H ₄	36.4 (121)	172.2 (br)	127.2 (91)	133.8 (10)	128.3 (12)	131.8 (2)	58.9 (br), 14.6 (br)	141.0, 133.7, 128.8 (2C), 125.9 (2C, br), 20.9
9i	Me	4-Cl-C ₆ H ₄	36.0 (121)	172.2 (br)	126.9 (91)	133.7 (9)	128.4 (12)	132.0 (2)	59.1 (br), 14.6 (br)	143.4, 129.7, 128.1 (2C), 126.8 (2C, br)
9l	Ph	Et	37.0 (120)	172.0 (br)	127.8 (83)	133.8 (10)	128.3 (12)	131.8 (2)	131.9, 127.9 (2C), 127.8 (2C), 127.0, 64.7 (br)	33.2 (br), 13.4
9m	Ph	Pr ⁱ	55.2 (119)	166.4 (11)	125.0 (93)	133.8 (10)	128.8 (13)	132.4 (2)	132.0, 128.1 (2C), 128.0 (2C), 127.3, 64.8	49.8 (9), 18.8, 18.4
9n	Ph	Ph	36.7 (120)	172.0 (br)	127.5 (75)	133.8 (9)	128.4 (12)	132.0 (<2)	132.0, 128.6, 128.0 (2C), 127.9 (2C), 65.0	144.3 (br), 132.1 (2C), 125.6 (2C, br), 124.2 (br)
9o	Ph	4-Me-C ₆ H ₄	36.8 (122)	172.0 (br)	126.7 (91)	133.7 (9)	128.3 (12)	131.8 (2)	128.8 (2C), 128.5, 127.8, 127.9 (2C), 64.8	140.7, 133.7 (2C), 127.0 (2C), 125.8, 20.9
9p	Ph	4-Cl-C ₆ H ₄	36.4 (121)	172.0 (br)	127.4 (59)	133.7 (9)	128.4 (12)	132.1 (2)	133.8, 132.0, 128.0 (2C), 127.9 (2C), 65.0	135.1 (2), 128.4, 127.2 (2C), 126.8 (2C)
30a	—	4-Me-C ₆ H ₄	36.7 (118)	171.8 (br)	127.7 (89)	133.8 (10)	128.2 (12)	131.8 (1)	78.2, 28.4 (3C)	141.3, 133.6, 128.7 (2C), 126.0 (2C), 20.9
30b	—	4-Cl-C ₆ H ₄	36.3 (118)	170.6 (br)	127.5 (66)	113.8 (9)	128.3 (12)	132.0 (<2)	78.6, 28.4 (3C)	132.1, 128.6, 128.0 (4C)

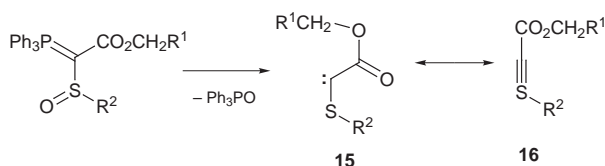
energy barrier to rotation of 58 ± 1 kJ mol⁻¹ and an energy difference between the two forms of 0.38 kJ mol⁻¹. A similar study of **9c** gave much more complex results and it appears that in this case there is restricted rotation of both the CO₂Et and S(O)Et groups. Even at 218 K sharp lines were still not obtained in the spectra and no quantitative information could be obtained.

The ylides **9** were subjected to FVP and underwent complete reaction at 600 °C to give a rather complex mixture of products as shown in Scheme 3. In all cases Ph₃PO was produced but this was usually accompanied by Ph₃P and, for **9a–c** only, by a small proportion of Ph₃PS (Table 1). The major non phosphorus-

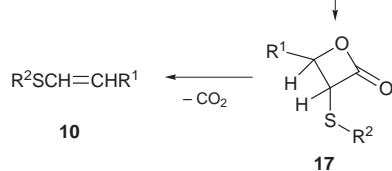
containing products were the alkenyl sulfides **10** whose identity was established by independent synthesis in the case of **10a** and **10i**. We believe that these are formed as shown in Scheme 4 by loss of Ph₃PO to give the alkoxy carbonyl sulfonyl carbenes **15** which undergo intramolecular CH insertion to give β -lactones **17** which then lose CO₂ to afford the products. Evidence in support of this mechanism was obtained by preparation and pyrolysis of the ¹³C labelled ylides **18** and **20** starting from 5% ¹³C-enriched ethyl bromoacetate. As expected FVP of the ylide **18** with the label on the ylide carbon led to product **19** with the label on =CHS, while FVP of **20** gave unlabelled products (Scheme 5).



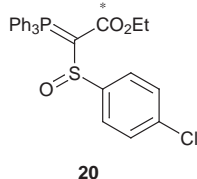
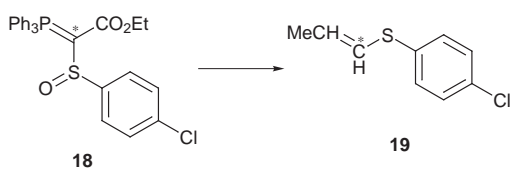
Scheme 3



Scheme 4



Scheme 4

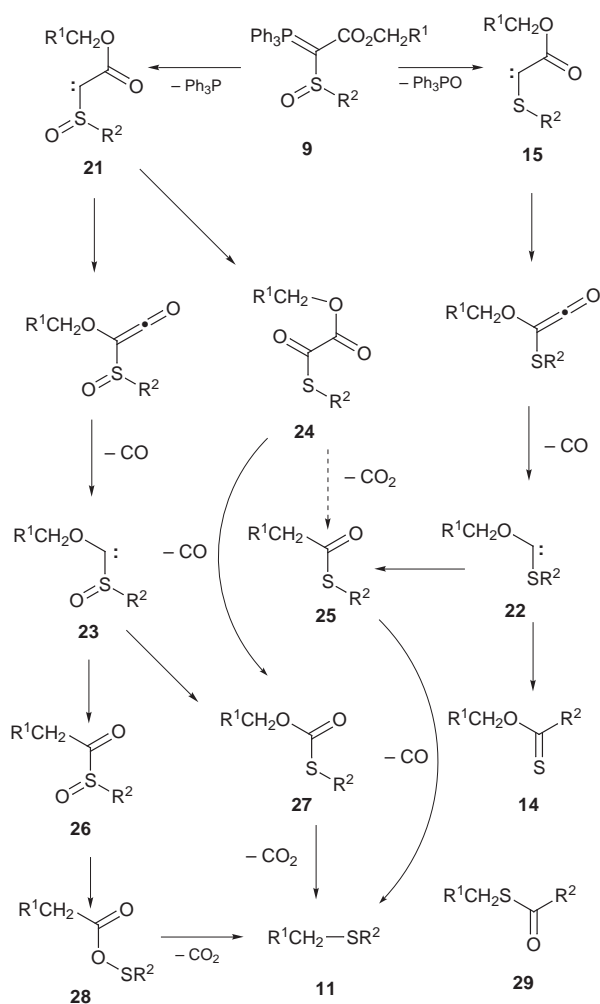


Scheme 5

Given that, as we infer, elimination to form the carbene precedes insertion, this is as far as we are aware the first report of a reaction involving a free alkoxy carbonyl sulfonyl carbene,⁷ since a study in which the apparent addition products of $\text{MeO}_2\text{C}(\text{Me})\text{C}:$ to alkenes were obtained by base-induced α -elimination from the α -chloro ester involved reaction in the presence of SnCl_4 .⁸ The behaviour observed here is in excellent agreement with that of bis(methoxycarbonyl)carbene generated by FVP of the diazomalonnate,⁹ which underwent insertion to give a β -lactone followed by loss of CO_2 to afford methyl acrylate. Photochemical generation of an alkoxy carbonyl carbene has allowed isolation of the β -lactone resulting from insertion in one instance,¹⁰ and the formation of β -lactams by insertion of (dialkylaminocarbonyl)carbenes is quite well known.¹¹ Close analogies can also be found in studies of carbenes derived from α -diazophosphonates¹² and α -diazophosphonamides¹³ where insertion to form four-membered rings is observed, and in the former case is accompanied by extrusion of metaphosphate to give alkenes. On the other hand a variety of alkoxy carbonyl carbenes have been generated and used in synthesis without any sign of the intramolecular insertion process.¹⁴ It appears that where other processes such as 1,2-hydrogen shift, ylide formation or intermolecular insertion are possible these predominate and only where no other process is possible does the intramolecular insertion occur.

The structure of the carbene **15** is of some interest since it might be considered to exist to some extent as the λ^4 - $\text{C}\equiv\text{S}$ form **16**. The λ^6 -compound $\text{CF}_3\text{C}\equiv\text{SF}_3$ is known,¹⁵ and evidence has been presented for both α -phosphinocarbenes¹⁶ and α -phosphinonitrenes¹⁷ existing and reacting to some extent in the λ^5 - $\text{P}\equiv\text{C}$ and λ^5 - $\text{P}\equiv\text{N}$ forms. Unfortunately **15** undergoes the intramolecular insertion readily under the conditions required for its generation and no measure of the relative importance of the form **16** could be made.

The other major products of pyrolysis of ylides **9** were the sulfides **11**, the disulfides **12**, the dithioacetals **13** probably formed by addition of R^2S^* to **10**, and compounds of formula $\text{R}^1\text{CH}_2\cdot\text{COS}\cdot\text{R}^2$ for which we propose the thioester structure **14** for the reasons given below. The most important of these products was **11** and for ylides **9d**, **f** and **j** this was the major product. The identity of **11i** and **p** was confirmed by independent synthesis. As shown in Scheme 6, this product could arise by



Scheme 6

a myriad of different routes all involving well-precedented processes in carbene chemistry. There is no clear correlation between the formation of **11** and the ratio of Ph_3PO to Ph_3P in a given case and although its formation from ylides where Ph_3PO is the sole phosphorus product shows that it must be formed from carbene **15** in these cases, it may well be formed from the sulfonyl carbene **21** in other cases.

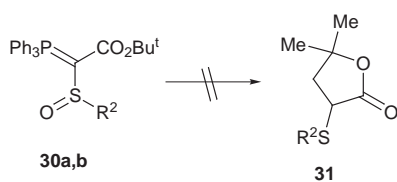
In an attempt to shed some light on which of the processes of Scheme 6 are feasible under the conditions involved we prepared representative monothiooxalates **24e** and **g** and the thioesters **25d** and **i** and examined their pyrolytic behaviour. At 600°C both compounds **24** gave the corresponding sulfides **11**, the disulfides **12** and the monothiocarbonates **27** thus establish-

ing the feasibility of the route from **24** to **27** to **11**. Under the same conditions **25d** was unchanged but at 750 °C it reacted to produce **11** and **12** while **25i** gave **11** at 600 °C. The finding that **25** is a possible precursor to **11** means that where the formation of **11** is associated with initial extrusion of Ph_3PO , the fragmentation probably goes *via* **22** and **25** as shown, while formation of **11** in association with initial extrusion of Ph_3P may be either *via* **24** and **27**, **23** and **27**, or **23**, **26** and **28**. In an attempt to investigate the possible involvement of **28** we attempted to prepare **28i** by reaction of 4-chlorobenzenesulfonyl chloride with silver propionate but this was unsuccessful. The formation of the disulfides **12** from FVP of both **24** and **25** suggests that generation of the radicals R^2S^\cdot is feasible under the conditions used and we believe that this is how both **12** and **13** are formed.

The remaining major products, formed in 8 of the 12 cases, had a molecular mass corresponding to **11** + 28 and the HRMS measurement on the compound derived from **9h** showed the extra mass to be due to CO and thus the compounds to have the overall formula $\text{R}^1\text{CH}_2\cdot\text{COS}\cdot\text{R}^2$. On this basis they could be either $\text{R}^1\text{CH}_2\text{C}(\text{O})\text{SR}^2$, $\text{R}^1\text{CH}_2\text{C}(\text{S})\text{OR}^2$, $\text{R}^1\text{CH}_2\text{OC}(\text{S})\text{R}^2$ or $\text{R}^1\text{CH}_2\text{SC}(\text{O})\text{R}^2$. The compounds all showed a characteristic ^{13}C NMR signal at δ_{C} 195.0–195.4. Although it is not easy to distinguish clearly between *S*-alkyl and *O*-alkyl thioesters on the basis of ^{13}C NMR chemical shifts,¹⁸ the first and last formulations could readily be excluded since the first is **25** and the shifts for **25e** (δ_{C} 198.1) and **25i** (δ_{C} 197.5) were clearly higher than those from the compounds of interest, while on the other hand synthesis of two examples of the last formulation **29** showed that they had lower shifts (**29e**, δ_{C} 191.7; **29i**, δ_{C} 190.8). We favour the formulation **14** for the pyrolysis products on the basis that the ^1H and ^{13}C NMR signals for R^1CH_2 clearly show that it is joined to oxygen rather than carbon (**14d**, δ_{H} 3.13; **14g**, δ_{C} 62.0). Furthermore the formation of this product is readily explained by a 1,2-shift of the R^2 group in the sulfinyl alkoxy carbene **22** (Scheme 6) and, as expected from this mechanism, the product from the labelled ylide **18** showed a five-fold enhancement of the signal at δ_{C} 195.0 while the product from **20** was unlabelled.

We have no satisfactory explanation for the anomalous behaviour of the ylide **9j** which gave Ph_3PO together with **11j** and the corresponding ethyl sulfide.

In an attempt to extend the scope of these studies we prepared five examples of benzyloxycarbonyl sulfinyl ylides **9l–p** (Tables 1 and 2) and the two *tert*-butoxycarbonyl sulfinyl ylides **30a,b**. These had spectroscopic properties in good agreement with the earlier examples (Table 2). FVP of **9l–p** was expected to provide access to the styryl sulfides **10** while the behaviour of **30** was of particular interest since with no α -hydrogen on the alkyl group they could not form β -lactones but might instead insert to give the γ -lactones **31** (Scheme 7). Intramolecular insertion



Scheme 7

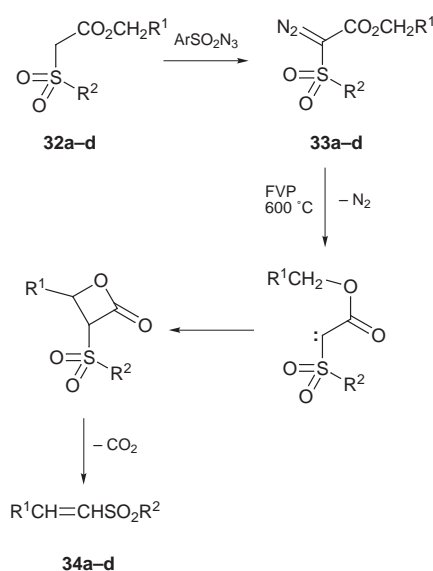
of a photochemically generated carbene into the β -CH of an alkoxy carbonyl group to form a γ -lactone has been reported before but is rather uncommon.^{10,19} In the event, the FVP of these ylides at 500 or 600 °C gave disappointing results. For **9l** both Ph_3PO and Ph_3P were produced together with a low yield of **10l** but this was accompanied by a significant yield of benzyl alcohol. For **9m–p** Ph_3PO and benzyl alcohol were obtained as the only identifiable products and loss of the alkoxy carbonyl group also occurred for **30a,b** where the products were 2-methylpropan-2-ol and the disulfides, R^2SSR^2 .

Table 3 Preparation of diazo compounds **33** and **35** and results of their pyrolysis

Compound	R ¹	R ²	Yield (%)	FVP temp. (°C)	Product	Yield (%)
33a	H	Et	17	600	34a	30
33b	Me	Et	50	600	34b	10
33c	H	Ph	54	400	34c	<5
33d	Me	Ph	47	400	—	—
35a	H	CH ₂ Ph	36	400	36a	51
35b	Me	CH ₂ Ph	37	400	36b	72
35c	H	Pr ⁱ	30	400	37	47
35d	H	CH ₂ SH	25	400	38	50

Although the pyrolytic behaviour of the ylides **9** had turned out to be more complex than expected, the overall formation of **10** from **7** and **8** in two steps represents an unusual and useful method for C=C double bond formation and we sought to extend the scope of this reaction by preparing and pyrolysing suitably functionalised diazo compounds. In an attempt to evaluate the relative involvement of **15** and **21** in Scheme 6, diazo exchange of β -sulfinyl and β -sulfenyl esters was attempted but this was uniformly unsuccessful in agreement with literature precedent,²⁰ although it is worth noting that formation of the first stable diazo compounds from β -sulfinyl esters has recently been achieved by using constrained cyclic systems.²¹ On the other hand diazo exchange of the β -sulfonyl esters **32** proceeded smoothly using 4-acetamidobenzene-sulfonyl azide²² to give the diazo compounds **33** in reasonable yield (Table 3). Four further examples of functionalised α -alkoxycarbonyl diazo compounds **35a–d** were obtained by diazotisation of readily available amino acid esters using the method originally reported for preparation of ethyl diazoacetate from ethyl glycinate.²³ These compounds proved to be rather unstable, slowly losing N_2 at room temperature to give the same products as from FVP, and so only spectroscopic characterisation was possible.

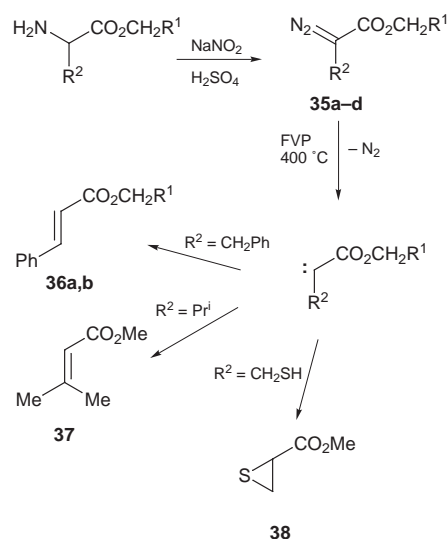
When **33a** and **b** were subjected to FVP at 600 °C, the expected alkenyl sulfones **34** were formed albeit in low yield (Table 3), most probably by the route shown in Scheme 8. On



Scheme 8

the other hand **33c** and **d** decomposed completely under these conditions. By reducing the furnace temperature to 400 °C, a very low yield of phenyl vinyl sulfone could be obtained from **33c** while for **33d** no products could be definitely identified. The rhodium-catalysed decomposition of **33d** in the presence of

propan-2-ol has been reported to lead to the product from intermolecular insertion into OH and under these conditions no products from intramolecular CH insertion were detected.²⁴ For the four amino acid-derived diazo compounds **35**, FVP at 400 °C gave products attributable to the corresponding carbenes but in each case a competing process had predominated and no products from intramolecular insertion into CH of the ester function were detected (Scheme 9). For **35a** and **b**



Scheme 9

the products were the corresponding cinnamates **36** formed by a 1,2-hydrogen shift. The same process has been reported in solution both by base or acid induced decomposition of **35a** and **b**²⁵ and using a rhodium catalyst.²⁶ The valine-derived compound **35c** behaved similarly to give **37**, again resulting from a 1,2-hydrogen shift. In the case of the cysteine-derived compound **35d**, the thirane ester **38** was formed apparently from intramolecular insertion of the carbene into the SH bond. It is interesting to compare this result with the work of Maycock and Stoodley²⁷ who treated the methyl ester of cysteine with nitrous acid and observed the direct formation of **38** which they attributed to intramolecular nucleophilic attack of SH on the diazonium function in an intermediate diazonium salt. Proof that the reaction did not involve the diazo compound **35d** came from the observation that **38** was obtained in enantiomerically pure form. In our case, the preparation of **35d** was conducted under less acidic conditions which favoured loss of a proton from the initial diazonium salt to give the isolable diazo compound which could then be pyrolysed to give **38** by SH insertion.

In conclusion, we have shown that the pyrolytic behaviour of stabilised ylides **9** with alkoxycarbonyl and sulfinyl groups present is considerably more complex than for the simpler sulfinyl ylides **4** and involves loss of both Ph_3PO and Ph_3P to give the alkenyl sulfides **10** as major products together with sulfides **11** and thioesters **14**. The intramolecular insertion process leading to **10** also occurs for the carbenes derived from alkoxycarbonyl sulfonyl diazo compounds. Although the reactions are unlikely to be of great preparative value, they have given a useful insight into the reactivity of alkoxycarbonyl sulfinyl-, sulfinyl- and sulfonyl-carbenes which was previously little known.

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. Infra red spectra were recorded as Nujol mulls for solids and as thin films for liquids on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^1H at 300 MHz and for ^{13}C at 75 MHz using a Bruker AM300

instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl_3 with internal Me_4Si as reference for ^1H and ^{13}C and external 85% H_3PO_4 as reference for ^{31}P . Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. Mass spectra were obtained on an AEI/Kratos MS-50 spectrometer using electron impact at 70 eV. GC-MS data were obtained using a Hewlett Packard 5890A chromatograph coupled to a Finnigan Incos mass spectrometer. Toluene was dried by storing over sodium wire.

The starting phosphonium salts and ylides **7** were commercially available or were prepared using standard methods. The following starting materials do not appear to have been fully characterised before:

(Propoxycarbonylmethyl)triphenylphosphonium iodide

Propyl chloroacetate (34.1 g, 0.25 mol) was added slowly to a stirred solution of sodium iodide (37.5 g, 0.25 mol) in acetone (150 cm^3). After 3 h the solvent was evaporated and the residue partitioned between water and toluene (200 cm^3). The toluene layer was dried over magnesium sulfate and then triphenylphosphine (65.6 g, 0.25 mmol) was added and the mixture stirred for 14 h. The product was filtered off and dried to give colourless crystals (95.4 g, 78%), mp 147–148 °C (Found: C, 56.6; H, 4.85. $\text{C}_{23}\text{H}_{24}\text{IO}_2\text{P}$ requires C, 56.3; H, 4.9%); δ_{H} 8.2–7.7 (15 H, m), 5.30 (2 H, d, J 14), 4.01 (2 H, t, J 7), 1.51 (2 H, sextet, J 7) and 0.73 (3 H, t, J 7); δ_{P} +20.3.

(Benzyloxycarbonylmethyl)triphenylphosphonium iodide

The procedure as above using benzyl chloroacetate gave yellow crystals (51%), mp 129–130 °C (Found: C, 60.2; H, 4.7. $\text{C}_{27}\text{H}_{24}\text{IO}_2\text{P}$ requires C, 60.2; H, 4.5%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1736, 1587, 1454, 1437, 1321, 1303, 1159, 1110, 756, 737, 722 and 692; δ_{H} 7.8–7.5 (15 H, m), 7.3–7.0 (5 H, m), 5.20 (2 H, d, J 13) and 4.98 (2 H, s); δ_{C} 162.8 (d, J 4, CO), 134.6 (d, J 2, C-4 of P-Ph), 133.2 (d, J 11, C-2 of P-Ph), 129.6 (d, J 13, C-3 of P-Ph), 127.9 (3 C), 127.8 (2 C), 127.3, 116.4 (d, J 89, C-1 of P-Ph), 67.7 (CH_2Ph) and 32.6 (d, J 55, CH_2P); δ_{P} +20.0; m/z 410 ($\text{M}^+ - \text{HI}$, 0.5%), 301 (8), 277 (100), 262 (23), 183 (26), 152 (8), 108 (13) and 91 (57).

(tert-Butoxycarbonylmethyl)triphenylphosphonium chloride

A solution of *tert*-butyl chloroacetate (10.0 g, 66 mmol) and triphenylphosphine (17.3 g, 66 mmol) in dry toluene (100 cm^3) was stirred at room temperature for 12 h. The resulting precipitate was filtered off to give the product as colourless crystals (22.8 g, 83%), mp 189 °C (lit.,²⁸ 185 °C); δ_{H} 8.2–7.8 (15 H, m), 5.53 (2 H, d, J 15) and 1.22 (9 H, s); δ_{C} 163.1 (d, J 4, CO), 135.1 (d, J 3, C-4 of P-Ph), 133.9 (d, J 11, C-2 of P-Ph), 130.2 (d, J 13, C-3 of P-Ph), 118.2 (d, J 89, C-1 of P-Ph), 84.5 (CMe_3), 33.7 (d, J 54, CH_2) and 27.5 (Me); δ_{P} +20.6; m/z 376 ($\text{M}^+ - \text{HCl}$, 8%), 319 (53), 301 (100), 275 (25), 262 (12), 183 (76) and 165 (48).

(Benzyloxycarbonylmethylene)triphenylphosphorane

A solution of (benzyloxycarbonylmethyl)triphenylphosphonium iodide (30 g, 55 mmol) in water (250 cm^3) was treated with sodium hydroxide (1 equiv.) to give after extraction with dichloromethane, drying over magnesium sulfate and evaporation and recrystallisation from ethyl acetate, the *title ylide* (11.3 g, 50%) as colourless crystals, mp 115–120 °C (HRMS: found M^+ , 410.1471. $\text{C}_{27}\text{H}_{23}\text{O}_2\text{P}$ requires M , 410.1436); δ_{H} 7.75–7.55 (6 H, m), 7.5–7.25 (9 H, m), 7.2–7.1 (5 H, s), 5.04 (2 H, s) and 3.00 (1 H, br s); δ_{C} 170.6 (d, J 12, CO), 138.5, 132.7 (d, J 10, C-2 of P-Ph), 131.9 (d, J 2, C-4 of P-Ph), 128.6 (d, J 12, C-3 of P-Ph), 127.9 (2 C), 127.6 (2 C), 127.6 (d, J 92, C-1 of P-Ph), 126.9, 63.8 (CH_2Ph) and 30.3 (d, J 125, $\text{CH}=\text{P}$); δ_{P} +17.4; m/z 410 (M^+ , 0.1%), 379 (0.1), 301 (3), 277 (100), 262 (5), 201 (18), 183 (15), 152 (8) and 108 (30).

(*tert*-Butoxycarbonylmethylene)triphenylphosphorane

The above method using (*tert*-butoxycarbonylmethyl)triphenylphosphonium chloride gave the *title ylide* (51%) as colourless crystals, mp 150 °C (lit.,²⁹ 154–155 °C); δ_{H} 7.7–7.6 (6 H, m), 7.5–7.35 (9 H, m), 2.75 (1 H, br s) and 1.20 (9 H, br s); δ_{C} 171.0 (d, *J* 9, CO), 132.9 (d, *J* 10, C-2 of P-Ph), 131.7 (C-4 of P-Ph), 128.5 (d, *J* 12, C-3 of P-Ph), 128.3 (d, *J* 91, C-1 of P-Ph), 76.3 (CMe₃), 31.3 (d, *J* 121, CH=P) and 28.7 (Me); δ_{P} +16.9.

{Ethoxycarbonyl-[¹³C]methylene}triphenylphosphorane

A solution of ethyl [5%-²⁻¹³C]bromoacetate and an equimolar quantity of triphenylphosphine in toluene was heated at 90 °C for 3 h. The resulting phosphonium salt (δ_{P} +20.4) was filtered off, dissolved in water and treated with sodium hydroxide (1 equiv.) to give after extraction with dichloromethane, drying and evaporation the required ylide (δ_{P} +17.3).

{Ethoxy[¹³C]carbonylmethylene}triphenylphosphorane

This was prepared as above starting from ethyl [5%-¹⁻¹³C]-bromoacetate.

The sulfinyl chlorides **8** were prepared by treatment of the corresponding thiols with acetic acid (1 equiv.) and sulfuric chloride (2 equiv.) at –40 °C according to the literature method⁶ and had physical and spectroscopic properties in accordance with the literature data.

Preparation of sulfinyl ylides

A solution of the appropriate stabilised ylide **7** (30 mmol) and triethylamine (3.0 g, 30 mmol) in dry toluene (100 cm³) was stirred at 0 °C under nitrogen while a solution of the appropriate sulfinyl chloride **8** (30 mmol) in dry toluene (10 cm³) was added dropwise. After the addition the mixture was allowed to warm up to room temperature over 12 h and then filtered, evaporated and the residue triturated with ethyl acetate to afford the products as follows:

[(Methoxycarbonyl)(methylsulfinyl)methylene]triphenylphosphorane 9a. From (methoxycarbonylmethylene)triphenylphosphorane and methanesulfinyl chloride as yellow crystals (13%), mp 123–125 °C (HRMS: found $M^+ - \text{MeSO}$, 333.1020. C₂₂H₂₁O₃PS requires $M - \text{MeSO}$, 333.1044); $\nu_{\text{max}}/\text{cm}^{-1}$ 1715, 1587, 1440, 1310, 1264, 1200, 1112, 1040, 997, 895, 858, 773, 758, 723 and 693; δ_{H} 7.7–7.4 (15 H, m), 3.52 (3 H, br s) and 1.85 (3 H, s); δ_{P} +27.6; m/z 333 ($M^+ - \text{MeSO}$, 8%), 301 (55), 277 (100), 262 (22), 201 (55), 199 (38), 183 (55) and 152 (30).

[(Ethylsulfinyl)(methoxycarbonyl)methylene]triphenylphosphorane 9b. From (methoxycarbonylmethylene)triphenylphosphorane and ethanesulfinyl chloride as colourless crystals (35%), mp 134–136 °C (HRMS: found $M^+ - \text{Me}$, 395.0850. C₂₃H₂₃O₃PS requires $M - \text{Me}$, 395.0871); $\nu_{\text{max}}/\text{cm}^{-1}$ 1598, 1484, 1440, 1378, 1275, 1252, 1182, 1110, 1082, 1041, 1023, 1000, 921, 760, 745, 718 and 695; δ_{H} 7.7–7.4 (15 H, m), 3.52 (3 H, br s), 2.18 (2 H, q, *J* 7) and 0.98 (3 H, t, *J* 7); δ_{P} +27.4; m/z 395 ($M^+ - \text{Me}$, 23%), 367 (17), 365 (72), 301 (4), 277 (5), 262 (46), 201 (5), 183 (100), 152 (14) and 108 (66).

[(Ethoxycarbonyl)(ethylsulfinyl)methylene]triphenylphosphorane 9c. From (ethoxycarbonylmethylene)triphenylphosphorane and ethanesulfinyl chloride as colourless crystals (44%), mp 140–143 °C (HRMS: found $M^+ - \text{O}$, 408.1307. C₂₄H₂₅O₃PS requires $M - \text{O}$, 408.1313); $\nu_{\text{max}}/\text{cm}^{-1}$ (CH₂Cl₂) 3040, 2970, 2920, 1640, 1595, 1482, 1436, 1365, 1232, 1190, 1170, 1100, 1070, and 865; δ_{H} 7.9–7.5 (15 H, m), 4.02 (2 H, br q, *J* 7), 2.21 (2 H, q of d, *J* 7, 2), 1.01 (3 H, t, *J* 7) and 0.90 (3 H, br s); δ_{C} see Table 2; δ_{P} +27.5; m/z 408 ($M^+ - \text{O}$, 45%), 379 (100), 301 (7), 277 (8), 262 (37), 183 (38), 152 (5), 108 (14) and 77 (4).

[(Methoxycarbonyl)(phenylsulfinyl)methylene]triphenylphosphorane 9d. From (methoxycarbonylmethylene)triphenylphosphorane and benzenesulfinyl chloride as colourless crystals (64%), mp 212–218 °C (HRMS: found $M^+ + \text{H} - \text{O}$, 443.1214. C₂₇H₂₃O₃PS requires $M + \text{H} - \text{O}$, 443.1235); $\nu_{\text{max}}/\text{cm}^{-1}$ 1602, 1578, 1475, 1430, 1280, 1180, 1104, 1080, 1022, 994, 816, 754, 740, 715 and 692; δ_{H} 7.85–7.5 (15 H, m), 7.4–7.1 (5 H, m) and 3.65 (3 H, br s); δ_{C} see Table 2; δ_{P} +28.2; m/z 443 (5%), 442 ($M^+ - \text{O}$, 18), 365 (5), 278 (18), 277 (42), 263 (14), 262 (74), 201 (11), 183 (42) and 86 (100).

[(Ethoxycarbonyl)(phenylsulfinyl)methylene]triphenylphosphorane 9e. From (ethoxycarbonylmethylene)triphenylphosphorane and benzenesulfinyl chloride as colourless crystals (71%), mp 167–170 °C (HRMS: found $M^+ - \text{O}$, 456.1319. C₂₈H₂₅O₃PS requires $M - \text{O}$, 456.1313); $\nu_{\text{max}}/\text{cm}^{-1}$ 1605, 1435, 1267, 1108, 1083, 1026, 740, 721 and 692; δ_{H} 7.8–7.5 (17 H, m), 7.4–7.2 (3 H, m), 4.07 (2 H, q, *J* 7) and 0.96 (3 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +28.1; m/z 456 ($M^+ - \text{O}$, 25%), 411 (3), 379 (4), 302 (7), 277 (100), 262 (78), 218 (7), 201 (20), 183 (42) and 152 (13).

[(Methoxycarbonyl)(4-methylphenylsulfinyl)methylene]triphenylphosphorane 9f. From (methoxycarbonylmethylene)triphenylphosphorane and 4-methylbenzenesulfinyl chloride as colourless crystals (30%), mp 215–216 °C (HRMS: found $M^+ + \text{H} - \text{O}$, 457.1385. C₂₈H₂₅O₃PS requires $M + \text{H} - \text{O}$, 457.1391); $\nu_{\text{max}}/\text{cm}^{-1}$ 1605, 1480, 1432, 1310, 1265, 1182, 1105, 1082, 1022, 998, 918, 808, 758, 745, 717 and 694; δ_{H} 7.85–7.5 (15 H, m), 7.20 and 7.05 (4 H, AB pattern, *J* 8), 3.64 (3 H, s) and 2.28 (3 H, br s); δ_{C} see Table 2; δ_{P} +28.3; m/z 457 (8%), 456 ($M^+ - \text{O}$, 32), 425 (3), 365 (4), 277 (6), 263 (14), 262 (100), 211 (4), 201 (3) and 183 (44).

[(Ethoxycarbonyl)(4-methylphenylsulfinyl)methylene]triphenylphosphorane 9g. From (ethoxycarbonylmethylene)triphenylphosphorane and 4-methylbenzenesulfinyl chloride as colourless crystals (41%), mp 200–202 °C (HRMS: found $M^+ + \text{H} - \text{O}$, 471.1529. C₂₉H₂₇O₃PS requires $M + \text{H} - \text{O}$, 471.1548); $\nu_{\text{max}}/\text{cm}^{-1}$ 1610, 1480, 1436, 1360, 1262, 1107, 1083, 998, 807, 753, 718 and 693; δ_{H} 7.85–7.5 (15 H, m), 7.21 and 7.04 (4 H, AB pattern, *J* 8), 4.09 (2 H, br q, *J* 7), 2.28 (3 H, s) and 0.97 (3 H, br t, *J* 7); δ_{C} see Table 2; δ_{P} +28.35; m/z 471 (4%), 470 ($M^+ - \text{O}$, 13), 425 (2), 379 (2), 303 (2), 285 (2), 263 (13), 262 (100), 185 (11) and 183 (37).

[(4-Methylphenylsulfinyl)(propoxycarbonyl)methylene]triphenylphosphorane 9h. In this case a solution of (propoxycarbonylmethyl)triphenylphosphonium iodide (6.66 g, 13.6 mmol) was stirred in dry THF (100 cm³) at room temperature while dry triethylamine (1.9 cm³, 13.6 mmol) was added. After 30 min, the mixture was filtered and dry triethylamine (1.9 cm³, 13.6 mmol) was added to the filtrate. The solution was stirred at 0 °C while 4-methylbenzenesulfinyl chloride (2.37 g, 13.6 mmol) was added over 30 min. After the addition the mixture was allowed to warm up to room temperature over 12 h and then filtered, evaporated and the residue triturated with ethyl acetate to afford the product as colourless crystals (0.20 g, 3%). Due to the extremely low yield only spectroscopic characterisation was possible; δ_{H} 7.6–7.5 (9 H, m), 7.45–7.35 (6 H, m), 7.07 and 6.91 (4 H, AB pattern, *J* 8), 3.90 (2 H, br s), 2.23 (3 H, s) and 1.7–0.3 (5 H, v br); δ_{P} +28.2; m/z 485 ($M^+ - \text{Me}$, 3%), 274 (2), 262 (46), 196 (5), 183 (57), 165 (17), 152 (10), 135 (25), 121 (21), 108 (38) and 43 (100).

[(4-Chlorophenylsulfinyl)(ethoxycarbonyl)methylene]triphenylphosphorane 9i. From (ethoxycarbonylmethylene)triphenylphosphorane and 4-chlorobenzenesulfinyl chloride as colourless crystals (72%), mp 191–194 °C (HRMS: found $M^+ - \text{O}$, 490.0937. C₂₈H₂₄³⁵ClO₃PS requires $M - \text{O}$, 490.0923); $\nu_{\text{max}}/\text{cm}^{-1}$ 1602, 1438, 1364, 1267, 1104, 1065, 1005, 820, 750, 716

and 691; δ_{H} 7.85–7.5 (15 H, m), 7.22 (4 H, s), 4.07 (2 H, br q, *J* 7) and 0.92 (3 H, br t, *J* 7); δ_{C} see Table 2; δ_{P} +28.3; *m/z* 492/490 ($\text{M}^+ - \text{O}$, 6/18%), 445 (2), 379 (3), 303 (3), 277 (10), 262 (100), 201 (4), 183 (48) and 108 (32).

{(4-Chlorophenylsulfinyl)(ethoxycarbonyl)[^{13}C]methylene}triphenylphosphorane 18. From {ethoxycarbonyl[5%- ^{13}C]methylene}triphenylphosphorane and 4-chlorobenzenesulfinyl chloride as colourless crystals with identical physical and spectroscopic properties to **9i** except for a five-fold enhancement of the ylide doublet at δ_{C} 36.0.

{(4-Chlorophenylsulfinyl){ethoxy[^{13}C]carbonyl}methylene}triphenylphosphorane 20. From {ethoxy[5%- ^{13}C]carbonylmethylene}triphenylphosphorane and 4-chlorobenzenesulfinyl chloride as colourless crystals with identical physical and spectroscopic properties to **9i** except for a five-fold enhancement of the carbonyl signal at δ_{C} 172.2.

{(4-Bromophenylsulfinyl)(methoxycarbonyl)methylene}triphenylphosphorane 9j. From (methoxycarbonylmethylene)triphenylphosphorane and 4-bromobenzenesulfinyl chloride as colourless crystals (53%), mp 172–173 °C (HRMS: found $\text{M}^+ - \text{O}$, 520.0228. $\text{C}_{27}\text{H}_{22}^{79}\text{BrO}_3\text{PS}$ requires $M - \text{O}$, 520.0261; $\nu_{\text{max}}/\text{cm}^{-1}$ 1718, 1573, 1435, 1313, 1226, 1203, 1158, 1115, 1069, 1031, 1002, 894, 870, 831, 759, 739, 723, 692 and 630; δ_{H} 7.85–7.5 (15 H, m), 7.37 and 7.18 (4 H, AB pattern, *J* 8) and 3.63 (3 H, br s); δ_{P} +28.2; *m/z* 522/520 ($\text{M}^+ - \text{O}$, 6/6%), 365 (1), 301 (25), 278 (50), 277 (100), 262 (80), 201 (18), 183 (60), 152 (15) and 108 (20).

{(4-Bromophenylsulfinyl)(ethoxycarbonyl)methylene}triphenylphosphorane 9k. From (ethoxycarbonylmethylene)triphenylphosphorane and 4-bromobenzenesulfinyl chloride as colourless crystals (60%), mp 190–192 °C (HRMS: found $\text{M}^+ - \text{CH}_3$, 535.0169. $\text{C}_{28}\text{H}_{24}^{79}\text{BrO}_3\text{PS}$ requires $M - \text{CH}_3$, 535.0132; $\nu_{\text{max}}/\text{cm}^{-1}$ 1722, 1604, 1440, 1365, 1314, 1265, 1228, 1207, 1187, 1112, 1032, 1000, 882, 828, 750, 735, 720, 690 and 632; δ_{H} 7.85–7.5 (15 H, m), 7.32 and 7.14 (4 H, AB pattern, *J* 8), 4.06 (2 H, br q, *J* 7) and 0.92 (3 H, br t, *J* 7); δ_{P} +28.3; *m/z* 537/535 ($\text{M}^+ - \text{Me}$, 3/3%), 379 (2), 303 (2), 277 (48), 262 (100), 201 (18), 199 (12) and 183 (73).

[(Benzyloxycarbonyl)(ethylsulfinyl)methylene]triphenylphosphorane 9l. From (benzyloxycarbonylmethylene)triphenylphosphorane and ethanesulfinyl chloride as yellow crystals (17%), mp 115–117 °C (Found: C, 71.5; H, 5.6. $\text{C}_{29}\text{H}_{27}\text{O}_3\text{PS}$ requires C, 71.6; H, 5.6%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1590, 1282, 1242, 1101, 1040, 908 and 750; δ_{H} 7.7–7.1 (20 H, m), 5.0 (2 H, br s), 2.18 (2 H, q, *J* 7) and 0.97 (3 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +27.5; *m/z* 470 ($\text{M}^+ - \text{O}$, 2%), 441 (3), 294 (7), 278 (40), 277 (100), 262 (8), 201 (18), 199 (14), 185 (15) and 183 (25).

[(Benzyloxycarbonyl)(propan-2-ylsulfinyl)methylene]triphenylphosphorane 9m. From (benzyloxycarbonylmethylene)triphenylphosphorane and propan-2-ylsulfinyl chloride as yellow crystals (10%), mp 122–125 °C (HRMS: found $\text{M}^+ - \text{O}$, 484.1616. $\text{C}_{30}\text{H}_{29}\text{O}_3\text{PS}$ requires $M - \text{O}$, 484.1626; $\nu_{\text{max}}/\text{cm}^{-1}$ 1620, 1320, 1275, 1112, 1063, 1012, 752, 730 and 700; δ_{H} 7.7–6.9 (20 H, m), 5.02 and 4.88 (2 H, AB pattern, *J* 12), 4.35 (1 H, m), 1.28 (3 H, d, *J* 8) and 1.02 (3 H, d, *J* 8); δ_{C} see Table 2; δ_{P} +24.1; *m/z* 484 ($\text{M}^+ - \text{O}$, 0.1%), 441 (0.3), 294 (0.5), 277 (35), 201 (7), 199 (5), 108 (18) and 91 (100).

[(Benzyloxycarbonyl)(phenylsulfinyl)methylene]triphenylphosphorane 9n. From (benzyloxycarbonylmethylene)triphenylphosphorane and benzenesulfinyl chloride as colourless crystals (6%), mp 145–147 °C (HRMS: found $\text{M}^+ - \text{O}$, 518.1462. $\text{C}_{33}\text{H}_{27}\text{O}_3\text{PS}$ requires $M - \text{O}$, 518.1469; $\nu_{\text{max}}/\text{cm}^{-1}$ 1603, 1440, 1260, 1105, 1050, 902, 752, 720 and 696; δ_{H} 7.55–6.95 (25 H, m)

and 5.06 (2 H, br s); δ_{C} see Table 2; δ_{P} +28.3; *m/z* 518 ($\text{M}^+ - \text{O}$, 1%), 441 (5), 427 (1), 411 (9), 383 (18), 339 (5), 303 (63), 273 (58), 262 (100) and 183 (84).

[(Benzyloxycarbonyl)(4-methylphenylsulfinyl)methylene]triphenylphosphorane 9o. From (benzyloxycarbonylmethylene)triphenylphosphorane and 4-methylbenzenesulfinyl chloride as yellow crystals (24%), mp 160–162 °C (HRMS: found $\text{M}^+ - \text{O}$, 532.1619. $\text{C}_{34}\text{H}_{29}\text{O}_3\text{PS}$ requires $M - \text{O}$, 532.1626; $\nu_{\text{max}}/\text{cm}^{-1}$ 1605, 1268, 1110, 1052, 906, 757, 725 and 698; δ_{H} 7.55–7.1 (20 H, m), 7.05 and 6.88 (4 H, AB pattern, *J* 8), 5.07 (2 H, br s) and 2.23 (3 H, s); δ_{C} see Table 2; δ_{P} +28.45; *m/z* 532 ($\text{M}^+ - \text{O}$, 97%), 441 (3), 425 (5), 397 (3), 303 (20), 262 (100) and 183 (22).

[(Benzyloxycarbonyl)(4-chlorophenylsulfinyl)methylene]triphenylphosphorane 9p. From (benzyloxycarbonylmethylene)triphenylphosphorane and 4-chlorobenzenesulfinyl chloride as yellow crystals (68%), mp 133–135 °C (Found: C, 70.2; H, 4.7%; $\text{M}^+ - \text{O}$, 552.1084. $\text{C}_{33}\text{H}_{26}^{35}\text{ClO}_3\text{PS}$ requires C, 69.7; H, 4.6%; $M - \text{O}$, 552.1080; $\nu_{\text{max}}/\text{cm}^{-1}$ 1604, 1266, 1106, 1086, 1010, 819, 750, 723 and 696; δ_{H} 7.6–7.15 (20 H, m), 7.08 and 7.02 (4 H, AB pattern, *J* 9) and 5.05 (2 H, br s); δ_{C} see Table 2; δ_{P} +28.2; *m/z* 554/552 ($\text{M}^+ - \text{O}$, 7/16%), 303 (13), 301 (16), 262 (95), 183 (40), 108 (82) and 91 (100).

[(*tert*-Butoxycarbonyl)(4-methylphenylsulfinyl)methylene]triphenylphosphorane 30a. From (*tert*-butoxycarbonylmethylene)triphenylphosphorane and 4-methylbenzenesulfinyl chloride as yellow crystals (18%), mp 140 °C (HRMS: found $\text{M}^+ - \text{O}$, 498.1815. $\text{C}_{31}\text{H}_{31}\text{O}_3\text{PS}$ requires $M - \text{O}$, 498.1782; $\nu_{\text{max}}/\text{cm}^{-1}$ 1610, 1304, 1252, 1170, 1112, 1070, 815, 730 and 700; δ_{H} 7.85–7.2 (15 H, m), 7.21 and 7.02 (4 H, AB pattern, *J* 8), 2.26 (3 H, s) and 1.14 (9 H, s); δ_{C} see Table 2; δ_{P} +28.5; *m/z* 498 ($\text{M}^+ - \text{O}$, 0.1%), 427 (0.2), 303 (0.1), 301 (0.2), 277 (100), 246 (8), 201 (22), 199 (20) and 183 (18).

[(*tert*-Butoxycarbonyl)(4-chlorophenylsulfinyl)methylene]triphenylphosphorane 30b. From (*tert*-butoxycarbonylmethylene)triphenylphosphorane and 4-chlorobenzenesulfinyl chloride as yellow crystals (21%), mp 153 °C (HRMS: found $\text{M}^+ - \text{O}$, 518.1204. $\text{C}_{30}\text{H}_{28}^{35}\text{ClO}_3\text{PS}$ requires $M - \text{O}$, 518.1236; $\nu_{\text{max}}/\text{cm}^{-1}$ 1645, 1246, 1161, 1106, 1064, 820, 760, 722 and 697; δ_{H} 7.9–7.4 (15 H, m), 7.22 (4 H, s) and 1.13 (9 H, s); δ_{C} see Table 2; δ_{P} +28.2; *m/z* 520/518 ($\text{M}^+ - \text{O}$, 2/5%), 462 (2), 445 (2), 318 (3), 301 (8), 277 (68), 262 (100), 183 (54), 144 (36) and 108 (50).

Flash vacuum pyrolysis of ylides 9

The apparatus used was as described previously.³⁰ All pyrolyses were conducted at pressures in the range 10^{-3} – 10^{-1} Torr and were complete within 1 h. Under these conditions the contact time in the hot zone was estimated to be ≈ 10 ms.

In all cases the phosphorus containing products collected at the furnace exit and the more volatile products were recovered from the cold trap. Yields were determined by calibration of the ^1H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 and comparing integrals, a procedure estimated to be accurate to $\pm 10\%$.

FVP of **9a** (215 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3P , Ph_3PO and Ph_3PS in a ratio of 80 : 14 : 6: Ph_3P ; δ_{P} –5.4; *m/z* 262 (M^+ , 12%), 183 (45), 152 (16) and 108 (100). Ph_3PO ; δ_{P} +28.6; *m/z* 277 ($\text{M}^+ - \text{H}$, 100%), 201 (28), 183 (27) and 152 (10). Ph_3PS ; δ_{P} +43.6; *m/z* 294 (M^+ , 91%), 262 (15), 217 (15) and 183 (100).

In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as methyl vinyl sulfide **10a** (20%); δ_{H} 6.46 (1 H, dd, *J* 16, 10), 5.20 (1 H, d, *J* 10), 4.97 (1 H, d, *J* 16) and 2.27 (3 H, s); δ_{C} 132.9, 108.4, 13.6; *m/z* 74 (M^+ , 8%), 73 (100), 59 (4), 50 (8)

and 45 (30), acetaldehyde (5%); δ_{H} 9.81 (1 H, q, *J* 2) and 2.22 (3 H, d, *J* 2); δ_{C} 198.9 and 29.9, dimethyl disulfide **12a** (2%); *m/z* 94 (M^+ , 58%), 79 (45), 64 (12) and 45 (100), and 1,1-bis(methylthio)ethane **13a** (10%); *m/z* 122 (M^+ , 33%), 107 (3), 75 (100) and 59 (30).

FVP of the ylide **9b** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3P , Ph_3PO and Ph_3PS in a ratio of 67:20:13. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as ethyl vinyl sulfide **10b** (10%); δ_{H} 6.37 (1 H, dd, *J* 16, 10), 5.17 (1 H, d, *J* 10), 4.84 (1 H, d, *J* 16), 2.73 (2 H, q, *J* 7) and 1.32 (3 H, t, *J* 7); *m/z* 88 (M^+ , 40%), 73 (16), 60 (54), 59 (83), 58 (70) and 45 (100) and diethyl disulfide **12b** (2%); *m/z* 122 (M^+ , 60%), 94 (47) and 66 (100).

FVP of the ylide **9c** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3P , Ph_3PO and Ph_3PS in a ratio of 60:30:10. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as ethyl prop-1-enyl sulfide **10c** (36%, *E:Z* = 4:3); δ_{H} (*E*) 5.9–6.0 (1 H, m), 5.7–5.5 (1 H, m), 2.66 (2 H, q, *J* 7), 1.75 (3 H, dd, *J* 5, 1) and 1.32 (3 H, t, *J* 7); (*Z*) 5.9–6.0 (1 H, m), 5.7–5.5 (1 H, m), 2.70 (2 H, q, *J* 7), 1.72 (3 H, dd, *J* 5, 1) and 1.29 (3 H, t, *J* 7); δ_{C} (*E*) 124.9, 122.2, 25.7, 17.5 and 13.6, (*Z*) 124.4, 122.8, 26.6, 14.5 and 13.5; *m/z* 102 (M^+ , 53%), 87 (8), 74 (21), 73 (58), 59 (16), 45 (100) and 41 (65) and acetaldehyde (2%); δ_{H} and δ_{C} as for product from **9a**.

Analysis of the pyrolysate produced at 500 °C showed the presence of ethyl prop-1-enyl sulfide **10c** (34%), diethyl disulfide **12c** (2%); *m/z* 122 (M^+ , 100%), 94 (68) and 66 (86), and *O*-ethyl propanethioate **14c** (3%); *m/z* 118 (M^+ , 24%), 89 (85) and 61 (100).

FVP of the ylide **9d** (200 mg) at 500 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3PO and Ph_3P in a ratio of 93:7. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as phenyl vinyl sulfide **10d** (14%); δ_{H} 7.5–7.3 (5 H, m), 6.68 (1 H, dd, *J* 17, 9), 5.44 (1 H, d, *J* 9) and 5.42 (1 H, d, *J* 17), methyl phenyl sulfide **11d** (22%); δ_{H} 7.5–7.3 (5 H, m) and 2.52 (3 H, s); *m/z* 124 (M^+ , 100%), diphenyl disulfide **12d** (5%); *m/z* 218 (M^+ , 66%) and 109 (100), 1,1-bis(phenylthio)ethane **13d** (2%); *m/z* 246 (M^+ , 12%), 137 (100), 123 (9) and 109 (65), and *O*-methyl benzenecarbothioate **14d** (16%); δ_{H} 7.5–7.3 (5 H, m) and 3.13 (3 H, s); *m/z* 152 (M^+ , 53%), 151 (18), 124 (100), 123 (84), 109 (40) and 77 (10).

FVP of the ylide **9e** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist entirely of Ph_3PO . In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as phenyl prop-1-enyl sulfide **10e** (10%); δ_{H} 7.5–7.2 (5 H, m), 6.3–5.8 (2 H, m) and 2.1–2.0 (3 H, m); δ_{C} 123.6 (*E*), 121.7 (*Z*), 18.5 (*E*) and 14.7 (*Z*); *m/z* 150 (M^+ , 100%), 149 (55), 135 (51), 134 (25), 116 (18), 110 (16), 105 (15) and 91 (20), ethyl phenyl sulfide **11e** (5%); δ_{H} 2.95 (2 H, q, *J* 7) and 1.30 (3 H, t, *J* 7); δ_{C} 27.7 and 14.4; *m/z* 138 (M^+ , 100%), 123 (68), 110 (78), 109 (33) and 77 (22), diphenyl disulfide **12e** (10%); *m/z* 218 (M^+ , 43%), 185 (13), 154 (15) and 109 (100), 1,1-bis(phenylthio)propane **13e** (15%); *m/z* 260 (M^+ , 3%), 151 (100), 137 (38), 123 (25) and 109 (62), and *O*-ethyl benzenecarbothioate **14e** (6%); *m/z* 166 (M^+ , 22%), 138 (36), 137 (100) and 109 (74).

FVP of the ylide **9f** (200 mg) at 500 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3PO and Ph_3P in a ratio of 90:10. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as 4-methylphenyl vinyl sulfide **10f** (11%); δ_{H} 7.4–7.1 (4 H, m), 6.56 (1 H, dd, *J* 17, 9), 5.30 (1 H, d, *J* 9), 5.26 (1 H, d, *J* 17) and 2.31 (3 H, s); *m/z* 150 (M^+ , 100%), 135 (98), 123 (14), 105 (30) and 91 (23),

methyl 4-methylphenyl sulfide **11f** (25%); δ_{H} 7.4–7.1 (5 H, m), 2.42 (3 H, s) and 2.27 (3 H, s); *m/z* 138 (M^+ , 100%), 123 (32) and 91 (75), bis(4-methylphenyl) disulfide **12f** (3%); *m/z* 123 (M^+ , 100%), and *O*-methyl 4-methylbenzenecarbothioate **14f** (5%); δ_{H} 7.4–7.1 (4 H, m), 2.99 (3 H, s) and 2.29 (3 H, s); *m/z* 166 (M^+ , 51%), 137 (100), 123 (12), 121 (8), 93 (18) and 91 (36).

FVP of the ylide **9g** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3PO and Ph_3P in a ratio of 90:10. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as 4-methylphenyl prop-1-enyl sulfide **10g** (51%); δ_{H} 7.4–7.2 (4 H, m), 6.30 (1 H, half AB pattern of q, *J* 9, 1), 6.02 (1 H, half AB pattern of q, *J* 9, 6), 2.35 (3 H, s) and 1.83 (3 H, dd, *J* 6, 1); *m/z* 164 (M^+ , 100%), 149 (86), 134 (21), 123 (21), 119 (18) and 91 (45), ethyl 4-methylphenyl sulfide **11g** (2%); *m/z* 152 (M^+ , 100%), 137 (64), 124 (25) and 91 (32), bis(4-methylphenyl) disulfide **12g** (3%); *m/z* 246 (M^+ , 12%), 245 (18), 214 (2), 182 (8) and 123 (100) and *O*-ethyl 4-methylbenzenecarbothioate **14g** (17%); δ_{C} 195.4, 62.0 and 14.1; *m/z* 180 (M^+ , 22%), 151 (100), 136 (10), 123 (37) and 91 (32).

FVP of the ylide **9h** (180 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3P and Ph_3PO in a ratio of 60:40. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as 4-methylphenyl but-1-enyl sulfide **10h** (34%, *E:Z* = 3:2) (HRMS: found M^+ , 178.0806. $\text{C}_{11}\text{H}_{14}\text{S}$ requires M , 178.0816); δ_{H} 7.37 and 7.19 (4 H, AB pattern, *J* 8), 6.35–5.7 (2 H, m), 2.37 (3 H, s), 2.25 (2 H, m) and 1.07 (3 H, t, *J* 7); δ_{C} (key peaks only) (major isomer) 120.9, 26.2, 21.0 and 13.4; (minor isomer) 123.0, 22.5, 21.1 and 13.6; *m/z* 178 (M^+ , 100%), 163 (21), 148 (25), 135 (18), 129 (22), 124 (50), 105 (18) and 91 (90), bis(4-methylphenyl) disulfide **12h** (2%); *m/z* 246 (M^+ , 12%), 182 (2) and 123 (100) and *O*-propyl 4-methylbenzenecarbothioate **14h** (3%) (HRMS: found M^+ , 194.0789. $\text{C}_{11}\text{H}_{14}\text{OS}$ requires M^+ , 194.0765); δ_{C} 195.2; *m/z* 194 (M^+ , 22%), 165 (88), 137 (12), 123 (100) and 91 (42).

FVP of the ylide **9i** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist of Ph_3P and Ph_3PO in a ratio of 60:40. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as (*E*)- and (*Z*)-4-chlorophenyl prop-1-enyl sulfide **10i** (17%, *E:Z* = 3:2); δ_{H} 7.34 (4 H, s), 6.35–5.8 (2 H, m) and 1.84 (3 H, d, *J* 5); δ_{C} (key peaks only) 122.9, 121.1, 18.5 and 14.6; *m/z* 186/184 (M^+ , 35/100%), 4-chlorophenyl ethyl sulfide **11i** (3%); δ_{C} 27.9 and 14.3, and *O*-ethyl 4-chlorobenzenecarbothioate **14i** (4%); δ_{C} 195.0, 52.0 and 13.9; *m/z* 202/200 (M^+ , 4/13%), 184 (29), 171 (78), 155 (27), 143 (55) and 108 (100).

FVP of the labelled ylide **18** (200 mg) at 600 °C gave a product in the cold trap whose main constituents were identified by ^{13}C NMR as being the same as for **9i**. The (*E*)- and (*Z*)-4-chlorophenyl prop-1-enyl sulfide **19** showed enhancement of the ArS-C= peaks at δ_{C} 122.9 and 121.1, 4-chlorophenyl ethyl sulfide **11i** was unlabelled, and the carbonyl peak at δ_{C} 195.0 due to **14i** was also enhanced.

FVP of the labelled ylide **20** (200 mg) at 600 °C gave a product in the cold trap whose main constituents were identified by ^{13}C NMR as being the same as for **9i**. The products **10i**, **11i** and **14i** were all unlabelled.

FVP of the ylide **9j** (200 mg) at 500 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist entirely of Ph_3PO together with some unreacted starting material. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as 4-bromophenyl methyl sulfide **11j** (11%); δ_{H} 7.36 and 7.07 (4 H, AB pattern, *J* 9) and 2.46 (3 H, s); *m/z* 204/202 (M^+ , 88/92%), 189/187 (45/43), 171/169 (11/13), 158/156 (12/12), 122 (28), 109 (99) and 108 (100) and 4-bromophenyl

ethyl sulfide (2%); m/z 218/216 (M^+ , 44/46%), 203/201 (15/14), 190/188 (19/18), 122 (47) and 109 (100).

FVP of the ylide **9k** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ^{31}P NMR and GC-MS to consist entirely of Ph_3PO . In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as 4-bromophenyl prop-1-enyl sulfide **10k** (53%); δ_{H} 7.5–7.0 (4 H, m), 6.2–6.0 (2 H, m) and 1.95–1.75 (3 H, m); m/z 230/228 (M^+ , 39/35%), 189/187 (8/9), 185/183 (8/10), 149 (100), 134 (50), 116 (35) and 109 (65), 4-bromophenyl ethyl sulfide **11k** (11%); m/z 218/216 (M^+ , 44/46%), 203/201 (15/14), 190/188 (19/18), 122 (47) and 109 (100) and *O*-ethyl 4-bromobenzenecarbothioate **14k** (10%); m/z 246/244 (M^+ , 9/10%), 217/215 (65/68), 189/187 (22/24), 136 (100) and 108 (92).

FVP of **9l** (120 mg) at 500 °C gave a solid at the furnace exit which was shown by NMR and GC-MS to consist of Ph_3PO and Ph_3P in a ratio of 60:40. In the cold trap was a liquid whose main constituents were identified by NMR, GC-MS and comparison with authentic samples as ethyl styryl sulfide **10l** (20%); δ_{H} (*E*) 6.75 and 6.48 (1 H, AB pattern, *J* 16); (*Z*) 6.47 and 6.28 (1 H, AB pattern, *J* 10); m/z 164 (M^+ , 20%), 135 (40), 103 (5), 91 (100) and 86 (30), diethyl disulfide **12l** (25%); m/z 122 (M^+ , 33%), 94 (30), 66 (80) and 36 (100) and benzyl alcohol (10%); δ_{H} 4.70 (2 H, s); m/z 108 (M^+ , 42%).

Preparation and FVP of authentic products and proposed intermediates

Methyl vinyl sulfide 10a. This was prepared by a literature method³¹ and had the following spectroscopic data; δ_{H} 6.46 (1 H, dd, *J* 16, 10), 5.20 (1 H, d, *J* 10), 4.97 (1 H, d, *J* 16) and 2.27 (3 H, s); δ_{C} 132.9, 108.5 and 13.5.

4-Chlorophenyl prop-2-enyl sulfide. Reaction of equimolar quantities of 4-chlorobenzenethiol, 3-bromopropene and sodium ethoxide in ethanol at room temperature for 18 h followed by addition to water, extraction with ether, evaporation and distillation gave a colourless liquid (81%), bp (oven temp.) 145–155 °C at 16 Torr (HRMS: found M^+ , 184.0125. $\text{C}_9\text{H}_9^{35}\text{ClS}$ requires *M*, 184.0113); δ_{H} 7.38 (4 H, s), 6.2–5.7 (1 H, m), 5.3–5.0 (2 H, m) and 3.56 (2 H, dt, *J* 7, 1); δ_{C} 134.4, 133.2 (CH=CH₂), 132.1, 131.1 (2 C), 128.8 (2 C), 117.8 (CH=CH₂) and 37.3; m/z 186/184 (M^+ , 32/100%), 169 (15), 149 (25), 143 (36) and 108 (50).

(*E*)- and (*Z*)-4-Chlorophenyl prop-1-enyl sulfide 10i. Reaction of 4-chlorophenyl prop-2-enyl sulfide with sodium ethoxide (3 equiv.) in boiling ethanol for 18 h followed by addition to water, extraction with ether, evaporation and distillation gave a colourless liquid (85%), bp (oven temp.) 110–120 °C at 3 Torr (HRMS: found M^+ , 184.0107. $\text{C}_9\text{H}_9^{35}\text{ClS}$ requires *M*, 184.0113); δ_{H} 7.34 (4 H, s), 6.35–5.8 (2 H, m) and 1.84 (3 H, d, *J* 5); δ_{C} 135.2, 134.9, 133.4, 131.9, 131.8, 129.8, 129.4, 129.0, 128.9, 128.8, 122.9 (*E*), 121.1 (*Z*), 18.5 (*E*) and 14.6 (*Z*); m/z 186/184 (M^+ , 30/100%), 171 (18), 149 (50), 143 (22), 139 (18), 134 (28), 115 (22) and 108 (45).

4-Chlorophenyl ethyl sulfide 11i. Reaction of equimolar quantities of 4-chlorobenzenethiol, bromoethane and potassium hydroxide in ethanol at room temperature for 3 h followed by addition to water, extraction with ether, evaporation and distillation gave a colourless liquid (70%), bp (oven temp.) 75–85 °C at 2.5 Torr (lit.,³² 123 °C at 18 Torr); δ_{H} 7.37 (4 H, s), 2.95 (2 H, q, *J* 7) and 1.30 (3 H, t, *J* 7); δ_{C} 135.2, 131.7, 130.3 (2 C), 128.9 (2 C), 27.9 and 14.3.

Benzyl 4-chlorophenyl sulfide 11p. Reaction of equimolar quantities of 4-chlorobenzenethiol, benzyl chloride and sodium ethoxide in ethanol at room temperature for 30 min followed by

addition to water, extraction with ether and evaporation gave a colourless solid (38%), mp 47–49 °C (lit.,³³ 52–53 °C); δ_{H} 7.3–7.1 (9 H, m) and 4.05 (2 H, s); δ_{C} 137.6, 135.3, 133.0, 131.9 (2 C), 129.5 (2 C), 129.3 (2 C), 129.1 (2 C), 127.9 and 39.8.

***O*-Ethyl *S*-phenyl monothiooxalate 24e.** Reaction of equimolar quantities of benzenethiol, ethyl oxalyl chloride and triethylamine in toluene at room temperature for 30 min followed by filtration, evaporation and distillation gave a colourless liquid (70%), bp (oven temp.) 180 °C at 3.5 Torr (HRMS: found M^+ , 210.0345. $\text{C}_{10}\text{H}_{10}\text{O}_3\text{S}$ requires *M*, 210.0351); $\nu_{\text{max}}/\text{cm}^{-1}$ 3060, 2984, 1755, 1745, 1700, 1580, 1478, 1441, 1270, 1240, 1020, 982, 858, 749 and 690; δ_{H} 7.60 (5 H, s), 4.48 (2 H, q, *J* 7) and 1.41 (3 H, t, *J* 7); δ_{C} 183.8, 159.1, 134.1 (2 C), 130.0, 129.4 (2 C), 125.7, 63.6 and 13.8; m/z 210 (M^+ , 27%), 137 (11), 123 (24), 110 (72), 109 (100) and 84 (22).

***O*-Ethyl *S*-(4-methylphenyl) monothiooxalate 24g.** Reaction as above using 4-methylbenzenethiol gave a colourless liquid (70%), bp (oven temp.) 150–155 °C at 4 Torr (HRMS: found M^+ , 224.0507. $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$ requires *M*, 224.0507); $\nu_{\text{max}}/\text{cm}^{-1}$ 2984, 1765, 1737, 1701, 1495, 1266, 1235, 1025, 1015, 1180, 859, 809 and 765; δ_{H} 7.42 and 7.30 (4 H, AB pattern, *J* 9), 4.41 (2 H, q, *J* 7), 2.38 (3 H, s) and 1.36 (3 H, t, *J* 7); δ_{C} 183.8, 158.9, 140.1, 133.8 (2 C), 130.0 (2 C), 122.1, 63.3, 21.0 and 13.6; m/z 224 (M^+ , 45%), 152 (10), 137 (32), 124 (65), 123 (100), 91 (95), 79 (37) and 77 (45).

***S*-Phenyl thioacetate 25d.** A solution of benzenethiol (4.07 g, 37 mmol) and triethylamine (3.76 g, 37 mmol) in dichloromethane (30 cm³) was stirred at 0 °C while acetyl chloride (3.04 g, 38 mmol) was added dropwise. After 1 h the solution was washed with water, dried and evaporated and the residue distilled to give a colourless liquid (5.1 g, 90%), bp (oven temp.) 125 °C at 2 Torr (lit.,³⁴ 228–230 °C); δ_{H} 7.51 (5 H, s) and 2.41 (3 H, s); δ_{C} 193.7, 134.3 (2 C), 129.2, 129.0 (2 C), 127.8 and 30.0.

***S*-Phenyl propanethioate 25e.** Reaction of equimolar quantities of benzenethiol, propionyl chloride and triethylamine in dichloromethane at 0 °C for 3 h followed by washing with water, drying, evaporation and distillation gave a colourless liquid (80%), bp (oven temp.) 125 °C at 2.5 Torr (lit.,³⁵ 170–180 °C at 10 Torr); δ_{H} 7.45–7.35 (5 H, m), 2.67 (2 H, q, *J* 7) and 1.21 (3 H, t, *J* 7); δ_{C} 198.1, 134.4 (2 C), 129.2, 129.1 (2 C), 127.8, 37.0 and 9.5.

***S*-(4-Chlorophenyl) propanethioate 25i.** Reaction of equimolar quantities of 4-chlorobenzenethiol, propionyl chloride and triethylamine in toluene at room temperature for 3 h followed by filtration, evaporation and distillation gave a colourless liquid (81%), bp (oven temp.) 85–90 °C at 2.5 Torr (HRMS: found M^+ , 200.0055. $\text{C}_9\text{H}_9^{35}\text{ClOS}$ requires *M*, 200.0063); δ_{H} 7.47 (4 H, s), 2.71 (2 H, q, *J* 7) and 1.23 (3 H, t, *J* 7); δ_{C} 197.5, 135.7 (2 C), 135.6, 129.4 (2 C), 126.3, 37.1 and 9.6; m/z 202/200 (M^+ , 8/24%), 172 (15), 157 (6), 144 (42), 108 (20) and 57 (100).

***S*-Ethyl benzenecarbothioate 29e.** This was prepared by the literature method³⁶ as a colourless liquid (72%), bp (oven temp.) 100 °C at 0.15 Torr (lit.,³⁶ 117 °C at 0.12 Torr); δ_{H} 8.0–7.85 (2 H, m), 7.55–7.3 (3 H, m), 3.05 (2 H, q, *J* 7) and 1.31 (3 H, t, *J* 7); δ_{C} 191.7, 137.0 (4ry), 133.0, 128.4 (2 C), 126.9 (2 C), 23.2 and 14.6.

***S*-Ethyl 4-chlorobenzenecarbothioate 29i.** Reaction of equimolar quantities of 4-chlorobenzoyl chloride, ethanethiol and triethylamine in toluene at room temperature for 3 h followed by filtration, evaporation and distillation gave a colourless liquid (82%), bp (oven temp.) 120–130 °C at 3 Torr (HRMS:

found M^+ , 200.0078. $C_9H_9^{35}ClOS$ requires M , 200.0063; δ_H 7.47 (4 H, s), 2.71 (2 H, q, J 7) and 1.23 (3 H, t, J 7); δ_C 190.8, 139.6, 135.5, 128.8 (2 C), 128.5 (2 C), 23.6 and 14.7; m/z 202/200 (M^+ , 2/6%), 139 (100), 111 (37) and 75 (28).

FVP of **24e** (500 mg) at 750 °C gave products both at the furnace exit and in the cold trap which were combined. By 1H NMR, GC-MS and comparison with authentic samples the products were: the unreacted starting material (~15%), diphenyl disulfide **12e** (~10%); m/z 218 (M^+ , 38%), 185 (9), 154 (12), 141 (5), 109 (100) and 65 (52), *O*-ethyl *S*-phenyl thiocarbonate **27e** (~20%); δ_H 7.5–7.1 (5 H, m), 4.29 (2 H, q, J 7) and 1.32 (3 H, t, J 7); m/z 182 (M^+ , 16%), 138 (12), 123 (30), 110 (100), 109 (78) and 65 (45), ethyl phenyl sulfide **11e** (~15%); δ_H 7.5–7.1 (5 H, m), 2.93 (2 H, q, J 7) and 1.32 (3 H, t, J 7); m/z 138 (M^+ , 100%), 123 (80), 110 (69), 109 (48) and 66 (32) and benzenethiol (~40%); δ_H 7.5–7.1 (5 H, m) and 3.43 (1 H, br s); m/z 110 (M^+ , 100%), 109 (40), 84 (27), 77 (20) and 66 (41).

FVP of **24g** (440 mg) at 600 °C gave liquid products both at the furnace exit and in the cold trap. By GC-MS and comparison with authentic samples the furnace exit products were: the unreacted starting material (~50%), bis(4-methylphenyl) disulfide **12g** (~10%); m/z 246 (M^+ , 12%), 182 (1), 124 (15), 123 (100), 121 (8), 91 (18), 79 (38) and 77 (37), and *O*-ethyl *S*-(4-methylphenyl) thiocarbonate **27g**. The products in the cold trap were shown by 1H NMR, GC-MS and comparison with authentic samples to be: *O*-ethyl *S*-(4-methylphenyl) thiocarbonate **27g** (combined yield ~15%); δ_H 7.35–7.05 (4 H, m), 4.33 (2 H, q, J 7), 2.32 (3 H, s) and 1.30 (3 H, t, J 7); m/z 196 (M^+ , 12%), 152 (15), 137 (20), 124 (55), 123 (50) and 91 (100), ethyl 4-methylphenyl sulfide **11g** (~10%); δ_H 7.35–7.05 (4 H, m), 2.92 (2 H, q, J 7), 2.32 (3 H, s) and 1.28 (3 H, t, J 7); m/z 152 (M^+ , 78%), 137 (52), 124 (23), 123 (28) and 91 (100), and 4-methylbenzenethiol (~15%); δ_H 7.35–7.05 (4 H, m), 3.33 (1 H, br s) and 2.32 (3 H, s); m/z 124 (M^+ , 52%), 123 (30), 108 (3) and 91 (100).

FVP of **25d** at 600 °C gave the unreacted starting material. FVP of **25d** (470 mg) at 750 °C gave a solid at the furnace exit and a liquid in the cold trap. By 1H NMR, GC-MS and comparison with authentic samples the solid was found to consist mainly of diphenyl sulfide; m/z 186 (M^+ , 100%), 185 (88), 184 (52), 152 (10), 109 (7) and 77 (12) and diphenyl disulfide **12d**; m/z 218 (M^+ , 58%), 185 (16), 154 (15) and 109 (100), while the liquid was mainly benzenethiol; δ_H 7.3–7.1 (5 H, m) and 3.44 (1 H, s); m/z 110 (M^+ , 100%), 109 (48), 84 (29), 77 (20) and 66 (45), and methyl phenyl sulfide **11d**; δ_H 7.3–7.1 (5 H, m) and 2.47 (3 H, s); m/z 124 (M^+ , 100%), 109 (46), 91 (40) and 78 (42).

FVP of **25i** (330 mg) at 600 °C gave an oil at the furnace exit which was shown by 1H NMR and GC-MS to be mainly the unreacted starting material with ~10% conversion to 4-chlorophenyl ethyl sulfide **11i**; δ_H 7.37 (4 H, s), 1.32 (2 H, q, J 7) and 1.32 (3 H, t, J 7); m/z 174/172 (M^+ , 34/100%), 157 (52, M^+ – Me), 143 (38, M^+ – Et) and 108 (36).

Preparation of sulfonyl esters³⁷

Methyl ethylsulfonylacetate 32a. Methyl ethylsulfonylacetate (4.0 g, 30 mmol), benzoic acid (3.6 g, 30 mmol) and benzyltriethylammonium chloride (1.1 g, 5 mmol) were dissolved in CH_2Cl_2 (50 cm^3) and a solution of potassium permanganate (9.2 g, 58 mmol) in water (100 cm^3) was added. The mixture was stirred vigorously for 12 h and then decolourised by addition of aqueous sodium metabisulfite. The mixture was filtered through Celite and the organic layer separated. This was then washed with 1 M aqueous hydrazine dihydrochloride (50 cm^3) and 2 M sodium hydroxide (2 \times 50 cm^3). Drying, evaporation and kugelrohr distillation of the residue gave methyl ethylsulfonylacetate **32a** (3.9 g, 79%) as a colourless liquid, mp 40 °C (lit.,³⁸ 42–44 °C); δ_H 4.02 (2 H, s), 3.83 (3 H, s), 3.28 (2 H, q, J 7) and 1.43 (3 H, t, J 7); δ_C 163.6 (CO), 56.4 (CH_2CO), 53.3 (OCH_3), 48.1 (CH_2CH_3) and 6.5 (CH_2CH_3).

Ethyl ethylsulfonylacetate 32b. This was prepared as above using ethyl ethylsulfonylacetate to give a colourless liquid (66%), bp 161 °C at 7 Torr (lit.,³⁹ 110 °C at 0.3 Torr); δ_H 4.25 (2 H, q, J 7), 4.02 (2 H, s), 3.30 (2 H, q, J 7), 1.40 (3 H, t, J 7) and 1.31 (3 H, t, J 7); δ_C 162.7 (CO), 62.1 (OCH_2), 56.2 (CH_2CO), 48.6 (SCH_2CH_3), 13.5 (OCH_2CH_3) and 6.1 (SCH_2CH_3).

Methyl phenylsulfonylacetate 32c. This was prepared as above using methyl phenylsulfonylacetate to give a colourless liquid (60%), bp 160 °C at 0.3 Torr (lit.,⁴⁰ 145 °C at 0.01 Torr); δ_H 8.0–7.9 (2 H, m), 7.8–7.5 (3 H, m), 4.15 (2 H, s) and 3.67 (3 H, s); δ_C 162.9 (CO), 138.7 (4ry), 134.4, 129.3 (2 C), 128.4 (2 C), 60.7 (CH_2) and 52.9 (CH_3).

Ethyl phenylsulfonylacetate 32d. This was prepared as above using ethyl phenylsulfonylacetate to give a colourless liquid (52%), bp 155 °C at 0.3 Torr (lit.,⁴¹ 134–135 °C at 0.01 Torr); δ_H 8.0–7.9 (2 H, m), 7.8–7.5 (3 H, m), 4.18 (2 H, s), 4.13 (2 H, q, J 8) and 1.18 (3 H, t, J 8); δ_C 162.2 (CO), 138.3 (4ry), 133.8, 128.8 (2 C), 128.0 (2 C), 61.7 (OCH_2), 60.4 (SCH_2) and 13.3 (CH_3).

Preparation of sulfonyl diazo esters

This was carried out by diazo exchange using 4-acetylaminobenzenesulfonyl azide.²²

Methyl ethylsulfonyl(diazo)acetate 33a. A solution of methyl ethylsulfonylacetate (4.7 g, 28 mmol) and 4-acetylaminobenzenesulfonyl azide (6.7 g, 28 mmol) in dry acetonitrile was stirred at 0 °C while triethylamine (8.6 g, 85 mmol) was added gradually. After the addition the mixture was stirred at room temperature for 12 h and then evaporated. Trituration of the residue with ether–light petroleum led to separation of 4-acetylaminobenzenesulfonamide and the filtrate was evaporated and subjected to column chromatography on silica using ether to give *the title compound* (0.9 g, 17%) as yellow crystals, mp 41–45 °C (HRMS: found M^+ , 192.0196. $C_8H_8N_2O_4S$ requires M , 192.0203); ν_{max}/cm^{-1} 2420, 2110, 1700, 1595, 1430, 1270, 1205, 1140, 1080, 905, 795, 740, 710 and 605; δ_H 3.86 (3 H, s), 3.42 (2 H, q, J 7) and 1.42 (3 H, t, J 7); δ_C 159.9 (CO), 71.6 ($C=N_2$), 52.5 (OMe), 50.5 (CH_2) and 6.7 (CH_3); m/z 192 (M^+ , 28%), 161 (11), 153 (5), 135 (5), 100 (70) and 59 (100).

Ethyl ethylsulfonyl(diazo)acetate 33b. The method above starting from ethyl ethylsulfonylacetate gave *the title compound* (50%) as yellow crystals, mp 37 °C (HRMS: found M^+ , 206.0363. $C_8H_8N_2O_4S$ requires M , 206.0361); ν_{max}/cm^{-1} 2460, 2100, 1700, 1440, 1365, 1330, 1280, 1210, 1140, 1070, 1000, 850, 775, 740, 710 and 600; δ_H 4.37 (2 H, q, J 7), 3.43 (2 H, q, J 7), 1.44 (3 H, t, J 7) and 1.36 (3 H, t, J 7); δ_C 159.5 (CO), 71.6 ($C=N_2$), 62.0 (CH_2), 50.5 (CH_2), 13.7 (CH_3) and 6.8 (CH_3); m/z 206 (M^+ , 73%), 180 (7), 161 (24), 153 (16), 135 (13), 114 (100), 94 (39), 78 (24) and 66 (80).

Methyl phenylsulfonyl(diazo)acetate 33c. The method above starting from methyl phenylsulfonylacetate gave *the title compound* (54%) as yellow crystals, mp 48–51 °C (HRMS: found M^+ , 240.0201. $C_9H_8N_2O_4S$ requires M , 240.0203); ν_{max}/cm^{-1} 2820, 2420, 2100, 1700, 1575, 1500, 1430, 1380, 1150, 1085, 720, 675 and 600; δ_H 8.0–8.1 (2 H, m), 7.7–7.5 (3 H, m) and 3.75 (3 H, s); δ_C 159.9 (CO), 141.6 (4ry), 134.2, 129.2 (2 C), 127.8 (2 C), 75.8 ($C=N_2$) and 52.9 (CH_3); m/z 240 (M^+ , 33%), 180 (7), 141 (28), 125 (72), 105 (74), 97 (35) and 77 (100).

Ethyl phenylsulfonyl(diazo)acetate 33d. The method above starting from ethyl phenylsulfonylacetate gave *the title compound* (47%) as yellow crystals, mp 41–45 °C (HRMS: found M^+ , 254.0352. $C_{10}H_{10}N_2O_4S$ requires M^+ , 254.0359); ν_{max}/cm^{-1} 2480, 2100, 1700, 1440, 1270, 1200, 1150, 1090, 1060, 1000, 730, 710, 670 and 590; δ_H 8.0–8.1 (2 H, m), 7.7–7.5 (3 H, m), 4.20

(2 H, q, *J* 7) and 1.24 (3 H, t, *J* 7); δ_{C} 158.9 (CO), 141.0 (4ry), 133.6, 128.6 (2 C), 127.2 (2 C), 75.3 (C=N₂), 61.8 (CH₂) and 13.5 (CH₃); *m/z* 254 (M⁺, 12%), 209 (7), 180 (3), 141 (24), 134 (26), 105 (29), 89 (9) and 77 (100).

Preparation of diazo compounds from amino acid ester hydrochlorides²³

Methyl 2-diazo-3-phenylpropionate 35a. A solution of (\pm)-phenylalanine methyl ester hydrochloride (5.0 g, 23 mmol) and sodium nitrite (1.60 g, 23 mmol) in water (20 cm³) containing sodium acetate (10 mg, 0.13 mmol) was prepared in a separating funnel. To this solution 2 M sulfuric acid (0.05 cm³) and ether (5 cm³) were added and the mixture shaken well and the organic layer separated. This addition of acid and ether and separation was repeated until reaction was complete as indicated by the appearance of brown fumes and the ether extract no longer being yellow. The combined ether extracts were then washed with aqueous sodium carbonate, dried and evaporated without heating. The residue was purified by column chromatography on silica using ether–light petroleum (bp 40–60 °C) (1 : 1) to give the product as a yellow oil (1.35 g, 36%); $\nu_{\text{max}}/\text{cm}^{-1}$ 2085 (C=N₂) and 1690 (CO); δ_{H} 7.4–7.2 (5 H, m), 3.85 and 3.72 (2 H, AB pattern, *J* 5) and 3.78 (3 H, s); *m/z* 190 (M⁺, 4%), 162 (M⁺ – N₂, 38), 139 (12), 131 (70), 103 (100), 91 (35) and 77 (56).

Ethyl 2-diazo-3-phenylpropionate 35b. This compound was prepared as above from (\pm)-phenylalanine ethyl ester hydrochloride as a yellow oil (37%) whose IR and ¹H NMR spectra were in excellent agreement with the literature data;⁴² $\nu_{\text{max}}/\text{cm}^{-1}$ 2070 (C=N₂) and 1675 (CO); δ_{H} 7.4–7.2 (5 H, m), 4.25 (2 H, q, *J* 7), 3.64 (2 H, s) and 1.28 (3 H, t, *J* 7); *m/z* 204 (M⁺, 2%), 176 (M⁺ – N₂, 35), 148 (14), 131 (100), 118 (10), 103 (60), 91 (30) and 77 (40).

Methyl 2-diazo-3-methylbutyrate 35c. This compound was prepared as above from (\pm)-valine methyl ester hydrochloride as a yellow oil (30%); $\nu_{\text{max}}/\text{cm}^{-1}$ 2075 (C=N₂) and 1690 (CO); δ_{H} 3.70 (3 H, s), 3.15 (1 H, septet, *J* 7), 1.27 (3 H, d, *J* 7) and 1.15 (3 H, d, *J* 7); *m/z* 142 (M⁺, 0.5%), 114 (M⁺ – N₂, 35), 83 (78), 73 (34), 59 (60), 55 (100) and 44 (96).

Methyl 2-diazo-3-mercaptopropionate 35d. This compound was prepared as above from (*S*)-cysteine methyl ester hydrochloride as a yellow oil (25%); $\nu_{\text{max}}/\text{cm}^{-1}$ 2070 (C=N₂) and 1685 (CO); δ_{H} 3.9–3.7 (3 H, m, CH₂ and SH) and 3.74 (3 H, s); *m/z* 118 (M⁺ – N₂, 60%), 86 (95), 73 (8), 59 (100), 55 (25) and 45 (20).

Flash vacuum pyrolysis of diazo compounds

FVP of **33a** (200 mg) at 600 °C gave a colourless oil in the cold trap whose main constituent was shown to be ethyl vinyl sulfone **34a** (30%); δ_{H} 6.63 (1 H, dd, *J* 10, 16), 6.45 (1 H, d, *J* 16), 6.19 (1 H, d, *J* 10), 3.00 (2 H, q, *J* 7) and 1.35 (3 H, t, *J* 7); δ_{C} 135.5, 130.8, 48.6 and 7.0; *m/z* 120 (M⁺, 2%), 78 (53), 63 (100) and 45 (65).

FVP of **33b** (205 mg) at 600 °C gave an oil in the cold trap which was mainly a 2 : 1 mixture of (*E*)- and (*Z*)-ethyl propenyl sulfone **34b** (10%); *m/z* 134 (M⁺, 13%), 105 (8), 89 (17) and 39 (100). (*E*)-isomer; δ_{H} 6.92 (1 H, half AB pattern of q, *J* 16, 8), 6.30 (1 H, half AB pattern of q, *J* 16, 2), 3.02 (2 H, q, *J* 8), 2.00 (3 H, dd, *J* 8, 2) and 1.30 (3 H, t, *J* 8); δ_{C} 144.5, 128.5, 48.9, 17.5 and 7.1. (*Z*)-isomer; δ_{H} 6.57 (1 H, half AB pattern of q, *J* 13, 8), 6.22 (1 H, half AB pattern of q, *J* 13, 2), 3.03 (2 H, q, *J* 8), 2.19 (3 H, dd, *J* 8, 2) and 1.30 (3 H, t, *J* 8); δ_{C} 144.6, 128.1, 49.8, 14.3 and 6.9.

FVP of **33c** (500 mg) at 400 °C gave an oil at the furnace exit which contained some phenyl vinyl sulfone **34c** (<5%); δ_{H} 7.7–7.3 (5 H, m), 6.68 (1 H, dd, *J* 18, 10), 6.48 (1 H, d, *J* 18) and 6.04

(1 H, d, *J* 10); *m/z* 168 (M⁺, 5%), 125 (55), 77 (100), 51 (85) and 27 (55).

FVP of **35a** (50 mg) at 400 °C gave methyl cinnamate **36a** (51%) as a mixture of (*E*)- and (*Z*)-isomers (ratio 1.2 : 1) identified by spectroscopic comparison with an authentic sample; δ_{H} (*E*) 7.70 and 6.46 (2 H, AB pattern, *J* 16), 7.6–7.5 (2 H, m), 7.4–7.3 (3 H, m) and 3.73 (3 H, s); δ_{H} (*Z*) 7.6–7.5 (2 H, m), 7.4–7.3 (3 H, m), 6.97 and 5.97 (2 H, AB pattern, *J* 11) and 3.82 (3 H, s).

FVP of **35b** (50 mg) at 400 °C gave ethyl cinnamate **36b** (72%) as a mixture of (*E*)- and (*Z*)-isomers (ratio 1 : 1) identified by spectroscopic comparison with an authentic sample; δ_{H} 7.68 and 6.45 (2 H, AB pattern, *J* 17, *E*), 7.6–7.5 (2 H, m, *E* and *Z*), 7.45–7.25 (3 H, m, *E* and *Z*), 6.95 and 5.95 (2 H, AB pattern, *J* 12, *Z*), 4.28 (2 H, q, *J* 7), 4.18 (2 H, q, *J* 7), 1.35 (3 H, t, *J* 7) and 1.24 (3 H, t, *J* 7).

FVP of **35c** (50 mg) at 400 °C gave methyl 3-methylbut-2-enoate **37** (47%); δ_{H} 5.67 (1 H, s), 3.70 (3 H, s), 2.15 (3 H, s) and 1.88 (3 H, s) (good agreement with literature values⁴³).

FVP of **35d** (52 mg) at 400 °C gave methyl thiirane-carboxylate **38** (50%); δ_{H} 3.70 (3 H, s), 3.32 (1 H, dd, *J* 8, 6), 2.80 (1 H, dd, *J* 6, 1) and 2.60 (1 H, dd, *J* 8, 1) (good agreement with literature values²⁷); δ_{C} 171.2, 52.8, 28.4 and 23.2.

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