

Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 3.¹ Preparation of *o*-Methoxyphenyl- and *o*-Methylsulfanylphenyl-alkynes and their Cyclisation to Benzofurans and Benzothiophenes

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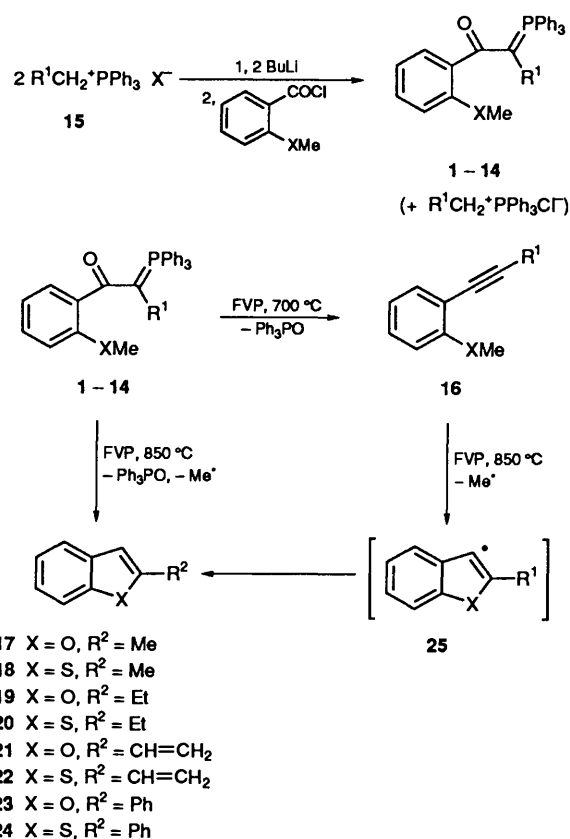
Fourteen new β -oxo phosphorus ylides **1–14** bearing *o*-methoxybenzoyl or *o*-(methylsulfanyl)benzoyl groups have been prepared and their pyrolytic behaviour studied. While flash vacuum pyrolysis (FVP) at 700 °C brings about extrusion of Ph_3PO to give the expected alkynes **16**, this is accompanied at 850 °C by loss of Me^\cdot and cyclisation of the resulting radicals to afford 2-substituted benzofurans or benzothiophenes **17–24**. Where the substituent R^1 on the ylidic carbon of the starting material is phenyl, this is incorporated unchanged into the heterocyclic products. Where R^1 is Et or Pr the vinyl products are formed by intramolecular abstraction of a β -hydrogen atom following cyclisation. For $\text{R}^1 = \text{Me}$, Pr, Bu and C_5H_{11} the cyclisation is followed by hydrogen atom abstraction from the alkyl group leading to its fragmentation and giving products with 2-methyl, ethyl and vinyl substituents. In these cases the products can be accounted for by a radical chain reaction involving the unusual homolytic substitution of a carbon radical at a saturated carbon atom.

We recently described the successful use of flash vacuum pyrolysis (FVP) to bring about the thermal extrusion of Ph_3PO from a range of β -oxo phosphorus ylides bearing H or alkyl groups on the ylidic position, a transformation not possible using conventional pyrolysis.² This allows the ylide pyrolysis route to be used to generate a wide range of terminal and aliphatic alkynes. In view of the rich thermal chemistry of functionalised alkynes, we sought to design systems in which the alkyne generation could be followed by further secondary thermal processes allowing direct construction of more complex target compounds in a single pyrolysis step. In this paper we report the first example of this approach, in which the generation of alkynes bearing a 2-methoxyphenyl or 2-methylsulfanylphenyl group is accompanied by loss of methyl radical and cyclisation to give substituted benzofurans and benzothiophenes.³ There has been considerable recent interest in synthesis of benzofurans by cyclisation of 2-oxy functionalised phenylalkynes including, for example, reaction of the 2-methoxy compounds with LiI in collidine⁴ and Pd/Cu catalysed reaction of the 2-hydroxy compounds.⁵

Results and Discussion

The required stabilised ylides **1–14** were readily prepared by acylation of the appropriate alkylidene triphenylphosphoranes (2 equiv.), generated by butyllithium treatment of the phosphonium salts **15**, with either 2-methoxy- or 2-methylsulfanylbenzoyl chloride. The reaction involves transylidation to regenerate one molecule of phosphonium salt as shown.⁶ The ylides were obtained as stable high-melting solids with the expected spectroscopic properties including characteristic ³¹P NMR shifts in the ylide region, $\delta_{\text{p}} + 13$ –18.

When these compounds were subjected to FVP at 700 °C and 10^{-2} mmHg in a conventional flow system (contact time ≈ 10 ms), extrusion of Ph_3PO took place to give the alkynes **16** as expected from our previous work.² In some cases, such as **1**, additional fragmentation to give the benzofuran was already observed to occur to some extent at 700 °C. When the ylides **1–14** were subjected to FVP at the higher temperature of 850 °C, loss of Ph_3PO was accompanied by cyclisation to give the desired benzofurans and benzothiophenes **17–24** (Table 1).



Isolation of the alkyne **16** from low-temperature pyrolysis and re-pyrolysis of this at 850 °C was confirmed to give the same products as the direct ylide pyrolysis at 850 °C in several of the cases listed.

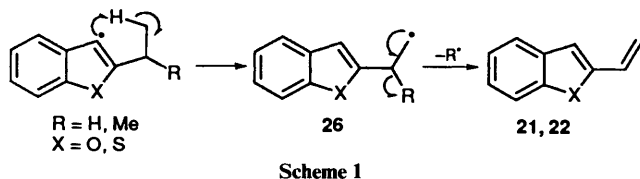
Only for **13** and **14**, however, did the cyclisation proceed without change to the R^1 group, giving 2-phenylbenzofuran **23** and 2-phenylbenzothiophene **24**, respectively. In all the other cases with aliphatic R^1 , the products were one or more of **17–22** with $\text{R}^2 = \text{Me}$, Et or vinyl. It seems most likely that the

Table 1 FVP of the ylides 1–14 at 850 °C to give 17–24

R ¹	X	Yield of products (%)				
		17/18	19/20	21/22	23/24	
1	Me	O	8	20	—	—
2	Me	S	14	17	—	—
3	Et	O	—	—	83	—
4	Et	S	—	—	49	—
5	Pr ⁱ	O	—	—	60	—
6	Pr ⁱ	S	—	—	24	—
7	Pr	O	9	52	10	—
8	Pr	S	6	45	9	—
9	Bu	O	4	30	25	—
10	Bu	S	10	31	23	—
11	C ₅ H ₁₁	O	3	14	21	—
12	C ₅ H ₁₁	S	10	28	14	—
13	Ph	O	—	—	—	80
14	Ph	S	—	—	—	53

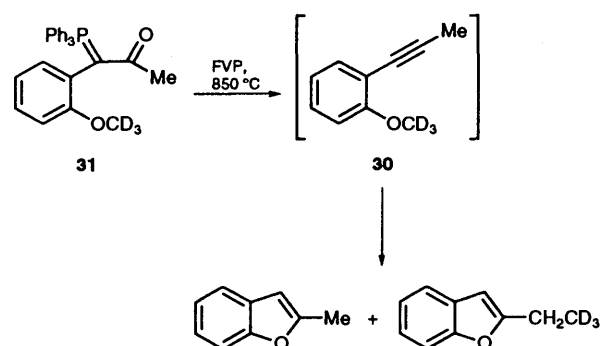
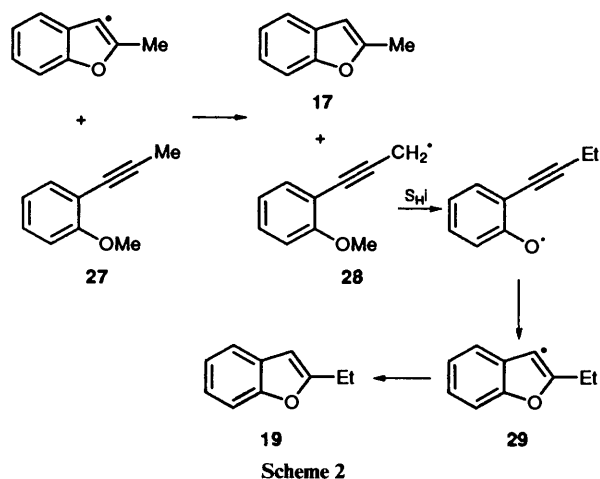
products arise from thermal loss of methyl radical from the alkynes **16** since this is a well precedented process, conversion of anisole into phenol at 640 °C in a flow system having been reported as early as 1949.⁷ An alternative mechanism, involving isomerisation of the alkyne to a vinylidene which then inserts into the OMe or SMe bond, has some precedent in the thermal conversion of *o*-ethynylphenol into benzofuran⁸ and of *o*-ethynylanisole into 2-methylbenzofuran⁹ but is clearly not involved here, since it would lead to 2,3-disubstituted products which were not detected in any of the experiments.

Cyclisation of the radical resulting from loss of Me[•] from **16** initially gives **25** in each case. For R¹ = Ph, this cannot readily undergo any intramolecular reaction and simply abstracts a hydrogen atom from another molecule (possibly on condensation in the cold trap) to give **23** and **24** in good yield. The results for **3–6** are also readily explained since, in these cases, the intermediates **25** can undergo intramolecular H atom abstraction from the β-position of the alkyl group *via* a five-membered ring transition state, accompanied by loss of either H[•] or Me[•] to give the observed vinyl products (Scheme 1).

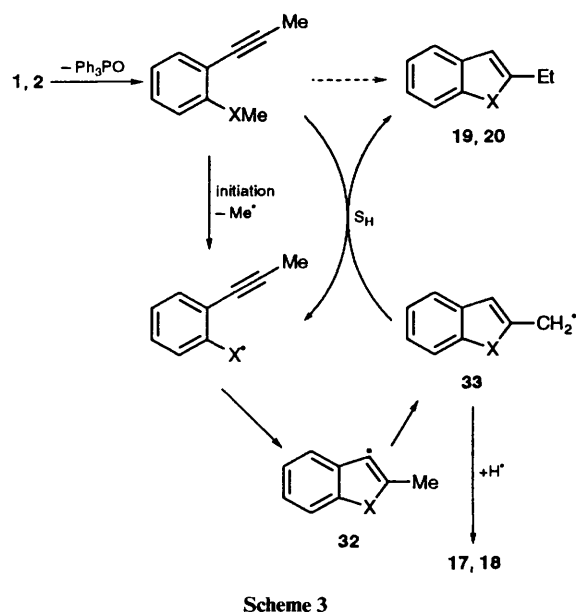


The products observed in the remaining reactions are rather harder to explain. The pyrolysis of **27** under comparable conditions to give **17** (29%) and **19** (15%) was reported by Barton and Groh in 1985.⁹ These authors explained the formation of **19** by the sequence shown in Scheme 2 where the 2-methylbenzofuran-3-yl radical, formed by loss of Me[•] and cyclisation, abstracts a hydrogen atom from a molecule of the starting material to give **17** and the prop-2-ynyl radical **28**. This was then postulated to undergo intramolecular homolytic substitution resulting in methyl transfer followed by cyclisation to **29** which abstracted H[•] to give **19**. On the basis of the new results presented here, we believe this mechanism to be unlikely since **29** is almost certainly produced as an intermediate in the pyrolysis of **3** and goes on, as shown in Scheme 1, to give a high yield of 2-vinylbenzofuran **21**, a product not formed from either **1** or **27**.

In order to confirm that the second carbon of the ethyl group in **19** and **20** does indeed come from the X-methyl group of **16**, we examined the behaviour of the trideuteriomethoxyalkyne **30**, readily generated by FVP of the ylide **31** analogous to the



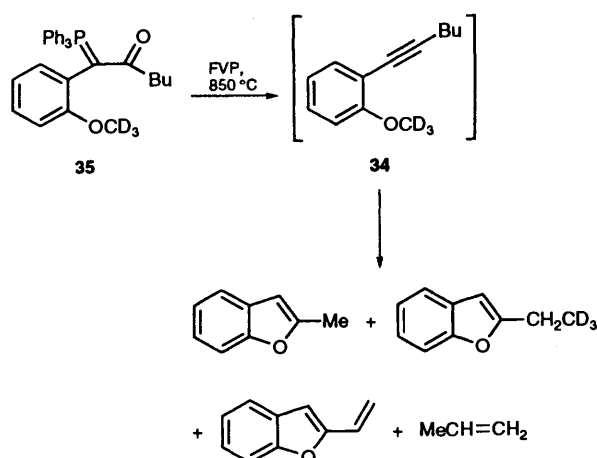
isomeric structure to **1**. At 850 °C the products were 2-methylbenzofuran and 2-(2,2,2-trideuterioethyl)benzofuran as shown. Bearing this in mind together with the need to avoid **29** as an intermediate, an alternative explanation for the formation of **19** and **20** in the pyrolysis of **1**, **27** and **2** is shown in Scheme 3.



The sequence begins with loss of Me[•] and cyclisation to give **32** as proposed in Barton's mechanism, but this now undergoes intramolecular abstraction to give the more stable benzylic radical **33**. Homolytic substitution by this on the alkyne then gives the ethyl products and generates a new aryloxy or arylsulfanyl radical ready for cyclisation to **32**. An attraction of this route is that it provides for a chain reaction and so the

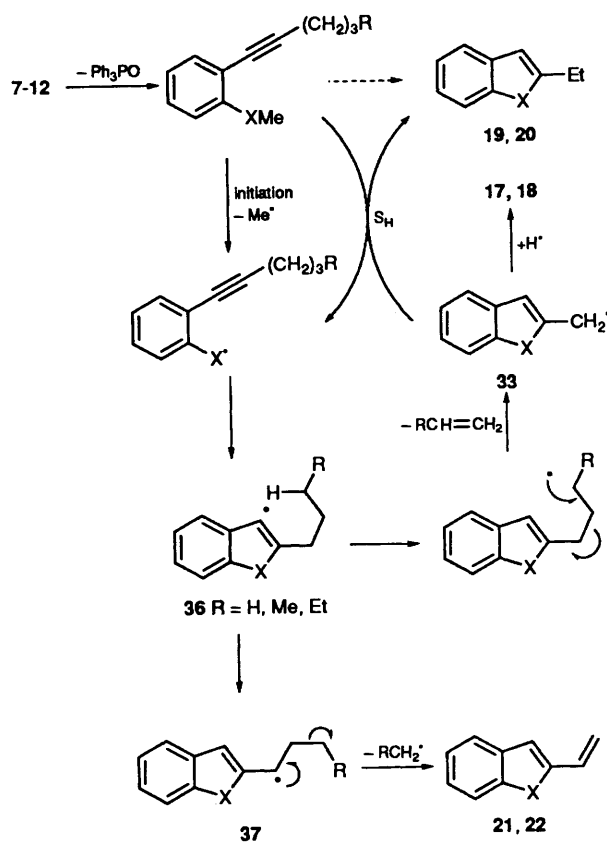
initial loss of Me[•] is only required as an initiation step. The occurrence of intermolecular reactions is, of course, uncommon under FVP conditions but it appears to be necessary here, since there is no obvious intramolecular mechanism for the formation of **19** and **20**. The homolytic substitution of a carbon radical on ArXMe to generate ArX[•] as required both by Barton's mechanism and our own also appears to be without precedent. Indeed, homolytic substitution of a carbon radical on a carbon centre of any type seems to be little known,¹⁰ although the processes proposed here do have the apparent driving force of producing a more stable aryloxy or arylsulfanyl radical from a less stabilised carbon radical.

The pyrolysis of **7–12** with longer alkyl substituents is quite remarkable in producing only the heterocyclic products **17–22** with Me, Et and vinyl as the 2-substituent. No trace of benzofurans or benzothiophenes with 2-propyl, -butyl, -pentyl or -allyl substituents was detected by ¹H NMR or GCMS. Additional evidence as to the mechanism of these processes was again obtained from the fragmentation of the deuteriated alkyne **34** formed by FVP of **35** at 850 °C. The 2-ethyl-



benzofuran was again fully deuteriated at the 2-position suggesting involvement of **33** in its formation; the vinyl product was not deuteriated, and propene was isolated in reasonable yield by careful analysis of the most volatile products while still cold. But-1-ene was similarly identified spectroscopically in the pyrolysis of **11**. These observations are fully consistent with the sequence shown in Scheme 4 which is simply an extension of the ideas involved in Scheme 3. Initiation by loss of Me[•] followed by cyclisation gives **36** which can undergo intramolecular abstraction of H[•] from the 3-position of the alkyl group since this involves a favourable six-membered ring transition state. Subsequent β-scission of the resulting radical gives **33** with elimination of the alkene. Interaction of this with the starting material as before gives the ethyl products and forms a new radical ready for cyclisation to **36**, again making a chain reaction possible. The formation of 2-methyl products **17** and **18** here may involve either abstraction of H[•] by **33** or secondary thermal degradation of ethyl compounds **19** and **20**, a process demonstrated by Barton to occur for **19** to an extent of 25% at 800 °C.⁹ The formation of the vinyl products **21** and **22** can be explained by an alternative reaction of **36**, abstraction of H[•] from the 1-position of the alkyl group. Although this is clearly less favourable than abstraction from the 3-position, it does produce a benzylic radical **37** which can undergo immediate β-scission as shown, with loss of Me[•], Et[•] or Pr[•], to afford the vinyl products.

We have demonstrated that pyrolysis of appropriate, readily



Scheme 4

accessible stabilised ylides allows direct formation of 2-substituted benzofurans and benzothiophenes and these can be formed as a single product in moderate to good yield with 2-phenyl and vinyl substituents. These reactions should be readily applicable to construction of more highly substituted examples. The other cases examined are not of great synthetic value but clearly involve novel sequences of radical reactions subsequent to cyclisation and, on the basis of the evidence available, it appears that these may represent further examples of the rarely encountered S_H2 reaction at a methyl carbon atom. In the context of a separate study to be reported shortly,¹¹ we have recently observed that FVP of methyl 2-naphthylacetate at 900 °C gives a 20% yield of 2-ethylnaphthalene, together with the 2-methyl and 2-vinyl products, and its formation might also involve a chain reaction with homolytic substitution of 2-naphthylmethyl on the starting material and loss of CO₂.

Experimental

M.p.s were recorded on a Kofler hot-stage microscope and are uncorrected. IR spectra were recorded for solutions in chloroform in matched sodium chloride cells of path-length 0.1 mm, on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ¹H at 80 MHz using a Bruker WP80 instrument, for ¹³C at 75 MHz and for ²H at 46 MHz on a Bruker AM300 instrument, and for ³¹P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl₃ with internal Me₄Si as reference for ¹H and ¹³C and external 85% H₃PO₄ as reference for ³¹P, except for ²H spectra which were run in CHCl₃ with internal CDCl₃ (δ_D 7.3) as reference. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz. Mass spectra were obtained on an A.E.I. MS-902 spectrometer using electron impact at 70 eV. Gas chromatography was performed using a

Pye Unicam 4500 instrument with flame ionisation detector and a 2 m × 4.5 mm column of 2% NPGS on Chromosorb W with N₂ as carrier gas. Dry THF was freshly distilled from potassium benzophenone ketyl under N₂.

Preparation of β-Oxoalkylidene(triphenyl)phosphoranes 1–14.—A suspension of the appropriate alkyl(triphenyl)phosphonium bromide **15** (25 mmol) in dry THF was stirred at room temperature (RT) under N₂ while a solution of BuLi in hexane (26 mmol) was added slowly to it by syringe. This was followed after 30 min by addition of the appropriate acid chloride (12.5 mmol) in dry THF (10 cm³). After 3 h the mixture was added to water (250 cm³) and extracted with ether (4 × 50 cm³). Drying and evaporation of the extract gave the ylide which crystallised with time. In cases of difficulty crystallisation could be induced by trituration with a small quantity of ethyl acetate. The following compounds were prepared by this method.

1-(2-Methoxybenzoyl)ethylidene(triphenyl)phosphorane 1. Prepared from ethyl(triphenyl)phosphonium bromide and 2-methoxybenzoyl chloride as colourless crystals (73%), m.p. 203–207 °C (Found: C, 79.6; H, 6.0. C₂₈H₂₅O₂P requires C, 79.2; H, 5.9%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2960, 1596, 1580, 1500, 1480, 1435, 1386, 1375, 1240, 1182, 1147, 1104, 1057, 1028, 992, 828 and 692; δ_{H} 7.9–7.2 (17 H, m), 7.0–6.75 (2 H, m), 3.86 (3 H, s) and 1.48 (3 H, d, *J* 15); δ_{P} +17.1; *m/z* 424 (M⁺, 5%), 423 (5), 393 (4), 317 (6), 289 (7), 277 (5), 262 (100), 201 (6) and 183 (40).

1-(2-Methoxybenzoyl)propylidene(triphenyl)phosphorane 3. Prepared from propyl(triphenyl)phosphonium bromide and 2-methoxybenzoyl chloride as pale yellow crystals (66%), m.p. 195–197 °C (Found: C, 79.4; H, 6.3. C₂₉H₂₇O₂P requires C, 79.4; H, 6.2%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3060, 2960, 1597, 1578, 1496, 1478, 1434, 1389, 1227, 1146, 1104, 1049, 1027 and 691; δ_{H} 7.9–7.1 (17 H, m), 7.0–6.8 (2 H, m), 3.88 (3 H, s), 1.87 (2 H, d of *q*, *J* 22, 7) and 0.59 (3 H, t, *J* 7); δ_{P} +16.5; *m/z* 438 (M⁺, 7%), 423 (56), 407 (3), 287 (2), 277 (21), 263 (22), 262 (100) and 183 (30).

1-(2-Methoxybenzoyl)-2-methylpropylidene(triphenyl)phosphorane 5. Prepared from isobutyl(triphenyl)phosphonium bromide and 2-methoxybenzoyl chloride as pale yellow crystals (48%), m.p. 220–222 °C (Found: C, 79.6; H, 6.5. C₃₀H₂₉O₂P requires C, 79.6; H, 6.5%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2958, 1597, 1577, 1490, 1466, 1434, 1402, 1327, 1240, 1102, 1050, 1028, 1018 and 692; δ_{H} 7.9–7.1 (17 H, m), 7.0–6.8 (2 H, m), 3.88 (3 H, s), 2.6–2.0 (1 H, m) and 0.74 (6 H, d, *J* 7); δ_{P} +13.3; *m/z* 452 (M⁺, 13%), 437 (28), 436 (100), 421 (7), 303 (3), 279 (20), 277 (10), 263 (20), 262 (85), 200 (13) and 183 (23).

1-(2-Methoxybenzoyl)butylidene(triphenyl)phosphorane 7. Prepared from butyl(triphenyl)phosphonium bromide and 2-methoxybenzoyl chloride as colourless crystals (66%), m.p. 190–192 °C (Found: C, 79.7; H, 6.4. C₃₀H₂₉O₂P requires C, 79.6; H, 6.5%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3056, 2956, 1596, 1578, 1495, 1478, 1434, 1388, 1276, 1230, 1147, 1103, 1053, 1040, 1027 and 692; δ_{H} 7.9–7.1 (17 H, m), 7.0–6.8 (2 H, m), 3.88 (3 H, s), 2.0–1.5 (2 H, m), 1.00 (2 H, m) and 0.36 (3 H, t, *J* 7); δ_{P} +16.5; *m/z* 452 (M⁺, 12%), 424 (50), 423 (100), 407 (3), 375 (2), 287 (8), 277 (2), 263 (18), 262 (67) and 183 (22).

1-(2-Methoxybenzoyl)pentylidene(triphenyl)phosphorane 9. Prepared from pentyl(triphenyl)phosphonium bromide and 2-methoxybenzoyl chloride as pale yellow crystals (44%), m.p. 166–168 °C (Found: C, 79.7; H, 6.7. C₃₁H₃₁O₂P requires C, 79.8; H, 6.7%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3060, 2958, 1597, 1580, 1496, 1478, 1436, 1390, 1238, 1146, 1104, 1058, 1042, 1029 and 692; δ_{H} 7.9–7.1 (17 H, m), 7.0–6.8 (2 H, m), 3.88 (3 H, s), 2.0–1.5 (2 H, m), 1.15–0.6 (4 H, m) and 0.42 (3 H, t, *J* 7); δ_{P} +16.5; *m/z* 466 (M⁺, 13%), 435 (5), 424 (25), 423 (100), 407 (3); 389 (2), 287 (9), 262 (80), 183 (30) and 108 (22).

1-(2-Methoxybenzoyl)hexylidene(triphenyl)phosphorane 11. Prepared from hexyl(triphenyl)phosphonium bromide and 2-methoxybenzoyl chloride as colourless crystals (42%), m.p. 153–154 °C (Found: C, 80.1; H, 7.1. C₃₂H₃₃O₂P requires C, 80.0; H, 6.9%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2955, 2925, 1597, 1496, 1478, 1435, 1389, 1238, 1178, 1114, 1103, 1060, 1028, 998 and 691; δ_{H} 7.9–7.2 (17 H, m), 7.0–6.8 (2 H, m), 3.86 (3 H, s), 2.0–1.5 (2 H, m), 1.5–0.6 (6 H, m) and 0.57 (3 H, t, *J* 7); δ_{P} +16.6; *m/z* 480 (M⁺, 10%), 450 (3), 424 (50), 423 (100), 407 (2), 403 (2), 345 (2), 287 (8), 277 (12), 263 (16), 262 (54), 201 (6), 183 (22) and 108 (12).

α-(2-Methoxybenzoyl)benzylidene(triphenyl)phosphorane 13. Prepared from benzyl(triphenyl)phosphonium chloride and 2-methoxybenzoyl chloride as colourless crystals (64%), m.p. 211–212 °C (Found: C, 81.3; H, 5.7. C₃₃H₂₇O₂P requires C, 81.5; H, 5.6%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3060, 2960, 1597, 1580, 1500, 1438, 1378, 1280, 1242, 1140, 1104, 1029, 970 and 693; δ_{H} 7.8–7.2 (17 H, m), 6.8–6.6 (7 H, m) and 3.66 (3 H, s); δ_{P} +14.8; *m/z* 486 (M⁺, 56%), 469 (6), 455 (18), 379 (14), 352 (6), 351 (8), 337 (4), 303 (3), 277 (5), 263 (45), 262 (100), 224 (20), 208 (32), 207 (20), 201 (13) and 183 (60).

1-(2-Methylsulfanylbenzoyl)ethylidene(triphenyl)phosphorane 2. Prepared from ethyl(triphenyl)phosphonium bromide and 2-methylsulfanylbenzoyl chloride as brown crystals (38%), m.p. 210–215 °C (Found: C, 76.1; H, 5.8. C₂₈H₂₅OPS requires C, 76.3; H, 5.7%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2975, 1584, 1500, 1460, 1435, 1375, 1186, 1146, 1104, 992, 818 and 690; δ_{H} 7.95–7.15 (19 H, m), 2.46 (3 H, s) and 1.52 (3 H, d, *J* 16); δ_{P} +17.8; *m/z* 425 (M⁺ – Me, 40%), 461 (81), 337 (7), 407 (3), 277 (33), 263 (22), 262 (45), 183 (60) and 91 (100).

1-(2-Methylsulfanylbenzoyl)propylidene(triphenyl)phosphorane 4. Prepared from propyl(triphenyl)phosphonium bromide and 2-methylsulfanylbenzoyl chloride as colourless crystals (60%), m.p. 206–208 °C (Found: C, 76.3; H, 5.9. C₂₉H₂₇OPS requires C, 76.6; H, 6.0%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2960, 2920, 1582, 1490, 1460, 1436, 1385, 1320, 1188, 1147, 1103, 1027, 945, 842 and 692; δ_{H} 7.9–7.1 (19 H, m), 2.46 (3 H, s), 1.88 (2 H, d of *q*, *J* 21, 7) and 0.59 (3 H, t, *J* 7); δ_{P} +17.0; *m/z* 439 (M⁺ – Me, 100%), 287 (6), 277 (8), 263 (86), 262 (84), 183 (76), 162 (46) and 108 (50).

1-(2-Methylsulfanylbenzoyl)-2-methylpropylidene(triphenyl)phosphorane 6. Prepared from isobutyl(triphenyl)phosphonium bromide and 2-methylsulfanylbenzoyl chloride as colourless crystals (46%), m.p. 219–221 °C (Found: C, 76.7; H, 6.3. C₃₀H₂₉OPS requires C, 76.9; H, 6.2%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2960, 2922, 1482, 1455, 1437, 1385, 1325, 1102, 1015 and 692; δ_{H} 7.9–7.1 (19 H, m), 2.42 (3 H, s), 2.7–2.0 (1 H, m) and 0.82 (6 H, d, *J* 7); δ_{P} +13.9; *m/z* (M⁺, 2%), 454 (33), 453 (100), 433 (6), 301 (5), 287 (2), 279 (8), 277 (8), 263 (28), 262 (32), 191 (18) and 183 (31).

1-(2-Methylsulfanylbenzoyl)butylidene(triphenyl)phosphorane 8. Prepared from butyl(triphenyl)phosphonium bromide and 2-methylsulfanylbenzoyl chloride as pale yellow crystals (71%), m.p. 169–171 °C (Found: C, 76.7; H, 6.2. C₃₀H₂₉OPS requires C, 76.9; H, 6.2%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3057, 2956, 2922, 1583, 1490, 1460, 1435, 1385, 1185, 1148, 1102, 1040, 1026, 1000, 888 and 690; δ_{H} 7.9–7.05 (19 H, m), 2.46 (3 H, s), 2.0–1.5 (2 H, m), 1.0 (2 H, m) and 0.34 (3 H, t, *J* 8); δ_{P} +17.1; *m/z* 468 (M⁺, 3%), 454 (45), 453 (80), 440 (30), 439 (60), 419 (3), 287 (10), 278 (50), 277 (100), 263 (45), 262 (54), 201 (66), 199 (44), 185 (45) and 183 (52).

1-(2-Methylsulfanylbenzoyl)pentylidene(triphenyl)phosphorane 10. Prepared from pentyl(triphenyl)phosphonium bromide and 2-methylsulfanylbenzoyl chloride as colourless crystals (52%), m.p. 145–146 °C (Found: C, 76.85; H, 6.35. C₃₁H₃₁OPS requires C, 77.1; H, 6.5%); $\nu_{\max}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2960, 2922, 1584, 1490, 1460, 1435, 1386, 1187, 1145, 1103, 1080, 1042, 998, 835 and 692; δ_{H} 8.0–7.2 (19 H, m), 2.48 (3 H, s), 2.1–1.6 (2 H, m),

1.2–0.6 (4 H, m) and 0.42 (3 H, t, *J* 8); δ_{P} +17.0; *m/z* 482 (M^+ , 4%), 468 (50), 467 (100), 440 (40), 439 (70), 405 (2), 287 (10), 262 (50) and 183 (35).

1-(2-Methylsulfanylbenzoyl)hexylidene(triphenyl)phosphorane **12**. Prepared from hexyl(triphenyl)phosphonium bromide and 2-methylsulfanylbenzoyl chloride as colourless crystals (30%), m.p. 154–156 °C Found: C, 77.0; H, 6.8. $\text{C}_{32}\text{H}_{33}\text{OPS}$ requires C, 77.4; H, 6.7%; $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2958, 2922, 1585, 1492, 1462, 1437, 1386, 1188, 1144, 1104, 1048 and 693; δ_{H} 8.0–7.2 (19 H, m), 2.47 (3 H, s), 2.1–1.6 (2 H, m), 1.2–0.6 (6 H, m) and 0.57 (3 H, t, *J* 8); δ_{P} +17.05; *m/z* 496 (M^+ , 2%), 481 (100), 439 (72), 287 (6), 262 (36) and 183 (30).

α -(2-Methylsulfanylbenzoyl)benzylidene(triphenyl)phosphorane **14**. Prepared from benzyl(triphenyl)phosphonium chloride and 2-methylsulfanylbenzoyl chloride as yellow crystals (14%), m.p. 216–219 °C (Found: C, 78.55; H, 5.6. $\text{C}_{33}\text{H}_{27}\text{OPS}$ requires C, 78.9; H, 5.4%; $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ 3058, 2980, 1590, 1495, 1436, 1375, 1244, 1175, 1142, 1118, 1103, 1000, 968 and 693; δ_{H} 7.8–6.7 (24 H, m) and 2.42 (3 H, s); δ_{P} +15.5; *m/z* 502 (M^+ , 9%), 487 (63), 467 (4), 455 (2), 379 (4), 352 (3), 277 (18), 262 (45), 240 (5), 226 (20), 225 (100), 197 (25) and 183 (36).

Flash Vacuum Pyrolysis of the Ylides 1–14, 31 and 35.—The apparatus and general procedure used was as described previously.² All pyrolyses were conducted at pressures of 10^{-3} – 10^{-2} mmHg and were complete within 1 h. Except for **13** where preparative TLC was required, all other heterocyclic products were collected directly from the cold trap free of Ph_3PO which collected at the furnace exit. Yields were determined by addition of an accurately weighed quantity of CH_2Cl_2 to the product solution in CDCl_3 and comparison of ^1H NMR integrals, a procedure estimated to be accurate to $\pm 10\%$.

(a) FVP of **1** (100 mg) at 700 °C gave Ph_3PO at the furnace exit and in the cold trap of colourless liquid which proved to be a 6:4 mixture of 2-methylbenzofuran **17**; δ_{H} 7.5–7.1 (4 H, m), 6.35 (1 H, q, *J* 1) and 2.40 (3 H, d, *J* 1) [lit.,¹² (CCl_4) 7.07 (4 H, m), 6.02 (1 H, m) and 2.36 (1 H, d, *J* 1)], and 1-(2-methoxyphenyl)propyne **16**; δ_{H} 7.5–6.8 (4 H, m), 3.90 (3 H, s) and 2.14 (3 H, s).

FVP of **1** (245 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzofuran **17** (8%); δ_{H} as above, and 2-ethylbenzofuran **19** (20%); δ_{H} 7.5–6.8 (4 H, m), 6.35 (1 H, m), 2.78 (2 H, q, *J* 7) and 1.31 (3 H, t, *J* 7) [lit.,¹² (CCl_4) 7.4–6.8 (4 H, m), 6.3–6.17 (1 H, m), 2.78 (2 H, q, *J* 8) and 1.34 (3 H, t, *J* 8)].

FVP of the trideuteriomethoxy ylide **31** (150 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved to be a mixture of 2-methylbenzofuran (28%); δ_{H} as above, and 2-(2,2,2-trideuterioethyl)benzofuran (20%); δ_{H} 7.5–6.8 (4 H, m), 6.35 (1 H, m) and 2.78 (2 H, br s); δ_{D} 1.33 (s).

(b) FVP of **3** (560 mg) at 700 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved to be mainly 1-(2-methoxyphenyl)but-1-yne **16** (70%); δ_{H} 7.6–6.8 (4 H, m), 3.90 (3 H, s), 2.52 (2 H, q, *J* 7) and 1.28 (3 H, t, *J* 7).

FVP of **3** (100 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved to be almost pure 2-vinylbenzofuran **21** (83%); δ_{H} 7.55–7.1 (4 H, m), 6.61 (1 H, dd, *J* 17, 11), 6.54 (1 H, s), 5.92 (1 H, dd, *J* 17, 2) and 5.34 (1 H, dd, *J* 11, 2) [lit.,¹³ 7.51–7.01 (4 H, m), 6.59 (1 H, dd, *J* 17, 11), 6.49 (1 H, s), 5.95 (1 H, d, *J* 17) and 5.31 (1 H, d, *J* 11)].

(c) FVP of **5** (129 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be almost pure 2-vinylbenzofuran **21** (60%).

(d) FVP of **7** (120 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC

and ^1H NMR to be a mixture of 2-methylbenzofuran **17** (9%), 2-ethylbenzofuran **19** (52%) and 2-vinylbenzofuran **21** (10%).

(e) FVP of **9** (100 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzofuran **17** (4%), 2-ethylbenzofuran **19** (30%) and 2-vinylbenzofuran **21** (25%).

FVP of the trideuteriomethoxy ylide **35** (46 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved to be a mixture of 2-methylbenzofuran (11%), 2-vinylbenzofuran (15%); δ_{H} as above, 2-(2,2,2-trideuterioethyl)benzofuran (9%); δ_{H} and δ_{D} as in (a) above, and propene (26%); δ_{H} 5.9–5.75 (1 H, m), 5.1–4.9 (2 H, m) and 1.72 (3 H, d of m, *J* 6).

(f) FVP of **11** (500 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzofuran **17** (3%), 2-ethylbenzofuran **19** (14%) and 2-vinylbenzofuran **21** (21%). Careful analysis of the most volatile products from a later pyrolysis of **11** showed the presence of but-1-ene ($\approx 10\%$); δ_{H} 5.95–5.75 (1 H, m), 5.05–4.85 (2 H, m), 2.15–2.0 (2 H, m) and 1.00 (3 H, t, *J* 7); δ_{C} 140.6, 113.1, 26.7 and 14.1.

(g) FVP of **13** (310 mg) at 850 °C gave a solid at the furnace exit shown by GCMS to consist mainly of Ph_3PO and 2-phenylbenzofuran **23**. This was isolated by preparative TLC (80%), m.p. 118–120 °C (lit.,¹⁴ 120–121 °C); δ_{H} 7.9–7.2 (9 H, m) and 6.97 (1 H, s); δ_{C} 111.1 (C-7) and 101.3 (C-3).

(h) FVP of **2** (270 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzothiophene **18** (14%); δ_{H} 7.9–7.1 (4 H, m), 6.93 (1 H, s) and 2.52 (3 H, s) and 2-ethylbenzothiophene **20** (17%); δ_{H} 7.9–7.1 (4 H, m), 6.93 (1 H, s), 2.87 (2 H, q, *J* 7) and 1.33 (3 H, t, *J* 7).

(i) FVP of **4** (240 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be almost pure 2-vinylbenzothiophene **22** (49%); δ_{H} 7.8–7.2 (4 H, m), 7.08 (1 H, s), 6.87 (1 H, dd, *J* 17, 11), 5.63 (1 H, d, *J* 17) and 5.24 (1 H, d, *J* 11) [lit.,¹⁵ 7.80–6.97 (5 H, m), 6.97–6.53 (1 H, dd, *J* 17, 11), 5.60 (1 H, d, *J* 17) and 5.24 (1 H, d, *J* 11)].

(j) FVP of **6** (300 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be almost pure 2-vinylbenzothiophene **22** (24%); δ_{H} as above.

(k) FVP of **8** (400 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzothiophene **18** (6%), 2-ethylbenzothiophene **20** (45%) and 2-vinylbenzothiophene **22** (9%).

(l) FVP of **10** (200 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzothiophene **18** (10%), 2-ethylbenzothiophene **20** (31%) and 2-vinylbenzothiophene **22** (23%).

(m) FVP of **12** (250 mg) at 850 °C gave Ph_3PO at the furnace exit and in the cold trap a colourless liquid which proved by GC and ^1H NMR to be a mixture of 2-methylbenzothiophene **18** (10%), 2-ethylbenzothiophene **20** (28%) and 2-vinylbenzothiophene **22** (14%).

(n) FVP of **14** (150 mg) at 850 °C gave Ph_3PO at the furnace exit and in the trap a pale brown solid which proved to be 2-phenylbenzothiophene **24** (53%), m.p. 173–175 °C (lit.,¹⁶ 175.5–176 °C); δ_{H} 8.0–7.25 (10 H, m); *m/z* 210 (M^+ , 100%), 208 (70), 178 (20), 165 (30) and 163 (30).

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