

Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 14.¹ Tandem cyclisation of intermediate aryloxy and arylthio radicals leading to tri- and tetra-cyclic aromatic heterocycles

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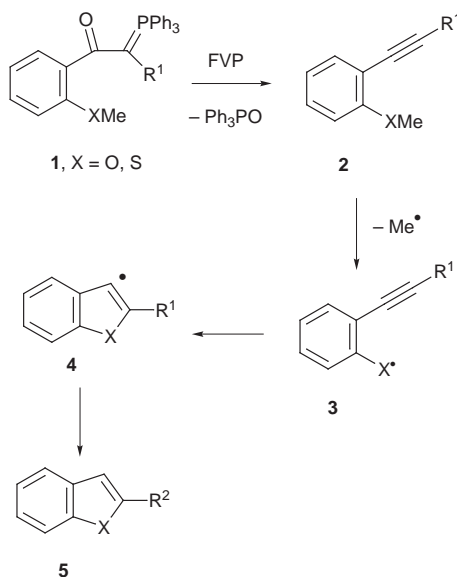
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Seven new stabilised phosphorus ylides **8–14** designed to undergo thermal tandem cyclisation have been prepared. Upon flash vacuum pyrolysis at 850 °C, loss of Ph₃PO and Me[•] results in tandem cyclisation to give benzothieno[3,2-*b*]benzothiophene **16** in the case of **11** while for **8** an abstraction–rearrangement–extrusion sequence leads to 2-phenylbenzofuran **18**. For **9** and **10** both types of process occur to give respectively benzothieno[3,2-*b*]benzofuran **27**, prepared here for the first time, and 2-phenylbenzothiophene **29**. For **12** and **13**, initial cyclisation is followed by intramolecular addition and aromatisation to give the tricyclic products **31** and **32**, while for **14** intramolecular homolytic substitution leads to the tetracyclic benzonaphthofuran **34** and, by rearrangement, to the isomer **37**. Fully assigned ¹³C NMR spectra are presented for all seven ylides.

In Part 3 of this series,² we reported that the ylides **1** with an *ortho*-methoxy or methylthio substituent underwent the normal extrusion of Ph₃PO upon flash vacuum pyrolysis (FVP) at 700 °C to give the alkynes **2** (Scheme 1). However at the higher

coupling with another radical, addition and substitution. Thus, conversion of the phosphonium salts **6** and **7** into the corresponding ylides with butyllithium followed by acylation with 2-methoxy- or 2-methylthio-benzoyl chloride afforded the set of four ylides **8–11** (Scheme 2). In a similar way acylation with

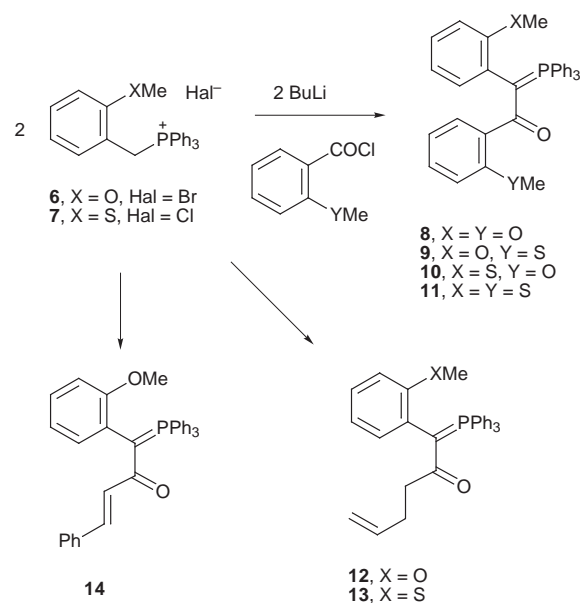


Scheme 1

temperature of 850 °C, benzofurans and benzothiophenes **5** were formed as the final products, probably by loss of Me[•] to give **3** which underwent intramolecular reaction by way of **4**. For R¹ = Ph, hydrogen atom abstraction by **4** gave **5** with R² = R¹, while for R¹ = alkyl, a variety of radical degradation processes led to **5** with R² = Me, Et and vinyl. It occurred to us that, by a suitable choice of R¹, the reactive centre in **4** could be used in a more constructive way and form the basis of a tandem cyclisation approach to polycyclic heteroaromatic products. We now describe the successful application of this idea.³

Results and discussion

The compounds prepared were chosen with a view to examining three possible modes of reaction of the radical centre in **4**:



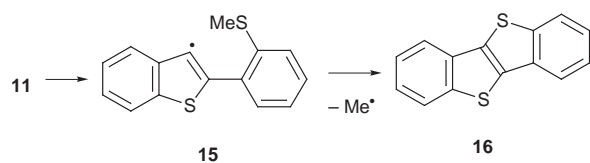
Scheme 2

pent-4-enoyl chloride gave the ylides **12** and **13** and reaction of **6** with cinnamoyl chloride gave **14**. The ylides were obtained in moderate yield as stable crystalline solids which gave the expected analytical and spectroscopic data including ³¹P NMR signals at δ_p +14–15; the highly informative ¹³C NMR spectra (Table 1) provided ready confirmation of the structures with the magnitude of the coupling from phosphorus forming a consistent pattern.

The four ylides **8–11** were subjected to FVP at 850 °C in the expectation that loss of a second methyl radical at the stage of **4** would lead to radical coupling to form a tetracyclic system. However only for the bis(methylthio) compound **11** did this proceed in the expected way with loss of Me[•] from the inter-

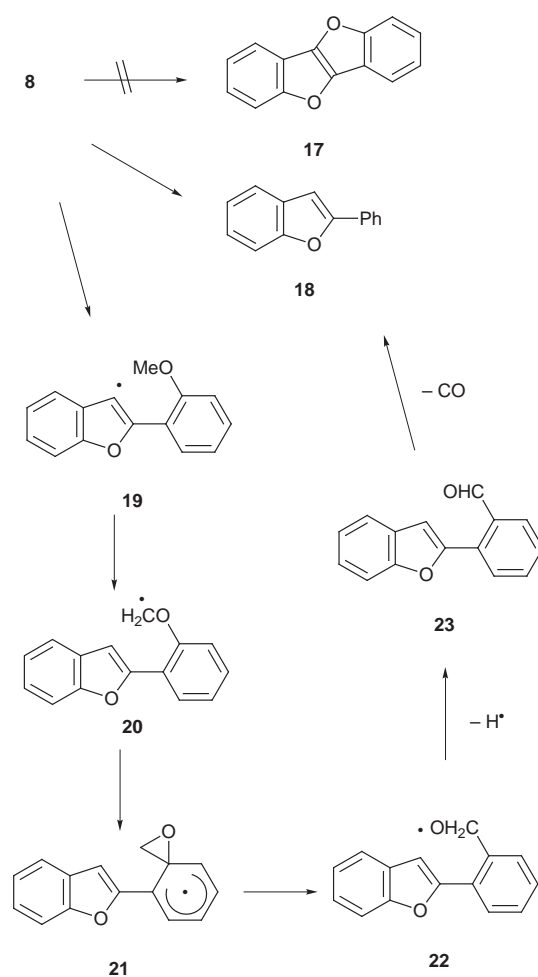
Table 1 ^{13}C NMR spectra of ylides **8–14** [δ_{C} ($J_{\text{P-C}}$)]

	CO	P=C	P-Phenyl				P=C-R signals	O=C-R signals
			C-1	C-2	C-3	C-4		
8	185.0 (7)	67.9 (110)	127.4 (90)	133.6 (9)	128.0 (12)	131.0 (2)	158.1 (3), 136.2 (6), 127.9, 127.2 (11), 119.65, 109.1, 53.9	156.3, 128.6, 127.9, 126.8, 119.56, 110.6, 55.5
9	185.8 (7)	67.6 (109)	127.0 (90)	133.7 (10)	128.1 (12)	131.2 (2)	158.1 (2), 136.7 (6), 127.9, 127.1 (10), 119.9, 109.3, 54.1	143.2 (12), 136.5, 127.3, 127.2 (2), 126.2, 123.8, 17.1
10	186.0 (7)	69.4 (106)	126.7 (90)	134.0 (10)	128.0 (12)	131.3 (2)	144.1 (4), 135.9 (4), 135.4 (11), 127.75, 122.8, 122.5, 15.2	155.8, 127.9, 126.71, 126.69, 119.6, 110.4, 55.6
11	186.7 (7)	69.5 (105)	126.5 (90)	134.1 (10)	128.0 (12)	131.3 (<2)	143.7 (4), 136.4 (4), 135.5 (11), 127.5, 123.4, 122.9, 15.2	143.4 (12), 136.1, 127.45, 126.95, 126.9 (2), 124.0, 17.5
12	189.3 (5)	65.0 (111)	127.4 (93)	133.6 (9)	128.0 (12)	131.0 (2)	158.8 (3), 137.0 (5), 127.6, 127.3 (11), 120.0, 109.8, 54.3	139.7, 113.6, 36.6 (10), 30.7
13	189.9 (5)	67.1 (109)	127.0 (90)	133.7 (10)	128.0 (12)	131.2 (1)	145.0 (5), 135.9 (3), 135.5 (12), 127.0 (2), 123.1, 122.3, 14.9	139.6, 113.6, 36.7 (10), 30.4
14	179.7 (5)	71.1 (110)	127.2 (87)	133.9 (10)	128.4 (12)	131.5 (2)	158.9 (3), 137.4 (5), 128.2 (1), 126.2 (12), 120.3, 110.1, 54.3	137.4, 134.3, 128.5, 128.0, 127.7, 126.5 (12)

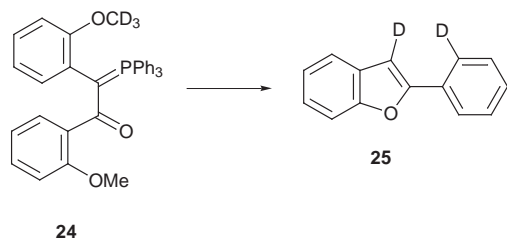
**Scheme 3**

mediate **15** to give benzothieno[3,2-*b*]benzothiophene **16** in 36% yield after chromatographic separation from Ph_3PO (Scheme 3). In contrast to this, the dimethoxy compound **8** did not give any of the expected benzofurobenzofuran **17** and instead the product was identified as 2-phenylbenzofuran **18** isolated in 52% yield (Scheme 4). We believe that this arises from the route shown in which the intermediate radical **19** abstracts a hydrogen atom intramolecularly to give the aryloxymethyl radical **20** and this then rearranges by way of the spiro intermediate **21** to the arylmethoxy radical **22**. This may then lose a hydrogen atom to give the aldehyde **23** which could lose CO under the conditions used to afford **18**. The rearrangement of aryloxymethyl to arylmethoxy radicals has been shown to occur readily under similar conditions.⁴ Evidence in support of this mechanism was obtained by examining the deuterium labelled ylide **24**. The deuterium NMR spectrum of the product obtained upon FVP of ylide **24** at 850 °C showed two singlets of equal intensity at δ_{D} 7.80 and 6.96 corresponding to the expected 2',3-dideuterio product **25** (Scheme 5).

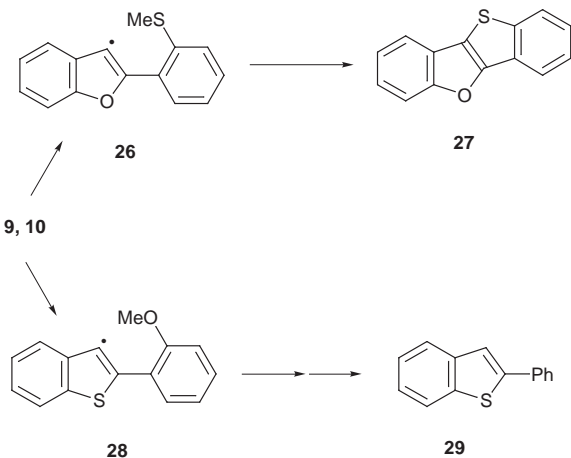
The two ylides **9** and **10** with methoxy and methylthio groups behaved according to the pattern established for **8** and **11** and they both gave the same mixture of two products: benzothieno[3,2-*b*]benzofuran **27** (20%) and 2-phenylbenzothiophene **29** (20%) (Scheme 6). If the initially formed alkyne loses Me^\cdot from the OMe group then cyclisation gives **26** which behaves in the same way as **15** and gives the tetracyclic product whereas if Me^\cdot is lost from the SMe group, the resulting intermediate **28** can undergo the same series of reactions as **19** to give **29**. The fact that the two products **27** and **29** are formed in equal amounts shows that there is no significant selectivity in which methyl group is lost first. Rather remarkably the fundamental heterocyclic compound **27** appears to be previously unknown and was fully characterised for the first time. The reason for the difference in behaviour between **15** and **26** on one hand and **19** and **28** on the other is unclear but it may be that the larger sulfur atom in the former two cases places the methyl group too far away for intramolecular abstraction to take place.

**Scheme 4**

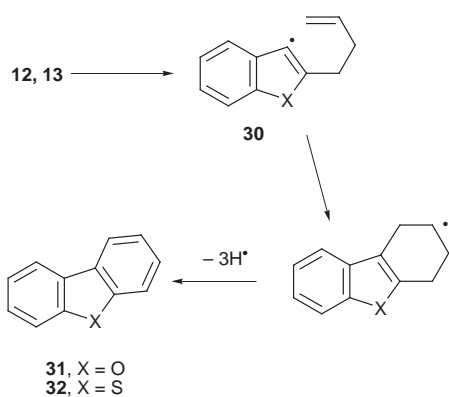
We now turned our attention to the pentenoyl ylides **12** and **13** and FVP of these took the expected course to give dibenzofuran **31** (36%) and dibenzothiophene **32** (28%) respectively, by way of addition in the intermediate **30** followed by aromatisation (Scheme 7). Finally the cinnamoyl ylide **14** was found to give mainly the naphthobenzofuran **34** (44%) expected from intramolecular homolytic aromatic substitution in the intermediate **33**, but this was accompanied by an isomeric product



Scheme 5



Scheme 6



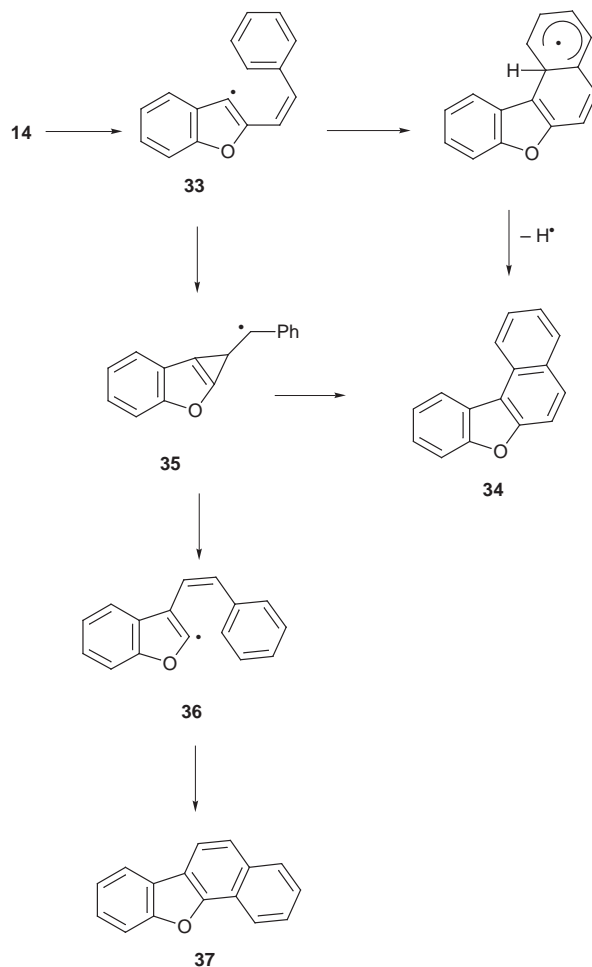
Scheme 7

(14%) to which we assign the structure **37**. This may be formed as shown by intramolecular addition of the intermediate **33** to give the stable benzylic radical **35** which may open in the opposite direction to give **36** which is then set up for substitution to afford **37** (Scheme 8).

In summary we have shown that, by using suitably designed starting materials, the pyrolytic synthesis of benzofurans and benzothiophenes may be extended to provide a useful tandem cyclisation approach to polycyclic heteroaromatic products and further studies on the scope and limitations of the method will be reported shortly.

Experimental

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. UV-visible spectra were recorded using a Pye-Unicam SP-800 instrument. Infra red spectra were recorded for solutions in CHCl_3 in matched sodium chloride cells of path length 0.1 mm, on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^1H at 300 MHz, for ^{13}C at 75 MHz and for ^2H at 46 MHz on a Bruker AM300 instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. 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



Scheme 8

for ^{31}P . The ^2H spectra were run either in CH_2Cl_2 with internal CD_3COCD_3 ($\delta_{\text{D}} = 2.20$) as reference or in CHCl_3 with internal CDCl_3 ($\delta_{\text{D}} = 7.30$) 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 AEI 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 $2\text{ m} \times 4.5\text{ mm}$ column of 2% NPGS on Chromosorb W with N_2 as carrier gas. Dry THF was freshly distilled from potassium benzophenone ketyl under N_2 .

The required quaternary phosphonium salts **6** and **7** were prepared according to the literature method,⁵ while the acid chlorides were freshly prepared from the corresponding carboxylic acids by heating under reflux with an excess of thionyl chloride for 2 h, evaporation and Kugelrohr distillation. (2-Trideuteriomethoxybenzyl)triphenylphosphonium bromide was prepared by reaction of 2-hydroxybenzyl alcohol with CD_3I and KOH in ethanol (94%) followed by treatment of the product with PBr_3 in toluene and then Ph_3P in toluene (74% overall); δ_{H} 8.0–7.7 (15 H, m), 7.6–7.25 (2 H, m), 7.0–6.7 (2 H, m) and 5.19 (2 H, d, J 14); δ_{D} (CHCl_3) 3.83 (s).

Preparation of ylides

A solution of the appropriate phosphonium salt (25.7 mmol) in dry THF (100 cm^3) was stirred under N_2 while a 2.5 M solution of butyllithium in hexane (26 mmol) was added. After 15 min a solution of the appropriate acid chloride (12.8 mmol) in dry THF (10 cm^3) was added dropwise and the resulting mixture stirred for 3 h. It was then added to water (250 cm^3) and the mixture extracted with diethyl ether ($2 \times 100\text{ cm}^3$) and ethyl acetate (100 cm^3). The combined extracts were washed with

water ($2 \times 100 \text{ cm}^3$), dried over MgSO_4 and evaporated to give a yellow solid. This was recrystallised from diethyl ether–hexane to give the products as follows:

[(2-Methoxybenzoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 8. From **6** and 2-methoxybenzoyl chloride as yellow crystals (83%), mp 209–211 °C (Found: C, 79.2; H, 5.7. $\text{C}_{34}\text{H}_{29}\text{O}_3\text{P}$ requires C, 79.0; H, 5.7%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3060, 2960, 1598, 1580, 1503, 1485, 1437, 1380, 1250, 1104, 1050, 1030, 972 and 693; δ_{H} 7.85–6.20 (23 H, m), 3.68 (3 H, s) and 3.20 (3 H, s); δ_{C} see Table 1; δ_{P} +14.1; m/z 516 (M^+ , 70%), 499 (12), 486 (40), 485 (100), 409 (24), 395 (6), 381 (10), 377 (17), 367 (11), 351 (10), 337 (15), 278 (28), 277 (80), 254 (60), 238 ($\text{M}^+ - \text{Ph}_3\text{PO}$, 50) and 183 (60).

[(2-Methoxybenzoyl)(2-trideuteriomethoxyphenyl)methylene]triphenylphosphorane 24. From (2-trideuteriomethoxybenzoyl)triphenylphosphonium bromide and 2-methoxybenzoyl chloride as yellow crystals with identical ^{31}P and ^1H NMR spectra to **8** save for the absence of the signal at δ_{H} 3.20.

[(2-Methylthiobenzoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 9. From **6** and 2-methylthiobenzoyl chloride as yellow crystals (44%), mp 197–199 °C (Found: C, 76.5; H, 5.5. $\text{C}_{34}\text{H}_{29}\text{O}_2\text{PS}$ requires C, 76.7; H, 5.5%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3058, 2975, 1584, 1565, 1500, 1480, 1434, 1375, 1280, 1248, 1145, 1107, 1050, 1030, 1000, 970 and 692; δ_{H} 7.9–6.2 (23 H, m), 3.22 (3 H, s, OMe) and 2.47 (3 H, s, SMe); δ_{C} see Table 1; δ_{P} +14.8; m/z 532 (M^+ , 13%), 517 (13), 501 (14), 488 (3), 409 (4), 382 (4), 337 (4), 277 (20), 262 (50), 255 (100), 183 (65) and 108 (40).

[(2-Methoxybenzoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 10. From **7** and 2-methoxybenzoyl chloride as yellow crystals (27%), mp 187–189 °C (Found: C, 76.4; H, 5.6. $\text{C}_{34}\text{H}_{29}\text{O}_2\text{PS}$ requires C, 76.7; H, 5.5%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1590, 1439, 1311, 1184, 1120, 1071, 995, 862, 755, 721 and 695; δ_{H} 8.1–6.6 (23 H, m), 3.86 (3 H, s, OMe) and 2.04 (3 H, s, SMe); δ_{C} see Table 1; δ_{P} +14.2; m/z 532 (M^+ , 18%), 517 (32), 485 (58), 377 (7), 277 (18), 270 (16), 262 (66), 239 (22), 183 (75), 135 (75) and 77 (100).

[(2-Methylthiobenzoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 11. From **7** and 2-methylthiobenzoyl chloride as yellow crystals (38%), mp 183–185 °C (Found: C, 74.0; H, 5.4. $\text{C}_{34}\text{H}_{29}\text{OPS}_2$ requires C, 74.4; H, 5.3%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1514, 1436, 1273, 1143, 1101, 1037, 962, 747, 712 and 692; δ_{H} 8.1–6.65 (23 H, m), 2.50 (3 H, s) and 2.04 (3 H, s); δ_{C} see Table 1; δ_{P} +14.6; m/z 548 (M^+ , 38%), 533 (60), 501 (100), 425 (10), 277 (67), 262 (69), 240 (42), 224 (34) and 183 (75).

[(2-Methoxyphenyl)(pent-4-enoyl)methylene]triphenylphosphorane 12. From **6** and pent-4-enoyl chloride as yellow crystals (58%), mp 129–131 °C (Found: C, 79.7; H, 6.3. $\text{C}_{31}\text{H}_{29}\text{O}_2\text{P}$ requires C, 80.15; H, 6.3%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1508, 1249, 1106, 1025, 978, 922, 747, 721 and 693; δ_{H} 7.9–7.2 (16 H, m), 7.15–6.45 (3 H, m), 6.1–5.65 (1 H, m), 5.2–4.8 (2 H, m), 3.37 (3 H, s) and 2.4–2.25 (4 H, m); δ_{C} see Table 1; δ_{P} +14.1; m/z 464 (M^+ , 7%), 433 (6), 409 (15), 382 (5), 277 (100), 262 (36), 201 (25), 199 (20) and 183 (80).

[(2-Methylthiophenyl)(pent-4-enoyl)methylene]triphenylphosphorane 13. From **7** and pent-4-enoyl chloride as yellow crystals (37%), mp 142–145 °C (Found: C, 77.3; H, 5.8. $\text{C}_{31}\text{H}_{29}\text{OPS}$ requires C, 77.5; H, 6.1%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1528, 1186, 1102, 972, 907, 751, 720 and 693; δ_{H} 8.0–7.35 (15 H, m), 7.2–6.8 (4 H, m), 6.2–5.65 (1 H, m), 5.2–4.8 (2 H, m), 2.45–2.2 (4 H, m) and 2.24 (3 H, s); δ_{C} see Table 1; δ_{P} +14.2; m/z 480 (M^+ , 22%), 465 (6), 433 (30), 425 (26), 409 (15), 333 (4), 277 (100), 262 (18), 201 (30), 199 (27) and 183 (55).

[(Cinnamoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 14. From **6** and cinnamoyl chloride as orange crystals (31%), mp 203–204 °C (Found: C, 81.4; H, 5.7%; M^+ , 512.1868. $\text{C}_{35}\text{H}_{29}\text{O}_2\text{P}$ requires C, 82.0; H, 5.7%); M , 512.1905; $\nu_{\text{max}}/\text{cm}^{-1}$ 3058, 2960, 1630, 1590, 1573, 1496, 1478, 1435, 1372, 1240, 1105, 1048, 1028, 980, 954 and 692; δ_{H} 7.75–7.05 (23 H, m), 7.0–6.7 (2 H, m), 6.42 (1 H, half AB pattern, J 8) and 3.24 (3 H, s); δ_{C} see Table 1; δ_{P} +15.1; m/z 512 (M^+ , 7%), 481 (54), 409 (3), 368 (13), 351 (5), 337 (6), 303 (9), 277 (8), 263 (18), 262 (48) and 183 (100).

Flash vacuum pyrolysis of ylides

The apparatus used was as described previously.⁶ All pyrolyses were conducted with a furnace temperature of 850 °C and at pressures in the range 10^{-3} to 10^{-1} Torr and were complete within 2 h. Under these conditions the contact time in the hot zone was estimated to be ≈ 10 ms. The entire pyrolysate was washed out of the cold trap and the products separated by preparative TLC (silica, light petroleum (bp 40–60 °C)–diethyl ether, 9:1).

FVP of the ylide **11** (500 mg) gave Ph_3PO and benzo[thieno[3,2-*b*]]benzothiophene **16** (36%) as colourless crystals, mp 213–215 °C (lit.,⁷ 216 °C); δ_{H} 8.1–7.8 (4 H, m) and 7.6–7.3 (4 H, m); δ_{C} 142.3, 133.4 and 133.1 (all 2 C, 4ry) and 125.0, 124.9, 124.0 and 121.6 (all 2 CH); m/z 240 (M^+ , 100%), 208 (8), 195 (16), 169 (5), 163 (12), 152 (8) and 120 (40).

FVP of the ylide **8** (500 mg) gave Ph_3PO and 2-phenylbenzofuran **18** (52%); δ_{H} 7.95–7.15 (9 H, m) and 7.00 (1 H, s); δ_{C} 155.9, 154.9, 141.3, 128.8 (2 C), 128.5, 126.5, 124.9 (2 C), 124.2, 122.9, 120.9, 111.2 and 101.3; m/z 194 (M^+ , 100%), 166 (32), 165 (48), 139 (10), 115 (10), 63 (50) and 51 (65), which was identical by GC to an authentic sample.⁸

FVP of the ylide **24** (500 mg) gave Ph_3PO and 3-deuterio-2-(2-deuteriophenyl)benzofuran **25**; δ_{D} (CH_2Cl_2) 7.80 (1 D, 2-DPh) and 6.96 (1 D, 3-D).

FVP of the ylide **9** (2 g) gave Ph_3PO and two other products identified as benzo[thieno[3,2-*b*]]benzofuran **27** (20%) as colourless crystals, mp 126.5–127.5 °C (Found: C, 74.95; H, 3.6%; M^+ , 224.0295. $\text{C}_{14}\text{H}_8\text{OS}$ requires C, 75.0; H, 3.6%; M , 224.0296); δ_{H} 8.02 (1 H, d, J 6), 7.88 (1 H, d, J 5), 7.73 (1 H, d, J 6), 7.67 (1 H, d, J 5), 7.48 (1 H, t, J 5) and 7.42–7.33 (3 H, m); δ_{C} 158.8, 153.0, 142.0, 125.1, 124.1 and 118.6 (all 4ry) and 124.9 (3 C), 124.3, 123.3, 119.7, 119.6 and 112.5 (all CH); m/z 224 (M^+ , 100%), 195 (12), 169 (3), 152 (12), 112 (12), 98 (4) and 76 (5), and 2-phenylbenzothiophene **29** (20%); m/z 210 (M^+ , 100%), 178 (12), 165 (28) and 105 (20).

FVP of the ylide **10** (200 mg) gave identical results to **9**.

FVP of the ylide **12** (200 mg) gave Ph_3PO and one other major product identified by GCMS, NMR and TLC comparison with an authentic sample as dibenzofuran **31** (36%); δ_{C} 156.1 and 124.2 (both 2 C, 4ry) and 127.1, 122.7, 120.6 and 111.7 (all 2 CH); m/z 168 (M^+ , 100%), 139 (42), 113 (4), 87 (3) and 63 (6).

FVP of the ylide **13** (200 mg) gave Ph_3PO and one other major product identified by GCMS, NMR and TLC comparison with an authentic sample as dibenzothiophene **32** (28%); δ_{H} 8.16 (2 H, m), 7.85 (2 H, m) and 7.5–7.4 (4 H, m); δ_{C} 139.4 and 135.6 (both 2 C, 4ry) and 126.7, 124.3, 122.8 and 121.6 (all 2 CH); m/z 184 (M^+ , 100%), 158 (3), 152 (7), 139 (11), 113 (3), 92 (12) and 79 (8).

FVP of the ylide **14** (210 mg) gave Ph_3PO and a red oil (58%) shown by GCMS to consist of two components of m/z 218 corresponding to isomeric benzonaphthofurans. The major isomer (44%) was naphtho[2,1-*b*]]benzofuran (“ γ -brazan”) **34**; δ_{H} 8.58 (1 H, d, J 8), 8.32 (1 H, m), 8.0–7.8 (2 H, m), 7.8–7.6 (2 H, m) and 7.6–7.3 (4 H, m); δ_{C} 155.6 and 154.2 (both 4ry, C–O), 129.1, 128.4, 127.0, 125.8, 124.3, 123.3, 123.0, 121.8, 112.6 and 111.7 (all CH) [remaining four 4ry signals uncertain] (lit.,⁹ δ_{C} 155.8 and 154.2; lit.,¹⁰ identical 10 CH signals); m/z 218 (M^+ ,

100%), 203 (1), 190 (6), 189 (42), 188 (11), 187 (12), 163 (11), 150 (3), 139 (4) and 109 (40) [lit.,⁹ m/z 218 (100%), 190 (31), 189 (58), 164 (4) and 163 (13)]. The minor product (14%) appeared to be naphtho[1,2-*b*]benzofuran (“ α -brazan”) **37**; δ_{H} 8.39 (1 H, d, *J* 8); m/z 218 (100%), 202 (2), 190 (5), 189 (38), 188 (10), 187 (11), 163 (10), 150 (3), 139 (4) and 109 (60). The UV spectrum of the mixture confirmed the presence of both isomers; $\lambda_{\text{max}}/\text{nm}$ 240, 252, 261, 281, 324, 333 and 340 (lit.,¹¹ λ_{max} **34**: 240, 252, 280, 316 and 339; **37**: 260, 295, 324, 334 and 340).

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