Flash vacuum pyrolysis of oxo-stabilised phosphonium ylides containing methoxythiophene and methylthiophene groups

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Abstract
Ten new oxo-stabilised phosphonium ylides containing substituted thiophene groups, as well as two deuterium-labelled analogues, are prepared and fully characterised. Upon flash vacuum pyrolysis at 800 °C, the simpler examples undergo extrusion of Ph_3PO coupled with domino cyclisation to give thieno[3,2-*b*]furan and thieno[3,4-*b*]furan products but the corresponding approach to a thieno[2,3-*b*]furan fails. One ylide designed to give a thieno[3,4-*b*]furan instead gives phenylbutadiyne and 2-phenyl-3-vinylthiophene at 725 °C and the mechanism of this unusual process is elucidated by deuterium labelling. Attempts to access more complex heterocyclic products from extended methoxythienyl ylides failed. Two ylides bearing a 3-methyl-2-thienylacryloyl group gave 5-benzylbenzothiophene, 5-(α-methylbenzyl)benzothiophene and fluoreno[3,4-*b*]thiophene upon FVP at 800 °C and the mechanism was again elucidated by deuterium labelling.

Keywords: Flash vacuum pyrolysis; Phosphonium ylide; Thienofuran; Benzothiophene; Fluorenothiophene; Radical cyclisation

1   Introduction
Flash vacuum pyrolysis (FVP) is now well established as an important method, both for generation of reactive intermediates and preparation of stable products [1]. As a synthetic method it has had a particular impact in the area of heterocyclic chemistry, allowing convenient formation of many otherwise inaccessible products in high yield [2]. For some years we have made a detailed study of oxo-stabilised phosphonium ylides as suitable precursors for synthesis of fused ring heterocycles by FVP in a process involving thermal extrusion of Ph_3PO to form an alkyne, simultaneous radical generation, and then a sequence of domino cyclisation processes leading to tri-, tetra- and pentacyclic fused ring aromatic heterocycles. Recent examples showing the versatility of the method include pyrolysis of nearly 40 compounds of structure **1** to give the corresponding products **2** (Scheme 1) including representatives of 24 different heterocyclic ring systems [3], cascade processes of up to eight steps [4], and introduction of nitrogen, either by starting from pyridine-containing ylides **3** which react to afford **4** [5], or by using a nitrogen-based cyclising radical which unexpectedly leads to both five- and six-membered ring heterocycles as illustrated by pyrolysis of ylide **5** to give both the quinoline **6** and the furocarbazole natural product Eustifoline D **7** [6–8]. In terms of the mechanism of these processes, this is illustrated for the case of a generalised ylide in Scheme 2 and is supported by the results of isotopic labelling [9].
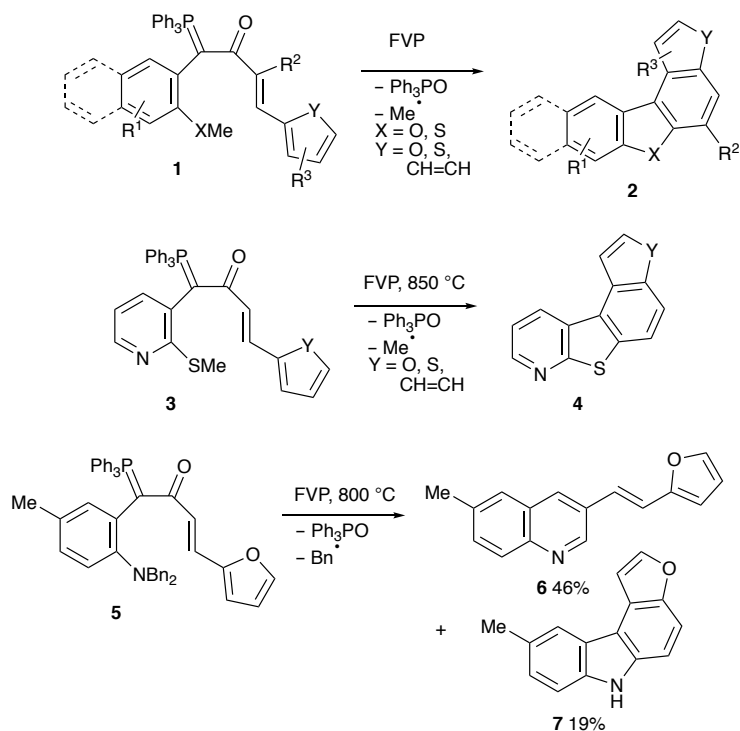
Scheme 1. Previous syntheses of fused ring heterocycles by oxo ylide pyrolysis
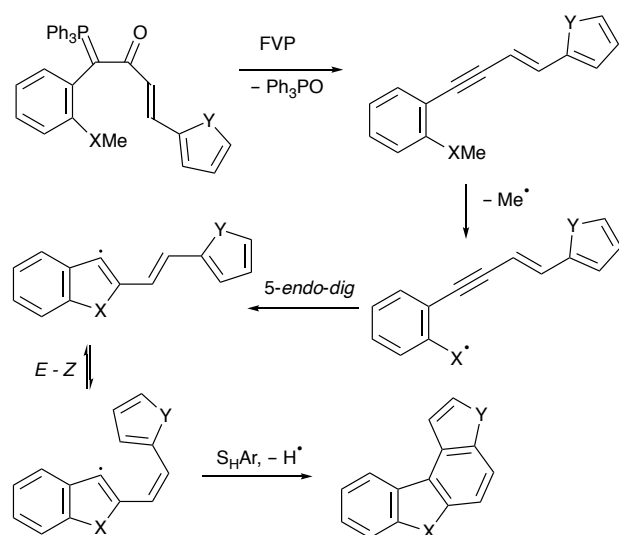
Scheme 2. Typical mechanism for generation of a tetracyclic product

In this paper we report the synthesis and FVP behaviour of a range of thiophene-containing oxo-stabilised ylides. In view of the success in replacing the starting benzene ring of **1** with pyridine in **3**, we were interested to see whether the thermodynamically stable thiophene ring could also be used and thus we examined a range of methoxythienyl ylides as a potential route to fused ring thiophene products. The expected thienofurans are relatively inaccessible heterocycles [10] and typical routes to thieno[3,2-*b*]furans [11–14] and thieno[3,4-*b*]furans [14–16] often involve several steps and require certain groups to be present. We have also recently encountered unexpected rearrangements of thiophenes under FVP conditions [17], and we include here also an account of further unexpected thermal processes involving oxo ylides containing a methylthienyl group.

2 Experimental

2.1 General

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 1710 instrument. NMR spectra were obtained for ^{1}H at 200 or 300 MHz, for ^{13}C at 50 or 75 MHz and for ^{31}P at 121 MHz all using Varian Gemini instruments. ^{2}H NMR spectra were run at 46 MHz in CHCl$_3$. All other spectra were run on solutions in CDCl$_3$ with internal Me$_4$Si as reference for ^{1}H and ^{13}C and external H$_3$PO$_4$ 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 A. E. I. Kratos MS–50 spectrometer using electron impact at 70 eV. GCMS was carried out using a Hewlett Packard 5890A coupled to a Finnigan–Incos 50 mass spectrometer. Elemental analysis was carried out on a Carlo-Erba 1106 elemental analyser.

Flash vacuum pyrolysis (FVP) was carried out as previously reported [18] in a conventional flow system by subliming the starting material through a horizontal quartz tube (30 × 2.5 cm) externally heated by a tube furnace to 700–800 °C and maintained at a pressure of 2–9 × 10^{-2} torr by a rotary vacuum pump. The contact time in the hot zone under these conditions is estimated to be ~10^{-2} s. The apparatus used is illustrated and a detailed experimental procedure is given in a recent publication [19]. Products were collected in a liquid N$_2$ cooled U-shaped trap and purified as noted.

2.2 Preparation of Simple Methoxythienyl Ylides

2.2.1. 4-Methoxy-3-thenoyl chloride

This was prepared by heating a mixture of 4-methoxythiophene-3-carboxylic acid [20] (3.0 g, 19 mmol) and thionyl chloride (2.1 cm^3, 30 mmol) under reflux for 2 h followed by evaporation under reduced pressure and kugelrohr distillation of the residue at 20 Torr to give the product (2.85 g, 85%) as a pale yellow crystalline solid, mp 47–48 ºC (Found: C, 40.9; H, 2.6. C$_6$H$_5$ClO$_2$S requires C, 40.8; H, 2.9%); v_{max}/cm^{-1} 1781, 1541, 1408, 1389, 1214, 1179, 1150, 1010, 911, 886, 815, 789 and 718; δ_H 8.38 (1H, d, J 3, 2-H), 6.33 (1H, d, J 3, 5-H) and 3.90 (3H, s, OMe); δ_C 158.3 (C), 157.5 (C), 140.5 (CH), 126.5 (C), 99.0 (CH) and 58.2 (Me); m/z 178 ([37]Cl-M$^+$, 11%), 176 ([35]Cl-M$^+$, 29), 141 (100), 126 (17), 98 (5) and 53 (14).

2.2.2. 4-Trideuteriomethoxy-3-thenoyl chloride

This was prepared as in 2.2.1 using 4-trideuteriomethoxythiophene-3-carboxylic acid [20] (0.38 g, 2.4 mmol) and thionyl chloride (0.73 cm^3, 10 mmol) to give the product (0.18 g, 40%) as a pale yellow crystalline solid, mp 44–47 ºC; δ_H 8.37 (1H, d, J 4, 2-H) and 6.33 (1H, d, J 4, 5-H).

2.2.3. [(3-Methoxy-2-thenoyl)benzylidene]triphenylphosphorane 8

A suspension of benzyltriphenylphosphonium chloride (10 g, 26.0 mmol) in dry THF (70 cm^3) was stirred under N$_2$ while a solution of butyllithium in hexanes (10.4 cm^3, 2.5 M, 26.0 mmol) was added. The resulting deep red solution was stirred for a further 2 h before adding a solution of 3-methoxy-2-thenoyl chloride [21] (2.30 g, 13.0 mmol) in dry THF (20 cm^3). After stirring for a further 24 h the mixture was added to water (100 cm^3) and extracted with diethyl ether (2 × 150 cm^3) and ethyl acetate (2 × 150 cm^3). The combined extracts were washed with water (100 cm^3), dried and evaporated to give a yellow oil which was triturated with diethyl ether to

give a yellow solid. This was dissolved in ethyl acetate (250 cm^3), the hot solution filtered and the solid obtained on evaporation recrystallised to give the product (3.03 g, 47%) as bright yellow crystals, mp 189–190 ºC (Found: C, 75.4; H, 5.0. C$_{31}$H$_{25}$O$_2$PS requires C, 75.6; H, 5.1%); ν_{max}/cm^{-1} 1592, 1543, 1510, 1351, 1237, 1104, 998, 967, 849, 750 and 690; δ_H 7.75–7.63 (6H, m, Ph), 7.60–7.25 (9H, m, Ph), 7.02 (1H, d, J 6, 5-H), 6.92–6.85 (5H, m, Ph), 6.66 (1H, d, J 6, 4-H), and 3.38 (3H, s, OMe); δ_C 177.4 (d, J 6, CO), 155.0 (thienyl C-3), 138.1 (d, J 11, C-1 of C-Ph), 134.9 (d, J 4, 2CH), 133.9 (d, J 10, C-2 of PPh), 131.5 (d, J 2, C-4 of PPh), 128.6 (d, J 12, C-3 of PPh), 127.3 (d, J 92, C-1 of PPh), 127.0 (2CH), 124.9 (CH), 124.7 (CH), 123.3 (d, J 14, thienyl C-2), 116.3 (thienyl C-4), 74.0 (d, J 109, C=P) and 58.2 (OMe); δ_P +15.9; m/z 492 (M$^+$, 30%), 461 (5), 277 (58), 262 (100), 230 (19), 214 (24), 183 (45), 165 (12), 141 (19), 108 (13) and 91 (6).

2.2.4   [(3-Methoxy-2-thenoyl)-1-propylidene]triphenylphosphorane 9

This was prepared as in 2.2.3 using propyltriphenylphosphonium bromide (10 g, 26.0 mmol), butyllithium in hexanes (10.4 cm^3, 2.5 M, 26.0 mmol) and 3-methoxy-2-thenoyl chloride [21] (2.30 g, 13.0 mmol) to give the product (1.71 g, 30%) as red-orange crystals, mp 222–224 ºC (Found: C, 72.7; H, 5.4. C$_{27}$H$_{25}$O$_2$PS requires C, 73.0; H, 5.7%); ν_{max}/cm^{-1} 1542, 1494, 1445, 1235, 1181, 1104, 1047, 1016, 930, 834, 744, 710 and 695; δ_H 7.85–7.60 (6H, m, Ph), 7.60–7.35 (9H, m, Ph), 7.13 (1H, d, J 6, 5-H), 6.89 (1H, d, J 6, 4-H), 3.90 (3H, s, OMe), 2.19 (2H, dq, J 23, 7, CH$_2$) and 0.73 (3H, t, J 7, CH$_3$); δ_C 177.5 (d, J 7, CO), 153.7 (thienyl C-3), 133.8 (d, J 10, C-2 of PPh), 131.5 (d, J 2, C-4 of PPh), 128.7 (d, J 12, C-3 of PPh), 127.7 (d, J 91, C-1 of PPh), 123.8 (d, J 10, thienyl C-2), 123.7 (CH), 116.8 (thienyl C-4), 71.2 (d, J 100, C=P), 58.9 (OMe), 20.7 (d, J 13, CH$_2$) and 14.2 (Me); δ_P +16.5; m/z 444 (M$^+$, 7%), 429 (34), 287 (8), 277 (22), 262 (100), 201 (7), 183 (35), 152 (7), 141 (23), 127 (7) and 108 (12).

2.2.5   [(4-Methoxy-3-thenoyl)benzylidene]triphenylphosphorane 10

This was prepared as in 2.2.3 using benzyltriphenylphosphonium chloride (6.14 g, 15.8 mmol), butyllithium in hexanes (6.34 cm^3, 2.5 M, 15.8 mmol) and 4-methoxy-3-thenoyl chloride (1.40 g, 7.9 mmol) to give the product (3.35 g, 86%) as very pale yellow crystals, mp 166–168 ºC (Found: C, 75.3; H, 5.0. C$_{31}$H$_{25}$O$_2$PS requires C, 75.6; H, 5.1%); ν_{max}/cm^{-1} 1592, 1491, 1432, 1238, 1216, 1158, 1107, 1030, 1001, 970, 874, 854, 761, 750 and 690; δ_H 7.71–7.53 (6H, m, Ph), 7.52–7.32 (9H, m, Ph), 6.98 (1H, d, J 3, 2-H), 6.84 (5H, br s, Ph), 5.97 (1H, d, J 3, 5-H) and 3.61 (3H, s, OMe); δ_C 180.6 (d, J 8, CO), 156.8 (thienyl C-4), 138.0 (d, J 12, C-1 of C-Ph), 135.7 (d, J 13, thienyl C-3), 134.5 (d, J 5, 2CH), 133.8 (d, J 10, C-2 of PPh), 131.5 (d, J 2, C-4 of PPh), 128.6 (d, J 12, C-3 of PPh), 127.0 (d, J 91, C-1 of PPh), 127.0 (2CH), 124.9 (CH), 124.5 (thienyl C-2), 95.7 (thienyl C-5), 74.1 (d, J 107, C=P) and 57.2 (OMe); δ_P +16.0; m/z 492 (M$^+$, 25%), 461 (3), 277 (40), 262 (100), 236 (6), 201 (10), 183 (39), 141 (24) and 69 (45).

2.2.6   [(4-Trideuteriomethoxy-3-thenoyl)benzylidene]triphenylphosphorane 11

This was prepared as in 2.2.3 using benzyltriphenylphosphonium chloride (0.78 g, 2 mmol), butyllithium in hexanes (0.8 cm^3, 2.5 M, 2 mmol) and 4-trideuteriomethoxy-3-thenoyl chloride (0.18 g, 1 mmol) to give a pale yellow oil which was triturated with diethyl ether to give pale yellow needles which were recrystallised from ethyl acetate to give the product (0.3 g, 61%) as very pale yellow crystals, mp 163.5–168

ºC; δ_H 7.71–7.53 (6H, m, Ph), 7.52–7.32 (9H, m, Ph), 6.98 (1H, d, J 3, 2-H), 6.84 (5H, br s, Ph) and 5.84 (1H, d, J 3, 5-H); δ_P +15.9.

2.2.7 [(4-Methoxy-3-thenoyl)-1-propylidene]triphenylphosphorane 12

This was prepared as in 2.2.3 using propyltriphenylphosphonium bromide (6.14 g, 15.9 mmol), butyllithium in hexanes (6.35 cm^3, 2.5 M, 15.9 mmol) and 4-methoxy-3-thenoyl chloride (1.40 g, 7.9 mmol) to give the product (3.09 g, 88%) as very pale yellow needles, mp 226–228 ºC (Found: C, 72.8; H, 5.6. C$_{27}$H$_{25}$O$_2$PS requires C, 73.0; H, 5.7%); ν_{max}/cm^{-1} 1545, 1495, 1364, 1321, 1276, 1198, 1178, 1153, 1103, 1031, 990, 942, 882, 855, 827, 776, 695 and 623; δ_H 7.82–7.60 (6H, m, Ph), 7.60–7.38 (9H, m, Ph), 7.21 (1H, d, J 3, 2-H), 6.18 (1H, d, J 3, 5-H), 3.87 (3H, s, OMe), 1.98 (2H, dq, J 23, 7, CH$_2$) and 0.63 (3H, t, J 7, CH$_3$); δ_C 181.5 (d, J 8, CO), 156.6 (thienyl C-4), 136.3 (d, J 13, thienyl C-3), 133.8 (d, J 10, C-2 of PPh), 131.6 (d, J 2, C-4 of PPh), 128.7 (d, J 12, C-3 of PPh), 127.3 (d, J 89, C-1 of PPh), 121.8 (thienyl C-2), 96.1 (thienyl C-5), 70.0 (d, J 100, C=P), 57.6 (OMe), 21.0 (d, J 13, CH$_2$) and 18.8 (Me); δ_P +17.3; m/z 444 (M$^+$, 10%), 429 (24), 410 (6), 386 (8), 368 (10), 262 (67), 236 (24), 183 (23), 137 (21), 123 (16), 111 (18), 97 (32), 81 (52) and 69 (100).

2.2.8 [(2-Methoxy-3-thenoyl)benzylidene]triphenylphosphorane 13

This was prepared as in 2.2.3 using benzyltriphenylphosphonium chloride (10.00 g, 26 mmol), butyllithium in hexanes (10.4 cm^3, 2.5 M, 26 mmol) and 2-methoxy-3-thenoyl chloride [22] (2.30 g, 13 mmol) in dry THF (10 cm^3). After stirring for a further 24 h the mixture was added to water (200 cm^3) and extracted with diethyl ether (2 × 100 cm^3) and ethyl acetate (2 × 75 cm^3). The combined extracts were washed with water (100 cm^3), dried, decolourised with charcoal and evaporated to give a pale yellow solid which was recrystallised from ethyl acetate to give the product (1.07 g, 17%) as pale yellow prisms, mp 182–185 ºC (Found: C, 75.3; H, 5.5. C$_{31}$H$_{25}$O$_2$PS requires C, 75.6; H, 5.1%); ν_{max}/cm^{-1} 1548, 1495, 1440, 1398, 1334, 1267, 1224, 1105, 1002, 969, 933, 762 and 702; δ_H 7.63–7.57 (6H, m, Ph), 7.50–7.32 (9H, m, Ph), 6.88–6.79 (5H, m, Ph), 6.69 (1H, d, J 6, 4-H), 6.25 (1H, d, J 6, 5-H) and 3.52 (3H, s, OMe); δ_C 180.4 (d, J 6, CO), 163.5 (thienyl C-2), 138.2 (d, J 12, C-1 of C-Ph), 134.4 (d, J 4, 2CH), 133.8 (d, J 10, C-2 of PPh), 131.5 (d, J 2, C-4 of PPh), 128.6 (d, J 12, C-3 of PPh), 127.9 (CH), 127.4 (d, J 91, C-1 of PPh), 127.0 (2CH), 124.4 (CH), 124.0 (d, J 12, thienyl C-3), 109.3 (thienyl C-5), 74.0 (d, J 109, C=P) and 61.5 (OMe); δ_P +15.6; m/z 492 (M$^+$, 54%), 461 (22), 379 (9), 277 (52), 262 (100), 214 (28), 199 (23) and 183 (46).

2.3 Pyrolysis of Simple Methoxythienyl Ylides

2.3.1 FVP of [(3-methoxy-2-thenoyl)benzylidene]triphenylphosphorane 8

FVP of the title compound (1.10 g) at 800 ºC and 3.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant to give a brown oil which solidified with time. This was then distilled at 160 ºC/0.01 Torr to give a clear yellow oil which solidified on cooling. This was recrystallised from ethanol to give the product, *2-phenylthieno[3,2-b]furan* **14** (0.20 g, 45%) as pale brown plates, mp 115–118 ºC (Found: C, 72.1; H, 4.1. C$_{12}$H$_8$OS requires C, 72.0; H, 4.0%) (HRMS: found M$^+$, 200.0292. C$_{12}$H$_8$OS requires M, 200.0296); ν_{max}/cm^{-1} 1594, 1335, 1304, 1163, 1043, 1014, 873, 827, 737 and 647; δ_H 7.76 (2H, d, J 7, Ph), 7.43 (2H, t, J 7, Ph), 7.32 (1H, d, J 7, Ph), 7.20 (1H, d, J 5, 6-

H), 7.15 (1H, d, J 5, 5-H) and 7.05 (1H, s, 3-H); δ_C 158.0 (C), 157.8 (C), 131.3 (C), 129.0 (2CH), 128.0 (CH), 125.4 (CH), 125.3 (C), 124.1 (2CH), 111.1 (CH) and 101.2 (CH); *m/z* 200 (M$^+$, 72%), 186 (24), 171 (100), 146 (18), 127 (13), 102 (39), 85 (24) and 77 (25).

2.3.2   FVP of [(3-methoxy-2-thenoyl)-1-propylidene]triphenylphosphorane 9

FVP of the title compound (0.64 g) at 800 ºC and 3.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant to give a pale brown oil, (0.10 g) which was found by ^{1}H NMR, ^{13}C NMR and GCMS to be a moderately complex mixture of products including triphenylphosphine and benzothiophene indicating some carbon skeleton fragmentation. However, two of the expected products were seen:

1. major product (28%): *2-vinylthieno[3,2-b]furan* **15**; δ_H 7.13 (1H, d, *J* 5, 6-H), 7.00 (1H, d, *J* 5, 5-H), 6.54 (1H, s, 3-H), 6.52 (1H, dd, *J* 16, 11, vinyl-H), 5.78 (1H, d, *J* 16, vinyl-H) and 5.21 (1H, d, *J* 11, vinyl-H); δ_C 157.1 (C), 156.2 (C), 131.4 (CH), 125.2 (CH), 124.8 (C), 112.3 (CH$_2$), 110.2 (CH) and 103.6 (CH); *m/z* 150 (M$^+$, 100%), 121 (43), 96 (47), 78 (17), 75 (10), 70 (20) and 45 (15);

2. minor product (9%): *2-ethylthieno[3,2-b]furan* **16**; δ_H 7.24 (1H, d, *J* 5, 6-H), 7.05 (1H, d, *J* 5, 5-H), 6.32 (1H, s, 3-H), 2.75 (2H, d, *J* 8, CH$_2$) and 1.27 (3H, t, *J* 8, CH$_3$); *m/z* 152 (M$^+$, 40%), 137 (100), 109 (10), 97 (9), 69 (13), 65 (12), 53 (11), 45 18) and 39 (19).

2.3.3   FVP of [(4-methoxy-3-thenoyl)-1-propylidene]triphenylphosphorane 12

FVP of the title compound (0.5 g) at 800 ºC and 5.0–9.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow oil which was kugelrohr distilled to give the product, *2-vinylthieno[3,4-b]furan* **17** (0.04 g, 25%) as an unstable pale yellow oil, bp (oven temp.) 170 ºC at 0.7 Torr (HRMS: Found M$^+$, 150.0133. C$_8$H$_6$OS requires M, 150.0139); δ_H 6.87 (1H, d, *J* 2, 4-H), 6.68 (1H, d, *J* 2, 6-H), 6.52 (1H, dd, *J* 18, 10, vinyl-H), 6.24 (1H, s, 3-H), 5.88 (1H, d, *J* 18, vinyl-H) and 5.38 (1H, d, *J* 10, vinyl-H); δ_C 163.1 (C), 156.5 (C), 136.0 (C), 125.9 (CH), 116.2 (CH), 107.6 (CH$_2$), 101.4 (CH) and 94.6 (CH); *m/z* 150 (M$^+$, 23%), 121 (18), 105 (12), 85 (19), 71 (21), 57 (56) and 43 (100).

2.3.4   FVP of [(4-methoxy-3-thenoyl)benzylidene]triphenylphosphorane 10

FVP of the title compound (0.5 g) at 725 ºC and 5.0–9.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:19) as eluant gave two fractions;

1. A mixture of two products, partially separable by preparative TLC;

(a) *2-phenyl-3-vinylthiophene* **18** (HRMS: Found M$^+$, 186.0498. C$_{12}$H$_{10}$S requires M, 186.0503); δ_H 7.62 (2H, d, *J* 7, ArH), 7.45 (1H, s, ArH), 7.4–7.25 (3H, m, ArH), 7.13 (1H, s, ArH), 6.69 (1H, dd, *J* 18, 11, vinyl-H), 5.62 (1H, d, *J* 18, vinyl-H) and 5.23 (1H, d, *J* 11, vinyl-H); δ_C 145.1 (C), 141.5 (C), 134.6 (C), 131.3 (CH), 129.1 (2CH), 127.9 (CH), 126.1 (2CH), 122.1 (CH), 120.8 (CH) and 113.9 (CH$_2$); *m/z* 186 (M$^+$, 100%), 171 (8), 152 (9), 141 (6), 115 (13) and 102 (1);

(b) *1-phenyl-1,3-butadiyne* **19** (HRMS: Found M$^+$, 126.0474. C$_{10}$H$_6$ requires M, 126.0470); ν_{max}/cm^{-1} 2200 (C≡C); δ_H 7.52 (2H, d, ArH), 7.4–7.3 (3H, m, ArH) and 2.45 (1H, s, CH) [Lit. [23] 7.42–7.2 (5H), 2.37 (1H)]; δ_C 133.0 (2CH), 129.7 (CH), 128.7 (2CH), 121.3 (C), 75.5 (C≡C), 73.6 (C≡C), 71.4 (C≡CH) and 68.3 (C≡C) [Lit.

[23] 132.7, 129.5, 128.4, 120.9, 75.3, 73.5, 71.3, 68.1]; m/z 126 (M$^+$, 78%), 98 (16), 87 (13), 74 (57) and 50 (100);

2. *1-(4-methoxy-3-thienyl)-2-phenylethyne* **20** (HRMS: Found M$^+$, 214.0457. C$_{13}$H$_{10}$OS requires M, 214.0452); δ_H 7.60–7.52 (2H, m, Ph), 7.42 (1H, d, J 4, 2-H), 7.38–7.30 (3H, m, Ph), 6.22 (1H, d, J 4, 5-H) and 3.88 (3H, s, OMe); δ_C 158.2 (CO), 131.9 (2CH), 128.4 (4CH), 123.4 (C), 115.0 (C), 96.6 (CH), 91.5 (C≡C), 82.1 (C≡C) and 58.0 (OMe); m/z 214 (M$^+$, 100%), 184 (10), 171 (25), 141 (50), 126 (50), 115 (43), 98 (18) and 86 (21).

2.3.5 FVP of [(4-trideuteriomethoxy-3-thenoyl)benzylidene]triphenylphosphorane 11

FVP of the title compound (0.3 g) at 725 ºC and 3.0–7.0 × 10^{-2} Torr gave a yellow-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave mainly *1-(4-trideuteriomethoxy-3-thienyl)-2-phenylethyne* **21** (0.1 g, 76%) as a brown oil, δ_H 7.42 (1H, d, J 4, 2-H) and 6.22 (1H, d, J 4, 5-H); δ_D 3.88 (CD$_3$O); m/z 217 (M$^+$,100%), 171 (19), 144 (34), 140 (8), 126 (22) and 117 (5), together with small amounts of *1-phenylbutadiyne* **19** and *4-deuterio-3-(2,2-dideuteriovinyl)-2-phenylthiophene* **22**.

2.3.6 Repyrolysis of product 21 at 800 ºC

FVP of the above product (0.1 g) at 800 ºC and 3.0–7.0 × 10^{-2} Torr gave a yellow-brown oily solid at the furnace exit. ^{1}H NMR, ^{2}H NMR and GCMS analysis indicated the presence of *1-phenyl-1,3-butadiyne* **19**, δ_H 2.45 (C≡CH); m/z 126 (M$^+$,100%), 98 (16), 87 (12), 76 (21), 74 (30), 63 (22) and 50 (22), and *4-deuterio-3-(2,2-dideuteriovinyl)-2-phenylthiophene* **22**; δ_H 6.67 (1H, br s, vinyl-H); δ_D 7.50 (1D, s, ArD), 5.68 (1D, s, vinyl-D) and 5.34 (1D, s, vinyl-D); m/z 189 (M$^+$,100%), 172 (9), 154 (15), 144 (12), 121 (15), 117 (23), 103 (23) and 77 (30).

2.4 Preparation of Methoxythienyl Cinnamoyl Ylides

2.4.1 3-Methoxy-2-thiophenemethanol 23 [24]

A solution of methyl 3-methoxythiophene-2-carboxylate [25] (2.0 g, 12 mmol) in dry diethyl ether (75 cm^3) was added dropwise to a stirred suspension of lithium aluminium hydride (0.33 g, 9 mmol) in dry diethyl ether (75 cm^3) under N$_2$. The reaction mixture was heated under reflux for 4 h then cooled. Water (50 cm^3) was added cautiously with stirring. The mixture was extracted with diethyl ether (3 × 50 cm^3), the combined extracts washed with water, dried with anhydrous Na$_2$CO$_3$, and evaporated to give the product (1.38 g, 80%) as a clear, colourless oil, unstable to distillation. (HRMS: Found M$^+$ 144.0240. C$_6$H$_8$O$_2$S requires M, 144.0245); ν_{max}/cm^{-1} 3392, 1559, 1382, 1252, 1154, 1116, 1000, 872, 707 and 667; δ_H 7.14 (1H, d, J 6, 5-H), 6.83 (1H, d, J 6, 4-H), 4.70 (2H, s, CH$_2$), 3.85 (3H, s, OMe) and 2.15 (1H, s, OH); δ_C 155.1 (C-3), 123.3 (C-5), 119.5 (C-2), 116.4 (C-4), 58.9 (CH$_2$) and 56.1 (OMe); m/z 144 (M$^+$, 79%), 127 (100), 115 (7), 111 (28), 100 (6), 97 (8), 85 (11) and 75 (33).

2.4.2 (3-Methoxy-2-thienylmethyl)triphenylphosphonium chloride 24

A solution of 3-methoxy-2-thiophenemethanol **23** (13.45 g, 93 mmol) and triphenylphosphine (60.0 g, 228 mmol) in dry acetonitrile (60 cm^3) was stirred under N$_2$ at 70 ºC while dry carbon tetrachloride (9.0 cm^3, 93 mmol) was added steadily *via* a syringe. A vigorous exothermic reaction resulted. The solution was heated under

reflux for a further 2 h, during which time a creamy white precipitate formed. This was filtered off, washed with cold acetonitrile and recrystallised from acetonitrile to give the product (27.60 g, 70%) as colourless prisms, mp 233–234.5 ºC; (Found: C, 67.9; H, 5.0. $C_{24}H_{22}ClOPS$ requires C, 67.8; H, 5.2%); ν_{max}/cm^{-1} 1587, 1554, 1439, 1389, 1260, 1112, 1049, 997, 928, 812, 738 and 691; δ_H 7.98–7.84 (3H, m, Ph), 7.82–7.64 (12H, m, Ph), 7.33 (1H, dd, J 6, 3, 5-H), 6.91 (1H, d, J 6, 4-H), 4.98 (2H, d, J 11, CH_2P) and 3.48 (3H, s, OMe); δ_C 159.3 (d, J 9, C-3), 136.6 (d, J 2, C-4 of Ph), 135.4 (d, J 10, C-2 of Ph), 131.5 (d, J 13, C-3 of Ph), 127.0 (d, J 5, C-5), 119.6 (d, J 85, C-1 of Ph), 116.9 (d, J 3, C-4), 103.8 (d, J 10, C-2), 58.9 (OMe) and 22.9 (d, J 53, CH_2); δ_P +20.6.

2.4.3   4-Methoxy-3-thiophenemethanol 27 [24]

This was prepared as in 2.4.1 using methyl 4-methoxythiophene-3-carboxylate [20] (0.40 g, 2.3 mmol) and lithium aluminium hydride (0.10 g, 2.6 mmol) to give the product (0.3 g, 91%) as a clear, colourless oil, bp (oven temp.) 70 ºC at 0.6 Torr (HRMS: Found M^+ 144.0239. $C_6H_8O_2S$ requires M, 144.0245); ν_{max}/cm^{-1} 3382, 2933, 1562, 1479, 1413, 1348, 1208, 1179, 1133, 1040, 857, 781, 731 and 602; δ_H 7.20 (1H, d, J 3, 2-H), 6.43 (1H, d, J 3, 5-H), 4.57 (2H, s, CH_2), 3.83 (3H, s, OMe) and 2.19 (1H, s, OH); δ_C 156.3 (C-4), 132.8 (C-3), 122.1 (C-2), 97.1 (C-5), 58.3 and 57.4; m/z 144 (M^+, 100%), 127 (32), 115 (34), 111 (35), 101 (10), 97 (10), 84 (9), 73 (9) and 55 (7).

2.4.4   (4-Methoxy-3-thienylmethyl)triphenylphosphonium chloride 28

This was prepared as in 2.4.2 using 4-methoxy-3-thiophenemethanol 27 (3.5 g, 24 mmol), triphenylphosphine (12.59 g, 48 mmol), acetonitrile (30 cm^3) and carbon tetrachloride (2.34 cm^3, 24 mmol) to give the product (5.3 g, 52%) as colourless prisms, mp 266–267 ºC (dec.); (Found: C, 67.5; H, 5.1. $C_{24}H_{22}ClOPS$ requires C, 67.8; H, 5.2%); ν_{max}/cm^{-1} 2022, 1588, 1547, 1439, 1345, 1257, 1227, 1200, 1172, 1046, 997, 891, 866, 824, 767, 751, 721 and 694; δ_H 7.88–7.50 (15H, m, Ph), 7.38 (1H, m, H-2), 6.02 (1H, d, J 5, H-5), 5.27 (2H, d, J 19, CH_2P) and 3.24 (3H, s, OMe); δ_C 156.2 (d, J 2, C-4), 135.2 (d, J 2, C-4 of Ph), 134.5 (d, J 10, C-2 of Ph), 130.3 (d, J 12, C-3 of Ph), 127.4 (d, J 8, C-2), 118.2 (d, J 87, C-1 of Ph), 117.5 (d, J 9, C-3), 96.9 (C-5), 57.2 (OMe) and 22.8 (d, J 50, CH_2P); δ_P +21.2.

2.4.5   [(3-Methoxy-2-thienyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 25

A suspension of (3-methoxy-2-thienylmethyl)triphenylphosphonium chloride 24 (5.0 g, 11.8 mmol) in dry THF (50 cm^3) was stirred under N_2 while a solution of butyllithium in hexanes (4.7 cm^3, 2.5 M, 11.8 mmol) was added. The resulting deep red solution was stirred for a further 2 h before adding a solution of 3-phenylpropenoyl chloride (0.98 g, 5.9 mmol) in dry THF (10 cm^3). After stirring for a further 12 h the mixture was added to water (100 cm^3) and extracted with diethyl ether (2 × 100 cm^3) and ethyl acetate (2 × 200 cm^3). The combined extracts were washed with water (100 cm^3), dried and evaporated to give a red oil which crystallised on cooling with dry ice to give a red-brown crystalline solid. This was recrystallised from ethyl acetate to give the product (1.97 g, 64%) as yellow-brown prisms, mp 206–209 ºC (dec.) (Found: C, 76.1; H, 5.2. $C_{33}H_{27}O_2PS$ requires C, 76.4; H, 5.3%); ν_{max}/cm^{-1} 1631, 1559, 1520, 1437, 1382, 1348, 1266, 1202, 1110, 1065, 974, 888, 828, 738 and 689; δ_H 7.69–7.59 (6H, m, Ph), 7.52–7.34 (12H, m, ArH, Ph

and vinyl-H), 7.29–7.18 (3H, m, ArH), 7.07 (1H, d, J 16, vinyl-H), 6.99 (1H, dd, J 6, 1, 5'-H), 6.50 (1H, d, J 6, 4'-H) and 3.38 (3H, s, OMe); δ_C 182.0 (d, J 9, CO), 155.8 (d, J 6, thienyl C-3), 137.2 (C-1 of C-Ph), 134.8 (CH), 133.8 (d, J 10, C-2 of PPh), 131.6 (d, J 2, C-4 of PPh), 128.5 (2CH), 128.4 (d, J 13, C-3 of PPh), 128.1 (2CH), 127.8 (CH), 126.9 (d, J 90, C-1 of PPh), 126.2 (d, J 12, -CH=), 124.0 (d, J 3, thienyl C-5), 117.8 (d, J 13, thienyl C-2), 115.9 (d, J 2, thienyl C-4), 62.3 (d, J 113, C=P) and 58.1 (OMe); δ_P +17.8; m/z 518 (M$^+$,19%), 503 (3), 487 (6), 368 (5), 277 (100), 262 (39), 240 (17), 201 (20), 183 (38) and 152 (12).

2.4.6 [(3-Methoxy-2-thienyl)(3-(5-methyl-2-thienyl)propenoyl)methylene]tri--phenylphosphorane 26

This was prepared as in 2.4.5 using (3-methoxy-2-thienylmethyl)triphenylphosphonium chloride 24 (9.0 g, 21 mmol), butyllithium in hexanes (8.4 cm^3, 2.5 M, 21 mmol) and 3-(5-methyl-2-thienyl)propenoyl chloride [26] (2.05 g, 10.5 mmol) to give the product (0.97 g, 23%) as yellow-orange needles, mp 184–185.5 ºC (Found: C, 71.1; H, 5.0. C$_{32}$H$_{27}$O$_2$PS$_2$ requires C, 71.4; H, 5.1%); ν_{max}/cm^{-1} 1620, 1551, 1502, 1361, 1209, 1107, 1067, 962, 883, 803, 747, 720 and 692; δ_H 7.75–7.67 (6H, m, Ph), 7.67–7.34 (10H, m, Ph and vinyl-H), 7.02 (1H, dd, J 6, 2, 5'-H), 6.83 (1H, d, J 5, 3-H), 6.79 (1H, d, J 16, vinyl-H), 6.60 (1H, d, J 5, 4-H), 6.52 (1H, d, J 6, 4'-H), 3.40 (3H, s, OMe) and 2.42 (3H, s, ArMe); δ_C 182.0 (d, J 8, CO), 155.8 (d, J 5, MeO-thienyl C-3), 140.7 (C), 140.5 (C), 133.8 (d, J 10, C-2 of PPh), 131.6 (d, J 2, C-4 of PPh), 128.6 (CH), 128.5 (d, J 13, C-3 of PPh), 128.3 (CH), 127.0 (d, J 91, C-1 of PPh), 126.0 (CH), 124.4 (d, J 11, -C=), 124.1 (d, J 4, MeO-thienyl C-5), 117.8 (d, J 12, MeO-thienyl C-2), 115.9 (d, J 2, MeO-thienyl C-4), 61.9 (d, J 115, C=P), 58.1 (OMe) and 15.7 (Me); δ_P +17.8; m/z 538 (M$^+$, 18%), 507, (6), 277 (18), 262 (40), 183 (28), 151 (28), 111 (33), 91 (72), 71 (65) and 57 (100).

2.4.7 [(4-Methoxy-3-thienyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 29

This was prepared as in 2.4.5 using (4-methoxy-3-thienylmethyl)triphenylphosphonium chloride 28 (5.0 g, 11.8 mmol), butyllithium in hexanes (4.7 cm^3, 2.5 M, 11.8 mmol) and 3-phenylpropenoyl chloride (0.98 g, 5.9 mmol) to give a yellow crystalline powder which was recrystallised from ethyl acetate to give the product (2.24 g, 73%) as yellow prisms, mp 238–240 ºC (dec.) (Found: C, 76.1; H, 5.2. C$_{33}$H$_{27}$O$_2$PS requires C, 76.4; H, 5.3%); ν_{max}/cm^{-1} 1627, 1545, 1511, 1437, 1348, 1186, 1152, 1107, 1071, 1032, 976, 934, 858, 848, 783, 762, 751, 726 and 694; δ_H 7.69–7.58 (6H, m, Ph), 7.51–7.38 (12H, m, ArH, Ph and vinyl-H), 7.28–7.17 (3H, m, ArH), 6.97 (1H, dd, J 4, 3, 2'-H), 6.93 (1H, d, J 16, vinyl-H), 5.84 (1H, d, J 4, 5'-H) and 3.31 (3H, s, OMe); δ_C 180.7 (d, J 8, CO), 157.9 (thienyl C-4), 137.3 (C-1 of C-Ph), 134.5 (CH), 133.9 (d, J 10, C-2 of PPh), 131.6 (d, J 2, C-4 of PPh), 129.4 (d, J 11, thienyl C-3), 128.5 (2CH), 128.4 (d, J 12, C-3 of PPh), 128.1 (2CH), 127.8 (CH), 127.1 (d, J 8, thienyl C-2), 126.9 (d, J 91, C-1 of PPh), 126.2 (d, J 12, -CH=), 95.3 (thienyl C-5), 66.1 (d, J 111, C=P) and 56.7 (OMe); δ_P +15.5; m/z 518 (M$^+$,21%), 386 (9), 368 (20), 326 (6), 277 (7), 262 (38), 236 (35), 208 (11), 183 (20), 152 (16), 131 (20), 111 (30), 97 (55), 83 (67), 69 (97) and 57 (100).

2.5 Preparation of Methylthienylacryloyl Ylides

2.5.1 3-(3-Methyl-2-thienyl)propenoyl chloride 33

A mixture of 3-(3-methyl-2-thienyl)propenoic acid [27] (5.00 g, 30 mmol) and oxalyl chloride (3.92 cm^3, 45 mmol) was heated under reflux for 2 h. The oxalyl chloride was removed under reduced pressure and the residue kugelrohr distilled to give the product (5.47g, 98%) as lemon-yellow needles, mp 64–66 ºC (Found: C, 51.8; H, 3.5. C$_8$H$_7$ClOS requires C, 51.5; H, 3.8%); ν_{max}/cm^{-1} 1731, 1592, 1412, 1274, 1246, 1088, 1045, 965, 936, 800, 742, 696, 655 and 629; δ_H 7.97 (1H, d, J 16, vinyl-H), 7.42 (1H, d, J 7, 5-H), 6.94 (1H, d, J 7, 4-H), 6.34 (1H, d, J 16, vinyl-H) and 2.39 (3H, s, Me); δ_C 165.9 (CO), 145.4 (C), 141.3 (CH), 132.8 (C), 131.9 (CH), 130.5 (CH), 119.5 (CH) and 14.4 (Me); m/z 188 (^{37}Cl-M$^+$, 7%), 186 (^{35}Cl-M$^+$, 22%), 168 (9), 151 (100), 123 (25), 97 (5) and 79 (11).

2.5.2 [(3-(3-Methyl-2-thienyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 35

A suspension of (2-methylthiobenzyl)triphenylphosphonium bromide **31** (8.0 g, 16.7 mmol) in dry THF (70 cm^3) was stirred under N$_2$ while a solution of butyllithium in hexanes (6.7 cm^3, 2.5 M, 16.7 mmol) was added. The resulting deep red solution was stirred for a further 2 h before adding a solution of 3-(3-methyl-2-thienyl)propenoyl chloride **33** (1.56 g, 8.3 mmol) in dry THF (10 cm^3). After stirring for a further 18 h the mixture was added to water (200 cm^3) and extracted with diethyl ether (2 × 100 cm^3) and ethyl acetate (2 × 100 cm^3). The combined extracts were washed with water (100 cm^3), dried and evaporated to give an orange solid which was recrystallised from ethyl acetate to give the product (3.90 g, 86%) as bright yellow-orange prisms, mp 220–222 ºC (Found: C, 74.4; H, 5.1. C$_{34}$H$_{29}$OPS$_2$ requires C, 74.4; H, 5.3%); ν_{max}/cm^{-1} 1614, 1500, 1435, 1355, 1197, 1099, 1078, 978, 961, 921, 852, 790, 755, 714 and 699; δ_H 7.82–7.52 (6H, m, Ph), 7.63 (1H, d, J 16, vinyl-H), 7.52–7.26 (9H, m, Ph), 7.08 (1H, t, J 8, 4'-H), 7.00 (1H, d, J 8, 6'-H), 6.95 (1H, d, J 7, 5-H), 6.90 (1H, d, J 8, 3'-H), 6.80 (1H, t, J 8, 5'-H), 6.72 (1H, d, J 7, 4-H), 6.44 (1H, d, J 16, vinyl-H) and 2.21 (6H, s, Me and SMe); δ_C 180.3 (d, J 6, CO), 145.2 (d, J 5, MeSC$_6$H$_4$ C-2), 137.9 (C), 136.5 (CH), 136.3 (d, J 3, CH), 135.0 (d, J 11, MeSC$_6$H$_4$ C-1), 134.0 (d, J 10, C-2 of PPh), 131.6 (d, J 3, C-4 of PPh), 130.9 (C), 128.4 (d, J 12, C-3 of PPh), 127.5 (d, J 3, CH), 127.0 (d, J 90, C-1 of PPh), 126.0 (d, J 9, CH), 125.7 (d, J 13, -CH=), 123.7 (CH), 123.5 (CH), 123.0 (CH), 71.4 (d, J 109, C=P), 15.3 (SMe) and 14.1 (Me); δ_P +15.7; m/z 548 (M$^+$, 31%), 533 (15), 501 (100), 405 (7), 383 (5), 277 (7), 262 (35), 250 (9), 183 (26), 151 (7) and 108 (8).

2.5.3 [(3-(3-Methyl-2-thienyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 34

This was prepared as in 2.5.2 using (2-methoxybenzyl)triphenylphosphonium bromide **30** (8.0 g, 17.0 mmol), butyllithium in hexanes (6.8 cm^3, 2.5 M, 17.0 mmol) and 3-(3-methyl-2-thienyl)propenoyl chloride **33** (1.61 g, 8.6 mmol) to give the product (4.16 g, 91%) as bright orange prisms, mp 227–229 ºC (Found: C, 76.5; H, 5.25. C$_{34}$H$_{29}$O$_2$PS requires C, 76.7; H, 5.5%); ν_{max}/cm^{-1} 1620, 1589, 1495, 1435, 1359, 1241, 1201, 1106, 1073, 1051, 1027, 961, 854, 802, 747 and 695; δ_H 7.70–7.49 (7H, m, Ph and vinyl-H), 7.48–7.25 (10H, m, 6'-H and Ph), 7.05 (1H, t, J 8, 4'-H), 6.93 (1H, d, J 7, 5-H), 6.80 (1H, t, J 8, 5'-H), 6.70 (1H, d, J 7, 4-H), 6.63 (1H, d, J 16, vinyl-H), 6.40 (1H, d, J 8, 3'-H), 3.22 (3H, s, OMe) and 2.21 (3H, s, Me); δ_C 179.6 (d, J 5, CO), 158.9 (d, J 3, MeOC$_6$H$_4$ C-2), 137.6 (C), 137.4 (d, J 6, CH), 136.7 (CH), 133.8 (d, J 10, C-2 of PPh), 131.4 (d, J 2, C-4 of PPh), 130.9 (C), 128.3 (d, J 12, C-3 of PPh), 128.0 (d, J 2, CH), 127.3 (d, J 91, C-1 of PPh), 126.5 (d, J 11, MeOC$_6$H$_4$ C-

1), 125.7 (d, *J* 12, -CH=), 125.6 (CH), 123.6 (CH), 120.3 (CH), 110.1 (d, *J* 2, CH), 70.1 (d, *J* 110, C=P), 54.3 (OMe) and 14.1 (Me); δ_P +15.4; *m/z* 532 (M$^+$, 52%), 501 (100), 367 (22), 277 (21), 262 (62), 201 (7), 183 (40), 165 (7) and 151 (14).

2.5.4 [(3-(3-Methyl-2-thienyl)propenoyl)(2-trideuteriomethoxyphenyl)methyl--ene]triphenylphosphorane 36

This was prepared as in 2.5.2 using (2-trideuteriomethoxybenzyl)triphenylphosphonium bromide **32** (2.0 g, 4.3 mmol), butyllithium in hexanes (1.7 cm^3, 2.5 M, 4.3 mmol) and 3-(3-methyl-2-thienyl)propenoyl chloride **33** (0.41 g, 2.2 mmol) to give the product (1.04 g, 88%) as bright yellow prisms, mp 227–230 ºC; ν_{max}/cm^{-1} 2065, 1619, 1495, 1490, 1376, 1266, 1245, 1201, 1100, 747 and 695; δ_D 3.24 (OCD$_3$); δ_H 7.64–7.52 (7H, m, Ph and vinyl-H), 7.48–7.26 (10H, m, 6'-H and Ph), 7.06 (1H, t, *J* 7, 4'-H), 6.94 (1H, d, *J* 6, 5-H), 6.81 (1H, t, *J* 5'-H), 6.71 (1H, d, *J* 6, 4-H), 6.63 (1H, d, *J* 16, vinyl-H), 6.41 (1H, d, *J* 7, 3'-H) and 2.20 (3H, s, Me); δ_C identical to **34** save for the absence of the signal at 54.3; δ_P +15.4; *m/z* 535 (M$^+$, 48%), 501 (100), 368 (20), 277 (15), 262 (69), 183 (58), 151 (22) and 69 (77).

2.6 Pyrolysis of Methylthienylacryloyl Ylides

2.6.1 FVP of [(3-(3-methyl-2-thienyl)propenoyl(2-methoxyphenyl)methylene]triphenylphosphorane 34

FVP of the title compound (0.5 g) at 800 ºC and 5.0–7.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow oil. GCMS, ^{1}H NMR, ^{13}C NMR and HRMS analysis indicated a mixture of three main products;

1. *5-benzylbenzothiophene* **37** (63%) (HRMS: Found M$^+$ 224.0652. C$_{15}$H$_{12}$S requires *M*, 224.0660); δ_H 4.03 (2H, s, CH$_2$); δ_C 41.8 (CH$_2$); *m/z* 224 (M$^+$, 99%), 206 (10), 189 (16), 179 (17), 147 (100), 111 (37) and 89 (72).

2. *5-(α-methylbenzyl)benzothiophene* **38** (21%) (HRMS: Found M$^+$ 238.0819. C$_{16}$H$_{14}$S requires *M*, 238.0816); δ_H 4.23 (1H, q, *J* 7, CH) and 1.64 (3H, d, *J* 7, CH$_3$); δ_C 44.7 (CH) and 22.1 (CH$_3$); *m/z* 238 (M$^+$, 44%), 223 (100), 208 (10), 189 (22), 179 (25), 111 (51), 89 (50) and 77 (58).

3. *fluoreno[3,4-b]thiophene* **39** (16%) (HRMS: Found M$^+$ 222.0512. C$_{15}$H$_{10}$S requires *M*, 222.0503); δ_H 3.90 (2H, s, CH$_2$); δ_C 37.2 (CH$_2$); *m/z* 222 (M$^+$, 100%), 189 (23), 176 (17), 150 (9), 111 (73) and 88 (23).

2.6.2 FVP of [(3-(3-methyl-2-thienyl)propenoyl)(2-methylthiophenyl)methyl-ene]triphenylphosphorane 35

FVP of the title compound (0.5 g) at 800 ºC and 2.0–7.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow oil. GCMS, ^{1}H NMR, and ^{13}C NMR analysis suggested a mixture of three main products:

1. *5-benzylbenzothiophene* **37** (52%); δ_H 4.01 (2H, s, CH$_2$); δ_C 41.8 (CH$_2$); *m/z* 224 (M$^+$, 95%), 208 (8), 189 (16), 179 (18), 147 (100), 111 (40) and 89 (68).

2. *5-(α-methylbenzyl)benzothiophene* **38** (23%); δ_H 4.19 (1H, q, *J* 7, CH) and 1.62 (3H, d, *J* 7, CH$_3$); δ_C 44.6 (CH) and 22.0 (CH$_3$); *m/z* 238 (M$^+$, 42%), 223 (100), 208 (9), 189 (19), 179 (26), 111 (67), 89 (72) and 77 (83).

3. *fluoreno[3,4-b]thiophene* **39** (25%); δ_H 3.82 (2H, s, CH$_2$); δ_C 37.1 (CH$_2$); *m/z* 222 (M$^+$, 90%), 189 (24), 176 (18), 150 (12), 110 (100), 98 (39) and 88 (40).

*2.6.3 FVP of [(3-(3-methyl-2-thienyl)propenoyl)(2-trideuteriomethoxyphenyl)meth-ylene]triphenylphosphorane* **36**

FVP of the title compound (0.5 g) at 800 ºC and 2.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow oil. GCMS, ^{1}H NMR, ^{2}H NMR and ^{13}C NMR analysis indicated a mixture of four products;

1. *5-benzylbenzothiophene* **37** δ_H 4.01 (2H, s, CH2); δ_C 41.8 (CH$_2$); *m/z* 224 (M$^+$, 100%).

2. *5-(α-deuteriobenzyl)benzothiophene* **40** δ_H 4.00 (1H, s, CHD); δ_D 4.18 (1D, d, *J* 2, CHD); δ_C 41.5 (t, *J* 20, CHD); *m/z* 225 (M$^+$, 100%).

3. *5-(α-trideuteriomethylbenzyl)benzothiophene* **41** δ_H 4.18 (1H, CH); δ_D 1.79 (3D, s, CD$_3$); δ_C 44.4 (CH); *m/z* 241 (M$^+$, 33%), 223 (100).

4. *fluoreno[3,4-b]thiophene* **39** δ_H 3.87 (2 H, CH$_2$); δ_C 37.2 (CH$_2$); *m/z* 222 (M$^+$, 100%).

3   Results and discussion

3.1   Synthesis and FVP of simple methoxythenoyl ylides

A series of methoxythenoyl ylides **8–13** were readily prepared by acylation of either benzylidene- or 1-propylidene-triphenylphosphorane in THF with the appropriate methoxythenoyl chlorides (Scheme 3). While 3-methoxy-2-thenoyl chloride required for **8** and **9** [21] and 2-methoxy-3-thenoyl chloride required for **13** [22] have been previously described, 4-methoxy-3-thenoyl chloride required for **10** and **12**, as well as its deuterium-labelled analogue required for **11**, have not. They were prepared by treatment of the corresponding 4-methoxythiophene-3-carboxylic acids with thionyl chloride and obtained as low melting solids.
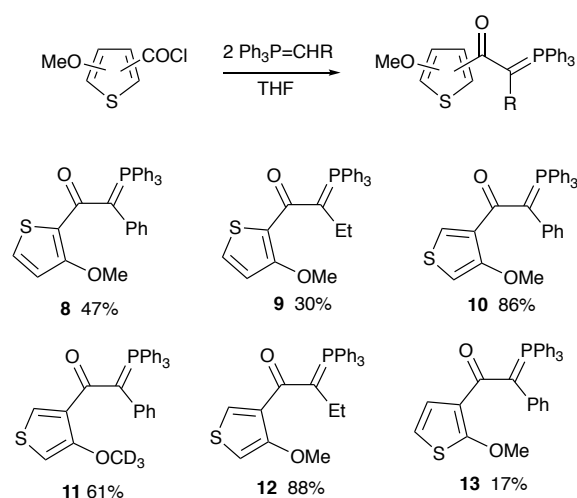

Scheme 3. Simple methoxythenoyl ylides prepared

The ylides **8–13** were obtained as high-melting crystalline solids which were stable on storage and showed the expected spectroscopic properties including ^{31}P NMR signals in the range +15.6–17.3 ppm and ^{13}C NMR spectra with phosphorus coupling

extending throughout the *P*-phenyl groups, the oxo ylide function and to at least the first carbon of both Ph/Et and thienyl groups. Importantly for the planned extrusion of Ph₃PO under FVP conditions, the value of the phosphorus coupling to the carbonyl group, $^2J_{p-CO}$ was 6–8 Hz, meaning that the extrusion should proceed readily since we recently showed [28] an empirical correlation with a cut off of 10 Hz.

The expected process upon FVP of ylides **8** and **9** (Scheme 4) involves cyclisation of the alkyne-containing thienyloxy radical to give the thieno[3,2-*b*]furyl radical which then gives an isolable product in which the substituent may be the same or different. According to our previous work [29,30], ylides with R = Ph should give the furan product with R^1 = Ph by simple hydrogen atom abstraction from the environment, while for R = Et, the main product should be R^1 = vinyl formed by intramolecular hydrogen atom abstraction and loss of H·.
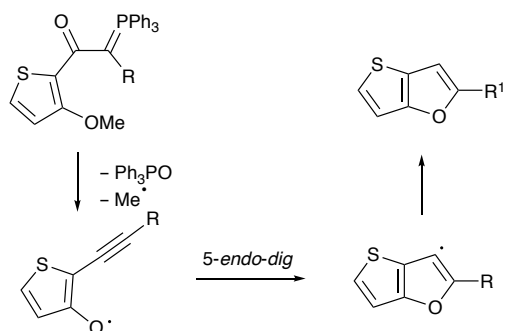
Scheme 4. Expected mechanism of formation of thieno[3,2-*b*]furans

For the ylides **8** and **9** and also the isomeric system **12**, FVP at 800 °C resulted in complete reaction to give, after chromatographic separation of Ph₃PO, heterocyclic products with the expected thienofuran structures (Scheme 5). In the case of **8**, the product was fully characterised as 2-phenylthieno[3,2-*b*]furan **14** formed in moderate yield. It should be noted that there is a single literature report of this compound [31], but the spectroscopic data given there appears to be erroneous, particularly the absence of the expected two ^{13}C NMR signals above 150 ppm for the quaternary carbons directly attached to oxygen which for our product appeared at 158.0 and 157.8 ppm.
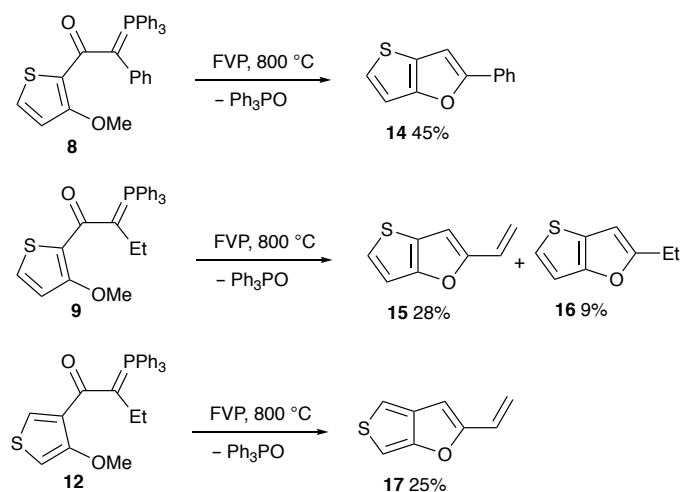
Scheme 5. FVP of ylides **8**, **9** and **12** to give thienofuran products

For the ethyl ylide **9**, the product was obtained as an oil consisting of a mixture of components but the major product was identified spectroscopically as the expected 2-vinylthieno[3,2-*b*]furan **15** accompanied by a little of the corresponding ethyl compound **16** formed by hydrogen atom abstraction by the intermediate radical. In the case of the isomeric system **12**, chromatographic separation followed by vacuum distillation gave 2-vinylthieno[3,4-*b*]furan in pure form as an unstable liquid.

To our surprise, the phenyl ylide **10** with the structure analogous to **12**, behaved in a completely different way. Initial FVP at 800 °C led to formation of Ph₃PO but the other products were clearly not the expected thienofuran and could not be immediately identified. For this reason, FVP at the lower temperature of 725°C was examined and the deuterium labelled analogue **11** was also prepared. Chromatographic separation of the product mixture obtained at 725 °C (Scheme 6) gave the alkyne **20** expected from extrusion of Ph₃PO, together with 2-phenyl-3-vinylthiophene **18** and 1-phenylbuta-1,3-diyne **19**. The identity of the diyne was confirmed by excellent agreement of both ^{1}H and ^{13}C NMR data with reported values [23]. The isolation of alkyne **20** and the fact that it was converted into **18** and **19** upon being re-subjected to FVP at 800 °C strongly suggest that the first stage of the pyrolytic process is proceeding as expected and that compounds **18** and **19** are formed as a result of secondary pyrolytic breakdown of **20.**
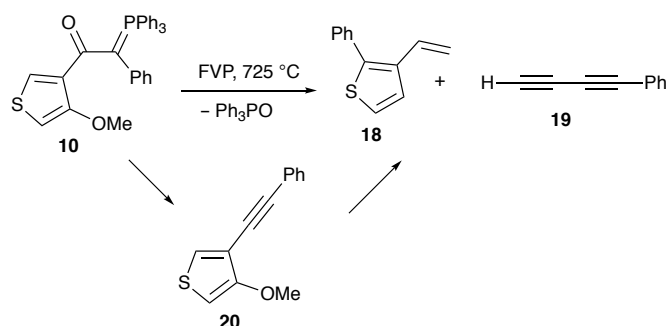

Scheme 6. Anomalous behaviour of ylide **10** upon FVP

It was therefore of great interest to examine FVP of the deuterium-labelled ylide **11**. At 725 °C it gave the labelled alkyne **21** together with unlabelled phenylbutadiyne **19** and 2-phenyl-3-vinylthiophene **22** bearing two deuterium atoms on the terminal position of the vinyl group and a third on position 4 of the thiophene ring (Scheme 7). As for the unlabelled pyrolysis mixture, re-pyrolysis at 800 °C led to complete conversion of **21** into **19** and **22**.
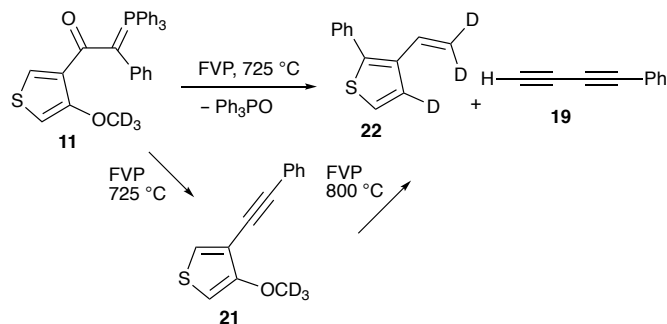

Scheme 7. Result of FVP of the deuterium-labelled ylide **11**

Based on these results, and particularly the fact that **19** is formed in unlabelled form, we believe that the diyne results from fragmentation of **21** (or **20**) as shown in Scheme 8.
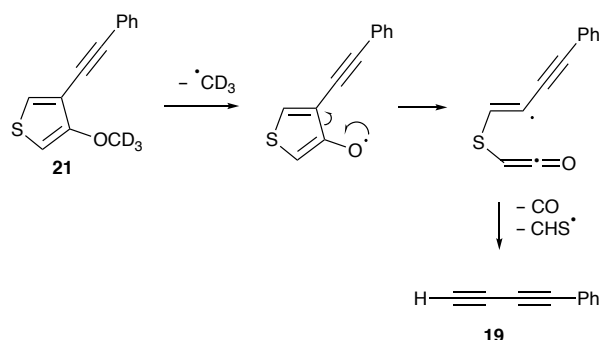
Scheme 8. Suggested mechanism for formation of diyne **19**

The formation of **18** is more surprising and harder to explain but a mechanism that is consistent with the deuterium labelling pattern of **22** is shown in Scheme 9. The key feature of this is isomerisation of the alkyne function in **21** (or **20**) to a vinylidene, a well precedented process under these conditions [32], and then triplet reactivity of this leading to a series of radical abstraction and rearrangement steps.
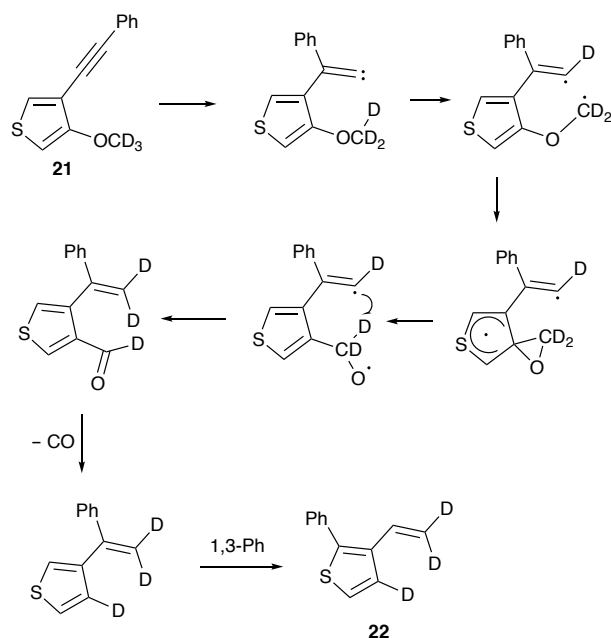
Scheme 9. Proposed mechanism for formation of labelled vinylthiophene **22**

Finally, in this section, FVP of the ylide **13**, isomeric with **8** and **10** did not lead to any useful products. There was extensive decomposition at 75 °C to give products including Ph_3PO, Ph_3P and Ph_3PS together with biphenyl and dibenzothiophene.

3.2 Synthesis and FVP of methoxythienyl cinnamoyl ylides

Based on the encouraging cyclisation behaviour observed for ylides **8** and **9** and to a lesser extent **10** and **12**, synthesis of extended analogues capable of domino

cyclisation to give polycyclic products was now planned. Since **13** did not give good results, no extended ylides with the 2-methoxy-3-thienyl structure were examined.

In contrast to the simple ylides which could be prepared in one step from a commercial phosphonium salt and a thiophene-containing acid chloride, the extended ylides required the methoxythiophene group to be located in the phosphonium salt and thus involved multi-stage synthesis (Scheme 10). As we noted some time ago [24], attempted lithium aluminium hydride reduction of methoxythiophene esters is not without complication. Any contact of compounds such as **23** with acid leads to oligomerisation so completely non-acidic conditions must be used. The readily available methyl 3-methoxythiophene-2-carboxylate [25] was thus reduced with a neutral/basic work-up [24] to give **23** and this was followed by combined chlorination and phosphonium salt formation, also under non-acidic conditions using Ph_3P/CCl_4. The resulting phosphonium salt **24** was then deprotonated and acylated with 0.5 equiv. of either cinnamoyl chloride or the thiophene-containing analogue [26] to give, respectively, ylides **25** and **26**.
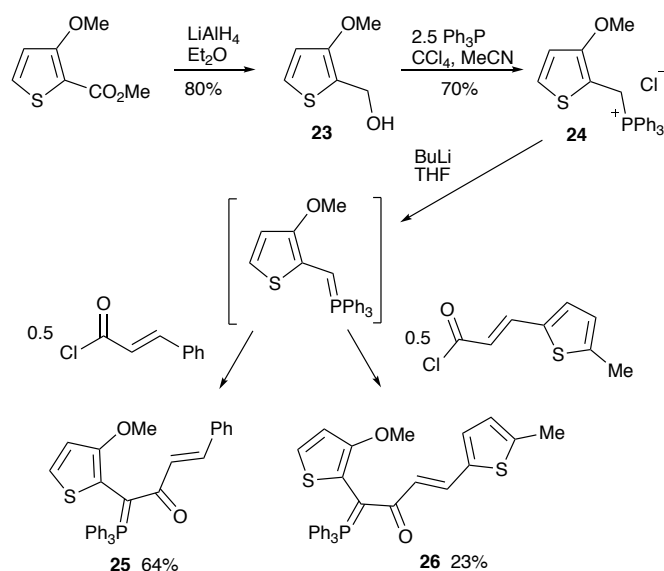
Scheme 10. Synthesis of extended methoxythienyl ylides **25** and **26**

The ylide **29** with the isomeric structure was likewise prepared (Scheme 11) starting from methyl 4-methoxythiophene-3-carboxylate [20] by $LiAlH_4$ reduction under non-acidic conditions [24] to give **27**, chlorination and phosphonium salt formation to give **28** followed by deprotonation and treatment with 0.5 equiv. cinnamoyl chloride. The three ylides **25**, **26** and **29** were obtained as high-melting stable crystalline solids with values of $^2J_{\text{P–CO}}$ of 8–9 Hz leading us to predict [28] successful extrusion of Ph_3PO upon FVP.
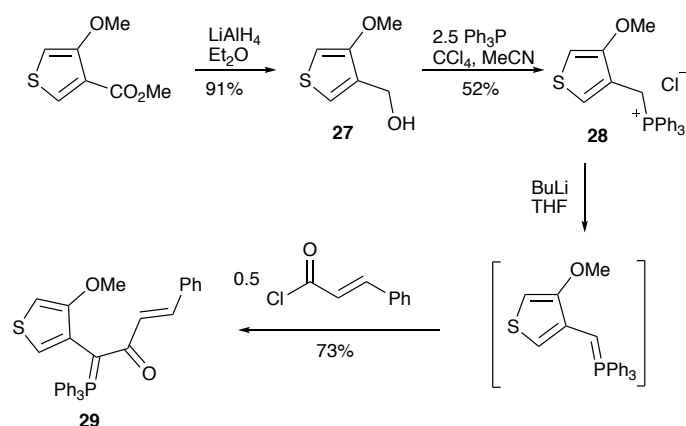
Scheme 11. Synthesis of extended methoxythienyl ylide **29**

Unfortunately, however no useful products were obtained from FVP of any of the three ylides. In each case there was extensive decomposition in the range 700–750 °C with no identifiable heterocyclic products obtained.

3.3   Synthesis and FVP of methoxythienylacryloyl ylides

In a previous study, ylides bearing a 2-methylcinnamoyl group were found to give rise to naphthalenes upon FVP in a process involving incorporation of the methyl group into a benzene ring at the stage of the 2-methylstyrylalkyne [33,34]. In a single example the same reaction was also observed for a thiophene analogue. We wanted to see whether this behaviour could be combined with benzofuran or benzothiophene formation in a single domino cyclisation process and so designed the ylides **34** and **35** containing both the required features. The new acid chloride **33** was first prepared by treating the corresponding acrylic acid [27] with oxalyl chloride and fully characterised. This was then used to acylate the ylides derived by treatment of phosphonium salts **30** and **31** with butyllithium to give **34** and **35** respectively Scheme 12). In order to elucidate the unexpected pyrolysis behaviour, the deuterium-labelled salt **32** was similarly used to generate the labelled ylide **36**. All three ylides were formed in excellent yield as stable solids and the $^2J_{P-CO}$ values of 5–6 Hz again suggested successful thermal extrusion of Ph$_3$PO [28].
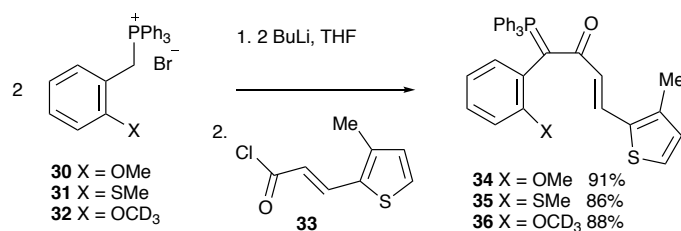

Scheme 12. Synthesis of 3-methyl-2-thienylacryloyl ylides **34–36**

In the event, FVP of both the OMe ylide **34** and the SMe ylide **35** led to complete reaction at 800 °C and, most surprisingly, the products were the same in each case (Scheme 13). Chromatographic separation of Ph$_3$PO left a mixture containing 5-benzylbenzothiophene **37**, 5-(α-methylbenzyl)benzothiophene **38** and fluoreno[3,4-*b*]thiophene **39**.
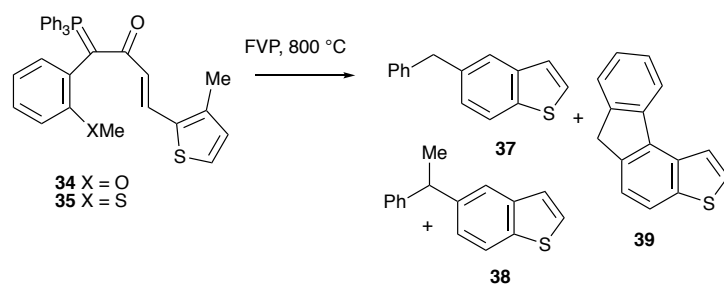
Scheme 13. FVP of ylides **34** and **35**

Interestingly two of these products, **37** and **39** were formed in our previous work [34] by FVP of the ylide with the same structure as **34** or **35** but with XMe replaced by H. The spectroscopic data obtained in the two studies were identical. Since, in addition to explaining the formation of **37** and **39** here, we have to explain the disappearance of the XMe group and also the appearance of the extra methyl group in product **38** the FVP result starting with the deuterium-labelled ylide **36** was of great interest.
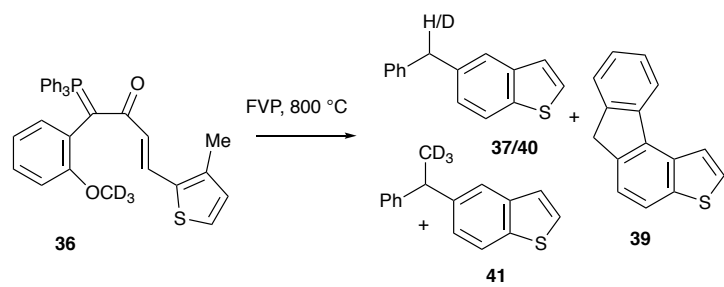

Scheme 14. FVP of deuterium-labelled ylide **36**

When this was performed, it gave a clear result (Scheme 14): the same three products were formed as for the unlabelled compound and by a combination of ^{1}H, ^{2}H and ^{13}C NMR and GCMS analysis, it was determined that 5-benzylbenzothiophene **37** was partly monodeuterated at the benzylic position (**40**), the tetracyclic product **39** was unlabelled and the 5-(α-methylbenzyl)benzothiophene was fully trideuterated, i.e. **41**.

Our proposal for the mechanisms involved which is supported by the deuterium-labelling results (Scheme 15) starts with extrusion of Ph$_3$PO and formation of a thienylmethyl radical which can undergo cyclisation to form **42** already containing the carbon skeleton required for products **37** and **39**. However, in contrast to the previous study, this intermediate now has the OMe/SMe group ideally placed to suffer an intramolecular hydrogen atom abstraction, thus setting in motion a series of steps that ultimately results in loss of the XMe group most likely as CH$_2$X, either formaldehyde or thioformaldehyde. The possibility of 1,3-hydrogen shifts may be used to explain the partial loss of the deuterium atom from the benzylic position. It should be noted that such loss of a methoxy group to be replaced by hydrogen was previously observed in our earlier studies on benzofuran and benzothiophene formation [9]. Once this group is lost formation of products **37** and **39** is readily explained. The only reasonable source of the methyl group in product **38** is from the original OMe or SMe group of the ylides and this was confirmed by the formation of the trideuteriomethyl compound **41** from ylide **36**. Although such an intramolecular process seems inherently unlikely in the gas phase, it has good precedent in this area of work with the formation of benzofuran bearing a 2-CH$_2$CD$_3$ group from a range of

OCD$_3$-containing ylides that gave rise to a benzofurylmethyl radical intermediate [29, 30]. Once the new methyl group has been attached, reactivity is restored to the benzylic centre by formation of a stable radical in order to promote the loss of the adjacent XMe group as before to produce **38**.
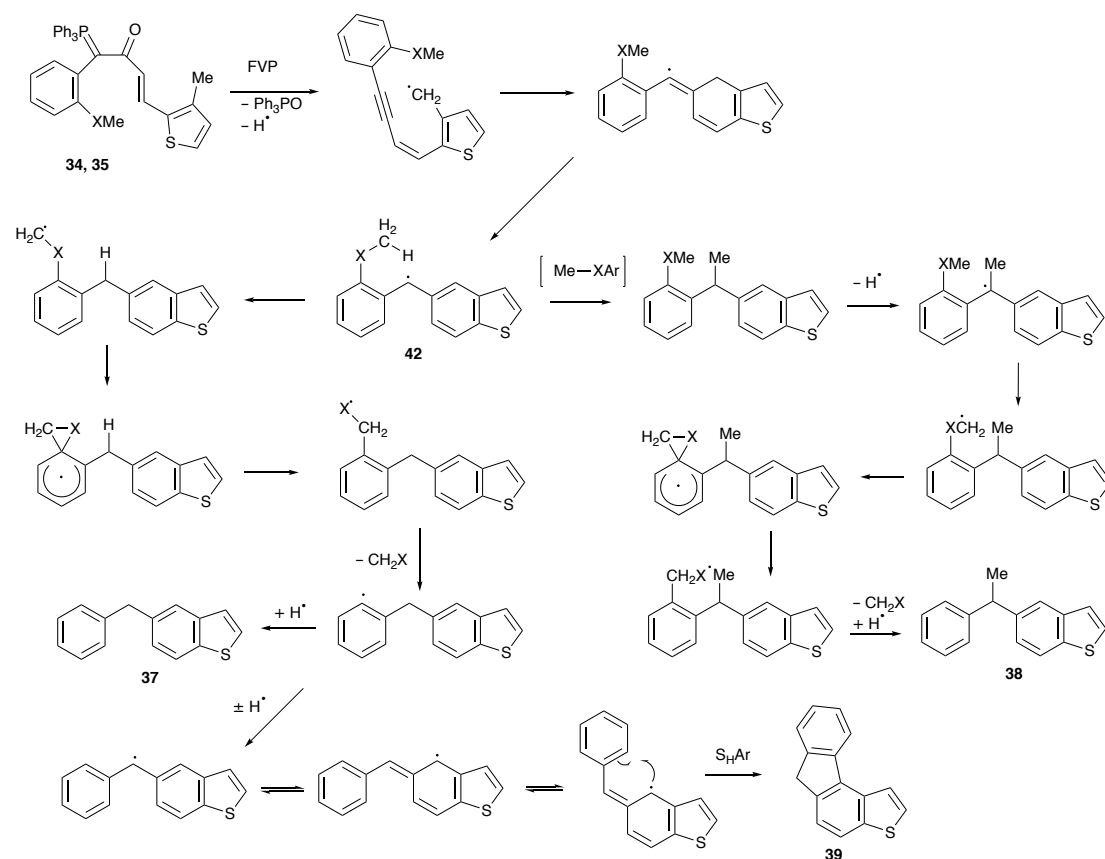
Scheme 15. Proposed mechanism for FVP of **34** and **35** to give **37**, **38** and **39**

4   Conclusion

While the studies on FVP of simpler methoxythienyl ylides **8**, **9** and **12** led to successful formation of the expected thienofuran products, the approach clearly has limitations with the isomeric ylide **13** affording no fused ring product and ylide **10** closely related to **12** giving a completely different and unexpected result which is nonetheless of significant mechanistic interest. Attempts to capitalise on these promising findings by moving to more extended ylides such as **25**, **26** and **29** unfortunately met with failure. The ylides were successfully prepared and characterised but gave no useful products upon FVP probably due to the increased fragility of their structures under the relatively harsh conditions required for reaction. The two ylides **34** and **35**, where two competing thermal cyclisation processes are possible, unexpectedly underwent benzothiophene formation based on cyclisation of the thienylmethyl group with complete loss of the normal cyclisation-initiating groups OMe and SMe, thus giving some idea of the relative ease of these two competing processes.

Acknowledgements

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Highlights

- Ten new oxo-stabilised phosphonium ylides are prepared
- FVP of simple examples gives thieno[3,2-*b*]furan and thieno[3,4-*b*]furan products
- Unexpected fragmentation and rearrangement occurs under milder conditions in one case to give phenylbutadiyne and a phenylvinylthiophene
- FVP of 3-methyl-2-thienylacryloyl ylides gives benzylthiophene and fluoreno[3,4-*b*]thiophene products

Graphical Abstract