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 \( \text{Ph}_3\text{PO} \) coupled with domino cyclisation to give thieno[3,2-\text{b}]furan and thieno[3,4-\text{b}]furan products but the corresponding approach to a thieno[2,3-\text{b}]furan fails. One ylide designed to give a thieno[3,4-\text{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 methoxymethyl ylides failed. Two ylides bearing a 3-methyl-2-thienylacryloyl group gave 5-benzylbenzothiophene, 5-(\( \alpha \)-methylbenzyl)benzothiophene and fluoreno[3,4-\text{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 \( \text{Ph}_3\text{PO} \) 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

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.

Scheme 2. Typical mechanism for generation of a tetracyclic product
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 °C (Found: C, 40.9; H, 2.6. C$_6$H$_5$ClO$_2$S requires C, 40.8; H, 2.9%); $\nu$$_{max}$/cm$^{-1}$ 1781, 1541, 1408, 1389, 1214, 1179, 1150, 1010, 911, 886, 815, 789 and 718; $\delta$$_H$ 8.38 (1H, d, J 3, 2-H), 6.33 (1H, d, J 3, 5-H) and 3.90 (3H, s, OMe); $\delta$$_C$ 158.3 (C), 157.5 (C), 140.5 (CH), 126.5 (C), 99.0 (CH) and 58.2 (Me); m/z 178 ($^{35}$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] (0.18 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 °C; $\delta$$_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 °C (Found: C, 75.4; H, 5.0. C$_3$H$_5$O$_2$PS requires C, 75.6; H, 5.1%); $\nu_{\text{max}}$ cm$^{-1}$ 1592, 1543, 1510, 1351, 1237, 1104, 998, 967, 849, 750 and 690; $\delta_{\text{H}}$ 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); $\delta_{\text{C}}$ 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); $\delta_{\text{H}}$ +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-propyldiene]triphenylphosphorane 9

This was prepared as in 2.2.3 using propyltriphenyolphosphonium 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] (2.3 g, 13.0 mmol) to give the product (1.71 g, 30%) as red-orange crystals, mp 222–224 °C (Found: C, 72.7; H, 5.4. C$_7$H$_{23}$O$_2$PS requires C, 73.0; H, 5.7%); $\nu_{\text{max}}$ cm$^{-1}$ 1542, 1494, 1445, 1235, 1181, 1104, 1047, 1016, 930, 834, 744, 710 and 695; $\delta_{\text{H}}$ 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$_3$); $\delta_{\text{C}}$ 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); $\delta_{\text{H}}$ +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 benzyltriphenyolphosphonium chloride (6.14 g, 15.8 mmol), butyllithium in hexanes (6.34 cm$^3$, 2.5 M, 15.8 mmol) and 4-methoxy-3-thienoyl chloride (1.40 g, 7.9 mmol) to give the product (3.35 g, 86%) as very pale yellow crystals, mp 166–168 °C (Found: C, 75.3; H, 5.0. C$_3$H$_5$O$_2$PS requires C, 75.6; H, 5.1%); $\nu_{\text{max}}$ cm$^{-1}$ 1592, 1491, 1432, 1238, 1216, 1158, 1107, 1030, 1001, 970, 874, 854, 761, 750 and 690; $\delta_{\text{H}}$ 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); $\delta_{\text{C}}$ 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); $\delta_{\text{H}}$ +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 benzyltriphenyolphosphonium chloride (0.78 g, 2 mmol), butyllithium in hexanes (0.8 cm$^3$, 2.5 M, 2 mmol) and 4-trideuteriomethoxy-3-thienoyl 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 (0.5 g, 61%) as very pale yellow crystals, mp 163.5–168
This was recrystallised from ethanol to give the product, oily solid at the furnace exit. Column chromatography of the title compound (1.10 g) at 800 °C; δH 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); δp +15.9.

2.2.7 [(4-Methoxy-3-thenoyl)-1-propyldiene]triphenylphosphorane 12
This was prepared as in 2.2.3 using propyltriphenylphosphonium bromide (6.14 g, 15.9 mmol), butyllithium in hexanes (6.35 cm3, 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 °C (Found: C, 72.8; H, 5.6. C27H23O2PS requires C, 73.0; H, 5.7%). νmax/cm−1 1545, 1495, 1364, 1321, 1276, 1198, 1178, 1153, 1103, 1031, 990, 942, 882, 855, 827, 776, 695 and 623; δH 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, CH2) and 0.63 (3H, t, J 7, CH3); δC 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, CH2) and 18.8 (Me); δp +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)benzyldiene]triphenylphosphorane 13
This was prepared as in 2.2.3 using benzyltriphenylphosphonium chloride (10.00 g, 26 mmol), butyllithium in hexanes (10.4 cm3, 2.5 M, 26 mmol) and 2-methoxy-3-thenoyl chloride [22] (2.30 g, 13 mmol) in dry THF (10 cm3). After stirring for a further 24 h the mixture was added to water (200 cm3) and extracted with diethyl ether (2 × 100 cm3) and ethyl acetate (2 × 75 cm3). The combined extracts were washed with water (100 cm3), 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 °C (Found: C, 75.3; H, 5.5. C33H25O2PS requires C, 75.6; H, 5.1%). νmax/cm−1 1548, 1495, 1440, 1398, 1334, 1267, 1224, 1105, 1002, 969, 933, 762 and 702; δH 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); δC 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); δp +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)benzyldiene]triphenylphosphorane 8
FVP of the title compound (1.10 g) at 800 °C 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 °C/0.01 Torr to give a clear yellow oil which solidified on cooling. This was recrystallised from ethanol to give the product, 2-phenyl thiophene[3,2-b]furan 14 (0.20 g, 45%) as pale brown plates, mp 115–118 °C (Found: C, 72.1; H, 4.1. C12H16O requires C, 72.0; H, 4.0%). (HRMS: found M+, 200.0292. C12H16O requires M, 200.0296; νmax/cm−1 1594, 1335, 1304, 1163, 1043, 1014, 873, 827, 737 and 647; δH 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); δC 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 °C 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 ¹H NMR, ¹³C 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; δH 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); δC: 157.1 (C), 156.2 (C), 131.4 (CH), 125.2 (CH), 124.8 (C), 112.3 (CH₂), 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; δH 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, CH₂) and 1.27 (3H, t, J 8, CH₃); 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 °C 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 to give 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 °C at 0.7 Torr (HRMS: Found M⁺, 150.0133. C₈H₆O₂S requires M⁺, 150.0139); δH 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); δC: 163.1 (C), 156.5 (C), 136.0 (C), 125.9 (CH), 116.2 (CH), 107.6 (CH₂), 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 °C 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 two fractions;
1. A mixture of two products, partially separable by preparative TLC;
   (a) 2-phenyl-3-vinylthiophene 18 (HRMS: Found M⁺, 186.0498. C₁₂H₁₀S requires M⁺, 186.0503); δH 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); δC: 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 (CH₂); 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. C₁₀H₆ requires M⁺, 126.0470); νmax/cm⁻¹ 2200 (C=C; δH 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)]; δC 133.0 (2CH), 129.7 (CH), 128.7 (2CH), 121.3 (C), 75.5 (C=C), 73.6 (C=C), 71.4 (C=C) and 68.3 (C=C) [Lit.
A syringe. A vigorous exothermic reaction resulted. The solution was heated under triphenylphosphine (60.0 g, 228 mmol) in dry acetonitrile (60 cm$^3$). A solution of 3

$\delta$H, 6.83 (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); $\delta$C 158.2 (CO), 131.9 (2CH), 128.4 (4CH), 123.4 (C), 115.0 (C), 96.6 (CH), 91.5 (C=CH), 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 °C 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, $\delta$H 7.42 (1H, d, J 4, 2-H) and 6.22 (1H, d, J 4, 5-H); $\delta$D 3.88 (CD$_2$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-phenyliophene 22.

2.3.6 Repyrolysis of product 21 at 800 °C

FVP of the above product (0.1 g) at 800 °C 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, $\delta$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-phenyliophene 22; $\delta$H 6.67 (1H, br s, vinyl-H); $\delta$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$^+$ 144.024. C$_6$H$_9$O$_2$S requires M, 144.0245); $\nu_{max}$/cm$^{-1}$ 3392, 1559, 1382, 1252, 1154, 1116, 1000, 872, 707 and 667; $\delta$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); $\delta$C 155.1 (C-3), 123.3 (C-5), 119.5 (C-2), 116.4 (C-4), 58.9 (CH$_3$) 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 °C 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 °C; (Found: C, 67.9; H, 5.0. C₂₂H₂₄ClOPS requires C, 67.8; H, 5.2%); υmax/cm⁻¹ 1587, 1554, 1439, 1389, 1260, 1112, 1049, 997, 928, 812, 738 and 691; δH 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, CH₂P) and 3.48 (3H, s, OMe); δC 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, CH₂); ΔδH +21.6.

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 °C at 0.6 Torr (HRMS: Found M⁺ 144.0239. C₆H₅O₂S requires M⁺, 144.0245); υmax/cm⁻¹ 3382, 2933, 1562, 1479, 1413, 1348, 1208, 1179, 1133, 1040, 857, 781, 731 and 602; δH 7.20 (1H, d, J 3, 2-H), 6.43 (1H, d, J 3, 5-H), 4.57 (2H, s, CH₂), 3.83 (3H, s, OMe) and 2.19 (1H, s, OH); δC 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 (17), 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 cm³) and carbon tetrachloride (2.34 cm³, 24 mmol) to give the product (5.3 g, 52%) as colourless prisms, mp 266–267 °C (dec.); (Found: C, 76.5; H, 5.1. C₃₃H₂₄ClOPS requires C, 67.8; H, 5.2%); υmax/cm⁻¹ 2022, 1588, 1547, 1439, 1345, 1257, 1227, 1200, 1172, 1046, 997, 891, 866, 824, 767, 751, 721 and 694; δH 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, CH₂P) and 3.24 (3H, s, OMe); δC 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, CH₂P); ΔδH +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 cm³) was stirred under N₂ while a solution of butyllithium in hexanes (4.7 cm³, 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 cm³). After stirring for a further 12 h the mixture was added to water (100 cm³) and extracted with diethyl ether (2 x 100 cm³) and ethyl acetate (2 x 200 cm³). The combined extracts were washed with water (100 cm³), 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 °C (dec.) (Found: C, 76.1; H, 5.2. C₃₃H₃₇O₃PS requires C, 76.4; H, 5.3%); υmax/cm⁻¹ 1631, 1559, 1520, 1437, 1382, 1348, 1266, 1202, 1110, 1065, 974, 888, 828, 738 and 689; δH 7.69–7.59 (6H, m, Ph), 7.52–7.34 (12H, m, ArH, Ph.
2.5.1

2.5

152 (16), 131 (20), 111 (30), 97 (55), 83 (67), 69 (97) and 57 (100). (MCH=), 95.3 (thienyl C), 127.8 (CH), 131.6 (d, J 5, 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), 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); δp +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]triphenylphosphorane 26

This was prepared as in 2.4.5 using (3-methoxy-2-thienylmethyl)triphenylphosphonium chloride 24 (9.0 g, 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 °C (Found: C, 71.1; H, 5.0. C13H11O2PS2 requires C, 71.4; H, 5.1%); νmax/cm⁻¹ 1620, 1551, 1502, 1361, 1209, 1067, 962, 883, 803, 747, 720 and 692; δH 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); δC 182.0 (d, J 8, CO), 155.8 (d, J 6, 4 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); δp +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) 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 °C (dec.) (Found: C, 76.1; H, 5.2. C13H11O2PS requires C, 76.4; H, 5.3%); νmax/cm⁻¹ 1627, 1545, 1511, 1437, 1348, 1186, 1152, 1071, 1032, 976, 934, 858, 848, 783, 762, 751, 726 and 694; δH 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); δC 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); δp +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 cm³, 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 (5.47 g, 98%) as lemon-yellow needles, mp 64–66°C (Found: C, 51.8; H, 3.5. C₈H₇ClOS requires C, 51.5; H, 3.8%); νmax/cm⁻¹ 1731, 1592, 1412, 1274, 1246, 1088, 1045, 965, 936, 800, 742, 696, 655 and 629; δH 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); δC 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 (37Cl-M⁺, 7%), 186 (35Cl-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 cm³) was stirred under N₂ while a solution of butyllithium in hexanes (6.7 cm³, 2.5 M, 16.7 mmol) was added. The resulting deep red solution was stirred for another 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 cm³). After stirring for a further 18 h the mixture was added to water (200 cm³) and extracted with diethyl ether (2 × 100 cm³) and ethyl acetate (2 × 100 cm³). The combined extracts were washed with water (100 cm³), 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°C (Found: C, 74.4; H, 5.1. C₃H₂O₃PS requires C, 74.4; H, 5.3%); νmax/cm⁻¹ 1614, 1500, 1435, 1355, 1197, 1099, 1078, 978, 961, 921, 852, 790, 755, 714 and 699; δH 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); δC 180.3 (d, J 6, CO), 145.2 (d, J 5, MeSC₆H₄ C-2), 137.9 (C), 136.5 (CH), 136.3 (d, J 3, CH), 135.0 (d, J 11, MeSC₆H₄ 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); δδ +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 cm³, 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°C (Found: C, 76.5; H, 5.25. C₃H₂O₂PS requires C, 76.7; H, 5.5%); νmax/cm⁻¹ 1620, 1589, 1495, 1435, 1359, 1241, 1201, 1106, 1073, 1051, 1027, 961, 854, 802, 747 and 695; δH 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); δC 179.6 (d, J 5, CO), 158.9 (d, J 3, MeOC₆H₄ 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, MeOCH₂C₆H₄ 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); δH +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 cm³, 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 °C; νmax/cm⁻¹ 2065, 1619, 1495, 1490, 1376, 1266, 1245, 1201, 1100, 747 and 695; δδ 3.24 (OCD₃); δH 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); δC identical to 34 save for the absence of the signal at 54.3; δH +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 °C 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, ¹H NMR, ¹³C NMR and HRMS analysis indicated a mixture of three main products;
1. 5-benzylbenzothiophene 37 (63%) (HRMS: Found M⁺ 224.0652. C₁₃H₁₂S requires M, 224.0660); δH 4.03 (2H, s, CH₂); δC 41.8 (CH₂); 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. C₁₄H₁₄S requires M, 238.0816); δH 4.23 (1H, q, J 7, CH) and 1.64 (3H, d, J 7, CH₃); δC 44.7 (CH) and 22.1 (CH₃); 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. C₁₃H₁₀S requires M, 222.0503); δH 3.90 (2H, s, CH₂); δC 37.2 (CH₂); 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)methylene]triphenylphosphorane 35
FVP of the title compound (0.5 g) at 800 °C 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, ¹H NMR, and ¹³C NMR analysis suggested a mixture of three main products:
1. 5-benzylbenzothiophene 37 (52%); δH 4.01 (2H, s, CH₂); δC 41.8 (CH₂); 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%); δH 4.19 (1H, q, J 7, CH) and 1.62 (3H, d, J 7, CH₃); δC 44.6 (CH) and 22.0 (CH₃); 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_1H 3.82 (2H, s, CH₂); δ_C 37.1 (CH₂); 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-trideuteriethoxyphenyl)methylene]triphenylphosphorane 36
FVP of the title compound (0.5 g) at 800 °C 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, ¹H NMR, ²H NMR and ¹³C NMR analysis indicated a mixture of four products;
1. 5-benzylbenzothiophene 37 δ_H 4.01 (2H, s, CH₂); δ_C 41.8 (CH₂); m/z 224 (M⁺, 100%).
2. 5-(α-deuteriobenzyl)benzothiophene 40 δ_H 4.00 (1H, s, CHD); δ_D 4.18 (1H, 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 (3H, s, CD₃); δ_C 44.4 (CH); m/z 241 (M⁺, 33%), 223 (100).
4. fluoreno[3,4-b]thiophene 39 δ_H 3.87 (2H, CH₂); δ_C 37.2 (CH₂); 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 ³¹P NMR signals in the range +15.6–17.3 ppm and ¹³C 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 Ph$_3$PO under FVP conditions, the value of the phosphorus coupling to the carbonyl group, $^{2}J_{P-CO}$ was $6-8$ Hz, meaning that the extrusion should proceed readily since we recently showed \cite{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 \cite{29,30}, ylides with $R = \text{Ph}$ should give the furan product with $R^1 = \text{Ph}$ by simple hydrogen atom abstraction from the environment, while for $R = \text{Et}$, the main product should be $R^1 = \text{vinyl}$ 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 Ph$_3$PO, 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 \cite{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 ¹H and ¹³C 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 wellprecedented 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 Ph₃PO, Ph₃P and Ph₃PS 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 Ph₃P/CCl₄. 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 LiAlH₄ 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 J_P-CO of 8–9 Hz leading us to predict [28] successful extrusion of Ph₃PO upon FVP.
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 $J_{P, CO}$ values of 5–6 Hz again suggested successful thermal extrusion of Ph3PO [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 Ph3PO left a mixture containing 5-benzylbenzothiophene 37, 5-(α-methylbenzyl)benzothiophene 38 and fluoreno[3,4-$b$]thiophene 39.
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/SMMe 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 SMMe 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](image)

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.
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References


Highlights

- Ten new oxo-stabilised phosphonium ylides are prepared
- FVP of simple examples gives thieno[3,2-\textit{b}]furan and thieno[3,4-\textit{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-\textit{b}]thiophene products

Graphical Abstract