# Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 2.[1] Two-step Conversion of Acid Chlorides into Acetylenic Esters and Terminal Alkynes

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The known thermal extrusion of Ph_3PO from α-acyl-α-ethoxycarbonyl ylides 1 to give acetylenic esters 2 can be accomplished in excellent yield by using flash vacuum pyrolysis (FVP) at 500 °C. Upon raising the furnace temperature to 750 °C, this reaction is accompanied by the unexpected loss of the ethoxycarbonyl group to give the terminal alkynes 7 in moderate yield. A mechanism is proposed for this reaction based on isotopic labelling studies. Ten new examples of ylides 1 have been prepared for the first time.

Thermal extrusion of Ph_3PO from the stabilised ylides 1 provides a potentially attractive synthesis of acetylenic esters 2 (see Scheme 1). This transformation was first reported in 1961

Scheme 1
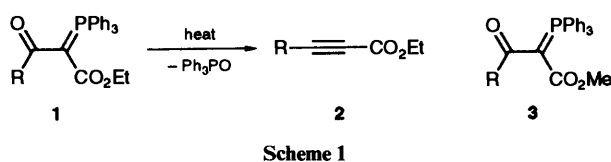
when Märkl[2] described the conversion of 11 examples of methoxycarbonyl ylides 3 to the corresponding acetylenic esters in 65–80% yields by heating at 220–260 °C under vacuum. Others have since used this method to gain access to a wide variety of acetylenic esters,[3–5] including functionalised examples,[6] bis-acetylenic esters of interest for polymer synthesis,[7] and intermediates in natural product synthesis.[8] Since the ylides 1 are readily formed by treating an acid chloride 4 with the commercially available ethoxycarbonylmethylenetriphenylphosphorane 5, this provides a convenient two-step method for conversion of 4 into 2 (see Scheme 2).

Scheme 2
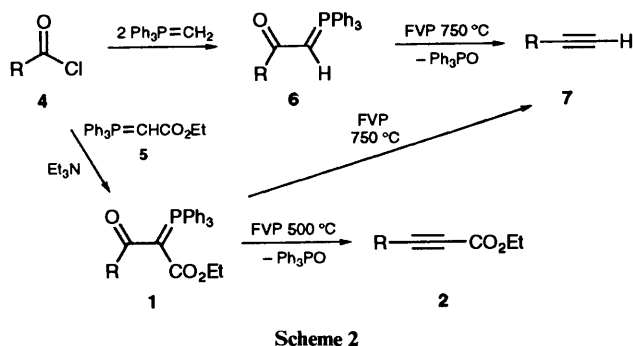
In Part 1 of this series,[1] we reported that the use of flash vacuum pyrolysis (FVP) allows efficient conversion of ylides 6 into terminal alkynes 7, a transformation not possible using conventional pyrolysis, and since 6 is readily prepared by treatment of acid chloride 4 with methylenetriphenylphosphorane, this allows the two-step conversion of 4 into 7 (see Scheme 2). In this paper, we examine the effect of FVP conditions on the transformation of 1 to 2 and describe the quite unexpected observation that, by simply raising the furnace temperature, the pyrolysis of 1 can be induced to give terminal alkynes 7 directly.[9]

Table 1 Formation of ylides 1 and FVP to give 2 and 7

R	Yield of 1 from 4 (%)	Yield of 2 from 1 (%)	Yield of 7 from 1 (%)
a Ph	71	—	48
b 4-MeC_6H_4	82	91	58
c 4-$MeOC_6H_4$	70	92	16
d 4-ClC_6H_4	92	92	46
e 4-$NO_2C_6H_4$	91	88	—
f 2-MeC_6H_4	64	90	34
g 2-$MeOC_6H_4$	73	88	—
h 2-$MeSC_6H_4$	69	82	38
i 2-Furyl	82	90	40
j 2-Thienyl	71	83	34
k 3-Me-2-thienyl	71	88	28
l 3-Thienyl	69	86	66
m Cyclohexyl	55	66	40

Results and Discussion

The stabilised ylides 1 were readily prepared in good to excellent yield (see Table 1) by reaction of ethoxycarbonylmethylenetriphenylphosphorane 5 with 1 equiv. of acid chloride 4 in the presence of triethylamine. They were obtained as stable crystalline solids showing the expected physical and spectroscopic characteristics. The ^{13}C NMR spectra, in particular, were highly informative, providing ready confirmation of the structures and showing that the coupling to phosphorus extends throughout the phenyl groups, to the ester carbonyl, and through the acyl carbonyl to the first carbon atom of the R group (see Table 2).

When the ylides 1 were subjected to FVP at 500 °C, the expected extrusion was observed. Triphenylphosphine oxide collected at the furnace exit and the acetylenic esters 2 were recovered directly from the cold trap in pure form and excellent yield (see Table 1). The method is suitable for preparation of multigram quantities of acetylenic esters as illustrated by the pyrolysis of most of the ylides on a 5–20 g scale and in the case of 2i the preparation of 12 g of product. The identity and purity of the acetylenic esters were readily checked by ^{1}H and ^{13}C NMR (see Table 3) which showed the expected patterns with no significant impurities detectable. The yields compare favourably with a previous study using conventional pyrolysis[4] where 2i and 2j were obtained from 4 in 37 and 45% overall yields, respectively.

When the same ylides 1 were subjected to FVP at 750 °C, Ph_3PO was again eliminated but this was accompanied by complete loss of the CO_2Et group to give the terminal alkynes 7 in moderate yield (Table 1). As before, the Ph_3PO accumulated at the furnace exit and the more volatile alkynes were recovered directly from the cold trap in pure form. Only in the cases of 1e

Table 2 ¹³C NMR spectra of ylides 1, δ_C (J_{P-C})

| R | RCO | P=C | Ester | | | PPh | | | | R signals |
			CO	CH₂	CH₃	C-1	C-2	C-3	C-4	
1b 4-MeC₆H₄	193.3 (5)	68.7 (111)	167.6 (14)	58.4	13.7	126.6 (93)	133.4 (10)	128.6 (13)	131.7 (3)	140.3 (9), 139.5, 128.6, 127.9, 21.5
1c 4-MeOC₆H₄	192.5 (5)	68.2 (111)	167.6 (14)	58.4	13.8	126.6 (93)	133.3 (10)	128.6 (12)	131.7 (2)	161.1, 135.5 (9), 130.7, 112.5, 55.2
1e 4-NO₂C₆H₄	191.1 (6)	70.3 (109)	167.2 (13)	58.6	13.5	125.3 (93)	133.2 (10)	128.7 (13)	132.1 (2)	149.8 (9), 147.7, 128.6 (2C), 122.6 (2C)
1f 2-MeC₆H₄	194.2 (5)	72.4 (110)	167.3 (16)	58.6	13.4	126.8 (92)	133.4 (10)	128.6 (12)	131.8 (2)	144.4 (9), 134.1, 129.6, 126.7, 125.6, 124.8, 19.4
1g 2-MeOC₆H₄	191.0 (5)	72.3 (113)	167.5 (16)	58.4	13.5	126.5 (93)	133.6 (10)	128.5 (13)	131.7 (3)	156.1, 134.7 (9), 128.8, 127.6, 120.3, 110.6, 55.7
1h 2-MeSC₆H₄	191.8 (5)	72.6 (111)	167.0 (15)	58.6	13.5	126.0 (93)	133.6 (10)	128.5 (13)	131.8 (3)	145.6 (9), 134.4, 128.0, 127.8, 126.7, 125.2, 17.5
1j 2-Thienyl	182.9 (6)	69.5 (114)	167.2 (14)	58.7	13.8	126.6 (94)	133.3 (10)	128.6 (13)	131.7 (2)	146.5 (11), 130.7, 129.0, 126.5
1k 3-Thienyl	186.1 (5)	70.1 (111)	167.4 (14)	58.6	13.7	126.5 (93)	133.3 (10)	128.6 (13)	131.7 (2)	144.6 (10), 128.9, 128.3, 123.0
1l 3-Me-2-thienyl	185.4 (7)	70.8 (110)	167.2 (14)	58.6	13.8	126.2 (93)	133.4 (10)	128.6 (13)	131.8 (2)	140.7 (10), 137.7, 130.0, 125.6, 15.3
1m Cyclohexyl	201.0 (2)	70.0 (110)	167.4 (15)	58.1	13.7	127.3 (94)	133.0 (10)	128.3 (12)	131.3 (3)	46.0 (6), 29.7 (2C), 26.3 (3C)

Table 3 ^{13}C NMR spectra of acetylenic esters 2, δ_C

R	$\equiv C-$	Ester CO	CH$_2$	CH$_3$	R signals
2b 4-MeC$_6$H$_4$	86.4, 80.6	154.0	61.9	14.1	141.3, 132.9 (2C), 129.4 (2C), 116.6, 21.6
2c 4-MeOC$_6$H$_4$	86.8, 80.3	154.2	61.8	14.1	161.6, 134.8 (2C), 114.3 (2C), 111.4, 55.3
2d 4-ClC$_6$H$_4$	84.3, 81.3	153.4	61.8	13.7	136.6, 133.8 (2C), 128.7 (2C), 117.8
2e 4-NO$_2$C$_6$H$_4$	84.3, 82.7	153.2	62.6	14.1	148.6, 133.7 (2C), 126.3, 123.8 (2C)
2f 2-MeC$_6$H$_4$	84.4, 84.2	153.6	61.4	13.6	141.6, 132.9, 130.2, 129.3, 125.4, 119.0, 20.0
2h 2-MeSC$_6$H$_4$	86.1, 82.9	153.3	61.6	13.6	143.6, 133.5, 130.6, 124.1, 123.9, 117.2, 14.6
2i 2-Furyl	85.9, 76.4	153.7	62.2	14.1	146.3, 134.6, 121.0, 111.6
2j 2-Thienyl	85.0, 80.0	153.8	62.1	14.1	136.4, 131.1, 127.5, 119.4
2k 3-Me-2-thienyl	87.5, 80.0	154.0	61.9	14.1	148.0, 130.0, 129.6, 115.0, 15.1
2l 3-Thienyl	80.9, 80.3	153.3	61.4	13.5	133.2, 129.5, 125.8, 118.1
2m Cyclohexyl	92.7, 73.1	154.0	61.7	14.1	31.5 (2C), 28.9, 25.6, 24.7 (2C)

**Table 4** ^{13}C NMR spectra of terminal alkynes 7, δ_C

R	R–C$\equiv$C	$\equiv C$–H	R signals
7a Ph	83.7	77.1	132.1 (2C), 128.3 (2C), 128.8, 122.2
7b 4-MeC$_6$H$_4$	83.8	76.4	138.9, 132.0 (2C), 129.1 (2C), 119.1, 21.5
7d 4-ClC$_6$H$_4$	82.5	78.2	137.8, 133.3 (2C), 128.7 (2C), 120.6
7f 2-MeC$_6$H$_4$	82.5	80.9	140.8, 132.5, 129.4, 128.7, 125.5, 120.9, 20.6
7h 2-MeSC$_6$H$_4$	81.0	83.5	141.9, 133.1, 129.3, 124.32, 124.26, 120.3, 15.1
7j 2-Thienyl	77.0	81.2	133.1, 128.0, 127.5, 126.9
7k 3-Me-2-thienyl	76.7	83.3	143.7, 129.0, 126.0, 117.3, 14.8
7l 3-Thienyl	78.8	76.9	130.1, 130.0, 125.4, 121.2
7m Cyclohexyl	89.0	67.8	32.6 (2C), 28.8, 25.8, 24.8 (2C)

and **1g** was the transformation unsuccessful, intractable products being formed in these cases due to the thermal lability of the nitro and methoxy groups; this also explains the low yield obtained from **1c**. As a method for the overall conversion of **4** into **7** this is certainly competitive with the FVP of **6**, since **5** is commercially available and the need to use butyllithium under an inert atmosphere is avoided. The identity and purity of the terminal alkynes **7** was again readily confirmed by ^{13}C NMR spectroscopy (see Table 4) which showed no significant impurities to be present.

The mechanism of loss of the ester group is of some interest. As shown in Scheme 3, this could either involve direct pericyclic

Scheme 3
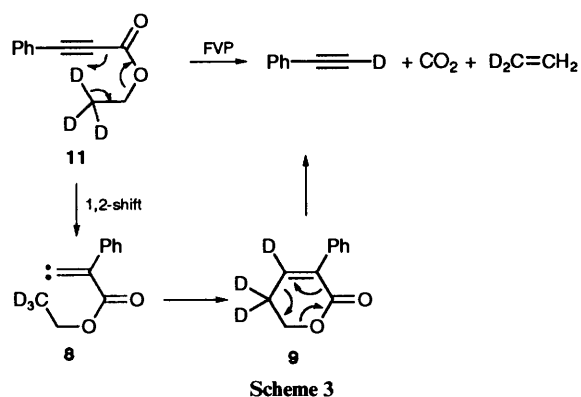
elimination of CO$_2$ and ethene, or a 1,2-shift of either the ester or phenyl group to give the vinylidene **8** which can then undergo intramolecular insertion to give the dihydropyranone **9** which subsequently fragments to give the same products. The involvement of vinylidenes in the pyrolysis of 3-unsubstituted propiolate esters has been reported before.[10] Alternatively the reaction might proceed, as shown in Scheme 4, analogously to the pyrolysis of diphenylmethyl propiolate to give benzophenone and methyleneketene,[11] by an ene-type reaction involving the C(1)-H of the ethyl group to give acetaldehyde

Scheme 4
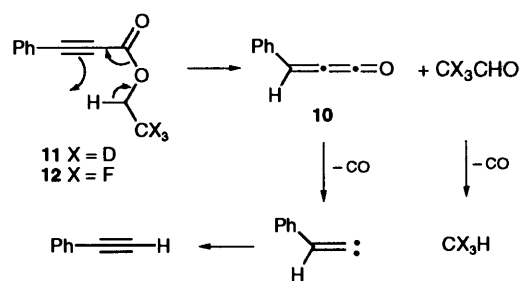
and benzylideneketene **10** both of which could then lose CO to give the final products shown. Careful analysis of the most voltatile fraction from FVP of ethyl phenylpropiolate at 750 °C showed no sign of acetaldehyde or methane (which has been detected in other FVP experiments by a signal at δ_H 0.18 despite its boiling point of -160 °C) but definite evidence for the presence of ethene (δ_H 5.40). More significantly, FVP of the [2,2,2-^{2}H$_3$]ethyl derivative **11** resulted mainly in the formation of PhC$\equiv$CD, consistent with either of the mechanistic routes of Scheme 3, but this was accompanied by some PhC$\equiv$CH (ratio $\approx 4:1$), indicating at least some involvement of the mechanism of Scheme 4. In closely related systems, such as the 2,2,2-trifluoroethyl ester **12**, fragmentation occurs exclusively by the mechanistic route of Scheme 4 to give phenylacetylene and trifluoroacetaldehyde. Further studies on the mechanism of decomposition of a range of simple acetylenic esters will be reported in detail shortly.[12]

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. IR spectra were recorded for Nujol mulls or, where indicated, for solutions in chloroform in matched sodium chloride cells of path length 0.1 mm, on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^{1}H at 300 MHz, for ^{2}H at 46 MHz, and for ^{13}C at 75 MHz on

a Bruker AM300 instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl$_3$ with internal Me$_4$Si as reference for ^{1}H and ^{13}C and external 85% H$_3$PO$_4$ as reference for ^{31}P, except for ^{2}H spectra which were run in CHCl$_3$ with CDCl$_3$ (δ_D 7.3) as reference. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. Mass spectra were obtained on an A.E.I. MS-902 spectrometer using electron impact at 70 eV. Toluene was dried by storing over sodium wire. Ether refers to diethyl ether.

Preparation of (α-Acyl-α-ethoxycarbonylmethylene)triphenyl-phosphoranes **1**.—A solution of (ethoxycarbonylmethylene)-triphenylphosphorane **5** (10.0 g, 29 mmol) and triethylamine (3.0 g, 29 mmol) in dry toluene (150 cm^3) was stirred at room temperature while a solution of the appropriate acid chloride **4** (29 mmol) in dry toluene (20 cm^3) was added dropwise. After the addition, the mixture was stirred for 3 h and then the triethylamine hydrochloride was filtered off and the filtrate evaporated to afford the desired ylides which were recrystallised from ethyl acetate–ether. Using this procedure the following phosphoranes **1** were prepared, all of which are new compounds except for **1a**, **1i** and **1j**:

(α-*Benzoyl-α-ethoxycarbonylmethylene*)*triphenylphosphorane* **1a** as pale yellow crystals (71%), m.p. 140–141 °C (lit.,^{3} 142–143 °C); δ_H 8.0–7.3 (20 H, m), 3.70 (2 H, q, J 7) and 0.61 (3 H, t, J 7); δ_P +18.6.

(α-*Ethoxycarbonyl-α-4-methylbenzoylmethylene*)*triphenyl-phosphorane* **1b** as yellow crystals (82%), m.p. 177–179 °C (Found: C, 77.1; H, 5.9. C$_{30}$H$_{27}$O$_3$P requires C, 77.2; H, 5.8%); ν_{max}/cm^{-1} 1660, 1520, 1434, 1345, 1267, 1103, 1087, 1020, 992, 821, 765, 748, 718, 707 and 688; δ_H 7.8–7.7 (6 H, m), 7.62 and 7.14 (4 H, AB pattern, J 10), 7.55–7.4 (9 H, m), 3.68 (2 H, q, J 7), 2.35 (3 H, s) and 0.60 (3 H, t, J 7); δ_C, see Table 2; δ_P +18.7; m/z 466 (M$^+$, 100%), 438 (16), 421 (8), 419 (10), 391 (27), 390 (50), 375 (23), 303 (40), 301 (22), 278 (17), 277 (70), 262 (28), 260 (18), 219 (28), 201 (56) and 183 (47).

(α-*Ethoxycarbonyl-α-4-methoxybenzoylmethylene*)*triphenyl-phosphorane* **1c** as yellow crystals (70%), m.p. 165–167 °C (Found: C, 74.7; H, 5.4. C$_{30}$H$_{27}$O$_4$P requires C, 74.7; H, 5.6%); ν_{max}/cm^{-1} 1657, 1601, 1520, 1500, 1435, 1345, 1287, 1265, 1240, 1178, 1102, 1087, 1020, 830, 770, 743, 705 and 687; δ_H 7.8–7.7 (8 H, m), 7.6–7.4 (9 H, m), 6.88 (2 H, half AB pattern, J 7), 3.83 (3 H, s), 3.70 (2 H, q, J 7) and 0.62 (3 H, t, J 7); δ_C, see Table 2; δ_P +19.0; m/z 482 (M$^+$, 3%), 450 (6), 438 (4), 410 (4), 409 (16), 394 (3), 375 (4), 347 (4), 303 (36), 301 (16), 277 (6), 263 (50), 262 (100), 201 (18) and 183 (36).

(α-4-*Chlorobenzoyl-α-ethoxycarbonylmethylene*)*triphenyl-phosphorane* **1d** as colourless crystals (92%), m.p. 154–156 °C (Found: C, 71.3; H, 4.9. C$_{29}$H$_{24}$ClO$_3$P requires C, 71.5; H, 5.0%); ν_{max}/cm^{-1} 1662, 1530, 1480, 1435, 1342, 1268, 1128, 1104, 1088, 1010, 992, 842, 822, 768, 745, 730 and 690; δ_H 7.95–7.2 (19 H, m), 3.70 (2 H, q, J 7) and 0.62 (3 H, t, J 7); δ_P +18.7; m/z 486[(^{35}Cl)M$^+$, 47%], 457 (4), 441 (9), 413 (21), 375 (8), 303 (16), 277 (28), 262 (26), 201 (27), 183 (34), 163 (44), 139 (34) and 106 (100).

(α-*Ethoxycarbonyl-α-4-nitrobenzoylmethylene*)*triphenylphos-phorane* **1e** as yellow crystals (91%), m.p. 169–170 °C (Found: C, 70.2; H, 4.9; N, 2.8. C$_{29}$H$_{24}$NO$_5$P requires C, 70.0; H, 4.9; N, 2.8%); ν_{max}/cm^{-1} 1640, 1542, 1515, 1438, 1325, 1310, 1273, 1140, 1104, 1095, 1075, 993, 838, 752, 725, 699 and 683; δ_H 8.20 (2 H, half AB pattern, J 9), 7.95–7.4 (17 H, m), 3.65 (2 H, q, J 7) and 0.57 (3 H, t, J 7); δ_C, see Table 2; δ_P +18.2; m/z 497 (M$^+$, 85%), 496 (37), 468 (17), 452 (156), 450 (14), 424 (60), 396 (10), 375 (24), 347 (8), 303 (42), 301 (20), 277 (30), 262 (26), 260 (27), 201 (84) and 183 (100).

(α-*Ethoxycarbonyl-α-2-methylbenzoylmethylene*)*triphenyl-phosphorane* **1f** as yellow crystals (64%), m.p. 149–151 °C

(Found: C, 77.3; H, 6.0. C$_{30}$H$_{27}$O$_3$P requires C, 77.2; H, 5.8%); ν_{max}/cm^{-1} 1650, 1517, 1455, 1433, 1338, 1280, 1145, 1103, 1095, 1077, 745, 708 and 688; δ_H 7.8–7.7 (6 H, m), 7.6–7.4 (9 H, m), 7.26 (1 H, m), 7.17–7.07 (3 H, m), 3.62 (2 H, q, J 7), 2.40 (3 H, s) and 0.53 (3 H, t, J 7); δ_C, see Table 2; δ_P +17.3; m/z 466 (M$^+$, 40%), 438 (2), 421 (7), 419 (16), 393 (6), 375 (14), 347 (8), 303 (34), 301 (14), 277 (40), 262 (100), 201 (38) and 183 (70).

(α-*Ethoxycarbonyl-α-2-methoxybenzoylmethylene*)*triphenyl-phosphorane* **1g** as yellow crystals (73%), m.p. 171–172 °C (Found: C, 74.8; H, 5.8. C$_{30}$H$_{27}$O$_4$P requires C, 74.7; H, 5.6%); ν_{max}/cm^{-1} 1674, 1534, 1447, 1350, 1291, 1270, 1247, 1114, 1092, 1031, 769, 755 and 701; δ_H 7.85–7.75 (6 H, m), 7.6–7.4 (9 H, m), 7.3–7.2 (2 H, m), 6.95–6.85 (2 H, m), 3.87 (3 H, s), 3.60 (2 H, q, J 7) and 0.55 (3 H, t, J 7); δ_C, see Table 2; δ_P +17.2; m/z 482 (M$^+$, 100%), 453 (8), 437 (4), 435 (2), 410 (12), 409 (30), 381 (3), 375 (8), 303 (20), 301 (13), 277 (40), 262 (15), 201 (20) and 183 (20).

(α-*Ethoxycarbonyl-α-2-methylsulfanylbenzoylmethylene*)*tri-phenylphosphorane* **1h** as yellow crystals (69%), m.p. 143–144 °C (Found: C, 72.35; H, 5.4. C$_{30}$H$_{27}$O$_3$PS requires C, 72.3; H, 5.5%); ν_{max}/cm^{-1} 1648, 1520, 1435, 1343, 1285, 1150, 1100, 1080, 992, 742, 718 and 690; δ_H 8.0–7.7 (6 H, m), 7.6–7.4 (9 H, m), 7.3–7.15 (4 H, m), 3.63 (2 H, q, J 7), 2.40 (3 H, s) and 0.55 (3 H, t, J 7); δ_C, see Table 2; δ_P +17.3; m/z 498 (M$^+$, 0.5%), 483 (100), 452 (3), 410 (4), 409 (3), 303 (5), 301 (2), 277 (10), 262 (60), 201 (5) and 183 (20).

(α-*Ethoxycarbonyl-α-2-furoylmethylene*)*triphenylphosphorane* **1i** as colourless crystals (82%), m.p. 110–111 °C (lit.,^{13} 112–113 °C); ν_{max}/cm^{-1} 1656, 1568, 1513, 1434, 1328, 1270, 1180, 1100, 1066, 1015, 996, 758, 736 and 688; δ_H 8.0–7.1 (17 H, m), 6.4 (1 H, m), 3.75 (2 H, q, J 7) and 0.72 (3 H, t, J 7); δ_P +18.8; m/z 442 (M$^+$, 66%), 413 (18), 369 (36), 340 (18), 277 (72), 262 (69), 201 (36), 183 (100) and 152 (40).

(α-*Ethoxycarbonyl-α-2-thenoylmethylene*)*triphenylphosphor-ane* **1j** as yellow crystals (71%), m.p. 121–122 °C (lit.,^{14} 122.5–123 °C); ν_{max}/cm^{-1} 1660, 1504, 1440, 1352, 1343, 1284, 1107, 1080, 1002, 860, 792, 763, 735 and 697; δ_H 7.8–7.4 (15 H, m), 7.26 (1 H, m), 7.20 (1 H, m), 7.06 (1 H, m), 3.72 (2 H, q, J 7) and 0.69 (3 H, t, J 7); δ_C, see Table 2; δ_P +18.7; m/z 458 (M$^+$, 30%), 429 (2), 413 (3), 399 (22), 386 (60), 385 (90), 375 (30), 357 (33), 303 (40), 301 (40), 289 (17), 277 (60), 262 (50), 260 (50), 201 (30) and 183 (30).

(α-*Ethoxycarbonyl-α-3-methyl-2-thenoylmethylene*)*triphenyl-phosphorane* **1k** as yellow crystals (71%), m.p. 128–130 °C (Found: C, 71.7; H, 5.4. C$_{28}$H$_{25}$O$_3$PS requires C, 71.2; H, 5.3%); ν_{max}/cm^{-1} 1648, 1540, 1432, 1405, 1310, 1235, 1180, 1115, 1100, 1075, 780, 758, 733, 710 and 688; δ_H 7.9–7.65 (6 H, m), 7.6–7.4 (9 H, m), 7.2 and 6.80 (2 H, AB pattern, J 5), 3.73 (2 H, q, J 7), 2.47 (3 H, s) and 0.68 (3 H, t, J 7); δ_C, see Table 2; δ_P +18.5; m/z 472 (M$^+$, 60%), 426 (24), 399 (5), 375 (30), 347 (10), 303 (20), 301 (12), 277 (30), 275 (20), 263 (45), 262 (100), 260 (50), 201 (20) and 183 (50).

(α-*Ethoxycarbonyl-α-3-thenoylmethylene*)*triphenylphosphor-ane* **1l** as yellow crystals (69%), m.p. 117–118 °C (Found: C, 71.0; H, 4.7. C$_{27}$H$_{23}$O$_3$PS requires C, 70.7; H, 5.1%); ν_{max}/cm^{-1} 1653, 1515, 1505, 1432, 1406, 1315, 1280, 1130, 1100, 1077, 995, 860, 750, 705 and 690; δ_H 7.9–7.35 (16 H, m), 7.2–7.07 (2 H, m), 3.70 (2 H, q, J 7) and 0.67 (3 H, t, J 7); δ_C, see Table 2; δ_P +18.66; m/z 458 (M$^+$, 100%), 429 (6), 413 (9), 411 (8), 386 (30), 385 (60), 375 (8), 303 (28), 301 (30), 289 (6), 277 (64), 262 (36), 260 (20), 201 (60) and 183 (56).

(α-*Cyclohexylcarbonyl-α-ethoxycarbonylmethylene*)*triphenyl-phosphorane* **1m** as yellow crystals (55%), m.p. 181–183 °C (Found: C, 76.8; H, 6.9. C$_{29}$H$_{31}$O$_3$P requires C, 76.0; H, 6.8%); ν_{max}/cm^{-1} 1640, 1540, 1430, 1390, 1335, 1292, 1231, 1203, 1161, 1100, 1075, 928, 770, 752, 738, 715 and 687; δ_H 7.8–7.35 (15 H, m), 3.76 (2 H, q, J 7), 3.65 (1 H, m), 2.0–1.1 (10 H, m) and 0.72 (3 H, t, J 7); δ_C, see Table 2; δ_P +16.9; m/z 458 (M$^+$, 6%),

412 (4), 374 (42), 373 (100), 348 (12), 347 (11), 303 (30), 279 (11), 277 (12), 262 (15), 201 (9) and 183 (12).

Flash Vacuum Pyrolysis (FVP) of Ylides **1**.—The apparatus and general procedure used were as described previously.[1] All pyrolyses were carried out at 10^{-1}–10^{-2} mmHg.* For small scale preparations ($\leqslant 0.5$ g ylide **1**), the pyrolyses were complete within 0.5 h, while the larger scale experiments (5–20 g **1**) took up to 8 h. In all cases, an additional room temperature trapping tube[1] was used in the system which served to collect all the Ph$_3$PO produced and allowed isolation of the alkynes **2** and **7** directly from the cold trap in pure form.

Pyrolysis of ylides **1** *at* 500 °C *to give acetylenic esters* **2**.

2b FVP of the ylide **1b** (5.5 g) at 500 °C gave ethyl 4-methylphenylpropiolate **2b** (2.0 g, 91%) as a colourless liquid; δ_H 7.44 and 7.15 (4 H, AB pattern, *J* 8), 4.26 (2 H, q, *J* 7), 2.33 (3 H, s) and 1.32 (3 H, t, *J* 7); δ_C, see Table 3.

2c FVP of the ylide **1c** (20.0 g) at 500 °C gave ethyl 4-methoxyphenylpropiolate **2c** (7.8 g, 92%) as a colourless liquid; δ_H 7.52 and 6.87 (4 H, AB pattern, *J* 9), 4.27 (2 H, q, *J* 7), 3.80 (3 H, s) and 1.33 (3 H, t, *J* 7); δ_C, see Table 3.

2d FVP of the ylide **1d** (5.0 g) at 500 °C gave ethyl 4-chlorophenylpropiolate **2d** (1.98 g, 92%) as a colourless liquid; δ_H 7.47 and 7.32 (4 H, AB pattern, *J* 8), 4.29 (2 H, q, *J* 7) and 1.32 (3 H, t, *J* 7); δ_C, see Table 3.

2e FVP of the ylide **1e** (5.0 g) at 500 °C gave ethyl 4-nitrophenylpropiolate **2e** (1.94 g, 88%) as a colourless solid; δ_H 8.27 and 7.77 (4 H, AB pattern, *J* 9), 4.34 (2 H, q, *J* 7) and 1.38 (3 H, t, *J* 7); δ_C, see Table 3.

2f FVP of the ylide **1f** (5.0 g) at 500 °C gave ethyl 2-methylphenylpropiolate **2f** (1.80 g, 90%) as a colourless liquid; δ_H 7.6–7.1 (4 H, m), 4.29 (2 H, q, *J* 7), 2.46 (3 H, s) and 1.33 (3 H, t, *J* 7); δ_C, see Table 3.

2g FVP of the ylide **1g** (14.0 g) at 500 °C gave ethyl 2-methoxyphenylpropiolate **2g** (5.2 g, 88%) as a colourless liquid; δ_H 7.6–7.3 (2 H, m), 7.0–6.8 (2 H, m), 4.27 (2 H, q, *J* 7), 3.84 (3 H, s) and 1.31 (3 H, t, *J* 7).

2h FVP of the ylide **1h** (5.0 g) at 500 °C gave ethyl (2-methylsulfanyl)phenylpropiolate **2h** (1.80 g, 82%) as a colourless solid; δ_H 7.6–7.0 (4 H, m), 4.29 (2 H, q, *J* 7), 2.47 (3 H, s) and 1.33 (3 H, t, *J* 7); δ_C, see Table 3.

2i FVP of the ylide **1i** (36.0 g) at 500 °C gave ethyl (2-furyl)propiolate **2i** (12.0 g, 90%) as a colourless liquid; δ_H 7.52 (1 H, dd, *J* 2, 1), 6.93 (1 H, dd, *J* 4, 1), 6.47 (1 H, dd, *J* 4, 2), 4.31 (2 H, q, *J* 7) and 1.36 (3 H, t, *J* 7); δ_C, see Table 3.

2j FVP of the ylide **1j** (5.5 g) at 500 °C gave ethyl (2-thienyl)-propiolate **2j** (1.80 g, 83%) as a colourless liquid; δ_H 7.44 (1 H, d, *J* 4), 7.43 (1 H, d, *J* 5), 7.01 (1 H, dd, *J* 5, 4), 4.27 (2 H, q, *J* 7) and 1.34 (3 H, t, *J* 7); δ_C, see Table 3.

2k FVP of the ylide **1k** (16.5 g) at 500 °C gave ethyl (3-methyl-2-thienyl)propiolate **2k** (6.0 g, 88%) as a colourless liquid; δ_H 7.35 and 6.89 (2 H, AB pattern, *J* 5), 4.29 (2 H, q, *J* 7), 2.38 (3 H, s) and 1.34 (3 H, t, *J* 7); δ_C, see Table 3.

2l FVP of the ylide **1l** (16.0 g) at 500 °C gave ethyl (3-thienyl)propiolate **2l** (5.4 g, 86%) as colourless crystals; δ_H 7.70 (1 H, m), 7.28 (1 H, m), 7.14 (1 H, m), 4.25 (2 H, q, *J* 7) and 1.30 (3 H, t, *J* 7); δ_C, see Table 3.

2m FVP of the ylide **1m** (200 mg) at 500 °C gave ethyl cyclohexylpropiolate **2m** (52 mg, 66%) as a colourless oil (Found: M$^+$, 180.1165. $C_{11}H_{16}O_2$ requires *M*, 180.1150); δ_H 4.20 (2 H, q, *J* 7), 2.55 (1 H, m), 1.9–1.3 (10 H, m) and 1.32 (3 H, t, *J* 7); δ_C, see Table 3; *m/z* 180 (M$^+$, 16%), 151 (26), 135 (24), 107 (25), 91 (36), 79 (60), 67 (28) and 29 (100).

Pyrolysis of ylides **1** *at* 750 °C *to give terminal alkynes* **7**.

7a FVP of the ylide **1a** (200 mg) at 750 °C gave phenylethyne

7a (48%) as a colourless liquid (Found: M$^+$, 102.0459. C_8H_6 requires *M*, 102.0469); δ_H 7.55–7.25 (5 H, m) and 3.06 (1 H, s); δ_C, see Table 4.

7b FVP of the ylide **1b** (200 mg) at 750 °C gave 4-methylphenylethyne **7b** (58%) as a colourless liquid (Found: M$^+$, 116.0631. C_9H_8 requires *M*, 116.0626); δ_H 7.40 and 7.10 (4 H, AB pattern, *J* 8), 3.02 (1 H, s) and 2.34 (3 H, s); δ_C, see Table 4.

7c FVP of the ylide **1c** (200 mg) at 750 °C gave 4-methoxyphenylethyne **7c** (16%) as a colourless liquid; δ_H 7.40 and 6.80 (4 H, AB pattern, *J* 8), 3.73 (3 H, s) and 2.91 (1 H, s).

7d FVP of the ylide **1d** (306 mg) at 750 °C gave 4-chlorophenylethyne **7d** (46%) as a colourless liquid; δ_H 7.38 and 7.25 (4 H, AB pattern, *J* 9) and 3.06 (1 H, s); δ_C, see Table 4.

7f FVP of the ylide **1f** (200 mg) at 750 °C gave 2-methylphenylethyne **7f** (34%) as a colourless liquid (Found: M$^+$, 116.0609. C_9H_8 requires *M*, 116.0626); δ_H 7.50–7.0 (4 H, m), 3.19 (1 H, s) and 2.37 (3 H, s); δ_C, see Table 4; *m/z* 116 (M$^+$, 48%), 115 (100), 91 (10), 89 (15) and 73 (56).

7h FVP of the ylide **1h** (200 mg) at 750 °C gave 2-methylsulfanylphenylethyne **7h** (38%) as a colourless liquid; δ_H 7.5–7.0 (4 H, m), 3.44 (1 H, s) and 2.46 (3 H, s); δ_C, see Table 4; *m/z* 116 (M$^+$, 48%), 115 (100), 91 (10), 89 (15) and 73 (56).

7i FVP of the ylide **1i** (200 mg) at 750 °C gave 2-furylethyne **7i** (40%) as a colourless liquid; δ_H 7.33 (1 H, m), 6.60 (1 H, m), 6.32 (1 H, m) and 3.34 (1 H, s).

7j FVP of the ylide **1j** (200 mg) at 750 °C gave 2-thienylethyne **7j** (34%) as a colourless liquid (Found: M$^+$, 108.0030. C_6H_4S requires *M*, 108.0033); δ_H 7.4–6.9 (3 H, m) and 3.31 (1 H, s); δ_C, see Table 4.

7k FVP of the ylide **1k** (200 mg) at 750 °C gave 3-methyl-2-thienylethyne **7k** (28%) as a colourless liquid (Found: M$^+$, 122.0182. C_7H_6S requires *M*, 122.0190); δ_H 7.11 and 6.80 (2 H, AB pattern, *J* 5), 3.42 (1 H, s) and 2.32 (3 H, s); δ_C, see Table 4.

7l FVP of the ylide **1l** (200 mg) at 750 °C gave 3-thienylethyne **7l** (66%) as a colourless liquid; δ_H 7.5–7.4 (1 H, m), 7.35–7.1 (2 H, m) and 3.01 (1 H, s); δ_C, see Table 4.

7m FVP of the ylide **1m** (210 mg) at 750 °C gave cyclohexylethyne **7m** (20 mg, 40%) as a colourless liquid (Found: M$^+$, 108.0929. C_8H_{12} requires *M*, 108.0939); δ_H 2.38 (1 H, m), 2.04 (1 H, d, *J* 3), 1.9–1.65 (4 H, m) and 1.55–1.25 (6 H, m); δ_C, see Table 4; *m/z* 108 (M$^+$, 4%), 93 (24), 79 (35), 67 (14), 51 (12), 41 (40) and 39 (100).

FVP of Other Derivatives.—*FVP of* **2a**. FVP of ethyl phenylpropiolate (95 mg) at 750 °C gave phenylacetylene (70%); δ_H 7.55–7.45 (2 H, m), 7.4–7.3 (3 H, m) and 3.08 (1 H, s); δ_C 132.1 (2 C), 128.8, 128.3 (2 C), 122.1 (4°), 83.7 (–C≡) and 77.2 (≡CH), and a small proportion of ethene; δ_H 5.40.

FVP of **11**. FVP of [2,2,2-$^2H_3$]ethyl phenylpropiolate[12] (122 mg) at 750 °C gave phenylacetylene (15%); δ_H and δ_C as above, and phenyl[2-$^2H_1$]acetylene, PhC≡CD (60%); δ_H as above, but with peak at 3.08 absent; δ_D 3.14.

FVP of **12**. FVP of 2,2,2-trifluoroethyl phenylpropiolate[12] (115 mg) at 750 °C gave a yellow liquid which was shown by ^1H and ^{13}C NMR to be almost pure phenylacetylene (55%); δ_H and δ_C as above. Additional small signals indicated the presence of trifluoroacetaldehyde (2%); δ_H 9.45 (1 H, q, *J* 3), and its hydrate or cyclic trimer, 2,4,6-tris(trifluoromethyl)-1,3,5-trioxane (4%); δ_H 5.16 (1 H, q, *J* 4).

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* 1 mmHg = 133.322 Pa.

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