Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 4.[1] Stepwise Construction of Terminal 1,3-Diynes, Conjugated Diacetylenic Esters and a Triacetylenic Ester

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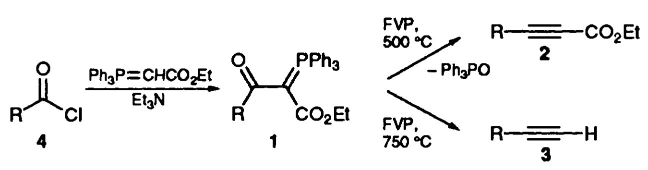
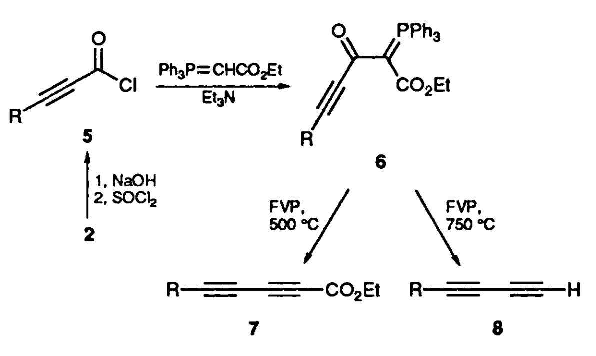
Thirteen examples of stabilised alkynoyl ylides **6** have been prepared and are found, upon flash vacuum pyrolysis (FVP) at 500 °C, to undergo extrusion of Ph_3PO to give the diacetylenic esters **7** in moderate yield. At 750 °C the same ylides afforded terminal 1,3-diynes **8** although often in poor yield. For R = 2-$MeSC_6H_4$ both **7** and **8** undergo secondary loss of $Me^{\bullet}$ and cyclisation to give 2-alkynylbenzothiophene derivatives **9** and **10** in low yield. The first example of an alkadiynoyl ylide **11** has been prepared and is converted by FVP at 500 °C into the triacetylenic ester **12**.

In part 2 of this series,[2] we reported that flash vacuum pyrolysis (FVP) of α-ethoxycarbonyl-β-oxo phosphorus ylides **1** at 500 °C results in clean extrusion of Ph_3PO to afford the acetylenic esters **2** in good yield, while at the higher temperature of 750 °C this is accompanied by cleavage of the ethoxycarbonyl group to give the terminal alkynes **3**, thus allowing convenient conversion of acid chlorides **4** into either compounds **2** or **3** in two simple steps. In this paper we describe the use of FVP to bring about the corresponding reactions of the homologous ylides **6**, readily formed by acylation of ethoxycarbonylmethylene(triphenyl)phosphorane with the acid chlorides **5** derived from hydrolysis and chlorination of **2**. The conventional pyrolysis of two examples of this type of ylide, **6b** and **6c**, was reported by Gough and Trippett in 1964[3] to give the acetylenic esters **7**, but in yields of only 16 and 9%, respectively, after chromatographic purification. Based on the encouraging results achieved with **1**,[2] we expected the use of FVP here to give improved yields of **7** and also to allow access to the terminal 1,3-diynes **8**.[4]





Results and Discussion

Thirteen examples of the alkynoyl ylides **6** were obtained in moderate to good yield by reaction of ethoxycarbonylmethylene(triphenyl)phosphorane with equimolar quantities of the appropriate acid chloride **5** and triethylamine in dry toluene at room temperature (Table 1). The acetylenic acids were readily obtained by hydrolysis of the acetylenic esters **2** obtained from ylide pyrolysis as reported previously.[2] For this reaction use of a two-phase system of ether–water and a phase-transfer catalyst gave excellent results. Although the acetylenic acids could be satisfactorily converted into the chlorides **5** by the literature method[5] of direct treatment with thionyl chloride in some instances, in others this resulted in some addition of the evolved HCl across the triple bond to give chlorocinnamic acids as significant impurities. This could be avoided completely by first converting the acids into the sodium salts and then treating these with an excess of either $SOCl_2$ or oxalyl chloride.

Table 1 Formation of ylides **6** and FVP to give **7** and **8**

	R	Yield of **6** from **5** (%)	Yield of **7** from **6** (%)	Yield of **8** from **6** (%)
a	Pr	68	37	47
b	Bu	61	—	33
c	Ph	88	53	18
d	4-MeC_6H_4	91	68	33
e	4-$MeOC_6H_4$	73	35	6
f	4-ClC_6H_4	81	24	21
g	2-MeC_6H_4	24	28	53
h	2-$MeOC_6H_4$	66	48	~0
i	2-$MeSC_6H_4$	58	6[a]	5[b]
j	2-Furyl	66	12	10
k	2-Thienyl	51	20	—
l	3-Me-2-thienyl	37	6	2
m	3-Thienyl	76	23	15

[a] 2-(Ethoxycarbonylethynyl)benzo[*b*]thiophene **9** (6%) also obtained.
[b] 2-Ethynylbenzo[*b*]thiophene **10** (5%) also obtained.

The ylides **6** were obtained as stable crystalline solids which showed the expected physical and spectroscopic properties including ^{31}P NMR signals in a remarkably narrow range of 17.3–17.5. The ^{13}C NMR spectra (Table 2) were particularly informative, providing ready confirmation of the expected structures and showing phosphorus coupling extending throughout the P–phenyl groups, to both carbonyl carbons and to the first carbon of the triple bond. The distinctive ylide carbon signals at $\delta_C \approx 75$ with a one bond coupling of 112–114 Hz are similar to but occur at slightly higher frequency than the signals for the corresponding ylides **1**.[2]

When the ylides **6** were subjected to FVP at 500 °C, the expected extrusion of Ph_3PO took place to give diacetylenic esters **7** in moderate yield (Table 1). In a few cases the two products collected separately in the cold trap but chromatographic separation was generally required to remove the Ph_3PO from the ester, resulting in some loss in yield. The

Table 2 ^{13}C NMR Spectra [$\delta(J_{P-C})$] of the ylides **6** and **11**

						Ester			P-Phenyl				
	R	≡C–*C*O	P=*C*	≡*C*–CO	≡*C*–R	CO	CH_2	CH_3	C-1	C-2	C-3	C-4	R signals
6a	Pr	173.0 (9)	74.7 (113)	81.5 (14)	91.3	166.9 (14)	58.7	13.8	125.6 (94)	133.2 (10)	128.5 (13)	131.8 (2)	21.6, 21.4, 13.7
6c	Ph	172.4 (9)	75.4 (113)	89.5 (15)	88.5	166.8 (14)	58.9	13.9	125.3 (94)	133.3 (10)	128.6 (12)	132.0 (2)	132.4, (2 C), 128.9, 128.1 (2 C), 122.4
6d	4-MeC_6H_4-	172.6 (9)	75.3 (114)	89.1 (14)	89.0	166.9 (14)	59.0	13.9	125.4 (94)	133.3 (10)	128.6 (13)	131.9 (3)	139.2, 132.5 (2 C), 128.9 (2 C), 119.4, 21.6
6e	4-$MeOC_6H_4$-	172.6 (9)	75.1 (113)	88.8 (14)	89.0	166.8 (14)	58.8	13.9	125.4 (94)	133.2 (10)	128.6 (12)	131.9 (< 2)	160.2, 134.2 (2 C), 114.3, 113.8 (2 C), 55.2
6f	4-ClC_6H_4-	172.1 (9)	75.6 (112)	90.4 (15)	87.1	166.8 (14)	58.9	13.8	125.2 (94)	133.3 (10)	128.6 (13)	132.0 (2)	134.9, 133.6 (2 C), 128.5 (2 C), 121.0
6g	2-MeC_6H_4-	172.6 (9)	75.2 (113)	93.2 (15)	87.6	166.8 (14)	58.9	13.9	125.6 (94)	133.3 (10)	128.6 (12)	131.9 (3)	141.6, 133.1, 129.3, 128.9, 125.3, 122.3, 20.7
6h	2-$MeOC_6H_4$-	172.5 (9)	75.2 (114)	93.5 (14)	85.3	166.9 (15)	58.9	13.9	125.4 (94)	133.3 (10)	128.6 (13)	131.9 (2)	160.8, 134.7, 130.5, 120.2, 111.7, 110.6, 55.7
6i	2-$MeSC_6H_4$-	172.1 (9)	75.2 (113)	95.4 (14)	85.8	166.7 (14)	58.9	13.9	125.3 (94)	133.2 (10)	128.6 (13)	131.9 (2)	142.8, 133.6, 129.3, 124.3, 124.0, 120.7, 15.2
6j	2-Furyl	171.7 (9)	75.1 (114)	94.1 (15)	78.7	166.7 (14)	59.2	13.8	125.1 (94)	133.3 (10)	128.6 (13)	132.1 (3)	144.6, 136.7, 118.3, 111.2
6k	2-Thienyl	172.0 (9)	75.3 (114)	93.7 (15)	82.1	166.8 (14)	59.1	14.0	125.2 (94)	133.3 (10)	128.6 (13)	132.0 (2)	134.1, 128.9, 127.1, 122.5
6l	3-Me-2-thienyl	172.2 (9)	75.1 (114)	96.2 (15)	82.3	166.8 (14)	59.0	14.0	125.4 (94)	133.3 (10)	128.6 (13)	132.0 (2)	145.6, 129.2, 128.0, 117.9, 15.2
6m	3-Thienyl	172.4 (9)	75.3 (113)	89.3 (15)	83.9	166.8 (14)	58.9	13.9	125.3 (94)	133.3 (10)	128.6 (13)	132.0 (2)	130.9, 130.2, 125.1, 121.6
11	4-$MeC_6H_4C{\equiv}C$	171.1 (9)	74.3 (126)	80.2 (15)	83.7	166.8 (14)	58.1	13.8	124.8 (94)	133.3 (10)	128.7 (12)	132.1 (< 2)	139.8, 132.6 (2 C), 129.1 (2 C), 118.5, 73.9, 65.8, 21.6

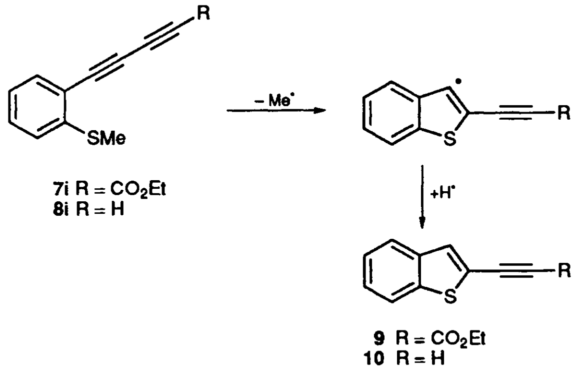
Table 3 ^{13}C NMR spectra (δ_C) of the diacetylenic esters **7** and the triacetylenic ester **12**

				Ester		
	R	≡C–	CO	CH_2	CH_3	R signals
7a	Pr	87.7, 72.4, 65.9, 64.1	153.2	62.3	14.0	21.42, 21.38, 13.4
7c	Ph	83.5, 72.1, 71.9, 70.9	152.9	62.5	14.0	133.1 (2 C), 130.5, 128.6 (2 C), 120.0
7d	4-MeC_6H_4-	83.1, 70.81, 70.77, 70.4	152.1	61.5	13.1	140.3, 132.2 (2 C), 128.5 (2 C), 116.0, 20.9
7e	4-$MeOC_6H_4$-	83.1, 70.7, 70.5, 70.3	152.1	61.3	13.0	160.3, 133.9 (2 C), 113.3 (2 C), 110.8, 54.4
7f	4-ClC_6H_4-	82.2, 73.1, 72.4, 70.6	152.8	62.5	14.0	136.9, 134.3 (2 C), 129.1 (2 C), 118.6
7g	2-MeC_6H_4-	82.6, 75.4, 72.3, 71.0	152.9	62.3	13.9	142.6, 133.4, 130.3, 129.7, 125.7, 119.7, 20.5
7h	2-$MeOC_6H_4$-	79.5, 74.7, 71.4, 70.4	152.0	61.3	13.0	161.2, 133.9, 131.0, 119.6, 109.8, 108.3, 54.8
7i	2-$MeSC_6H_4$-	80.8, 77.9, 73.6, 70.8	152.9	62.5	14.0	144.5, 134.3, 130.7, 124.7, 124.5, 118.3, 15.2
7j	2-Furyl	77.5, 75.1, 72.9, 70.3	152.7	62.6	14.0	145.9, 135.4, 120.8, 111.5
7l	3-Me-2-thienyl	78.5, (~77), 74.5, 71.1	152.9	62.3	13.9	148.4, 129.4, 129.3, 115.8, 15.1
7m	3-Thienyl	78.7, (~77), 71.9, 71.0	152.9	62.4	14.0	133.6, 130.2, 126.0, 119.3
7m	(CD_3SOCD_3)	79.3, 72.4, 71.2, 70.0	152.6	62.7	13.7	135.4, 130.5, 127.5, 118.9
12	4-MeC_6H_4-	80.3, 77.2, 73.1, 71.2, 68.5, 68.4	152.5	62.7	14.0	141.2, 133.3 (2 C), 129.4 (2 C), 116.7, 21.8

Table 4 ^{13}C NMR spectra (δ_C) of the terminal 1,3-diynes **8**

	R	≡C–H	≡C–	R signals
8a	Pr	64.4	78.3, 68.5, 64.8	21.5, 21.0, 13.4
8d	4-MeC_6H_4-	70.2	74.7, 72.2, 67.6	139.2, 131.9 (2 C), 128.5 (2 C), 117.2, 20.8
8f	4-ClC_6H_4-	71.8	74.5, 74.1, 67.9	135.8, 134.0 (2 C), 128.9 (2 C), 119.5
8g	2-MeC_6H_4-	71.8	74.5, 71.8, 68.3	142.1, 133.3, 129.6, 129.5, 125.7, 120.9, 20.6
8m	3-Thienyl	70.1	72.2, 69.5, 67.1	131.0, 129.2, 124.6, 119.2

heterocyclic substituted examples **6j–m** all gave poor yields and in the case of **6i** a significant by-product was identified spectroscopically as benzothiophene derivative **9**. This clearly results from a secondary reaction of **7i** as shown, involving loss of Me˙ cyclisation and hydrogen abstraction. This is in good agreement with the behaviour of (2-methylsulfanyl)phenylalkynes at 850 °C,[1] but the occurrence of this process at such a low temperature as 500 °C is surprising, particularly since the corresponding reaction of **6h** to give the benzofuran does not appear to occur at all under these conditions. The identity and purity of the diacetylenic esters was readily confirmed by their ^{13}C NMR spectra (Table 3). The four separate quaternary alkyne signals in each compound could not be assigned with certainty.



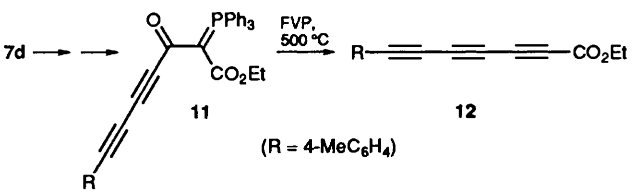
7i R = CO_2Et
8i R = H

9 R = CO_2Et
10 R = H

When the same ylides **6** were subjected to FVP at 750 °C, extrusion of Ph_3PO was accompanied by loss of the ester grouping as described previously for **1**,[2] to afford the terminal 1,3-diynes again in moderate yield (Table 1). The ^{13}C NMR data for selected examples are presented in Table 4. Apart from the poor yields for the heterocyclic examples and formation of the benzothiophene **10** from **6i**, results which are consistent with the results at 500 °C, the other noticeable feature is the very poor yields obtained for the methoxyphenyl derivatives **8e**, **h**.

Although the methoxy group can lose Me˙ under these conditions,[1] the absence of any benzofuran products corresponding to **10** in the case of **6h** indicates that other complex decomposition processes involving the diyne intervene.

The overall conversion of **2** *via* **5** and **6** into **7** is, of course, potentially just the first step in an iterative method for the construction of conjugated polyacetylenic esters and, by carrying out the final FVP at 750 °C, of terminal polyynes. We have successfully achieved the preparation of one triacetylenic ester by this method. Thus, hydrolysis and chlorination of the diacetylenic ester **7d** from FVP of **6d**, gave the diacetylenic acid chloride which upon reaction with $Ph_3P{=}CHCO_2Et$ afforded the ylide **11** in 68% yield. This compound, the first of its type, gave ^{13}C NMR data in good agreement with the pattern for **6** except for a substantial increase of the phosphorus coupling to the ylide carbon to 126 Hz for which we have no simple explanation. When this ylide was pyrolysed at 500 °C the triacetylenic ester **12** was formed in 30% yield and characterised spectroscopically. The six separate acetylenic signals in its ^{13}C NMR spectrum (Table 3) provide ready confirmation of the expected structure although the compound was too unstable to be obtained in analytically pure form. Although extension of this approach to higher polyynes would be of interest, the accumulating effect of poorer yields and increasing sensitivity of the products towards the FVP conditions mean that its usefulness beyond the formation of triynes is limited.



11 **12**

(R = 4-MeC_6H_4)

Experimental

M.p.s were recorded on a Reichert hot-stage microscope and are uncorrected. IR spectra were recorded for Nujol mulls on a

Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^1H at 300 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 $CDCl_3$ unless otherwise indicated, with internal Me_4Si as reference for ^1H and ^{13}C and external 85% H_3PO_4 as reference 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. MS-902 spectrometer using electron impact at 70 eV. Dry toluene was dried by storing over sodium wire.

Preparation of Acetylenic Acid Chlorides **5**.—A solution of the appropriate acetylenic ester **2** (30 mmol), obtained as described previously from FVP of **1**,[2] in ether (100 cm^3) was stirred vigorously with a solution of NaOH (1.25 g, 31 mmol) in water (100 cm^3) in the presence of benzyltriethylammonium chloride (0.1 g) for 5 days. The aqueous layer was separated, acidified with 2 mol dm^{-3} HCl and extracted with CH_2Cl_2. The extract was dried and evaporated to give the acetylenic acid (75–90%) which was converted directly into the acid chloride. For this, the acetylenic acid was converted into its sodium salt by dissolution in an aqueous solution of the calculated quantity of NaOH, filtering and evaporating the solution and vacuum drying the residue. A suspension of the salt (10 mmol) in dry ether (50 cm^3) was then heated under reflux with redistilled thionyl chloride (10 cm^3, 16.3 g, 137 mmol) for 6 h. Evaporation followed by Kugelrohr distillation of the residue afforded the desired acetylenic acid chloride **5** (75–85%) which was used without further purification for preparation of **6**.

Similar hydrolysis of **7d**, obtained from FVP of **6d**, conversion of the acid into its sodium salt and reaction of this with an excess of $SOCl_2$ in toluene at room temperature (RT) for 18 h afforded the diacetylenic acid chloride required for preparation of **11**.

Preparation of [Acyl(ethoxycarbonyl)methylene]triphenylphosphoranes **6** *and* **11**.—A solution of (ethoxycarbonylmethylene)triphenylphosphorane (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 **5** (29 mmol) in dry toluene (20 cm^3) was added dropwise to it. 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 were prepared.

Ethyl 3-oxo-2-triphenylphosphoranylideneoct-4-ynoate **6a**. Prepared as colourless crystals (68%), m.p. 134–136 °C (Found: C, 76.2; H, 6.1. $C_{28}H_{27}O_3P$ requires C, 76.0; H, 6.2%); ν_{max}/cm^{-1} 2218, 1672, 1505, 1435, 1340, 1250, 1100, 1078, 995, 755, 705 and 687; δ_H 7.95–7.45 (15 H, m), 3.88 (2 H, q, J 7), 2.39 (2 H, t, J 7), 1.62 (2 H, m), 1.02 (3 H, t, J 7) and 0.79 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 442 (M^+, 13%), 414 (60), 385 (32), 303 (25), 301 (22), 277 (100), 262 (65), 201 (38), 183 (95) and 152 (32).

Ethyl 3-oxo-2-triphenylphosphoranylidenenon-4-ynoate **6b**. Prepared as colourless crystals (61%), m.p. 137–138.5 °C (lit.,[3] 137–138 °C); δ_H 7.8–7.3 (15 H, m), 3.83 (2 H, q, J 7), 2.38 (2 H, t, J 7), 1.6–1.4 (4 H, m), 0.87 (3 H, t, J 7) and 0.78 (3 H, t, J 7); δ_P +17.3.

Ethyl 3-oxo-5-phenyl-2-triphenylphosphoranylidenepent-4-ynoate **6c**. Prepared as colourless crystals (88%), m.p. 173–174 °C (lit.,[3] 178–178.5 °C); ν_{max}/cm^{-1} 2208, 1678, 1520, 1490, 1444, 1350, 1274, 1212, 1108, 1090, 768, 759 and 695; δ_H 7.85–7.25 (20 H, m), 3.90 (2 H, q, J 7) and 0.82 (3 H, t, J 7); δ_C see Table 2; δ_P +17.5.

Ethyl 5-(4-methylphenyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6d**. Prepared as colourless crystals (91%), m.p. 175–176 °C (Found: C, 78.1; H, 5.3. $C_{32}H_{27}O_3P$ requires C, 78.4; H, 5.5%); ν_{max}/cm^{-1} 2190, 1660, 1505, 1430, 1335, 1258, 1200, 1100, 1082, 1020, 810, 752, 722 and 686; δ_H 7.75–7.65 (6 H, m), 7.55–7.4 (11 H, m), 7.10 (2 H, half AB pattern, J 8), 3.90 (2 H, q, J 7), 2.32 (3 H, s) and 0.81 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 490 (M^+, 97%), 475 (35), 462 (100), 461 (67), 447 (92), 433 (16), 417 (12), 389 (32), 377 (25), 301 (12), 277 (43), 262 (18), 261 (18), 201 (40) and 183 (90).

Ethyl 5-(4-methoxyphenyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6e**. Prepared as colourless crystals (73%), m.p. 159–161 °C (Found: C, 75.9; H, 5.4. $C_{32}H_{27}O_4P$ requires C, 75.9; H, 5.4%); ν_{max}/cm^{-1} 2185, 1655, 1600, 1510, 1350, 1290, 1242, 1168, 1100, 1090, 1022, 832, 752 and 690; δ_H 8.0–7.5 (17 H, m), 6.92 (2 H, half AB pattern, J 9), 3.94 (2 H, q, J 7), 3.81 (3 H, s) and 0.82 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 506 (M^+, 48%), 491 (12), 478 (34), 463 (70), 449 (8), 393 (27), 278 (28), 277 (60), 262 (22), 239 (30), 228 (18), 201 (25), 183 (100) and 159 (55).

Ethyl 5-(4-chlorophenyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6f**. Prepared as colourless crystals (81%), m.p. 164–165 °C (Found: C, 73.0; H, 4.6. $C_{31}H_{24}ClO_3P$ requires C, 72.9; H, 4.7%); ν_{max}/cm^{-1} 2196, 1662, 1508, 1478, 1430, 1335, 1258, 1202, 1101, 1083, 1010, 830, 813, 750, 720 and 688; δ_H 7.7–7.6 (6 H, m), 7.55–7.4 (11 H, m), 7.25 (2 H, half AB pattern, J 8), 3.86 (2 H, q, J 7) and 0.76 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 512 (^{37}Cl-M^+, 16%), 511 (21), 510 (^{35}Cl-M^+, 52%), 495 (12), 482 (45), 467 (40), 437 (10), 409 (18), 397 (12), 303 (16), 301 (14), 278 (20), 277 (57), 262 (25), 201 (40), 185 (77) and 183 (100).

Ethyl 5-(2-methylphenyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6g**. Prepared as colourless crystals (24%), m.p. 143–144 °C (Found: C, 78.4; H, 5.5. $C_{32}H_{27}O_3P$ requires C, 78.4; H, 5.5%); δ_H 7.75–7.65 (6 H, m), 7.6–7.4 (10 H, m), 7.25–7.05 (3 H, m), 3.87 (2 H, q, J 7), 2.55 (3 H, s) and 0.75 (3 H, t, J 7); δ_C see Table 2; m/z 490 (M^+, 62%), 475 (25), 462 (32), 461 (65), 447 (54), 445 (28), 417 (10), 389 (18), 377 (13), 375 (11), 303 (28), 301 (15), 277 (27), 262 (70), 203 (35), 201 (35) and 183 (100).

Ethyl 5-(2-methoxyphenyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6h**. Prepared as colourless crystals (66%), m.p. 154–156 °C (Found: C, 75.8; H, 5.2. $C_{32}H_{27}O_4P$ requires C, 75.9; H, 5.4%); ν_{max}/cm^{-1} 2190, 1655, 1505, 1337, 1268, 1242, 1100, 1080, 1013, 760, 727 and 688; δ_H 7.7–7.6 (6 H, m), 7.55–7.35 (10 H, m), 7.25 (1 H, m), 6.80 (2 H, m), 3.89 (2 H, q, J 7), 3.80 (3 H, s) and 0.80 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 506 (M^+, 16%), 477 (12), 463 (16), 449 (5), 433 (4), 405 (4), 331 (22), 303 (50), 301 (25), 277 (29), 262 (46), 201 (25) and 183 (100).

Ethyl 5-(2-methylsulfanylphenyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6i**. Prepared as colourless crystals (58%), m.p. 126–128 °C (Found: C, 73.8; H, 5.1. $C_{32}H_{27}O_3PS$ requires C, 73.5; H, 5.2%); ν_{max}/cm^{-1} 2182, 1658, 1502, 1430, 1360, 1337, 1272, 1245, 1200, 1100, 1082, 748, 718 and 685; δ_H 7.85–7.35 (16 H, m), 7.3–6.9 (3 H, m), 3.90 (2 H, q, J 7), 2.41 (3 H, s) and 0.79 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 522 (M^+, 11%), 507 (2), 493 (6), 475 (8), 465 (5), 447 (4), 375 (12), 331 (22), 303 (40), 279 (17), 277 (19), 262 (43), 201 (28), 198 (37) and 183 (100).

Ethyl 5-(2-furyl)-3-oxo-2-triphenylphosphoranylidenepent-4-ynoate **6j**. Prepared as colourless crystals (66%), m.p. 161–162 °C (Found: C, 75.3; H, 5.0%; M^+, 466.1372. $C_{29}H_{23}O_4P$ requires C, 74.7; H, 5.0%; M^+, 466.1334); ν_{max}/cm^{-1} 2190, 1632, 1510, 1435, 1325, 1285, 1238, 1103, 1095, 1080, 1018, 746, 721 and 683; δ_H 7.9–7.2 (16 H, m), 6.82 (1 H, m), 6.42 (1 H, m), 3.95 (2 H, q, J 7) and 0.90 (3 H, t, J 7); δ_C see Table 2; δ_P +17.4; m/z 466 (M^+, 24%), 451 (5), 438 (30), 423 (35), 409 (5), 365 (8), 353 (12), 303 (14), 301 (12), 262 (42), 201 (20), 185 (28) and 183 (100).

Ethyl 3-oxo-5-(2-thienyl)-2-triphenylphosphoranylidenepent-4-ynoate **6k**. Prepared as colourless crystals (51%), m.p. 161–163 °C (Found: C, 72.35; H, 5.1. $C_{29}H_{23}O_3PS$ requires C, 72.2; H, 4.8%); ν_{max}/cm^{-1} 2180, 1668, 1498, 1432, 1320, 1258, 1218, 1165, 1102, 1080, 840, 752, 720 and 688; δ_H 8.0–7.3 (17 H, m), 7.09 (1 H, dd, *J* 5, 3), 4.01 (2 H, q, *J* 7) and 0.93 (3 H, t, *J* 7); δ_C see Table 2; δ_P +17.5; *m/z* 482 (M^+, 100%), 467 (20), 454 (95), 453 (45), 439 (50), 425 (16), 409 (10), 381 (20), 369 (25), 303 (11), 301 (13), 277 (18), 262 (15), 201 (20) and 183 (80).

Ethyl 5-(3-*methyl*-2-*thienyl*)-3-*oxo*-2-*triphenylphosphoranylidenepent*-4-*ynoate* **6l**. Prepared as colourless crystals (37%), m.p. 154–156 °C (Found: C, 72.3; H, 5.0. $C_{30}H_{25}O_3PS$ requires C, 72.6; H, 5.1%); ν_{max}/cm^{-1} 2185, 1660, 1512, 1440, 1370, 1332, 1266, 1197, 1108, 1092, 760, 728 and 698; δ_H 8.0–7.45 (15 H, m), 7.31 and 6.92 (2 H, AB pattern, *J* 5), 3.96 (2 H, q, *J* 7), 2.46 (3 H, s) and 0.84 (3 H, t, *J* 7); δ_C see Table 2; δ_P +17.4; *m/z* 496 (M^+, 23%), 468 (18), 453 (17), 439 (8), 395 (6), 383 (25), 303 (18), 301 (12), 262 (25), 239 (20), 201 (26), 184 (85) and 183 (100).

Ethyl 3-*oxo*-5-(3-*thienyl*)-2-*triphenylphosphoranylidenepent*-4-*ynoate* **6m**. Prepared as colourless crystals (76%), m.p. 137–139 °C (Found: C, 72.3; H, 4.45. $C_{29}H_{23}O_3PS$ requires C, 72.2; H, 4.8%); ν_{max}/cm^{-1} 2196, 1662, 1504, 1435, 1327, 1255, 1210, 1160, 1100, 1080, 788, 752, 735 and 690; δ_H 7.7–7.6 (6 H, m), 7.55–7.35 (9 H, m), 7.25–7.1 (3 H, m), 3.89 (2 H, q, *J* 7) and 0.80 (3 H, t, *J* 7); δ_C see Table 2; δ_P +17.4; *m/z* 482 (M^+, 74%), 467 (16), 454 (65), 453 (37), 439 (55), 425 (12), 409 (12), 381 (20), 375 (10), 369 (15), 303 (13), 301 (22), 277 (38), 262 (100), 201 (35) and 183 (98).

Ethyl 7-(4-*methylphenyl*)-3-*oxo*-2-*triphenylphosphoranylidenehepta*-4,6-*diynoate* **11**. Prepared as colourless crystals (68%), m.p. 169–180 °C (Found: M^+, 514.1715. $C_{34}H_{27}O_3P$ requires M^+, 514.1698); ν_{max}/cm^{-1} 2208, 1660, 1520, 1433, 1343, 1288, 1234, 1180, 1100, 1080, 818, 760, 720 and 682; δ_H 7.9–7.3 (17 H, m), 7.15 (2 H, half AB pattern, *J* 8), 3.89 (2 H, q, *J* 7), 2.36 (3 H, s) and 0.86 (3 H, t, *J* 7); δ_C see Table 2; δ_P +17.3; *m/z* 514 (M^+, 27%), 487 (25), 486 (100), 471 (15), 457 (10), 441 (7), 414 (20), 401 (11), 301 (8), 277 (38), 261 (18), 229 (14), 201 (15) and 183 (66).

Flash Vacuum Pyrolysis of Ylides.—The apparatus used was as described previously.[6] All pyrolyses were conducted at pressures in the range 10^{-3}–10^{-1} Torr and were complete within 1 h. Under these conditions the contact time in the hot zone was estimated to be ≈10 ms. In some cases Ph_3PO collected at the furnace exit and the volatile products were recovered from the cold trap. Where necessary, in the case of less volatile products, the entire pyrolysate was washed out together and separated by preparative TLC. Yields were determined by calibration of the ^1H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 and comparing integrals, a procedure estimated to be accurate to ±10%.

Conversion of ylides **6** *into acetylenic esters* **7** *at* 500 °C. *Compound* **7a**. FVP of the ylide **6a** (212 mg) at 500 °C gave ethyl octa-2,4-diynoate **7a** (29 mg, 37%) as a colourless liquid; δ_H 4.24 (2 H, q, *J* 7), 2.33 (2 H, t, *J* 7), 1.60 (2 H, sextet, *J* 7), 1.32 (3 H, t, *J* 7) and 1.02 (3 H, t, *J* 7); δ_C see Table 3.

Compound **7c**. FVP of the ylide **6c** (448 mg) at 500 °C followed by preparative TLC on silica using ether gave ethyl 5-phenylpenta-2,4-diynoate **7c** (53%) as a colourless liquid (Found: M^+, 198.0686. $C_{13}H_{10}O_2$ requires M^+, 198.0681); δ_H 7.65–7.2 (5 H, m), 4.27 (2 H, q, *J* 7) and 1.32 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 198 (M^+, 22%), 154 (9), 153 (52), 126 (100), 113 (10), 98 (15) and 75 (36).

Compound **7d** FVP of the ylide **6d** (476 mg) at 500 °C gave ethyl 5-(4-methylphenyl)penta-2,4-diynoate **7d** (68%) as a colourless liquid (Found: M^+, 212.0851. $C_{14}H_{12}O_2$ requires M^+, 212.0837); δ_H 7.42 and 7.15 (4 H, AB pattern, *J* 8), 4.27 (2 H, q, *J* 7), 2.38 (3 H, s) and 1.32 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 212 (M^+, 10%), 193 (4), 167 (38), 140 (100), 139 (84), 135 (27), 119 (32) and 91 (38).

Compound **7e** FVP of the ylide **6e** (192 mg) at 500 °C gave a liquid which was purified by preparative TLC on silica using ether to afford ethyl 5-(4-methoxyphenyl)-penta-2-4-diynoate **7e** (35%) as a colourless liquid (Found: M^+, 228.0775. $C_{14}H_{12}O_3$ requires M^+, 228.0786); δ_H 7.50 and 6.88 (4 H, AB pattern, *J* 9), 4.28 (2 H, q, *J* 7), 3.82 (3 H, s) and 1.34 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 228 (M^+, 12%), 201 (4), 183 (18), 168 (8), 156 (100), 140 (19), 112 (18) and 86 (47).

Compound **7f**. FVP of the ylide **6f** (192 mg) at 500 °C gave a liquid which was purified by preparative TLC on silica using ether—hexane (3:7) to afford ethyl 5-(4-chlorophenyl)penta-2,4-diynoate **7f** (24%) as a colourless liquid (Found: M^+, 232.0303. $C_{13}H_9ClO_2$ requires M^+, 232.0291); δ_H 7.63 and 7.47 (4 H, AB pattern, *J* 9), 4.36 (2 H, q, *J* 7) and 1.37 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 232 (^{35}Cl–M^+, 3%), 187 (15), 162 (55), 160 (100), 159 (45), 149 (6) and 123 (60).

Compound **7g**. FVP of the ylide **6g** (250 mg) at 500 °C followed by preparative TLC on silica using ether gave ethyl 5-(2-methylphenyl)penta-2,4-diynoate **7g** (28%) as a colourless liquid (Found: M^+, 212.0829. $C_{14}H_{12}O_2$ requires M^+, 212.0837); δ_H 7.50 (1 H, m), 7.35–7.15 (3 H, m), 4.29 (2 H, q, *J* 7), 2.47 (3 H, s) and 1.36 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 212 (M^+, 23%), 167 (27), 140 (65), 139 (100), 137 (12), 127 (18) and 115 (12).

Compound **7h**. FVP of the ylide **6h** (448 mg) at 500 °C followed by preparative TLC on silica using ether gave ethyl 5-(2-methoxyphenyl)penta-2,4-diynoate **7h** (48%) as a colourless liquid (Found: M^+, 228.0787. $C_{14}H_{12}O_3$ requires M^+, 228.0786); δ_H 7.7–7.65 (2 H, m), 7.15–6.9 (2 H, m), 4.35 (2 H, q, *J* 7), 3.97 (3 H, s) and 1.37 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 228 (M^+, 50%), 183 (27), 156 (100), 155 (95), 127 (32), 126 (30), 86 (80) and 84 (90).

Compound **7i** FVP of the ylide **6i** (193 mg) at 500 °C gave a colourless oil which was separated by preparative TLC on silica with ether-hexane (3:7) to give two products: ethyl 5-(2-methylsulfanylphenyl)penta-2,4-diynoate **7i** (6%) as a colourless liquid (Found: M^+, 244.0558. $C_{14}H_{12}O_2S$ requies M^+, 244.0558); δ_H 7.5–7.0 (4 H, m), 4.30 (2 H, q, *J* 7), 2.50 (3 H, s) and 1.35 (3 H, t, *J* 7); δ_C see Table 3, and 2-(ethoxycarbonylethynyl)-benzothiophene **9** (6%); δ_H 7.9–7.1 (5 H, m), 4.35 (2 H, q, *J* 7) and 1.40 (3 H, t, *J* 7); $\delta_C(CD_3SOCD_3)$ 153.7 (CO), 141.5 (C), 138.5 (C), 133.6, 126.8, 125.2, 124.6, 122.2 (all CH), 119.4 (C), 85.8 and 79.9 (≡CH–), 62.3 (CH_2) and 14.1 (CH_3).

Compound **7j**. FVP of the ylide **6j** (240 mg) at 500 °C followed by preparative TLC on silica using ether gave ethyl 5-(2-furyl)penta-2,4-diynoate **7j** (12%) as a colourless liquid (Found: M^+, 188.0461. $C_{11}H_8O_3$ requires M^+, 188.0473); δ_H 7.48 (1 H, dd, *J* 2, 1), 6.90 (1 H, dd, *J* 4, 1), 6.44 (1 H, dd, *J* 4, 2), 4.28 (2 H, q, *J* 7) and 1.34 (3 H, t, *J* 7); δ_C see Table; *m/z* 188 (M^+, 100%), 143 (75) and 116 (80).

Compound **7k**. FVP of the ylide **6k** (174 mg) at 500 °C gave a liquid which was purified by preparative TLC on silica using ether–light petroleum (b.p. 40–60 °C) (4:1) to afford ethyl 5-(2-thienyl)penta-2,4-diynoate **7k** (20%) as a colourless liquid (Found: M^+, 204.0250. $C_{11}H_8O_2S$ requires M^+, 204.0245); δ_H 7.5–7.3 (2 H, m), 7.0 (1 H, m), 4.22 (2 H, q, *J* 7) and 1.24 (3 H, t, *J* 7); *m/z* 204 (M^+, 23%), 160 (8), 159 (36) and 132 (100).

Compound **7l**. FVP of the ylide **6l** (300 mg) at 500 °C gave a liquid which was purified by preparative TLC on silica using ether–hexane (3:7) to afford ethyl 5-(3-methyl-2-thienyl)penta-2,4-diynoate **7l** (6%) as a colourless liquid; δ_H 7.28 and 6.87 (2 H, AB pattern, *J* 5), 4.27 (2 H, q, *J* 7), 2.35 (3 H, s) and 1.32 (3 H, t, *J* 7); δ_C see Table 3.

Compound **7m**. FVP of the ylide **6m** (348 mg) at 500 °C gave a liquid which was purified by preparative TLC on silica using ether–hexane (3:7) to afford ethyl 5-(3-thienyl)penta-2,4-diynoate **7m** (23%) as a colourless liquid (Found: M^+, 204.0249. $C_{11}H_8O_2S$ requires M^+, 204.0245); δ_H 7.85 (1 H, dd, *J* 3, 2), 7.41 (1 H, d, *J* 3), 7.33 (1 H, d, *J* 2), 4.34 (2 H, q, *J* 7) and 1.35 (3 H, t, *J* 7); δ_C see Table 3; *m*/*z* 204 (M^+, 15%), 159 (26), 132 (100) and 131 (40).

Compound **12**. FVP of the ylide **11** (230 mg) at 500 °C gave a solid which consisted mainly of ethyl 7-(4-methylphenyl)hepta-2,4,6-triynoate **12** (30%); δ_H 7.9–7.5 (4 H, m), 4.32 (2 H, q, *J* 7), 2.41 (3 H, s) and 1.33 (3 H, t, *J* 7); δ_C see Table 3; *m*/*z* 236 (M^+, 12%), 191 (21), 164 (100) and 162 (11).

Conversion of the ylides **6** *into the* 1,3-*diynes* **8** *at* 750 °C. Compound **8a**. FVP of the ylide **6a** (340 mg) at 750 °C gave hepta-1,3-diyne **8a** (47%) as a colourless liquid; δ_H 2.17 (2 H, t of d, *J* 7, 1), 1.88 (1 H, t, *J* 1), 1.50 (2 H, sextet, *J* 7), and 0.94 (3 H, t, *J* 7); δ_C see Table 4; *m*/*z* 92 (M^+, 42%), 91 (100), 65 (17), 63 (32) and 62 (17).

Compound **8b**. FVP of the ylide **6b** (232 mg) at 750 °C gave oct-1,3-diyne **8b** (33%) as a colourless liquid; δ_H 2.30 (2 H, t, *J* 7), 1.98 (1 H, s), 1.7–1.3 (4 H, m) and 0.94 (3 H, t, *J* 7).

Compound **8c**. FVP of the ylide **6c** (253 mg) at 750 °C gave phenylbutadiyne **8c** (18%) as a colourless liquid; δ_H 7.65–7.3 (5 H, m) and 2.46 (1 H, s).

Compound **8d**. FVP of the ylide **6d** (343 mg) at 750 °C followed by preparative TLC on silica using ether–hexane (3 : 7) gave (4-methylphenyl)butadiyne **8d** (33%) as a colourless liquid (Found: M^+, 140.0626. $C_{11}H_8$ requires *M*$^+$, 140.0626); δ_H 7.43 and 7.14 (4 H, AB pattern, *J* 8), 2.38 (1 H, s) and 2.28 (3 H, s); δ_C see Table 4; *m*/*z* 140 (M^+, 68%), 139 (100), 113 (9), 98 (4), 89 (7) and 86 (13).

Compound **8e**, FVP of the ylide **6e** (500 mg) at 750 °C followed by preparative TLC on silica using ether–hexane (3 : 7) gave (4-methoxyphenyl)butadiyne **8e** (6%) as a colourless liquid (Found: M^+, 156.0557. $C_{11}H_8O$ requires *M*$^+$, 156.0575); δ_H 7.48 and 6.90 (4 H, AB pattern, *J* 9), 3.86 (3 H, s) and 2.47 (1 H, s); *m*/*z* 156 (M^+, 17%), 152 (21), 147 (21), 135 (260), 111 (10), 109 (13), 84 (30) and 73 (100).

Compound **8f**. FVP of the ylide **6f** (380 mg) at 750 °C gave pale yellow crystals of (4-chlorophenyl)butadiyne **8f** (21%) (Found: M^+, 160.0029. $C_{10}H_5Cl$ requires *M*$^+$, 160.0080); δ_H 7.57 and 7.42 (4 H, AB pattern, *J* 9) and 2.54 (1 H, s); δ_C see Table 4; *m*/*z* 160 (^{35}Cl-M^+, 4%), 97 (5), 84 (68) and 66 (100).

Compound **8g**. FVP of the ylide **6g** (280 mg) at 750 °C gave (2-methylphenyl)butadiyne **8g** (53%) as a pale yellow solid; δ_H 7.7–7.5 (1 H, m), 7.4–7.25 (3 H, m), 2.56 (1 H, s) and 2.50 (3 H, s); δ_C see Table 4; *m*/*z* M^+ not observed.

Compound **8h**. FVP of the ylide **6h** (220 mg) at 750 °C followed by preparative TLC on silica using ethyl acetate gave a colourless liquid which contained some (2-methoxyphenyl)-butadiyne **8h** (Found: M^+, 156.0572. $C_{11}H_8O$ requires *M*$^+$, 156.0575) and which did display the expected ^1H NMR peaks at δ_H 3.83 (3 H, s) and 2.47 (1 H, s) but was contaminated with a compound showing ^1H NMR peaks in the aromatic region only.

Compound **8i**. FVP of the ylide **6i** (540 mg) at 750 °C gave a colourless oil which was shown by GCMS and ^1H NMR to contain two products: (2-methylsulfanylphenyl)butadiyne **8i** (5%); δ_H 7.8–7.0 (4 H, m), 2.60 (1 H, s) and 2.47 (3 H, s); *m*/*z* 172 (M^+, 68%), 171 (100), 170 (25), 127 (30), 113 (35), 98 (22) and 87 (25), and 2-ethynylbenzothiophene **10** (5%); δ_H 7.9–7.1 (5 H, m) and 2.5 (1 H, s); *m*/*z* 158 (M^+, 100%), 132 (3), 115 (16), 114 (25) and 93 (6).

Compound **8j**. FVP of the ylide **6j** (340 mg) at 750 °C gave (2-furyl)butadiyne **8j** (10%) as a colourless liquid (Found: M^+, 116.0258. C_8H_4O requires *M*$^+$, 116.0262); δ_H 7.40 (1 H, m), 6.78 (1 H, m), 6.40 (1 H, m) and 2.67 (1 H, s).

Compound **8l**. FVP of the ylide **6l** (320 mg) at 750 °C gave (3-methyl-2-thienyl)butadiyne **8l** (2%) as a colourless liquid; δ_H 7.13 and 6.76 (2 H, AB pattern, *J* 5), 2.60 (1 H, s) and 2.28 (3 H, s).

Compound **8m**. FVP of the ylide **6m** (480 mg) at 750 °C gave a liquid which was purified by preparative TLC on silica using ether–hexane (1 : 1) to afford (3-thienyl)butadiyne **8m** (15%) as a colourless liquid (Found: M^+, 132.0020. C_8H_4S requires *M*$^+$, 132.0034); δ_H 7.42 (1 H, m), 7.1–6.9 (2 H, m) and 2.35 (1 H, s); δ_C see Table 4; *m*/*z* 132 (M^+, 20%), 121 (4), 88 (20), 86 (90), 85 (68), 84 (100) and 73 (32).

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