# Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 8.[1] Preparation of symmetrical and unsymmetrical 1,3-diynes from alkynoyl ylides and oxalyl diylides

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Seven examples of the alkynoyl phosphorus ylides 5 have been prepared and are found, upon flash vacuum pyrolysis (FVP) at 750 °C, to undergo extrusion of Ph_3PO to give the unsymmetrical 1,3-diynes 9 in moderate yield. Six examples of the oxalyl diylides 6 have been prepared and their fully assigned ^{13}C NMR spectra are presented. Upon FVP, those with R = aryl undergo two-fold extrusion of Ph_3PO to give symmetrical 1,3-diynes 13 but this requires the unusually severe temperature of 900 °C. In contrast those with R = CO_2Me, CO_2Et or $COPh$ undergo complete reaction at 500 °C but afford only Ph_3PO and fragmentation products.

In Part 1 of this series,[2] we described the use of flash vacuum pyrolysis (FVP) to bring about the extrusion of Ph_3PO from the β-oxo phosphorus ylides 1 to give the alkynes 2, a transformation which, for R^1 = H or alkyl, is not possible using conventional pyrolysis. Since 1 is readily prepared in two steps from an alkyl halide and an acid chloride, this provides a useful overall synthesis of the alkynes. We later showed that FVP also gives excellent results for the ester stabilised ylides 3[3] and their alkynoyl analogues 4,[4] affording acetylenic and diacetylenic esters respectively, with the added advantage that the corresponding terminal alkynes and 1,3-diynes could be obtained simply by increasing the pyrolysis temperature in each case. In this paper we describe the preparation of alkynoyl ylides 5, including examples with R^1 = alkyl which have not been reported before, and their behaviour upon FVP. A brief
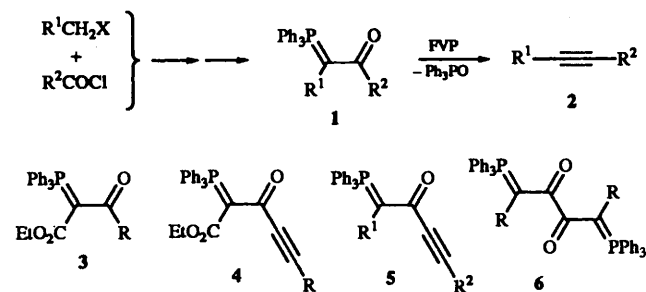
report by Gough and Trippett in 1964 described the conventional pyrolysis of six examples of 5 with an α-stabilising group (R^1 = CO_2Et, CN, Ph, R^2 = Ph, Bu) to give the diynes in 9–30% yield.[5] On the basis of our previous work we expected the use of FVP to give improved yields and, more importantly, to be successful for R^1 = alkyl, thus allowing preparation of purely aliphatic 1,3-diynes. The efficient synthesis of unsymmetrical 1,3-diynes is a rather difficult process which is of continuing interest.[6] We also report the preparation of six oxalyl diylides 6 and their behaviour upon FVP which is expected to provide an efficient route to symmetrical 1,3-diynes.

Results and discussion

Six examples of the alkynoyl ylides 5 were obtained (see Scheme 1), by treatment of the ylides 7, generated from the corresponding phosphonium salts and BuLi, with alkynoyl
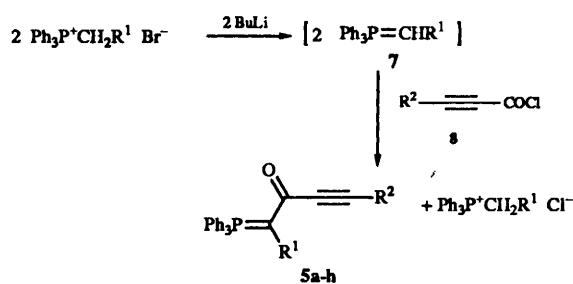
Scheme 1

Table 1 Formation of the ylides 5 and FVP to give 9

	R^1	R^2	Yield of 5 from 7 (%)	δ_P	Yield of 9 from 5 (%)
a	Me	Bu	31	18.5	49
b	Et	Bu	30	18.4	45
c	Pr	Bu	24	18.3	42
d	Pr^i	Bu	26	17.8	15
e	Ph	Bu	65	16.0	46
f	Bu	Ph	54	18.6	61
g	Ph	Ph	39	16.3	70
h	$4\text{-}NO_2C_6H_4$	$4\text{-}MeOC_6H_4$	72	16.4	52

chlorides 8 (0.5 equiv.) in THF at room temperature (Table 1). The reaction proceeds with transylidation[7] to regenerate 1 mol equiv. of phosphonium salt. The compounds were obtained in disappointing yield, particularly where both R^1 and R^2 were aliphatic groups, due to partial hydrolysis and decomposition during the recrystallisation needed to remove all traces of the phosphonium salt. The compounds showed the expected spectroscopic properties including ^{31}P NMR signals at δ_P + 17.8–18.6 for R^1 = alkyl and + 16.0–16.4 for R^1 = aryl and IR absorptions in the range 2188–2200 cm^{-1} for the C≡C bond. As expected the ^{13}C NMR spectra of selected compounds (Table 2) were particularly informative with phosphorus coupling extending throughout the P-phenyl groups, through the carbonyl to the first acetylenic carbon, and in most cases to the first carbon of R^1. The ylide carbon in 5h gave a signal of particularly low intensity which could not be observed.

When the ylides 5 were subjected to FVP at 750 °C, Ph_3PO accumulated at the furnace exit and the desired 1,3-diynes 9

**Table 2** ^{13}C NMR spectra of the ylides **5**, δ_C $(J_{P,C})$

						P-Phenyl				
	R^1	R^2	C=O	P=C	CO–C≡	≡C–	C-1	C-2	C-3	C-4	R^1 and R^2 signals
5b	Et	Bu	168.4 (10)	73.9 (102)	80.5 (19)	89.3	125.7 (90)	133.6 (10)	128.7 (12)	131.9 (2)	30.4, 21.9, 21.8, 18.9, 18.3, 13.6
5c	Pr	Bu	169.2 (11)	71.0 (103)	81.2 (19)	88.5	126.1 (90)	133.6 (10)	128.6 (12)	131.8 (<2)	30.8 (12), 30.5, 27.3, 21.9, 18.9, 13.7, 13.6
5g	Ph	Ph	168.5 (11)	78.3 (114)	90.3 (18)	87.0	125.7 (91)	133.8 (10)	128.6 (12)	131.9 (2)	137.2 (11), 134.5 (2C, 4), 132.2 (2C), 128.3 127.9 (2C), 127.2 (2C), 125.4, 122.8
5h			169.0 (9)	—*	88.3 (22)	88.7	125.0 (92)	133.7 (10)	129.0 (12)	132.4 (2)	145.9 (12), 144.6, 133.4 (2C, 5), 122.2 (2C) 160.2, 133.8 (2C), 114.0 (3C†), 55.3

* This signal was of extremely low intensity and could not be observed. † The signals for C-1, C-3 and C-5 of the 4-methoxyphenyl group are coincident in $CDCl_3$; in CD_3SOCD_3 they come at δ_C 113.0 (C-1) and 114.4 (C-3,5).

Table 3 ^{13}C NMR spectra of the 1,3-diynes **9** and **13**, δ_C

|	R^1	R^2	–C≡	R^1 signals	R^2 signals
9a	Me	Bu	76.9, 73.0, 65.2, 64.5	4.2	30.3, 21.9, 18.8, 13.5
9b	Et	Bu	78.6, 77.6, 65.3, 64.8	13.45, 12.9	30.4, 22.0, 18.9, 13.53
9c	Pr	Bu	77.5, 77.3, 65.5, 65.3	21.94, 21.2, 13.48	30.4, 21.89, 18.9, 13.54
9d	Pr^i	Bu	82.5, 78.3, 65.1, 64.6	18.8, 22.6 (2C)	30.4, 21.9, 18.9, 13.5
9e	Ph	Bu	84.8, 74.7, 74.5, 65.1	132.5 (2C), 128.8, 128.3 (2C), 122.1	30.3, 22.0, 19.3, 13.6
9g (= 13a)	Ph	Ph	81.5, 73.9	132.5 (2C), 129.2, 128.4 (2C), 121.8	(R^2 = R^1)
9h	4-NO$_2$C$_6$H$_4$	4-MeOC$_6$H$_4$	84.9, 78.7, 77.2, 72.2	147.3, 134.4* (2C), 129.1, 123.7 (2C)	160.9, 133.1* (2C), 114.3 (2C), 113.0
13b	4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	80.8, 74.6	135.6, 133.7 (2C), 128.9 (2C), 120.1	(R^2 = R^1)

* Assignment may be interchanged.
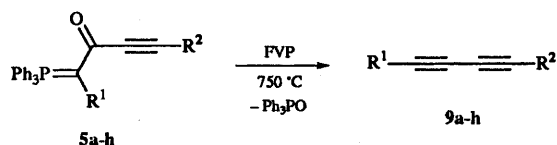
were obtained directly from the cold trap in pure form, except in the case of **9h** where the less volatile diyne collected with the Ph$_3$PO and had to be separated by preparative TLC. The identity and purity of the products was clear from the ^{13}C NMR data (Table 3) which are in good agreement with expectation and showed no significant contamination from isomeric hydrocarbons. The yields were only moderate (see Table 1) with the balance of the material being accounted for by non-volatile decomposition products left in the inlet tube and varying amounts of tar at the furnace exit. The particularly low yield in the case of **9d** may be due to elimination of propene from the secondary alkyl group which leads to further radical decomposition. The yields do, however, compare favourably with those obtained using conventional pyrolysis in the two cases previously studied (**9e** 23%, **9g** 24%),[5] and it is likely on the basis of previous work that conventional pyrolysis of **9a–d** and **9f** with aliphatic R^1 would fail completely. In this context it is interesting to note that under FVP conditions there is no significant difference in the yield of diyne obtained from the isomeric ylides **9e** and **9f**. Despite the disappointing overall yields, the preparation and FVP of **5** does represent a viable approach to the synthesis of unsymmetrical 1,3-diynes including purely aliphatic examples. The donor–acceptor substituted diaryldiyne **9h**, prepared here for the first time, is likely to be of interest as a potential second-harmonic generator for non-linear optics.[8]

Simultaneous formation of both triple bonds of a 1,3-diyne should, in principle, be possible by two-fold extrusion of Ph$_3$PO from the oxalyl diylides [1,4-bis(triphenyl-phosphoranylidene)butane-2,3-diones] **6**. Accordingly, we have prepared representative examples of this compound class and examined their behaviour upon FVP. The first compound of this type, **6e**, was prepared by Gough and Trippett[5] by treatment of Ph$_3$P=CHCO$_2$Et (4 equiv.) with oxalyl chloride,

but was reported not to give the expected diyne upon conventional pyrolysis. In a later study, Mehrotra and co-workers[9] reported the preparation of **6** (R = H, Me, Et) and **6d** by reaction of the appropriate ylides **10** with EtSC(O)-C(O)SEt, and went on to describe their use for the formation of transition metal complexes.[10] Most recently, Bestmann and co-workers described the formation of **6** (R = H) from oxalic acid and Ph$_3$P=C(SiMe$_3$)$_2$.[11]

In our hands the reaction of a range of simple non-stabilised ylides **10** (R = Me, Et, Pr, Pr^i), generated from the corresponding phosphonium salts and BuLi, with oxalyl chloride at temperatures as low as $-60\,^\circ$C resulted in a vigorous and complex reaction from which only Ph$_3$PO could be isolated. Use of semi-stabilised ylides gave somewhat better results, and treatment of **10** (4 equiv.) with oxalyl chloride in THF at room temperature (see Scheme 2) afforded the diylides
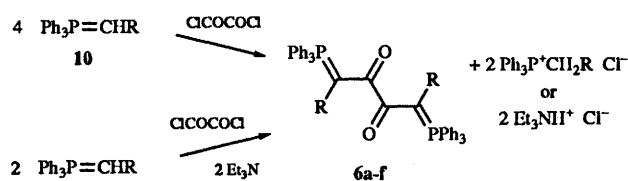

Scheme 2

6a–c albeit in disappointing yield (Table 4). The compounds were rather difficult to obtain in pure form and repeated recrystallisation was not successful in removing the last traces of the phosphonium salt produced in the transylidation process and also some Ph$_3$PO resulting from hydrolysis. Despite this, spectroscopic examination revealed that the materials obtained did consist overwhelmingly of the desired compounds. In particular, the ^{31}P NMR signals at δ_P +14.4–14.5 and the highly informative ^{13}C NMR spectra (Table 5) were in good agreement with expectation. In the latter spectra, the ylide carbon gave a signal at $\delta_C \approx 70$ ($^1J_{C,P}$ 102–105 Hz) and phosphorus coupling was also observed throughout the P-phenyl rings and to the first two positions of the R groups. The carbonyl signals were particularly characteristic, coming as double doublets in the range δ_C 185–190. By analogy with

Table 4 Formation of the diylides **6** and FVP to give **13**

	R	Yield of **6** (%)	δ_P	Yield of **13** from **6** (%)
a	Ph	32	14.4	64
b	4-ClC$_6$H$_4$	58	14.5	10
c	4-BrC$_6$H$_4$	21	14.4	—
d	CO$_2$Me	69	16.3	—
e	CO$_2$Et	73	16.0	—
f	COPh	64	17.6	—

similar compounds we assign the smaller coupling constant (4–5 Hz) to the two-bond coupling to the nearer phosphorus and the larger value of 12–13 Hz to $^3J_{C,P}$.

For the synthesis of **6d–f** we first examined the reaction of **10** (4 equiv.) with oxalyl chloride as used in the original preparation of **6e**.[5] While this was successful, better yields could be obtained by use of triethylamine as base rather than **10** itself. Thus, these compounds were prepared in moderate yield (Table 4) from **10** (2 equiv.) and Et$_3$N (2 equiv.) as shown in Scheme 2. Again the ^{31}P and ^{13}C (Table 5) NMR spectra provided clear confirmation of the structures. The properties of **6e** were in good agreement with those previously reported,[5] but those of **6d** were not. Mehrotra and co-workers[9] reported a melting point of 136 °C for **6d** and claimed that it was too insoluble for NMR spectra to be obtained. In contrast our sample had a melting point of 273–274 °C and was readily soluble in CDCl$_3$, giving all the expected analytical and spectroscopic data. We conclude that the material obtained by Mehrotra and co-workers was not, in fact, **6d**. It is interesting to note that, while our work was in progress, Capuano and co-workers reported the formation of a quite different product from Ph$_3$P=CHCOPh

11 (H$_2$O) **12**
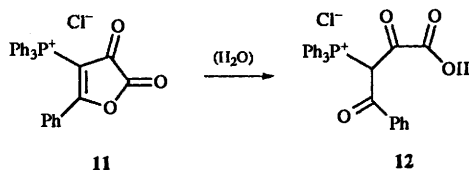
and oxalyl chloride.[12] When this ylide (1 equiv.) is added to oxalyl chloride, the hygroscopic cyclic phosphonium salt **11** is formed which is readily hydrolysed to afford **12**. Formation of this type of product was avoided in our work by reversing the order of addition and always adding oxalyl chloride to an excess of the ylides.

Some difficulty was experienced in obtaining satisfactory mass spectra of the diylides **6** which is not surprising in view of their high molecular mass (M_r 722–914) and expected thermal lability. In most cases electron-impact ionisation even at 20 eV gave M$^+$ − Ph$_3$PO and/or M$^+$/2 as the highest prominent peaks, but use of FAB did give M + H$^+$ signals for **6a** and **6b**.

When the diylides **6a** and **6b** were subjected to FVP they proved to be extraordinarily resistant towards extrusion, coming through the furnace largely unchanged even up to 850 °C. Only at 900 °C was reaction complete to give the desired diynes **13a** and **13b** in yields of 64 and 10%, respectively. The poor yield in the latter case was partly due to the need for chromatographic separation of this less volatile diyne from

6 FVP 900 °C − 2Ph$_3$PO R———≡———≡———R **13**
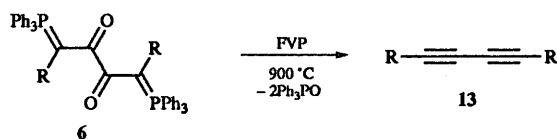
Ph$_3$PO. Both these products gave the expected ^{1}H and ^{13}C (Table 3) NMR data but **13b** was not obtained in sufficient

purity for full characterisation. Unfortunately, **6c** could not be obtained in sufficient purity for its pyrolysis to be examined.

A completely different pattern of behaviour was observed for the more highly stabilised examples **6d–f**. All these compounds underwent complete reaction upon FVP at 500 °C to give a high yield of Ph$_3$PO. Unfortunately, however, none of the desired diynes could be detected. The only products isolated from the cold trap were methanol from **6d**, ethanol and acetaldehyde from **6e** and benzoic acid from **6f**. In Part 2 of this series[3] we described the thermal loss of acetylenic ethyl ester groups upon FVP at 750 °C to give the corresponding terminal alkynes and this was shown to proceed at least in part by a mechanism involving loss of acetaldehyde and CO. It therefore seems likely that the expected diyne diesters **13d** and **13e** may be formed here, but are not stable under the conditions used and fragment by concerted and radical routes to give methanol, ethanol and acetaldehyde as the only non-gaseous products. At present we have no simple explanation for the formation of benzoic acid from **6f**, but this product has also been obtained from FVP of a variety of other benzoyl-containing polyoxo ylides and diylides and further evidence on the mechanisms involved will be reported shortly.

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. IR spectra were recorded for solids as Nujol mulls and for liquids as thin films unless otherwise indicated, on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^{1}H 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$_4$Si as reference for ^{1}H and ^{13}C and external 85% H$_3$PO$_4$ 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 or, where noted, using FAB on a Fisons VG Autospec instrument. Toluene was dried by storage over sodium wire and dry THF was freshly distilled from potassium benzophenone ketyl.

Preparation of alkynoyl ylides 5

A suspension of the appropriate phosphonium salt **7** (25 mmol) in dry THF (100 cm^3) was stirred at room temperature under N$_2$ while a solution of BuLi in hexane (26 mmol) was added slowly by syringe. This was followed after 30 min by addition of the appropriate alkynoyl chloride **8** (prepared from the corresponding alkynoic acid as described previously[4]) (12.5 mmol) in dry THF (10 cm^3). After 3 h the mixture was added to water (250 cm^3) and extracted with diethyl ether (2 × 50 cm^3) and ethyl acetate (2 × 50 cm^3). Drying and evaporation of the extract gave the ylide which crystallised with time. In cases of difficulty crystallisation could be induced by trituration with a small quantity of ethyl acetate. The compounds were recrystallised from ethyl acetate. The following compounds were prepared by this method.

2-Triphenylphosphoranylidenenon-4-yn-3-one 5a. From ethyl-(triphenyl)phosphonium bromide and hept-2-ynoyl chloride as pale yellow crystals (31%), mp 186–187 °C (Found: C, 81.55; H, 7.0. C$_{27}$H$_{27}$OP requires C, 81.4; H, 6.8%); ν_{max}/cm^{-1} 2220, 1500, 1435, 1358, 1178, 1109, 988, 811, 755, 730 and 697; δ_H 7.75–7.25 (15 H, m), 2.34 (2 H, t, J 7), 1.81 (3 H, d, J 15), 1.7–1.4 (4 H, m) and 0.89 (3 H, t, J 7); δ_P +18.5; m/z 398 (M$^+$, 30%), 369 (6), 355 (15), 341 (5), 327 (12), 317 (12), 277 (12), 262 (62), 201 (15) and 183 (100).

3-Triphenylphosphoranylidenedec-5-yn-4-one 5b. From prop-yl(triphenyl)phosphonium bromide and hept-2-ynoyl chloride as pale yellow crystals (30%), mp 148–150 °C (Found: C, 81.6; H, 7.1. C$_{28}$H$_{29}$OP requires C, 81.5; H, 7.1%); ν_{max}/cm^{-1} 2200,

Table 5 ^{13}C NMR spectra of the diylides **6**, δ_C ($J_{P,C}$)

	R	COCO ($^2J,^3J$)	P=C	P-Phenyl				R signals
				C-1	C-2	C-3	C-4	
6a	Ph	188.2 (5,13)	68.5 (105)	125.4 (95)	133.7 (10)	128.2 (12)	130.2 (2)	136.7 (11), 136.0 (2C, 5), 127.2, 126.9 (2C)
6b	4-ClC$_6$H$_4$	187.9 (5,13)	67.8 (104)	126.0 (90)	133.6 (10)	128.4 (12)	131.4 (<2)	137.0 (2C, 4), 135.5 (12), 130.6, 127.1 (2C)
6c	4-BrC$_6$H$_4$	185.5 (4,12)	70.7 (102)	124.9 (90)	133.6 (10)	128.5 (12)	131.8 (<2)	137.2 (2C, 4), 135.1 (11), —*
6d	CO$_2$Me	193.3 (3,11)	66.1 (113)	126.0 (93)	133.7 (10)	128.4 (12)	131.7 (<2)	167.7 (16), 49.8
6e	CO$_2$Et	193.6 (4,11)	65.8 (112)	126.4 (93)	133.8 (10)	128.3 (13)	131.5 (<2)	167.3 (15), 58.2, 14.1
6f	COPh	191.7 (4,14)	82.4 (99)	125.5 (92)	133.5 (10)	128.5 (13)	131.4 (<2)	191.6 (12), 144.2 (5), 129.4, 128.7 (2C) 127.7 (2C)

* Due to peak overlap the signals due to C-3, 4 and 5 of the 4-bromophenyl groups could not be definitely assigned.

1495, 1433, 1362, 1155, 1095, 1020, 940, 748, 730 and 690; δ_H 7.8–7.4 (15 H, m), 2.35 (2 H, t, *J* 7), 2.3–1.9 (2 H, m), 1.7–1.3 (4 H, m), 0.90 (3 H, t, *J* 7) and 0.85 (3 H, t, *J* 7); δ_C see Table 2; δ_P +18.4; *m/z* 412 (M$^+$, 18%), 398 (4), 397 (100), 369 (3), 355 (4), 331 (4), 303 (3), 301 (2), 287 (5), 279 (4), 263 (5), 262 (20), 201 (5) and 183 (20).

4-Triphenylphosphoranylideneundec-6-yn-5-one 5c. From butyl(triphenyl)phosphonium bromide and hept-2-ynoyl chloride as pale yellow crystals (24%), mp 155–157 °C (Found: C, 82.0; H, 7.45. C$_{29}$H$_{31}$OP requires C, 81.7; H, 7.3%); v_{max}/cm^{-1} 2205, 1496, 1435, 1360, 1162, 1098, 1016, 759 and 690; δ_H 7.85–7.25 (15 H, m), 2.35 (2 H, t, *J* 7), 2.3–1.9 (2 H, m), 1.6–1.1 (6 H, m), 0.90 (3 H, t, *J* 7) and 0.68 (3 H, t, *J* 7); δ_C see Table 2; δ_P +18.3; *m/z* 426 (M$^+$, 8%), 411 (2), 398 (48), 397 (100), 303 (2), 301 (2), 287 (6), 277 (6), 263 (5), 262 (30), 201 (6) and 183 (35).

2-Methyl-3-triphenylphosphoranylidenedec-5-yn-4-one 5d. From isobutyl(triphenyl)phosphonium bromide and hept-2-ynoyl chloride as pale yellow crystals (26%), mp 196–198 °C (Found: C, 82.0; H, 7.25. C$_{29}$H$_{31}$OP requires C, 81.7; H, 7.3%); v_{max}/cm^{-1} 2208, 1434, 1320, 1183, 1104, 1062, 1030, 868, 759, 742 and 692; δ_H 7.75–7.25 (15 H, m), 2.35 (2 H, t, *J* 7), 2.1–1.7 (1 H, m), 1.6–1.4 (4 H, m), 1.28 (6 H, d, *J* 7) and 0.90 (3 H, t, *J* 7); δ_P +17.8; *m/z* 426 (M$^+$, 12%), 412 (33), 411 (100), 384 (7), 379 (5), 277 (16), 262 (37), 201 (12) and 183 (40).

1-Phenyl-1-triphenylphosphoranylideneoct-3-yn-2-one 5e. From benzyl(triphenyl)phosphonium chloride and hept-2-ynoyl chloride as colourless crystals (65%), mp 200–202 °C (lit.,[5] 207–208 °C); δ_H 7.75–7.25 (15 H, m), 7.0 (5 H, m), 2.10 (2 H, m), 1.3–1.05 (4 H, m) and 0.73 (3 H, t, *J* 7); δ_P +16.0.

1-Phenyl-4-triphenylphosphoranylideneoct-1-yn-3-one 5f. From pentyl(triphenyl)phosphonium bromide and phenylpropynoyl chloride as pale yellow crystals (54%), mp 191–193 °C (Found: C, 83.6; H, 6.2. C$_{32}$H$_{29}$OP requires C, 83.5; H, 6.3%); v_{max}/cm^{-1} 2195, 1493, 1436, 1360, 1165, 1107, 1083, 997, 891, 765, 749 and 693; δ_H 7.75–7.25 (20 H, m), 2.5–2.1 (2 H, m), 1.4–1.1 (4 H, m) and 0.69 (3 H, t, *J* 7); δ_P +18.6; *m/z* 460 (M$^+$, 3%), 431 (3), 418 (45), 417 (100), 363 (4), 287 (7), 277 (5), 262 (25), 247 (7) and 183 (23).

1,4-Diphenyl-4-triphenylphosphoranylidenebut-1-yn-3-one 5g. From benzyl(triphenyl)phosphonium chloride and phenylpropynoyl chloride as yellow crystals (39%), mp 238–240 °C (lit.,[5] 241–242 °C); δ_H 7.75–7.25 (15 H, m) and 7.2–7.0 (10 H, m); δ_C see Table 2; δ_P +16.3.

1-(4-Methoxyphenyl)-4-(4-nitrophenyl)-4-triphenylphosphoranylidenebut-1-yn-3-one 5h. From 4-nitrobenzyl(triphenyl)phosphonium bromide and 4-methoxyphenylpropynoyl chloride[4] as orange crystals (72%), mp 228–230 °C (Found: C, 75.1; H, 4.6; N, 2.5. C$_{35}$H$_{26}$NO$_4$P requires C, 75.7; H, 4.7; N, 2.5%); v_{max}/cm^{-1} 2188, 1602, 1505, 1440, 1342, 1253, 1172, 1110, 1022, 842, 726 and 698; δ_H 7.88 and 6.77 (4 H, AB pattern, *J* 8), 7.65–7.5 (9 H, m), 7.5–7.4 (6 H, m), 7.25–7.1 (4 H, m) and 3.77 (3 H, s); δ_C see Table 1; δ_P +16.4; *m/z* (20 eV) no peak observed above 278 (Ph$_3$PO).

Flash vacuum pyrolysis of the ylides 5 to give the diynes 9

The apparatus used was as described previously.[2] All pyrolyses were conducted at pressures in the range 10^{-3}–10^{-1} Torr. Under these conditions the contact time in the hot zone was estimated to be $\approx$ 10 ms. In most cases Ph$_3$PO collected at the furnace exit and the more 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 ^{1}H NMR spectra by adding an accurately weighed quantity of a solvent such as CH$_2$Cl$_2$ and comparing integrals, a procedure estimated to be accurate to ± 10%.

Compound 9a. FVP of the ylide **5a** (105 mg) at 750 °C gave nona-2,4-diyne **9a** (49%) as a yellow liquid; δ_H 2.25 (2 H, t, *J* 7), 1.82 (3 H, s), 1.6–1.4 (4 H, m) and 0.91 (3 H, t, *J* 7); δ_C see Table 3.

Compound 9b. FVP of the ylide **5b** (200 mg) at 750 °C gave deca-3,5-diyne **9b** (45%) as a yellow liquid (Found: M, 134.1103. C$_{10}$H$_{14}$ requires *M*, 134.1096); δ_H 2.35 (4 H, m), 1.6–1.45 (6 H, m), 1.25 (3 H, t, *J* 7) and 1.0 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 134 (M$^+$, 55%), 117 (13), 105 (28) and 91 (100).

Compound 9c. FVP of the ylide **5c** (210 mg) at 750 °C gave undeca-4,6-diyne **9c** (42%) as a yellow liquid (Found: M, 148.1248. C$_{11}$H$_{16}$ requires *M*, 148.1252); δ_H 2.25 (2 H, t, *J* 7), 2.22 (2 H, t, *J* 7), 1.6–1.35 (6 H, m), 0.98 (3 H, t, *J* 7) and 0.89 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 148 (M$^+$, 32%), 119 (12), 105 (45) and 91 (100).

Compound 9d. FVP of the ylide **5d** (102 mg) at 750 °C gave 2-methyldeca-3,5-diyne **9d** (15%) as a yellow liquid (Found: M, 148.1264. C$_{11}$H$_{16}$ requires *M*, 148.1252), δ_H 2.27 (2 H, t, *J* 7), 2.2 (1 H, m), 1.7–1.3 (4 H, m), 1.18 (6 H, d, *J* 6) and 0.91 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 148 (M$^+$, 36%), 133 (15), 117 (82), 105 (75) and 91 (100).

Compound 9e. FVP of the ylide **5e** (253 mg) at 750 °C gave 1-phenylocta-1,3-diyne **9e** (46%) as a yellow liquid (Found: M, 182.1100. C$_{14}$H$_{14}$ requires *M*, 182.1096); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 2220, 1590, 1480, 1145, 1105, 1060, 1015, 900 and 800; δ_H 7.5–7.4 (2 H, m), 7.3–7.2 (3 H, m), 2.35 (2 H, t, *J* 7), 1.6–1.4 (4 H, m) and 0.94 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 182 (M$^+$, 84%), 167 (40), 165 (52), 153 (35), 152 (58), 139 (100) and 126 (33).

Compound 9e. FVP of the ylide **5f** (107 mg) at 750 °C gave 1-phenylocta-1,3-diyne **9e** (61%) as a yellow liquid identical in all respects with that prepared from **5e** above.

Compound 9g. FVP of the ylide **5g** (113 mg) at 750 °C gave diphenylbutadiyne **9g** (70%) as colourless crystals, mp 85–86 °C (lit.,[13] 87–88 °C); v_{max}/cm^{-1} 3030, 2218, 2146, 1590, 1480, 1432, 1062, 1018, 920, 750 and 680 (lit.,[14] 3040, 2220, 2150, 1586, 1480, 1430, 1060, 1022, 910, 750 and 685); δ_H 7.5–7.4 (4 H, m), 7.3–7.2 (6 H, m); δ_C see Table 3.

Compound 9h. FVP of the ylide **5h** (500 mg) at 750 °C gave 1-(4-methoxyphenyl)-4-(4-nitrophenyl)buta-1,3-diyne **9h** (52%) as an orange solid, mp 247.5–249 °C (Found: C, 72.8; H, 3.7; N, 5.0; M, 277.0737. C$_{17}$H$_{11}$NO$_3$ requires C, 73.6; H, 4.0; N, 5.1%; *M*, 277.0739); v_{max}/cm^{-1} 2215, 1600, 1510, 1340, 1252, 1178, 1033, 856 and 833; δ_H 8.20, 7.65, 7.50 and 6.87 (4 × 2 H, each

half AB pattern, J 8) and 3.84 (3 H, s); δ_C see Table 3; m/z 277 (M$^+$, 100%), 262 (14), 247 (12), 231 (42), 216 (12), 200 (8), 188 (40) and 187 (78).

Preparation of the oxalyl diylides 6a–c

A suspension of the appropriate phosphonium salt (24 mmol) in dry THF (100 cm^3) was stirred at room temperature under N$_2$ while a solution of BuLi in hexane (25 mmol) was added slowly by syringe. This was followed after 30 min by addition of oxalyl chloride (0.76 g, 6 mmol) in dry THF (10 cm^3). After 3 h the mixture was added to water (250 cm^3) and extracted with diethyl ether (2 × 50 cm^3) and ethyl acetate (2 × 50 cm^3). Drying and evaporation of the extract gave the diylide which crystallised with time and was recrystallised from ethyl acetate. The following compounds were prepared by this method.

1,4-Diphenyl-1,4-bis(triphenylphosphoranylidene)butane-2,3-dione 6a. From benzyl(triphenyl)phosphonium chloride as yellow crystals (32%), mp 271–273 °C (Found: M + H$^+$, 759.2603. C$_{52}$H$_{40}$O$_2$P$_2$ requires M + H, 759.2582); v_{max}/cm^{-1} 1528, 1435, 1377, 1353, 1190, 1102, 1010 and 693; δ_H 7.6–7.25 (30 H, m) and 7.05 (10 H, s); δ_C see Table 5; δ_P +14.4; m/z 480 (M$^+$ − Ph$_3$PO, 4%), 380 (30), 379 (M$^+$/2, 100), 351 (1), 278 (3), 277 (8), 262 (3), 201 (6), 183 (15) and 165 (11); m/z (FAB, glycerol) 759 (M + H$^+$, 12%), 379 (M$^+$/2, 100) and 183 (6).

1,4-Bis(4-chlorophenyl)-1,4-bis(triphenylphosphoranylidene)-butane-2,3-dione 6b. From 4-chlorobenzyl(triphenyl)phosphonium chloride as yellow crystals (58%), mp 135 °C (Found: C, 75.1; H, 4.6; ^{35}Cl$_2$ − M + H$^+$, 827.1819. C$_{52}$H$_{38}$Cl$_2$O$_2$P$_2$ requires C, 75.5; H, 4.6%; M + H, 827.1802); v_{max}/cm^{-1} 1500, 1435, 1375, 1323, 1188, 1100, 963, 835, 750, 722 and 693; δ_H 7.7–7.2 (30 H, m) and 6.91 (8 H, s); δ_C see Table 5; δ_P +14.5; m/z 548 (M$^+$ − Ph$_3$PO, 0.5%), 514 (1), 486 (1), 413 (M$^+$/2, 28), 278 (65), 277 (100), 262 (12), 236 (9), 201 (28), 199 (24), 183 (25), 163 (68) and 136 (40); m/z (FAB, glycerol) 827 (^{35}Cl$_2$ − M + H$^+$, 10%), 415 (^{37}Cl − M$^+$/2, 36) and 413 (^{35}Cl − M$^+$/2, 100).

1,4-Bis(4-bromophenyl)-1,4-bis(triphenylphosphoranylidene)-butane-2,3-dione 6c. From 4-bromobenzyl(triphenyl)phosphonium bromide as colourless crystals (21%), correct elemental analysis could not be obtained owing to partial hydrolysis and decomposition on attempted recrystallisation; v_{max}/cm^{-1} 1705, 1435, 1195, 1180, 1096, 1063, 961, 748, 711 and 688; δ_H 7.5–7.2 (30 H, m) and 7.05 and 6.83 (8 H, AB pattern, J 9); δ_C see Table 5; δ_P +14.4; m/z 457 (M$^+$/2, 0.2%), 379 (1), 350 (1), 278 (48), 277 (100), 271 (2), 269 (2), 262 (3), 201 (30), 199 (15), 185 (9), 183 (10) and 152 (6).

Preparation of oxalyl diylides 6d–f

A solution of the appropriate ylide 10 (12 mmol) in dry toluene (100 cm^3) containing triethylamine (1.2 g, 12 mmol) was stirred at room temperature while oxalyl chloride (0.76 g, 6 mmol) in dry toluene (10 cm^3) was added slowly. After 3 h the mixture was added to water (250 cm^3) and extracted with diethyl ether (2 × 50 cm^3) and ethyl acetate (2 × 50 cm^3). Drying and evaporation of the extract gave the ylide which was recrystallised from ethyl acetate. The following compounds were prepared by this method.

Dimethyl 3,4-dioxo-2,5-bis(triphenylphosphoranylidene)-hexane-1,6-dioate 6d. From methoxycarbonylmethylene-(triphenyl)phosphorane as colourless crystals (69%), mp 273–274 °C (Found: C, 73.3; H, 5.4; M$^+$/2, 361.0964. C$_{44}$H$_{36}$O$_6$P$_2$ requires C, 73.1; H, 5.0%; M/2, 361.0993); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 1660, 1545, 1350, 1300, 1190, 1107, 1091 and 910; δ_H 7.85–7.75 (12 H, m), 7.5–7.35 (18 H, m) and 3.30 (6 H, s); δ_C see Table 5; δ_P +16.35; m/z (20 eV) 444 (M$^+$ − Ph$_3$PO, 0.2%), 361 (M$^+$/2, 30), 301 (3), 277 (18), 262 (100) and 183 (9).

Diethyl 3,4-dioxo-2,5-bis(triphenylphosphoranylidene)hexane-1,6-dioate 6e. From ethoxycarbonylmethylene(triphenyl)-phosphorane as colourless crystals (73%), mp 243–245 °C (lit.,[5] 248–249 °C) (Found: C, 73.6; H, 5.5. C$_{46}$H$_{40}$O$_6$P$_2$ requires C, 73.6; H, 5.4%); v_{max}/cm^{-1} 1668, 1545, 1436, 1372, 1301, 1206, 1103, 1078, 756, 720 and 692; δ_H 7.9–7.75 (12 H, m), 7.5–7.3 (18 H, m), 3.81 (4 H, br s) and 0.70 (6 H, t of d, J 7, 2); δ_C see Table 5; δ_P +16.0; m/z 722 (M$^+$ − 28, 0.2%), 417 (0.7), 400 (1), 376 (100), 302 (12), 279 (38), 277 (90), 263 (76), 201 (17), 199 (8) and 183 (35).

1,6-Diphenyl-2,5-bis(triphenylphosphoranylidene)hexane-1,3,4,6-tetraone 6f. From benzoylmethylene(triphenyl)-phosphorane as yellow crystals (64%), mp 146–148 °C (Found: C, 80.0; H, 5.3; M − Ph$_3$PO, 536.1491. C$_{54}$H$_{40}$O$_4$P$_2$ requires C, 79.6; H, 4.9%; M − Ph$_3$PO, 536.1541); v_{max}/cm^{-1} (CH$_2$Cl$_2$) 2990, 1583, 1512, 1410, 1345, 1305, 1196, 1150, 1120, 1092, 1047, 955 and 860; δ_H 7.65–7.15 (40 H, m); δ_C see Table 5; δ_P +17.6; m/z 536 (M$^+$ − Ph$_3$PO, 33%), 508 (2), 452 (3), 431 (6), 403 (4), 301 (8), 277 (100) and 262 (35).

Flash vacuum pyrolysis of the diylides 6 to give the diynes 13

This was carried out as described above for 5.

Compound 13a. FVP of the diylide 6a at 850 °C and below gave only part reaction and some unchanged diylide was recovered. FVP of 6a (265 mg) at 900 °C gave Ph$_3$PO at the furnace exit and in the cold trap 1,4-diphenylbutadiyne 13a (45 mg, 64%) identical in all respects with that prepared from 5g above.

Compound 13b. FVP of the diylide 6b at 850 °C and below gave only part reaction and some unchanged diylide was recovered. FVP of 6b (150 mg) at 900 °C gave a solid at the furnace exit which proved to be a mixture of Ph$_3$PO and the desired diyne. These were separated using preparative TLC (SiO$_2$, Et$_2$O–hexane, 1:1) to give slightly impure 1,4-bis(4-chlorophenyl)butadiyne 13b (4.8 mg, 10%) as an oily solid; δ_H 7.45 and 7.32 (8 H, AB pattern, J 8.5); δ_C see Table 3.

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