Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 5.[1] Selective Extrusion of Ph_3PO from β,γ,β'-Trioxo Ylides to give Diacylalkynes

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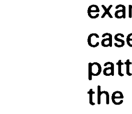
Sixteen examples of the previously unknown trioxo ylides **7** have been prepared by acylation of stabilised phosphorus ylides **8** with α-oxo acid chlorides **9**. Extrusion of Ph_3PO from these is readily achieved using FVP at 500 °C in most cases, to afford the diacylalkynes **10** in moderate yield. Three examples failed to give the expected alkynes and the nature of the processes involved in these cases is uncertain. Fully assigned ^{13}C NMR spectra are presented for the ylides and an unexpected pattern is observed in the value of J_{P-C} for the three carbonyl carbons depending on the nature of the substituents present. There is some correlation between the value of $^2J_{P-C}$ for the central carbonyl carbon and the success of the pyrolysis although this is not complete. The method has been used to prepare a specifically ^{13}C labelled acetylenic diester **14**.

In previous papers in this series we have examined the use of flash vacuum pyrolysis (FVP) to bring about thermal extrusion of Ph_3PO from a variety of stabilised phosphorus ylides **1**, thus providing convenient synthetic methods for a variety of substituted alkynes $R^1C{\equiv}CR^2$. It has long been known that for ylides **2**, stabilised by both ester and keto carbonyl groups, phosphine oxide extrusion involves loss of oxygen exclusively from the latter to give acetylenic esters.[2] This is most probably due to these compounds existing predominantly in the configuration shown with the keto carbonyl *syn* to phosphorus and the ester carbonyl *anti* to it, as recently demonstrated in the solid state by an X-ray structure determination.[3] Pyrolysis of ylides stabilised by two keto or aldehyde carbonyls has only been examined in a few cases. For examples such as **3**–**5**[4] and **6**,[5] selectivity is poor and, unless the two groups are identical as in **3** and **4**, mixtures of the two isomeric alkynes, $R^1COC{\equiv}CR^2$ and $R^1C{\equiv}CCOR^2$ are produced. In this paper we describe the preparation and behaviour upon FVP of the first examples of the higher homologues **7**, stabilised by an ester or keto group on one side of phosphorus and an α-diketone or α-keto ester group on the other.[6]



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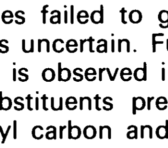

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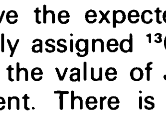
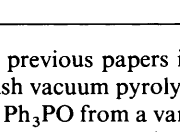


3 $R^1 = R^2 = Me$
4 $R^1 = R^2 = Ph$
5 $R^1 = Me, R^2 = Ph$
6 $R^1 = H, R^2 = CF_3, C_2F_5, C_3F_7$



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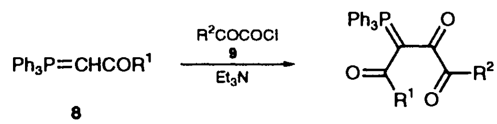
Results and Discussion

A total of 16 examples of the trioxo ylides **7** were obtained in good to excellent yield as shown in Scheme 1, by reaction of stabilised ylides **8** with 1 equiv. of the acid chlorides **9** in the presence of triethylamine in toluene at room temperature (Table 1). For R^2 = Me it was found to be preferable to use a solution of pyruvoyl chloride in toluene prepared *in situ* by reaction of sodium pyruvate with oxalyl chloride. Repeated attempts to obtain **7** ($R^1 = R^2$ = Me) were unsuccessful. The new ylides



8 **7**

Scheme 1

were stable crystalline solids which showed the expected analytical and spectroscopic properties including ^{31}P NMR signals at δ_P +15–18. Their ^{13}C NMR spectra, in particular, were highly informative and provided ready confirmation of the expected structures (Table 2). Doublets due to the ylide carbon are observed in the range δ_C 80–86 ($^1J_{P-C} \approx 100$ Hz) for **7a**–**h** (R^1 = Ph, Me or Bu^t) and at δ_C 66–70 ($^1J_{P-C} \approx 110$ Hz) for **7i**–**p** (R^1 = OMe or OEt). Phosphorus coupling is also observed throughout the P-phenyl groups and to the first carbon of R^1.

The pattern of phosphorus coupling to the three carbonyl carbons is somewhat surprising, but does form a quite consistent pattern (Table 2). In most cases, the assignment of these signals could be made based on the observed chemical shifts or by extrapolation across the series. When ambiguity remained the signals have been assigned to conform to the pattern of observed P–C coupling constants. For **7a**–**d** (R^1 = Ph), the three-bond coupling to R^2CO is largest with smaller couplings to the other two carbonyls. For **7i**–**p** (R^1 = OMe or OEt), the three-bond coupling to R^2CO and the two-bond coupling to R^1CO are both large and the remaining value is small. A marked difference occurs for **7e**–**h** (R^1 = Me or Bu^t), where the two-bond coupling to R^2CO*C*O is now large and the remaining two values small. The reason for this pattern is not entirely clear but it presumably reflects the differing electron distribution in the trioxo ylide system depending on the groups present. As described below there is also a good correlation between the magnitude of the two-bond coupling to R^2CO*C*O and the behaviour upon FVP.

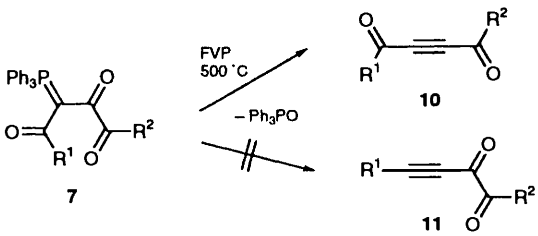
When the ylides **7** were subjected to FVP at 500 °C, extrusion of Ph_3PO took place across the central position as shown in Scheme 2 to give diacylalkynes **10** in moderate yield in most cases (Table 3). Because of the small scale of operations, the boiling points of the liquid products, all well known compounds, were not determined but no significant impurities were detected by ^1H or ^{13}C NMR and in no case was any of the isomeric product **11** detected. For **7i**–**p** this is as expected, since these compounds are assumed to exist predominantly in the form **12** with the ester CO *anti* to phosphorus, as is already well

Table 1 Preparation of the ylides **7**

	R^1	R^2	Yield (%)	δ_P		R^1	R^2	Yield (%)	δ_P
7a	Ph	Ph	82	16.5	**7i**	OMe	Ph	68	15.7
7b	Ph	Me	58	16.6	**7j**	OMe	Me	87	15.3
7c	Ph	OMe	87	17.8	**7k**	OMe	OMe	82	16.3
7d	Ph	OEt	70	15.6	**7l**	OMe	OEt	98	16.5
7e	Me	Ph	51	15.6	**7m**	OEt	Ph	71	15.6
7f	Me	OMe	86	16.2	**7n**	OEt	Me	56	15.2
7g	Me	OEt	68	16.2	**7o**	OEt	OMe	80	16.2
7h	Bu^t	Ph	78	17.4	**7p**	OEt	OEt	91	16.2

Table 3 Formation and ^{13}C NMR (δ_C) spectra of the diacylalkynes **10**

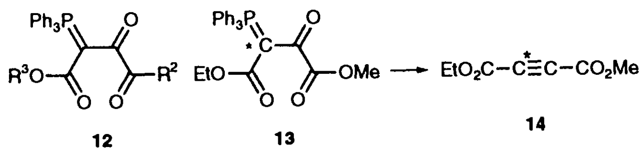
	R^1	R^2	Yield (%)	C≡C	C=O	R signals
10a	Ph	Ph	40	85.8	176.5	135.8 (4ry), 135.2, 129.8 (2 C), 129.0 (2 C)
10b	Ph	Me	0	—		
10c	Ph	OMe	23	80.11, 80.08	176.0, 152.7	135.6 (4ry), 135.2, 129.8 (2 C), 129.0 (2 C), 53.4
10d	Ph	OEt	44	80.5, 79.7	176.1, 152.2	135.6 (4ry), 135.2, 129.7 (2 C), 128.9 (2 C), 63.1, 14.0
10e	Me	Ph	0	—		
10f	Me	OMe	0	—		
10g	Me	OEt	67	80.8, 78.0	182.5, 152.2	63.0, 32.3, 13.9
10h	Bu^t	Ph	43	85.4, 78.2	188.8, 176.5	135.7 (4ry), 135.1, 129.6 (2 C), 128.9 (2 C), 45.2, 25.6 (3 C)
10i	OMe	Ph	67	(as **10c**)		
10j	OMe	Me	38	81.0, 77.5	182.6, 152.7	53.4, 32.3
10k	OMe	OMe	59	74.4	152.0	54.0
10l	OMe	OEt	61	75.1, 74.3	152.3, 151.8	63.1, 53.5, 13.9
10m	OEt	Ph	52	(as **10d**)		
10n	OEt	Me	23	81.4, 78.5	183.1, 152.8	63.6, 33.0, 14.5
10o	OEt	OMe	70	(as **10l**)		
10p	OEt	OEt	63	74.7	151.8	63.1, 13.9



Scheme 2

known for the simpler analogues **2**. The good selectivity for **10** as opposed to **11** is somewhat more surprising in cases **7a**, **c** and **d**. The pattern of behaviour for the remaining compounds is harder to explain. For **7b**, **e** and **f** none of the expected alkynes **10** were formed and the complex mixtures produced, including such components as acetaldehyde and acetophenone (**7b**), benzoic acid (**7b**, **e**) benzaldehyde (**7e**) and methanol (**7f**) indicate the occurrence of indiscriminate fragmentation processes. For **7e–h** we had expected poor results owing to the high value of $^2J_{P-C}$ to the central carbonyl. In the course of an extensive study of the magnitude of this coupling in relation to the pyrolysis behaviour for very many stabilised ylides, we have observed a good correlation such that ylides with $^2J_{P-C} > 10$ Hz do not generally eliminate Ph_3PO to give alkynes while those with $^2J_{P-C} < 10$ Hz do. Based on this, pyrolysis of **7g** and **h** should also have given poor results and FVP of **7b** was expected to be successful. In fact, significant unidentified side-products were formed from **7h** and the presence of a methyl group either as R^1 or R^2 seems to be undesirable explaining the failure of the pyrolysis of **7b** and the formation of significant quantities of ethanol and methanol as by-products in the FVP of **7g** and **7j**, respectively. The dependence of the FVP behaviour on the values of R^1, R^2 and $^2J_{P-C}$ clearly needs further investigation.

Despite the problems encountered in some cases, this method does allow convenient preparation of multigram quantities of diacylalkynes and we have already described the use of **10a** and **i** prepared in this way for cycloaddition with $Bu_3P{\cdot}CS_2$.[7] A further illustration of the value of this method is provided by the preparation of the specifically ^{13}C labelled unsymmetrical acetylene diester **14** which was required for a mechanistic study on the higher temperature fragmentation of acetylenic esters.[8] Beginning from ethyl bromoacetate labelled with 5% ^{13}C on the $BrCH_2$ carbon, the required labelled ylide **13** was readily prepared and, upon FVP, afforded the spectroscopically pure labelled diester (5 × enhancement of δ_C 75.1) in 55% yield. This labelled material could not be so readily prepared by other methods.



Experimental

M.p.s were recorded on a Kofler hot-stage microscope and are uncorrected. IR spectra were recorded for solids on Nujol mulls or solutions in CH_2Cl_2 and for liquids on thin films using a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^{1}H at 200 MHz and for ^{13}C at 50 MHz using a Varian Gemini 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_4Si as reference for ^{1}H 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. GC–MS data were obtained using a Hewlett Packard 5890A chromatograph

Table 2 ^{13}C NMR spectra [$\delta_C(J_{P-C})$], of the ylides **7**

	R[1]	R[2]	P=*C*	*CO*–R[1]	*CO*–COR[2]	CO–*CO*R[2]	P-Phenyl C-1	C-2	C-3	C-4	R signals
7a	Ph	Ph	84.2 (97)	193.4 (7)	190.3 (5)	193.5 (13)	124.1 (92)	133.4 (10)	128.8 (13)	132.3 (< 2)	141.9 (8), 134.3, 132.7, 130.6, 129.0 (4 C), 127.9 (2 C), 127.5 (2 C)
7b	Ph	Me	80.2 (99)	193.5 (8)	191.3 (5)	201.4 (11)	124.1 (92)	133.5 (10)	128.8 (13)	132.4 (3)	143.2 (8), 131.0, 128.6 (2 C), 128.1 (2 C), 25.6
7c	Ph	OMe	82.3 (100)	192.9 (7)	182.3 (6)	166.2 (15)	124.1 (92)	133.5 (10)	128.9 (13)	132.4 (2)	141.8 (8), 131.1, 129.1 (2 C), 127.9 (2 C), 51.4
7d	Ph	OEt	82.7 (100)	193.0 (7)	182.6 (6)	165.9 (15)	124.1 (92)	133.6 (10)	128.9 (13)	132.4 (2)	141.8 (8), 131.1, 129.2 (2C), 128.0 (2 C), 61.0, 13.6
7e	Me	Ph	86.3 (102)	195.2 (5)*	190.2 (13)	193.4 (5)*	124.5 (92)	133.5 (10)	128.7 (13)	132.2 (2)	133.8, 133.1, 129.7 (2 C), 128.1 (2 C), 30.2 (5)
7f	Me	OMe	84.5 (104)	195.0 (6)	182.4 (13)	167.1 (6)	124.6 (93)	133.4 (10)	128.8 (13)	132.3 (2)	51.9, 29.5 (5)
7g	Me	OEt	84.5 (105)	195.1 (6)	182.6 (13)	166.8 (5)	124.8 (93)	133.5 (10)	128.8 (12)	132.2 (2)	61.3, 29.5 (5), 13.8
7h	Bu^t	Ph	85.9 (102)	206.9 (3)	185.1 (19)	193.0 (< 2)	125.3 (93)	133.7 (10)	128.4 (13)	131.9 (3)	134.6, 132.8, 129.9 (2 C), 127.6 (2 C), 43.9 (5), 26.6 (3 C)
7i	OMe	Ph	69.2 (109)	167.8 (14)	192.0 (4)	194.5 (11)	124.3 (93)	133.7 (10)	128.8 (13)	132.5 (3)	134.7, 132.6, 129.1 (2 C), 128.4 (2 C), 50.1
7j	OMe	Me	66.2 (109)	168.1 (14)	193.1 (4)	202.7 (11)	124.0 (93)	133.6 (10)	128.8 (13)	132.5 (3)	50.1, 25.9
7k	OMe	OMe	68.0 (111)	167.8 (15)*	184.3 (6)	167.5 (14)*	124.0 (93)	133.6 (10)	128.8 (13)	132.5 (2)	51.8, 50.3
7l	OMe	OEt	67.8 (111)	167.41 (15)*	184.6 (6)	167.45 (13)*	124.1 (94)	133.6 (10)	128.8 (13)	132.5 (3)	61.0, 50.3, 14.2
7m	OEt	Ph	69.0 (109)	167.0 (14)	192.0 (4)	194.5 (11)	124.4 (93)	133.7 (10)	128.8 (12)	132.5 (2)	134.7, 133.6, 129.3 (2 C), 128.3 (2 C), 59.2, 13.4
7n	OEt	Me	66.0 (108)	167.9 (13)	193.2 (4.5)	202.8 (10)	124.2 (93)	133.6 (10)	128.9 (14)	132.5 (3)	59.1, 26.0, 13.6
7o	OEt	OMe	67.8 (110)	167.8 (14)*	184.3 (6)	167.2 (13)*	124.2 (93)	133.6 (10)	128.8 (13)	132.5 (3)	59.1, 51.7, 13.7
7p	OEt	OEt	67.6 (111)	167.5 (15)*	184.7 (6)	167.2 (13)*	124.2 (93)	133.6 (10)	128.7 (13)	132.4 (2)	60.9, 59.1, 14.1, 13.7

* Assignments may be interchanged.

coupled to a Finnigan Incos mass spectrometer. Toluene was dried over sodium.

The required stabilised ylides **8** are commercially available, with the exception of pivaloylmethylene(triphenyl)phosphorane (R^1 = Bu^t) which was prepared by reaction of Ph_3P with 1-bromopinacolone in boiling toluene followed by treatment of the resulting phosphonium salt with aqueous NaOH.

The acid chlorides **9** are commercially available (R^2 = OMe, OEt) or were prepared by treatment of the appropriate α-keto acid sodium salt with 1 equiv. of oxalyl chloride (R^2 = Ph, Me). In the first case the reaction was carried out in dry ether and was followed by filtration, evaporation and distillation of the product. In the last case the instability of the desired pyruvoyl chloride meant that it was preferable to perform the reaction in dry toluene, filter the solution under dry N_2 and use it directly for the ylide preparation.

Preparation of β,γ,β′-*Trioxo Phosphorus Ylides*.—A solution of the appropriate stabilised ylide **8** (10 mmol) and triethylamine (1.01 g, 10 mmol) in dry toluene (50 cm^3) was stirred at room temperature while a solution of the appropriate acid chloride **9** (10 mmol) in dry toluene (10 cm^3) was added dropwise to it. After the addition, the mixture was stirred for 3 h and then poured into water (100 cm^3). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 × 50 cm^3). The combined organic phase and extracts were dried and evaporated to give the desired ylides which were recrystallised from ethyl acetate. Using this method the following were prepared.

1,4-*Diphenyl*-3-*triphenylphosphoranylidenebutane*-1,2,4-*trione* **7a**. Prepared as yellow crystals (82%), m.p. 158–160 °C (Found: C, 79.4; H, 5.0. $C_{34}H_{25}O_3P$ requires C, 79.7; H, 4.9%); ν_{max}/cm^{-1} (CH_2Cl_2) 3020, 1780, 1665, 1585, 1515, 1475, 1428, 1310, 1210, 1170, 1100, 995, 860 and 830; δ_H 8.15–7.0 (25 H, m); δ_C see Table 2; δ_P +16.5; *m*/*z* 512 (M^+, 0.5%), 456 (0.5), 407 (75), 379 (3), 277 (80), 262 (10), 234 (12), 183 (33), 129 (75), 105 (83) and 77 (100).

1-*Phenyl*-2-*triphenylphosphoranylidenepentane*-1,3,4-*trione* **7b** prepared as yellow crystals (58%), m.p. 164–166 °C (Found: C, 77.4; H, 5.0. $C_{29}H_{23}O_3P$ requires C, 77.3; H, 5.1%); ν_{max}/cm^{-1}(CH_2Cl_2) 1685, 1580, 1510, 1320, 1300, 1155, 1116, 1090, 1010, 985 and 858; δ_H 7.8–7.2 (20 H, m) and 1.98 (3 H, s); δ_C see Table 2; δ_P +16.6; *m*/*z* (20 eV) 407 (M^+ − MeCO, 2%), 277 (100), 262 (6), 201 (8), 172 (20), 157 (8), 129 (30) and 105 (26).

Methyl 2,4-*dioxo*-4-*phenyl*-3-*triphenylphosphoranylidenebutanoate* **7c**. Prepared as colourless crystals (87%), m.p. 129–131 °C (Found: C, 74.7; H, 4.9. $C_{29}H_{23}O_4P$ requires C, 74.7; H, 5.0%); ν_{max}/cm^{-1}(CH_2Cl_2) 3000, 1714, 1580, 1520, 1472, 1420, 1338, 1302, 1195, 1170, 1122, 1092, 1014, 985 and 855; δ_H 7.8–7.3 (20 H, m) and 3.17 (3 H, s); δ_C see Table 2; δ_P +17.8; *m*/*z* 466 (M^+, 0.2%), 408 (5), 381 (2), 380 (2), 304 (2), 278 (33), 277 (76), 236 (6), 201 (12), 183 (11), 129 (12), 105 (29), 85 (66) and 84 (100).

Ethyl 2,4-*dioxo*-4-*phenyl*-3-*triphenylphosphoranylidenebutanoate* **7d**. Prepared as colourless crystals (70%), m.p. 123–125 °C (Found: C, 75.3; H, 5.4. $C_{30}H_{25}O_4P$ requires C, 75.0; H, 5.2%); ν_{max}/cm^{-1}(CH_2Cl_2) 1707, 1580, 1515, 1420, 1330, 1300, 1186, 1120, 1092, 1010, 985, 918 and 856; δ_H 7.85–7.2 (20 H, m), 3.58 (2 H, q, *J* 7) and 1.02 (3 H, t, *J* 7); δ_C see Table 2; δ_P +15.6; *m*/*z* 480 (M^+, 0.5%), 407 (7), 379 (2), 304 (2), 278 (45), 277 (100), 201 (25), 199 (22), 183 (25), 152 (18), 129 (33), 105 (32) and 77 (92).

1-*Phenyl*-3-*triphenylphosphoranylidenepentane*-1,2,4-*trione* **7e**. Prepared as brown crystals (51%), m.p. 170–172 °C (Found: C, 77.4; H, 5.3. $C_{29}H_{23}O_3P$ requires C, 77.3; H, 5.1%); ν_{max}/cm^{-1}(CH_2Cl_2) 3000, 1700, 1654, 1575, 1530, 1470, 1420, 1355, 1300, 1208, 1165, 1092, 987, 908 and 832; δ_H 8.0–7.25 (20 H, m) and 2.32 (3 H, d, *J* 4); δ_C see Table 2; δ_P +15.6; *m*/*z* 450 (M^+, 0.5%), 345 (3), 303 (2), 278 (18), 277 (42), 201 (12), 199 (14), 183 (10), 105 (22) and 77 (100).

Methyl 2,4-*dioxo*-3-*triphenylphosphoranylidenepentanoate* **7f**. Prepared as yellow crystals (86%), m.p. 130–132 °C (Found: C, 71.7; H, 5.3%; M − CO_2Me, 345.1056. $C_{24}H_{21}O_4P$ requires C, 71.3; H, 5.2%; *M* − CO_2Me, 345.1044); ν_{max}/cm^{-1}(CH_2Cl_2) 2930, 1710, 1535, 1470, 1414, 1352, 1280, 1190, 1092, 1033, 1015, 986, 918, 860 and 800; δ_H 7.75–7.4 (15 H, m), 3.44 (3 H, s) and 2.26 (3 H, s); δ_C see Table 2; δ_P +16.2; *m*/*z* 404 (M^+, 1%), 376 (5), 375 (4), 345 (25), 318 (18), 303 (83), 277 (100), 201 (25), 183 (35) and 152 (16).

Ethyl 2,4-*dioxo*-3-*triphenylphosphoranylidenepentanoate* **7g**. Prepared as yellow crystals (68%), m.p. 138–140 °C (Found: C, 72.0; H, 5.7. $C_{25}H_{23}O_4P$ requires C, 71.8; H, 5.5%); ν_{max}/cm^{-1} 1712, 1600, 1575, 1262, 1210, 1100, 1045, 861, 740, 720 and 690; δ_H 8.0–7.5 (15 H, m), 3.93 (2 H, q, *J* 7), 2.32 (3 H, s) and 1.22 (3 H, t, *J* 7); δ_C see Table 2; δ_P +16.2; *m*/*z* 418 (M^+, 2%), 390 (15), 375 (2), 361 (2), 345 (100), 317 (10), 303 (83), 279 (37), 278 (37), 277 (78), 262 (22), 201 (23) and 183 (47).

5,5-*Dimethyl*-1-*phenyl*-3-*triphenylphosphoranylidenehexane*-1,2,4-*trione* **7h**. Prepared as yellow crystals (78%), m.p. 168–170 °C (Found: C, 77.8; H, 6.25. $C_{32}H_{29}O_3P$ requires C, 78.0; H, 5.9%); ν_{max}/cm^{-1} 1654, 1525, 1430, 1360, 1340, 1300, 1260, 1210, 1140, 1090, 832, 737, 702, 680 and 648; δ_H 7.75–7.15 (20 H, m) and 1.32 (9 H, s); δ_C see Table 2; δ_P +17.4; *m*/*z* 477 (M^+ − Me, 0.2%), 436 (M^+ − C_4H_8, 0.5), 435 (1), 387 (10), 303 (16), 277 (100), 201 (20), 183 (18), 158 (26) and 105 (50).

Methyl 3,4-*dioxo*-4-*phenyl*-2-*triphenylphosphoranylidenebutanoate* **7i**. Prepared as colourless crystals (68%), m.p. 205–207 °C (Found: C, 74.8; H, 5.0. $C_{29}H_{23}O_4P$ requires C, 74.7; H, 5.0%); ν_{max}/cm^{-1}(CH_2Cl_2) 2980, 1645, 1572, 1518, 1472, 1412, 1320, 1270, 1175, 1092, 1072, 1015, 988 and 960; δ_H 8.15–7.5 (20 H, m) and 3.21 (3 H, s); δ_C see Table 2; δ_P +15.7; *m*/*z* 438 (M^+ − CO, 10%), 406 (4), 361 (2), 277 (100), 262 (8), 201 (8), 152 (8), 122 (27), 105 (27) and 92 (36).

Methyl 3,4-*dioxo*-2-*triphenylphosphoranylidenepentanoate* **7j**. Prepared as colourless crystals (87%), m.p. 153–155 °C (Found: C, 71.2; H, 5.3. $C_{24}H_{21}O_4P$ requires C, 71.3; H, 5.2%); ν_{max}/cm^{-1}(CH_2Cl_2) 2925, 1690, 1650, 1600, 1470, 1412, 1338, 1290, 1172, 1090, 1060, 988, 941 and 872; δ_H 7.8–7.4 (15 H, m), 3.30 (3 H, s) and 2.38 (3 H, s); δ_C see Table 2; δ_P +15.3; *m*/*z* 405 ($M + 1^+$, 8%), 361 (8), 333 (24), 301 (30), 277 (100), 201 (25), 183 (44), 152 (18) and 77 (45).

Dimethyl 2-*oxo*-3-*triphenylphosphoranylidenebutanedioate* **7k**. Prepared as colourless crystals (82%), m.p. 174–176 °C (Found: C, 69.1; H, 5.2%; M − CO_2Me, 361.0992. $C_{24}H_{21}O_5P$ requires C, 68.6; H, 5.0%; *M* − CO_2Me, 361.0994); ν_{max}/cm^{-1}(CH_2Cl_2) 2970, 2930, 1715, 1650, 1540, 1470, 1415, 1350, 1270, 1180, 1095, 985 and 952; δ_H 7.75–7.4 (15 H, m), 3.83 (3 H, s) and 3.28 (3 H, s); δ_C see Table 2; δ_P +16.3; *m*/*z* 420 (M^+, 0.5%), 361 (52), 301 (4), 277 (5), 201 (22), 183 (20) and 152 (10).

1-*Ethyl* 4-*methyl* 2-*oxo*-3-*triphenylphosphoranylidenebutanedioate* **7l**. Prepared as colourless crystals (98%), m.p. 173–174 °C (Found: C, 68.8; H, 5.45. $C_{25}H_{23}O_5P$ requires C, 69.1; H, 5.3%); ν_{max}/cm^{-1}(Nujol) 1728, 1663, 1582, 1440, 1432, 1350, 1278, 1180, 1153, 1101, 1088, 1021, 753, 710 and 691; δ_H 8.0–7.5 (15 H, m), 4.38 (2 H, q, *J* 7), 3.38 (3 H, s) and 1.38 (3 H, t, *J* 7); δ_C see Table 2; δ_P +16.5; *m*/*z* 434 (M^+, 1%), 375 (4), 362 (23), 361 (100), 301 (5), 293 (16), 201 (6), 183 (17), 165 (8) and 77 (12).

Ethyl 3,4-*dioxo*-4-*phenyl*-2-*triphenylphosphoranylidenebutanoate* **7m**. Prepared as colourless crystals (71%), m.p. 168–169 °C (Found: C, 74.4; H, 5.9%; M − CO, 452.1551. $C_{30}H_{25}O_4P$ requires C, 75.0; H, 5.2%; *M* − CO, 452.1541); ν_{max}/cm^{-1} (CH_2Cl_2) 1640, 1530, 1470, 1425, 1353, 1327, 1270, 1200, 1160, 1090 and 980; δ_H 8.15–7.45 (20 H, m), 3.76 (2 H, q, *J* 7) and 0.59 (3 H, t, *J* 7); δ_C see Table 2; δ_P +15.6; *m*/*z* 452 (M^+ − CO, 10%), 376 (26), 375 (100), 301 (9), 277 (20) and 262 (62).

Ethyl 3,4-*dioxo*-2-*triphenylphosphoranylidenepentanoate* **7n**.

Prepared as colourless crystals (56%), m.p. 138–140 °C (Found: C, 72.4; H, 5.5%; M − COMe, 375.1118. $C_{25}H_{23}O_4P$ requires C, 71.8; H, 5.5%; *M* − COMe, 375.1150); $\nu_{max}/cm^{-1}(CH_2Cl_2)$ 1690, 1638, 1532, 1468, 1415, 1355, 1320, 1250, 1146 and 1092; δ_H 7.8–7.4 (15 H, m), 3.83 (2 H, q, *J* 7), 2.32 (3 H, s) and 0.78 (3 H, t, *J* 7); δ_C see Table 2; δ_P +15.2; *m/z* 418 (M^+, 0.2%), 375 (M^+ − COMe, 100), 347 (5), 303 (28), 301 (36), 277 (67), 262 (70), 201 (37), 183 (86) and 165 (40).

4-*Ethyl* 1-*methyl* 2-*oxo*-3-*triphenylphosphoranylidenebutanedioate* **7o**. Prepared as colourless crystals (90%), m.p. 115–118 °C (Found: C, 69.45; H, 5.6. $C_{25}H_{23}O_5P$ requires C, 69.1; H, 5.3%); $\nu_{max}/cm^{-1}(CH_2Cl_2)$ 2940, 1718, 1648, 1548, 1360, 1260, 1190, 1163, 1094, 1080 and 988; δ_H 7.75–7.4 (15 H, m), 3.85 (3 H, s), 3.83 (2 H, q, *J* 7) and 0.77 (3 H, t, *J* 7); δ_C see Table 2; δ_P +16.2; *m/z* 434 (M^+, 0.2%), 376 (18), 303 (3), 301 (1), 278 (20), 277 (42), 201 (8), 183 (6), 91 (22), 85 (67) and 84 (100).

Diethyl 2-*oxo*-3-*triphenylphosphoranylidenebutanedioate* **7p**. Prepared as colourless crystals (91%), m.p. 136–138 °C (Found: C, 70.0; H, 5.6. $C_{26}H_{25}O_5P$ requires C, 69.6; H, 5.6%); ν_{max}/cm^{-1} 1735, 1725, 1672, 1540, 1438, 1342, 1278, 1190, 1095, 1020, 760, 745, 718 and 698; δ_H 8.0–7.5 (15 H, m), 4.38 (2 H, q, *J* 7), 3.89 (2 H, q, *J* 7), 1.37 (3 H, t, *J* 7) and 0.78 (3 H, t, *J* 7); δ_C see Table 2; δ_P +16.2; *m/z* 448 (M^+, 0.2%), 403 (0.2), 376 (16), 375 (100), 347 (4), 303 (12), 279 (4), 201 (6), 195 (3), 183 (11) and 165 (8).

Flash Vacuum Pyrolysis of the Ylides **7**.—The apparatus used was as described previously.[9] All pyrolyses were conducted at pressures in the range 10^{-3}–10^{-1} Torr and were complete within 1 h for ⩽0.5 g of ylide or 3–4 h for 1–5 g ylide. 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 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 or distillation. For small-scale pyrolyses 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%. The apparently low overall yield of products in some cases is accounted for by the formation of gaseous products and/or by a substantial non-volatile polymeric residue in the inlet tube.

(a) FVP of the ylide **7a** (5.0 g) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be a mixture of Ph_3PO and the desired product. Chromatography on silica (ethyl acetate) gave pure dibenzoylacetylene **10a** (0.9 g, 40%) as pale yellow crystals, m.p. 110–111 °C (lit.,[10] 112 °C); δ_H 8.4–8.2 (4 H, m) and 7.8–7.3 (6 H, m); δ_C see Table 3.

(b) FVP of the ylide **7b** (124 mg) at 500 °C gave a solid at the furnace exit which proved to be a mixture of Ph_3PO and Ph_3P, and in the cold trap a liquid which was shown by ^1H and ^{13}C NMR and GCMS to contain a complex mixture of products including acetaldehyde, acetophenone, benzoic acid, 1-phenylpent-1-ene-3,4-dione and 1-phenylpent-2-ene-1,4-dione. The desired acetylbenzoylacetylene **10b** was not present.

(c) FVP of the ylide **7c** (200 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was methyl benzoylpropynoate **10c** (23%); δ_H 8.12 (2 H, m), 7.75–7.45 (3 H, m) and 3.90 (3 H, s); δ_C see Table 3.

(d) FVP of the ylide **7d** (215 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was ethyl benzoylpropynoate **10d** (44%); δ_H 8.1–8.2 (2 H, m), 7.7–7.45 (3 H, m), 4.35 (2 H, q, *J* 7) and 1.38 (3 H, t, *J* 7); δ_C see Table 3.

(e) FVP of the ylide **7e** (106 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be Ph_3PO and in the cold trap a solid which was shown by ^1H NMR and GCMS to contain mainly benzaldehyde (17%) and benzoic acid (45%) with further minor unidentified components. The expected acetylbenzoylacetylene **10e** was not present.

(f) FVP of the ylide **7f** (121 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be mainly Ph_3PO accompanied by ≈5% Ph_3P. The material in the cold trap was shown by ^1H NMR and GCMS to contain mainly methanol with further minor unidentifed components. The expected methyl 3-acetylpropynoate **10f** was not present.

(g) FVP of the ylide **7g** (142 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be Ph_3PO and in the cold trap ethyl 3-acetylpropynoate **10g** (67%) as a colourless liquid; δ_H 4.26 (2 H, q, *J* 7), 2.36 (3 H, s) and 1.30 (3 H, t, *J* 7); δ_C see Table 3; *m/z* 140 (M^+, 1%), 125 (21), 111 (3), 95 (28), 80 (8), 67 (9) and 53 (100), accompanied by ethanol (≈20%).

(h) FVP of ylide **7h** (92 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap contained several unidentified components but the major one was the desired benzoylpivaloylacetylene (43%); δ_H 8.2–8.0 (2 H, m), 7.7–7.5 (3 H, m) and 1.34 (9 H, s); δ_C see Table 3; *m/z* (GCMS) 199 (M^+ − Me, 1%), 159 (6), 158 (84), 130 (5), 105 (42), 102 (28), 77 (45) and 57 (100).

(i) FVP of the ylide **7i** (1.0 g) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be a mixture of Ph_3PO and the desired product. Kugelrohr distillation gave methyl benzoylpropynoate **10i** (0.27 g, 67%) as a colourless solid, m.p. 68–69 °C (lit.,[11] 65–66 °C); δ_H 8.4–8.2 (2 H, m), 7.8–7.5 (3 H, m) and 3.97 (3 H, s); δ_C see Table 3.

(j) FVP of the ylide **7j** (140 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be Ph_3PO and in the cold trap methyl 3-acetylpropynoate **10j** (38%) as a colourless liquid; δ_H 3.80 (3 H, s) and 2.40 (3 H, s); δ_C see Table 3, accompanied by methanol (≈40%).

(k) FVP of the ylide **7k** (500 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was dimethyl butynedioate **10k** (59%); δ_H 3.84 (6 H, s); δ_C see Table 3.

(l) FVP of the ylide **7l** (503 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was ethyl methyl butynedioate **10l** (61%); δ_H 4.37 (2 H, q, *J* 7), 3.89 (3 H, s) and 1.35 (3 H, t, *J* 7); δ_C see Table 3.

(m) FVP of the ylide **7m** (500 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was ethyl benzoylpropynoate **10m** (52%); δ_H 8.3–8.2 (2 H, m), 7.8–7.5 (3 H, m), 4.42 (2 H, q, *J* 7) and 1.39 (3 H, t, *J* 7); δ_C see Table 3.

(n) FVP of the ylide **7n** (400 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was ethyl 3-acetylpropynoate **10n** (23%); δ_H 4.32 (2 H, q, *J* 7), 2.45 (3 H, s) and 1.36 (3 H, t, *J* 7); δ_C see Table 3.

(o) FVP of the ylide **7o** (1.10 g) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was ethyl methyl butynedioate **10o** (88%); δ_H 4.28 (2 H, q, *J* 7), 3.82 (3 H, s) and 1.31 (3 H, t, *J* 7); δ_C see Table 3.

(p) FVP of the ylide **7p** (503 mg) at 500 °C gave a solid at the furnace exit which was shown by ^1H and ^{31}P NMR to be pure Ph_3PO. The colourless liquid in the cold trap was diethyl butynedioate **10p** (63%); δ_H 4.37 (2 H, q, *J* 7) and 1.35 (3 H, t, *J* 7); δ_C see Table 3.

(q) ^{13}C *Labelled ethyl methyl acetylenedicarboxylate* **14**. This compound was prepared as for **10o** by FVP of ylide **13** made from (ethoxycarbonylmethylene)triphenylphosphorane derived from ethyl bromoacetate labelled with 5% ^{13}C at the Br*C*H_2 position. The product was obtained in 55% yield on the pyrolysis and had spectroscopic properties identical with those of the unlabelled compound **10o** above, except for a five times enhancement of the signal at δ_C 75.1.

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