

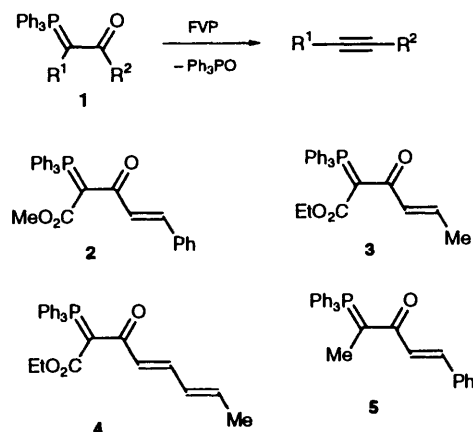
## Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 6.<sup>1</sup> Pyrolysis of Substituted Cinnamoyl Ylides as a Route to Conjugated Enynes

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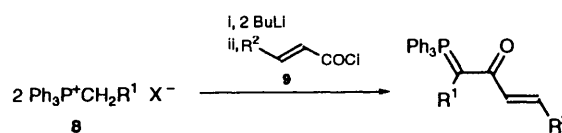
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The substituted cinnamoyl ylides **6** and **7**, readily prepared in one step from the quaternary phosphonium salts **8** and cinnamoyl chlorides **9**, undergo extrusion of  $\text{Ph}_3\text{PO}$  upon FVP to give the 1,3-enynes **12** and **13** in moderate yield. At 500 °C there is little double bond isomerisation, but at 700 °C this does occur to give almost 1:1 mixtures of *E* and *Z* isomers. In a few cases, including those with a nitrophenyl group present, the yields are poor or the reactions fail completely. An attempt to improve upon the poor yield of 1-phenylbutenyne by use of an ester stabilised ylide was only partly successful since the severe conditions required for loss of the ester group resulted in significant isomerisation to naphthalene. The fully assigned  $^{13}\text{C}$  NMR spectra for 20 enynes are reported. One example of the isomeric  $\beta,\gamma$ -unsaturated- $\delta$ -oxo ylides, **14** has been prepared and is found to undergo loss of  $\text{Ph}_3\text{P}$  on FVP at 700 °C to give indene and benzene in low yield.

In previous parts of this series we have described the successful use of flash vacuum pyrolysis (FVP) to bring about thermal extrusion of  $\text{Ph}_3\text{PO}$  from the stabilised ylides **1** to give alkynes, a process which, for  $\text{R}^1 = \text{H}$  or alkyl, is not possible using conventional pyrolysis. Since the ylides **1** are readily prepared as stable crystalline solids by acylation of  $\text{Ph}_3\text{P}=\text{CHR}^1$  with an acid chloride  $\text{R}^2\text{COCl}$ , this provides convenient access to a wide range of substituted alkynes. In early work using conventional pyrolysis, Märkl<sup>2</sup> successfully obtained an enyne from **2**. Gough and Trippett likewise converted the ylides **3** and **4** into the corresponding enyne and dienyne, but under the same conditions the ylide **5** lacking the additional ester stabilisation



gave no enyne.<sup>3</sup> In this paper we describe the synthesis of a range of substituted cinnamoyl ylides **6** and **7** and their conversion by means of FVP into *E*- and *Z*-1,3-enynes. Although the conjugated enynes are of considerable interest as synthetic intermediates, they have most commonly been prepared by direct formation of the C(2)–C(3) single bond by metal-induced coupling of alkyne and alkene fragments.<sup>4</sup> The approach used here which allows overall coupling of an alkyl halide  $\text{R}^1\text{CH}_2\text{X}$ , *via* the phosphonium salt **8**, with an acid chloride **9** to give enyne  $\text{R}^1\text{C}\equiv\text{C}-\text{CH}=\text{CHR}^2$ , in just three steps would seem to offer an attractive alternative, particularly if some control of the configuration of the double bond in the product were possible by varying the pyrolysis temperature.

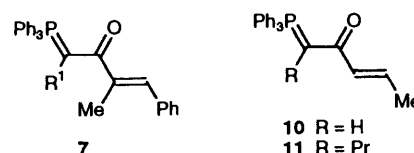


Scheme 1

### Results and Discussion

A total of 21 ylides **6** were obtained in moderate to good yield, as shown in Scheme 1, by reaction of the quaternary phosphonium salts **8** (2 equiv.) with butyllithium to generate the corresponding ylides, followed by acylation with substituted cinnamoyl chlorides **9** (Table 1). The acylation proceeds with 'transylidation' to regenerate one molecule of the starting phosphonium chloride.<sup>5</sup> Use of  $\alpha$ -methylcinnamoyl chloride likewise afforded two examples of the ylides **7**. All the ylides were obtained as yellow or orange crystalline solids showing the expected  $^{31}\text{P}$  NMR signals in the range  $\delta_{\text{p}} +14$ –19. Upon prolonged storage they have all been found to be perfectly stable with the exception of **6a** which is markedly light sensitive and deteriorates appreciably within a few weeks.

Apart from the ester-stabilised examples **2**–**4** mentioned earlier, the only previous report of the formation of enynes by pyrolysis of stabilised ylides is our previous paper<sup>6</sup> in which crotonyl chloride derived ylides **10** and **11** gave the

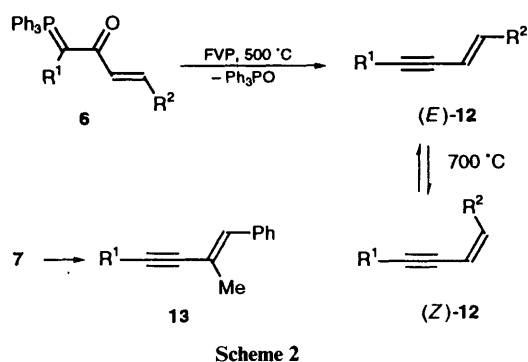


corresponding enynes in yields of 59 and 82%, respectively, upon FVP at 750 °C. Under these conditions the extrusion was accompanied by 10–15% isomerisation of the double bond to give the *Z*-enynes. Pyrolysis of two examples of **1** ( $\text{R}^2 = \text{cyclobutyl}$ ) at 800–850 °C led to extrusion of ethene in addition to  $\text{Ph}_3\text{PO}$  to give vinylalkynes. Since the simpler ylides **1** ( $\text{R}^1, \text{R}^2 = \text{H}$  or alkyl) sublimed unchanged at 600 °C,<sup>6</sup> we first investigated FVP of **6a**–**g** at 700 °C. With the exception of **6a**, this led to clean extrusion of  $\text{Ph}_3\text{PO}$ , as shown in Scheme 2, to give moderate yields of the desired enynes **12** (Table 1). However, examination of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of these

Table 1 Formation of the ylides **6** and **7** and FVP to give compounds **12** and **13**

	R <sup>1</sup>	R <sup>2</sup>	Yield (%)	$\delta_p$	Formation of enynes at			
					500 °C		700 °C	
					Yield (%)	E/Z ratio	Yield (%)	E/Z ratio
<b>6a</b>	H	Ph	59	15.6			8	58/42
<b>6b</b>	Me	Ph	49	15.6			53	57/43
<b>6c</b>	Et	Ph	60	18.0			33	56/44
<b>6d</b>	Pr	Ph	49	17.8	42	95/5	21	53/47
<b>6e</b>	Pr <sup>i</sup>	Ph	53	16.2			67	56/44
<b>6f</b>	Bu	Ph	66	18.0	58	96/4	25	50/50
<b>6g</b>	Ph	Ph	66	16.0	85	97/3	99	57/43
<b>6h</b>	2-MeOC <sub>6</sub> H <sub>4</sub>	Ph	31	15.1	54	93/7		
<b>6i</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	37	15.9	16	88/12		
<b>6j</b>	2-Thienyl	Ph	46	16.6	66	90/10		
<b>6k</b>	Me	2-ClC <sub>6</sub> H <sub>4</sub>	56	18.0	< 5			
<b>6l</b>	Me	4-ClC <sub>6</sub> H <sub>4</sub>	34	15.9	~ 0			
<b>6m</b>	Me	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	30	18.4	~ 0			
<b>7a</b>	Me	—	63	17.8	67	95/5		
<b>6n</b>	Ph	4-MeC <sub>6</sub> H <sub>4</sub>	66	15.6	82	> 95/5		
<b>6o</b>	Ph	4-ClC <sub>6</sub> H <sub>4</sub>	66	16.0	39	97/3		
<b>6p</b>	Ph	2-ClC <sub>6</sub> H <sub>4</sub>	74	16.1	58	95/5		
<b>6q</b>	Ph	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	60	16.4	19	77/23		
<b>6r</b>	Ph	3,4-OCH <sub>2</sub> OC <sub>6</sub> H <sub>3</sub>	81	15.7	58	85/15		
<b>6s</b>	Ph	2-Furyl	55	15.9	55	90/10		
<b>6t</b>	Ph	2-Thienyl	77	15.8	47	85/15		
<b>6u</b>	Ph	5-Me-2-thienyl	58	15.7	34	79/21		
<b>7b</b>	Ph	—	48	14.7	55	95/5		
<b>6v</b>	EtO <sub>2</sub> C	Ph	47	17.6			18 <sup>a</sup>	67/33

<sup>a</sup> Yield of **12a** formed at 800 °C.



products showed that a substantial degree of isomerisation had occurred in each case, giving almost 1:1 mixtures of *E*- and *Z*-**12**. The precise ratio of isomers in each case was readily determined from integration of the lower frequency half of the AB pattern due to the =CH—C≡C protons in the <sup>1</sup>H spectra which consistently occurred at *ca.* 0.5 ppm lower frequency for the *Z*-isomers. A significant 5-bond coupling of *ca.* 2 Hz, through the triple bond to the protons on the first carbon of R<sup>1</sup>, was also observed for these signals. Analysis of the <sup>13</sup>C NMR data and comparison with those of the pure *E*-isomers obtained at 500 °C (*vide infra*) allowed full assignment of the signals due to each isomer of **12b–g** which form a highly consistent pattern (Table 2).

Recently, Hickson and McNab have published a detailed study of the thermal *E/Z* isomerisation of a variety of styryl derivatives under FVP conditions.<sup>7</sup> Cinnamyl alcohol, methyl cinnamate and cinnamaldehyde were each found to be converted into the *Z* isomers to an extent of < 10% at 700 °C, while for cinnamitrile the conversion was 14% at 700 °C rising to the equilibrium composition of 40% at 900 °C. The styrylalkynes **12** are obviously most similar to the last example in having a comparatively low steric requirement for the C≡CR<sup>1</sup>

group, as for C≡N. The equilibrium composition of 42–50% *Z* isomer observed here (Table 1) is in good agreement with the value for cinnamitrile, and the fact that it is reached at a significantly lower temperature may perhaps be attributed to the formation of **12** in an excited state by the extrusion of Ph<sub>3</sub>PO.

In order to reduce the unwanted double bond isomerisation, compounds **6d**, **f** and **g** were subjected to FVP at 500 °C. This again resulted in complete extrusion of Ph<sub>3</sub>PO to give the enynes, but these were now formed almost exclusively (> 95%) as the *E* isomers. These conditions were then applied to the remaining ylides **6h–u**. In most cases, this gave the desired enynes in moderate yield with little double bond isomerisation (Table 1). Again the <sup>13</sup>C NMR data formed a highly consistent pattern and could for the most part be fully assigned without ambiguity (Table 2). It was surprising to discover that **6k**, **l** gave little or none of the enynes, particularly since the closely related compound **6b** behaved well at 700 °C. The failure of the reaction for **6m** is not so surprising since the thermal lability of nitro groups is well known and this is also reflected in the poor yields obtained from **6i** and **q**. Pyrolysis of the two examples **7a**, **b** proceeded in a straightforward manner to give the enynes **13** with little double bond isomerisation.

The consistently poor yield obtained for **6a**, which prevented access to **12a** in reasonable quantity, seems to be partly due to the instability of this ylide, and FVP even at 500 °C was accompanied by extensive decomposition in the inlet tube of the pyrolysis set-up and the formation of a significant proportion of Ph<sub>3</sub>P. In an attempt to circumvent this problem, the ester-stabilised ylide **6v** was prepared since, as we recently reported,<sup>8</sup> pyrolysis of  $\alpha$ -ethoxycarbonyl  $\beta$ -oxo ylides at 750 °C leads to loss of the whole ester group to afford terminal alkynes. The compound was readily obtained by a slightly different method to the other examples, involving treatment of Ph<sub>3</sub>P=CHCO<sub>2</sub>Et with cinnamoyl chloride and triethylamine. When this was subjected to FVP at 700 °C, the expected enyne **12v** was

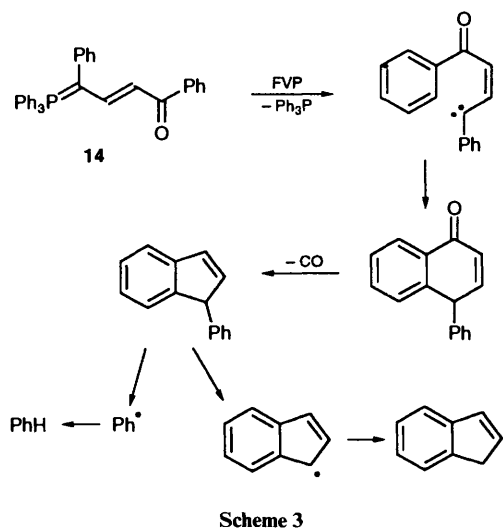
Table 2 <sup>13</sup>C NMR spectra ( $\delta_c$ ) of the 1,3-enynes **12** and **13**

R <sup>1</sup>	R <sup>2</sup>	Enyne signals						R <sup>1</sup> signals						R <sup>2</sup> signals					
		C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6
(E)-12a	H	143.1	106.9	84.1	79.3	—	—	135.8	126.3	128.7	128.9	128.9	133.4	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
(Z)-12a	H	140.6	106.3	— <sup>a</sup>	— <sup>a</sup>	—	—	133.4	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	136.5	126.0	128.6	128.2	128.2	128.2	128.2
(E)-12b	Ph	140.1	108.8	88.3	78.9	4.5	4.5	136.5	126.0	128.4	128.3	128.3	136.6	126.0	128.4	128.3	128.3	128.3	128.3
(Z)-12b	Me	137.3	108.1	93.2	78.3	4.8	4.8	136.5	126.0	128.6	128.1	128.1	136.5	126.0	128.6	128.1	128.1	128.1	128.1
(E)-12c	Et	140.0	108.8	94.2	79.0	13.3	13.9	136.7	126.0	128.4	128.2	128.2	136.7	126.0	128.4	128.2	128.2	128.2	128.2
(Z)-12c	Et	137.3	108.1	98.9	78.6	13.6	13.7	136.5	126.0	128.6	128.1	128.1	136.5	126.0	128.6	128.1	128.1	128.1	128.1
(E)-12d	Ph	140.0	108.9	92.9	79.9	21.6	22.2	136.7	126.0	128.4	128.2	128.2	136.7	126.0	128.4	128.2	128.2	128.2	128.2
(Z)-12d	Pr	137.2	108.2	98.0	79.4	21.9	22.0	136.6	126.0	128.6	128.0	128.0	136.6	126.0	128.6	128.0	128.0	128.0	128.0
(E)-12e	Pr <sup>†</sup>	139.9	108.8	98.3	78.8	21.3	23.0	136.7	126.0	128.5	128.1	128.1	136.7	126.0	128.5	128.1	128.1	128.1	128.1
(Z)-12e	Pr <sup>†</sup>	137.3	108.2	102.8	78.4	21.5	22.6	136.7	126.0	128.5	128.1	128.1	136.7	126.0	128.5	128.1	128.1	128.1	128.1
(E)-12f	Bu	139.9	108.9	93.0	79.7	19.3	30.9	136.5	126.0	128.6	128.1	128.1	136.5	126.0	128.6	128.1	128.1	128.1	128.1
(Z)-12f	Bu	137.2	108.2	97.8	79.2	19.6	30.6	136.7	126.0	128.4	128.2	128.2	136.7	126.0	128.4	128.2	128.2	128.2	128.2
(E)-12g	Ph	141.3	108.1	91.7	88.9	123.4	131.5	136.5	126.0	128.6	128.1	128.1	136.5	126.0	128.6	128.1	128.1	128.1	128.1
(Z)-12g	Ph	138.7	107.4	95.8	88.2	123.5	131.4	136.7	126.0	128.4	128.2	128.2	136.7	126.0	128.4	128.2	128.2	128.2	128.2
(E)-12h	2-MeOC <sub>6</sub> H <sub>4</sub>	140.9	108.4	92.9	88.2	112.5	159.8	136.3	126.2	128.7	128.5	128.5	136.3	126.2	128.7	128.5	128.5	128.5	128.5
(E)-12i	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	143.4	107.1	94.4	89.8	123.9	132.1	135.8	126.5	128.9	128.4	128.4	135.8	126.5	128.9	128.4	128.4	128.4	128.4
(E)-12j	2-Thienyl	141.2	107.7	92.8	84.9	—	123.5	137.1	127.3	127.1	127.1	127.1	137.1	127.1	127.1	127.1	127.1	127.1	127.1
(E)-12n	Ph	141.3	107.0	91.4	89.1	123.5	131.5	133.6	126.2	129.4	138.7	138.7	133.6	126.2	129.4	138.7	138.7	138.7	138.7
(E)-12o	Ph	139.8	108.8	92.3	88.5	123.2	131.5	134.8	127.4	128.9	134.3	134.3	134.8	127.4	128.9	134.3	134.3	134.3	134.3
(E)-12p	Ph	137.0	110.7	92.6	88.6	123.1	131.6	134.3	133.2	130.0	129.5	129.5	134.3	133.2	130.0	129.5	129.5	129.5	129.5
(E)-12q	Ph	135.7	113.6	93.6	88.1	122.8	131.7	132.6	147.5	124.8	130.0	130.0	132.6	147.5	124.8	130.0	130.0	130.0	130.0
(E)-12r	Ph	140.9	108.4	91.3	89.0	123.5	131.4	130.9	105.1	148.2	128.1	128.1	130.9	105.1	148.2	128.1	128.1	128.1	128.1
(E)-12s	Ph	143.0	106.1	92.4	88.9	123.4	131.4	—	152.2	111.9	110.1	110.1	—	152.2	111.9	110.1	110.1	110.1	110.1
(E)-12t	Ph	134.0	107.3	92.1	88.7	123.3	131.4	—	141.5	127.8	127.1	127.1	—	141.5	127.8	127.1	127.1	127.1	127.1
(E)-12u	Ph	134.6	105.8	91.7	89.0	123.5	131.4	—	140.7	126.0	126.9	126.9	—	140.7	126.0	126.9	126.9	126.9	126.9
(E)-13a	Me	136.1	119.8	84.8	83.5	4.3	4.3	137.0	128.3	128.9	126.9	126.9	137.0	128.3	128.9	126.9	126.9	126.9	126.9
(E)-13b	Ph	136.1	119.8	93.2	88.4	123.4	131.5	136.8	128.3	129.0	127.2	127.2	136.8	128.3	129.0	127.2	127.2	127.2	127.2

† Assignments may be interchanged. <sup>a</sup> Signals not definitely assigned. <sup>b</sup> Additional signals 133.4, 129.7, 120.5 and 55.7. <sup>c</sup> Signal for OCH<sub>2</sub>O at 101.3. <sup>d</sup> Signal for Me at 15.7.

obtained in impure form. Complete loss of the ester group to give the desired terminal enyne **12a** (18%) was only achieved at 800 °C, at which temperature significant side-reactions took place. The most important of these was the formation of naphthalene (8%) together with a bright blue colour attributed to a trace quantity of azulene. These products probably result from the previously reported isomerisation of **12a** to styryl-vinylidene which undergoes intramolecular addition and rearrangement to give naphthalene and azulene.<sup>9</sup> At 850 °C the yield of **12a** fell to 12% and that of naphthalene increased to 20%. It is therefore clear that this method is of little value in preparing the terminal enyne **12a**.

Finally, it was of interest to examine the pyrolytic behaviour of the vinylogous oxo ylide **14** which is isomeric with **6g**. This previously unknown compound was readily prepared<sup>10</sup> in 62% yield by acylation of benzylidene(triphenyl)phosphorane with  $\beta$ -chloroacrylophenone and resembled **6** in most of its physical and spectroscopic properties. Extrusion of  $\text{Ph}_3\text{PO}$  from this ylide would give diphenylcyclobutadiene and should not be favoured. In fact, **14** underwent predominant loss of  $\text{Ph}_3\text{P}$  on FVP at 700 °C to give a complex mixture of products among which indene and benzene were the largest single components, formed in yields of 12 and 9%, respectively. One possible mechanism for the formation of these two products is shown in Scheme 3 in which extrusion of  $\text{Ph}_3\text{P}$  is followed by



intramolecular addition of the resulting carbene, extrusion of CO and fragmentation to give phenyl and indenyl radicals which then abstract a hydrogen atom. The products could, of course, be formed from a variety of other fragmentation pathways, and further study of a wider range of ylides analogous to **14** might elucidate the mechanisms involved.

## Experimental

M.p.s were recorded on a Kofler hot-stage microscope and are uncorrected. IR spectra were recorded for solids on Nujol mulls and for liquids on thin films using a Perkin-Elmer 1420 instrument. NMR spectra were obtained for  $^1\text{H}$  at 200 MHz and for  $^{13}\text{C}$  at 50 MHz using a Varian Gemini instrument and for  $^{31}\text{P}$  at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in  $\text{CDCl}_3$  with internal  $\text{Me}_4\text{Si}$  as reference for  $^1\text{H}$  and  $^{13}\text{C}$  and external 85%  $\text{H}_3\text{PO}_4$  as reference for  $^{31}\text{P}$ . 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 coupled to a Finnigan Incos

mass spectrometer. Dry THF was freshly distilled from potassium benzophenone ketyl under  $\text{N}_2$ .

The required quaternary phosphonium salts were commercially available or were readily prepared by reaction of the appropriate halide with  $\text{Ph}_3\text{P}$  in boiling toluene. The cinnamoyl chlorides were freshly prepared from the corresponding acids by treatment with an excess of  $\text{SOCl}_2$ , evaporation and Kugelrohr distillation.

*Preparation of Substituted Cinnamoylalkylidene(triphenyl)-phosphoranes.*—A suspension of the appropriate quaternary phosphonium salt (25 mmol) in dry THF (150  $\text{cm}^3$ ) was stirred at room temperature under nitrogen while butyllithium in hexane (26 mmol) was added dropwise to it by syringe. After 15 min a solution of the appropriate cinnamoyl chloride (12.5 mmol) in dry THF (10  $\text{cm}^3$ ) was added dropwise to the mixture which was then stirred for 8 h before being added to water (250  $\text{cm}^3$ ). Extraction of the aqueous mixture with ether (3  $\times$  100  $\text{cm}^3$ ) followed by drying of the combined extracts and evaporation gave the required phosphoranes which were recrystallised from ethyl acetate. Using this method the following compounds were prepared.

**Cinnamoylmethylene(triphenyl)phosphorane 6a.** Prepared as yellow crystals (59%), m.p. 157–160 °C (lit.,<sup>11</sup> non-crystalline) (Found: M, 406.1495.  $\text{C}_{28}\text{H}_{23}\text{OP}$  requires M, 406.1486);  $\nu_{\text{max}}/\text{cm}^{-1}$  1634, 1517, 1440, 1103, 973, 885, 760, 729 and 690;  $\delta_{\text{H}}$  7.8–7.2 (21 H, m), 6.93 (1 H, half AB pattern,  $J$  18) and 4.05 (1 H, br s);  $\delta_{\text{P}}$  +15.6;  $m/z$  406 ( $\text{M}^+$ , 100%), 405 (55), 378 (21), 377 (20), 363 (7), 353 (5), 329 (6), 303 (70), 275 (58), 262 (60), 202 (12), 185 (15) and 183 (65).

**1-Cinnamoylethylidene(triphenyl)phosphorane 6b.** Prepared as yellow crystals (49%), m.p. 205–206 °C (lit.,<sup>5</sup> 205–208 °C);  $\nu_{\text{max}}/\text{cm}^{-1}$  1630, 1438, 1167, 1103, 982, 908, 847, 738 and 690;  $\delta_{\text{H}}$  7.8–7.2 (22 H, m) and 1.82 (3 H, d,  $J$  16);  $\delta_{\text{P}}$  +15.6;  $m/z$  420 ( $\text{M}^+$ , 7%), 278 (50), 277 (100), 262 (80), 201 (30), 183 (50), 152 (20) and 131 (30).

**1-Cinnamoylpropylidene(triphenyl)phosphorane 6c.** Prepared as yellow prisms (60%), m.p. 211–213 °C (Found: C, 83.2; H, 6.3.  $\text{C}_{30}\text{H}_{27}\text{OP}$  requires C, 82.9; H, 6.3%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1631, 1495, 1165, 1101, 975, 921, 860, 763, 729 and 691;  $\delta_{\text{H}}$  7.7–7.25 (22 H, m), 2.17 (2 H, d, of q,  $J$  22, 7) and 0.96 (3 H, t,  $J$  7);  $\delta_{\text{P}}$  +18.0;  $m/z$  434 ( $\text{M}^+$ , 64%), 419 (99), 357 (11), 343 (7), 331 (6), 315 (2), 302 (14), 287 (22), 279 (9) and 262 (100).

**1-Cinnamoylbutylidene(triphenyl)phosphorane 6d.** Prepared as yellow needles (49%), m.p. 187–189 °C (lit.,<sup>12</sup> 204–207 °C);  $\nu_{\text{max}}/\text{cm}^{-1}$  1632, 1501, 1438, 1164, 1106, 1082, 975, 720 and 692;  $\delta_{\text{H}}$  7.75–7.2 (22 H, m), 2.2–1.95 (2 H, m), 1.32 (2 H, sextet,  $J$  7) and 0.70 (3 H, t,  $J$  7);  $\delta_{\text{P}}$  +17.8;  $m/z$  448 ( $\text{M}^+$ , 12%), 420 (20), 419 (100), 278 (40), 277 (80), 262 (60), 201 (10), 183 (40) and 131 (25).

**1-Cinnamoyl-2-methylpropylidene(triphenyl)phosphorane 6e.** Prepared as yellow crystals (53%), m.p. 219–220 °C (Found: C, 83.2; H, 6.6.  $\text{C}_{31}\text{H}_{29}\text{OP}$  requires C, 83.0; H, 6.5%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1626, 1430, 1181, 1103, 1073, 977, 748, 697 and 686;  $\delta_{\text{H}}$  7.7–7.25 (22 H, m), 2.10 (1 H, d of septets,  $J$  25, 7) and 1.30 (6 H, d,  $J$  7);  $\delta_{\text{P}}$  +16.2;  $m/z$  448 ( $\text{M}^+$ , 15%), 435 (15), 434 (45), 279 (26), 277 (56), 262 (100), 201 (15), 183 (58) and 131 (58).

**1-Cinnamoylpentylidene(triphenyl)phosphorane 6f.** Prepared as yellow needles (66%), m.p. 179–180 °C (Found: C, 83.4; H, 6.8.  $\text{C}_{32}\text{H}_{31}\text{OP}$  requires C, 83.1; H, 6.8%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1634, 1157, 1097, 968, 852, 746, 721 and 690;  $\delta_{\text{H}}$  7.7–7.25 (22 H, m), 2.10 (2 H, d of t,  $J$  22, 7), 1.29 (2 H, m), 1.10 (2 H, sextet,  $J$  7) and 0.96 (3 H, t,  $J$  7);  $\delta_{\text{P}}$  +18.0;  $m/z$  462 ( $\text{M}^+$ , 15%), 434 (11), 420 (30), 419 (100), 289 (6), 287 (6), 277 (48), 262 (44), 201 (13) and 183 (36).

**$\alpha$ -Cinnamoylbenzylidene(triphenyl)phosphorane 6g.** Prepared as yellow crystals (66%), m.p. 228–230 °C (Found: C, 84.9; H, 5.7.  $\text{C}_{34}\text{H}_{27}\text{OP}$  requires C, 84.6; H, 5.6%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1640,

1580, 1490, 1430, 1205, 1100, 970, 750 and 690;  $\delta_{\text{H}}$  7.75–7.1 (21 H, m), 7.02 (5 H, s) and 6.93 (1 H, half AB pattern, *J* 16);  $\delta_{\text{C}}$  179.7 (d, *J* 5, CO), 137.1 (d, *J* 11, C-1 of  $\alpha$ -phenyl), 136.9 (C-1 of cinnamoyl Ph), 134.8 (2 C), 134.7 (2 C, d, *J* 4, C-2 of  $\alpha$ -phenyl), 133.6 (6 C, d, *J* 10, C-2 of P-Ph), 131.5 (3 C, d, *J* 2, C-4 of P-Ph), 128.5 (6 C, d, *J* 12, C-3 of P-Ph), 128.3 (2 C), 127.9, 127.5 (3 C), 126.6 (3 C, d, *J* 91, C-1 of P-Ph), 126.1, 125.3 and 76.2 (d, *J* 109, ylide C);  $\delta_{\text{P}}$  +15.95; *m/z* 482 ( $\text{M}^+$ , 100%), 481 (34), 454 (3), 405 (5), 379 (13), 363 (3), 351 (8), 303 (7), 278 (10), 277 (22), 262 (60), 204 (65) and 183 (28).

$\alpha$ -Cinnamoyl-2-methoxybenzylidene(triphenyl)phosphorane **6h**. Prepared as orange crystals (31%), m.p. 203–204 °C (Found: C, 81.4; H, 5.7%; M, 512.1868.  $\text{C}_{35}\text{H}_{29}\text{O}_2\text{P}$  requires C, 82.0; H, 5.7%; M, 512.1905);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) 3058, 2960, 1630, 1590, 1573, 1496, 1478, 1435, 1372, 1240, 1105, 1048, 1028, 980, 954 and 692;  $\delta_{\text{H}}$  7.75–7.05 (23 H, m), 7.0–6.7 (2 H, m), 6.42 (1 H, half AB pattern, *J* 8) and 3.24 (3 H, s);  $\delta_{\text{P}}$  +15.1; *m/z* 512 ( $\text{M}^+$ , 7%), 481 (54), 409 (3), 368 (13), 351 (5), 337 (6), 303 (9), 277 (8), 263 (18), 262 (48) and 183 (100).

$\alpha$ -Cinnamoyl-4-nitrobenzylidene(triphenyl)phosphorane **6i**. Prepared as orange crystals (37%), m.p. 266–267 °C (Found: C, 77.1; H, 4.9; N, 2.6.  $\text{C}_{34}\text{H}_{26}\text{NO}_3\text{P}$  requires C, 77.4; H, 5.0; N, 2.7%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1623, 1570, 1475, 1360, 1097 and 975;  $\delta_{\text{H}}$  7.85 and 7.05 (4 H, AB pattern, *J* 8), 7.7–7.2 (21 H, m) and 6.90 (1 H, half AB pattern, *J* 16);  $\delta_{\text{P}}$  +15.9; *m/z* 527 ( $\text{M}^+$ , 1.5%), 293 (2), 279 (23), 278 (70), 277 (100), 263 (15), 262 (50), 250 (19), 249 (50), 202 (75), 201 (60), 199 (40) and 183 (50).

$\alpha$ -Cinnamoyl-2-thienylmethylene(triphenyl)phosphorane **6j**. Prepared as yellow crystals (46%), m.p. 196–199 °C (Found: M, 488.1401.  $\text{C}_{32}\text{H}_{25}\text{OPS}$  requires M, 488.1364);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) 1624, 1570, 1490, 1426, 1365, 1338, 1212, 1187, 1164, 1100, 972, 900 and 832;  $\delta_{\text{H}}$  7.75–7.10 (22 H, m), 6.97 (1 H, m), 6.72 (1 H, m) and 6.52 (1 H, m);  $\delta_{\text{P}}$  +16.6; *m/z* 488 ( $\text{M}^+$ , 50%), 438 (3), 408 (9), 308 (11), 277 (12), 263 (10), 262 (40), 210 (100) and 183 (35).

1-(2-Chlorocinnamoyl)ethylidene(triphenyl)phosphorane **6k**. Prepared as orange crystals (56%), m.p. 194–196 °C (Found: C, 76.7; H, 5.3.  $\text{C}_{29}\text{H}_{24}\text{ClOP}$  requires C, 76.6; H, 5.3%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1620, 1470, 1370, 1150, 1100, 1038, 970 and 845;  $\delta_{\text{H}}$  7.75–7.3 (16 H, m), 7.25–7.05 (5 H, m) and 1.82 (3 H, d, *J* 20);  $\delta_{\text{P}}$  +18.0; *m/z* 456 ( $^{37}\text{Cl} - \text{M}^+$ , 12%), 455 (15), 454 ( $^{35}\text{Cl} - \text{M}^+$ , 35), 453 (12), 419 (32), 405 (5), 391 (9), 377 (4), 343 (8), 317 (15), 289 (22), 278 (28), 277 (72), 263 (48), 262 (100), 201 (36) and 183 (95).

1-(4-Chlorocinnamoyl)ethylidene(triphenyl)phosphorane **6l**. Prepared as yellow crystals (34%), m.p. 213–214 °C (Found: C, 76.2; H, 5.3.  $\text{C}_{29}\text{H}_{24}\text{ClOP}$  requires C, 76.6; H, 5.3%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1622, 1478, 1150, 1098, 972 and 842;  $\delta_{\text{H}}$  7.8–7.15 (19 H, m) and 1.80 (3 H, d, *J* 16);  $\delta_{\text{P}}$  +15.9; *m/z* 456 ( $^{37}\text{Cl} - \text{M}^+$ , 25%), 455 (21), 454 ( $^{35}\text{Cl} - \text{M}^+$ , 52), 453 (21), 393 (8), 317 (8), 287 (12), 278 (8), 277 (23), 264 (25), 263 (19) and 262 (100).

1-(2-Nitrocinnamoyl)ethylidene(triphenyl)phosphorane **6m**. Prepared as orange crystals (30%), m.p. 177–181 °C (Found: C, 74.2; H, 5.1; N, 2.9.  $\text{C}_{29}\text{H}_{24}\text{NO}_3\text{P}$  requires C, 74.8; H, 5.2; N, 3.0%);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) 1602, 1518, 1492, 1430, 1378, 1342, 1300, 1160, 1100, 966, 860 and 832;  $\delta_{\text{H}}$  7.8–7.2 (21 H, m) and 2.02 (3 H, d, *J* 20);  $\delta_{\text{P}}$  +18.4; *m/z* 465 ( $\text{M}^+$ , 2%), 317 (7), 289 (10), 278 (40), 277 (85), 263 (45), 262 (100), 201 (42), 199 (21), 185 (55), 184 (60) and 183 (95).

1-( $\alpha$ -Methylcinnamoyl)ethylidene(triphenyl)phosphorane **7a**. Prepared as yellow crystals (63%), m.p. 120–122 °C (Found: C, 83.2; H, 6.3.  $\text{C}_{30}\text{H}_{27}\text{OP}$  requires C, 82.9; H, 6.3%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1485, 1438, 1369, 1179, 1135, 1107, 1022, 762, 753, 718, 710 and 694;  $\delta_{\text{H}}$  7.77–7.16 (20 H, m), 6.74 (1 H, s), 2.16 (3 H, s) and 1.78 (3 H, d, *J* 16);  $\delta_{\text{P}}$  +17.8; *m/z* 434 ( $\text{M}^+$ , 2%), 317 (1), 279 (2), 277 (7), 262 (33), 201 (7), 183 (25), 162 (20), 145 (66), 117 (100) and 91 (60).

$\alpha$ -(4-Methylcinnamoyl)benzylidene(triphenyl)phosphorane **6n**. Prepared as yellow crystals (66%), m.p. 236–237 °C (Found: C,

84.9; H, 6.0.  $\text{C}_{35}\text{H}_{29}\text{OP}$  requires C, 84.7; H, 5.9%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1622, 1474, 1360, 1187, 1100 and 952;  $\delta_{\text{H}}$  7.75–7.15 (20 H, m), 7.03 (5 H, m), 6.87 (1 H, half AB pattern, *J* 16) and 2.28 (3 H, s);  $\delta_{\text{P}}$  +15.6; *m/z* 496 ( $\text{M}^+$ , 85%), 495 (50), 379 (10), 303 (8), 294 (8), 277 (21), 266 (17), 263 (27), 262 (100), 261 (12), 218 (70) and 183 (60).

$\alpha$ -(4-Chlorocinnamoyl)benzylidene(triphenyl)phosphorane **6o**. Prepared as yellow crystals (66%), m.p. 245–246 °C (Found: M, 516.1396.  $\text{C}_{34}\text{H}_{26}^{35}\text{ClOP}$  requires M, 516.1410);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) 1623, 1590, 1486, 1432, 1400, 1364, 1260, 1210, 1183, 1100, 974 and 818;  $\delta_{\text{H}}$  7.7–7.15 (20 H, m), 7.02 (5 H, m) and 6.83 (1 H, half AB pattern, *J* 16);  $\delta_{\text{P}}$  +16.05; *m/z* 518 ( $^{37}\text{Cl} - \text{M}^+$ , 23%), 517 (32), 516 ( $^{35}\text{Cl} - \text{M}^+$ , 64), 515 (32), 277 (45), 263 (23), 262 (100), 238 (30), 203 (30) and 183 (50).

$\alpha$ -(2-Chlorocinnamoyl)benzylidene(triphenyl)phosphorane **6p**. Prepared as orange crystals (74%), m.p. 241–243 °C (Found: C, 78.8; H, 5.05.  $\text{C}_{34}\text{H}_{26}\text{ClOP}$  requires C, 79.0; H, 5.1%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1620, 1587, 1474, 1360, 1184, 1100, 1030, 972 and 950;  $\delta_{\text{H}}$  7.7–7.2 (19 H, m), 6.98 (5 H, s), 7.05–6.95 (1 H, m) and 6.87 (1 H, half AB pattern, *J* 16);  $\delta_{\text{P}}$  +16.1; *m/z* 518 ( $^{37}\text{Cl} - \text{M}^+$ , 22%), 517 (30), 516 ( $^{35}\text{Cl} - \text{M}^+$ , 65), 515 (36), 482 (24), 481 (60), 379 (14), 351 (6), 278 (18), 277 (50), 263 (22), 262 (100), 238 (16), 203 (30) and 183 (60).

$\alpha$ -(2-Nitrocinnamoyl)benzylidene(triphenyl)phosphorane **6q**. Prepared as orange crystals (60%), m.p. 253–254 °C (Found: C, 77.7; H, 4.9; N, 2.6.  $\text{C}_{34}\text{H}_{26}\text{NO}_3\text{P}$  requires C, 77.4; H, 5.0; N, 2.7%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1600, 1566, 1480, 1342, 1098, 970 and 948;  $\delta_{\text{H}}$  7.85–7.2 (20 H, m), 6.98 (5 H, s) and 6.82 (1 H, half AB pattern, *J* 15);  $\delta_{\text{P}}$  +16.4; *m/z* 527 ( $\text{M}^+$ , 80%), 510 (3), 495 (2), 481 (10), 408 (6), 392 (5), 391 (5), 380 (25), 279 (100), 352 (30), 351 (50), 277 (28), 262 (50), 201 (25) and 183 (65).

$\alpha$ -(3,4-Methylenedioxcinnamoyl)benzylidene(triphenyl)phosphorane **6r**. Prepared as yellow crystals (81%), m.p. 220–222 °C (Found: M, 526.1765.  $\text{C}_{35}\text{H}_{27}\text{O}_3\text{P}$  requires M, 526.1698);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) 1621, 1600, 1485, 1430, 1372, 1338, 1228, 1204, 1180, 1100, 1037, 997, 976, 952, 930, 850 and 807;  $\delta_{\text{H}}$  7.7–7.2 (16 H, m), 6.98 (5 H, s), 6.85–6.6 (4 H, m) and 5.88 (2 H, s);  $\delta_{\text{P}}$  +15.7; *m/z* 526 ( $\text{M}^+$ , 97%), 525 (58), 405 (5), 379 (12), 351 (7), 303 (5), 278 (34), 277 (81), 264 (25), 263 (25), 262 (100), 248 (850) and 183 (60).

$\alpha$ -[3-(2-Furyl)propenoyl]benzylidene(triphenyl)phosphorane **6s**. Prepared as brown crystals (55%), m.p. 254–256 °C (Found: C, 81.6; H, 5.4.  $\text{C}_{32}\text{H}_{25}\text{O}_3\text{P}$  requires C, 81.3; H, 5.3%);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) 1625, 1492, 1430, 1362, 1217, 1178, 1100, 1010, 972, 950 and 812;  $\delta_{\text{H}}$  7.75–7.15 (17 H, m), 7.03 (5 H, s), 6.82 (1 H, half AB pattern, *J* 16) and 6.36 (2 H, m);  $\delta_{\text{P}}$  +15.9; *m/z* 472 ( $\text{M}^+$ , 72%), 443 (3), 418 (2), 415 (2), 389 (3), 379 (8), 351 (5), 278 (9), 277 (21), 263 (20), 262 (100), 201 (15), 194 (65) and 183 (40).

$\alpha$ -[3-(2-Thienyl)propenoyl]benzylidene(triphenyl)phosphorane **6t**. Prepared as orange crystals (77%), m.p. 241–243 °C (Found: C, 78.25; H, 5.1.  $\text{C}_{32}\text{H}_{25}\text{OPS}$  requires C, 78.7; H, 5.2%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1615, 1590, 1475, 1370, 1098 and 952;  $\delta_{\text{H}}$  7.7–7.3 (16 H, m), 7.1–6.85 (3 H, m), 7.00 (5 H, m) and 6.72 (1 H, half AB pattern, *J* 15);  $\delta_{\text{P}}$  +15.8; *m/z* 488 ( $\text{M}^+$ , 30%), 487 (20), 278 (40), 277 (80), 263 (30), 262 (100), 207 (30), 201 (15), 199 (15) and 183 (70).

$\alpha$ -[3-(5-Methyl-2-thienyl)propenoyl]benzylidene(triphenyl)phosphorane **6u**. Prepared as yellow crystals (58%), m.p. 138–140 °C (Found: C, 78.5; H, 5.3.  $\text{C}_{33}\text{H}_{27}\text{OPS}$  requires C, 78.9; H, 5.4%);  $\nu_{\text{max}}/\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) 1612, 1488, 1365, 1320, 1220, 1205, 1170, 1100, 1040 and 950;  $\delta_{\text{H}}$  7.75–7.3 (16 H, m), 7.02 (5 H, s), 6.85 (1 H, half AB pattern, *J* 3), 6.60 (1 H, half AB pattern, *J* 16), 6.56 (1 H, half AB pattern of q, *J* 3, 1) and 2.37 (3 H, d, *J* 1);  $\delta_{\text{P}}$  +15.7; *m/z* 502 ( $\text{M}^+$ , 57%), 501 (24), 474 (2), 379 (7), 351 (3), 279 (5), 278 (6), 277 (15), 263 (27), 262 (100), 224 (60), 201 (9), 185 (11), 184 (12) and 183 (56).

$\alpha$ -( $\alpha$ -Methylcinnamoyl)benzylidene(triphenyl)phosphorane **7b**.

Prepared as yellow crystals (48%), m.p. 115–116 °C (Found: C, 84.4; H, 6.0. C<sub>35</sub>H<sub>29</sub>OP requires C, 84.7; H, 5.9%);  $\nu_{\max}/\text{cm}^{-1}$  1590, 1467, 1363, 1122, 1100, 1068, 1026, 997 and 968;  $\delta_{\text{H}}$  7.75–7.1 (20 H, m), 6.97 (5 H, s), 6.68 (1 H, q, *J* 2) and 1.89 (3 H, d, *J* 2);  $\delta_{\text{P}}$  +14.7; *m/z* 496 (M<sup>+</sup>, 32%), 495 (36), 419 (2), 405 (2), 380 (6), 379 (22), 351 (11), 303 (36), 275 (10), 263 (24), 262 (100) and 183 (60).

**1,4-Diphenyl-4-triphenylphosphoranylidenebut-2-en-1-one 14.** Reaction as above but using  $\beta$ -chloroacrylophenone<sup>13</sup> in place of the cinnamoyl chloride gave yellow crystals (62%), m.p. 217–220 °C (Found: C, 84.6; H, 5.4. C<sub>34</sub>H<sub>27</sub>OP requires C, 84.6; H, 5.6%);  $\nu_{\max}/\text{cm}^{-1}$  1584, 1552, 1500, 1430, 1300, 1248, 1197, 1147, 1093, 1000, 982, 960, 908, 768, 719, 703 and 689;  $\delta_{\text{H}}$  7.7–7.1 (27 H, m);  $\delta_{\text{P}}$  +20.3; *m/z* 482 (M<sup>+</sup>, 5%), 405 (4), 377 (6), 279 (5), 262 (95), 220 (30), 201 (7), 191 (12) and 183 (100).

**Cinnamoyl(ethoxycarbonyl)methylene(triphenyl)phosphorane 6v.** A solution of ethoxycarbonylmethylene(triphenyl)phosphorane (5.0 g, 14 mmol) and triethylamine (1.43 g, 14.2 mmol) in dry toluene (50 cm<sup>3</sup>) was stirred at room temperature while cinnamoyl chloride (2.33 g, 14 mmol) in dry toluene (10 cm<sup>3</sup>) was added to it dropwise. After being stirred for 18 h, the solution was washed with water (3 × 50 cm<sup>3</sup>), dried and evaporated. Recrystallisation of the residue from ethyl acetate gave the *ylide* (3.2 g, 47%) as yellow crystals, m.p. 132–135 °C (lit.,<sup>14</sup> 118–120 °C) (Found: M, 478.1719. C<sub>31</sub>H<sub>27</sub>O<sub>3</sub>P requires M, 478.1698);  $\nu_{\max}/\text{cm}^{-1}$  1618, 1510, 1365, 1285, 1260, 1184, 1101, 990, 743, 718 and 688;  $\delta_{\text{H}}$  8.26 (1 H, half AB pattern, *J* 18), 7.75–7.25 (21 H, m), 3.77 (2 H, q, *J* 7) and 0.68 (3 H, t, *J* 7);  $\delta_{\text{P}}$  +17.6; *m/z* 478 (M<sup>+</sup>, 3%), 434 (8), 405 (3), 303 (5), 277 (10), 262 (20), 218 (5), 152 (20), 131 (15), 101 (15) and 86 (100).

**Flash Vacuum Pyrolysis of Ylides.**—The apparatus used was as described previously.<sup>6</sup> All pyrolyses were conducted at pressures in the range 10<sup>-3</sup>–5 × 10<sup>-2</sup> Torr and were complete within 1 h. Under these conditions the contact time in the hot zone was estimated to be ≈ 10 ms.

In all cases Ph<sub>3</sub>PO collected at the furnace exit and the more volatile products were recovered from the cold trap in sufficient purity for direct spectroscopic characterisation without any further purification being required. Yields were determined by calibration of the <sup>1</sup>H NMR spectra by adding an accurately weighed quantity of a solvent such as CH<sub>2</sub>Cl<sub>2</sub> and comparing integrals, a procedure estimated to be accurate to ± 10%.

(a) **Compound 6a.** FVP of the title compound (106 mg) at 700 °C gave 1-phenylbut-1-en-3-yne **12a** as a yellow oil (8%) composed of the following. Compound (*E*)-**12a** (58%);  $\delta_{\text{H}}$  7.52–7.22 (5 H, m), 7.06 (1 H, half AB pattern, *J* 16), 6.15 (1 H, d of d, *J* 16, 2) and 3.06 (1 H, d, *J* 2) [lit.,<sup>15</sup> (CCl<sub>4</sub>);  $\delta_{\text{H}}$  7.2 (5 H, m), 6.90 (1 H, d, *J* 18), 6.00 (1 H, d, of d, *J* 18, 3) and 2.92 (1 H, d, *J* 3)];  $\delta_{\text{C}}$  see Table 2. Compound (*Z*)-**12a** (42%);  $\delta_{\text{H}}$  7.52–7.22 (5 H, m), 6.72 (1 H, half AB pattern, *J* 12), 5.70 (1 H, d of d, *J* 12, 2) and 3.37 (1 H, d, *J* 2);  $\delta_{\text{C}}$  140.6 (C-1) and 106.3 (C-2), remaining signals assignment uncertain. For MS see FVP of **6v**.

(b) **Compound 6b.** FVP of the title compound (100 mg) at 700 °C gave 1-phenylpent-1-en-3-yne **12b** as a yellow oil (53%) (Found: M, 142.0786. C<sub>11</sub>H<sub>10</sub> requires M, 142.0783);  $\nu_{\max}/\text{cm}^{-1}$  3010, 2905, 2840, 2280, 2190, 1600, 1180, 1110 and 950 [lit.,<sup>16</sup> 2230, 2190 and 953]; *m/z* 142 (M<sup>+</sup>, 75%), 141 (100), 128 (8), 115 (70), 86 (47), 84 (77), 73 (48) and 63 (18) composed of the following. Compound (*E*)-**12b** (57%);  $\delta_{\text{H}}$  7.45–7.15 (5 H, m), 6.87 (1 H, half AB pattern, *J* 16), 6.15 (1 H, half AB pattern of q, *J* 16, 2) and 2.02 (3 H, d, *J* 2) [good agreement with lit.<sup>17</sup>];  $\delta_{\text{C}}$  see Table 2. Compound (*Z*)-**12b** (43%);  $\delta_{\text{H}}$  7.45–7.15 (5 H, m), 6.58 (1 H, d, half AB pattern, *J* 12), 5.70 (1 H, half AB pattern of q, *J* 12, 2) and 2.09 (3 H, d, *J* 2) [good agreement with lit.<sup>17</sup>];  $\delta_{\text{C}}$  see Table 2.

(c) **Compound 6c.** FVP of the title compound (104 mg) at

700 °C gave 1-phenylhex-1-en-3-yne **12c** as a yellow oil (33%) (Found: M, 156.0931. C<sub>12</sub>H<sub>12</sub> requires M, 156.0939);  $\nu_{\max}/\text{cm}^{-1}$  2905, 2195, 1660, 1600, 1312, 1164, 1092, 1050 and 950; *m/z* 156 (M<sup>+</sup>, 68%), 141 (100), 128 (33), 115 (77), 102 (8), 89 (10), 77 (15) and 63 (22) composed of the following. Compound (*E*)-**12c** (56%);  $\delta_{\text{H}}$  7.50–7.20 (5 H, m), 6.89 (1 H, half AB pattern, *J* 16), 6.18 (1 H, half AB pattern of t, *J* 16, 2), 2.54–2.32 (2 H, m) and 1.21 (3 H, t, *J* 8);  $\delta_{\text{C}}$  see Table 2. Compound (*Z*)-**12c** (44%);  $\delta_{\text{H}}$  7.50–7.20 (5 H, m), 6.58 (1 H, half AB pattern, *J* 12), 5.72 (1 H, half AB pattern of t, *J* 12, 2), 2.54–2.32 (2 H, m) and 1.24 (3 H, t, *J* 8);  $\delta_{\text{C}}$  see Table 2.

(d) **Compound 6d.** FVP of the title compound (270 mg) at 500 °C gave (*E*)-1-phenylhept-1-en-3-yne **12d** as a yellow oil (42%);  $\delta_{\text{H}}$  7.50–7.20 (5 H, m), 6.88 (1 H, half AB pattern, *J* 16), 6.17 (1 H, half AB pattern of t, *J* 16, 2), 2.48–2.35 (2 H, m), 1.70–1.50 (2 H, m) and 1.02 (3 H, t, *J* 8).

FVP of the title compound (96 mg) at 700 °C gave 1-phenylhept-1-en-3-yne **12d** as a yellow oil (21%) (Found: M, 170.1099. C<sub>13</sub>H<sub>14</sub> requires M, 170.1096);  $\nu_{\max}/\text{cm}^{-1}$  2900, 2840, 2290, 2190, 1590, 1165, 1065, 950 and 805; *m/z* 170 (M<sup>+</sup>, 52%), 155 (25), 141 (98), 139 (28), 128 (28), 115 (100), 102 (10), 91 (19), 89 (13) and 77 (15) composed of the following. Compound (*E*)-**12d** (53%);  $\delta_{\text{H}}$  as above;  $\delta_{\text{C}}$  see Table 2. Compound  $\delta_{\text{C}}$ (*Z*)-**12d** (47%);  $\delta_{\text{H}}$  7.50–7.20 (5 H, m), 6.55 (1 H, half AB pattern, *J* 12), 5.70 (1 H, half AB pattern of t, *J* 12, 2), 2.48–2.25 (2 H, m), 1.70–1.50 (2 H, m) and 1.04 (3 H, t, *J* 8);  $\delta_{\text{C}}$  see Table 2.

(e) **Compound 6e.** FVP of the title compound (107 mg) at 700 °C gave 5-methyl-1-phenylhex-1-en-3-yne **12e** as a yellow oil (67%) (Found: M, 170.1103. C<sub>13</sub>H<sub>14</sub> requires M, 170.1096);  $\nu_{\max}/\text{cm}^{-1}$  2950, 2905, 2860, 2200, 1590, 1310, 1050, 950 and 900; *m/z* 170 (M<sup>+</sup>, 23%), 155 (62), 141 (33), 128 (63), 115 (74), 102 (17), 91 (21), and 27 (100) composed of the following. Compound (*E*)-**12e** (56%);  $\delta_{\text{H}}$  7.90–7.20 (5 H, m), 6.78 (1 H, half AB pattern *J* 16), 6.08 (1 H, half AB pattern of d, *J* 16, 2), 2.82–2.55 (1 H, m) and 1.12 (6 H, d, *J* 8);  $\delta_{\text{C}}$  see Table 2. Compound (*Z*)-**12e** (44%);  $\delta_{\text{H}}$  7.90–7.2 (5 H, m), 6.47 (1 H, half AB pattern *J* 12), 5.60 (1 H, half AB pattern of d, *J* 12, 2), 2.82–2.55 (1 H, m) and 1.14 (6 H, d, *J* 8);  $\delta_{\text{C}}$  see Table 2.

(f) **Compound 6f.** FVP of the title compound (178 mg) at 500 °C gave (*E*)-1-phenyloct-1-en-3-yne **12f** as a yellow oil (58%);  $\delta_{\text{H}}$  7.4–7.2 (5 H, m), 6.87 (1 H, half AB pattern, *J* 16), 6.17 (1 H, half AB pattern of t, *J* 16, 2), 2.45–2.31 (2 H, m), 1.60–1.40 (4 H, m) and 0.95 (3 H, t, *J* 7).

FVP of the title compound (101 mg) at 700 °C gave 1-phenyloct-1-en-3-yne **12f** as a yellow oil (25%);  $\nu_{\max}/\text{cm}^{-1}$  2955, 2920, 2845, 2200, 1605, 1100, 1055 and 952 [lit.,<sup>18</sup> (*E*-isomer) 2190 and 960]; *m/z* 184 (M<sup>+</sup>, 23%), 155 (62), 141 (33), 128 (63), 115 (74), 102 (17), 91 (21), and 27 (100) composed of the following. Compound (*E*)-**12f** (50%);  $\delta_{\text{H}}$  7.4–7.2 (5 H, m), 6.87 (1 H, d, half AB pattern *J* 16), 6.17 (1 H, half AB pattern of t, *J* 16, 2), 2.55–2.31 (2 H, m), 1.68–1.40 (4 H, m) and 0.95 (3 H, t, *J* 7) [lit.,<sup>18</sup>  $\delta_{\text{H}}$ (CCl<sub>4</sub>) 7.12 (5 H, m), 6.70 (1 H, d, *J* 16), 5.99 (1 H, d, of t, *J* 16, 2), 2.45–2.13 (2 H, m), 1.70–1.10 (4 H, m) and 0.88 (3 H, t, *J* 7)];  $\delta_{\text{C}}$  see Table 2. Compound (*Z*)-**12f** (50%);  $\delta_{\text{H}}$  7.4–7.2 (5 H, m), 6.56 (1 H, d, half AB pattern *J* 12), 5.70 (1 H, half AB pattern of t, *J* 12, 2), 2.55–2.31 (2 H, m), 1.68–1.40 (4 H, m) and 0.95 (3 H, t, *J* 7);  $\delta_{\text{C}}$  see Table 2.

(g) **Compound 6g.** FVP of the title compound (192 mg) at 500 °C gave (*E*)-1,4-diphenylbut-1-en-3-yne as a yellow solid **12g** (85%); spectra as below.

FVP of the title compound (107 mg) at 700 °C gave 1,4-diphenylbut-1-en-3-yne **12g** as a yellow oil (99%);  $\nu_{\max}/\text{cm}^{-1}$  3005, 2190, 1588, 1476, 1242, 948 and 802 [lit.,<sup>16</sup> 953]; *m/z* 204 (M<sup>+</sup>, 73%), 127 (12), 103 (22), 91 (21), 77 (6) and 27 (100) composed of the following. Compound (*E*)-**12g** (57%);  $\delta_{\text{H}}$  7.75–7.20 (10 H, m), 7.06 and 6.40 (2 H, AB pattern, *J* 16) [lit.,<sup>15</sup>  $\delta_{\text{H}}$  7.55–7.10 (10 H, m), 7.03 and 6.27 (2 H, AB pattern, *J* 16)];  $\delta_{\text{C}}$

see Table 2. Compound (Z)-12g (43%);  $\delta_{\text{H}}$  7.75–7.20 (10 H, m), 6.72 and 5.93 (2 H, AB, pattern, J 12);  $\delta_{\text{C}}$  see Table 2.

(h) Compound 6h. FVP of the title compound (200 mg) at 500 °C gave (E)-4-(2-methoxyphenyl)-1-phenylbut-1-en-3-yne 12h as a yellow oil (54%);  $\delta_{\text{H}}$  7.70–7.20 (7 H, m), 7.04 and 6.44 (2 H, AB pattern, J 16), 6.92–6.82 (2 H, m) and 3.88 (3 H, s);  $\delta_{\text{C}}$  see Table 2.

(i) Compound 6i. FVP of the title compound (100 mg) at 500 °C, 14 m Torr, inlet 120 °C) gave (E)-4-(4-nitrophenyl)-1-phenylbut-1-en-3-yne 12i as a yellow oil (16%) (Found: M, 249.0779.  $\text{C}_{16}\text{H}_{11}\text{NO}_2$  requires M, 249.0790);  $\nu_{\text{max}}/\text{cm}^{-1}$  2924, 2190, 1588, 1517, 1339, 1107, 850 and 747;  $\delta_{\text{H}}$  8.21 and 7.62 (4 H, AB pattern, J 10), 7.50–7.30 (5 H, m) and 7.13 and 6.40 (2 H, AB pattern, J 16);  $\delta_{\text{C}}$  see Table 2;  $m/z$  249 ( $\text{M}^+$ , 48%), 219 (24), 202 (64), 189 (14), 176 (5), 150 (8), 105 (9), 86 (60), 84 (100) and 109 (10).

(j) Compound 6j. FVP of the title compound (200 mg) at 500 °C gave (E)-1-phenyl-4-(2-thienyl)but-1-en-3-yne 12j as a yellow oil (66%) (Found: M, 210.0497.  $\text{C}_{14}\text{H}_{10}\text{S}$  requires M, 210.0503);  $\nu_{\text{max}}/\text{cm}^{-1}$  3020, 2960, 2280, 1600, 1240, 1050, 950 and 890;  $\delta_{\text{H}}$  7.55–6.90 (9 H, m) and 6.35 (1 H, half AB pattern, J 16);  $\delta_{\text{C}}$  see Table 2;  $m/z$  210 ( $\text{M}^+$ , 49%), 165 (25), 152 (7), 139 (7), 84 (100), 77 (9) and 63 (13).

(k) Compound 7a. FVP of the title compound (280 mg) at 500 °C gave (E)-2-methyl-1-phenylpent-1-en-3-yne 13a as a yellow oil (67%) (Found: M, 156.0945.  $\text{C}_{12}\text{H}_{12}$  requires M, 156.0939);  $\nu_{\text{max}}/\text{cm}^{-1}$  2960, 2905, 2285, 2215, 1690, 1592, 1241 and 903;  $\delta_{\text{H}}$  7.45–7.19 (5 H, m), 6.80 (1 H, s), 2.07 (3 H, s) and 2.03 (3 H, s);  $\delta_{\text{C}}$  see Table 2;  $m/z$  156 ( $\text{M}^+$ , 72%), 155 (27), 141 (100), 128 (21), 115 (48), 105 (9), 91 (19), 84 (10) and 77 (23).

(l) Compound 6n. FVP of the title compound (1.14 g) at 480 °C gave (E)-1-(4-methylphenyl)-4-phenylbut-1-en-3-yne 12n as a light yellow solid (82%) (Found: M, 218.1080.  $\text{C}_{17}\text{H}_{14}$  requires M, 218.1096);  $\nu_{\text{max}}/\text{cm}^{-1}$  3005, 2950, 2900, 2180, 1585, 1478, 1110, 950 and 793;  $\delta_{\text{H}}$  7.52–7.12 (9 H, m), 7.01 and 6.34 (2 H, AB pattern, J 16) and 2.34 (3 H, s);  $\delta_{\text{C}}$  see Table 2;  $m/z$  218 ( $\text{M}^+$ , 100%), 217 (45), 203 (56), 202 (75), 189 (9), 178 (3), 165 (47), 141 (5), 126 (5), 119 (7), 115 (11), 105 (15) and 91 (16).

(m) Compound 6o. FVP of the title compound (160 mg) at 500 °C gave (E)-1-(4-chlorophenyl)-4-phenylbut-1-en-3-yne 12o as a yellow oil (39%) (Found: M, 238.0551.  $\text{C}_{16}\text{H}_{11}^{35}\text{Cl}$  requires M, 238.0547;  $\nu_{\text{max}}/\text{cm}^{-1}$  3020, 2965, 2910, 2295, 2195, 1590, 1478, 1004 and 950;  $\delta_{\text{H}}$  7.72–7.22 (9 H, m), 6.97 and 6.36 (2 H, AB pattern, J 16);  $\delta_{\text{C}}$  see Table 2;  $m/z$  240 ( $^{37}\text{Cl} - \text{M}^+$ , 6%), 238 ( $^{35}\text{Cl} - \text{M}^+$ , 17), 216 (20), 202 (100), 126 (9), 101 (21) and 77 (19).

(n) Compound 6p. FVP of the title compound (160 mg) at 500 °C gave (E)-1-(2-chlorophenyl)-4-phenylbut-1-en-3-yne 12p as a yellow oil (58%) (Found: M, 238.0545.  $\text{C}_{16}\text{H}_{11}^{35}\text{Cl}$  requires M, 238.0547);  $\nu_{\text{max}}/\text{cm}^{-1}$  3020, 2965, 2910, 2290, 2185, 1600, 1243 and 948;  $\delta_{\text{H}}$  7.61–7.16 (10 H, m) and 6.39 (1 H, half AB pattern, J 16);  $\delta_{\text{C}}$  see Table 2;  $m/z$  240 ( $^{37}\text{Cl} - \text{M}^+$ , 8%), 238 ( $^{35}\text{Cl} - \text{M}^+$ , 23), 202 (100), 126 (4), 101 (21), 88 (8) and 75 (9).

(o) Compound 6q. FVP of the title compound (120 mg) at 500 °C gave (E)-1-(2-nitrophenyl)-4-phenylbut-1-en-3-yne 12q as a light brown oil (19%) (Found: M, 249.0782.  $\text{C}_{16}\text{H}_{11}\text{NO}_2$  requires M, 249.0790);  $\nu_{\text{max}}/\text{cm}^{-1}$  3063, 2955, 2922, 2853, 2242, 2196, 1603, 1508, 1343, 1259 and 805;  $\delta_{\text{H}}$  8.08–7.92 (1 H, m), 7.68–7.22 (9 H, m) and 6.39 (1 H, half AB pattern, J 16);  $\delta_{\text{C}}$  see Table 2;  $m/z$  249 ( $\text{M}^+$ , 31%), 232 (9), 217 (18), 202 (36), 189 (19), 175 (14), 165 (15), 128 (50), 114 (31), 105 (100), 92 (52) and 77 (64).

(p) Compound 6r. FVP of the title compound (200 mg) at 500 °C gave (E)-1-(3,4-methylenedioxyphenyl)-4-phenylbut-1-en-3-yne 12r as a yellow oil (58%) (Found: M, 248.0829.  $\text{C}_{17}\text{H}_{12}\text{O}_2$  requires M, 248.0834);  $\nu_{\text{max}}/\text{cm}^{-1}$  2870, 2240, 2180, 1695, 1465, 1025 and 900;  $\delta_{\text{H}}$  7.50–7.12 (5 H, m), 7.0–6.71 (4 H, m), 6.19 (1 H, half AB pattern, J 16) and 5.95 (2 H, s);  $\delta_{\text{C}}$  see

Table 2;  $m/z$  248 ( $\text{M}^+$ , 82%), 218 (11), 189 (100), 163 (15), 150 (5), 139 (8), 121 (8) and 109 (10).

(q) Compound 6s. FVP of the title compound (160 mg) at 500 °C gave (E)-4-(2-furyl)-1-phenylbut-1-en-3-yne 12s as a yellow oil (55%) (Found: M, 194.0735.  $\text{C}_{14}\text{H}_{10}\text{O}$  requires M, 194.0729);  $\nu_{\text{max}}/\text{cm}^{-1}$  3010, 2240, 2180, 1588, 1478, 1008, 940 and 893;  $\delta_{\text{H}}$  7.45–7.20 (6 H, m), 6.79 and 6.29 (2 H, AB pattern, J 16) and 6.44–6.33 (2 H, m);  $\delta_{\text{C}}$  see Table 2;  $m/z$  194 (52%), 166 (14), 165 (100), 155 (11), 141 (31), 139 (24), 128 (13), 115 (42), 91 (25), 86 (50), 84 (73) and 77 (13).

(r) Compound 6t. FVP of the title compound (184 mg) at 500 °C gave (E)-4-phenyl-1-(2-thienyl)but-1-en-3-yne 12t as a yellow oil (47%) (Found: M, 210.0497.  $\text{C}_{14}\text{H}_{10}\text{S}$  requires M, 210.0503);  $\nu_{\text{max}}/\text{cm}^{-1}$  3020, 2970, 2285, 2240, 1586, 1478, 1010 and 900;  $\delta_{\text{H}}$  7.50–6.93 (9 H, m) and 6.19 (1 H, half AB pattern, J 16);  $\delta_{\text{C}}$  see Table 2;  $m/z$  210 ( $\text{M}^+$ , 57%), 184 (100), 165 (32), 152 (18), 139 (26), 105 (32) and 84 (63).

(s) Compound 6u. FVP of the title compound (190 mg) at 500 °C gave (E)-1-(5-methyl-2-thienyl)-4-phenylbut-1-en-3-yne 12u as a yellow oil (34%) (Found: M, 224.0675.  $\text{C}_{15}\text{H}_{12}\text{S}$  requires M, 224.0660);  $\nu_{\text{max}}/\text{cm}^{-1}$  3050, 2980, 2918, 2227, 1590, 1472, 1436, 1260, 1118 and 797;  $\delta_{\text{H}}$  7.52–7.25 (5 H, m), 7.04 and 6.06 (2 H, AB pattern, J 16), 6.83 and 6.64 (2 H, AB pattern, J 9) and 2.47 (3 H, s);  $\delta_{\text{C}}$  see Table 2;  $m/z$  224 ( $\text{M}^+$ , 100%), 223 (70), 222 (15), 208 (11), 198 (13), 189 (16), 178 (9), 165 (16), 151 (7), 105 (26) and 77 (15).

(t) Compound 7b. FVP of the title compound (158 mg) at 500 °C gave (E)-2-methyl-1,4-diphenylbut-1-en-3-yne 13b as a yellow oil (55%) (Found: M, 218.1100.  $\text{C}_{17}\text{H}_{14}$  requires M, 218.1092);  $\nu_{\text{max}}/\text{cm}^{-1}$  3005, 2905, 2195, 1948, 1591, 1478, 1063 and 912;  $\delta_{\text{H}}$  7.51–7.19 (10 H, m), 6.94 (1 H, q, J 1) and 2.16 (3 H, d, J 1);  $\delta_{\text{C}}$  see Table 2;  $m/z$  218 ( $\text{M}^+$ , 100%), 202 (88), 189 (13), 139 (8), 115 (18), 101 (10), 89 (11) and 77.

(u) Compound 6v. FVP of the title compound (250 mg) at 800 °C gave a yellow oil which contained 1-phenylbut-1-en-3-yne 12a (18%) as a 2:1 mixture of E and Z isomers;  $\delta_{\text{H}}$  and  $\delta_{\text{C}}$  spectra were identical with those of the products from 6a, together with naphthalene (8%).

FVP of the title compound (200 mg) at 850 °C gave a mixture shown by  $^1\text{H}$  NMR and GC-MS to contain compound (E)-12a (8%);  $m/z$  128 ( $\text{M}^+$ , 100%), 102 (38), 78 (22), 74 (22), 63 (40) and 51 (86), compound (Z)-12a (4%);  $m/z$  128 ( $\text{M}^+$ , 100%), 102 (32), 78 (16), 74 (15), 63 (28) and 51 (52), and naphthalene (20%);  $\delta_{\text{H}}$  7.88–7.80 (4 H, m) and 7.52–7.44 (4 H, m);  $m/z$  128 ( $\text{M}^+$ , 100%), 102 (22), 75 (18), 74 (18), 63 (32) and 51 (52).

(v) Compound 14. FVP of the title compound (205 mg) at 700 °C gave a solid at the furnace exit which was shown by  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy to be mainly  $\text{Ph}_3\text{P}$ . In the cold trap a colourless liquid was formed whose major constituents were shown by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and GC-MS comparison with authentic samples to be indene ( $\approx 12\%$ ) and benzene ( $\approx 9\%$ ).

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