

Flash Vacuum Pyrolysis of Stabilised Phosphorus Ylides. Part 1. Preparation of Aliphatic and Terminal Alkynes

R. Alan Aitken* and J. Ian Atherton

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9ST, UK

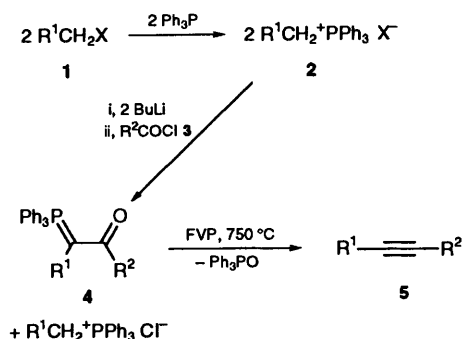
Thermal extrusion of Ph_3PO from β -oxoalkylenetriphenylphosphoranes **4** to give the alkynes **5**, which under conventional pyrolysis conditions is restricted to cases in which R^1 is an electron withdrawing group, has been successfully achieved for $\text{R}^1 = \text{H}$ or alkyl by using FVP. The method allows convenient construction of multigram quantities of the alkynes **5** from alkyl halides **1** and acid chlorides **3** in three steps with good overall yields. Under the conditions used the ylides with $\text{R}^2 = \text{cyclobutyl}$ also undergo loss of ethene to provide convenient access to the vinylalkynes **6**.

Thermal extrusion of triphenylphosphine oxide from α -oxo phosphorus ylides **4** to give the alkynes **5** was first described in 1959 when Trippett and Walker¹ reported the quantitative formation of diphenylacetylene upon heating compound **4** ($\text{R}^1 = \text{R}^2 = \text{Ph}$) at 300°C in the absence of solvent for 30 min. The method was later extended to cases in which $\text{R}^1 = \text{CN}$ and CO_2Et ,² and was used by Märkl to provide a useful synthesis of acetylenic esters ($\text{R}^1 = \text{CO}_2\text{Me}$).³ It is worth noting that the corresponding reaction of the related phosphinimine, $\text{Ph}_3\text{P}=\text{N}-\text{COPh}$, to give benzonitrile had already been described some 40 years earlier.⁴ More recently, this reaction has been used to gain access to a wide variety of alkynes for $\text{R}^1 = \text{aryl}$,⁵ CO_2R ,⁶ CN ,⁷ COSMe ,⁸ COR ,⁹ Br or Cl ,¹⁰ SR ,¹¹ SeAr ,¹² OAr ¹³ and $\text{PO}(\text{OPh})_2$.¹⁴ However, a serious limitation, which became apparent at an early stage,^{2,15} was that cases in which $\text{R}^1 = \text{H}$ or alkyl did not furnish the expected alkynes. Under conventional pyrolysis conditions, side-reactions, including partial extrusion of Ph_3P and isomerisation of the desired alkynes to allenes, occurred making the method useless for formation of simple aliphatic and terminal alkynes. In order to circumvent these problems, Bestmann described two separate ways in which compound **4** could be converted into compound **5** indirectly,^{16,17} but these involved additional steps with resultant reduction in the overall yield. In this paper we describe the successful application of flash vacuum pyrolysis (FVP), a technique which has recently given excellent results in a wide variety of thermal extrusion reactions,¹⁸ to the pyrolysis of examples of compound **4** where $\text{R}^1 = \text{H}$ and alkyl, thus providing convenient access to a variety of aliphatic and terminal alkynes.¹⁹

Results and Discussion

The required ylides **4** were readily prepared by reaction of quaternary phosphonium salts **2**, derived from alkyl halides **1**, with butyllithium followed by 0.5 equiv. of an acid chloride **3**. As shown, the reaction proceeds with transylidation²⁰ to give the desired stabilised ylide **4** and the quaternary phosphonium chloride. The latter is readily removed by aqueous work-up to give the ylides **4a-q** in acceptable yield. The examples prepared, all previously known compounds, were stable unreactive solids which showed the expected spectroscopic properties. Particularly informative were the ^{13}C NMR spectra, exemplified by the data from **4d**, **k**, **n** shown in Table 1. The pattern of phosphorus coupling which extends throughout the phenyl groups and to the first carbon of R^1 and R^2 provides ready confirmation of the structures.

When the ylides were subjected to FVP in a conventional flow-system at 10^{-2} mmHg (contact time ≈ 10 ms) they



sublimed unchanged at temperatures up to 600°C but at 750°C underwent complete reaction in the desired sense to give Ph_3PO and the alkynes **5** in moderate to excellent yield (Table 2). By a simple modification of the pyrolysis system, insertion of a spacer tube between the furnace exit and the cold trap, the alkynes were directly obtained in pure form in the cold trap, free of any Ph_3PO . The identity and purity of the alkynes was readily checked by ^1H and ^{13}C NMR (see Experimental section) which showed no major contaminants and, in particular, the complete absence of the isomeric allenes reported from conventional pyrolysis. Although for convenience pyrolyses were generally performed using 0.5 g of ylide, the feasibility of using this method to prepare multigram quantities of alkynes was demonstrated by the FVP of compound **4d** (18 g) to give compound **5d** (3.4 g, 82%) and compound **4n** (13.2 g) to give compound **5n** (3.7 g, 81%), each preparation being completed within 3 h.

Only for $\text{R}^2 = \text{cyclobutyl}$ was an additional fragmentation process observed: loss of ethene to afford vinylalkynes. Thus, for both compounds **4f** and **4m**, FVP at 750°C gave the expected cyclobutylalkynes **5** accompanied by a comparable amount of the vinylalkynes **6**, resulting from loss of ethene. By lowering the pyrolysis temperature, the proportion of the former increased but the latter had not been completely eliminated when, at

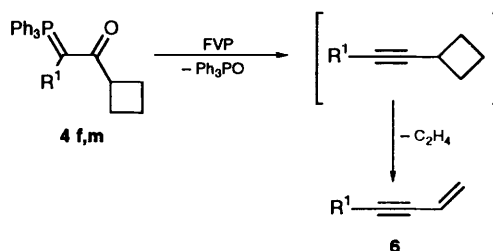


Table 1 ^{13}C NMR Spectra of selected ylides **4**, $\delta_{\text{C}}(J_{\text{P-C}})$

R ¹	R ²	C=O	P=C	P-Phenyl				R ¹ signals	R ² signals	
				C-1	C-2	C-3	C-4			
4d	H	Bu ^t	200.1 (<2)	47.2 (110)	127.8 (91)	132.9 (10)	128.6 (12)	131.6 (2)	—	40.5 (12), 28.7 (3 C)
4k	Pr	Bu ^t	193.5 (<2)	68.3 (104)	128.6 (93)	133.0 (9)	128.0 (12)	130.5 (2)	29.2 (13), 28.3, 13.7	39.9 (11), 28.7 (3 C)
4n	Pr	c-C ₆ H ₁₁	193.6 (<2)	64.0 (103)	128.4 (90)	133.3 (10)	128.3 (12)	131.0 (2)	29.1 (14), 28.3, 13.8	43.4 (10), 30.0 (2 C), 26.5 (3 C), 26.2

Table 2 FVP of ylides **4** at 750 °C to give alkynes **5**

	R ¹	R ²	Yield of 5 (%)	R ¹	R ²	Yield of 5 (%)	
a	H	Et	78	j	Pr	Pr ⁱ	93
b	H	Pr	59	k	Pr	Bu ^t	81
c	H	Pr ⁱ	72	l	Pr	MeCH=CH	82
d	H	Bu ^t	82	m	Pr	c-C ₄ H ₇	81 ^a
e	H	MeCH=CH	59	n	Pr	c-C ₆ H ₁₁	81
f	H	c-C ₄ H ₇	67 ^a	o	Bu	Bu	80
g	H	c-C ₆ H ₁₁	64	p	Bu	C ₅ H ₁₁	69
h	H	Ph	82	q	Me	2-Thienyl	64
i	Me	Me	74				

^a Yield of vinylalkyne **6** formed at 800–850 °C.

600 °C, the ylides began to sublime unchanged. On the other hand, FVP at 850 °C for compound **4f** and 800 °C for compound **4m** led to clean formation of the enynes **6** in good yield. In this transformation, the cyclobutanecarbonyl chloride used to prepare the ylides is acting as a convenient masked form of acryloyl chloride to provide access to the synthetically useful enynes. The homologous enynes **5e** and **5l** were readily prepared by using crotonyl chloride and in these cases 10–15% isomerisation to the *Z*-isomers was seen to have occurred under the pyrolysis conditions. The propynylthiophene **5q** has recently found use as a potential precursor of the simple natural product junipal.²¹ The high yield and purity of the products from this method was such that we found difficulty in reproducing the poor results obtained from conventional pyrolysis. In the case of compound **4n**, the ylide sublimed unchanged at 600 °C and 10⁻² mmHg, but increasing the severity of the conditions by introducing a nitrogen leak to bring the pressure up to 1 mmHg allowed complete reaction to give compound **5** at temperatures as low as 450 °C, albeit in slightly reduced yield. In contrast to many other FVP reactions, melting the substrate in the inlet tube did not adversely affect the outcome of the reaction. Only by resorting to destructive distillation of compound **4n** at 20 mmHg over an open flame was a mixture of hydrocarbons produced in 58% yield, which was shown by GLC to contain only 60% of compound **5n** together with at least four other components including alkenes or allenes as indicated by ¹H NMR signals in the range δ_{H} 4.5–6.5.

We have demonstrated the use of FVP to overcome the long standing limitation on the thermolysis of the ylides **4** to give the alkynes **5**, thus providing a convenient new route for *de novo* construction of aliphatic and terminal alkynes. The advantages of FVP should also prove beneficial in the pyrolysis of a wide variety of other stabilised phosphorus ylides and this will be described in subsequent Parts of this series.

Experimental

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

Perkin-Elmer 1420 instrument. NMR spectra were obtained for ¹H at 80 MHz using a Bruker WP80 instrument and for ¹³C and ³¹P at 20 MHz and 32 MHz, respectively, using a Varian CFT 20 instrument. The ¹³C data in Table 1 were obtained at 75 MHz on a Bruker AM300 instrument. All spectra were recorded using solutions in CDCl₃ with internal Me₄Si as reference for both ¹H and ¹³C NMR spectra and external 85% H₃PO₄ as reference for ³¹P spectra. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are in Hz. Mass spectra were obtained on an A.E.I. MS-902 spectrometer using electron impact at 70 eV. Dry THF was freshly distilled from potassium benzophenone ketyl under N₂.

Preparation of β -Oxoalkylenetriphenylphosphoranes 4.—A suspension of the appropriate alkyltriphenylphosphonium bromide **2** (25 mmol) in dry THF was stirred at room temp. under N₂ while a solution of BuLi in hexane (26 mmol) was added slowly by syringe. This was followed after 30 min by the addition of the appropriate acid chloride **3** (12.5 mmol) in dry THF (10 cm³). After 3 h the mixture was added to water (250 cm³) and extracted with diethyl ether (4 × 50 cm³). 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 following compounds were prepared by this method.

1-(Triphenylphosphoranylidene)butan-2-one 4a. (From methyltriphenylphosphonium bromide and propionyl chloride) as colourless crystals (35%), m.p. 215–218 °C (from Et₂O–CH₂Cl₂) (lit.,²² 221–222 °C); δ_{H} 7.9–7.5 (15 H, m), 3.52 (1 H, br s), 2.35 (2 H, qd, *J* 7 and 2) and 1.17 (3 H, t, *J* 7).

1-(Triphenylphosphoranylidene)pentan-2-one 4b. (From methyltriphenylphosphonium bromide and butyryl chloride) as colourless needles (33%), m.p. 144–145 °C (from Et₂O) (lit.,²³ 146 °C); δ_{H} 7.9–7.5 (15 H, m), 3.52 (1 H, br s), 2.33 (2 H, t, *J* 7), 1.70 (2 H, sextet, *J* 7) and 0.97 (3 H, t, *J* 7).

3-Methyl-1-(triphenylphosphoranylidene)butan-2-one 4c. (From methyltriphenylphosphonium bromide and isobutyryl chloride) as colourless crystals (42%), m.p. 172–173 °C (from Et₂O–hexane) (lit.,²⁴ 170–171 °C); δ_{H} 7.9–7.5 (15 H, m), 3.67

(1 H, br s), 2.55 (1 H, septet of d, J 7 and 2) and 1.18 (6 H, d, J 7).

3,3-Dimethyl-1-(triphenylphosphoranylidene)butan-2-one 4d. (From methyltriphenylphosphonium bromide and pivaloyl chloride) as colourless crystals (87%), m.p. 182–184 °C (from EtOAc–hexane) (lit.,²⁵ 181–182 °C); δ_{H} 7.96–7.5 (15 H, m), 3.82 (1 H, br s) and 1.23 (9 H, s).

(E)-1-(Triphenylphosphoranylidene)pent-3-en-2-one 4e. (From methyltriphenylphosphonium bromide and crotonyl chloride) as colourless crystals (47%), m.p. 163–165 °C (from EtOAc–hexane) (lit.,²⁶ 162–164 °C); δ_{H} 7.96–7.5 (15 H, m), 6.70 (1 H, half ABq, J 15 and 6), 6.35 (1 H, half ABm, J 15), 3.76 (1 H, br s) and 1.82 (3 H, d, J 6).

1-Cyclobutyl-2-(triphenylphosphoranylidene)ethan-1-one 4f. (From methyltriphenylphosphonium bromide and cyclobutanecarbonyl chloride) as colourless crystals (47%), m.p. 190–192 °C (from EtOAc–hexane) (lit.,²⁶ 185–190 °C); δ_{H} 7.9–7.5 (15 H, m), 3.63 (1 H, br s), 3.27 (1 H, m) and 2.3–1.7 (6 H, m).

1-Cyclohexyl-2-(triphenylphosphoranylidene)ethan-1-one 4g. (From methyltriphenylphosphonium bromide and cyclohexanecarbonyl chloride) as colourless crystals (47%), m.p. 162–164 °C (from EtOAc–hexane) (lit.,²³ 166 °C); δ_{H} 7.9–7.5 (15 H, m), 3.58 (1 H, br s) and 2.2–1.1 (11 H, m).

1-(Triphenylphosphoranylidene)acetophenone 4h. (From methyltriphenylphosphonium bromide and benzoyl chloride) as colourless crystals (83%), m.p. 177–178 °C (from Et₂O) (lit.,²⁷ 178–180 °C); δ_{H} 8.2–7.5 (20 H, m) and 4.51 (1 H, d, J 25).

3-(Triphenylphosphoranylidene)butan-2-one 4i. (From ethyltriphenylphosphonium bromide and acetyl chloride) as colourless crystals (35%), m.p. 169–170 °C (from Et₂O) (lit.,²⁵ 170.5–171.5 °C); δ_{H} 7.9–7.5 (15 H, m), 2.15 (3 H, br s) and 1.68 (3 H, d, J 16).

2-Methyl-4-(triphenylphosphoranylidene)heptan-3-one 4j. (From butyltriphenylphosphonium bromide and isobutyryl chloride) as colourless needles (43%), m.p. 139–140 °C (from Et₂O) (lit.,²⁸ 139–142 °C); δ_{H} 7.9–7.5 (15 H, m), 3.05 (1 H, septet, J 7), 2.2–1.7 (2 H, m), 1.4–1.0 (2 H, m), 1.11 (6 H, d, J 7) and 0.64 (3 H, t, J 7).

2,2-Dimethyl-4-(triphenylphosphoranylidene)heptan-3-one 4k. (From butyltriphenylphosphonium bromide and pivaloyl chloride) as colourless crystals (51%), m.p. 148–151 °C (from EtOAc–hexane) (lit.,²⁹ 152–153 °C); δ_{H} 7.9–7.5 (15 H, m), 2.3–1.75 (2 H, m), 1.3–1.0 (2 H, m), 1.26 (9 H, s) and 0.50 (3 H, t, J 7).

(E)-5-(Triphenylphosphoranylidene)oct-2-en-4-one 4l. (From butyltriphenylphosphonium bromide and crotonyl chloride) as yellow crystals (43%), m.p. 168–170 °C (from Et₂O) (lit.,²⁸ 168–170 °C); δ_{H} 7.9–7.5 (15 H, m), 6.75 (2 H, m), 2.25–2.0 (2 H, m), 1.87 (3 H, m), 1.5–1.1 (2 H, m) and 0.65 (3 H, t, J 7).

1-Cyclobutyl-2-(triphenylphosphoranylidene)pentan-1-one 4m. (From butyltriphenylphosphonium bromide and cyclobutanecarbonyl chloride) as colourless crystals (44%), m.p. 125–126 °C (from Et₂O–hexane) (lit.,³⁰ 126–128 °C); δ_{H} 7.9–7.5 (15 H, m), 3.60 (1 H, m), 2.5–1.6 (8 H, m), 1.13 (2 H, m) and 0.61 (3 H, t, J 7).

1-Cyclohexyl-2-(triphenylphosphoranylidene)pentan-1-one 4n. (From butyltriphenylphosphonium bromide and cyclohexanecarbonyl chloride) as colourless crystals (72%), m.p. 159–161 °C (from Et₂O–hexane) (lit.,³¹ 164–166 °C); δ_{H} 7.9–7.5 (15 H, m), 2.70 (1 H, br s), 2.06 (2 H, m), 2.0–1.1 (12 H, m) and 0.63 (3 H, t, J 7).

6-(Triphenylphosphoranylidene)decan-5-one 4o. (From pentyltriphenylphosphonium bromide and pentanoyl chloride) as colourless needles (37%), m.p. 149–151 °C (from Et₂O) (lit.,¹⁷ 107–108 °C); δ_{H} 7.9–7.5 (15 H, m), 2.45 (2 H, m), 2.2–0.9 (10 H, m), 0.95 (3 H, t, J 7) and 0.68 (3 H, t, J 7). We attribute the discrepancy in melting points in this case to the existence of

different polymorphic forms of the ylide, a phenomenon already observed by Bestmann in related examples.³²

5-(Triphenylphosphoranylidene)undecan-6-one 4p. (From pentyltriphenylphosphonium bromide and hexanoyl chloride) as pale yellow needles (35%), m.p. 120–123 °C (from EtOAc–hexane) (lit.,¹⁷ 124–126 °C); δ_{H} 7.9–7.5 (15 H, m), 2.42 (2 H, m), 2.2–0.9 (12 H, m), 0.91 (3 H, t, J 7) and 0.65 (3 H, t, J 7).

1-(2-Thienyl)-2-(triphenylphosphoranylidene)propan-1-one 4q. (From ethyltriphenylphosphonium bromide and 2-thienoyl chloride) as colourless crystals (28%), m.p. 175–177 °C (from EtOAc–Et₂O) (lit.,³³ 170–171 °C) (Found: C, 74.9; H, 5.2. Calc. for C₂₅H₂₁OPS: C, 75.0; H, 5.3%); ν_{max} /cm⁻¹ 1502, 1488, 1446, 1434, 1242, 1186, 1136, 1121, 974, 863, 746 and 708; δ_{H} 7.75–7.25 (17 H, m), 7.05 (1 H, m) and 1.95 (3 H, d, J 17); δ_{P} +18.7; m/z 400 (M⁺, 65%), 385 (3), 343 (3), 339 (4), 317 (5), 289 (6), 277 (20), 262 (100), 201 (15) and 183 (70).

Flash Vacuum Pyrolysis of the Ylides 4 to give the Alkynes 5.—Various set-ups are available for this technique.¹⁸ The apparatus used is similar to one which has been illustrated and described recently.³⁴ The sample was volatilised from a tube in a Büchi Kugelrohr oven through a 30 × 2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to temperatures in the range 250–1000 °C, the temperature being monitored by a Pt/Pt–13% Rh thermocouple situated at the centre of the furnace. The products were collected separately in this study by connecting the furnace tube *via* a 15 × 2.5 cm tube at room temperature (to collect the Ph₃PO) to a U-shaped trap cooled in liquid nitrogen (to collect the alkyne). The whole system was maintained at a pressure of 10⁻² mmHg by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions the contact time in the hot zone was estimated to be ≈ 10 ms.

The majority of the pyrolyses, performed using ≤ 0.5 g of compound 4, were complete in less than 30 min., while the two examples 4f and 4m performed on ≥ 10 g scale required 3 h. After the material had all sublimed the alkynes 5 were recovered directly from the cold trap and analysed by ¹H and ¹³C NMR. For the small scale pyrolyses, yields were determined by calibration of the ¹H NMR spectra by adding an accurately weighed quantity of a solvent such as CH₂Cl₂ and comparing integrals, a procedure estimated to be accurate to ± 10%. In the case of volatile products, especially compound 5a (b.p. + 8 °C), care had to be taken to keep the product cold during transfer from the trap.

But-1-yne 5a. FVP of the ylide 4a (120 mg) at 750 °C gave compound 5a (15 mg, 78%) as a colourless liquid; δ_{H} 2.25 (2 H, qd, J 7 and 3), 1.97 (1 H, t, J 3) and 1.18 (3 H, t, J 7).

Pent-1-yne 5b. FVP of the ylide 4b (500 mg) at 750 °C gave compound 5b (58 mg, 59%) as a colourless liquid; δ_{H} 2.20 (2 H, td, J 7 and 2), 1.97 (1 H, t, J 2), 1.57 (2 H, sextet, J 7) and 1.03 (3 H, t, J 7); δ_{C} 84.1 (C–2), 68.2 (C–1), 22.1 (C–4), 20.5 (C–3) and 13.4 (C–5).

3-Methylbut-1-yne 5c. FVP of the ylide 4c (500 mg) at 750 °C gave compound 5c (70 mg, 72%) as a colourless liquid; δ_{H} 2.60 (1 H, septet of d, J 7 and 2), 2.03 (1 H, d, J 2) and 1.21 (6 H, d, J 7); δ_{C} 93.0 (C–2), 66.5 (C–1), 31.0 (2 × Me) and 27.3 (C–3).

3,3-Dimethylbut-1-yne 5d. FVP of the ylide 4d (18.0 g) at 750 °C gave compound 5d (3.38 g, 82%) as a colourless liquid; δ_{H} 2.07 (1 H, s) and 1.26 (9 H, s); δ_{C} 90.1 (C–2), 67.3 (C–1), 22.9 (3 × Me) and 20.4 (C–3).

Pent-3-en-1-yne 5e. FVP of the ylide 4e (540 mg) at 750 °C gave compound 5e (55 mg, 59%) as a colourless liquid shown by ¹H NMR to be an 8:1 mixture of the *E* and *Z* isomers; *E* isomer: δ_{H} 6.20 (1 H, half ABq, J 15 and 6), 5.45 (1 H, half ABqd, J 15, 2 and 2), 2.70 (1 H, dm, J 2) and 1.76 (3 H, ddm, J 6

and 2); δ_C 128.4 (C-4), 110.1 (C-3), 82.5 (C-2), 75.45 (C-1) and 18.5 (C-5).

Butenyne 6f. FVP of the ylide **4f** (470 mg) at 750 °C gave a liquid (19 mg) which was a 1 : 1 mixture of ethynylcyclobutane **5f**; δ_H 3.01 (1 H, m), 2.4–1.9 (6 H, m) and 2.01 (1 H, s), and butenyne **6f**. FVP of the ylide **4f** (102 mg) at 850 °C gave entirely the butenyne **6f** (10 mg, 67%) as a colourless liquid; δ_H 5.8–5.4 (3 H, m) and 2.88 (1 H, d, *J* 1); δ_C 128.6 (C-4), 116.4 (C-3), 82.3 (C-2) and 77.8 (C-1).

Ethynylcyclohexane 5g. FVP of the ylide **4g** (500 mg) at 750 °C gave compound **5g** (89 mg, 64%) as a colourless liquid; δ_H 2.36 (1 H, m), 2.04 (1 H, d, *J* 3) and 1.9–1.25 (10 H, m); δ_C 88.75 ($\equiv C-$), 67.95 ($\equiv CH$), 32.7 (C-2, 6), 28.9 (C-1), 26.0 (C-3, 5) and 24.9 (C-4).

Ethynylbenzene 5h. FVP of the ylide **4h** (550 mg) at 750 °C gave compound **5h** (120 mg, 82%) as a colourless liquid; δ_H 7.7–7.55 (2 H, m), 7.5–7.35 (3 H, m) and 3.10 (1 H, s); δ_C 132.2 (C-2, 6), 128.8 (C-4), 128.4 (C-3, 5), 122.3 (C-1), 83.8 ($\equiv C-$) and 77.3 ($\equiv CH$).

But-2-yne 5i. FVP of the ylide **4i** (114 mg) at 750 °C gave compound **5i** (136 mg, 74%) as a colourless liquid; δ_H 1.75 (6 H, s); δ_C 74.5 and 3.3.

2-Methylhept-3-yne 5j. FVP of the ylide **4j** (500 mg) at 750 °C gave compound **5j** (103 mg, 93%) as a colourless liquid; δ_H 2.57 (1 H, m), 2.15 (2 H, td, *J* 6 and 2), 1.47 (1 H, septet of m, *J* 6), 1.16 (6 H, d, *J* 7) and 0.98 (3 H, t, *J* 6); δ_C 86.2 (C-3), 79.2 (C-4), 23.6 (2 \times Me), 22.8 (C-6), 20.9 (C-5), 20.8 (C-2) and 13.45 (C-7).

2,2-Dimethylhept-3-yne 5k. FVP of the ylide **4k** (510 mg) at 750 °C gave compound **5k** (127 mg, 81%) as a colourless liquid; δ_H 2.15 (2 H, t, *J* 7), 1.52 (2 H, sextet, *J* 7), 1.23 (9 H, s) and 0.98 (3 H, t, *J* 7); δ_C 89.1 (C-3), 78.7 (C-4), 31.6 (3 \times Me), 27.5 (C-2), 22.8 (C-6), 20.8 (C-5) and 13.4 (C-7).

Oct-2-en-4-yne 5l. FVP of the ylide **4l** (497 mg) at 750 °C gave compound **4l** (114 mg, 82%) as a colourless liquid, shown by 1H NMR to be a 7 : 1 mixture of *E* and *Z* isomers; *E* isomer: δ_H 6.15 (1 H, half ABq, *J* 16 and 6), 5.60 (1 H, half ABq, *J* 16 and 2), 2.30 (2 H, t, *J* 7), 1.77 (3 H, dd, *J* 6 and 2), 1.57 (2 H, sextet, *J* 7) and 1.00 (3 H, t, *J* 7); δ_C 137.6 (C-2), 111.6 (C-3), 88.25 (C-4), 79.5 (C-5), 22.5 (C-7), 21.5 (C-6), 18.3 (C-1) and 13.5 (C-8).

Hept-1-en-3-yne 6m. FVP of the ylide **4m** (100 mg) at 600 °C gave a mixture of pent-1-ynylcyclobutane **5m** and compound **6m** (3 : 1 ratio) as a colourless liquid. FVP of compound **4m** (473 mg) at 800 °C gave solely compound **6m** (91 mg, 81%) as a colourless liquid; δ_H 6.0–5.2 (3 H, m), 2.25 (2 H, t, *J* 6), 1.55 (2 H, sextet, *J* 6) and 0.99 (3 H, t, *J* 6); δ_C 125.2 (C-1), 117.9 (C-2), 90.9 (C-3), 79.7 (C-4), 22.3 (C-6), 21.5 (C-5) and 13.5 (C-7).

Pent-1-ynylcyclohexane 5n. FVP of the ylide **4n** (13.2 g) at 750 °C gave compound **5n** (3.73 g, 81%) as a colourless liquid; δ_H 2.30 (1 H, m), 2.13 (2 H, t, *J* 7), 1.8–1.2 (12 H, m) and 0.97 (3 H, t, *J* 7); δ_C 84.8 (C-1'), 79.9 (C-2'), 33.4 (C-2, 6), 29.35 (C-1), 26.2 (C-4), 25.1 (C-3, 5), 22.8 (C-4'), 20.9 (C-3') and 13.4 (C-5').

Dec-5-yne 5o. FVP of the ylide **4o** (505 mg) at 750 °C gave compound **2o** (133 mg, 80%) as a colourless liquid; δ_H 2.12 (4 H, t, *J* 6), 1.5–1.3 (8 H, m) and 0.93 (6 H, t, *J* 6); δ_C 80.2 (C-5, 6), 31.6 (C-2, 9), 22.1 (C-3, 8), 18.6 (C-4, 7) and 13.7 (C-1, 10).

Undec-5-yne 5p. FVP of the ylide **4p** (565 mg) at 750 °C gave compound **5p** (138 mg, 69%) as a colourless liquid; δ_H 2.13 (4 H, t, *J* 6), 1.6–1.2 (10 H, m) and 0.91 (6 H, t, *J* 6); δ_C 80.1 (C-5, 6), 31.6 (C-9), 31.3 (C-2), 29.1 (C-8), 22.4 (C-10), 22.1 (C-3), 18.9 (C-7), 18.6 (C-4), 14.05 (C-11) and 13.7 (C-1).

2-(Prop-1-ynyl)thiophene 5q. FVP of the ylide **4q** (455 mg) at 750 °C gave compound **5q** (89 mg, 64%) as a colourless liquid; δ_H 7.2–7.0 (2 H, m), 6.90 (1 H, dd, *J* 5 and 4) and 2.02 (3 H, s); δ_C 130.8, 126.7, 125.8, 124.4 (C-2), 89.9 ($\equiv C-$), 73.1 ($\equiv C-$) and 4.5 (Me).

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