Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 10.[1] Generation of 2-methylstyrylalkynes and their thermal cyclisation to 2-alkenylnaphthalenes

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A series of nine 2-methylcinnamoyl phosphorus ylides 7 have been prepared and are found upon FVP at 500 °C to undergo loss of Ph_3PO to afford the corresponding styrylalkynes 8 whose fully assigned ^{13}C NMR spectra are presented. FVP of the ylides at 900 °C leads to cyclisation to give substituted naphthalenes 9–18; the mechanism of these reactions may proceed either by initial hydrogen atom loss or an initial [1,7]hydrogen shift, but an alternative route involving an initial [1,3]hydrogen shift has been ruled out by examination of a deuterium labelled analogue. For the α-phenyl ylides 7d and 7i a further cyclisation leads to benzo[*c*]fluorene derivatives and this process has been extended to a thiophene analogue to give fluoreno[3,4-*b*]thiophene. The formation of 2-ethylnaphthalene as the main product from the α-methoxycarbonyl ylide 7e is due to a secondary thermal reaction of methyl 2-naphthylacetate which may involve a radical chain reaction featuring, as the propagation step, an unusual homolytic substitution at a methoxy carbon by a 2-naphthylmethyl radical.

In Part 6 of this series,[2] we described the thermal extrusion of Ph_3PO from a series of cinnamoylalkylidenetriphenylphosphoranes **1** using flash vacuum pyrolysis (FVP) at 500 °C to afford the styrylalkynes **2**. Since styrylacetylene has been implicated as an intermediate in the mechanistically intriguing thermal conversion of azulene into naphthalene,[3] we were interested to see whether secondary thermal reaction of the styrylalkynes **2** under more severe conditions might proceed by isomerisation to the vinylidene **3** and cyclisation as shown to afford specifically substituted naphthalenes **4** or azulenes **5**. Although this was generally not successful, we report here that styrylalkynes bearing an *ortho*-methyl group do undergo cyclisation at 900 °C to afford a new synthesis of 2-alkenylnaphthalenes.[4]

Results and discussion

The required ylide precursors **7a–i** were readily prepared by acylation of the appropriate ylides, $Ph_3P{=}CHR^1$, with 2-methyl- or 2,4,6-trimethyl-cinnamoyl chloride **6** (Table 1). When these were subjected to FVP at 500 °C and 10^{-2} Torr in a conventional flow system (contact time *ca.* 10^{-2} s), the expected extrusion of Ph_3PO took place in line with our previous results,[2] to afford the styrylalkynes **8** in variable yield and with little *E*–*Z* isomerisation (Table 1). The identity of these products was readily confirmed by their ^{13}C NMR spectra which form a highly consistent pattern (Table 2).

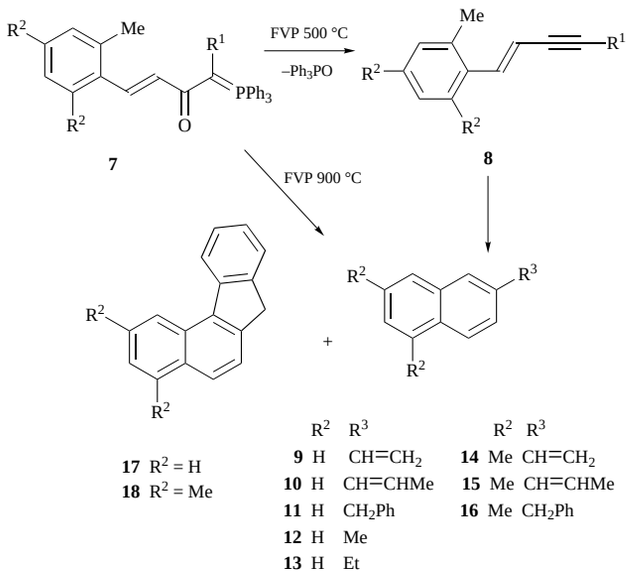
When the products **8** were repyrolysed at 900 °C or, more conveniently, when the ylides **7** were subjected directly to FVP at 900 °C, a variety of substituted naphthalenes **9**–**16** were produced in moderate yield (Scheme 1). As shown in Table 1, ylides **7a**, **7b**, **7f** and **7g** with R^1 = Me or Et gave the 2-vinyl products, while **7c** and **7 h** with $R^1 = Pr^i$ gave mainly the 2-propenylnaphthalenes, but accompanied by some vinyl products. For **7d** the main product was 2-benzylnaphthalene **11**, accompanied by 7*H*-benzo[*c*]fluorene **17** resulting from further cyclisation. The latter compound was identified spectroscopically,[5] and was also produced by separate FVP of an authentic sample of **11** at 950 °C, but only in low yield (7%), with the remainder of **11** being recovered unreacted.† This indicates that **17** is most probably a primary product of the cyclisation and is not derived from **11**. The products from methoxycarbonyl ylide **7e** are at first sight surprising, but they are in fact secondary fragmentation products of methyl 2-naphthylacetate **30**, since FVP of the latter at 900 °C produced a similar mixture of 2-methyl-, 2-ethyl- and 2-vinyl-naphthalenes.

A number of mechanistic possibilities for the formation of

† An early report of the thermal conversion of 2-benzylnaphthalene **11** into the isomeric benzo[*a*]fluorene (ref. 6) seems likely to be erroneous.

Table 1 Formation of ylides **7**, **24** and **27** and FVP at 500 and 900 °C

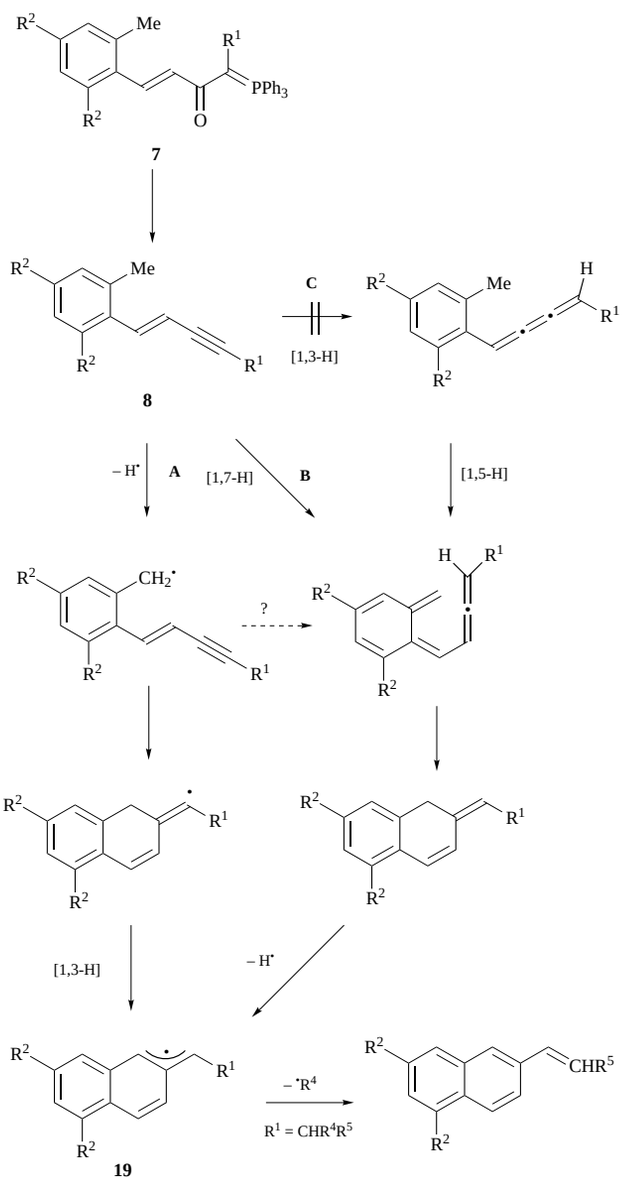
					8 at 500 °C		
	R^1	R^2	Yield (%)	δ_P	Yield (%)	*E* : *Z* ratio	Products at 900 °C (% yield)
7a	Me	H	41	17.7	15	85 : 15	**9** (15)
7b	Et	H	66	17.7	77	98 : 2	**9** (35)
24	—	—	41	17.8	—		**25** (21)
7c	Pr^i	H	54	16.0	75	>95 : 5	**10** (36), **9** (18)
7d	Ph	H	42	15.7	65	85 : 15	**11** (25), **17** (9)
7e	CO_2Me	H	77	18.9	92	97 : 3	**12** (21), **13** (58), **9** (7)
7f	Me	Me	36	18.1	48	>95 : 5	**14** (52)
7g	Et	Me	58	18.0	45	>95 : 5	**14** (56)
7h	Pr^i	Me	62	16.0	70	>95 : 5	**15** (31), **14** (21)
7i	Ph	Me	40	15.95	19	85 : 15	**16** (16), **18** (13)
27	—	—	57	15.8	—		**28** (20), **29** (14)



Scheme 1

the alkenylnaphthalene products are shown in Scheme 2. In route **A** initial loss of a benzylic hydrogen atom from the initially formed enyne **8** is followed by radical cyclisation and a subsequent [1,3]hydrogen shift to give the intermediate **19**. The feasibility of generation of benzylic radicals under the conditions used was confirmed by FVP of toluene at 900 °C which resulted in 6% conversion to bibenzyl. Alternatively, in route **B**, a [1,7]hydrogen shift, a well precedented process which has been of recent theoretical interest,[7] followed by a 6π electrocyclisation affords an intermediate which can readily lose the benzylic hydrogen atom to afford the same stabilised radical **19**. The first intermediate in route **B** could also be formed from the first intermediate in route **A** by rearrangement of the diradical implicit in the *E*–*Z* isomerisation of its double bond and hydrogen atom abstraction by the resulting allenyl radical. Finally in route **C**, isomerisation of **8** by a [1,3]hydrogen shift to the 1,2,3-triene would allow a subsequent [1,5]hydrogen shift and cyclisation as already reported for the closely related *o*-alkylphenylallenes.[8] This process is also closely analogous to the McMullen reaction reported by Brown and McMullen,[9] in which *o*-methylbenzylideneketene cyclises to 2-naphthol. Whatever the origin of **19**, it can account for most of the observed products either by loss of $H^{\bullet}$ or $Me^{\bullet}$ (for R^1 = Me, Et, Pr^i) or abstraction of a hydrogen atom (R^1 = Ph, CO_2Me). It is also possible, although apparently less likely, that the dihydronaphthalene product could be formed by direct addition of the benzylic hydrogen across the triple bond, as observed by Koller *et al.* for the related *o*-tolyl alkynyl ketones.[10]

In order to distinguish between these possibilities the trideuteriomethyl ylide **24** was prepared. As shown in Scheme

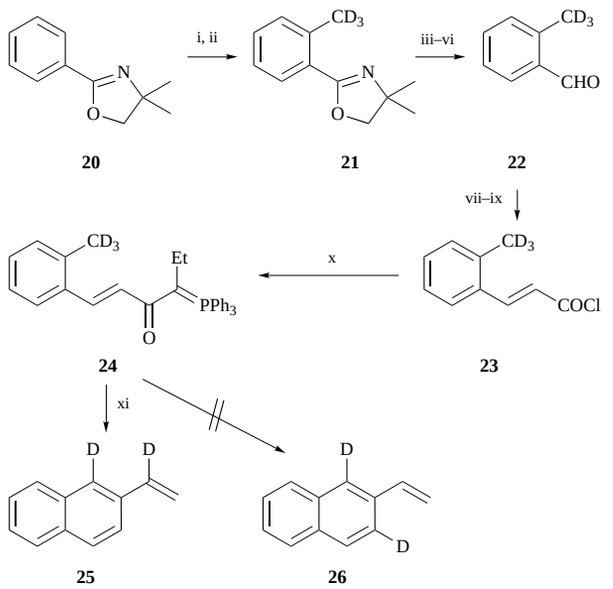


Scheme 2

3, a sample of *o*-[$^2H_3$]methylbenzaldehyde **22** was obtained by *ortho*-lithiation of 2-phenyl-4,4-dimethyloxazoline **20**, alkylation with CD_3I and reductive removal of the oxazoline.[11] Claisen condensation of this with ethyl acetate followed by hydrolysis, chlorination and treatment with Ph_3P=CHEt then afforded **24**. FVP of this at 900 °C produced a sample of [$^2H_2$]-2-vinylnaphthalene which, by reference to its fully assigned ^1H and ^{13}C NMR spectra,[12] was exclusively the 1,1′-isomer **25**. This is consistent with the formation of **19** by either

Table 2 ^{13}C NMR Spectra of 1,3-enynes **8**, δ_C

			Enyne signals				R^1 signals				Ar signals							
	R^1	R^2	C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4	C-5	C-6	2-Me	4-Me
8a	Me	H	137.9	109.7	87.9	79.2	4.5				137.9	135.5	130.4	128.2	124.8	126.1	19.8	
8b	Et	H	137.8	109.8	93.8	79.4	13.3	13.9			135.5	135.5	130.4	128.1	124.8	126.1	19.8	
8c	Pr^i	H	137.7	109.8	97.9	79.2	21.3	23.0			137.7	135.5	130.4	128.1	124.8	126.1	19.8	
8d	Ph	H	138.9	109.0	91.3	89.2	123.3	131.5	128.3	128.1	135.8	135.2	130.5	128.5	124.8	126.2	19.8	
8e	CO_2Me	H	145.6	105.5	86.6	81.7	154.5		52.7		136.6	134.0	130.8	129.9	125.3	126.4	19.7	
8f	Me	Me	138.6	113.8	87.4	79.1	4.0				136.8	136.0	128.9	133.0			20.4	20.4
8g	Et	Me	138.4	113.9	93.0	79.0	13.3	13.9			136.8	136.0	128.8	133.1			21.0	20.9
8h	Pr^i	Me	138.3	113.9	97.1	78.8	21.3	23.0			136.7	136.1	128.8	133.2			21.03	20.94
8i	Ph	Me	139.9	113.2	90.7	88.8	123.4	131.5	128.3	128.1	137.1	136.2	128.9	132.9			21.1	21.0

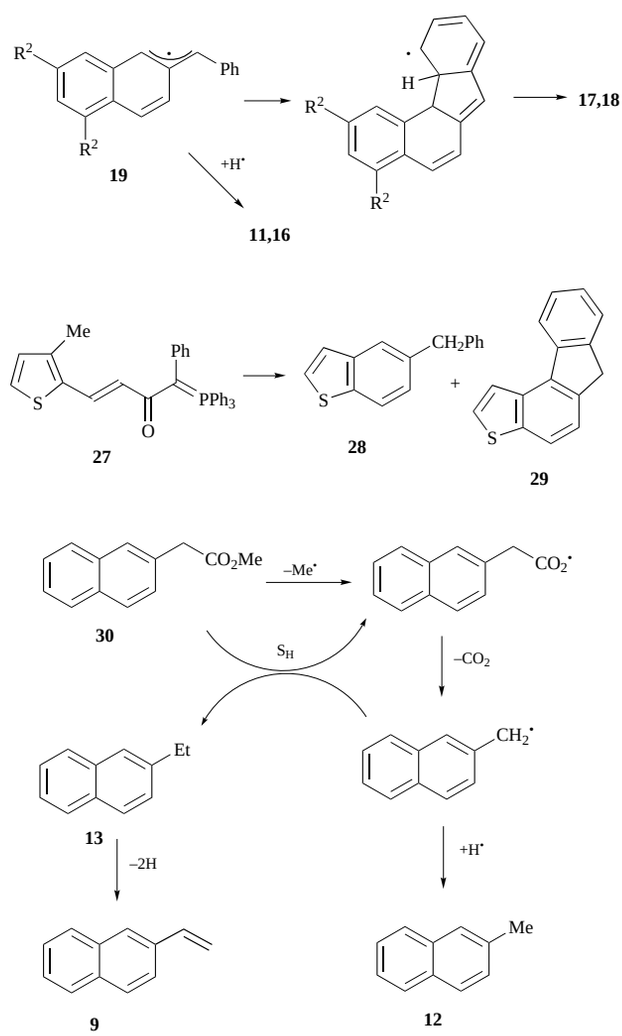


Scheme 3 *Reagents and conditions:* i, BuLi, −78 °C; ii, CD_3I; iii, Li, NH_3(l); iv, NCS; v, Al_2O_3; vi, SiO_2; vii, Na, EtOAc; viii, NaOH; ix, $SOCl_2$; x, 2 Ph_3P=CHEt; xi, FVP, 850 °C

route **A** or **B** but clearly rules out route **C** which would give the isomer **26**. The unusually severe conditions required to bring about the reaction (the enynes are recovered unchanged from FVP at temperatures up to 800 °C) perhaps favours the radical route **A**.

The results for the ylides **7d** and **7i** can also be explained by the formation of intermediate **19** as in Scheme 2. This can then either abstract a hydrogen atom to give **11** and **16** or alternatively undergo an intramolecular homolytic substitution followed by aromatisation to give the benzofluorenes **17** and **18**. The thiophene-based analogue **27** behaved in an analogous way to afford a mixture of two products characterised spectroscopically as 5-benzylbenzo[*b*]thiophene **28** and the fluorenothiophene **29**.

The mechanism involved for **7e**, which gives 2-ethylnaphthalene **13** as the main product in almost 60% yield, is not entirely clear. As mentioned above, the same products can be obtained from methyl 2-naphthylacetate **30** which is presumably formed by the mechanism of Scheme 2 followed by hydrogen atom abstraction by the radical **19**. The subsequent reaction of **30** may be similar to that involved in the degradation of the 2-alkyl group of 2-alkyl-3-benzofuryl radicals,[13] *i.e.* to involve a chain reaction as shown in Scheme 4 with, as an initiation step, loss of a methyl radical. The resulting carboxyl radical will readily lose CO_2 to give the stable 2-naphthylmethyl radical and, in the propagation step, **30** can suffer intermolecular homolytic substitution by this species to give **13** and generate a further carboxyl radical. Once the ester **30** is exhausted, the benzylic radical can abstract



Scheme 4

a hydrogen atom as a termination step to give **12**, and the vinylnaphthalene **9** is presumed to be a secondary thermal dehydrogenation product of **13**. As discussed in our previous paper,[13] intermolecular homolytic substitution by a carbon radical at a saturated carbon atom is very uncommon and would be expected to be especially disfavoured in the gas-phase, but the systems involved have the common feature of attack by a long-lived benzylic radical at an OMe group with formation of a new C–C bond and a delocalised oxygen-centred radical.

Despite the disappointing yields obtained in some cases, we believe this reaction to have some potential for the synthesis of specifically substituted naphthalenes and related systems by starting from suitably substituted 2-methylcinnamoyl ylides.

Experimental

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. Infra red spectra were recorded as Nujol mulls for solids and as thin films for liquids on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^{1}H at 80 MHz using a Bruker WP80 instrument, for ^{13}C at 50 MHz using a Varian Gemini instrument, for ^{2}H at 42 MHz using a Bruker AM300 instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in $CDCl_3$, with internal Me_4Si as reference for ^{1}H and ^{13}C and external 85% H_3PO_4 as reference for ^{31}P, except for ^{2}H spectra which were run in $CHCl_3$ with internal $CDCl_3$ (δ_D 7.30) as reference. 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 was carried out using a Hewlett Packard 5890A instrument coupled to a Finnigan-Incos 50 mass spectrometer. Preparative TLC was performed using 1 mm layers of silica (Merck Kieselgel 60–80 mesh) containing 0.5% Woelm fluorescent green indicator on glass plates. Dry THF was freshly distilled from potassium benzophenone ketyl under N_2.

The required quaternary phosphonium salts were all commercially available or were prepared by heating a solution of equimolar quantities of the appropriate alkyl halide and triphenylphosphine in toluene under reflux for 5 h.

Preparation of cinnamoyl chlorides

2-Methylcinnamoyl chloride. Based on the method of Young,[14] 2-methylbenzaldehyde (4.0 g, 33 mmol) was added to a suspension of sodium metal (0.76 g, 33 mmol) in ethyl acetate (60 cm^3) stirred at 0 °C. After stirring for 3 h at 0 °C, acetic acid was added dropwise until a bright yellow colouration was produced; water (70 cm^3) was then added and the mixture stirred for 20 min. The organic layer was separated, washed with aqueous sodium carbonate (2 × 50 cm^3), dried and evaporated to give ethyl 2-methylcinnamate (5.43 g, 87%) as a yellow oil. This was hydrolysed directly by addition of 2 M sodium hydroxide (25 cm^3) and heating under reflux for 2.5 h. The resulting solution was extracted with diethyl ether (25 cm^3), which was discarded, and then acidified by addition of conc. HCl (10 cm^3). The resulting suspension was extracted with CH_2Cl_2 (3 × 20 cm^3) which was dried and evaporated to give 2-methylcinnamic acid (3.25 g, 69%) as yellow crystals. This was heated under reflux in thionyl chloride (20 cm^3) for 2 h and then the excess thionyl chloride was evaporated. Kugelrohr distillation of the residue gave 2-methylcinnamoyl chloride (3.2 g, 89%) as a light yellow oil which was used directly for preparation of the ylides.

2,4,6-Trimethylcinnamoyl chloride. The procedure described above starting from 2,4,6-trimethylbenzaldehyde (5.0 g, 34 mmol) gave ethyl 2,4,6-trimethylcinnamate (6.7 g, 91%) which was hydrolysed to give crude 2,4,6-trimethylcinnamic acid (5.8 g, 99%). This was directly converted to 2,4,6-trimethylcinnamoyl chloride (4.15 g, 65%) using thionyl chloride.

4,4-Dimethyl-2-(2-trideuteriomethylphenyl)-4,5-dihydro-1,3-oxazole 21. This compound was prepared by modification of the method of Gschwend.[15] A solution of 4,4-dimethyl-2-phenyl-4,5-dihydro-1,3-oxazole **20** (1.58 g, 9 mmol) was stirred under nitrogen in dry THF (60 cm^3) at −70 °C. A solution of butyllithium in hexane (4.5 cm^3 of 2 M solution, 9 mmol) was added at this temperature which was maintained for 5 min after the addition and then warmed to room temperature. The solution was then cooled again to −70 °C and trideuteriomethyl iodide (1.40 g, 9.66 mmol) was added. The mixture was left to stir under nitrogen and allowed to warm to room temperature over 12 h. The mixture was then poured into saturated aqueous ammonium chloride (100 cm^3) and extracted with diethyl ether (3 × 100 cm^3) which was dried and evaporated to yield the crude product as a yellow oil. Kugelrohr distillation (85 °C/0.1 Torr) gave 4,4-dimethyl-2-(2-trideuteriomethylphenyl)-4,5-dihydro-1,3-oxazole **21** (2.17 g, 68%); δ_H 7.78–7.72 (1 H, m), 7.45–7.15 (3 H, m), 4.04 (2 H, s) and 1.38 (6 H, s); δ_D 2.52 (3 D, s); δ_C 162.8 (C-2), 131.2, 131.0 (both 4ry), 130.4, 129.8, 128.3, 125.5 (all CH), 78.6 (C-5), 67.8 (C-4) and 28.5 (2 C, Me).

2-Trideuteriomethylbenzaldehyde 22. The following reactions are based on the methods of Meyers *et al.*[11] A solution of **21** (2.17 g, 7.7 mmol) in dry THF (100 cm^3) was stirred while liquid ammonia (300 cm^3) was carefully added, and the mixture allowed to settle with stirring, before adding lithium metal (0.32 g, 45 mmol) in small pieces. The solution was allowed to stir for 1 h then water (10 cm^3) was added dropwise and the solution left to stir for 12 h. The mixture was partitioned between water and diethyl ether and the ethereal extract was separated, dried and evaporated to yield the crude amino alcohol (2.49 g) as a yellow oil; δ_H 7.36–7.03 (4 H, m), 3.61 (2 H, s), 3.28 (2 H, s) and 1.1 (6 H, s); δ_D 2.34 (3 D, s).

The crude amino alcohol was stirred with *N*-chlorosuccinimide (1.73 g, 9 mmol) in CH_2Cl_2 (100 cm^3) for 1 h. Alumina (75 g) was then added and the suspension left to stir vigorously overnight. The alumina was filtered off and washed thoroughly with CH_2Cl_2 (200 cm^3) and the combined filtrate was evaporated down to 5 cm^3 and then passed through a short column of silica using CH_2Cl_2 (500 cm^3) as eluent. The solution was dried and evaporated to yield a yellow oil. Kugelrohr distillation gave 2-trideuteriomethylbenzaldehyde **22** (0.292 g, 31%) as a colourless liquid, bp (oven temp.) 140 °C/0.05 Torr; δ_H 10.25 (1 H, s) and 7.82–7.20 (4 H, m); δ_D 2.65 (3 D, s).

2-Trideuteriomethylcinnamoyl chloride 23. The method of Young[14] as described above for the unlabelled compound was used with sodium metal (0.09 g, 4 mmol) in dry ethyl acetate (10 cm^3) and 2-trideuteriomethylbenzaldehyde **22** (0.40 g, 3.4 mmol). The product was Kugelrohr distilled (120 °C/0.05 Torr) to yield ethyl 2-trideuteriomethylcinnamate (0.36 g, 56%). Subsequent base hydrolysis provided the corresponding cinnamic acid; δ_H 10.12 (1 H, br s), 8.12 and 7.20 (2 H, AB pattern, *J* 16) and 7.75–7.1 (4 H, m) which was used directly to obtain 2-trideuteriomethylcinnamoyl chloride **23** (0.22 g, 57%) as a light yellow oil, bp 160°C/0.3 Torr.

3-(3-Methyl-2-thienyl)propenoyl chloride. Reaction of triethyl phosphonoacetate with sodium hydride in dry THF followed by addition of 3-methylthiophene-2-carbaldehyde gave ethyl 3-(3-methyl-2-thienyl)propenoate which was hydrolysed to 3-(3-methyl-2-thienyl)propenoic acid; this was then reacted with thionyl chloride as above to give the required acid chloride.

Preparation of substituted cinnamoylalkylidenetriphenylphosphoranes 7

A suspension of the appropriate quaternary phosphonium salt (25 mmol) in dry THF (150 cm^3) was stirred at room temperature under nitrogen while butyllithium in hexane (26 mmol) was added dropwise by syringe. After 15 min a solution of the appropriate cinnamoyl chloride (12.5 mmol) in dry THF (10 cm^3) was added dropwise and the mixture stirred for 8 h before adding to water (250 cm^3). Extraction with diethyl ether (3 × 100 cm^3) followed by drying and evaporation gave the product which was recrystallised from ethyl acetate.

[1-(2-Methylcinnamoyl)ethylidene)]triphenylphosphorane 7a. From ethyl(triphenyl)phosphonium bromide and 2-methylcinnamoyl chloride as yellow crystals (41%), mp 170–172 °C (Found: M^+, 434.1750. $C_{30}H_{27}OP$ requires *M*, 434.1800); ν_{max}/cm^{-1} (CH_2Cl_2) 1618, 1487, 1430, 1377, 1162, 1100, 1050, 970, 912 and 846; δ_H 7.8–7.3 (18 H, m), 7.2–7.1 (3 H, m), 2.38 (3 H, s) and 1.80 (3 H, d, *J* 16); δ_P 17.7; *m/z* 434 (M^+, 24%), 289 (5), 277 (19), 262 (100), 183 (35), 145 (13), 135 (13) and 108 (13).

[1-(2-Methylcinnamoyl)prop-1-ylidene]triphenylphosphorane 7b. From propyl(triphenyl)phosphonium bromide and 2-methylcinnamoyl chloride as yellow needles (66%), mp 169–171.5 °C (Found: C, 83.1; H, 6.6. $C_{31}H_{29}OP$ requires C, 83.0; H, 6.5%); ν_{max}/cm^{-1} 1627, 1436, 1162, 1104, 968, 918, 753, 720 and 690; δ_H

7.84–7.10 (21 H, m), 2.42 (3 H, s), 2.21 (2 H, d of q, *J* 22, 7) and 0.98 (3 H, t, *J* 7); δ_P 17.7; *m/z* 448 (M^+, 22%), 433 (78), 371 (3), 355 (4), 331 (6), 303 (10), 287 (14), 277 (41), 262 (100), 201 (20), 183 (90), 145 (50), 115 (38) and 108 (75).

[1-(2-Trideuteriomethylcinnamoyl)prop-1-ylidene]triphenylphosphorane 24. From propyl(triphenyl)phosphonium bromide and 2-trideuteriomethylcinnamoyl chloride **23** as yellow prisms (41%), mp 169–171 °C; δ_H 7.80–7.10 (21 H, m), 2.19 (2 H, d of q, *J* 22, 7) and 0.96 (3 H, t, *J* 7); δ_D 2.39; δ_P 17.8.

[1-(2-Methylcinnamoyl)-2-methylprop-1-ylidene]triphenylphosphorane 7c. From 2-methylpropyl(triphenyl)phosphonium bromide and 2-methylcinnamoyl chloride as yellow crystals (54%), mp 208–210 °C (Found: C, 83.0; H, 6.8. $C_{32}H_{31}OP$ requires C, 83.1; H, 6.8%); ν_{max}/cm^{-1} 1631, 1438, 1402, 1340, 1181, 1103, 1073, 971, 940, 869, 764, 730 and 693; δ_H 7.70–7.08 (21 H, m), 2.38 (3 H, s), 2.12 (1 H, d of septets, *J* 25, 7) and 1.32 (6 H, d, *J* 7); δ_P 16.0; *m/z* 462 (M^+, 18%), 447 (52), 385 (3), 303 (5), 277 (42), 262 (54), 218 (22), 201 (16), 183 (29), 145 (100), 116 (67) and 115 (58).

[2-Methylcinnamoyl(phenyl)methylene]triphenylphosphorane 7d. From benzyl(triphenyl)phosphonium chloride and 2-methylcinnamoyl chloride as yellow crystals (42%), mp 259–260 °C (Found: C, 84.5; H, 5.7. $C_{35}H_{29}OP$ requires C, 84.7; H, 5.9%); ν_{max}/cm^{-1} 1625, 1497, 1434, 1262, 1219, 1198, 1102, 972, 760, 715, 700 and 687; δ_H 7.8–7.3 (20 H, m), 7.0 (5 H, s), 6.90 (1 H, half AB pattern, *J* 16) and 2.33 (3 H, s); δ_P 15.7; *m/z* 496 (M^+, 36%), 495 (27), 481 (3), 403 (15), 379 (12), 351 (12), 303 (3), 278 (40), 277 (80), 262 (72), 201 (100) and 183 (48).

[1-(2,4,6-Trimethylcinnamoyl)ethylidene]triphenylphosphorane 7f. From ethyl(triphenyl)phosphonium bromide and 2,4,6-trimethylcinnamoyl chloride as yellow crystals (36%), mp 215–218 °C (Found: C, 82.5; H, 6.7%; M^+, 462.2135. $C_{32}H_{31}OP$ requires C, 83.1; H, 6.8%; *M*, 462.2113); ν_{max}/cm^{-1} (CH_2Cl_2) 1621, 1605, 1487, 1430, 1370, 1160, 1100, 1042, 980, 908, 850 and 819; δ_H 7.8–7.35 (16 H, m), 6.93 (1 H, half AB pattern, *J* 16), 6.88 (2 H, s), 2.38 (6 H, s), 2.26 (3 H, s) and 1.77 (3 H, d, *J* 16); δ_P 18.1; *m/z* 462 (M^+, 83%), 447 (10), 385 (11), 369 (18), 342 (8), 317 (33), 289 (94), 262 (100), 217 (18), 201 (22), 183 (86) and 108 (65).

[1-(2,4,6-Trimethylcinnamoyl)prop-1-ylidene]triphenylphosphorane 7g. From propyl(triphenyl)phosphonium bromide and 2,4,6-trimethylcinnamoyl chloride as yellow crystals (58%), mp 174–176 °C (Found: C, 83.4; H, 7.25. $C_{33}H_{33}OP$ requires C, 83.2; H, 7.0%); ν_{max}/cm^{-1} 1632, 1506, 1482, 1439, 1365, 1162, 1105, 762, 720 and 692; δ_H 7.8–7.3 (16 H, m), 7.0–6.75 (3 H, m), 2.37 (6 H, s), 2.25 (3 H, s), 2.3–1.8 (2 H, m) and 0.91 (3 H, t, *J* 7); δ_P 18.0; *m/z* 476 (M^+, 46%), 461 (98), 399 (8), 331 (16), 317 (11), 303 (81), 287 (34), 277 (11), 262 (100), 201 (19), 183 (73), 153 (19), 119 (14) and 108 (48).

[1-(2,4,6-Trimethylcinnamoyl)-2-methylprop-1-ylidene]triphenylphosphorane 7h. From 2-methylpropyl(triphenyl)phosphonium bromide and 2,4,6-trimethylcinnamoyl chloride as yellow crystals (62%), mp 192–194 °C (Found: C, 83.1; H, 7.2. $C_{34}H_{35}OP$ requires C, 83.2; H, 7.2%); ν_{max}/cm^{-1} 1634, 1489, 1442, 1183, 1102, 1074, 978, 869, 843, 722, 695 and 689; δ_H 7.75–7.3 (16 H, m), 6.90 (1 H, half AB pattern, *J* 16), 6.85 (2 H, s), 2.37 (6 H, s), 2.25 (3 H, s), 2.3–1.7 (1 H, m) and 1.24 (6 H, d, *J* 7); δ_P 16.0; *m/z* 490 (M^+, 40%), 475 (100), 461 (9), 413 (13), 397 (7), 357 (8), 345 (7), 303 (22), 287 (11), 279 (10), 262 (28), 231 (18), 201 (25), 183 (23), 167 (41) and 108 (31).

[2,4,6-trimethylcinnamoyl(phenyl)methylene]triphenylphosphorane 7i. From benzyl(triphenyl)phosphonium chloride and 2,4,6-trimethylcinnamoyl chloride as pale yellow crystals (40%), mp 199–201 °C (Found: C, 84.5; H, 6.5. $C_{37}H_{33}OP$ requires C, 84.7; H, 6.3%); ν_{max}/cm^{-1} 1635, 1506, 1436, 1212, 1101, 986, 951, 856, 840, 755, 709 and 693; δ_H 7.9–7.3 (16 H, m), 7.0 (5 H, m), 6.79 (2 H, s), 6.50 (1 H, half AB pattern, *J* 16) and 2.23 (9 H, s); δ_P 15.95; *m/z* 524 (M^+, 3%), 523 (2), 509 (1), 433 (1), 393 (1), 369 (2), 353 (1), 334 (1), 293 (2), 279 (40), 278 (55), 277 (100), 262 (4), 229 (4), 201 (50), 199 (50), 185 (40) and 183 (55).

[3-(3-methyl-2-thienyl)propenoyl(phenyl)methylene]triphenylphosphorane 27. From benzyl(triphenyl)phosphonium chloride and 3-(3-methyl-2-thienyl)propenoyl chloride as yellow crystals (57%), mp 235–238 °C (Found: C, 78.6; H, 5.15. $C_{33}H_{27}OPS$ requires C, 78.9; H, 5.4%); ν_{max}/cm^{-1} (CH_2Cl_2) 1610, 1590, 1475, 1430, 1352, 1200, 1100, 1070, 1036, 1000, 956, 852 and 830; δ_H 7.75–7.3 (16 H, m), 7.02 (5 H, s), 6.98 and 6.73 (2 H, AB pattern, *J* 3), 6.60 (1 H, half AB pattern, *J* 16) and 2.22 (3 H, s); δ_P 15.8; *m/z* 502 (M^+, 60%), 501 (25), 409 (2), 379 (8), 351 (7), 303 (4), 278 (16), 277 (45), 263 (20), 262 (100), 240 (18), 224 (60), 201 (14), 185 (12), 184 (10) and 183 (50).

[2-Methylcinnamoyl(methoxycarbonyl)methylene]triphenylphosphorane 7e. For this ylide a different method was used. A solution of the commercially available methoxycarbonylmethylenetriphenylphosphorane (1.67 g, 5 mmol) in toluene (30 cm^3) was stirred at room temp. while 2-methylcinnamoyl chloride (0.90 g, 5 mmol) in toluene (10 cm^3) was added dropwise. The mixture was stirred at 40 °C for 2 h and then added to water (100 cm^3). Separation of the organic layer, drying and evaporation gave the product as yellow crystals (77%), mp 210–211.5 °C (Found: C, 77.2; H, 5.3%; M^+, 478.1687. $C_{31}H_{27}O_3P$ requires C, 77.8; H, 5.7%; *M*, 478.1698); ν_{max}/cm^{-1} 2945, 1735, 1664, 1573, 1530, 1443, 1106, 764, 720 and 688; δ_H 8.13 (1 H, half AB pattern, *J* 16), 7.8–7.35 (17 H, m), 7.20–7.06 (3 H, m), 3.18 (3 H, s) and 2.36 (3 H, s); δ_P 18.9; *m/z* 478 (M^+, 43%), 463 (40), 450 (37), 417 (9), 385 (13), 361 (9), 333 (10), 301 (6), 277 (100), 262 (26), 172 (16), 159 (41) and 157 (45).

Preparation of 2-benzylnaphthalene 11

Following the literature procedure,[16] 2-benzoylnaphthalene (from Friedel–Crafts reaction of 2-naphthoyl chloride with benzene) was reduced with hydrazine hydrate in an autoclave at 210 °C for 24 h. Extraction with diethyl ether followed by distillation gave a colourless liquid (77%), bp 220 °C/10 Torr which solidified with time, mp 53–55 °C (lit.,[16] 58 °C); δ_H 7.85–7.6 (4 H, m), 7.5–7.25 (3 H, m), 7.25 (5 H, s) and 4.14 (2 H, s).

Preparation of methyl 2-naphthylacetate 30

This was prepared by treatment of 2-naphthylacetic acid with 1.5 equiv. thionyl chloride in methanol under reflux for 1 h, followed by evaporation and Kugelrohr distillation to give a colourless oil (75%), bp (oven temp.) 220–230 °C/20 Torr (lit.,[17] 136 °C/0.3 Torr); δ_H 7.85–7.7 (4 H, m), 7.5–7.35 (3 H, m), 3.79 (2 H, s) and 3.70 (3 H, s).

Flash vacuum pyrolysis of ylides 7

The apparatus used was as described previously.[18] All pyrolyses were conducted at pressures in the range 10^{-3}–10^{-1} Torr. Under these conditions the contact time in the hot zone was estimated to be *ca.* 10 ms. Unless otherwise stated, Ph_3PO collected at the furnace exit and the more volatile products were recovered from the cold trap. Yields were determined after calibration of the ^{1}H 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%.

Low temperature FVP to give enynes 8

***(E)*-1-(2-Methylphenyl)pent-1-en-3-yne 8a.** FVP of the ylide **7a** (95 mg) at 500 °C gave (E)-1-(2-*methylphenyl*)*pent*-1-*en*-3-*yne* **8a** as a yellow oil (15%) (HRMS: found M^+, 156.0941. $C_{12}H_{12}$ requires *M*, 156.0939); ν_{max}/cm^1 3000, 2905, 2840, 2300, 1585, 1425, 1180 and 1110; δ_H 7.75–7.02 (5 H, m), 6.03 (1 H, half AB pattern of q, *J* 16, 2), 2.32 (3 H, s) and 2.00 (3 H, d, *J* 2); δ_C see Table 2; *m/z* 156 (M^+, 78%), 141 (100), 128 (34), 115 (81), 91 (19), 77 (19), 63 (30) and 51 (30).

***(E)*-1-(2-Methylphenyl)hex-1-en-3-yne 8b.** FVP of the ylide **7b** (200 mg) at 500 °C gave (E)-1-(2-*methylphenyl*)*hex*-1-*en*-3-*yne* **8b** as a yellow oil (77%) (HRMS: found M^+, 170.1103. $C_{13}H_{14}$ requires *M*, 170.1092); ν_{max}/cm^{-1} 2900, 2230, 1595, 1469, 1438, 1309 and 947; δ_H 7.50–7.05 (5 H, m), 6.08 (1 H, half AB

pattern of t, *J* 16, 2), 2.41 (2 H, q of d, *J* 8, 2), 2.38 (3 H, s) and 1.22 (3 H, t, *J* 8); δ_C see Table 2; *m/z* 170 (M^+, 77%), 155 (100), 141 (52), 128 (51), 115 (47), 84 (32) and 77 (21).

(*E*)-1-(2-Methylphenyl)-5-methylhex-1-en-3-yne 8c. FVP of the ylide **7c** (70 mg) at 500 °C gave (E)-1-(2-*methylphenyl*)-5-*methylhex*-1-*en*-3-*yne* **8c** as a yellow oil (75%) (HRMS: found M^+, 184.1258. $C_{14}H_{16}$ requires *M*, 184.1252); ν_{max}/cm^{-1} 2900, 2300, 1680, 1596, 1314, 955, 853 and 816; δ_H 7.47–7.05 (5 H, m), 6.08 (1H, half AB pattern of d, *J* 16, 2), 2.75 (1 H, septet of d, *J* 7, 2), 2.36 (3 H, s) and 1.23 (6 H, d, *J* 7); δ_C see Table 2; *m/z* 184 (M^+, 100%), 169 (89), 154 (78), 141 (70), 128 (64), 115 (40) and 77 (24).

(*E*)-1-(2-Methylphenyl)-4-phenylbut-1-en-3-yne 8d. FVP of the ylide **7d** (116 mg) at 500 °C gave (E)-1-(2-*methylphenyl*)-4-*phenylbut*-1-*en*-3-*yne* **8d** as a yellow oil (65%) (HRMS: found M^+, 218.1093. $C_{17}H_{14}$ requires *M*, 218.1092); ν_{max}/cm^{-1} 2900, 2840, 2180, 1590, 1092, 1060, 948 and 800; δ_H 7.56–7.16 (10 H, m), 6.31 (1 H, half AB pattern, *J* 16) and 2.40 (3 H, s); δ_C see Table 2; *m/z* 218 (M^+, 100%), 202 (70), 189 (10), 141 (12), 115 (30) and 84 (42).

(*E*)-4-Methoxycarbonyl-1-(2-methylphenyl)but-1-en-3-yne 8e. FVP of the ylide **7e** (410 mg) at 500 °C gave (E)-4-*methoxycarbonyl*-1-(2-*methylphenyl*)*but*-1-*en*-3-*yne* **8e** as a light yellow oil (92%) (HRMS: found M^+, 200.0843. $C_{13}H_{12}O_2$ requires *M*, 200.0837); ν_{max}/cm^{-1} 2951, 2208, 1710, 1597, 1484, 1435, 1255, 1111, 1089 and 749; δ_H 7.52 and 6.13 (2 H, AB pattern, *J* 16), 7.50–7.45 (1 H, m), 7.30–7.13 (3 H, m), 3.83 (3 H, s) and 2.38 (3 H, s); δ_C see Table 2; *m/z* (20 eV) 200 (M^+, 25%), 185 (4), 182 (3), 169 (17), 155 (13), 141 (100), 129 (18), 115 (30), 91 (10) and 77 (8).

(*E*)-1-(2,4,6-Trimethylphenyl)pent-1-en-3-yne 8f. FVP of the ylide **7f** (103 mg) at 500 °C gave (E)-1-(2,4,6-*trimethylphenyl*)*pent*-1-*en*-3-*yne* **8f** as a yellow oil (48%) (HRMS: found M^+, 184.1257. $C_{14}H_{16}$ requires *M*, 184.1252); ν_{max}/cm^{-1} 2900, 2840, 2205, 1600, 1430, 1028, 955 and 856; δ_H 6.91 (1 H, half AB pattern, *J* 16), 6.88 (2 H, s), 5.68 (1 H, half AB pattern of q, *J* 16, 2), 2.26 (6 H, s), 2.25 (3 H, s) and 2.01 (3 H, d, *J* 2); δ_C see Table 2; *m/z* 184 (M^+, 74%), 182 (15), 170 (37), 169 (100), 167 (24), 156 (21), 155 (31), 154 (29), 153 (34), 152 (27), 141 (56), 128 (29), 115 (42) and 91 (22).

(*E*)-1-(2,4,6-Trimethylphenyl)hex-1-en-3-yne 8g. FVP of the ylide **7g** (80 mg) at 500 °C gave (E)-1-(2,4,6-*trimethylphenyl*)*hex*-1-*en*-3-*yne* **8g** as a yellow oil (45%) (HRMS: found M^+, 198.1412. $C_{15}H_{18}$ requires *M*, 198.1404); ν_{max}/cm^{-1} 2900, 2205, 1600, 1460, 1310, 1055, 952 and 852; δ_H 6.86 (1 H, half AB pattern, *J* 16), 6.82 (2 H, s), 5.67 (1 H, d of t, *J* 16, 2), 2.28 (2 H, m), 2.25 (9 H, s) and 1.23 (3 H, t, *J* 7); δ_C see Table 2; *m/z* 198 (M^+, 98%), 183 (40), 169 (100), 154 (41), 141 (49), 128 (31) and 115 (30).

(*E*)-5-Methyl-1-(2,4,6-trimethylphenyl)hex-1-en-3-yne 8h. FVP of the ylide **7h** (90 mg) at 500 °C gave (E)-5-*methyl*-1-(2,4,6-*trimethylphenyl*)*hex*-1-*en*-3-*yne* **8h** as a yellow oil (70%) (HRMS: found M^+, 212.1561. $C_{16}H_{20}$ requires *M*, 212.1560); ν_{max}/cm^{-1} 2905, 2850, 2200, 1600, 1450, 1310, 955 and 900; δ_H 6.90 (1 H, half AB pattern, *J* 16), 6.87 (2 H, s), 5.72 (1 H, d of d, *J* 16, 2), 2.76 (1 H, septet of d, *J* 7, 2), 2.32 (6 H, s), 2.30 (3 H, s) and 1.26 (6 H, d, *J* 7); δ_C see Table 2; *m/z* 212 (M^+, 100%), 197 (41), 182 (55), 169 (84), 156 (58), 141 (55), 128 (40) and 115 (39).

(*E*)-4-Phenyl-1-(2,4,6-trimethylphenyl)but-1-en-3-yne 8i. FVP of the ylide **7i** (100 mg) at 500 °C gave (E)-4-*phenyl*-1-(2,4,6-*trimethylphenyl*)*but*-1-*en*-3-*yne* **8i** as a yellow oil (19%) (HRMS: found M^+, 246.1416. $C_{19}H_{18}$ requires *M*, 246.1401); ν_{max}/cm^{-1} 2900, 2840, 2290, 1600, 1243, 1063, 956 and 802; δ_H 7.76–7.25 (5 H, m), 7.10 and 5.97 (2 H, AB pattern, *J* 16), 6.89 (2 H, s), 2.35 (6 H, s) and 2.29 (3 H, s); δ_C see Table 2; *m/z* 246 (M^+, 100%), 231 (67), 215 (75), 182 (19), 169 (36), 152 (23), 128 (32) and 115 (38).

High temperature FVP to give naphthalenes 9–16.

FVP of the ylide **7a** (125 mg) at 900 °C gave a solid at the furnace exit shown by ^1H and ^{31}P NMR spectroscopy and TLC to be Ph_3PO, and in the cold trap a colourless liquid (6.8 mg, 15%) which was mainly 2-vinylnaphthalene **9** [δ_H 7.9–7.1 (7 H, m), 6.91 (1 H, dd, *J* 18, 11), 5.86 (1 H, dd, *J* 18, 1) and 5.33 (1 H, dd, *J* 11, 1)].

FVP of the ylide **7b** (117 mg) at 900 °C gave a solid at the furnace exit shown by ^1H and ^{31}P NMR spectroscopy and TLC to be Ph_3PO, and in the cold trap a colourless liquid which was mainly 2-vinylnaphthalene; δ_H as above. GC–MS of the oil showed it to contain 2-vinylnaphthalene **9** (13.8 mg, 35%) [*m/z* 154 (M^+, 100%), 128 (29) and 76 (94)], indene (4.5 mg, 15%) [*m/z* 116 (M^+, 84%) and 115 (100)], naphthalene (2.6 mg, 8%) [*m/z* 128 (M^+, 100%) and 102 (15)] and traces of toluene [*m/z* 92 (M^+, 51%) and 91 (100)], ethylbenzene [*m/z* 106 (M^+, 38%) and 91 (100)], 2-methylstyrene [*m/z* 118 (M^+, 57%) and 117 (15)] and 2-propenylnaphthalene **10** [*m/z* 168 (M^+, 100%) and 153 (58)].

Repeat pyrolysis of **7b** (180 mg) at 850 °C followed by preparative TLC (Et_2O) thus gave pure 2-vinylnaphthalene **9** (14 mg, 23%) [δ_H as above; δ_C 136.9 (C-1′), 135.0 (C-2), 133.5 (C-8a), 133.1 (C-4a), 128.1 (C-4), 128.0 (C-8), 127.7 (C-5), 126.4 (C-1), 126.2 (C-7), 125.9 (C-6), 123.2 (C-3) and 114.2 (C-2′): lit.,[12] δ_C 136.9 (C-1′), 134.9 (C-2), 133.5 (C-8a), 133.1 (C-4a), 128.1 (C-4), 128.0 (C-8), 127.6 (C-5), 126.4 (C-1), 126.2 (C-7), 125.8 (C-6), 123.1 (C-3) and 114.1 (C-2)].

FVP of the ylide **24** (180 mg) at 850 °C and subsequent isolation by preparative TLC (Et_2O) gave 1,1′-dideuterio-2-vinylnaphthalene **25** (13 mg, 21%) [δ_H 7.9–7.15 (6 H, m), 5.86 (1 H, s) and 5.33 (1 H, s); δ_D 7.66 (1 D, s) and 6.79 (1 D, s); lit.,[12] δ_H 7.65 (H-1) and 6.80 (H-1′); δ_C 136.9 (C-1′, very weak), 134.9 (C-2), 133.5 (C-8a), 133.2 (C-4a), 128.1 (C-4), 128.0 (C-8), 127.7 (C-5), C-1 signal not present, 126.2 (C-7), 125.9 (C-6), 123.2 (C-3) and 114.0 (C-2′); *m/z* 156 (M^+, 100%), 155 (63), 154 (40), 129 (12), 116 (7) and 77 (38)].

FVP of the ylide **7c** (182 mg) at 900 °C gave a solid at the furnace exit shown by ^1H and ^{31}P NMR spectroscopy and TLC to be Ph_3PO, and in the cold trap a yellow liquid which was mainly 2-propenylnaphthalene **10** (24.1 mg, 36%) [δ_H 7.9–7.3 (7 H, m), 6.75–5.75 (2 H, m) and 2.0–1.85 (3 H, m)] and 2-vinylnaphthalene **9** (11.1 mg, 18%); δ_H as above. GC–MS confirmed the presence of **10** [*m/z* 168 (M^+, 100%) and 128 (29)], **9** [*m/z* 154 (M^+, 100%) and 153 (58)] and traces of indene [*m/z* 116 (M^+, 84%) and 115 (100)], naphthalene [*m/z* 128 (M^+, 100%) and 102 (15)] and toluene [*m/z* 92 (M^+, 51%) and 91 (100)].

FVP of the ylide **7d** (488 mg) at 900 °C gave a solid at the furnace exit shown by ^1H and ^{31}P NMR spectroscopy and TLC to be a mixture of Ph_3PO and two hydrocarbons. These were separated by preparative TLC (Et_2O) to give 2-benzylnaphthalene **11** (50.9 mg, 25%), identical by TLC with an authentic sample [δ_H 7.85–7.6 (4 H, m), 7.5–7.25 (3 H, m), 7.25 (5 H, s) and 4.14 (2 H, s)] and 7*H*-benzo[*c*]fluorene **17** (17.5 mg, 9%) [δ_H 8.72 (1 H, dd, *J* 8, 2), 8.34 (1 H, dd, *J* 7, 2), 7.9–7.2 (8 H, m) and 3.96 (2 H, s); lit.,[5] δ_H 8.69 (1 H, dd, *J* 8, 1), 8.31 (1 H, dd, *J* 8, 1), 7.86–7.10 (8 H, m) and 3.87 (2H, s)].

FVP of **11** at 950 °C gave mostly the unchanged starting material but this was accompanied by 7*H*-benzo[*c*]fluorene **17** (*ca.* 7%) [δ_H as above].

FVP of the ylide **7f** (189 mg) at 900 °C gave a solid at the furnace exit shown by ^1H and ^{31}P NMR spectroscopy and TLC to be Ph_3PO, and in the cold trap a colourless liquid (38.5 mg, 52%) which was mainly 5,7-dimethyl-2-vinylnaphthalene **14** (HRMS: found M^+, 182.1102. $C_{14}H_{14}$ requires *M*, 182.1096) [δ_H 7.95–7.8 (1 H, m), 7.7–7.3 (3 H, m), 7.10 (1 H, m), 6.88 (1 H, dd, *J* 18, 10), 5.83 (1 H, dd, *J* 18, 1), 5.30 (1 H, dd, *J* 10, 1), 2.60 (3 H, s) and 2.42 (3 H, s); δ_C 137.0 (C-1′), 135.5 (C-2), 134.0 (C-8a), 133.9 (C-4a), 129.1 (C-4), 128.5 and 128.3 (C-5 and 7), 126.3 (C-1), 125.4 (C-8), 124.2 (C-3), 122.1 (C-6), 113.8 (C-2′), 21.6 and 19.2 (both Me); *m/z* 182 (M^+, 100%), 167 (37), 165 (28), 152 (20), 84 (32) and 49 (35)].

FVP of the ylide **7g** (196 mg) at 900 °C gave a solid at the furnace exit shown by ^{1}H and ^{31}P NMR spectroscopy and TLC to be Ph_3PO, and in the cold trap a colourless liquid which was mainly 5,7-dimethyl-2-vinylnaphthalene **14** (42.0 mg, 56%) [δ_H and δ_C data as above].

FVP of the ylide **7 h** (230 mg) at 900 °C gave a solid at the furnace exit shown by ^{1}H and ^{31}P NMR spectroscopy and TLC to be a mixture of Ph_3PO and three hydrocarbons. These were separated by preparative TLC (Et_2O) to give a mixture (2 : 1) of (*E*)- and (*Z*)-5,7-dimethyl-2-propenylnaphthalene **15** (28.4 mg, 31%) (HRMS: found M^+, 196.1245. $C_{15}H_{16}$ requires *M*, 196.1252) [δ_H 7.9–7.7 (1 H, m), 7.65–7.3 (3 H, m), 7.05 (1 H, m), 6.75–5.75 (2 H, m), 2.59 (3 H, s), 2.42 (3 H, s) and 2.0–1.85 (3 H, m); *m/z* 196 (M^+, 78%), 181 (80), 165 (100), 152 (42), 141 (18), 128 (20), 115 (23), 89 (63), 82 (62) and 76 (55)] and 5,7-dimethyl-2-vinylnaphthalene **14** (17.5 mg, 21%) [δ_H and *m/z* data as above].

FVP of the ylide **7i** (440 mg) at 900 °C gave a solid at the furnace exit shown by ^{1}H and ^{31}P NMR spectroscopy and TLC to be a mixture of Ph_3PO and two hydrocarbons. These were separated by preparative TLC (Et_2O) to give 2-benzyl-5,7-dimethylnaphthalene **16** (33 mg, 16%) (HRMS: found M^+, 246.1417. $C_{19}H_{18}$ requires *M*, 246.1409) [δ_H 7.9–6.8 (10 H, m), 4.12 (2 H, s), 2.62 (3 H, s) and 2.44 (3 H, s); δ_C(non-aromatic signals only) 42.0, 21.6 and 19.2; *m/z* 246 (M^+, 100%), 231 (42) and 215 (45)] and 2,4-dimethyl-7*H*-benzo[*c*]fluorene **18** (26.6 mg, 13%) (HRMS: found M^+, 244.1258. $C_{19}H_{16}$ requires *M*, 244.1252) [δ_H 8.5–8.4 (2 H, m), 8.2–7.1 (6 H, m), 3.96 (2 H, s), 2.71 (3 H, s) and 2.63 (3 H, s); δ_C(non-aromatic signals only) 37.6, 22.2 and 20.2; *m/z* 244 (M^+, 100%), 229 (52) and 215 (45)].

FVP of the ylide **27** (462 mg) at 900 °C gave a solid at the furnace exit shown by ^{1}H and ^{31}P NMR spectroscopy and TLC to be a mixture of Ph_3PO and two other products. These were separated by preparative TLC (Et_2O) to give a liquid which proved by ^{1}H NMR spectroscopy and GC–MS to be a mixture of 5-benzylbenzo[*b*]thiophene **28** (41.6 mg, 20%) [δ_H 7.85–7.2 (10 H, m) and 4.07 (2 H, s); δ_C 41.8 (CH_2); *m/z* 226 (M^+, 16%), 225 (83), 224 (66), 222 (24), 208 (8), 189 (14), 178 (16), 147 (100), 121 (12), 111 (46), 89 (54), 86 (18) and 77 (19)] and 8*H*-fluoreno[3,4-*b*]thiophene **29** (27.7 mg, 14%) [δ_H 8.1–7.2 (8 H, m) and 3.93 (2 H, s); δ_C 37.2 (CH_2); *m/z* 224 (M^+, 20%), 223 (100), 222 (83), 222 (24), 189 (28), 176 (17), 163 (5), 150 (7), 111 (48), 89 (54), 98 (20), 88 (16) and 76 (7)].

FVP of the ylide **7e** (200 mg) at 830 °C gave a solid at the furnace exit which was shown by TLC to be Ph_3PO and in the cold trap a yellow oil (49 mg) which contained Ph_3PO and further components by ^{1}H NMR spectroscopy. The spectrum was identical to that below save for the presence of Ph_3PO.

Pyrolysis of 4-methoxycarbonyl-1-(2-methylphenyl)but-1-en-3-yne **8e** (70 mg) (obtained from low temperature pyrolysis of **7e**) at 830 °C gave a yellow oil (61 mg) which turned to a dark red colour on exposure to air. Analysis by ^{1}H NMR spectroscopy and GC–MS showed the presence of 2-methylnaphthalene **12** (21%) [δ_H 7.9–7.1 (7 H, m) and 2.48 (3 H, s); *m/z* 142 (M^+, 96%) and 141 (100)], 2-ethylnaphthalene **13** (58%) [δ_H 7.9–7.1 (7 H, m), 2.79 (2 H, q, *J* 8) and 1.31 (3 H, t, *J* 8); *m/z* 156 (M^+, 37%) and 141 (100)] and 2-vinylnaphthalene **9** (7%) [δ_H 7.9–7.1 (7 H, m), 6.91 (1 H, dd, *J* 18,11), 5.86 (1 H, dd, *J* 18,1) and 5.33 (1 H, dd, *J* 11,1); *m/z* 154 (M^+, 100%) and 153 (66)]. The spectrum also showed evidence of a small quantity of methanol [δ_H 3.47 (3 H, s) and 3.42 (1 H, br s)].

FVP of the ester **30** (116 mg) at 900 °C gave a liquid in the cold trap shown by ^{1}H NMR spectroscopy to contain 2-methylnaphthalene **12** (19.2 mg, 23%), 2-ethylnaphthalene **13** (17.1 mg, 19%) and 2-vinylnaphthalene **9** (14.9 mg, 17%); δ_H and *m/z* as above.

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References

1 Part 9, R. A. Aitken and N. Karodia, *Liebigs Ann. Recl.*, 1997, 779.
2 R. A. Aitken, C. Boeters and J. J. Morrison, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2473.
3 J. Becker, C. Wentrup, E. Katz and K.-P. Zeller, *J. Am. Chem. Soc.*, 1980, **102**, 5110.
4 Preliminary communication, R. A. Aitken, C. Boeters and J. J. Morrison, *Tetrahedron Lett.*, 1995, **36**, 1303.
5 D. W. Jones, R. S. Matthews and K. D. Bartle, *Spectrochim. Acta*, 1972, **28A**, 2053.
6 C. Graebe, *Ber. Dtsch. Chem. Ges.*, 1894, **27**, 952.
7 M. E. Gurskii, I. D. Gridnev, Yu. V. Il′ichev, A. V. Ignatenko and Yu. N. Bubnov, *Angew. Chem., Int. Ed. Eng.*, 1992, **31**, 781; H. Jiao and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1763.
8 H. Heimgartner, J. Zsindely, H.-J. Hansen and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 2924.
9 R. F. C. Brown and G. L. McMullen, *Aust. J. Chem.*, 1974, **27**, 2385.
10 M. Koller, M. Karpf and A. S. Dreiding, *Helv. Chim. Acta*, 1986, **69**, 560.
11 A. I. Meyers, R. J. Himmelsbach and M. Reuman, *J. Org. Chem.*, 1983, **48**, 4053.
12 A. R. Katritzky, G. J. Hitchings, R. W. King and D. W. Zhu, *Magn. Reson. Chem.*, 1991, **29**, 2.
13 R. A. Aitken and G. Burns, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2455.
14 W. C. Young, *Ber. Dtsch. Chem. Ges.*, 1892, **25**, 2102.
15 H. W. Gschwend and A. Hamdan, *J. Org. Chem.*, 1975, **40**, 2008.
16 W. Borsche, P. Hofmann and H. Kühn, *Liebigs Ann. Chem.*, 1943, **554**, 23.
17 G. B. Arrowsmith, G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1965, 2072.
18 R. A. Aitken and J. I. Atherton, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1281.

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