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Novel Thermal Cyclisation of *o*-Methylstyrylalkynes to give 2-Alkenylnaphthalenes

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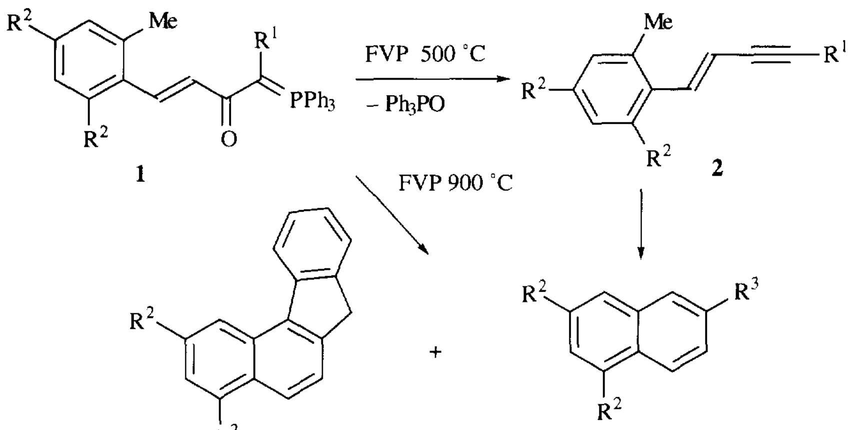
Abstract: Formation of *o*-methylstyrylalkynes by flash vacuum pyrolysis of the corresponding stabilised phosphorus ylides at 900 °C is accompanied by unexpected cyclisation to give 2-alkenylnaphthalenes and deuterium labelling has been used to elucidate the mechanisms involved.

In a recent paper we described the thermal extrusion of Ph_3PO from a series of cinnamoylalkylidenetriphenyl-phosphoranes using flash vacuum pyrolysis (FVP) at 500 °C to afford styrylalkynes.[1] Since styrylacetylene has been implicated as an intermediate in the mechanistically intriguing thermal conversion of azulene into naphthalene,[2] we were interested to see whether a secondary thermal cyclisation of the styrylalkynes might take place under more severe conditions to afford specifically substituted naphthalenes or azulenes. 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.

The required ylide precursors **1a-i**[3] were readily prepared by acylation of the appropriate ylides, $Ph_3P{=}CHR^1$, with 2-methyl- or 2,4,6-trimethyl-cinnamoyl chloride (Table 1). When these were subjected to FVP at 500 °C and 10^{-2} Torr in a conventional flow system (contact time $\approx 10^{-2}$ s), the expected extrusion of Ph_3PO took place in line with our previous results,[1] to afford the styrylalkynes **2** in variable yield and with little *E-Z* isomerisation (Table 1).

When these products were repyrolysed at 900 °C or, more conveniently, when ylides **1** were subjected directly to FVP at 900 °C, a variety of substituted naphthalenes **3-10** were produced in moderate yield. As shown in Table 1, ylides **1a**, **1b**, **1f** and **1g** with R^1 = Me or Et gave the 2-vinyl products, while **1c** and **1h** with R^1 = Pr^i gave mainly the 2-propenyl naphthalenes, but accompanied by some vinyl product. For **1d** the main product was 2-benzylnaphthalene **5**, accompanied by the product of a further cyclisation, benzo[*c*]fluorene **11**. The latter was identified spectroscopically[4] and was also produced by separate FVP of an authentic sample of **5**[5] at 950 °C, but only to a small extent (7%) with the remainder of **5** being recovered unreacted.[6] This indicates that **11** is most probably a primary product of the cyclisation and is not derived from **5**. The products from methoxycarbonyl ylide **1e** are at first sight surprising, but they are in fact secondary fragmentation products of methyl 2-naphthylacetate since FVP of the latter at 900 °C produced a similar mixture of 2-methyl, 2-ethyl and 2-vinylnaphthalenes. The mechanism of this transformation is unclear but we believe it to be similar to that involved in the degradation of the 2-alkyl group of 2-alkyl-3-benzofuryl radicals,[7] *i.e.* to involve intermolecular homolytic substitution by a 2-naphthylmethyl radical on methyl 2-naphthylacetate as the route to 2-ethylnaphthalene.



1 **2**

11 $R^2 = H$

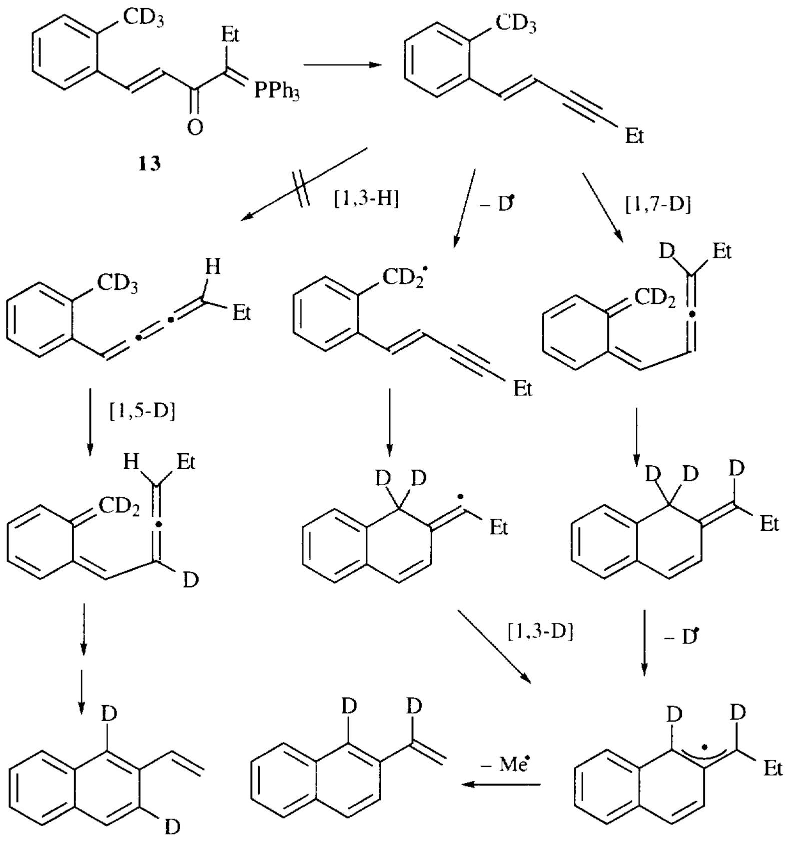
12 $R^2 = Me$

	R^2	R^3		R^2	R^3
3	H	CH=CH$_2$	**8**	Me	CH=CH$_2$
4	H	CH=CHMe	**9**	Me	CH=CHMe
5	H	CH$_2$Ph	**10**	Me	CH$_2$Ph
6	H	Me			
7	H	Et			

Table 1 Formation of ylides **1**, **13** and **17** and results of their FVP at 500 and 900 °C

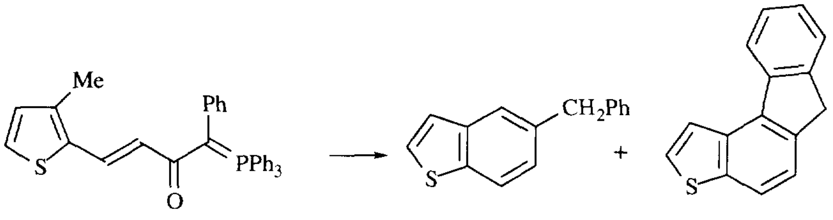
	R^1	R^2	Yield (%)	δ_P	**2** at 500 °C Yield (%)	**2** at 500 °C *E/Z* ratio	Products at 900 °C Yield (%)
1a	Me	H	41	17.7	15	85/15	**3** (15)
1b	Et	H	66	17.7	77	98/2	**3** (31)
1c	Pr^i	H	54	16.0	75	>95/5	**4** (36), **3** (18)
1d	Ph	H	42	15.7	65	85/15	**5** (25), **11** (9)
1e	CO$_2$Me	H	77	18.9	92	97/3	**7** (58), **6** (21), **3** (7)
1f	Me	Me	36	18.1	48	>95/5	**8** (52)
1g	Et	Me	58	18.0	45	>95/5	**8** (56)
1h	Pr^i	Me	62	16.0	70	>95/5	**9** (31), **8** (21)
1i	Ph	Me	40	15.95	19	85/15	**10** (16), **12** (13)
13	—	—	41	17.8	—		**15** (21)
17	—	—	57	15.8	—		**18** (20), **19** (14)

A number of mechanistic possibilities for the formation of the alkenylnaphthalene products are illustrated for the case of trideuteriomethyl ylide **13** related to **1b** below. Isomerisation of the initially formed enyne to the 1,2,3-triene would allow a subsequent [1,5] hydrogen shift and cyclisation to give **16** as already reported for the closely related *o*-alkylphenylallenes.[8] This process is also closely analogous to the McMullen reaction reported by Brown,[9] in which *o*-methylbenzylideneketene cyclises to 2-naphthol. Alternatively, a [1,7] hydrogen shift, a well precedented process which has been of recent theoretical interest,[10] followed by a 6π electrocyclisation affords an intermediate which can readily lose the benzylic hydrogen atom to afford the highly stabilised radical **14**. This can account for most of the observed products either by loss of H• or Me• (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 Dreiding for the related *o*-tolyl alkynyl ketones.[11] A further possibility is initial loss of a benzylic hydrogen atom followed by radical cyclisation as shown and subsequent [1,3] hydrogen shift to give the same intermediate **14**. 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.



16 **15** **14**

In order to distinguish between these possibilities the trideuteriomethyl ylide **13** was prepared. A sample of $[^2H]_3$-*o*-tolualdehyde was obtained by *ortho* lithiation of 2-phenyl-4,4-dimethyloxazoline, alkylation with CD_3I and reductive removal of the oxazoline.[12] Claisen condensation of this with ethyl acetate followed by hydrolysis, chlorination and treatment with $Ph_3P{=}CHEt$ then afforded **13**. 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[13] was exclusively the 1,1'-isomer **15**.[14] This clearly rules out the mechanism involving a [1,5] hydrogen shift but does not distinguish between the remaining two possibilities which both involve **14**.[15] The unusually severe conditions required to bring about the reaction (the enynes are recovered unchanged from FVP at temperatures up to 850 °C) perhaps favours the radical route.



17 **18** **19**

Despite the disappointing yield obtained in some cases we believe this reaction to have some potential for the synthesis of specifically substituted naphthalenes and related systems. This is illustrated by FVP of **17** which produced a mixture of 5-benzylbenzothiophene and the previously unknown 8*H*-fluoreno[3,4-*b*]thiophene **19**.

References and Notes

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14. **15**: δ_C as **3** except for the absence of 136.9 (C-1') and 126.4 (C-1); δ_H as **3** except for the absence of 7.65 (H-1) and 6.80 (H-1'); δ_D 7.66 (1 D) and 6.79 (1 D).
15. A referee has suggested an additional mechanistic variation which we cannot exclude, namely that the product shown as arising from the concerted [1,7] H shift might alternatively be formed in a homolytic process by rearrangement of the 1,2-diradical implicit in the *E/Z* isomerisation of the enyne followed by abstraction of the benzylic hydrogen atom by the resulting allenyl radical.

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