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Acephenanthrylenes from flash vacuum thermolysis of diarylmethylidenecycloproparenes

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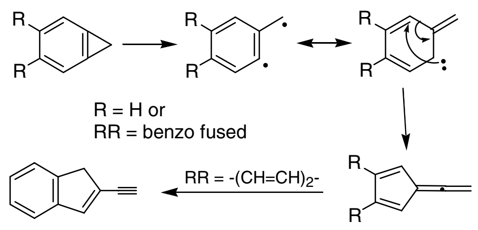
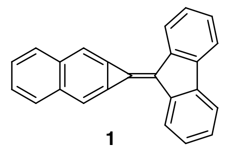
Abstract—Upon flash vacuum thermolysis at 750 °C fluorenylidenecyclopropa[*b*]naphthalene (**1**) undergoes opening of the three-membered ring and rearrangement to give a range of $C_{24}H_{14}$ polycyclic aromatic hydrocarbons. Dibenz[*e*.*l*]- and -[*e*.*k*]acephenanthrylene (**7**) and (**12**), respectively, have been identified while the plausible naphth[1,2-*e*]- and [2,3-*e*]acephenanthrylenes (**9**) and (**14**) were not detected. With diphenylmethylidenecyclopropa[*b*]naphthalene (**2**) cyclodehydrogenation and rearrangement also provide $C_{24}H_{14}$ polycycles; dibenz[*e*.*k*]acephenanthrylene (**12**) is identified and dibenz[*a*.*e*]aceanthrylene (**15**) is a proposed product.

The novel aromatic alkylidenecycloproparenes, for example, **1**,[1,2] and **2**[3] have continued to provide a source of fascination[4,5] since their discovery in 1984,[6] not least because the various derivatives have unexpected polarities,[1,7,8] fluorescence characteristics,[9] and unusual properties.[4,10,11] Recently, we described protocols that allow for the synthesis of an extensive series of 1-aryl- and 1-diarylmethylidene-1*H*-cyclopropa[*b*]naphthalenes, their polarities, and the linear dependence of their cycloproparenyl ^{13}C NMR chemical shifts upon the Hammett σ_p^+ constant of the remote aryl substituent.[7] Despite these various studies, there has been only one examination of an alkylidenecycloproparene under flash vacuum thermolysis (FVT) conditions, namely that specifically targeted[12] to provide propadienone **4** from fragmentation of the Meldrum's acid derivative **3**. Nonetheless, the behaviour of parent hydrocarbons 1*H*-cyclopropabenzene[13] and 1*H*-cyclopropa[*b*]naphthalene[14] were examined some considerable time ago and, as illustrated in Scheme 1, they ring open and contract by a Wolff-like rearrangement to fulvenallenes, with the benzo derivative from cyclopropa[*b*]naphthalene rearranging further to indenylethyne.



Scheme 1.



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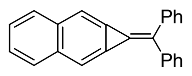

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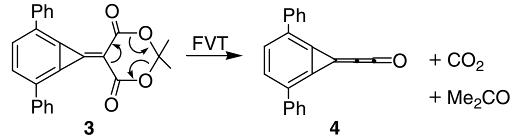

3 **4**

Herein, the results of FVT of fluorenylidene- (**1**) and diphenylmethylidene- (**2**) cyclopropa[*b*]naphthalene at 750 °C are provided. They demonstrate that comparable ring contraction to propatrienes is thwarted by preference for ring expansion that involves the terminal alkene substituent and formation of polycyclic aromatic hydrocarbons (PAHs) notably in the acephenanthrylene series.[15]

Keywords: Flash vacuum thermolysis; Strained molecules; Acephenanthrylenes; Polycyclic aromatic hydrocarbons.

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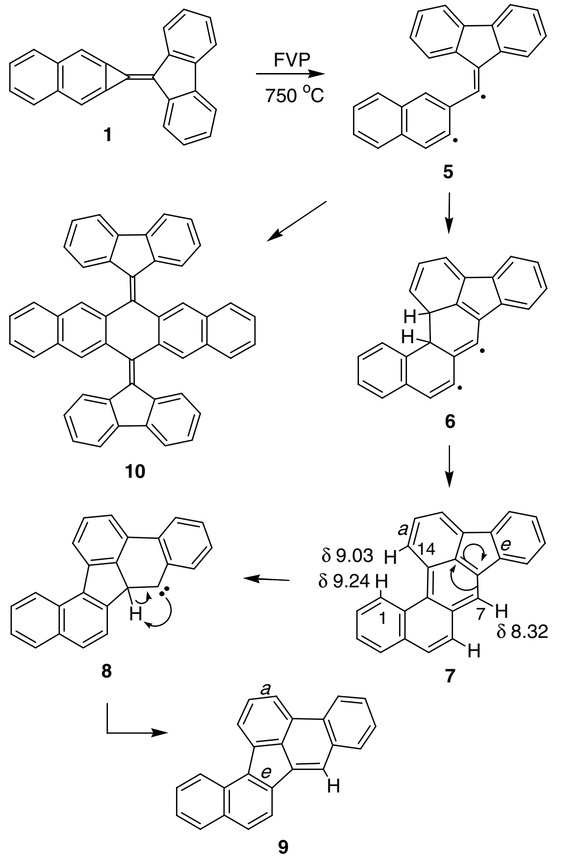
Alkylidenecycloproparenes **1** and **2** are easily available from the corresponding parent hydrocarbon[1,3,7] and each has thermal stability to temperatures above the melting point thereby allowing for sublimation into the hot zone of a conventional FVT apparatus[16] without decomposition. With the hot tube at 750 °C and a pressure of 2×10^{-2} mmHg, fluorenylidene **1** sublimes into the hot zone well below its melting point, and product is deposited almost immediately after the hot zone and before the cold trap. Conventional workup and separation (Supplementary data) gives PAH products. In contrast, diphenyl **2** (mp 112 °C) is vaporized slowly at 155 °C but it too deposits FVT products just beyond the hot zone.

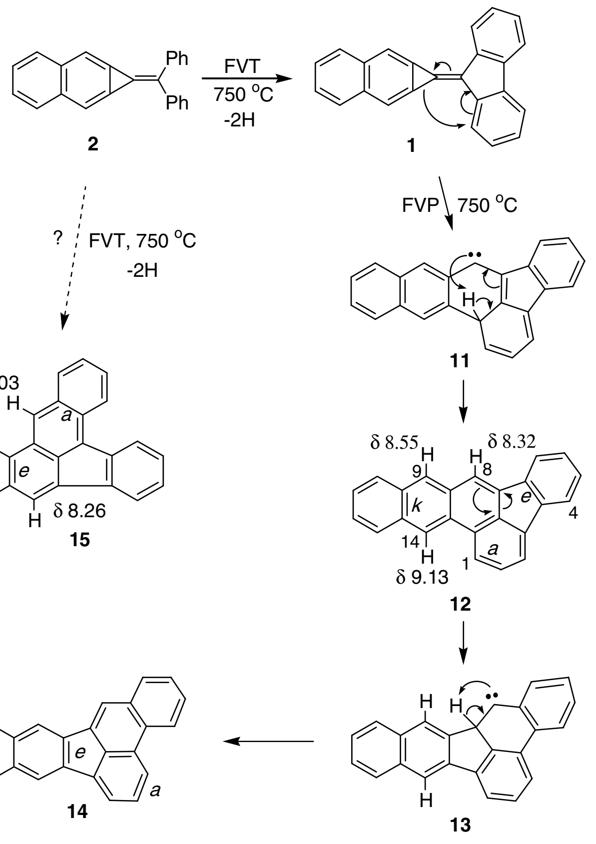
The crude product mixtures from **1** and **2** provided proton NMR spectra that clearly demonstrate loss of the molecular symmetry that is present in the substrates; no evidence was gained to support the formation of propatriene analogues of fulvenallene or their derivatives. The pyrolysate from **1** provided a yellow solid that comprised of at least six components. Careful chromatographic separations and subsequent crystallizations (Supplementary data) afforded dibenz[*e.l*]acephenanthrylene (**7**) as yellow crystals in a combined 47% yield. The ^{1}H NMR spectroscopic data were in full agreement with those reported by Cho.[17] In particular, the bay region protons H1 and H14 are doublets (J 8.5 Hz) at δ 9.24 and δ 9.03, respectively, and H7 appears as the only singlet at δ 8.32. Moreover, in the (previously unreported) ^{13}C NMR spectrum C1/C14 appeared at δ 119.4/121.2, and all 12 of the CH moieties and 9 of the 10 quaternary carbon atoms were discernable; one of the last is overlapped (Supplementary data). The formation of **7** is best rationalized by opening of the strained three-membered ring σ bond to give diradical **5**, which then cyclizes to **6** and aromatizes to **7** as shown in Scheme 2.

Subsequent chromatography fractions gave mixtures of **7** with a second PAH, but only traces (<4%) of the pure material were isolated; this was shown to be dibenz[*e.k*]acephenanthrylene (**12**)[18] identical to the material isolated from FVT of **2** (see Scheme 3 and below). The ^{1}H NMR spectrum of this compound displayed all of the peaks listed by Cho et al.[19,20] and, in particular, the three low field singlets at δ 8.27, 8.51 and 9.09, assigned to H8, H9 and H14, respectively, were observed at δ 8.32, 8.55 and 9.13. The ^{13}C NMR spectrum of **12** (previously unreported) displays 22 of the 24 carbons as distinct signals (Supplementary data) and the electronic absorption spectrum is fully in accord with the published data.[19] A later, slower moving fraction was obtained and this provided traces of a purple solid shown to be a dimer of **1** [m/z 604 (42%), 302 (100)] and proposed as the pentacene derivative **10**, from linear coupling of the ring opened diradical as occurs with Ag(I)-assisted ring opening of cycloproparenes.[21,22]

In contrast to the above, FVT of **2** is less easily achieved but provides, after careful chromatography, pale yellow needles of dibenz[*e.k*]acephenanthrylene (**12**)[18] in low



Scheme 2.



Scheme 3.

(7%) yield (Scheme 3). A second component, obtained as a different yellow crystalline $C_{24}H_{14}$ hydrocarbon (m/z 302) in 12% yield is tentatively proposed as dibenz[*a.e*]aceanthrylene (**15**) from its physical characteristics and ^{1}H NMR spectroscopic data that agree fully with those reported by Cho and Harvey,[19] and subsequently refined by them with Kim in 1993.[20] Again the identity of the low field singlets at δ 8.26 (H9) and 9.03 (H14) with those reported (δ 8.24 and 9.00, respectively) together with identical chemical shifts and coupling patterns for the remaining 12 protons supports the assignment. Whereas a straightforward mechanistic pathway exists for the formation of **12** via **1** and **11** (Scheme 3), with the only variable being the point at which cyclodehydrogenation between the two phenyl substituents takes place, no such easy-to-describe pathway exists for the **2**→**15** transformation.

Not all of the $C_{24}H_{14}$ hydrocarbon products from **1** and **2** were able to be separated by the facilities available. However, it seems clear that automerization[23] in analogy to that of acephenanthrylene itself[24] could transform the initial products **7** and **12** into the known[25,26] naphth[1,2-*e*]acephenanthrylene (**9**), and its [2,3-*e*] isomer (**14**),[27] respectively, as shown in Schemes 2 and 3.

While the results recorded here are open to further refinement, it is clear that the simple diarylmethylidenecycloproparenes readily transform into acephenanthrylenes upon FVT. The area is open to anyone who wishes to follow so that the full range of products may be delineated.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.12.047.

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