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The Ethyne-Ethylidene Rearrangement: Formation of 3-Ethynyl- and 1-Ethynylacenaphthylene on Flash Vacuum Pyrolysis of 1,7-Diethynylnaphthalene

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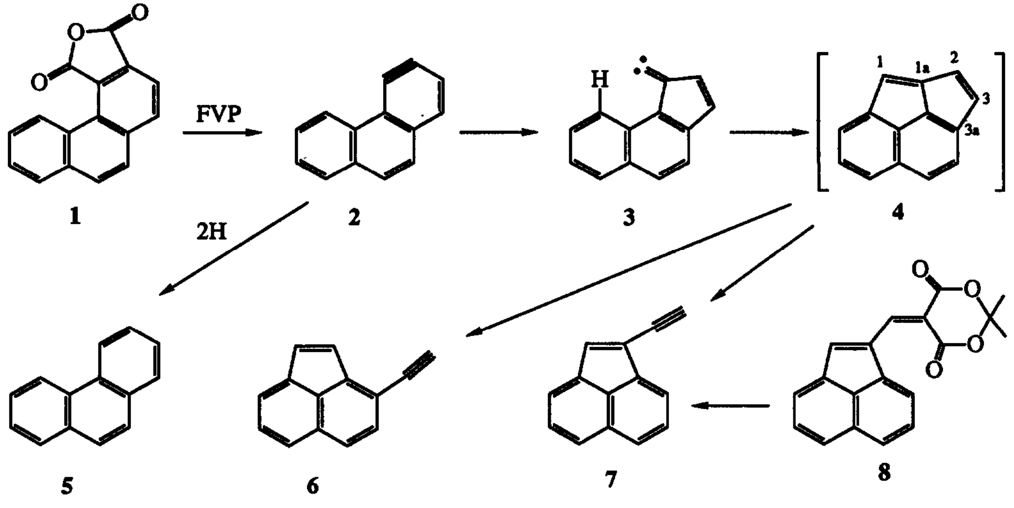
Abstract: 1,7-Diethynylnaphthalene on flash vacuum pyrolysis at 1100°C/0.05 mm gave 3-ethynylacenaphthylene and 1-ethynylacenaphthylene (80:20). This finding is interpreted in terms of initial formation of 3-ethynylacenaphthylene, ring closure of some of this compound to the hypothetical cyclopent[*bc*]acenaphthylene and cleavage to give 1-ethynyl- and 3-ethynylacenaphthylene.

Arylacetylenes, $\mathrm{ArC{\equiv}CH}$, undergo reversible rearrangement to arylidenecarbenes, $\mathrm{ArCH{=}C}$:, under the conditions of flash vacuum pyrolysis (FVP) (700-800°C/0.02 mm).[1] Carbenes formed in this way can be trapped intramolecularly by insertion into an aromatic C–H bond.[2] Thus, 1-ethynylnaphthalene on FVP at 850°/0.05 mm gave acenaphthylene (80%), and 2-ethynylbiphenyl at 700°/0.2mm gave a mixture of phenanthrene and 1,2-benzazulene (72:28, 99%). These findings have been extended by L.T. Scott and his co-workers[3] who used this process to convert two ethynyl groups into two aryl rings in an elegant synthesis of corannulene by pyrolysis of 7,10-diethynylfluoranthene at 1000°C/10^{-4} Torr.

The benzyne-cyclopentadienylidenecarbene rearrangement is analogous to the ethyne-ethylidene rearrangement. It occurs in benzyne and other arynes at high temperatures.[4,5,6] The arynes can be obtained by FVP of arene-1,2-dicarboxylic anhydrides and the exocyclic carbene formed on rearrangement of the aryne can be trapped intramolecularly.[7] We are currently exploring the limitations of these trapping reactions.

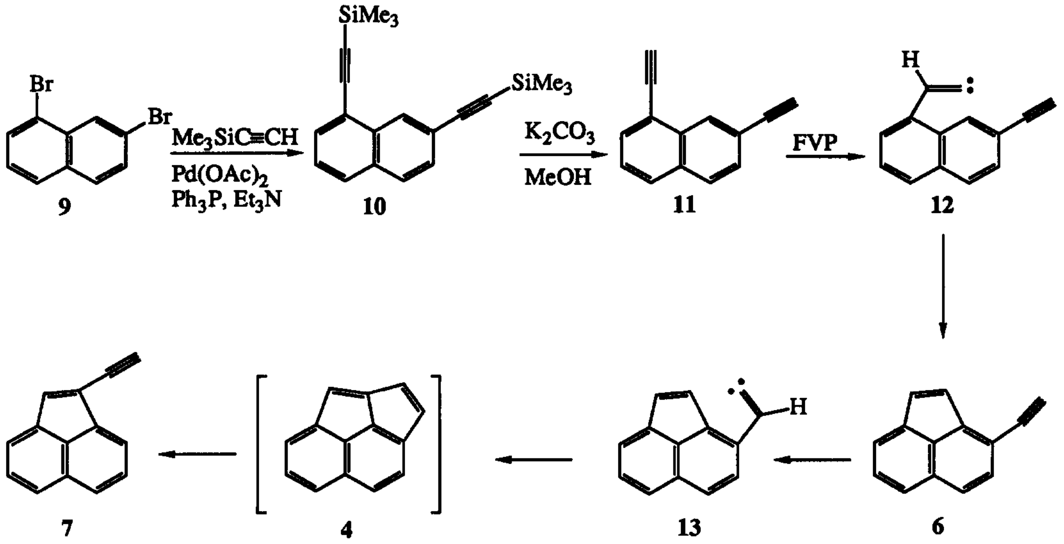
Pyrolysis of phenanthrene-3,4-dicarboxylic anhydride **1** (860°/0.02 mm) yielded 1-ethynylacenaphthylene **7**, 3-ethynylacenaphthylene **6** and phenanthrene **5**.[8] The mechanism proposed for this transformation (Scheme 1) involved ring contraction of 3,4-phenanthryne **2** and trapping of the carbene **3** to form the highly strained tetracyclic hydrocarbon cyclopent[*bc*]acenaphthylene **4**. Cleavage of the 1a-2 or the 3-3a bond in **4** gave the ethynyl derivatives. The phenanthrene **5** arose from a reductive process often observed in reactions like this where reactive intermediates abstract hydrogen from pyrolytic fragments.

We previously described FVP of the Meldrum's acid derivative **8** which at 860°/0.03 mm gave 1-ethynylacenaphthylene **7**.[8] There was no evidence that the proposed intermediate **4** was formed in this reaction but we now show that this temperature (860°) was too low to achieve isomerization of **7** to **6** *via* **4**.



Scheme 1

To investigate this matter further, we have developed a new synthesis of 3-ethynylacenaphthylene **6**. 2-Bromonaphthalene was brominated in poor yield to form 1,7-dibromonaphthalene **9** [9] and this was converted into 1,7-bis(trimethylsilylethynyl)naphthalene **10**.[10,11] Desilylation with K_2CO_3 in methanol gave 1,7-diethynylnaphthalene **11** [12] as an unstable oil which was pyrolysed immediately after isolation (Scheme 2).



Scheme 2

A sample of 1,7-diethynylnaphthalene **11** was pyrolysed at 860°, the pyrolysate was repyrolysed at 1050° and the resulting pyrolysate was again pyrolysed at 1100°. Each pyrolysate was examined using ^{1}H n.m.r. spectroscopy and the products were identified and their proportions estimated. Pyrolysis of 1,7-diethynylnaphthalene (15.8 mg, empty tube, 860°, 0.03 mm, 60-80°, 30 min) gave a yellow oil (14.5 mg) consisting of 1,7-diethynylnaphthalene (69%) (δ 3.51, s, 3.20, s, 2× $\equiv$CH) and 3-ethynylacenaphthalene (31%) (δ 7.17, d, *J* 5.3 Hz, H2; 7.06, d, *J* 5.3 Hz, H1; 3.40, s, $\equiv$CH); (14.5 mg; empty tube, 1050°, 0.03 mm, ambient, 10 min) yellow oil (9.6 mg) consisting of 1,7-diethynylnaphthalene (6%), 3-ethynylacenaphthylene (88%) and 1-ethynylacenaphthylene (6%) (δ 7.32, s, H2; 3.48, s, $\equiv$CH); (9.6 mg, packed tube, 1100°, 0.05 mm, ambient, 10 min, some blackening of tube) yellow oil (1.7 mg) consisting of 3-ethynylacenaphthylene (80%) and 1-ethynylacenaphthylene (20%). Analysis by HPLC[14] confirmed the presence of 1-ethynyl- and 3-ethynylacenaphthylene and showed that a trace of phenanthrene was present.

FVP of 1,7-diethynylnaphthalene (10.9 mg; packed tube, 1110°, 0.05 mm, ambient, 15 min, some blackening of tube) left an unsublimed residue of 6.6 mg and gave a pyrolysate as a yellow oil (1.5 mg) consisting of 3-ethynylacenaphthylene (80%) and 1-ethynylacenaphthylene (20%). The identities of the products were confirmed by their retention times on HPLC and a trace of phenanthrene was shown to be present.

It is proposed that the conversion of 1,7-diethynylnaphthalene into 1-ethynylacenaphthylene involves sequential ethyne-ethylidene rearrangements: The first leads to formation of the carbene **12** and insertion into the aryl C–H bond to form **6**. This cyclisation requires >860°. The second proceeds through the carbene **13** and considerable vibrational energy is required (> 1050°) to allow insertion into the olefinic C–H bond to form the strained tetracyclic intermediate **4**. From the earlier work[8] cleavage of **4** is expected to give **6** and **7** in a ratio of 30:70. We regard these findings as confirmatory evidence for the intermediacy of **4** and estimate that at 1100° about 28% of the material passing through the pyrolysis tube is converted into the tetracyclic intermediate. The possibilities that the rearrangement takes place by skeletal rearrangement of the acenaphthylene system or by migration of the ethynyl group in a series of shifts are considered unlikely. The presence of a trace of phenanthrene in the pyrolysate formed at 1100° points to the possibility of an alternative breakdown of the intermediate **4** *via* **3** and **2**.

Acknowledgements

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11. 1,7-Bis(trimethylsilylethynyl)naphthalene: Following the method of Austin *et al.*[10], 1,7-dibromonaphthalene (1.00 g, 3.5 mmol), ethynyltrimethylsilane (1.5 ml, 10.5 mmol), palladium acetate (25 mg) and triphenylphosphine (50 mg) were heated under reflux under nitrogen in deaerated triethylamine (20 ml) for 48 h. Triethylamine hydrobromide was removed by filtration, and the filtrate yielded a dark brown oil. Flash chromatography of this oil (silica, ethyl acetate/light petroleum 1:4) gave *1,7-bis(trimethylsilylethynyl)naphthalene* as a green oil (438 mg, 39%) (Found: *m/z* 320.14±0.003. $C_{20}H_{24}Si_2$ requires M, 320.1416). ν_{max} (film) 2153m cm^{-1} (C≡C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.30 and 0.35, 2×s, 2×SiMe_3; 7.40, dd, *J* 8.2, 7.4 Hz, 1H; 7.52, dd, *J* 8.4, 1.6 Hz, 1H; 7.53-7.69, m, 3H; 8.47, br s, H8. ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 0.11, 2×SiMe_3; 93.52, 100.41, 102.70, 105.63, 2×C≡C; 120.80, 121.49, 132.63, 133.04, C1, 4a, 7, 8a; 126.07, 128.30, 128.75, 129.16, 130.67, 131.40, C2-6 and C8. MS (EI): *m/z* 320 (M, 75%), 306 (30), 305 (100), 145 (27), 73 (41).

12. 1,7-Diethynylnaphthalene: Desilylation of 1,7-bis(trimethylsilylethynyl)naphthalene (93 mg) with anhydrous potassium carbonate (75 mg) in anhydrous methanol (3 ml)[10] for 3.5 h under nitrogen at room temperature afforded a green oil (51 mg). Purification by preparative TLC (ethyl acetate/light petroleum, 1:4) gave *1,7-diethynylnaphthalene* (23 mg, 50%) as a green oil which tended to darken on standing and was best used immediately. (Found: *m/z* 176.062±0.002. $C_{14}H_8$ requires 176.0626). ν_{max} 3294s (H–C≡), 2106w (C≡C) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.20 and 3.51, 2×H–C≡; 7.44, dd, *J* 8.3, 7.2 Hz, H3; 7.57, dd, *J* 8.5, 1.6 Hz, H6; 7.75, dd, *J* 7.2, 1.1 Hz, H2; 7.78-7.84, m, 2H, H4,5; 8.54, br s, H8. ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 78.21, 82.84, 2×H–C≡; 81.26, 84.02, 2×–C≡; 119.84, 120.66, 132.78, 133.10, C1, 4a, 7, 8a; 126.24, 128.52, 129.10, 129.31, 130.59, 131.94, C2-6 and C8. MS (EI): *m/z* 176 (M, 100%), 175 (11), 174 (10), 150 (11), 98 (4), 88 (12), 87 (5), 75 (12), 74 (6).

13. Pyrolysis apparatus: A silica tube (40 cm×2.5 cm i.d.) was heated with an external electric furnace (Lindberg Type 550035) which gave a hot zone of 30 cm. The tube could be packed with 5 mm lengths of silica tubing (8 mm o.d.). The temperature was measured with a chromel-alumel thermocouple placed on the outer surface at the centre of the tube, and the pressure was measured near the cold finger condenser containing liquid nitrogen. The sample was vaporized from a Pyrex test tube heated with an air bath. Conditions are reported as (tube temperature, pressure, air bath temperature, time to vaporize the sample).

14. HPLC (see reference 8 for instruments and column): CH_3CN/H_2O, 1:1 → 9:1, over 1 h at gradient 3. Retention times were compared directly with those from a pyrolysate of 4-phenylnaphtho[1,2-*c*]furan-1,3-dione: 1-ethynylacenaphthylene 22.76 min; 3-ethynylacenaphthylene 23.6 min; phenanthrene, 26.41 min.

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