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Thermolysis of Benzo[*c*]phenanthrene: Conversion of an Alternant $C_{18}H_{12}$ PAH into Non-alternant $C_{18}H_{10}$ PAHs.

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Abstract: The product composition of the pyrolysates obtained upon thermolysis of the alternant $C_{18}H_{12}$ PAH benzo[*c*]phenanthrene (**1**) is markedly pressure dependent. At 0.1-0.5 Torr (N_2 carrier gas, 1050-1150 °C) **1** is converted into the non-alternant $C_{18}H_{10}$ PAH's cyclopenta[*cd*]pyrene (**4**) and benzo[*ghi*]fluoranthene (**5**) which have been identified as abundant combustion effluents and are associated with fullerene formation.

In a recent Letter,[1] it has been reported that Flash Vacuum Thermolysis (FVT; unpacked quartz tube, 1000-1150 °C) of the alternant polycyclic aromatic hydrocarbon (PAH) 1-chlorobenzo[*c*]phenanthrene gave access to the non-alternant PAH benzo[*ghi*]fluoranthene (**5**,[2] yield 53%). Under similar conditions the parent compound benzo[*c*]phenanthrene (**1**)[3] was recovered unchanged. Hence, it was concluded[1] that the *peri* aryl C-H bonds of **1** are not labile enough to generate an aryl diradical, such as **7**, which may undergo cyclization to **5**.

Here we wish to report, however, that the pyrolysate product composition obtained for **1** is markedly pressure dependent. At 0.1-0.5 Torr (flow thermolysis, N_2 carrier gas) and T>1000 °C **1** is converted into the non-alternant $C_{18}H_{10}$ PAH's cyclopenta[*cd*]pyrene (**4**)[4] and benzo[*ghi*]fluoranthene (**5**,[2] Scheme 1).

Thermolysis of benzo[*c*]phenanthrene (**1**, 100 mg aliquots, unpacked quartz tube 40 cm, subl. temp. 120 °C, rate 0.1 gh^{-1})[4] gave only deposits behind the hot zone; no volatiles were found in the cold trap. ^1H NMR, IR, GC-MS and HPLC revealed that the pyrolysates consist of **1**, **4**, **5** and a small amount of phenanthrene (**6**)[5]. With increasing pressure and temperature an enhanced conversion of **1** is observed (Table 1). Although at 0.5 Torr and 1150 °C a thin carbon lining is formed on the hot surface of the quartz tube, the mass recovery remains

Scheme 1

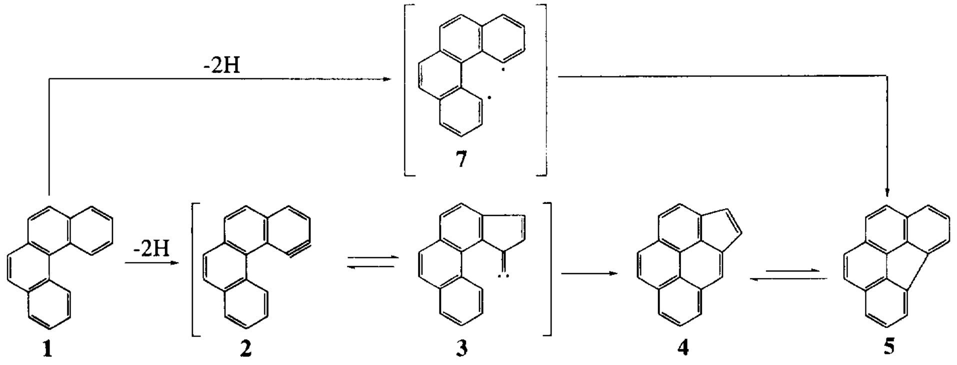

Table 1. Product Composition of the Pyrolysates obtained by Thermolysis of **1**.

p (Torr)	T (^{o}C)	**1** (%)	**4** (%)	**5** (%)	**6** (%)	**Mass Recovery** (%)
0.01	950	100	--	--	--	95
0.01	1050	90	3	4	3	95
0.01	1150	75	11	11	3	95
0.1	1050	72	12	12	4	91
0.1	1150	63	16	18	3	74
0.5	1050	59	17	20	4	73
0.5	1150	29	41	26	4	60

reasonable (60%). At 1.0 Torr only carbonization occurred! The conversion data concomitant with temperature and pressure suggest that both **4** and **5** arise *via* direct pathways from **1**. No clear shift in the product ratio **4/5**, as expected for a consecutive process, is found.

The formation of **4** from **1** can be rationalized by invoking the benzyne-cyclopentadienylidene carbene rearrangement,[6] *i.e.* the formation of 1,2-dehydrobenzo[*c*]phenanthrene (**2**) *via* homolysis of a *peri* aryl C-H bond[7] followed by loss of a vicinal hydrogen (Scheme 1). Benzyne derivative **2** will equilibrate with its carbene isomer **3**, which then gives **4** *via* intramolecular trapping (C-H insertion). Recently, a similar mechanism has been proposed for the FVT conversion of triphenylene into cyclopent[*hi*]acephenanthrylene.[8] The interconversion of **4** and **5** can occur *via* ring-contraction/ring-expansion, *i.e.* the exchange of a five- and a six-membered ring.[9] Notwithstanding, we expect that under the thermolysis conditions **5** will also be directly formed *via* the 1,12-diradical **7**[10] derived from **1** (Scheme 1). Independent thermolysis of **4** gave pyrolysates containing both **4** and **5** (0.01 Torr; 1050 ^{o}C, **4/5** 99/1% and 1150 ^{o}C, **4/5** 97/3%, 0.1 Torr; 1050 ^{o}C, **4/5** 98/2% and 1150 ^{o}C, **4/5** 94/6% and 0.5 Torr; 1050 ^{o}C, **4/5** 94/6% and 1150 ^{o}C, **4/5** 91/9% with mass recoveries in the range 95/65% for 0.01/0.5 Torr). It has already been established that **5** rearranges to **4** (FVT, 1175 ^{o}C; **4/5** 12/35%).[1]

The conversion of **1** into **4** and **5** provides an example that under high temperature conditions an alternant PAH can be efficiently converted into non-alternant PAH's. Both **4** and **5** have been identified as important combustion effluents[11] and are associated with fullerene formation.[12]

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