Preparative Flash Vacuum Thermolysis.[1] A Short Synthesis of Cyclopenta[*c,d*]pyrene

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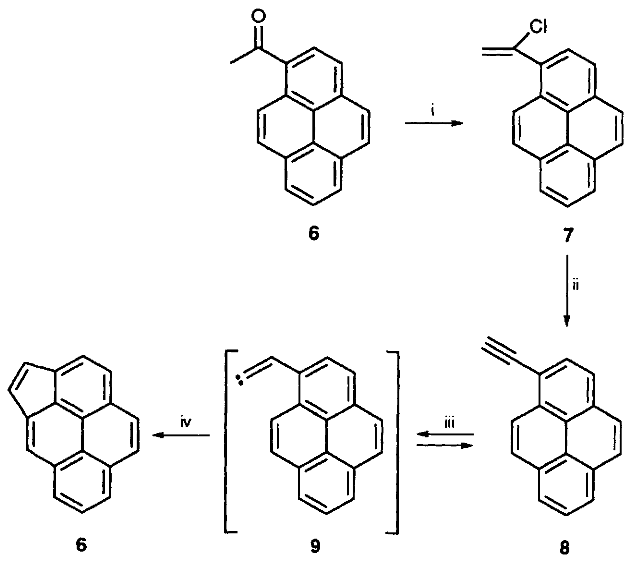
Flash vacuum thermolysis (FVT) of 1-chloro-1-(pyren-1-yl)ethene at 1000 °C gives the combustion emittant cyclopenta[*c,d*]pyrene in good yields; the identification of 1-(pyren-1-yl)ethyne as an intermediate in the range 600–900 °C indicates that cyclopenta[*c,d*]pyrene is formed *via* an ethynyl–ethylidene carbene rearrangement.

The significant formation of the non-alternant polycyclic aromatic hydrocarbon (PAH) cyclopenta[*c,d*]pyrene **10** in combustion processes, in combination with its mutagenic and carcinogenic activity,[2–6] has stimulated the development of synthetic approaches towards **10** to enable the systematic investigation of its chemical, physical and biological properties. Thus far, with the exception of the pyrolysis of 2-(pyren-1-yl)ethanol (850 °C), which only gives access to small amounts of **10**,[7] and a recommended route from 1,2,3,6,7,8-hexahydropyrene,[6] pyren-4-yl acetic acid has been the key synthon in all of the reported syntheses.[8] However invariably, all these preparations of **10** require lengthy or tedious procedures.

Here, we report a new efficient gram-scale synthesis of cyclopenta[*c,d*]pyrene **10** from 1-chloro-1-(pyren-1-yl)ethene **7** using FVT.[9] Our approach was based on the work of Brown and coworkers, who discovered the occurrence of ethynyl–ethylidene carbene rearrangements under the high temp. conditions of FVT.[10] Their observation that (1-naphthyl)-ethyne **4** is efficiently converted into acenaphthylene **5** in the dilute gas phase is of particular interest in relation to why cyclopenta-fused aromatics are formed as major combustion products. They found that **5** was formed from (1-naphthyl)-ethyne **4** *via* an intramolecular insertion of its ethylidene carbene tautomer into a *peri*-carbon–hydrogen bond.[10,11] However, the synthesis of **4** was only achieved in a low yield (18%).

Because of this somewhat troublesome access to the ethynyl moiety, we reasoned that treatment of 1-acetylnaphthalene **1** with phosphorus pentachloride[12] would give access to 1-(naphthyl)-1,1-dichloroethane **2** and 1-chloro-(1-naphthyl)-ethene **3** as suitable FVT precursors to **4** *via* elimination of hydrogen chloride. Both **2** and **3** were found to be excellent precursors for the generation of the ethynyl functionality† in **4** upon FVT.[1,13] At 800 °C, **4** was formed in 71% yield, while the reaction ultimately proceeded quantitatively to acenaphthylene **5** at 1000 °C (10^{-2} Torr, mass recovery 80%).



Scheme 1 *Reagents and conditions*: i, PCl_5, CH_2Cl_2, 5 h, reflux; $-HCl$; ii; FVT (600–700 °C, 10^{-2} Torr); iii, FVT (700–800 °C, 10^{-2} Torr); iv, FVT (800–1000 °C, 10^{-2} Torr); intramolecular C–H insertion, 1,2 H shift

Based on these observations we followed the same synthetic approach for the synthesis of cyclopenta[*c,d*]pyrene (**10**, Scheme 1). Treatment of 1-acetylpyrene **6**‡ with phosphorus pentachloride gave 1-chloro-1-(pyren-1-yl)ethene (**7**, 69%). Apparently, in this case, the primary product 1,1-dichloro-1-(pyren-1-yl)ethane eliminates quantitatively one molecule of hydrogen chloride under the reaction conditions.§ Then, 1-chloro-1-(pyren-1-yl)ethene **7** was slowly sublimed into the quartz tube at the temps. shown in Table 1 (10^{-2} Torr, sublimation temp. 130 °C; sublimation rate 1 g h^{-1}). In all cases, a solid was deposited closely behind the hotzone, while no volatile products, except hydrogen chloride, were found in the liquid N_2 cold trap. As the deposit changes from colourless to yellow to bright orange[14] with increase in temp., it signals the ultimate formation of cyclopenta[*c,d*]pyrene **10** as the only product. Spectroscopic analysis (^1H, ^{13}C, IR and GC–MS) of the pyrolysates shows that **7** is efficiently converted into 1-(pyren-1-yl)ethyne **8** in the range 600–900 °C, which is progressively transformed into cyclopenta[*c,d*]-pyrene **10** >700 °C (Table 1).¶ The mass recoveries remained excellent in the temperature range applied. For the assessment of FVT as the preparative method of choice for the synthesis of **10** 1.5 g of **7** was subjected to FVT at 1000 °C under the above conditions; pure cyclopenta[*c,d*]pyrene (**10**, 1.16 g, conversion 100%, mass recovery 90%) was obtained.

At the same time this FVT synthesis provides strong evidence that the route of formation of cyclopenta-fused polyaromatics in combustion processes,[2,3,4,15,16] must involve ethynyl substituted aromatics as intermediates. The formation of 1-(pyren-1-yl)ethyne **8** in the range 600–900 °C indicates that **10** is formed *via* intramolecular trapping of its 2-(pyren-1-yl)ethylidene carbene tautomer **9**. In the case of **4** and **8** this trapping can only lead to cyclopenta-fusion. While our present findings show that this is a highly efficient process, it remains to be seen whether the related FVT reactions with formation of a six-membered ring, as was recently reported in the synthesis of corannulenes,†,[17–19] has a similar selectivity. In connection with the environmental concern about thermal

Table 1 Product composition of the pyrolysate obtained by FVT of 1-chloro-1-(pyren-1-yl)ethene **7**.[a]

T/°C	**7** (%)	**8** (%)	**10** (%)	Mass recovery (%)
600	50	50	—	90
700	34	65	1	90
800	6	66	28	90
900	1	17	82	93
1000	—	—	100	90

[a] The product composition of the pyrolysate was established from integral ratios in the ^1H NMR spectrum and by capillary GC.

PAH formation while burning organics,[16] their build up *via* ethynyl intermediates must represent an important combustion mechanism.

Received, 23rd August 1993; Com. 3/05098J

Footnotes

† A similar approach was recently used for the synthesis of corannulenes.[17–19] Note, however, that the ring closure *via* the 1-chloro-1-ethene groups proceeded in only moderate yield (10–15%) under flow pyrolysis (1000 °C, 1.5 Torr, N_2).[18]

‡ To a cooled suspension (0 °C) of fresh aluminium chloride (4.00 g, 30 mmol) in dichloromethane (50 ml), 2.06 g (25 mmol) acetylchloride was added. Subsequently, 5.05 g (25 mmol) of solid pyrene was added in small portions at room temp. After stirring overnight the reaction mixture was hydrolysed with conc. HCl solution (0 °C). After workup, crude solid 1-acetylpyrene **6** was purified by recrystallization from methanol. Yield 5.00 g (10.02 mmol, 80% mp 89–90 °C). Satisfactory analytical data (^{1}H, ^{13}C NMR, GC–MS, IR) were obtained.

§ A mixture of 2.24 g (9.2 mmol) of **6** and 2.01 g (9.6 mmol) of phosphorus pentachloride in dichloromethane (50 ml) was refluxed for 6 h. After cooling to room temp. water (50 ml) was added. After workup, crude solid **7** was purified by flash chromatography (silica, eluent *n*-hexane : chloroform 9 : 1). Yield 1.66 g (6.4 mmol, 69% mp 73–74 °C). Satisfactory analytical data (^{1}H, ^{13}C NMR, GC–MS, IR) were obtained.

¶ Diagnostic for the formation of the ethynyl group in the case of **8** are the following spectroscopic data; δ_H (300 MHz; $CDCl_3$; $SiMe_4$) 3.64 (s, 1H), δ_C (75 MHz; $CDCl_3$) δ 82.8 (–*C*CH) and 82.6 (C*C*H), and IR(KBr) ν/cm^{-1} 3310 (ν-*CC-H*) and 2100 (ν *CC*-H). The spectroscopic data of **10** were in agreement with reported values.[6,8]

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