The Chemistry of Phenalenium Systems. XXXI.[1] The Synthesis, Dimerization, and Trapping of 6-Methylenebenzo[cd]pyrene

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(Received December 6, 1979)

The acetolysis of 6-mesyloxymethyl-6H-benzo[cd]pyrene (**6**) gave 7,7a-dihydrospiro[benzo[ghi]perylene-5-(6H),6'-[6H]benzo[cd]pyrene] (**13**), whereas, on formolysis, **6** gave spiro[benzo[ghi]perylene-5(6H),6'-[6H]benzo-[cd]pyrene], 6-hydroxymethyl-6H-benzo[cd]pyrene, and 6-methyl-6H-benzo[cd]pyrene as well as **13**. It might reasonably be supposed that the formation of **13** proceeds in a process involving four steps: (i) the formation of the intermediate 6H-6-benzo[cd]pyren-6-ylmethyl cation (**8**); (ii) the conversion of **8** into the reactive 6-methyl-enebenzo[cd]pyrene (**5**) by the loss of a proton; (iii) the head-to-head self-Diels-Alder dimerization of **5** to the initial dimer, 6,7-dihydrospiro[benzo[ghi]perylene-5(4aH),6'-[6H]benzo[cd]pyrene], and (iv) a 1,3-hydrogen shift to form **13**. When 6-methylbenzo[cd]pyren-6-yl tetrafluoroborate (**7**) was treated with triethylamine in chloroform, the spiro-dimer, **13**, was also obtained. The reaction of **7** with triethylamine in the presence of dimethyl acetylenedicarboxylate resulted in the formation of dimethyl benzo[ghi]perylene-5,6-dicarboxylate. These results strongly suggest the intermediate formation of **5** as a reactive compound.

In connection with our current interest in the chemistry of phenafulvenes (1-methylenephenalene) (**1**)[2,3] we have recently reported the formation of the parent phenafulvene (**1**: X=Y=H) as a reactive intermediate through the transition-metal-promoted isomerization of naphtho[1,8]tricyclo[4.1.0.0^{2,7}]heptene (**2**).[4] The formation of (**1**: X=Y=H) in this reaction has been confirmed by the isolation of its dimer, **3**, and by means of a trapping experiment with dimethyl acetylenedicarboxylate to give dimethyl 1,2-pyrenedicarboxylate (**4**).[4]

In order to learn how the stability of the parent phenafulvene changes with the annelation of benzene rings, we have tried to synthesize 6-methylenebenzo-[cd]pyrene (**5**) as a higher benzolog of **1**. By analogy with the parent phenafulvene, the compound **5** could not be isolated because of its pronounced reactivity. In the study reported herein, the synthesis of **5** as well as various types of evidence for the intermediate existence of **5** are reported.
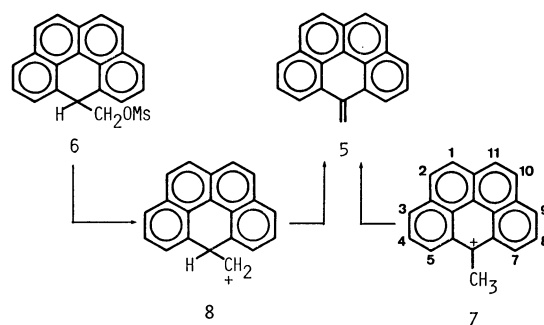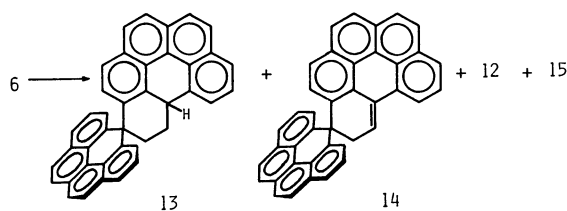

Scheme 1.
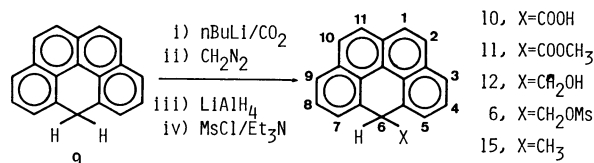
Scheme 2.
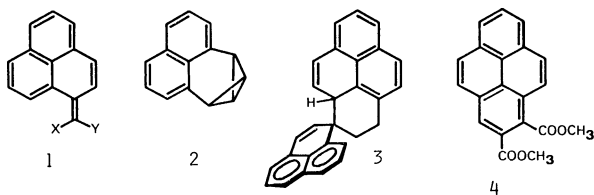
Results and Discussion

As is shown in Scheme 1, either the solvolysis of the mesylate **6**, or the proton abstraction of the 6-methylbenzo[cd]pyren-6-yl cation (**7**) appears to be an attractive route leading to **5**.

The synthesis of **6** was accomplished by the sequence of reactions shown in Scheme 2. The treatment of 6H-benzo[cd]pyrene (**9**) in tetrahydrofuran with butyl-lithium at −60 °C, followed by carboxylation with carbon dioxide, gave 6H-benzo[cd]pyrene-6-carboxylic acid (**10**) as the sole product. The exclusive formation of **10** is in good accordance with the highest Hückel charge density[6] at C-6 in the anion derived from **9**. The acid was converted into the methyl ester, **11**, with diazomethane under a nitrogen atmosphere,[7]

The ester, **11**, was reduced with lithium aluminium hydride to the alcohol, **12**, which, on treatment with mesyl chloride in the usual manner, then gave **6**.[8] The structures of **11**, **12**, and **6** were unambiguously confirmed by the respective spectroscopic properties given in the Experimental Section.

The acetolysis of **6** in gently refluxing glacial acetic acid led to 7,7a-dihydrospiro[benzo[ghi]perylene-5(6H), 6'-[6H]benzo[cd]pyrene] (**13**), a dimer of the desired **5**, in a 50% yield, whereas the formolysis of **6** at 50 °C gave **13** in only a 15% yield, along with a trace amount of the corresponding dehydrogenated dimer, spiro-[benzo[ghi]perylene-5(6H),6'-[6H]benzo[cd]pyrene] (**14**), in addition to **12** (26%) and 6-methyl-6H-benzo-[cd]pyrene (**15**), as is shown in Scheme 3. On the other hand, the formolysis of **6** at 80 °C gave **14** (15%), along with **12** and **15**, in yields similar to those of the above experiment. The elemental analysis and the molecular-weight determination of **13** clearly indicated it to be a dimer of **5**. The final structural proof of **13** was obtained from its ^{1}H-NMR spectrum, which showed one proton triplet at δ 5.01 (H-7a, J = 7.5 Hz), a four-proton multiplet at δ 2.38—2.68, and

Scheme 3.
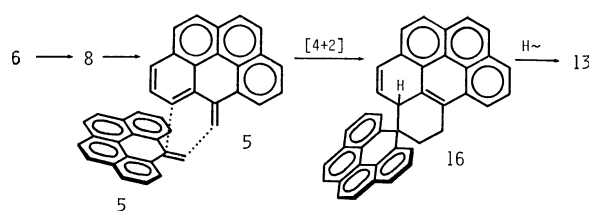
Scheme 4.

aromatic-proton multiplets at δ 7.00—7.94. The relation between the adjacent protons in the alicyclic moiety was confirmed by the aid of spin-decoupling experiments. Irradiation at about δ 2.6 changed the broad triplet at 5.01 into a broad singlet; conversely, irradiation at 5.01 changed the multiplet at 2.38—2.68 into the pseudo-symmetrical pattern of an AA′-BB′-like system. Furthermore, the electronic spectrum of 13 is very similar to that of 15, indicating the existence of a benzo[a]phenanthrene chromophore in 13. Although attempts to make an elemental analysis and mass-spectral measurement of 14 were unsuccessful because of its pronounced sensitivity to heat and air, the structure of 14 was established by means of the ¹H-NMR and electronic spectra and chemical evidence. The ¹H-NMR spectrum of 14 showed signals at δ 3.18 (H-6,6, d, 2H, J=5.0 Hz), 6.47 (H-7, t, 1H, J=5.0 Hz), and 7.03—7.93 (m, 19H). On the irradiation of the signals at δ 6.47, the doublet at δ 3.18 was converted into a clean singlet. A comparison of the electronic spectrum of 14 with that of 13 reflects the bathochromic shift anticipated for the introduction of an exo methylene double bond into the 6H-benzo[cd]pyrene π-system. An examination of the spectra of several 6-methylenebenzo[cd]pyrene derivatives[9] has shown the existence of the same chromophore in 14. Furthermore, 14 could easily be obtained from 13 by treatment with iodine in benzene. The structure of 15 was established through an independent synthesis (vide infra).

The difference in the product distributions between the acetolysis and the formolysis of 6 was explained by the fact that formic acid, as is generally known, gradually decomposes into water and carbon monoxide, even at room temperature.[10] Thus, the intermediate carbonium ion, 8, partly collapsed into an alcohol, 12, upon the nucleophilic attack of water. The formation of 15 was closely parallel to the precedent in which triphenylmethanol is reduced to triphenyl-methane by formic acid.[11]

A possible explanation for the formation of 13 from 6 might be that the reaction proceeds in a process involving four steps: (i) the initial formation of the intermediate carbonium ion, 8; (ii) the conversion of 8 into the reactive hydrocarbon, 5, by the loss of the proton; (iii) the head-to-head self-Diels-Alder dimerization of 5 to the initial dimer, 16, and (iv) a 1,3-hydrogen shift to form the observed dimer, 13 (Scheme 4). The ease of the hydrogen shift in the final step may be attributed to the difference in π-energy between the 1-vinylpyrene and benzo[a]phenanthrene π-moieties in 16 and 13 respectively.[12]

The second synthetic route, which consists of proton abstraction from the 6-methylbenzo[cd]pyren-6-yl cation, 7, would be a more favorable synthetic method for the labile 5. To this end, 6-methyl-6H-benzo-[cd]pyrene, 15, readily accessible from 9 through lithiation with butyllithium, followed by methylation with excess methyl iodide, was treated with trityl tetrafluoroborate in chloroform to give a 83% yield of 7. The structure of 7 was evident from its ¹H-NMR spectrum in trifluoroacetic acid, which exhibited signals at δ 3.87 (s, -CH₃), 8.33 (d, J=8.6 Hz, H-1,11), 8.57 (d, J=8.6 Hz, H-2,10), 8.41 (dd, J=7.0, 6.5 Hz, H-4,8), 9.12 (d, J=6.5 Hz, H-3,9), and 9.51 (d, J=7.0 Hz, H-5,7).

When the cation, 7, was treated with triethylamine in chloroform at 0 °C, the spiro dimer, 13, was obtained in a 42% yield. On the other hand, when the reaction was carried out at −10——15 °C, which is the practical lower limit for the reaction, the only product obtained was 13, and no hydrocarbon corresponding to 5 could be detected by TLC monitoring. The formation of 13 even at low temperatures, suggested the pronounced reactivity of the initial product, 5, for the self-Diels-Alder reaction as both 4π and 2π components. In order to confirm the transient existence of 5, we carried out a trapping experiment. The reaction of 7 with triethylamine in chloroform in the presence of two mole equivalents of dimethyl acetylenedicarboxylate at 0 °C resulted in the formation of the product in a 20% isolated yield; to this product we assigned the structure of dimethyl 5,6-benzo[ghi]perylenedicarboxylate (17) on the basis of its mass spectrum [m/e 392 (M⁺, 100%), 361 (M⁺—OCH₃, 28%), 274 (M⁺—2COOCH₃, 28%)], ¹H-NMR spectrum [δ 4.10 (s, -OCH₃), 4.17 (s, -OCH₃), 8.92 (dd, J₈,₉=7.5 Hz, J₈,₁₀=1.5 Hz, H-8), 9.41 (s, H-7), 7.87—8.28 (m, other aromatic protons)] and its electronic spectrum, which is closely similar to that of the parent benzo[ghi]perylene.[13]
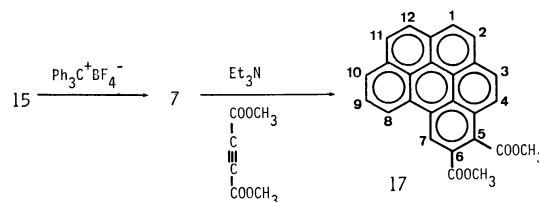
Scheme 5.

In conclusion, as in the case of the parent phena-fulvene 1: X=Y=H, all attempts to isolate 6-methyl-enebenzo[cd]pyrene 5 have thus far been unsuccessful, though it can be generated and trapped. Although it is well documented that nonalternant fulvenes, such

as tria-,[14] penta-,[15] and hepta-fulvenes,[16] belong to an extremely reactive group of substances, unsubstituted *exo*-cyclic methylene compounds with odd-alternant polycyclic benzenoid moieties, *e.g.*, **1** and **5**, also not have enough stability to permit isolation.[17]

Experimental

All the melting points were determined on a micro hot stage and are uncorrected. The mass spectra were obtained on a Hitachi RM-50 spectrometer operating at 20 or 70 eV. The electronic spectra were taken on a Hitachi 124 double-beam spectrometer. The NMR spectra were recorded with a Varian XL-100 (100 MHz) spectrometer and are given in δ-values with respect to tetramethylsilane as the internal standard.

6-Methoxycarbonyl-6H-benzo[cd]*pyrene* (**11**).   To a stirred solution of 6*H*-benzo[*cd*]pyrene (**9**) (4.2 g, 175 mmol) in 30 ml of dry THF, we added a hexane solution containing 17.5 mmol of butyllithium at -60 °C under nitrogen. The mixture was then stirred for 30 min at this temperature, and dry carbon dioxide gas was bubbled through the solution. The resulting mixture was warmed to 0 °C with a continuous bubbling of carbon dioxide. After having been acidified with dil hydrochloric acid, the reaction mixture was extracted with ether. The ether layer was washed with water and extracted with a saturated aqueous solution of sodium hydrogencarbonate. After having been washed with ether, the aqueous layer was acidified with concd hydrochloric acid to give colorless precipitates which, after filtration and methylation with diazomethane under nitrogen, yielded a crude ester, **11**. The product was chromatographed on alumina, eluted with hexane–benzene (1:1), and recrystallized from hexane–benzene to give pure **11** as pale yellow needles; mp 149—150 °C. MS: *m/e* 298 (M$^+$, 12%), 239 (M$^+$—COOCH$_3$, 100%); IR (KBr): 1725 cm^{-1}; NMR (CDCl$_3$): 3.51 (s, 3H, –CH$_3$), 5.81 (bs, 1H, H-6), 7.41—7.81 (m, 10H, other protons).

Found: C, 84.32; H, 4.72%. Calcd for C$_{21}$H$_{40}$O$_2$: C, 84.54; H, 4.73%.

6-Hydroxymethyl-6H-benzo[cd]*pyrene* (**12**).   A solution of **11** (1.19 g, 4.0 mmol) in 120 ml of dry ether was added, drop by drop, to a suspension of lithium aluminium hydride (152 mg) in 20 ml of dry ether at -20 °C over a 2-h period under nitrogen. After stirring for 3 h at this temperature, the reaction mixture was quenched with ether saturated with water and extracted with benzene. The combined organic layer was washed successively with dil hydrochloric acid, an aqueous solution of sodium hydrogencarbonate, and water, dried (Na$_2$SO$_4$), and evaporated under reduced pressure. The residue was recrystallized from hexane–benzene (2:3) under nitrogen to give 870 mg (80%) of **12** as brown prisms; mp 119.5—122 °C. MS: *m/e* 270 (M$^+$, 3.2%), 239 (M$^+$—CH$_2$OH, 100%); NMR (CDCl$_3$): 1.6 (bs, 1H, –OH), 3.60 (d, 2H, *J*=6.5 Hz, –CH$_2$–O), 4.67 (t, 1H, *J*=6.5 Hz, H-6), 7.49—7.91 (m, 10H, aromatic protons).

Found: C, 89.15; H, 5.39%. Calcd for C$_{20}$H$_{14}$: C, 88.86; H, 5.22%.

6-Mesyloxymethyl-6H-benzo[cd]*pyrene* (**6**).   To a stirred solution of **12** (270 mg, 1.0 mmol) in 6 ml of dry dichloromethane containing 1.6 mmol of triethylamine, we added, drop by drop, 1.3 mmol of methanesulfonyl chloride in 7 ml of dry dichloromethane at -10 °C over a 30-min period under nitrogen. After stirring for 2 h at this temperature, the solution was poured into ice water and the layers were separated. The organic layer and the combined dichloromethane extracts were washed successively with cold dil

hydrochloric acid, an aqueous solution of sodium hydrogen-carbonate, and water, and then dried (MgSO$_4$). The solvent was evaporated under reduced pressure, leaving 277 mg (80%) of crude **6**, which was subsequently dissolved in 5 ml of dichloromethane and 5 ml of hexane at the ambient temperature under nitrogen, while the solution was concentrated to a volume of 4 ml. The solution was cooled gradually to -40 °C, giving 172 mg of the analytically pure **6** as pale yellow needles; mp 120—122 °C. MS: *m/e* 348 (M$^+$, 3%), 252 (M$^+$—OMs, 33%), 239 (M$^+$—CH$_2$OMs, 100%); NMR (CDCl$_3$): 2.39 (s, 3H, –SO$_2$CH$_3$), 4.28 (d, 2H, *J*=6.5 Hz, –CH$_2$–SO$_2$–), 5.04 (bt, 1H, *J*=6.5 Hz, H-6), 7.57—7.97 (m, 10H, aromatic protons).

Found: C, 72.13; H, 4.61; S, 9.05%. Calcd for C$_{21}$H$_{16}$O$_3$S: C, 72.39; H, 4.63; S, 9.20%.

Acetolysis of **6**.   A solution of **6** (140 mg, 0.4 mmol) in 15 ml of dry acetic acid, containing 96 mg of anhydrous sodium dihydrogenphosphate as a buffer, was refluxed for 1 h under nitrogen. The reaction mixture was then poured into water and extracted with benzene. The extracts were washed with an aqueous solution of sodium hydrogencarbonate and water, and then dried, and the solvent was removed under reduced pressure. The residue was chromatographed on alumina containing 3% of water, eluting with hexane–benzene (9:1), to give 50 mg (50%) of the spiro-dimer, **13**, as pale yellow crystals; mp 158—162 °C (dec). MS: *m/e* 504 (M$^+$, 25%), 276 (benzo[*ghi*]perylene ion, 100%); UV λ_{max} nm (log ε) (hexane): 219 (4.74), 233 (4.63), 249 (4.19), 256 (4.24), 258 sh (4.22), 262 sh (4.43), 282 (4.67), 293 (4.63), 323 (4.13), 338 (4.00); NMR: see text.

Found: C, 94.98; H, 4.73%. Calcd for C$_{40}$H$_{20}$: C, 95.21; H, 4.79%.

Formolysis of **6**.   A solution of **6** (140 mg, 0.4 mmol) in 14 ml of 99% formic acid containing 96 mg of anhydrous sodium dihydrogenphosphate was heated to 40—50 °C over a 4-h period under nitrogen. After workup in the same manner as the acetolysis just described, the crude products were chromatographed on alumina containing 3% of water, eluting gradually with hexane, hexane–benzene (9:1), and benzene. The solvent of each fraction was then evaporated, leaving 4 mg of **15**, 15 mg (15%) of **13**, and 26 mg (26%) of **12**. The structures of **12** and **15** were confirmed from the NMR spectra to be identical with those of the respective authentic compounds.

Formolysis of **6** *at High Temperatures*.   A solution of **6** (140 mg, 0.4 mmol) in 14 ml of 99% formic acid containing 96 mg of anhydrous sodium dihydrogenphosphate was heated from room temperature to 80 °C over a 15-min period and then maintained at this temperature for 10 min under nitrogen. The solution was subsequently worked up, and the products were separated by the same procedures as above to give 8 mg of **15**, 15 mg (15%) of the dehydro spiro-dimer, **14**, as yellow crystals, and 23 mg (23%) of **12**. The dimer **14** is gradually decomposed around 80 °C. UV λ_{max} nm (log ε) (hexane): 216 (4.96), 232 (4.82), 265 sh (4.61), 279 (4.66), 320 (4.44), 334 (4.47), 390 (3.91), 413 (3.92); NMR: see text.

Dehydrogenation of **13**.   A solution of 55 mg (0.11 mmol) of the spiro-dimer, **13**, in 6 ml of benzene was treated with 38 mg (0.3 mmol) of iodine at room temperature for 30 min under nitrogen. The products were chromatographed on alumina containing 2.5% of water, eluting with benzene, and again on the same deactivated alumina with hexane–benzene (9:1), to give 20 mg (45%) of pure **14**, which was identical in every respect with the authentic sample.

6-Methyl-6H-benzo[cd]*pyrene* (**15**).   To a stirred solu-

tion of 6H-benzo[cd]pyrene (9) (1.56 g, 6.5 mmol) in 70 ml of dry THF, we added 6.5 mmol of butyllithium in hexane at −60 °C under nitrogen. After having been stirred for 30 min at this temperature, the reaction mixture was quenched by the addition of a large excess of methyl iodide. The mixture was stirred for 1 h at −50 °C, warmed to room temperature, and extracted with benzene. The extracts were washed successively with 2 mol dm⁻³ hydrochloric acid, a saturated aqueous solution of sodium hydrogencarbonate, and water, dried (MgSO₄), and evaporated. The residue was chromatographed on alumina with hexane–benzene (1:1). The solvent was evaporated, leaving a yellow solid which was recrystallized from cyclohexane under nitrogen to give pure 15 (1.51 g, 92%) as yellow crystals; mp 122—124 °C. MS: m/e 254 (M⁺, 17%), 239 (M⁺−CH₃, 100%); UV λ_{max} nm (log ε) (hexane): 268.5 (4.39), 278 (4.64), 289 (4.75), 312 (3.95), 325 (3.97), 338 (3.77); NMR: see text.

Found: C, 94.24; H, 5.55%. Calcd for C₂₀H₁₄: C, 94.45; H, 5.55%.

6-Methylbenzo[cd]pyren-6-yl Tetrafluoroborate (7). To a stirred solution of 15 (1.5 g, 6.0 mmol) in 40 ml of dry chloroform, we added finely powdered trityl tetrafluoroborate (2.05 g, 6.5 mmol) at room temperature. Black solids precipitated at once, after which the mixture was warmed at 50 °C for 2 h. After cooling, the black solid mass was collected by filtration and washed several times with dry chloroform in a dry box. The product was dried *in vacuo* to give 1.7 g (83%) of 7; mp >350 °C. NMR: see text.

Dimerization of 6-Methylenebenzo[cd]pyrene (5). To a suspension of the cation, 7 (340 mg, 1.0 mmol), in 20 ml of dry chloroform, we added, drop by drop, 150 mg (3.0 mmol) of dry triethylamine in 5 ml of dry chloroform at 0 °C over a 15-min period under nitrogen. After stirring for an additional hour, the reaction mixture was poured into 2 mol dm⁻³ hydrochloric acid and the organic layer was washed successively with an aqueous solution of sodium hydrogencarbonate and water, dried (MgSO₄), and evaporated at reduced pressure to give a residue which was subsequently chromatographed on alumina containing 2.5% of water with hexane–benzene (9:1) to give 105 mg (42%) of the pure dimer, 13, as pale yellow crystals, which were identical in every respect with the product of the acetolysis of 6.

Trapping of 5 by Dimethyl Acetylenedicarboxylate. To a suspension of 7 (170 mg, 0.5 mmol) in 15 ml of dry chloroform containing dimethyl acetylenedicarboxylate (120 mg, 1.0 mmol), we added, drop by drop, triethylamine (75 mg, 1.50 mmol) in 10 ml of dry chloroform at room temperature under nitrogen. After additional stirring for 3 h, the reaction mixture was poured into water. The organic layer was washed successively with water, 2 mol dm⁻³ hydrochloric acid, an aqueous solution of sodium hydrogencarbonate, and water, dried (MgSO₄), and evaporated. The residue was chromatographed on alumina with benzene to give

39 mg (20%) of crude 17. Pure 17 was obtained by recrystallization from hexane–benzene as reddish brown crystals; mp 239—240 °C. IR (KBr): 1725 cm⁻¹; MS and NMR: see text.

Found: C, 80.10; H, 4.19%. Calcd for C₂₆H₁₆O₄: C, 79.58; H, 4.11%.

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