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Some Reactions on 4*H*-Cyclopenta[*def*]phenanthrene-8,9-dione

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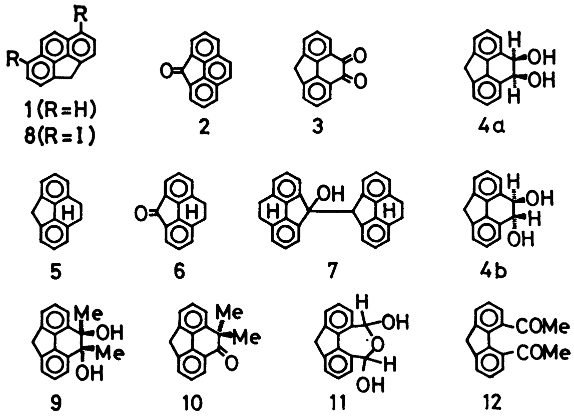
Synopsis. The oxidation of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene gave the 4-ketone by treatment with Triton B-oxygen, and afforded 8,9-diketone by the action of chromium (III) salt. The reduction of the quinone yielded the corresponding *meso*- and *dl*-diols.

The oxidation of 4*H*-cyclopenta[*def*]phenanthrene (**1**) has already been reported to give cyclopenta[*def*]phenanthren-4-one (**2**), 4*H*-cyclopenta[*def*]phenanthrene-8,9-dione (**3**), and other substances.[1,2] *meso*-8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene-8,9-diol (**4a**) was obtained from **1** by treatment with osmium tetraoxide.[3] The quinone, **3**, has been prepared by the oxidation of **1** with iodic acid.[4]

The present paper will deal with another route to form **3** and some related reactions.

The air-oxidation of 8,9-dihydro-4*H*-cyclopenta[*def*]-phenanthrene (**5**)[5] gave the expected 8,9-dihydrocyclopenta[*def*]phenanthren-4-one (**6**) in a moderate yield, accompanied by the formation of 8,8′,9,9′-tetrahydro-4,4′-bi(4*H*-cyclopenta[*def*]phenanthren)-4-ol (**7**). This reaction may be initiated by the dissociation of more acidic protons on the active 4-methylene[6] than the 8,9-protons.



Scheme 1.

The reexamination of the oxidation of **1** using iodic acid resulted in **2**, **3**, and 1,7-diiodo-4*H*-cyclopenta-[*def*]phenanthrene (**8**).[4] Pure **3** was also isolated easily by the reaction of **5** with sodium dichromate, in spite of the dominant formation of **2**, which can be converted into **5**.

The reduction of **3** with lithium aluminium hydride afforded two isomeric diols, **4a**[3] and *dl*-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene-8,9-diol (**4b**). The treatment of **3** with a large excess of methylmagnesium iodide gave only a single isomer, 8,9-dimethyl-4*H*-cyclopenta[*def*]phenanthrene-8,9-diol (**9**), of the expected diastereomeric diols. An inspection of the molecular model suggests that the attack of the second molecule of the Grignard reagent from the same side as in the first attack would be sterically hindered; hence, a *dl*-structure is tentatively assigned to **9**.

The pinacol-pinacolone rearrangement of **9** gave the expected 9,9-dimethyl-4*H*-cyclopenta[*def*]phenanthren-8-one (**10**). A similar transformation of **4a** and **4b** yielded only **3**. The oxidative cleavage of **4a** and **4b** afforded 6,10-dihydro-4*H*-fluoreno[4,5-*cde*]oxepin-4,6-diol (**11**),[7] and **9** was also converted into 4,5-diacetylfluorene (**12**). The UV absorbance at the characteristic maximum of **4a** (307 nm) is greater than those of **4b** (308 nm) and **9** (305 nm). This may result from the steric factor of the 8,9-substituents.

The reactivities of **4a** and **4b** towards periodic acid were compared to each other at 50 °C by measurements of the disappearance of the maximum at *ca.* 307 nm caused by the diol and the appearance of the peak at 298 nm of **11**. The reaction time of **4b** was twice that of **4a**. This difference in the reactivity is consistent with the assignments of the *meso*- and *dl*-configurations to **4a** and **4b** respectively.[8]

Experimental

All the melting points are uncorrected. The instruments used in this experiment were the same with those described elsewhere.[7]

*Air-oxidation of 8,9-Dihydro-4*H*-cyclopenta*[def]*phenanthrene (5).* Air was introduced into a solution of **5** (960 mg, 5 mmol) in pyridine (25 ml) containing Triton B (40%, 0.25 ml) at 17—19 °C for 20 h. After PhH (50 ml) has then been added, the reaction mixture was extracted with HCl (2 mol/l, 90 ml), and the PhH solution was washed with aqueous NaCl, dried over Na_2SO_4, and chromatographed on an alumina column, with PhH as the eluent. The first eluate was evaporated to dryness, and the residue was recrystallized from hexane to give 125 mg (13%) of **5**: mp 141—142 °C.

The second orange eluate afforded 714 mg (69%) of **6**: mp 141—143 °C (from HOEt); IR 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.03 (4H, s) and 6.91—7.39 (6H, m); MS, *m/e*, 206 (M^+). Found: C, 87.29: H, 4.82%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%.

The colorless portion of the alumina yielded 39 mg (4%) of **7**: mp 219—221 °C (dec) (from cyclohexane); IR 3335 cm^{-1} (OH); NMR ($CDCl_3$) δ 2.01 (1H, s, OH), 2.93 (4H, s), 2.97 (4H, s), 4.88 (1H, s), and 6.71—7.03 (12H, m); MS, *m/e*, 398 (M^+), 207, and 191. Found: C, 90.50; H, 5.31%. Calcd for $C_{30}H_{22}O$: C, 90.42; H, 5.57%.

*Oxidation of 4*H*-Cyclopenta*[def]*phenanthrene (1) with HIO_3.* The hydrocarbon **1** (1.0 g, 5.3 mmol) was treated with HIO_3 (4.3 g), H_2O (25 ml), and HOAc (30 ml) in dioxane (270 ml) by a method similar to that described elsewhere:[4] 407 mg (41%) of **1** was recovered by sublimation *in vacuo*: mp 114—115 °C. Upon separation by column chromatography, 62 mg (6%) of **2** (mp 169.5—170.0 °C; lit,[1] mp 170 °C) and 272 mg (24%) of **3** (mp 256 °C, dec: lit,[4] mp 260 °C, dec)

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were obtained.

In addition, a 50-mg portion (2%) of **8** was isolated: mp 216—217 °C (from cyclohexane); NMR (CS_2) δ 4.20 (2H, s, H_4), 7.39 (2H, d, J=7.8 Hz, H_3, H_5), 7.75 (2H, s, H_8, H_9), and 8.00 (2H, d, H_2, H_6); MS, *m/e*, 442 (M^+), 315, and 188. Found: C, 40.98; H, 2.15%. Calcd for $C_{15}H_8I_2$: C, 40.76; H, 1.82%.

*4*H-*Cyclopenta*[def]*phenanthrene-8,9-dione (**3**).* A solution of **5** (2.40 g, 12.5 mmol) in HOAc (200 ml) was refluxed with $Na_2Cr_2O_7 \cdot 2H_2O$ (5.0 g) for 45 min. Upon treatment with PhH and H_2O, the PhH solution of the resulting precipitate was chromatographed on a silica-gel column, with PhH as the eluent; the first eluate gave 0.43 g (18%) of **1**. The lower yellow band on the column was extracted with HOEt, giving 1.43 g (56%) of **2**.

The upper orange-red band was extracted with EtOAc to give 0.54 g (20%) of **3**.

meso- *(**4a**) and* dl-*8,9-Dihydro-4*H-*cyclopenta*[def]*phenanthrene-8,9-diols (**4b**).* Quinone, **3** (440 mg, 2 mmol), in ether (80 ml) was added to a suspension of $LiAlH_4$ (304 mg, 8 mmol) in ether (20 ml) at 0 °C, after which the mixture was stirred for 10 h at room temperature. Upon decomposition with aqueous NaCl and the evaporation of the ether, the residue was purified by fractional recrystallization from CH_2Cl_2 to give 244 mg (55%) of **4b**: mp 200.0—200.5 °C (dec); IR 3240 cm^{-1} (OH); UV_{max} (HOEt) 270 (log ε 4.10), 296 (3.45), and 308 nm (3.30); NMR ($CDCl_3$) δ 1.76 (2H, s, OH), 3.94 (2H, s), 5.18 (2H, s), and 7.17—7.49 (6H, m); MS, *m/e*, 224 (M^+), 206, and 178. Found: C, 80.40; H, 5.31%. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%.

In addition, 20 mg (5%) of **4a** was isolated; it was identical in all respects with the specimen obtained by the oxidation of **1** with OsO_4;[3] mp 183.5—184.5 °C (dec) (lit,[3] mp 180 °C, dec); IR 3395 and 3305 cm^{-1} (OH); UV_{max} (HOEt) 268 (log ε 4.14), 295 (3.40), and 307 nm (3.41); NMR ($CDCl_3$) δ 2.15 (2H, s, OH), 3.93 (2H, s), 5.08 (2H, s), and 7.28—7.62 (6H, m); MS, *m/e*, 224 (M^+), 206, and 178.

*8,9-Dimethyl-4*H-*cyclopenta*[def]*phenanthrene-8,9-diol (**9**).* A solution of **3** (550 mg, 2.5 mmol) in PhH (100 ml) was added to a mixture of MeMgI (prepared from MeI (1.2 ml, 20 mmol) and Mg) in ether at 15—20 °C, after which the new mixture was refluxed for an additional 5 h. Upon treatment with aqueous NH_4Cl, the resulting mixture was separated by means of a silica-gel column with PhH-EtOAc (95/5). The orange-red band on the column gave 72 mg (13%) of **3**. The upper light yellow band afforded 361 mg (57%) of **9**: mp 167.5—168.5 °C; IR 3470 cm^{-1} (OH); UV_{max} (HOEt) 273 (log ε 4.06), 294 (3.80), and 305 nm (3.16); NMR ($CDCl_3$) δ 1.50 (6H, s), 2.28 (2H, s, OH), 3.92 (2H, s), and 7.25—7.50 (6H, m); MS, *m/e*, 252 (M^+), 234, 189, and 165. Found: C, 80.55; H, 6.77%. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39%.

*Pinacol-Pinacolone Rearrangement of Diols. a) 9,9-Dimethyl-4*H-*cyclopenta*[def]*phenanthren-8-one (**10**):* A mixture of **9** (252 mg, 1 mmol) in HOAc (50 ml) containing H_2SO_4 (0.35 ml) was refluxed for 3 h to afford 132 mg (56%) of **10**: mp 99—100 °C (from aqueous DMF); IR 1662 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.57 (6H, s), 4.02 (2H, s), and 7.28—7.93 (6H, m); MS, *m/e*, 234 (M^+) and 219. Found: C, 87.20; H, 6.16%. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

b): A solution of **4a** (112 mg, 0.5 mmol) in HOAc (10 ml) was refluxed with H_2SO_4 (0.1 ml) for 10 min, giving 37 mg (34%) of **3**. Similarly, **4b** (112 mg, 0.5 mmol) gave 48 mg (43%) of **3**.

*4,5-Diacetylfluorene (**12**).* The diol **9** (252 mg, 1 mmol) was treated with $Pb(OAc)_4$ (0.5 g) in PhH (50 ml) at room temperature for 5 h to yield 148 mg (59%) of **12**: mp 167—168 °C; IR 1670 cm^{-1} (C=O); UV_{max} (HOEt) 246 (log ε 4.36), 275 (3,52), and 322 nm (3.86); NMR ($CDCl_3$) δ 2.67 (6H, s), 3.90 (2H, s), and 7.13—7.64 (6H, m); MS, *m/e*, 250 (M^+), 235, 207, 193, and 165. Found: C, 81.28; H, 5.84%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

In addition, 30 mg (12%) of **9** were recovered.

Glycol Scission of Diols. A solution of **4a** (1.34×10^{-4} mol/l HOEt, 4.00 ml) was mixed with an aqueous solution of H_5IO_6 (5.07×10^{-3} mol/l, 0.11 ml) in a quartz cell, which was maintained at 50±1 °C. After the prescribed times, the UV spectra were measured in the range from 290 to 340 nm. The spectrum after 120 min was identical with that of **11**:[7] UV_{max} (HOEt) 265 (log ε 4.16), 287 (3.66), and 298 (3.74).

Two solutions of **4b** and H_5IO_6 were treated as a manner similar to that described above; the end point of the reaction was observed after 240 min.

The similar treatment of **9** showed no significant change after 24 h.

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