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The Fries Rearrangement of 4*H*-Cyclopenta[*def*]phenanthrenyl Acetate

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A Fries rearrangement of 4*H*-cyclopenta[*def*]phenanthren-1-yl acetate gave 2- and 7-acetyl derivatives. The reaction of isomeric 2-acetoxy compound afforded 1- and 7-acetyl derivatives. The acetyl group of the 3- and 8-acetoxy compounds rearranged into the 2- and 9-positions, respectively. In addition, 1-, 2-, 3-, 4-isopropyl compounds were derived from the corresponding acetyl derivatives.

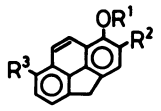
The Fries rearrangement is one of the important synthetic methods for obtaining acyl-substituted phenols from the corresponding acyloxy compounds. This reaction has been investigated widely, but has scarcely been applied to polycyclic aromatic hydrocarbons (PAH).[1,2]

4*H*-Cyclopenta[*def*]phenanthrene (CPP) is one of the interesting PAH; some reactions involving CPP derivatives have been reported.[3] Recently, we have reported Friedel–Crafts acetylations of methoxy-4*H*-cyclopenta[*def*]phenanthrenes.[4] The effect of the methoxyl group was different from that of the amino group on CPP.[5]

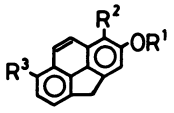
The present paper deals with a Fries rearrangement of acetoxy derivatives of CPP, **1a—5a**. This is expected to yield valuable informations concerning both the reactivities of the electrophilic substitution of substituted CPP, and the mechanism of the Fries rearrangement (Scheme 1). The reactants, **1a—5a**, were synthesized by a rearrangement of the corresponding acetyl derivatives, **6a—10a**,[6,7] with *m*-chloroperbenzoic acid (MCPB) in moderate yields. Also, **6a—10a** were converted into isopropyl compounds: **6d—10d** via **6b—10b** and **6c—10c** (Scheme 2).

The acetyl group of 4*H*-cyclopenta[*def*]phenanthren-1- (**1a**), 2- (**2a**), 3- (**3a**), and 8-yl acetate (**4a**) migrated upon stirring with aluminium chloride in nitrobenzene, giving 2-acetyl-1-hydroxy- (**1b**), 1-acetyl-2-hydroxy- (**2b**), 2-acetyl-3-hydroxy- (**3b**), 9-acetyl-8-hydroxy-4*H*-cyclopenta[*def*]phenanthrene (**4b**), respectively, in moderate yields (summarized in Table 1). The phenolic compounds, **1e—4e**, were isolated as by-products of the reactions.

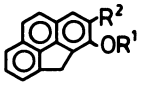
The reaction of **2a** afforded 7-acetyl-2-acetoxy compound, **2d**, accompanied by a trace amount of 7-acetyl-2-hydroxy derivative, **2c**, through a treatment in



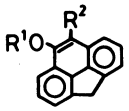
1a (R^1=Ac, R^2=R^3=H)
1b (R^1=R^3=H, R^2=Ac)
1c (R^1=R^2=H, R^3=Ac)
1d (R^1=R^3=Ac, R^2=H)
1e (R^1=R^2=R^3=H)



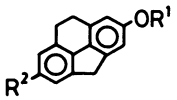
2a (R^1=Ac, R^2=R^3=H)
2b (R^1=R^3=H, R^2=Ac)
2c (R^1=R^2=H, R^3=Ac)
2d (R^1=R^3=Ac, R^2=H)
2e (R^1=R^2=R^3=H)



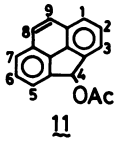
3a (R^1=Ac, R^2=H)
3b (R^1=H, R^2=Ac)
3e (R^1=R^2=H)



4a (R^1=Ac, R^2=H)
4b (R^1=H, R^2=Ac)
4e (R^1=R^2=H)



5a (R^1=Ac, R^2=H)
5c (R^1=H, R^2=Ac)
5d (R^1=R^2=Ac)
5e (R^1=R^2=H)



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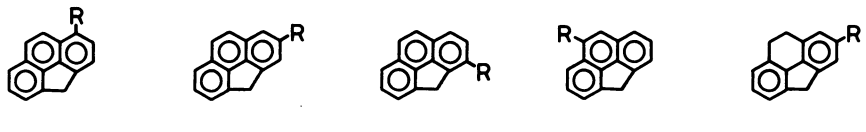
Scheme 1.



6a-6d 7a-7d 8a-8d 9a-9d 10a-10d

a: R=Ac b: R= -CMe2 (OH) c: R= -C=CH2 (Me) d: R=Pr-i

Scheme 2.

Table 1. The Fries Rearrangements of **1a—5a**

Reactant	Solv.	Temp °C	Time h	Product/%		Recovd/%	
1a	$PhNO_2$	r.t.	2	**1b**(85)			
2a	$C_2H_4Cl_2$	r.t.	3	**2c**(trace)	**2d**(34)	**2a**(2)	**2e**(18)
2a	$C_2H_4Cl_2$	refl.	1	**2b**(33)			
2a	$PhNO_2$	40	2	**2b**(65)		**2a**(10)	**2e**(9)
3a	$PhNO_2$	40	2	**3b**(62)		**3a**(20)	**3e**(3)
4a[a]	$PhNO_2$	r.t.	3	**4b**(51)			**4e**(trace)
5a[a]	PhCl	refl.	1	**5c**(8)		**5a**(10)	

a) Isolated yield.

1,2-dichloroethane at room temperature. On the other hand, **2b** was the main product under reflux conditions, similar to the case in nitrobenzene. Similar trends were observed in a reaction of **1a** in 1,2-dichloroethane.

A Fries rearrangement of the 8,9-dihydro-2-acetoxy derivative **5a** yielded 6-acetyl-2-hydroxy compound, **5c**, as the solely isolated product. A reaction of 4-acetoxy compound, **11**, gave no identified products.

These results fairly differ from reactions of the amino[5] and methoxy derivatives[4] of CPP. One of the remarkable results of Fries rearrangements in nitrobenzene is that the acetyl group is introduced into the adjacent position to the original acetoxyl group of **1a—4a**. This is similar to the cases of 1-, 2-, and 8-amines[5] and 1- and 2-ethers.[4] On the other hand, **2a** gives diacetyl derivative **2d** under relatively mild conditions using 1,2-dichloroethane; position 7 in the parent CPP is the most reactive position to electrophile.[3,8] These can be explained by the fact that the formations of **1d** and **2d** are kinetically controlled and those of **1b** and **2b** are thermodynamically controlled. The driving force of thermodynamic stabilities of the compounds would be caused by the formation of a chelating ring between the vicinal acetyl and the hydroxyl groups.

From the predominant formations of **1b—4b** by reactions in nitrobenzene it is postulated that the solvent prefers the formation of thermodynamically-controlled products, in spite of the fact that the attack of the electrophile on the ortho position of substituent requires more energy and may attack the other positions.[9] The solvated acetyl chloride-aluminium chloride complex is the attacking species in the Friedel-Crafts acetylation using nitrobenzene as a solvent.[10] Also, in this case, the solvated reactant-aluminium chloride complex furnishs the rearrangement by moving the acetyl group from the oxygen atom to the adjacent carbon in the solvated state under the reaction conditions.

The following mechanisms have been proposed for the Fries rearrangement:[1] (i) an intramolecular reaction, (ii) a Friedel-Crafts acetylation by acyl chloride to the aryl-$OAlCl_2$ formed from the original acyloxy compound with aluminium chloride, or (iii) a disproportionation reaction of two acyloxy derivatives (these would operate simultaneously). A brief experiment involving a cross-Fries rearrangement between **1e** and **2a** in the presence of aluminium chloride in nitrobenzene afforded a mixture of **1b** and **2b** in a ratio of ca 4:1; this supports the idea that the reaction proceeds via an intermolecular mechanism. The disproportionation mechanism (iii) would be one of the reasonable mechanisms, since fair amounts of **1e** and **2e** were obtained as by-products during the formations of **1d** and **2d**. The production of **1b—4b** in nitrobenzene has been explained by the intramolecular mechanism (i), since the yields of **1b—4b** are moderately high, in spite of the adjacent attack being restricted due to the steric factor.[9]

The acetates, **1a—5a**, were synthesized by Baeyer–Villiger rearrangements of 1- (**6a**),[6] 2- (**7a**),[6] 3- (**8a**),[6,7] 8- (**9a**),[6] and 8,9-dihydro-2-acetyl-4*H*-cyclopenta[*def*]-phenanthrene (**10a**)[6] with MCPB. The alkaline hydrolyses of **1a—5a** afforded phenols **1e—5e**. Reactions of **6a—10a** with methylmagnesium iodide gave the corresponding 2-substituted 2-propanol isomers, **6b—10b**. The alcohols were converted into propylene derivatives **6c—10c** by treatments with acetic anhydride. The olefins gave isopropyl compounds, **6d—10d**, by hydrogenation with Raney nickel.

Experimental

All of the melting points are uncorrected. The ^{1}H NMR spectra were obtained with a Jeol C-60 HL or a Varian VXR-300 spectrometers in $CDCl_3$ from TMS. The IR (KBr-pellet) and mass spectra were recorded on a Jasco IR-G and a Hitachi M-80 apparatus.

Acetyl compounds **6a—10a** were obtained according to the method described elsewhere.[6] Oxime of **6a**: mp 206.0—207.5 °C; yield 74%; IR, 3200 cm^{-1}; ^{1}H NMR (C_6D_6), δ=2.33 (3H, s), 3.88 (2H, s), 7.30—7.66 (5H, m), 7.82 (1H, d, J=9.0 Hz), 8.22 (1H, bs), and 8.58 (1H, d, J=9.0 Hz); MS, m/z 247 (M$^+$), 230, and 189. Found: C, 82.86; H, 5.40%. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30%.

Oxime of **7a**: mp 193—194 °C; yield 95%; IR, 3250 cm^{-1}; ^{1}H NMR, δ=2.51 (3H, s), 4.39 (2H, s), 7.66—7.75 (2H, m), 7.86 (1H, d, J=8.7 Hz), 7.87 (2H, s), 7.98 (1H, bs), and 8.08 (2H, s); MS, m/z 247 (M$^+$), 231, and 189. Found: C, 82.60; H, 5.53; N, 5.92%. Calcd for $C_{17}H_{13}NO$: N, 5.66%.

Oxime of **8a**:[7] yield 77%; mp 151.5—152.0 °C; IR, 3300 cm^{-1}; ^{1}H NMR (C_6D_6), δ=2.24 (3H, s), 4.23 (2H, s), 7.36—7.89 (7H, m), and 8.52 (1H, bs); MS, m/z 247 (M$^+$), 231, 214, and 189. Found: C, 82.87; H, 5.60%.

Oxime of **10a**: mp 181.0—181.5 °C; yield 88%; IR, 3250 cm^{-1}; ^{1}H NMR, δ=2.34 (3H, s), 3.16 (4H, s), 3.91 (2H, s), 7.12 (1H, d, J=7.2 Hz), 7.21 (1H, t, J=7.2 Hz), 7.35 (1H, d, J=7.2 Hz), 7.41 (1H, s), 7.62 (1H, s), and 8.20 (1H, bs); MS, m/z 249 (M$^+$), 232, 217, and 191. Found: C, 82.15; H, 6.37%. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 5.30%.

3-Acetoxy-4*H*-cyclopenta[*def*]phenanthrene (3a) by the Baeyer-Villiger Rearrangement of the Corresponding Ketone. Typical Procedure. A mixture of **8a**[6,7] (1.392 g, 6 mmol) in $CHCl_3$ (100 ml, percolated through alumina before use) was cooled in a refrigerator; MCPB (690 mg, 4 mmol) was added and stirred. Additional MCPB (690 mg) was added after 8 and 16 h (total 2.07 g, 12 mmol). The stirring was continued for 3 d below 5 °C. After treatment with aqueous sodium hydrogencarbonate, the organic layer was evaporated. The residue was chromatographed on SiO_2 with benzene and the first colorless eluate gave **3a** (1.027 g, 69%); mp 109—110 °C (EtOH); IR, 1753 and 1193 cm^{-1}; ^{1}H NMR, δ=2.42 (3H, s), 4.23 (2H, s), 7.26 (1H, d, J=8.4 Hz), and 7.51—7.84 (6H, m); MS, m/z 248 (M$^+$), 206, 205, 189, and 177. Found: C, 82.43; H, 4.82%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

1a; yield 67%; mp 130—131 °C; IR, 1752 and 1205 cm^{-1}; ^{1}H NMR, δ=2.50 (3H, s), 4.35 (2H, s), 7.36 (1H, d, J=7.6 Hz), 7.64—7.74 (4H, m), and 7.83—7.88 (2H, m); MS, m/z 248 (M$^+$), 206, 205, 177, and 176. Found: C, 82.40; H, 4.92%.

2a; yield 67%; mp 111.5—112.5 °C; IR, 1751, 1219, and 1206 cm^{-1}; ^{1}H NMR, δ=2.41 (3H, s), 4.37 (2H, s), 7.44 (1H, s), 7.54 (1H, s), 7.62—7.77 (2H, m), and 7.78—7.89 (3H, m); MS, m/z 248 (M$^+$), 206, 205, 177, and 176. Found: C, 82.50; H, 5.00%.

5a; yield 74%; mp 124.5—125.0 °C; IR, 1751 and 1203 cm^{-1}; ^{1}H NMR, δ=2.25 (3H, s), 3.13 (4H, s), 3.83 (2H, s), 6.72 (1H, s), 6.94 (1H, s), and 6.98—7.31 (3H, m); MS, m/z 250 (M$^+$), 208, 207, 191, and 189. Found: C, 81.85; H, 5.71%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

11; obtained by acetylation of the corresponding alcohol[11] in 85% yield; mp 93—94 °C; IR, 1723 and 1223 cm^{-1}; ^{1}H NMR, δ=2.22 (3H, s), 6.93 (1H, s), and 7.30—7.65 (8H, m); MS, m/z 248 (M$^+$), 206, and 189. Found: C, 82.52; H, 4.78%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

4a;[12] yield 81%; mp 97—98 °C. Hydrolysis of **4a** gave **4e**,[12] in 68% yield; mp 167—168 °C.

4*H*-Cyclopenta[*def*]phenanthren-1-ol (1e). The acetate **1a** (620 mg, 2.5 mmol) was dissolved in EtOH (10 ml) and a solution of KOH (2.5 g) in H_2O (10 ml) was added in a small portion into a warmed (60—70 °C) solution of **1a**. After 5 min, the resulting mixture was allowed to stand at room temperature and acidified by HCl to give **1e**; 489 mg (95%); mp 148—149 °C (cyclohexane); IR, 3340 cm^{-1}; ^{1}H NMR, δ=4.22 (2H, s), 5.23 (1H, s), 6.93 (1H, d, J=7.8 Hz), and 7.39—7.84 (7H, m); MS, m/z 206 (M$^+$) and 189. Found: C, 87.46; H, 4.90%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%.

2e; yield 95%; mp 169—170 °C; IR, 3320 cm^{-1}; ^{1}H NMR, δ=4.23 (2H, s), 5.02 (1H, s), 7.14 (1H, s), 7.18 (1H, s), and 7.44—7.70 (5H, m); MS, m/z 206, 189, and 176. Found: C, 87.53; H, 4.66%.

3e;[7] yield 93%; mp 165—166 °C; IR, 3350 and 3250 cm^{-1}; ^{1}H NMR, δ=4.29 (2H, s), 5.05 (1H, s), 7.15 (1H, d, J=7.8 Hz), and 7.59—7.92 (6H, m); MS, m/z 206, 189, and 176. Found: C, 87.09; H, 4.64%.

5e; yield 96%; mp 155—156 °C; IR, 3200 cm^{-1}; ^{1}H NMR, δ=3.01 (4H, s), 3.83 (2H, s), 4.76 (1H, s), 6.62 (1H, s), 6.83 (1H, s), and 7.05—7.36 (3H, m); MS, m/z 208 (M$^+$), 191, and 189. Found: C, 86.34; H, 6.04%. Calcd for $C_{15}H_{12}O$: 86.51; H, 5.81%.

Fries Rearrangements of 1a—5a and 7. Typical Procedure. Into a mixture of powdered $AlCl_3$ (64 mg, 0.48 mmol) in $PhNO_2$ (5 ml) was added a solution of **1a** (50 mg, 0.2 mmol) in $PhNO_2$ (5 ml) and stirred for 2 h at room temperature. Upon stirring with aq. HCl for 3 h, the reaction mixture was analyzed with a suitable hydrocarbon as an internal standard by means of gas chromatography (Shimadzu 6AMFP apparatus attached a column containing Silicone SE-30).

A pure specimen of **1b** was obtained by the reaction of **1e** (41 mg, 0.2 mmol) in $C_2H_4Cl_2$ (10 ml) with Ac_2O (0.023 ml, 0.24 mmol) and $AlCl_3$ (64 mg, 0.48 mmol) at room temperature for 30 min, yield 40 mg (80%); mp 178—179 °C; IR, 3450, 2690, 1639, and 1385 cm^{-1}; ^{1}H NMR, δ=2.66 (3H, s), 4.03 (2H, s), 7.48—7.70 (5H, m), 7.94 (1H, d, J=9.0 Hz), and 13.76 (1H, s); MS, m/z 248 (M$^+$), 233, 205, and 176. Found: C, 82.21; H, 5.04%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

Compound **1d** was isolated from the reaction of **1a** (248 mg, 1 mmol) with Ac_2O–$AlCl_3$ in $CHCl_3$; yield 221 mg (76%); mp 155—156 °C; IR, 1751, 1660, and 1195 cm^{-1}; ^{1}H NMR, δ=2.39 (3H, s), 2.78 (3H, s), 4.27 (2H, s), 7.35 (1H, d, J=7.8 Hz), 7.58—7.70 (2H, m), 7.81 (1H, d, J=9.0 Hz), 8.15

(1H, d, J=7.8 Hz), and 8.91 (1H, d, J=9.0 Hz). Found: C, 78.40; H, 4.99%. Calcd for $C_{19}H_{14}O_3$: C, 78.60; H, 4.85%.

Diketone **1d** was hydrolyzed with aqueous KOH in EtOH to give **1c**; yield 38%; mp 183—185 °C; IR, 3250, 1645, and 1254 cm^{-1}; ^{1}H NMR (DMSO-d_6), δ=2.76 (3H, s), 4.32 (2H, s), 7.09 (1H, d, J=7.5 Hz), 7.59 (1H, d, J=7.5 Hz), 7.80 (1H, d, J=7.5 Hz), 8.10 (1H, d, J=9.6 Hz), 8.86 (1H, d, J=7.5 Hz), 8.70 (1H, d, J=9.6 Hz), and 9.90 (1H, s); MS, m/z 248 (M$^+$), 233, 217, 205, and 189. Found: C, 82.55; H, 5.06%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

Fries Rearrangement of 2a. Acetate **2a** (50 mg, 0.2 mmol) was treated with $AlCl_3$ (64 mg, 0.48 mmol) in $C_2H_4Cl_2$ (10 ml) at room temperature for 3 h. The composition of the reaction mixture was submitted to GC. The main portion was chromatographed on SiO_2 with benzene to give **2d**; yield 12 mg (20%); mp 196—197 °C; IR, 1758, 1659, and 1201 cm^{-1}; ^{1}H NMR, δ=2.40 (3H, s), 2.79 (3H, s), 4.27 (2H, s), 7.38 (1H, s), 7.52 (1H, s), 7.62 (1H, d, J=7.8 Hz), 7.88 (1H, d, J=9.0 Hz), 8.09 (1H, d, J=7.8 Hz), and 8.34 (1H, d, J=9.0 Hz); MS, m/z 290 (M$^+$), 248, 233, 205, and 176. Found: C, 78.86; H, 5.16%. Calcd for $C_{19}H_{14}O_3$: 78.60; H, 4.85%.

The diketone **2d** was hydrolyzed to give **2c**; yield 80%; mp 129—130 °C; IR, 3260, 1637, and 1217 cm^{-1}; ^{1}H NMR, δ=3.00 (3H, s), 4.27 (2H, s), 5.25 (1H, s), and 7.10—8.10 (6H, m). Found: C, 82.52; H, 4.96%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

The isomeric **2b** was obtained by the reaction of **2e** (103 mg, 0.5 mmol) with Ac_2O (0.057 ml, 0.6 mmol) and $AlCl_3$ (200 mg, 1.5 mmol) in $C_2H_4Cl_2$ (40 ml) at room temperature for 30 min; yield 87 mg (70%); mp 153.5—154.5 °C; IR, 3450, 2580, 1607, and 1210 cm^{-1}; ^{1}H NMR, δ=2.95 (3H, s), 4.17 (2H, s), 7.20 (1H, s), 7.45—7.84 (3H, m), 7.88 (1H, d, J=9.0 Hz), 8.02 (1H, d, J=9.0 Hz), and 14.27 (1H, s); MS, m/z 248 (M$^+$), 233, and 176. Found: C, 82.48; H, 4.71%.

Fries Rearrangement of 3a. A reaction of **3a** (50 mg, 0.2 mmol) was carried out similar as described above. The reaction mixture yielded **3b**; yield 12 mg (24%); mp 176—177 °C; IR, 3400, 3200, 1640, and 1300 cm^{-1}; ^{1}H NMR, δ=2.84 (3H, s), 4.33 (2H, s), 7.61—7.77 (5H, m), 8.33 (1H, s), and 12.59 (1H, s); MS, m/z 248 (M$^+$), 233, 205, and 176. Found: C, 82.04; H, 4.98%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

Fries Rearrangement of 4a. Compound **4a** (50 mg, 0.2 mmol) was treated in a manner similar to that described above, giving 25.5 mg (51%) of **4b**; mp 152.5—153.5 °C; IR, 3400, 2650, 1639, 1447, and 1380 cm^{-1}; ^{1}H NMR, δ=2.99 (3H, s), 4.27 (2H, s), 7.58—7.68 (3H, m), 7.83 (1H, d, J=7.2 Hz), 8.00 (1H, d, J=8.0 Hz), 8.22 (1H, d, J=8.0 Hz), and 16.62 (1H, s); MS, m/z 248 (M$^+$), 233, and 176. Found: C, 82.02; H, 4.79%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

The Reaction of 5a. Compound **5a** (125 mg, 0.5 mmol) was treated with $AlCl_3$ (160 mg, 1.2 mmol) in PhCl (10 ml) with refluxing for 1 h to give 10 mg (8%) of **5c** and 12 mg (10%) of **5a**. **5c**; mp 186—187 °C; IR, 3300, 1650, 1575, 1368, and 1288 cm^{-1}; ^{1}H NMR, δ=2.62 (3H, s), 3.12 (4H, s), 3.85 (2H, s), 5.45 (1H, s), 6.64 (1H, s), 6.83 (1H, s), 7.72 (1H, s), and 7.90 (1H, s); MS, m/z 250 (M$^+$), 235, 207, and 189.

Diketone **5d** was obtained by a treatment of **5c** with Ac_2O in benzene; mp 116.0—116.5 °C; IR, 3550, 1757, 1665, and 1200 cm^{-1}; ^{1}H NMR, δ=2.34 (3H, s), 2.65 (3H, s), 3.19 (4H, s), 3.93 (2H, s), 6.90 (1H, s), 7.11 (1H, s), 7.80 (1H, s), and 7.98 (1H, s); MS, m/z 292 (M$^+$), 250, 235, and 207. Found: C, 77.84; H, 5.40%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

Reaction of 11. Compound **11** (248 mg, 1.0 mmol) in PhCl (30 ml) was refluxed with $AlCl_3$ (170 mg, 1.3 mmol) for 1 h; only **11** (120 mg, 48%) was isolated from the reaction mixture.

2-(4*H*-Cyclopenta[*def*]phenanthren-1-yl)-2-propanol (6b). A mixture of **6a** (1.872 g, 8 mmol) in PhH (30 ml) was added dropwise into MeMgI (prepared from 2.0 g (12 mmol) of CH_3I and 290 mg (12 mg atom) of Mg in ether); the mixture was refluxed for 4 h. Upon the usual treatment, the residue was chromatographed on SiO_2 with PhH giving 1.517 g (76%) of **6b**, 263 mg (14%) of **6c** (mp 50—51 °C), and 56 mg (3%) of **6a**. **6b**; mp 113.0—114.5 °C; IR, 3270 and 1148 cm^{-1}; ^{1}H NMR, δ=1.83 (6H, s), 2.09 (1H, bs), 4.20 (2H, s), 7.52—7.86 (5H, m), 7.76 (1H, d, J=9.0 Hz), and 8.47 (1H, d, J=9.0 Hz); MS, m/z 248 (M$^+$), 233, 230, 215, and 189. Found: C, 87.29; H, 6.73%. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50%.

7b; yield 38%; mp 88—89 °C; IR, 3370 and 1168 cm^{-1}; ^{1}H NMR, δ=1.62 (6H, s), 2.43 (1H, s), 4.05 (2H, s), and 7.35—7.75 (7H, m); MS, m/z 248 (M$^+$), 233, 230, 215, and 189. Found: C, 87.20; H, 6.79%.

8b; yield 81% (crude); IR, 3420 and 1170 cm^{-1}; ^{1}H NMR, δ=1.79 (6H, s), 2.01 (1H, s), 4.54 (2H, s), and 7.57—7.80 (7H, m); MS, m/z 248 (M$^+$), 230, 215, 202, and 189. Found: C, 86.99; H, 6.46%.

9b; yield 86%; mp 108—109 °C; IR, 3320 and 1150 cm^{-1}; ^{1}H NMR, δ=1.93 (6H, m), 2.07 (1H, s), 4.33 (2H, s), 7.58—7.80 (5H, m), 7.84 (1H, s), and 8.40 (1H, m); MS, m/z 248 (M$^+$), 233, 230, 215, and 189. Found: C, 87.01; H, 6.63%.

1-Isopropenyl-4*H*-cyclopenta[*def*]phenanthrene (6c). A mixture of **6b** (248 mg, 1 mmol) in Ac_2O (4 ml) was refluxed for 5 h giving 209 mg (91%) of **6c** by column chromatography; mp 50.5—51.0 °C; IR, 1622 cm^{-1}; ^{1}H NMR, δ=2.32 (3H, s), 4.34 (2H, s), 5.23—5.24 (1H, m), 5.45—5.46 (1H, m), 7.53 (1H, d, J=7.3 Hz), 7.61—7.71 (3H, m), 7.82 (1H, d, J=7.7 Hz), 7.83 (1H, d, J=9.1 Hz), and 8.05 (1H, d, J=9.1 Hz); MS, m/z 230 (M$^+$), 215, and 189. Found: C, 93.87; H, 5.93%. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13%.

7c; yield 68%; mp 65—66 °C; IR, 1612 cm^{-1}; ^{1}H NMR, δ=2.32 (3H, s), 4.27 (2H, s), 5.14 (1H, m), 5.42 (1H, m), and 7.50—7.90 (7H, m); MS, m/z 230 (M$^+$), 215, and 189. Found: C, 93.88; H, 5.86%.

8c; yield 26% from crude **8b**; mp 29.5—30.0 °C; IR, 1620 cm^{-1}; ^{1}H NMR, δ=2.32 (3H, s), 4.26 (2H, s), 5.20 (1H, s), 5.36 (1H, s), and 7.34—7.68 (7H, m); MS, m/z 230 (M$^+$), 215, and 189. Found: C, 93.64; H, 6.17%.

9c; yield 63%; mp 31.0—31.5 °C; IR, 1632 and 1624 cm^{-1}; ^{1}H NMR, δ=2.33 (3H, s), 4.30 (2H, s), 5.25 (1H, m), 5.40 (1H, m), and 7.47—8.00 (7H, m); MS, m/z 230 (M$^+$), 215, 213, and 189. Found: C, 93.58; H, 6.05%.

10c; yield 84% from **1e**; mp 55—56 °C; IR, 1614 cm^{-1}; ^{1}H NMR, δ=2.16 (3H, s), 3.08 (4H, s), 3.76 (2H, s), 4.92 (1H, s), 5.20 (1H, s), 6.87—7.13 (4H, m), and 7.33 (1H, s); MS, m/z 232 (M$^+$), 217, and 191. Found: C, 92.86; H, 7.14%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%.

1-Isopropyl-4*H*-cyclopenta[*def*]phenanthrene (6d). A solution of **6c** (115 mg, 0.5 mmol) in EtOH (60 ml) was shaken with Raney nickel (W-7, 0.15 g) under an atmosphere of hydrogen for 15 min at room temperature to give **6d** (60 mg, 52%); mp 70—71 °C; ^{1}H NMR, δ=1.45 (6H, d, J=6.6 Hz), 3.73 (1H, sep, J=6.6 Hz), 4.21 (2H, s), 7.14—7.73 (6H, m),

and 7.90 (1H, d, J=9.0 Hz); MS, m/z 232 (M^+), 217, 215, 202, and 189. Found: C, 93.27; H, 7.21%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%.

7d; yield 47%; mp 75—76 °C; ^{1}H NMR, δ=1.35 (6H, d, J=7.0 Hz), 3.00 (1H, sep, J=7.0 Hz), 4.14 (2H, s), and 7.30—7.75 (7H, m); MS, m/z 232 (M^+), 217, 202, and 189. Found: C, 93.27; H, 7.21%.

8d; yield 52%; mp 45.5—46.0 °C; ^{1}H NMR, δ=1.44 (6H, d, J=7.0 Hz), 3.37 (1H, sep, J=7.0 Hz), 4.34 (2H, s), and 7.54—7.82 (7H, m); MS, m/z 232 (M^+), 217, 202, and 189. Found: C, 93.02; H, 7.27%.

9d; yield 32%; mp 33.5—34.0 C; ^{1}H NMR, δ=1.50 (6H, d, J=6.6 Hz), 3.71 (1H, sep, J=6.6 Hz), 4.24 (2H, s), and 7.30—7.92 (7H, m); MS, m/z 232 (M^+), 217, 202, and 189. Found: C, 93.12; H, 6.68%.

10d; yield 60%; mp 97.5—98.0 °C; ^{1}H NMR, δ=1.30 (6H, d, J=6.9 Hz), 2.96 (1H, sep, J=6.9 Hz), 3.13 (4H, s), 3.86 (2H, s), 7.00 (1H, s), 7.07—7.18 (2H, m), 7.23 (1H, s), and 7.31 (1H, d, J=7.3 Hz); MS, m/z 234 (M^+), 219, 202, 191, and 189. Found: C, 92.26; H, 7.88%. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74%.

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