Friedel-Crafts Acetylations of Methoxy-4*H*-cyclopenta[*def*]-phenanthrenes and the 4-Ketones

Masahiro MINABE,* Masaaki YOSHIDA, Yutaka TAKABAYASHI, and Masatoshi MASUDA
Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321
(Received June 27, 1987)

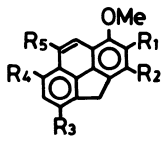
Acetylations of 2- and 3-methoxy-4*H*-cyclopenta[*def*]phenanthrene gave predominantly the 1- and 8-acetyl derivatives, respectively. The acetylation of the 1-methoxy compound afforded the 2-, 3-, 5-, 7-, and 8-yl ketones and the reaction of the 8-methoxy derivative yielded the 1- and 3-acetyl derivatives. Similar reactions of 1-, 2-, 3-, and 8-methoxy-4*H*-cyclopenta[*def*]phenanthren-4-one occurred mainly at the 2-, 1-, 8-, and 9-positions, respectively.

The hydrocarbon, 4*H*-cyclopenta[*def*]phenanthrene is one of the interesting polycyclic aromatic hydrocarbons[1] because of the combination of their ring moieties and for carcinogenic screening tests. Our previous papers concerned the electrophilic substitution of electron-attractive acetyl-, bromo-, and nitro-4*H*-cyclopenta[*def*]phenanthrenes[2] and the bromination of cyclopentaphenanthrenamine derivatives having an electron-donating property.[3]

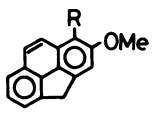
The present paper deals with the Friedel–Crafts acetylations of 1- (**1a**), 2- (**2a**), 3- (**3a**), 8-methoxy- (**4a**), and 8,9-dihydro-2-methoxy-4*H*-cyclopenta[*def*]-phenanthrene(**5a**) in order to obtain further information regarding the reactivities of the parent hydrocarbon with electrophiles. It also concerns the acylation of the methoxy ketones, **6a—10a** (Scheme 1).

Acetylations of **1a—4a** were carried out according to the modified Perrier procedure[4] by means of the addition of a substrate into the resulting mixture of acetic anhydride and aluminium chloride. The reaction mixture was analyzed by means of gas chromatographic technique (Table 1). The reaction of **1a** afforded 2- (**1b**), 3- (**1c**), 5- (**1d**), 7- (**1e**), and 8-acetyl compound (**1f**). The reactions of **2a** and **3a** gave predominantly 2-methoxy-1-acetyl compound **2b** and 3-methoxy-8-acetyl derivative **3b**, respectively. The acetylation of **4a** yielded two isomers, **4b** and **4c**. Similar trends were observed in the case of acetyl chloride as the acylating agent.[5]

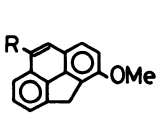
The orientations on these reactions can be explained by the combination of reactivities of methoxynaphthalene[6] and of parent 4*H*-cyclopenta[*def*]phenanthrene;[7] electrophile attacks mainly the 1- and 3-positions of the latter accompanied by a substitution at the 2- and 8-positions. The formations of **1c**, **1d**, and **1e** from **1a** are due to the original reactivity of the parent hydrocarbon. Also, the production of **1b** and **1f** (and a part of **1c**) are due to the 1-methoxy group



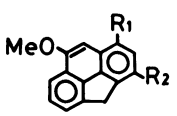
1a (all of R=H)
1b (R_1=Ac, other R=H)
1c (R_2=Ac, other R=H)
1d (R_3=Ac, other R=H)
1e (R_4=Ac, other R=H)
1f (R_5=Ac, other R=H)



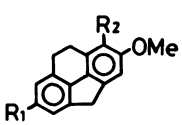
2a (R=H)
2b (R=Ac)



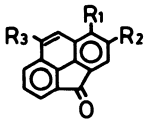
3a (R=H)
3b (R=Ac)



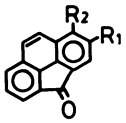
4a (R_1=R_2=H)
4b (R_1=Ac, R_2=H)
4c (R_1=H, R_2=Ac)



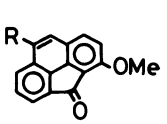
5a (R_1=R_2=H)
5b (R_1=Ac, R_2=H)
5c (R_1=R_2=Ac)



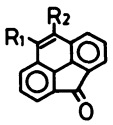
6a (R_1=OMe, R_2=R_3=H)
6b (R_1=OH, R_2=Ac, R_3=H)
6c (R_1=OMe, R_2=H, R_3=Ac)



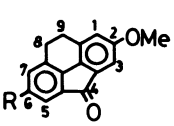
7a (R_1=OMe, R_2=H)
7b (R_1=OMe, R_2=Ac)
7c (R_1=OH, R_2=Ac)



8a (R=H)
8b (R=Ac)



9a (R_1=OMe, R_2=H)
9b (R_1=OH, R_2=Ac)



10a (R=H)
10b (R=Ac)

Scheme 1.

Table 1. The Friedel-Crafts Acetylation of **1a—4a**

Reactant	[$AlCl_3$] / [Reactant]	Solvent / ml	Temp / °C	Yield / %	Isomer distribution/%						Recovd. / %
					1-	2- (**1b**)	3- (**1c**)	5- (**1d**)	7- (**1e**)	8- (**1f**)	
1a	2.2	60	20	11		30	12	2	16	40	89
1a	2.2	60	75	19		14	23	7	14	42	78
1a	3.3	60	20	42		66	4	1	7	24	55
					(**2b**)						
2a	2.2	60	20	80	100						14
										(**3b**)	
3a	2.2	180	20	92						100	5
					(**4b**)		(**4c**)				
4a	2.2	90	20	8	37		63				88
4a	2.2	90	75	40	31		69				60
4a	3.3	90	20	86	67		33				13

which may accelerate the 2- and 8-positions by a resonance effect, as is 1-methoxynaphthalene. The reactions of **2a**, **3a**, and **4a** are postulated to be those of 2-methoxynaphthalene derivatives in which the 1-, 6-, and 8-positions are accelerated.

The methoxyl group on **2a** and **3a** enhances the acylation more than the case of **1a** and **4a**. Experiments at different temperatures show that the formation of **1b** is kinetically controlled and that the formations of **1c** and **1d** are thermodynamically controlled. Also **4b** and **4c** are formed from **4a** under kinetic and thermodynamic controls under these conditions. The molar ratio of aluminium chloride against the substrate influences not only the reaction rate but also the regioselectivities.[6] An increase in the ratio causes an acceleration of the reaction and gives kinetically-controlled products, such as **1b** and **4b**.

The acetylation of **5a** afforded predominantly **5b**. The second attack of the reagent occurred at the 1-position, giving 1,6-diacetyl compound **5c**. The reactivity at the 6-position of **5a** is accelerated by the methoxy group more than that of the 7-position of 2-methoxyfluorene.[8]

4*H*-Cyclopenta[*def*]phenanthren-4-one is less reactive to electrophile than the parent hydrocarbon and the reaction of the ketone occurs mainly at the 8-position accompanied by the minor 2-isomer.[9] The next interesting point concerns the Friedel-Crafts acetylations of 4-oxo derivatives of **1a—5a**. The reaction of **6a** afforded **6b** as the main product and **6c** as the minor product. The acetylation of **7a** occurred giving 1-acetyl-2-methoxy compound **7b** and the acetyl phenol **7c**. The isomeric **8a** gave the corresponding **8b**, and the another isomer, **9a** yielded **9b**. Also, the substitution of **10a** produced **10b**.

Because of the low reactivity due to the 4-carbonyl, the reaction required a long time in the presence of a large amount of acylating complex. A substitution adjacent to the methoxyl group causes a fission of the methyl group followed by the formation of a chelate ring, such as **6b**, **7c**, or **9b**, under these conditions.

The reactive position of **6a**, **7a**, **8a**, and **10a** are similar to that of **1a**, **2a**, **3a**, and **5a**, respectively. On the other hand, the excited position of **9a** to the electrophile is the 9-position, differing from the case of **4a**, but the same as that of *N*-acetyl-4*H*-cyclopenta[*def*]phenanthren-8-amine.[3] This should be simply interpreted as indicating that the 8-methoxy group is not an effective electron-donating group compared to the amino and acetylamino groups, and affects only on the adjacent 9-position of the deactivated ketone.

Experimental

All the melting points are uncorrected. The ^1H NMR spectra were measured using a Jeol JNM C-60 HL or a Varian VXR-300 spectrometer in $CDCl_3$ using TMS as an internal reference. The IR (KBr-pellet), UV data (cyclohexane), and mass spectra were recorded on a Jasco IR-G, a Shimadzu UV-180, and a Hitachi M-80 spectrometer, respectively.

1-Methoxy-4*H*-cyclopenta[*def*]phenanthrene (1a).[10] To a mixture of 4*H*-cyclopenta[*def*]phenanthren-1-ol[11] (434 mg, 2.1 mmol) in acetone (5 ml) was added aq KOH (1.12 g, 20 mmol) in H_2O (1 ml), and Me_2SO_4 (0.66 ml, 7 mmol) was added dropwise at room temperature giving 434 mg (90%) of **1a**: mp 99—100 °C (lit,[10] mp 96—98 °C); IR, 1241 cm^{-1}; ^1H NMR, δ=4.06 (3H, s), 4.29 (2H, s), 7.01 (1H, d, J=7.6 Hz), 7.58—7.66 (3H, m), 7.78—7.82 (2H, m), and 8.02 (1H, d, J=9.0 Hz); UV, λ_{max} 352 (log ε 3.62), 345 (3.16), 335 (3.45), 328 (3.16), 311 (4.13), 298 (4.08), 270 (4.36), 261 (4.44), and 252 nm (4.42); MS, m/z 220 (M^+) and 205. Found: C, 87.08; H, 5.69%. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49%.

2a; yield 95%; mp 86—87 °C; IR, 1192 cm^{-1}; ^1H NMR, δ=3.99 (3H, s), 4.31 (2H, s), 7.28 (1H, s), 7.36 (1H, s), 7.54—7.66 (2H, m), and 7.75—7.84 (3H, m); UV, λ_{max} 357 (log ε 3.53), 350 (3.17), 339 (3.33), 333 (3.08), 324 (3.03), 301 (3.99), 289 (4.00), 280 (4.12), and 257 nm (4.87); MS, m/z 220 (M^+), 205, and 177. Found: C, 87.22; H, 5.76%.

3a; yield 87%; mp 47—48 °C; IR, 1242 cm^{-1}; ^1H NMR, δ=4.01 (3H, s), 4.24 (2H, s), 7.06 (1H, d, J=8.4 Hz), and 7.39—7.72 (6H, m); UV, λ_{max} 349 (log ε 3.37), 342 (2.99), 333 (3.26), 312 (4.14), 300 (4.16), 277 (4.11), and 250 nm (4.70); MS, m/z 220 (M^+) and 205. Found: C, 87.43; H, 5.36%.

4a; yield 88%; mp 129—130 °C; IR, 1148 cm^{-1}; ^1H NMR, δ=4.12 (3H, s), 4.33 (2H, s), 7.04 (1H, s), 7.56—7.73 (5H, m), and 8.00 (1H, dd, J=7.9, 0.7 Hz); UV, λ_{max} 346 (log ε 3.29), 339 (2.92), 330 (3.19), 309 (3.92), 297 (4.08), and 248 nm (4.74); MS, m/z 220 (M^+), 205, and 177. Found: C, 87.06; H, 5.29%.

5a; yield 87%; mp 67—68 °C; IR, 1134 cm^{-1}; ^1H NMR, δ=3.11 (4H, s), 3.85 (5H, s), 6.71 (1H, d, J=1.6 Hz), 6.93 (1H, d, J=1.6 Hz), 7.07—7.15 (2H, m), and 7.30 (1H, d, J=6.9 Hz); UV, λ_{max} 281 nm (log ε 4.39); MS, m/z 222 (M^+), 207, and 178. Found: C, 86.70; H, 6.64%. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%.

1-Methoxy-4*H*-cyclopenta[*def*]phenanthren-4-one (6a). To a mixture of **1a** (770 mg, 3.5 mmol) in pyridine (50 ml) was bubbled oxygen in the presence of Triton B (40% in MeOH, 0.35 ml) for 5 h at room temperature to give **6a** (663 mg, 81%); mp 186.5—187.5 °C; IR, 1706, 1626, and 1240 cm^{-1}; ^1H NMR, δ=4.08 (3H, s), 6.85 (1H, d, J=7.8 Hz), 7.54—7.79 (4H, m), 8.87 (1H, d, J=8.1 Hz), and 7.92 (1H, d, J=9.1 Hz); UV, λ_{max} 390 (log ε 3.05), 371 (3.13), 315 (4.21), 302 (4.14), and 243 nm (4.87). Found: C, 82.03; H, 4.32%. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

7a; yield 75%; mp 140—141 °C; IR, 1712, 1628, and 1268 cm^{-1}; ^1H NMR δ=3.95 (3H, s), 7.24 (1H, d, J=1.7 Hz), 7.43 (1H, d, J=1.7 Hz), 7.44—7.49 (1H, m), 7.63—7.73 (3H, m), and 7.83 (1H, d, J=8.1 Hz); UV, λ_{max} 404 (log ε 2.84), 380 (2.85), 360 (2.87), 326 (3.84), 311 (3.72), 295 (3.74), and 242 nm (5.09). Found: C, 82.08; H, 4.19%.

8a; yield 56%; mp 123—124 °C; IR, 1704, 1624, and 1268 cm^{-1}; ^1H NMR, δ=4.14 (3H, s), 7.02 (1H, d, J=8.4 Hz), and 7.30—7.82 (6H, m); UV, λ_{max} 415 (log ε 3.14), 392 (3.22), 311 (3.73), 296 (4.22), and 231 nm (4.79). Found: C, 82.02; H, 4.21%.

9a; yield 89%; mp 201.5—202.5 °C; IR, 1704, 1626, and 1268 cm^{-1}; ^1H NMR, δ=4.04 (3H, s), 6.81 (1H, s), and 7.35—8.08 (6H, m); UV, λ_{max} 428 (log ε 2.81), 418 (2.79), 404 (2.95), 381 (2.95), 321 (3.67), 286 (4.02), 260 (4.10), and 236 nm (4.98). Found: C, 81.84; H, 4.05%.

10a; yield 90%; mp 116.5—117.5 °C; IR, 1702 and 1592 cm^{-1}; ^1H NMR, δ=3.00 (4H, s), 3.81 (3H, s), 6.75 (1H, d, J=1.8 Hz), 6.94 (1H, d, J=1.8 Hz), 7.05 (1H, t, J=7.4 Hz), 7.15 (1H, d, J=7.4 Hz), and 7.30 (1H, d, J=7.4 Hz); UV, λ_{max} 453 (log ε 2.96), 311 (3.58), 300 (3.85), 276 (4.75), and 266 nm (4.61). Found: C, 81.30; H, 5.32%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%.

Friedel-Crafts Acetylation of 1a—4a. General Procedure. To aluminium chloride (2.2—3.3 mmol) in 1,2-dichloroethane (60—180 ml), acetic anhydride (1.1 mmol) was added at 20 °C (or 75 °C) and the mixture was stirred until it became a homogeneous solution (30 min). All of the finely-powdered methoxy compound (1.0 mmol) was added and stirred for 5 min.

Upon the usual treatment of the reaction mixture, a part of the organic layer was submitted to GC (Shimadzu 6AMFP apparatus attached a column containing Dexsil 300 GC (5%), at 250 °C) after the addition of 2-acetyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene as an internal standard.

Acetylation of 1a. To a mixture of Ac_2O (0.07 ml, 0.7 mmol) and $AlCl_3$ (150 mg, 1.1 mmol) in $PhNO_2$ (30 ml), **1a** (107 mg, 0.49 mmol) was added at room temperature, followed by stirring for 30 min. Upon the usual treatment, the organic layer was distilled with steam and the residue was chromatographed on silica gel with benzene. The first colorless band afforded 42 mg (39%) of **1a**, mp 98—100 °C.

The second light yellow band gave a trace amount of **1d**: mp 149—150 °C (EtOH); IR, 1664 and 1270 cm^{-1}; ^1H NMR, δ=2.61 (3H, s), 4.08 (3H, s), 4.46 (2H, s), 6.85 (1H, d, J=7.8 Hz), 7.39—7.91 (4H, m), and 7.84 (1H, d, J=7.8 Hz); UV, λ_{max} 377 (log ε 3.67), 360 (3.71), 329 (4.06), and 243 nm (4.53); MS, m/z 262 (M^+), 247, and 204. Found: C, 82.40; H, 5.43%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

The next yellow band was collected and gave the following three compounds: **1f** (24 mg, 19%); mp 154—155 °C (EtOH); IR, 1656 and 1274 cm^{-1}; ^1H NMR, δ=2.86 (3H, s), 4.07 (3H, s), 4.24 (2H, s), 6.98 (1H, d, J=7.8 Hz), 7.43—7.81 (3H, m), and 8.64—8.95 (2H, m); UV, λ_{max} 377 (log ε 3.67), 360 (3.71), 329 (4.06), and 243 nm (4.53); MS, m/z 262 (M^+) and 149. Found: C, 82.31; H, 5.55%.

1e (trace); mp 155—156 °C (EtOH); IR, 1664 and 1246 cm^{-1}; ^1H NMR, δ=2.82 (3H, s), 4.07 (3H, s), 4.32 (2H, s), 7.06 (1H, d, J=7.8 Hz), 7.63 (1H, d, J=7.8 Hz), 7.71 (1H, d, J=7.5 Hz), 8.21 (1H, d, J=9.2 Hz), 8.23 (1H, d, J=7.5 Hz), and 8.86 (1H, d, J=9.2 Hz); UV, λ_{max} 360 (log ε 3.30), 316 (4.06), 300 (4.15), and 250 nm (4.80); MS, m/z 262 (M^+) and 149. Found: C, 82.20; H, 5.25%.

1c (35 mg, 27%); mp 138—139 °C (EtOH); IR, 1668 and 1234 cm^{-1}; ^1H NMR, δ=2.77 (3H, s), 4.09 (3H, s), 4.48 (2H, s), 7.43 (1H, s), and 7.56—8.16 (5H, m); UV, λ_{max} 364 (log ε 3.36), 347 (3.34), 300 (3.90), and 260 nm (4.51); MS, m/z 262 (M^+), 247, and 149. Found: C, 82.21; H, 5.45%.

The next yellow band yielded a trace amount of **1b**; mp 78—79 °C; IR, 1672 and 1380 cm^{-1}: ^1H NMR, δ=2.81 (3H, s), 4.12 (3H, s), 4.30 (2H, s), 7.46—7.98 (5H, m), and 8.02 (1H, d, J=9.0 Hz); UV, λ_{max} 364 (log ε 3.02), 346 (3.12), 301 (4.19), 274 (4.70), and 266 nm (4.72); MS, m/z 262 (M^+), 247, and 149. Found: C, 82.35; H, 5.51%.

The Reaction of 2a. A mixture of Ac_2O (0.09 ml, 0.9 mmol) and $AlCl_3$ (190 mg, 1.4 mmol) in $PhNO_2$ (40 ml) was stirred with **2a** (140 mg, 0.64 mmol) at 20 °C for 30 min. Upon the treatment as described above, **2a** (17 mg, 12%, mp 82—84 °C) and **2b** (139 mg, 83%) were isolated by means of silica-gel column chromatography. **2b**; mp 128—129 °C; IR, 1656 and 1386 cm^{-1}; ^1H NMR, δ=2.72 (3H, s), 4.06 (3H, s), 4.34 (2H, s), 7.47 (1H, s), 7.57—7.68 (2H, m), 7.80 (1H, d, J=7.8 Hz), 7.88 (1H, d, J=9.1 Hz), and 8.06 (1H, d, J=9.1 Hz); UV, λ_{max} 364 (log ε 3.46), 347 (3.43), 299 (4.02), and 257 nm (4.67); MS, m/z 262 (M^+), 247, 232, 189, 176, and 149. Found: C, 82.65; H, 5.62%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

Acetylation of 3a. A solution of **3a** (220 mg, 1 mmol) was added into a mixture of Ac_2O (0.11 ml, 1.2 mmol) and $AlCl_3$ (290 mg, 2.2 mmol) in $PhNO_2$ (120 ml), and the resulting mixture was stirred at 20 °C for 30 min giving **3b** (240 mg, 92%); mp 156—157 °C; IR, 1650, 1258, and 1234 cm^{-1}; ^1H NMR, δ=2.84 (3H, s), 4.13 (3H, s), 4.37 (2H, s), 7.31 (1H, d, J=8.6 Hz), 7.71—7.73 (2H, m), 7.91 (1H, d, J=8.6 Hz), 8.48 (1H, s), and 8.81—8.84 (1H, m); UV, λ_{max} 332 (log ε 4.28), 286 (4.16), and 252 nm (4.62); MS, m/z 262 (M^+), 247, 223, 176, and 149. Found: C, 82.25; H, 5.39%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

Acetylation of 4a. A mixture of **4a** (116 mg, 0.53 mmol) was mixed with a mixture of Ac_2O (0.07 ml, 0.7 mmol) and $AlCl_3$ (150 mg, 1.1 mmol) in $C_2H_4Cl_2$ (30 ml) and stirred at 20 °C for 30 min. Upon the usual treatment, the resulting

residue was chromatographed on a silica-gel column. The first colorless eluate afforded 14 mg (12%) of **4a**, mp 129—130 C. The first fraction of yellow band gave 77 mg (56%) of **4b**; mp 160—161 °C; IR, 1654, 1246, and 1151 cm^{-1}; ^1H NMR, δ=2.81 (3H, s), 4.18 (3H, s), 4.37 (2H, s), 7.57—7.75 (3H, m), 8.05 (1H, d, J=7.8 Hz), 8.22 (1H, d, J=7.6 Hz), and 8.33 (1H, s); UV, λ_{max} 373 (log ε 3.93), 356 (3.83), 328 (4.12), 314 (4.04), 284 (4.13), 273 (4.15), and 258 nm (4.66); MS, m/z 262 (M^+), 247, 219, 176, and 149. Found: C, 82.50; H, 5.56%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

The second fraction yielded 32 mg (23%) of **4c**; mp 151—153 °C; IR, 1666, 1270, and 1149 cm^{-1}; ^1H NMR, δ=2.76 (3H, s), 4.14 (3H, s), 4.65 (2H, s), 7.04 (1H, s), 7.65—7.80 (3H, m), 8.02 (1H, d, J=7.7 Hz), and 8.10 (1H, d, J=8.4 Hz); UV, λ_{max} 336 (log ε 4.28), 323 (4.33), 280 (4.23), and 260 nm (4.58); MS, m/z 262 (M^+), 247, 204, 176, and 149. Found: C, 82.40; H, 5.63%.

Friedel-Crafts Reaction of 5a. A 1,2-dichloroethane (30 ml) solution of **5a** (111 mg, 0.5 mmol), Ac_2O (0.07 ml, 0.7 mmol), and $AlCl_3$ (150 mg, 1.1 mmol) was stirred at room temperature. Upon column chromatography (SiO_2), 54 mg (41%) of **5b** and a trace amount of **5c** were isolated. **5b**; mp 109—110 °C; IR, 1660 and 1286 cm^{-1}; ^1H NMR, δ=2.62 (3H, s), 3.13 (4H, s), 3.85 (3H, s), 3.90 (2H, s), 6.74 (1H, s), 6.96 (1H, s), 7.77 (1H, s), and 7.95 (1H, s); UV, λ_{max} 341 (log ε 4.47) and 326 nm (4.49); MS, m/z 264 (M^+), 249, and 221. Found: C, 81.57; H, 5.89%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

5c; mp 167—168 °C; IR, 1668, 1642, and 1286 cm^{-1}; ^1H NMR, δ=2.62 (3H, s), 2.63 (3H, s), 3.16 (4H, s), 3.95 (3H, s), 4.14 (2H, s), 6.83 (1H, s), 7.77 (1H, s), and 7.95 (1H, s); MS, m/z 306 (M^+), 291, 279, 247, 206, and 167. Found: C, 78.59; H, 5.80%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%.

In an another experiment with a long reaction time (1h), a small amount of 1,6-diacetyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthren-2-ol was obtained in addition to **5b** and **5c**: mp 228—230 °C; IR, 1666, 1631, and 1220 cm^{-1}; ^1H NMR, δ=2.62 (3H, s), 2.73 (3H, s), 3.12 (4H, s), 4.08 (2H, s), 6.76 (1H, s), 7.73 (1H, s), 7.94 (1H, s), and 13.13 (1H, s); MS, m/z 292 (M^+), 277, 249, 206, and 176. Found: C, 77.81; H, 5.68%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

The Friedel-Crafts Acetylation of 6a. Ketone **6a** (117 mg, 0.5 mmol) was added into a mixture of Ac_2O (0.32 ml, 3 mmol) and $AlCl_3$ (800 mg, 6 mmol) in $C_2H_4Cl_2$ (7.5 ml) and stirred at room temperature for 72 h. Upon the usual treatment, the residue was chromatographed on silica gel and the light yellow band afforded 89 mg (68%) of **6b**: mp 270.5—272.0 °C (from benzene); IR, 2600, 1706, 1630, and 1230 cm^{-1}; ^1H NMR, δ=2.79 (3H, s), 7.70—7.75 (1H, m), 7.82 (1H, d, J=9.0 Hz), 7.88 (1H, d, J=7.9 Hz), 7.98 (1H, d, J=8.0 Hz), 8.10 (1H, d, J=9.0 Hz), 8.21 (1H, s), and 14.85 (1H, s). Found: C, 78.06; H, 3.85%. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84%.

The next yellow band yielded 21 mg (15%) of **6c**: mp 229—230 °C (from cyclohexane); IR, 1694, 1668, and 1272 cm^{-1}; ^1H NMR, δ=2.79 (3H, s), 4.07 (3H, s), 6.76 (1H, d, J=7.8 Hz), 7.43—7.80 (3H, m), 8.42 (1H, s), and 8.73—8.89 (1H, m). Found: C, 78.68; H, 4.35%. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%.

Reaction of 7a. A mixture of **7a** (117 mg, 0.5 mmol), Ac_2O (0.16 ml, 1.7 mmol), and $AlCl_3$ (400 mg, 3 mmol) in $C_2H_4Cl_2$ (7.5 ml) was stirred at room temperature for 10 h giving **7b** (71 mg, 51%) and **7c** (37 mg, 28%), respectively.

7b: mp 176.5—177.5 °C (from benzene-hexane) which was confirmed by oxidation of **2b** with oxygen in the presence of Triton B (40%) in pyridine; IR, 1718, 1668, and 1272 cm^{-1}; ^1H NMR, δ=2.69 (3H, s), 4.04 (3H, s), 7.51—7.54 (1H, m), 7.57 (1H, s), and 7.74—7.87 (4H, m); UV, λ_{max} 400 (log ε 2.98), 331 (3.82), 317 (3.75), 296 (4.00), and 244 nm (4.98). Found: C, 78.23; H, 4.43%. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%.

7c: mp 213.0—213.5°C (from benzene); IR, 2630, 1706, 1624, and 1200 cm^{-1}; ^1H NMR, δ=3.91 (3H, s), 7.24 (1H, s), 7.32—8.04 (5H, m), and 14.14 (1H, s); UV, λ_{max} 440 (log ε 3.06), 392 (3.13), 346 (3.94), 330 (3.80), 313 (3.83), 300 (3.95), 270 (4.33), and 249 nm (4.74). Found: C, 77.82; H, 3.53%. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84%.

Reaction of 8a. A mixture of **8a** (234 mg, 1 mmol), Ac_2O (0.32 ml, 3.4 mmol), and $AlCl_3$ (800 mg, 6 mmol) in $C_2H_4Cl_2$ (15 ml) was stirred at room temperature for 10 h. The usual procedure afforded 14 mg (6%) of **8a** and 254 mg (92%) of **8b**. **8b**: mp 166.0—166.5 °C (from benzene-hexane); IR, 1702, 1662, and 1258 cm^{-1}; ^1H NMR, δ=2.80 (3H, s), 4.26 (3H, s), 7.18 (1H, d, J=8.8 Hz), 7.65—7.67 (1H, m), 7.82 (1H, d, J=7.0 Hz), 7.91 (1H, d, J=8.8 Hz), 8.32 (1H, s), and 8.92 (1H, d, J=8.4 Hz); UV, λ_{max} 383 (log ε 3.20), 334 (4.14), 303 (4.25), and 252 nm (4.67). Found: C, 78.28; H, 4.12%. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%.

Reaction of 9a. Ketone **9a** (58.5 mg, 0.25 mmol) was treated with Ac_2O (0.16 ml, 1.7 mmol) and $AlCl_3$ (400 mg, 3 mmol) in $C_2H_4Cl_2$ (7.5 ml) at room temperature for 10 h to yield 34 mg (52%) of **9b** and 16 mg (27%) of **9a**. **9b**: mp 210.0—210.5 °C (from benzene-hexane); IR, 2650, 1708, 1664, and 1384 cm^{-1}; ^1H NMR, δ=2.97 (3H, s), 7.60—7.70 (3H, m), 7.91 (1H, d, J=6.7 Hz), 8.12 (1H, dd, J=8.0, 4.3 Hz), 8.27 (1H, d, J=8.0 Hz), and 16.61 (1H, s); UV, λ_{max} 359 (log ε 3.87), 325 (3.88), and 231 nm (4.75). Found: C, 78.02; H, 3.89%. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84%.

Reaction of 10a. A mixture of **10a** (321 mg, 1.36 mmol), Ac_2O (0.32 ml, 3.4 mmol), and $AlCl_3$ (800 mg, 6 mmol) in $C_2H_4Cl_2$ (30 ml) was stirred at room temperature for 34 h to give 25 mg (8%) of **10a** and 256 mg (68%) of **10b**, respectively. **10b**: mp 220—221 °C (red needles from benzene-hexane); IR, 1704, 1668, and 1264 cm^{-1}; ^1H NMR, δ=2.58 (3H, s), 3.06 (4H, s), 3.84 (3H, s), 6.80 (1H, s), 6.99 (1H, s), 7.89 (1H, s), and 7.91 (1H, s); UV, λ_{max} 452 (log ε 3.25), 340 (4.07), 326 (4.09), 291 (4.59), and 254 nm (4.26). Found: C, 77.47; H, 5.27%. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07%.

Friedel-Crafts Acetylation of 4*H*-Cyclopenta[*def*]phenanthren-4-one. A mixture of the ketone (404 mg, 2 mmol), Ac_2O (4.4 ml, 47 mmol), and $AlCl_3$ (10.6 g, 79 mmol) in $C_2H_4Cl_2$ (15 ml) was stirred at room temperature for 20 d to give the recovered ketone (195 mg, 48%) and 8-acetyl-4*H*-cyclopenta[*def*]phenanthren-4-one (45 mg, 9%); mp 171.5—173.0 °C (from cyclohexane); IR, 1706 and 1664 cm^{-1}; ^1H NMR, δ=2.84 (3H, s), 7.61—7.67 (2H, m), 7.83—7.90 (2H, m), 7.99 (1H, d, J=8.0 Hz) 8.43 (1H, s), and 8.89 (1H, d, J=8.4 Hz); UV, λ_{max} 340 (log ε 3.17), 307 (4.13), and 240 nm (4.82). Found: C, 83.04; H, 3.88%. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09%.

The authors wish to thank Emeritus Professor Kazuo Suzuki and Professor Takashi Toda Utsunomiya University for their valuable discussion.

References

1) M. Minabe and K. Suzuki, *Yuki Gosei Kagaku Kyokai Shi*, **44**, 421 (1986).
2) M. Yoshida, H. Hirota, M. Minabe, and K. Suzuki, *J. Chem. Eng. Data*, **26**, 220 (1981).
3) M. Yoshida, M. Minabe, W. Ookawa, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **56**, 1259 (1983).
4) G. Perrier, *Ber.*, **33**, 815 (1900).
5) I. Hashimoto, *Nippon Kagaku Kaishi*, **1982**, 1179.
6) R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc. C*, **1966**, 181; C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc. B*, **1968**, 1112.
7) M. Yoshida, K. Hishida, M. Minabe, and K. Suzuki, *J. Org. Chem.*, **45**, 1783 (1980).
8) G. W. Gray, J. B. Hartley, and A. Ibbotson, *J. Chem. Soc.*, **1955**, 1686.
9) M. Yoshida, M. Kobayashi, M. Minabe, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **54**, 1159 (1981).
10) A. Sieglitz and W. Schidlo, *Chem. Ber.*, **96**, 1098 (1963).
11) M. Minabe, M. Yoshida, T. Amimoto, T. Nagata, and M. Kobori, *Bull. Chem. Soc. Jpn.*, **61**, 879 (1988).