Michael Addition of 4*H*-Cyclopenta[*def*]phenanthrene to 9,9′-Bifluorenylidene and the Related Reactions

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The compound 9-(4*H*-cyclopenta[*def*]phenanthren-4-yl)-9,9′-bifluorene was synthesized by the Michael addition of 4*H*-cyclopenta[*def*]phenanthrene to 9,9′-bifluorenylidene and also by other reactions. In addition, five kinds of trimers which consisted of 4*H*-cyclopenta[*def*]phenanthrene and fluorene were obtained by the same reactions. The conformation of these trimers is assigned to be the *gauche-gauche* form.

The Michael addition of fluorene (**1**) to 9,9′-bifluorenylidene (**2**) has been reported in detail.[1] In our previous publication,[2] the ring expansions on the active methylene of 4*H*-cyclopenta[*def*]phenanthrene (**3**) were shown to have a property similar to that of **1**. The acidities of methylene protons of hydrocarbons **1** and **3** have been investigated closely, with their analogues, by determination of the dissociation constant in some solvents.[3]

The present paper deals with the Michael additions of **3** and **1** to some fulvalenes in order to compare with additions of **1** to **2**, and also to clarify the conformations of the resulting trimers.

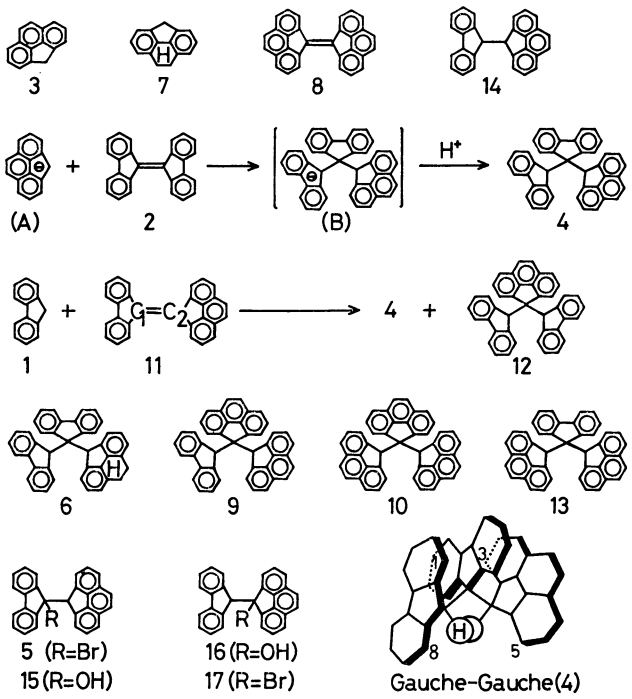
Results and Discussion

The Michael addition of **3** to **2** gave 9-(4*H*-cyclopenta[*def*]phenanthren-4-yl)-9,9′-bifluorene (**4**); the yield of **4** increased (10—35%) with the increase of base concentration (2—10% of sodium ethoxide). This reaction proceeded rapidly under a potassium hydroxide–aqueous pyridine system to give **4** in a reasonable yield. The addition can be explained by the nucleophilic attack of carbanion (A) on the highly-polarized acceptor **2** to form carbanion (B) followed by protonation to give **4** (Scheme 1).

Compound **4** was also prepared by the reaction of 9-lithiofluorene with bromide **5**, and also by dehydrogenation of 9-(8,9-dihydro-4*H*-cyclopenta[*def*]-phenanthren-4-yl)-9,9′-bifluorene (**6**), which was obtained by the addition of hydrocarbon **7**[4] to **2**.

The Michael reactions of fulvalene **8**[5] with **1** and with **3** yielded 4-(9-fluorenyl)-4,4′-bi(4*H*-cyclopenta-[*def*]phenanthrene) (**9**) and 4,4′ : 4′,4″-ter(4*H*-cyclopenta[*def*]phenanthrene) (**10**), respectively. The addition of **1** to unsymmetrical ethylene **11**[5] afforded isomeric **4** and 4,4-di(9-fluorenyl)-4*H*-cyclopenta[*def*]-phenanthrene (**12**) in a ratio of 75 to 25. Furthermore, the reaction of **3** with **11** gave 9,9-di(4*H*-cyclopenta[*def*]phenanthren-4-yl)fluorene (**13**) (73%) and **9** (27%).

The methine protons in the NMR spectrum of hydrocarbon **14** appear as two doublets about 0.3 ppm apart. In addition, the methine signals of alcohol **15** and bromide **5** shift to lower fields than those of alcohol **16** and bromide **17**, respectively. These findings may be explained as due to the difference of the acidities between the methylene protons of fragmental hydrocarbons **1** and **3**.[3] Also, this presumption would be extended reasonably to the reactivity of fulvalene **11**: the electron distribution on the central double bond of **11** lies to the **3** moiety. Therefore, the carbanion preferentially attacks the C_1 atom rather than the C_2 atom on **11**.



Scheme 1.

The assignment of the methine protons in the NMR spectra of the trimers was confirmed by comparison[6] with the corresponding deuterated compounds, as summarized in Table 1. The methine protons of **6** are observed as a two-proton singlet, which suggests that the electronic property of a methine proton on the **7** moiety of **6** is equivalent to that of a **1** segment. The two methine protons of the unsymmetrical trimers, such as **4** and **9**, are observed as two separate singlets, which may be regarded as the case of **14**. The two methine protons of **4** and **9** are assigned so that the methine on the leaflet of **3** corresponds to the peak in lower field and the methine on the leaflet of **1** to the one in higher field.

The compound **4** would be symmetrical with respect to the central fluorenylidene plane as in the analogues, **10**, **12**, and **13**, whose methine proton NMR

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TABLE 1. PROTON NMR SPECTRA OF THE MICHAEL ADDUCTS IN PYRIDINE-d_5

Compd	Methine (δ)	Aromatic (δ)
4	5.65 (1H, s), 5.93 (1H, s)	5.68 (2H, d, J=7.2 Hz), 6.46—8.78 (22H, m)
6[a]	5.35 (2H, s)	2.94 (4H, s, $-CH_2-CH_2-$), 4.87 (1H, d, J=7.8 Hz), 5.24 (1H, d, J=7.8 Hz), 6.18—8.70 (20H, m)
9	5.89 (1H, s), 6.18 (1H, s)	5.36 (1H, d, J=6.6 Hz), 5.48 (1H, d, J=6.6 Hz), 6.10—8.83 (22H, m)
10	6.41 (2H, s)	5.45 (2H, d, J=7.2 Hz), 6.52—8.90 (22H, m)
12	5.73 (2H, s)	5.44 (2H, d, J=7.8 Hz), 6.08—8.83 (22H, m)
13	6.14 (2H, s)	5.74 (2H, d, J=7.2 Hz), 6.54—8.86 (22H, m)

a) Measured in DMSO-d_6.

spectra showed a two-proton singlet. An examination of molecular scale models of **4** suggests that the *gauche-gauche* form is more appropriate to the conformation of **4** at the ground state than the *anti-anti* form, due to the steric interaction of the bulky aromatic rings.

The anomalous spread of the aromatic signal zone in the spectrum of **4** is probably attributable to the torsional conformation.[1] The signals at higher fields would be assigned to be the 1-proton of the outside 9-fluorenyl plane and the 3-proton of the 4*H*-cyclopenta[*def*]phenanthren-4-yl plane, because of being located in the shielding zone of the adjacent central aromatic ring,[1,7,8] as simulated in Scheme 1. On the contrary, the peaks at lower fields are due to the 8-proton of the 9-fluorenyl plane and the 5-proton of the 4*H*-cyclopenta[*def*]phenanthren-4-yl plane. The broad aromatic zone on the spectrum of **4** is observed to become narrower with the elevation of temperature. At a high temperature, the central sp^3-sp^3 single bonds may be released from the torsion, which would increase the probability of the *eclipsed-eclipsed* form. Therefore, the shielding effect of the central aromatic ring decreases and results in some reducing of the signal zone. A similar view can be applied to the other analogues: **6**, **9**, **10**, **12**, and **13**.

Experimental

All the melting points are uncorrected. The melting points of deuterated compounds in this series are identical with those of the parent hydrocarbons.

The IR spectra were obtained as KBr disks using a IR-G spectrophotometer (JASCO). The mass spectra were measured with a RMU-6E apparatus (Hitachi). The proton NMR spectra were recorded with a JNM-C-60HL (60 MHz) spectrometer (JEOL) using TMS as an internal reference. The deuterium incorporation was determined from the average value of five peaks on the NMR spectra.

*Michael Reaction of 9,9'-Bifluorenylidene (**2**) with 4H-Cyclopenta[def]phenanthrene (**3**).* To a soln of KOH (0.05 g) in H_2O (1 ml) and pyridine (9 ml), there was added 492 mg (1.5 mmol) of **2** and 285 mg (1.5 mmol) of **3**. The mixture was stirred for 1 h at room temperature under an atmosphere of nitrogen.

The reaction mixture was then poured into HCl (2%, 150 ml) and extracted with benzene (150 ml). The organic layer was dried over Na_2SO_4 and evaporated to dryness, and the residual materials were separated by means of silica-gel column chromatography (2.0×50 cm) in cyclohexane. The first and second eluates gave 34 mg of **3** (mp 114—116 °C) and 72 mg of **2** (mp 185—187 °C), respectively.

The third eluate was evaporated off and the residue was recrystallized from EtOAc to afford 554 mg (71%) of **4**: mp 259—260 °C (dec); MS, *m/e*, 518 (M^+), 353, and 329. Found: C, 94.91; H, 4.94%. Calcd for $C_{41}H_{26}$: C, 94.95; H, 5.05%.

*Michael Reaction between **2** and 8,9-Dihydro-4H-cyclopenta[def]phenanthrene (**7**).* A mixture of **2** (492 mg, 1.5 mmol), **7** (288 mg, 1.5 mmol), and aq K_2CO_3 (1.1 g in 2 ml) in pyridine (8 ml) was heated in a sealed tube at 95—98 °C for 24 h. The reaction mixture was treated in a manner similar to the above to yield 273 mg (35%) of **6**: mp 253—254 °C (dec); MS, *m/e*, 520 (M^+) and 494. Found: C, 94.65; H, 5.46%. Calcd for $C_{41}H_{28}$: C, 94.58; H, 5.42%.

*Michael Addition of **1** to 4,4'-Bi(4H-cyclopenta[def]phenanthren-4-ylidene) (**8**).* A mixture of **1** (249 mg, 1.5 mmol), **8** (564 mg, 1.5 mmol), and aq KOH (0.3 g in 1 ml) in pyridine (9 ml) was refluxed for 8 h under an atmosphere of nitrogen to give 520 mg (64%) of **9**: mp 319—320 °C (dec); MS, *m/e*, 542 (M^+) and 353. Found: C, 95.16; H, 4.67%. Calcd for $C_{43}H_{26}$: C, 95.17; H, 4.83%.

*Addition of **3** to **8**.* To a soln of $NaOPr^n$ prepared from metallic sodium (0.3 g) and *n*-PrOH (13 ml), there were added 564 mg (1.5 mmol) of **8** and 285 mg (1.5 mmol) of **3**. The resulting mixture was refluxed for 8 h under an atmosphere of nitrogen to yield 738 mg (87%) of **10**: mp 327—328 °C (dec); MS, *m/e*, 566 (M^+). Found: C, 95.11; H, 4.30%. Calcd for $C_{45}H_{26}$: C, 95.37; H, 4.63%.

*Michael Reaction of 4-(9-Fluorenylidene)-4H-cyclopenta[def]phenanthrene (**11**) with **1**.* A mixture of **11** (528 mg, 1.5 mmol) and **1** (249 mg, 1.5 mmol) in EtOH (10 ml) containing NaOEt (1.0 g) was heated in a sealed tube at 95—98 °C for 8 h. After cooling, the precipitates were collected and separated by silica-gel column chromatography to afford 381 mg (49%) of the mixture, which consisted of **4** (75% by NMR) and **12** (25%).

*Michael Addition of **3** to **11**.* A mixture of **3** (285 mg) and **11** (528 mg) was allowed to react under the conditions similar to those of **1** and **11** to yield the products (545 mg, 67%), which consisted of **13** (73% by NMR) and **9** (27%).

*9-(4H-Cyclopenta[def]phenanthren-4-yl)-9,9'-bifluorene (**4**).*

a): A soln of 9-lithiofluorene (prepared from 870 mg of **1** according to the procedure described elsewhere[9]) was added dropwise to a soln of bromide **5** (1.00 g, 2.3 mmol) in benzene–xylene (1 : 1, 60 ml) at 0 °C with stirring for 10 min. After being boiled for an additional 2 h, the reaction mixture was treated with aq NH_4Cl (5%, 50 ml), dried over Na_2SO_4, and then evaporated to dryness *in vacuo*. The residue was recrystallized from cyclohexane to afford 550 mg (46%) of **4**, which was identical in all respects with the specimen obtained by the Michael addition of **3** to **2**.

b): A soln of **6** (281 mg, 0.54 mmol) in 10 ml of *p*-cymene was refluxed with Pd–C (5%, 50 mg) for 40 h. The reaction

mixture was filtered and the filtrate was then steam distilled. The residue was chromatographed in cyclohexane on a silica-gel column to give 99 mg (35%) of **4**: mp 259—260 °C (dec).

*4,4-Di(9-fluorenyl)-4*H*-cyclopenta*[def]*phenanthrene (12).* A mixture of 9-lithiofluorene and bromide **17** was treated in a manner similar to that used for **4**, giving **12** in a yield of 50%: mp 286—287 °C (dec); MS, *m/e*, 518 (M^+), 353, and 165. Found: C, 94.73; H, 5.06%. Calcd for $C_{41}H_{26}$: C, 94.95; H, 5.05%.

*9,9-Di(4*H*-cyclopenta*[def]*phenanthren-4-yl)fluorene (13).* Compound **13** was prepared by the reaction of **3** with **5** according to a procedure similar to the above: yield 42%; mp 308—309 °C (dec); MS, *m/e*, 542 (M^+), 353, and 189. Found: C, 95.08; H, 4.89%. Calcd for $C_{43}H_{26}$: C, 95.17; H, 4.83%.

*9-(4*H*-Cyclopenta*[def]*phenanthren-4-yl)-9-fluorenol (15).*[5] A soln of fluorenone (5.4 g, 30 mmol) in xylene (60 ml) was allowed to react with 4-lithio-4*H*-cyclopenta[*def*]phenanthrene[10] (prepared from 5.7 g of **3** with LiBu^n in xylene) at 0 °C. The resulting mixture was refluxed for 1 h to afford 9.85 g (89%) of **15**: mp 188—189 °C (lit,[5] 188—189 °C); IR: 3310 cm^{-1} (–OH); MS, *m/e*, 370 (M^+); NMR (benzene-d_6): δ 1.94 (1H, s, –OH), 5.27 (1H, s, >CH–), and 6.50—7.65 (16H, m, Ar–H).

*4-(9-Fluorenyl)-4*H*-cyclopenta*[def]*phenanthren-4-ol (16).* To a soln of 4*H*-cyclopenta[*def*]phenanthren-4-one (3.0 g, 14.7 mmol) in benzene–xylene (1 : 1, 80 ml), there was added dropwise a soln of 9-lithiofluorene (prepared from 2.5 g of **1**) at 0 °C with stirring for 10 min. The mixture was boiled for an additional 2 h to yield 2.77 g (51%) of **16**: mp 202—203 °C; IR, 3275 cm^{-1} (–OH); MS, *m/e*, 370 (M^+); NMR (benzene-d_6): δ 1.98 (1H, s, –OH), 4.96 (1H, s, >CH–), and 6.60—7.50 (16H, m, Ar–H). Found: C, 90.80; H, 4.90%. Calcd for $C_{28}H_{18}O$: C, 90.78; H, 4.90%.

*4-(9-Fluorenylidene)-4*H*-cyclopenta*[def]*phenanthrene (11).*[5] A soln of **15** (0.8 g, 2.2 mmol) in AcOH (30 ml) containing concd HCl (0.2 ml) was refluxed for 1 h to give 500 mg (66%) of **11**: mp 197—198 °C (dec) (lit,[5] mp 196 °C, dec); MS, *m/e*, 352 (M^+).

Compound **16** was also converted into **11** in a 68% yield.

*4-(9-Fluorenyl)-4*H*-cyclopenta*[def]*phenanthrene (14).* A mixture of **11** (100 mg, 0.28 mmol), Zn powder (1 g), and concd HCl (1 ml) in AcOH (30 ml) was refluxed for 1.5 h to give 97 mg (96%) of **14**: mp 208—209 °C (from EtOAc); MS, *m/e*, 354 (M^+), 189, and 165; NMR (benzene-d_6): δ 5.04 (1H, d, J=4.2 Hz), 5.35 (1H, d), and 6.85—7.79 (16H, m). Found: C, 94.60; H, 5.01%. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%.

*9-Bromo-9-(4*H*-cyclopenta*[def]*phenanthren-4-yl)fluorene (5).* Dry HBr was bubbled into a soln of **15** (3.7 g, 10 mmol) in AcOH (135 ml) for 1 h. The reaction mixture was allowed to stand overnight and the precipitate was filtered, dried, and then recrystallized from benzene–cyclohexane (1 : 1) to afford 3.73 g (86%) of **5**: mp 185—187 °C (dec); MS, *m/e*, 434, 432 (M^+), 354, and 352; NMR (benzene-d_6) δ 5.53 (1H, s, >CH–) and 6.46—7.66 (16H, m, Ar–H). Found: C, 77.39; H, 3.74%. Calcd for $C_{28}H_{17}Br$: C, 77.60; H, 3.95%.

*4-Bromo-4-(9-fluorenyl)-4*H*-cyclopenta*[def]*phenanthrene (17).* Compound **17** was produced from **16** by a method similar to the above in a 78% yield: mp 171—172 °C (dec); MS, *m/e*, 434, 432 (M^+), 354, and 352; NMR (benzene-d_6): δ 5.24 (1H, s, >CH–) and 6.60—7.60 (16H, m, Ar–H). Found: C, 77.90; H, 3.96%. Calcd for $C_{28}H_{17}Br$: C, 77.60; H, 3.95%.

Syntheses of Deuterated Compounds. Hydrocarbon **3** was deuterated by the method applied in **1**[11] to give 4,4-dideuterio **3** (**3**-4,4-d_2) in a 92% yield. The deuterium incorporation was calculated to be 97% by NMR.

Also, **7**-4,4-d_2 was obtained in a 93% yield (deuterium incorporation, 97%).

Deuterated compounds of **4**, **6**, **9**, **10**, **12**, and **13** were prepared by the Michael reaction using corresponding substrates in a NaOEt–EtOD or NaOD–D_2O–pyridine system. The deuterium contents of these compounds were found to be *ca.* 100% at the methine protons.

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