A Facile Synthesis of 4*H*-Cyclopenta[*def*]phenanthrene

Masahiro MINABE,* Masaaki YOSHIDA, and Tokuei TAKAYANAGI
Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321
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Synopsis. A facile and cheap method for synthesis of 4*H*-cyclopenta[*def*]phenanthrene was achieved from fluorene as the starting material via di-*t*-butylfluorene.

In order to learn how to facilely obtain 4*H*-cyclopenta[*def*]phenanthrene (**1**) is one of the important reasons for studing the chemistry of **1**.[1] About ten procedures have been proposed for the synthesis of **1**; usually pyrene[2] and diphenic acid[3] are used as the starting materials in more facile methods. The preparation from tetralin is cheap but needs a long sequence.[4]

We wish to report here on a convenient, cheap method to make **1** from fluorene (**2**).

Hydrocarbon **2** is known to react with electrophile, mainly at the 2,7-positions, accompanied by a minor amount of the 2,5-positional isomer. For the preparation of the 4-substituted fluorene, it is necessary to block the 2,7-positions by the positional protecting group. The *t*-butyl group is convenient for the protection;[5] the synthesis of 4-bromofluorene by this method has been reported by Kajigaeshi et al.[6]

The sequence of the preparation of **1** from **2** is summarized in Scheme 1. We first planned to make 4-iodofluorene via **4e**;[6] however, trans-*t*-butylations of **4e** and **7** were difficult. The second plan, to convert **4e** into **4f**, was not effective due to the low yield. The final design was a route through **4a**.[6] The chloromethylation of **3** using chloromethyl methyl ether in the presence of titanium tetrachloride gave **4a** in a good yield accompanied by the formation of dimeric **8**. The conversion of **4a** to **4c**[6] was furnished by a treatment of potassium cyanide in DMF to give **4b**[6] followed by acidic hydrolysis to form **4c** in good yields, respectively.

The ring closure of the acid chloride **4d** gave the phenol **5** which was so unstable as to change into reddish materials containing the quinone. Crude **5** was submitted to a reduction using hydriodic acid-red phosphorus in acetic acid, giving a mixture of **1**, **6a**, and maybe **6b**. The mixture was directly treated with aluminium chloride in toluene, yielding expected hydrocarbon **1**.

This procedure can give **1** from **2** via 8-steps in a total yield of 12—13%, and be facile comparable to the method from diphenic acid[3] (40—50% yield through 10-steps). However, the available diphenic acid is more costly (more than three times) than commercial fluorene. The preparation is the most facile and cheap way to obtain **1** within the established procedures.

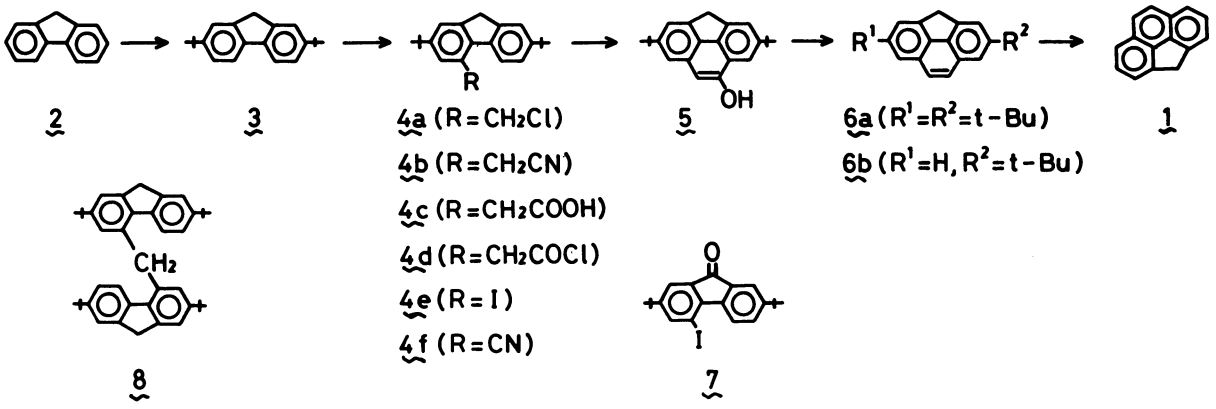
Experimental

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

Compounds **3** and **4e** were synthesized according to a method similar to that given in the literature.[6] ^{1}H NMR of **4e**, δ=1.35 (9H, s) 1.38 (9H, s), 3.87 (2H, s), 7.47—7.56 (3H, m), 7.80 (1H, s), and 8.66 (1H, d, J=8.5 Hz).

Trans-*t*-butylation of 4e. A mixture of **4e** (808 mg, 2 mmol) and $AlCl_3$ (200 mg, 1.5 mmol) in toluene (20 ml) was stirred at 50 °C for 6 h; only **2** was isolated from the resulting mixture: 73.2 mg (22%); mp 112—114 °C.

2,7-Di-*t*-butyl-4-iodo-9-fluorenone (7). A mixture of **4e** (2.02 g, 5 mmol) and $KMnO_4$ (4.42 g, 28 mmol) in acetone (100 ml) was stirred at room temperature for 10 h. After decomposition with aqueous $NaHSO_3$, the resulting mixture was extracted with benzene and chromatographed on a SiO_2 column. The yellow eluate was evaporated to give 1.85 g (89%) of **7**: mp 140.5—141.5 °C (hexane); IR, 1710 cm^{-1}; ^{1}H NMR, δ=1.32 (9H, s), 1.34 (9H, s), 7.58 (1H, dd, J=8.1, 2.0 Hz), 7.69 (1H, d, J=1.7 Hz), 7.73 (1H, d, J=2.0 Hz), 7.82 (1H, d, J=1.7 Hz), and 8.41 (1H, d, J=8.1 Hz); UV, λ_{max} 410 (log ε 3.01), 336 (3.00), 305 (3.62), 274 (4.74), 264 (4.68), and 240 (4.40); MS, m/z 418 (M^+) and



Scheme 1.

403. Found: C, 60.11; H, 5.29%. Calcd for $C_{21}H_{23}OI$: C, 60.29; H, 5.06%.

A mixture of **7** (418.5 mg, 1 mmol) and $AlCl_3$ (540 mg, 4 mmol) in toluene (10 ml) was stirred at 70 °C for 40 h, but no specific material was obtained except **7** (262 mg, 62%, mp 139.5—141.5 °C).

4-Cyano-2,7-di-*t*-butylfluorene (4f). A mixture of **4e** (809 mg, 2 mmol), KCN (263 mg, 4 mmol), and CuCN (361 mg, 4 mmol) in DMF (10 ml) was refluxed for 17 h. The mixture was extracted with benzene, washed with dil. HCl, successively with water, dried, and chromatographed on SiO_2 giving **4f** (110 mg, 20%); mp 192—193 °C (hexane); IR, 2250 cm^{-1}; ^1H NMR, δ=1.37 (9H, s), 1.38 (9H, s), 3.88 (2H, s), 7.49 (1H, dd, J=8.1, 1.8 Hz), 7.60—7.61 (2H, m), 7.74 (1H, s), and 8.29 (1H, d, J=8.1 Hz); UV, λ_{max} 329 (log ε 4.24), 316 (4.15), 273 (4.37), and 241 (4.27); MS, m/z 303 (M^+) and 270. Found: C, 86.92; H, 8.09; N, 4.43%. Calcd for $C_{22}H_{25}N$: C, 87.14; H, 8.24; N, 4.62%.

4-Chloromethyl-2,7-di-*t*-butylfluorene (4a).[6] To a mixture of **3** (2.78 g, 10 mmol) in CS_2 (100 ml), there was added chloromethyl methyl ether (2.30 ml, 30 mmol), and successively added $TiCl_4$ (1.30 ml, 11.6 mmol) for 5 min with ice-cooling. Upon stirring for 2 h at the temperature, the reaction was quenched by pouring into ice-water, and the organic layer was evaporated and purified by sublimation in vacuo to yield **4a** (2.84 g, 87%); mp 98.5—99.5 °C (lit,[6] mp 90—93 °C); UV, λ_{max} 310 (log ε 4.05) and 273 (4.34); ^1H NMR,[6] δ=1.38 (9H, s), 1.39 (9H, s), 3.89 (2H, s), 5.00 (2H, s), 7.31 (1H, s), 7.46 (1H, d, J=8.3 Hz), 7.54 (1H, s), 7.59 (1H, s), and 7.90 (1H, d, J=8.3 Hz).

The residue of sublimation afforded **8**: mp 230—231 °C; IR, 1260 cm^{-1}; ^1H NMR, δ=1.18 (18H, s), 1.34 (18H, s), 3.95 (4H, s), 4.87 (2H, s), 7.00 (2H, s), 7.23—7.26 (2H, m), 7.46 (2H, s), 7.59 (2H, s), and 7.64 (2H, d, J=8.0 Hz); MS, m/z 568 (M^+), 553, and 269. Found: C, 90.83; H, 9.37%. Calcd for $C_{43}H_{52}$: C, 90.79; H, 9.21%.

4-Cyanomethyl-2,7-di-*t*-butylfluorene (4b).[6] A solution of **4a** (655 mg, 2 mmol) in DMF (20 ml) was stirred at room temperature with KCN (260 mg, 4.0 mmol) in H_2O (0.35 ml) for 24 h. Upon decomposition with dil. HCl, the residue was extracted with benzene and chromatographed on SiO_2 to give 530 mg (84%) of **4b**: mp 187—188 °C (lit,[6] mp 186—187 °C); UV, λ_{max} 304 (log ε 4.07), 292 (4.11), 285 (4.29), and 274 (4.44).

2,7-Di-*t*-butyl-9*H*-fluorene-4-acetic acid (4c).[6] A solution of **4b** (318 mg, 1 mmol) in AcOH (10 ml) was refluxed with conc. H_2SO_4 (0.8 ml) and H_2O (0.8 ml) for 3.5 h. Upon dilution with H_2O, the precipitate was recrystallized from benzene–cyclohexane to give **4c** (298 mg, 89%): mp 178—179 °C (lit,[6] mp 177—178 °C); UV, λ_{max} 335 (log ε 2.66), 305 (4.01), 293 (4.05), 285 (4.30), and 273 (4.45).

2,6-Di-*t*-butyl-4*H*-cyclopenta[*def*]phenanthren-8-ol (5) through Acid Chloride 4d. A mixture of **4c** (170 mg, 0.5 mmol) in $SOCl_2$ (5 ml) was refluxed for 30 min giving oily **4d**: IR, 1792 cm^{-1}; ^1H NMR, δ=1.39 (18H, s), 3.87 (2H, s), 4.55 (2H, s), and 7.13—7.54 (5H, m).

The above oil was added dropwise into a mixture of $AlCl_3$ (100 mg, 8 mmol) in $C_2H_4Cl_2$ (10 ml) at −8 °C, and the resulting mixture was stirred for 2 h giving 119 mg (75%) of **5**: mp>200 °C; IR, 3420 cm^{-1}; ^1H NMR, δ=1.45 (18H, s), 4.19 (2H, s), 6.94 (1H, s), 7.36 (1H, s), 7.50 (1H, s), 7.69 (1H, s), and 7.96 (1H, s).

The alcohol **5** was easily decomposed into red by standing for a few hour, and was failed to measure of the elemental analysis: the main portion may be 2,6-di-*t*-butyl-4*H*-cyclopenta[*def*]phenanthrene-8,9-dione (IR, 1671 cm^{-1}; MS, m/z 332, 318).

Reduction of 5. Carboxylic acid **4c** (340 mg, 1.0 mmol) was converted into **5** by a method similar to above; the resulting crude **5** was dissolved in AcOH (50 ml) and refluxed with HI (57%, 10 ml) and red phosphorus (1.0 g) for 90 h. Upon the usual treatment, a part of the resulting mixture was submitted GLPC (5% Dexsil 300 GC on Chromosorb, 1.0 Kg cm^{-2}, 230 °C): **1** (retention time 2.4 min, 8%) and **6a** (14.2 min, 31%) were confirmed by comparison with the authentic specimens. The major peak (6.3 min, 56%) might correspond to the monoalkylated compound **6b**.

The separation of the residual part of the mixture gave small amount of 2,6-di-*t*-butyl-4*H*-cyclopenta[*def*]phenanthrene (**6a**): mp 224—225 °C; IR, 1342 and 1210 cm^{-1}; ^1H NMR, δ=1.51 (18H, s), 4.31 (2H, s), 7.76 (2H, s), and ca. 7.8 (4H, s); MS, m/z 302 (M^+), 288, and 287. (Found: C, 91.80; H, 8.29%. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67%.)

4*H*-Cyclopenta[*def*]phenanthrene (1). Acid **4c** (672 mg, 2 mmol) was treated in a way similar to the above, yielding a mixture of **6a**, **6b**, and **1**. The reaction mixture was dried, dissolved in toluene (40 ml), and stirred with $AlCl_3$ (36 mg, 0.3 mmol) at room temperature for 1.5 h giving 104 mg (27% based on **4c**) of **1**, mp 114—115 °C. This is identical in all respects with the authentic specimen.

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