Selective Preparation of Fluorene Derivatives Using the *t*-Butyl Function as a Positional Protective Group[1)]

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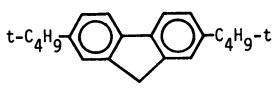
(Received July 8, 1985)

Several 4-substituted 2,7-di-*t*-butylfluorene derivatives (**3**) were prepared by electrophilic substitutions of 2,7-di-*t*-butylfluorene (**1**). 4-Substituted fluorene (**4**), such as 4-bromo- (**4a**), 4-methyl (**4e**), and 4-acetylaminofluorene (**4j**), were obtained by the trans-*t*-butylations of **3**. Although we attempted to synthesize 1,8-disubstituted fluorene from 3,6-di-*t*-butylfluorene (**2**) which was derived from 2,2′-diiodo-4,4′-di-*t*-butyldiphenylmethane (**5**), by the same methods, we obtained only 2,7-disubstituted fluorene derivatives (**8**); it turned out electrophilic substitutions of **2** gave 2,7-disubstituted 3,6-di-*t*-butylfluorene derivatives.

It is difficult to prepare 4-substituted fluorenes by direct electrophilic substitutions on the fluorene ring because such substitutions occur predominantly at the 2- or 2,7-positions having the highest electron density. Therefore, 4-substituted fluorenes usually have been prepared via 4-fluorenonecarboxylic acid, the dehydrated fused-ring compound of diphenic acid, in a tedious synthetic procedure.[2)]

Recently, Tashiro[3)] have reported that many kinds of aromatic compounds can be selectively prepared by using *t*-butyl function as a positional protective group. We now report a convenient preparation of the 4-substituted fluorenes by electrophilic substitutions of 2,7-di-*t*-butylfluorene (**1**) and subsequent Lewis acid-catalyzed trans-*t*-butylations, using the Tashiro's method. Furthermore, we report also an attempted preparation of 1,8-disubstituted fluorenes by electrophilic substitutions of 3,6-di-*t*-butylfluorene (**2**) which is prepared from diphenylmethane via several steps.



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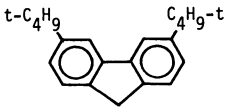

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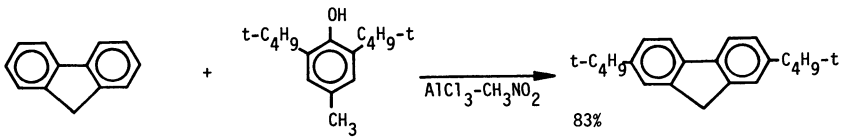
Results and Discussion

Electrophilic Substitutions of 2,7-Di-*t*-butylfluorene (1). Although starting material **1** has been prepared from the reaction of fluorene with *t*-butyl chloride in the presence of $AlCl_3$ in nitrobenzene/carbon disulfide,[4)] this method is not so appropriate because of contamination of 2-*t*-butylfluorene. Now we could obtained **1** by the $AlCl_3$/Nitromethane-catalyzed *t*-butylation[3)] of fluorene with 2,6-di-*t*-butyl-*p*-cresol in good yield under mild conditions.

The reactions of **1** with electrophiles afforded 4-substituted 2,7-di-*t*-butylfluorenes (**3**) regioselectively. In these reactions, the electrophilic attack to **1** did not occur at 1-, 3-, 6-, and 8-positions in the fluorene ring blocked by the bulky *t*-butyl groups. Thus, the reaction of **1** with bromine in the presence of iron powder in carbon tetrachloride gave 4-bromo-2,7-di-*t*-butylfluorene (**3a**). The reaction of **1** with iodine, periodic acid, and sulfuric acid in acetic acid/carbon tetrachloride at 70—80 °C gave 4-iodo-2,7-di-*t*-butylfluorene (**3b**). 4-Chloromethyl-2,7-di-*t*-butylfluorene (**3c**) was obtained by the $ZnCl_2$-catalyzed chloromethylation of **1** with chloromethyl methyl ether. The reaction of **1** with fuming nitric acid in acetic anhydride/acetic acid at −40 °C to −20 °C gave a



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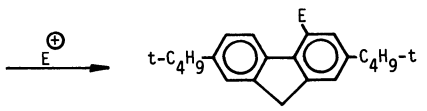


3

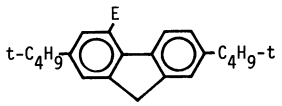
	E	Yield(%)
3a :	Br	95
3b :	I	87
3c :	CH_2Cl	62
3d :	NO_2	22

Scheme 1.

mixture of 4-nitro-2,7-di-*t*-butylfluorene (**3d**) and 7-nitro-2-*t*-butylfluorene. Compound **3d** was separated from the mixture by column chromatography over alumina (Scheme 1).

Attempts to synthesize 4-acetyl and 4-chloro derivatives of **1** were unsuccessful. Furthermore, any 4,5-disubstituted products were not obtained by the electrophilic substitutions of **1**. It seems that 4-substituent prevent further substitution of electrophile on 5-position owing to its steric hindrance.

Several derivatives **3** were also obtained from the subsequent reactions of **3c** and **3d**. The reduction of **3c** with $LiAlH_4$ in tetrahydrofuran afforded 4-methyl-2,7-di-*t*-butylfluorene (**3e**). The reaction of **3c** with NaCN in acetonitrile afforded 4-cyanomethyl-2,7-di-*t*-butylfluorene (**3f**), and subsequent hydrolysis of **3f** gave 4-carboxymethyl-2,7-di-*t*-butylfluorene (**3g**). 4-Hydroxymethyl-2,7-di-*t*-butylfluorene (**3h**) was also obtained by treating **3c** with $AgNO_3$ in water/acetone. And then, the reduction of **3d** with tin and hydrochloric acid in ethanol gave 4-amino-2,7-di-*t*-butylfluorene (**3i**). 4-Acetylamino-2,7-di-*t*-butylfluorene (**3j**) was obtained from **3i** and acetic anhydride.



	E
3e :	CH_3
3f :	CH_2CN
3g :	CH_2COOH
3h :	CH_2OH
3i :	NH_2
3j :	$NHCOCH_3$

Trans-*t*-butylations of 3. $AlCl_3$-catalysed trans-*t*-butylations[3] of **3a, 3e,** and **3j** were carried out at 50 °C for 3—6 h in benzene to afford the desired 4-bromofluorene (**4a**), 4-methylfluorene (**4e**), and 4-acetylaminofluorene (**4j**), respectively (Scheme 2).

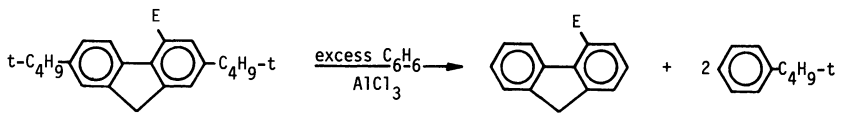
Compounds **4a**[5] and **4j**[6], have already been prepared from 4-fluorenonecarboxylic acid by means of successive conversion of the functional groups. However, our method is more useful because these compounds can be prepared in only three steps from fluorene as starting material which is easily available. Although **4e** have been obtained by passing 2,2-dimethylbiphenyl over Pd–charcoal at 450 °C,[7] the above preparative conditions are too severe as an experimental procedure in laboratory in comparison with our method.

While we tried to prepare other derivatives **4** from **3** except above **3a, 3e,** and **3j**, these products **4** were not obtained because the trans-*t*-butylation of **3** with $AlCl_3$ in benzene did not proceed satisfactory owing to the deficient electron densities in the fluorene ring substituted with electron-attractive groups, or the products were difficult to isolate from the reaction mixture.

Synthesis of 3,6-Di-*t*-butylfluorene (2). The preparations of 1,8-disubstituted fluorene are also difficult by direct electrophilic substitutions to the fluorene ring because of the same reason described about the preparation of 4-substituted fluorenes. From the facts that several **4**'s were obtained from **1**, we also expected that 1-substituted and 1,8-disubstituted 3,6-di-*t*-butylfluorenes may be obtained by electrophilic substitutions of **2** in which the bulky *t*-butyl groups should block 2-, 4-, 5-, and 7-positions in the fluorene ring.

Thus, 2,2′-diiodo-4,4′-di-*t*-butyldiphenylmethane (**5**) was prepared by iodination of 4,4′-di-*t*-butyldiphenylmethane[8] with iodine, periodic acid, and sulfuric acid in acetic acid, and then by heating **5** with activated copper powder[9] crude **2** was obtained in fairly good yield. Furthermore, in order to obtain pure **2**, the crude **2** was oxidized with bubbling oxygen in the *N,N*-dimethylformamide solution in the presence of Triton B to afford 3,6-di-*t*-butyl-9-fluorenone (**6**) which can be easily purified by recrystallization. And then **6** is reduced with $NaBH_4$ in ethanol to give 3,6-di-*t*-butyl-9-fluorenol (**7**). The pure **2** could be obtained by reduction of **7** with hydroiodic acid in acetic acid as colorless columnar crystals (Scheme 3).

Electrophilic Substitutions of 3,6-Di-*t*-butylfluorene (2). The reaction of **2** with *N*-bromosuccinimide in propylene carbonate at 70—75 °C gave a dibromo-substituted 3,6-di-*t*-butylfluorene (**8a**). Compound **8a** was also obtained from the reaction of **2**



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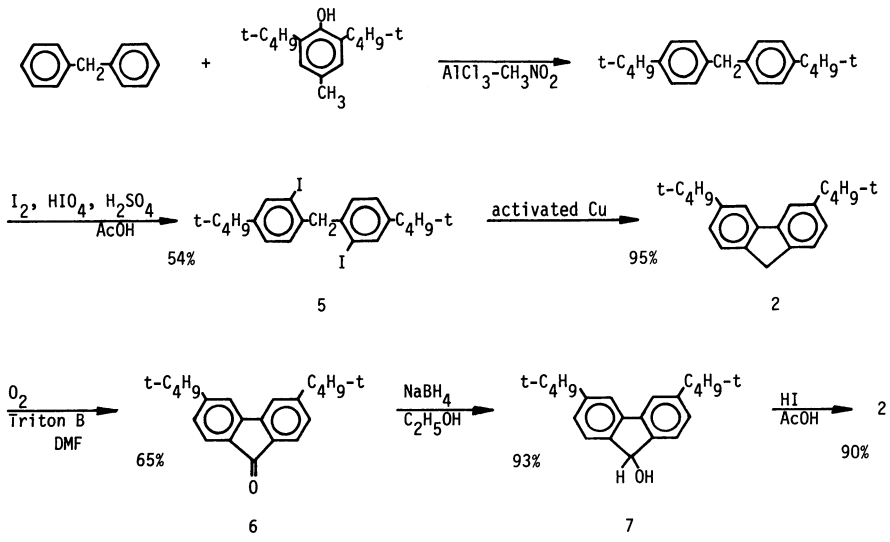
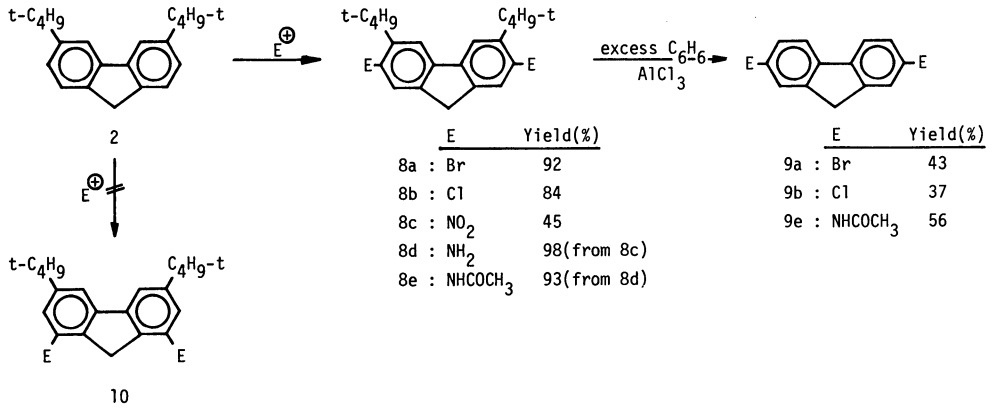
	E	Yield(%)
4a :	Br	45
4e :	CH_3	30
4j :	$NHCOCH_3$	94

Scheme 2.



Scheme 3.



Scheme 4.

with bromine in carbon tetrachloride in the presence of iron powder. When **2** was treated with chlorine in carbon tetrachloride in the presence of iron powder, a dichloro-substituted 3,6-di-*t*-butylfluorene (**8b**) was obtained. The reaction of **2** with fuming nitric acid and sulfuric acid in acetic anhydride at 10—20 °C afforded a dinitro-substituted 3,6-di-*t*-butylfluorene (**8c**). Furthermore, the reduction of **8c** with zinc powder and aqueous $CaCl_2$ in ethanol gave a diamino-substituted 3,6-di-*t*-butylfluorene (**8d**). Then a bis(acetylamino)-substituted 3,6-di-*t*-butylfluorene (**8e**) was obtained by acetylation of **8d** with acetic anhydride. It could be confirmed that products, **8a, 8b, 8c, 8d**, and **8e** were all symmetrical-type compounds by their ^1H NMR spectra which showed only two singlets in aromatic regions.

Subsequently, the trans-*t*-butylations of **8a, 8b**, and **8e** were carried out in the usual way. However, all resultant products were 2,7-disubstituted fluorenes. That is, the reactions of **8a, 8b**, and **8e** with $AlCl_3$ in benzene at 50 °C gave 2,7-dibromofluorene[10] (**9a**), 2,7-dichlorofluorene[10] (**9b**), and 2,7-bis(acetylamino)-fluorene[11] (**9e**), which were identical with authentic samples, respectively.

Because it can not be considered that 1,8-groups of 1,8-disubstituted 3,6-di-*t*-butylfluorene (**10**) immigrate into the 2,7-positions under the treating conditions, the substitution reactions with electrophiles should proceed at the 2,7-positions. Thus we recognized the above compounds, **8a—e**, as 2,7-disubstituted 3,6-di-*t*-butylfluorenes. That is, it turned out that although the 2,7-positions in **2** have been blocked by bulky *t*-butyl groups the electrophilic attack to **2** occurs predominantly at 2,7-positions having the highest electron density,[12] rather than at the 1,8-positions which are not hindered sterically (Scheme 4).

Furthermore, ^1H NMR spectra of the acetylamino compounds, **3j, 4j, 8e**, and **9e**, in CF_3COOH showed two acetylmethyl signals due to the two conformers

which appear at room temperature on the NMR time scale by the restricted rotation around the N–CO bond. We have already investigated about the *cis*, *trans*-isomerism of the protonated ring-substituted acetanilides by measurements of their NMR spectra in CF_3COOH.[13]

Experimental

All melting points are uncorrected. NMR spectra were determined on a JEOL-MH-100 spectrometer with Me_4Si as internal standard. IR spectra were measured as KBr pellets on a Nippon Bunko IR-A spectrometer.

2,7-Di-*t*-butylfluorene (1). To a solution of fluorene (34.0 g, 0.2 mol) and 2,6-di-*t*-butyl-*p*-cresol (44 g, 0.2 mol) in nitromethane (300 ml) was added at 10—15 °C $AlCl_3$–nitromethane catalyst [$AlCl_3$ (40 g, 0.3 mol)/nitromethane (60 ml)] over a period of 40 min. After the reaction mixture was stirred for 15 min more, it was poured into a large amount of ice-water. The aqueous layer was extracted with ether and the combined organic phase was washed with water, and concentrated to remove nitromethane. The residue was dissolved in ether, washed with 10% NaOH solution to remove *p*-cresol, and then washed with water, dried over $MgSO_4$, and evaporated in vacuo to obtain a black oily product which was column-chromatographed on alumina using benzene as an eluent to give **1**; yield: 46 g (83%); colorless needles; mp 120—122 °C (from ethanol) (lit,[4] mp 122—123 °C). IR (KBr): 1257 cm^{-1} (*t*-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.38 (18H, s, *t*-C_4H_9×2), 3.87 (2H, s, 9-CH_2), 7.39 (2H, d, J=7 Hz, 3- and 6-H), 7.58 (2H, s, 1- and 8-H), and 7.68 (2H, d, J=8 Hz, 4- and 5-H). Found: C, 90.45; H, 9.50%. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41%.

4-Bromo-2,7-di-*t*-butylfluorene (3a). To a mixture of **1** (4.5 g, 16 mmol) and catalytic amount of iron powder in CCl_4 (20 ml) was added dropwise a solution of bromine (2.8 g, 18 mmol) in CCl_4 (5 ml) at 5—8 °C under stirring. After the reaction mixture was stirred for more 3 h at 15—20 °C, it was poured into water. The mixture was extracted with ether, and the ether solution was washed with 10% NaOH solution, dried over $MgSO_4$, and evaporated in vacuo to afford the residue which was recrystallized from ethanol to give **3a** as colorless needles; yield: 5.4 g (95%); mp 125—127 °C. IR (KBr): 1260 cm^{-1} (*t*-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.39, 1.41 (each 9H, s, *t*-C_4H_9×2), 3.96 (2H, s, 9-CH_2), 7.48—7.72 (4H, m, H_{arom}), and 8.60 (1H, d, J=8Hz, 5-H). Found: C, 70.57; H, 7.03%. Calcd for $C_{21}H_{25}Br$: C, 70.58; H, 7.05%.

4-Iodo-2,7-di-*t*-butylfluorene (3b). To a solution of **1** (2.3 g, 8 mmol) and iodine (1.0 g, 4 mmol) in a 2:1 acetic acid-CCl_4 (12 ml) was added 98% H_2SO_4 (0.2 ml) and water (1.6 ml), and the mixture was heated for 3 h at 70—80 °C. After the reaction mixture was poured into water, it was extracted with ether. The ether solution was washed with $NaHSO_3$ solution to remove unreacted iodine, and washed with Na_2CO_3 solution and then with water, and dried over $MgSO_4$. The solution was evaporated in vacuo to leave the residue which was recrystallized from ethanol to give **3b** as yellow needles; yield: 2.8 g (87%); mp 109—110 °C. IR (KBr): 1260 cm^{-1} (*t*-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.40 (18H, s, *t*-C_4H_9×2), 3.88 (2H, s, 9-CH_2), 7.44—7.92 (4H, m, H_{arom}), and 8.74 (1H, d, J=8 Hz, 5-H). Found: C, 62.34; H, 6.12%. Calcd for $C_{21}H_{25}I$: C, 62.38; H, 6.23%.

4-Chloromethyl-2,7-di-*t*-butylfluorene (3c). A mixture of **1** (7 g, 25 mmol), chloromethyl methyl ether (8 g, 0.1 mol), and $ZnCl_2$ (1.7 g, 13 mmol) was stirred for 20 min at room temperature. The reaction mixture was poured into water, extracted with ether, and dried over $MgSO_4$. The ether solution was evaporated in vacuo to give the residue which was recrystallized from hexane affording **3c** as colorless needles; yield: 5.1 g (62%); mp 90—93 °C. IR (KBr): 1260 cm^{-1} (*t*-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.36 (18H, s, *t*-C_4H_9×2), 3.88 (2H, s, 9-CH_2), 5.00 (2H, s, CH_2Cl), 7.28—7.68 (4H, m, H_{arom}), and 9.94 (1H, d, J=8 Hz, 5-H). Found: C, 80.92; H, 8.23%. Calcd for $C_{22}H_{27}Cl$: C, 80.93; H, 8.33%.

4-Nitro-2,7-di-*t*-butylfluorene (3d). To a solution of **1** (2.3 g, 8 mmol) in acetic anhydride (40 ml) was added dropwise at −40—−20 °C a mixture of fuming HNO_3 (1 g) and acetic acid (1.15 g) over a period of 30 min under stirring. After the reaction mixture was stirred for 2 h more at −20—0 °C, it was poured into an ice-cold water. The precipitated solid was filtered, washed with water, and column chromatographed on alumina using petroleum benzine as an eluent to give **3d** in the second fraction; yield: 0.6 g (22%); yellow needles; mp 135—137 °C (from ethanol). IR (KBr): 1255 (*t*-C_4H_9), 1340, 1520 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$) δ=1.36, 1.38 (each 9H, s, *t*-C_4H_9×2), 3.89 (2H, s, 9-CH_2), 7.34 (1H, d, J=8 Hz, 6-H), 7.49, 7.66, 7.80 (each 1H, s, H_{arom}), and 7.94 (1H, d, J=8 Hz, 5-H). Found: C, 77.77; H, 7.73; N, 4.05%. Calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33%.

4-Methyl-2,7-di-*t*-butylfluorene (3e). To a solution of **3c** (0.5 g, 1.5 mmol) in tetrahydrofuran (10 ml) was added a small portions of $LiAlH_4$ (0.07 g, 2 mmol) under stirring, and the mixture was refluxed for 5 h and then allowed to stand. To the solution was added a 3:2 tetrahydrofuran–water (2 ml) and then a few drops of diluted H_2SO_4. The reaction mixture was extracted with ether, washed with water, and dried over $MgSO_4$. The ether solution was evaporated in vacuo to give **3e** as colorless needles; yield: 0.38 g (87%); mp 133—135 °C (from ethanol). IR (KBr): 1260 cm^{-1} (*t*-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.34 (18H, s, *t*-C_4H_9×2), 2.68 (3H, s, CH_3), 3.84 (2H, s, 9-CH_2), 7.06—7.54 (4H, m, H_{arom}), and 7.70 (1H, d, J=8 Hz, 5-H). Found: C, 90.08; H, 9.70%. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65%.

4-Cyanomethyl-2,7-di-*t*-butylfluorene (3f). To a solution of **3c** (3.9 g, 12 mmol) in acetonitrile (60 ml) was added a solution of NaCN (1.2 g, 24 mmol) in water (3 ml). After the mixture was refluxed for 3 h, it was poured into water. The precipitated solid was filtered, washed with water, and recrystallized from ethanol to give **3f** as colorless crystals; yield: 3.1 g (83%); mp 186—187 °C. IR (KBr): 1260 (*t*-C_4H_9), 2240 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ=1.36 (18H, s, *t*-C_4H_9×2), 3.82 (2H, s, 9-CH_2), 4.04 (2H, s, CH_2CN), and 7.20—7.56 (5H, m, H_{arom}). Found: C, 86.81; H, 8.74; N, 4.23%. Calcd for $C_{23}H_{27}N$: C, 87.01; H, 8.57; N, 4.41%.

4-Carboxymethyl-2,7-di-*t*-butylfluorene (3g). To a solution of **3f** (3.7 g, 12 mmol) in ethylene glycol (60 ml) was added a solution of NaOH (4.8 g, 0.12 mol) in water (30 ml). The mixture was heated for 30 h at 150—160 °C with an oil bath and then poured into water. The precipitated solid was dissolved in hot water and filtered off under

heating. After the filtrate was acidified with hydrochloric acid, the resultant precipitate was filtered and recrystallized from hexane to give **3g** as colorless crystals; yield: 1.7 g (41%); mp 177—178 °C. IR (KBr): 1255 (t-C_4H_9), 1700 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ=1.36 (18H, s, t-C_4H_9×2), 3.88 (2H, s, 9-CH_2), 4.04 (2H, s, $C\underline{H}_2COOH$), 6.36 (1H, br.s, COOH), 7.24, 7.55, 7.62 (each 1H, s, H_{arom}), 7.42, and 7.80 (each 1H, d, J=9 Hz, 5- and 6-H). Found: C, 81.96; H, 8.44%. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39%.

4-Hydroxymethyl-2,7-di-*t*-butylfluorene (3h). To a solution of **3c** (1.6 g, 5 mmol) in acetone (24 ml) was added a solution of $AgNO_3$ (2.3 g, 13 mmol) in water (10 ml). The mixture was refluxed for 12 h and then acetone was distilled. The residue obtained was extracted with ether, washed with water, and dried over $MgSO_4$. The ether solution was evaporated in vacuo to give **3h** as colorless needles; yield: 0.4 g (27%); mp 150—151 °C (from petroleum benzine). IR (KBr): 1265 (t-C_4H_9), 3280 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ=1.36 (18H, s, t-C_4H_9×2), 3.82 (2H, s, 9-CH_2), 5.04 (2H, s, $C\underline{H}_2OH$), and 7.24—7.60 (5H, m, H_{arom}). Found: C, 85.43; H, 9.30%. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15%.

4-Amino-2,7-di-*t*-butylfluorene (3i). To a solution of **3d** (3.23 g, 10 mmol) and concentrated hydrochloric acid (d=1.19; 10 ml) in ethanol (50 ml) was gradually added tin powder (2.37 g). After the mixture was refluxed for 1 h, it was poured into a large amount of ice-cold water, basified with 10% NaOH solution and extracted with chloroform. The chloroform solution was washed with water, dried over $MgSO_4$, and evaporated in vacuo to give **3i** as pink prisms; yield: 2.8 g (95%); mp 148—150 °C (from methanol). IR (KBr): 1265 (t-C_4H_9), 3350, 3450 cm^{-1} (NH_2); ^1H NMR ($CDCl_3$) δ=1.36, 1.39 (each 9H, s, t-C_4H_9×2), 3.85 (2H, s, 9-CH_2), 4.01 (2H, br.s, NH_2), 6.68, 7.02, 7.52 (each 1H, s, H_{arom}), 7.33, and 7.55 (each 1H, d, J=9 Hz, 5- and 6-H). Found: C, 85.74; H, 9.29; N, 4.67%. Calcd for $C_{21}H_{27}N$: C, 85.95; H, 9.28; N, 4.77%.

4-Acetylamino-2,7-di-*t*-butylfluorene (3j). To a solution of **3i** (1.17 g, 4 mmol) in benzene (20 ml) was added acetic anhydride (0.8 ml). The mixture was stirred at 40—50 °C for 15 min and then poured into water. The resultant precipitate was filtered, washed with water, and recrystallized from hexane to give **3j** as colorless needles; yield: 1.3 g (95%); mp 189—190 °C. IR (KBr): 1270 (t-C_4H_9), 1650 (CO), 3230, 3300 cm^{-1} (NH); ^1H NMR (CF_3COOH) δ=1.42 (18H, s, t-C_4H_9×2), 2.18, 2.60 (total 3H, s, $COCH_3$), 3.73, 3,83 (total 2H, 9-CH_2), 7.17—7.68 (5H, m, H_{arom}), 8.85, and 9.70 (total 1H, br.s, NH). Found: C, 82.29; H, 8.74; N, 4.26%. Calcd for $C_{23}H_{29}NO$: C, 82.34; H, 8.71; N, 4.18%.

4-Bromofluorene (4a). A solution of **3a** (1.08 g, 3 mmol) and $AlCl_3$ (0.04 g, 0.3 mmol) in benzene (18 ml) was stirred at 50 °C for 6 h, and then the mixture was quenched with water. The organic layer was extracted with ether, washed with water, dried with $MgSO_4$, and evaporated in vacuo at 100 °C to leave t-butylbenzene. Compound **4a** was obtained from residue as colorless needles; yield: 0.33 g (45%); mp 55—57 °C (from methanol) (lit,[5] 59 °C). ^1H NMR ($CDCl_3$) δ=3.86 (2H, s, 9-CH_2), 6.96—7.56 (6H, m, H_{arom}), and 8.56 (1H, d, J=8 Hz, 5-H). Found: C, 63.59; H, 3.72%. Calcd for $C_{13}H_9Br$: C, 63.70; H, 3.70%.

4-Methylfluorene (4e). A solution of **3e** (0.58 g, 2 mmol) and $AlCl_3$ (0.03 g, 0.2 mmol) in benzene (12 ml) was stirred at 50 °C for 4 h, and then it was treated and worked up as described above to afford **4e** as colorless crystals; yield: 0.1 g (30%); mp 68—70 °C (from methanol) (lit,[7] 70.4—71.2 °C). ^1H NMR ($CDCl_3$) δ=2.73 (3H, s, CH_3), 3.93 (2H, s, 9-CH_2), and 7.17—7.98 (7H, m, H_{arom}). Found: C, 93.34; H, 6.65%. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71%.

4-Acetylaminofluorene (4j). To a solution of **3j** (0.67 g, 0.2 mmol) in benzene (30 ml) was added $AlCl_3$ (0.87 g, 6.6 mmol). After the reaction mixture was stirred for 3 h at 50 °C, it was treated and worked up as described above to give **4j** as a light brown crystals; yield: 0.42 g (94%); mp 197—198 °C (from benzene) (lit,[6] 199—200 °C). IR (KBr): 1630, 1650 (CO), 3160, 3220 cm^{-1} (NH); ^1H NMR (CF_3COOH) δ=2.21, 2.64 (total 3H, s, $COCH_3$), 3.86, 3.97 (total 2H, s, 9-CH_2), 7.18—7.71 (7H, m, H_{arom}), 8.98, and 9.76 (total 1H, br.s, NH). Found: C, 80.40; H, 5.88: N, 6.38%. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27%.

2,2′-Diiodo-4,4′-di-*t*-butyldiphenylmethane (5). To a solution of 4,4′-di-t-butyldiphenylmethane (17.6 g, 63 mmol), periodic acid (7.6 g, 34 mmol), water (35 ml), and 98% H_2SO_4 (4.9 ml), and the mixture was poured into ice-water, it was extracted with ether. The ether solution was washed with $NaHSO_3$ solution to remove iodine, and washed with Na_2CO_3 and then with water, and dried over $MgSO_4$. The solution was evaporated in vacuo to leave the residue which was column-chromatographed on alumina using petroleum benzine as an eluent to give **5**; yield: 17.6 g (54%); colorless plates; mp 88—90 °C (from ethanol). IR (KBr): 1260 cm^{-1} (t-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.28 (18H, s, t-C_4H_9×2), 4.20 (2H, s, CH_2), 6.76 (2H, d, J=8 Hz, 6- and 6′-H), 7.20 (2H, dd, J=2 and 8 Hz, 5- and 5′-H), and 7.76 (2H, d, J=2 Hz, 3- and 3′-H). Found: C, 46.61; H, 4.91%. Calcd for $C_{20}H_{24}I$: C, 46.35; H, 4.67%.

3,6-Di-*t*-butylfluorene (2) by Ullmann Reaction of 5. To melted **5** (30 g, 60 mmol) was added slowly the activated copper powder[13] (30 g, 0.47 mol) and the mixture was heated at 230 °C for 4 h. After cooling, the reaction mixture was extracted with acetone and the acetone solution was filtered to remove the copper powder. The filtrate was concentrated in vacuo to give crude **2** as oily material; yield: 30 g (95%).

3,6-Di-*t*-butylfluorenone (6). To a solution of crude **2** (15 g, 54 mmol) in dimethylformamide (150 ml) was added Triton B (4 ml), and oxygen gas was bubbled into the reaction mixture with heating at 90 °C. The above mixture was poured into the water, acidified with dil. hydrochloric acid, and extracted with benzene. The benzene solution was evaporated in vacuo to give **6** as yellow needles; yield: 10 g (65%); mp 208—209 °C (from petroleum benzine). IR (KBr): 1250 (t-C_4H_9), 1700 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ=1.36 (18H, s, t-C_4H_9×2), 7.16 (2H, dd, J=8 and 2 Hz, 2- and 7-H), 7.62 (2H, d, J=2 Hz, 4- and 5-H), and 7.64 (2H, d, J=8 Hz, 1- and 8-H). Found: C, 86.19; H, 8.41%. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27%.

3,6-Di-*t*-butyl-9-fluorenol (7). Sodium borohydride (7.5 g, 0.2 mol) was added to the solution of **6** (10.2 g, 35 mmol) in ethanol (400 ml). The mixture was heated and stirred for 30 min until **6** was dissolved perfectly. The reaction mixture was evaporated in vacuo, and to the residue was added water, and then it was extracted with

benzene. The benzene solution was washed with water, dried with $MgSO_4$, and evaporated in vacuo to give **7** as colorless prisms; yield: 9.6 g (93%); mp 120—123 °C (from ethanol). IR (KBr): 1255 (t-C_4H_9), 3240 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ=1.32 (18H, s, t-C_4H_9×2), 1.76 (1H, br.s, OH), 5.38 (1H, br.s, 9-H), 7.28 (2H, dd, J=8 and 2 Hz, 2- and 7-H), 7.48 (2H, d, J=8 Hz, 1- and 8-H), and 7.64 (2H, d, J=2 Hz, 4- and 5-H). Found: C, 85.48; H, 9.02%. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90%.

3,6-Di-*t*-butylfluorene (2) from 7. To a solution of **7** (13.2 g, 45 mmol) in acetic acid (550 ml) was added hydroiodic acid (57%, 53 g, 0.24 mol) and the mixture was refluxed for 2 h. The reaction mixture was poured into ice-cold water, extracted with ether. The ether solution was washed with $NaHSO_3$ solution, Na_2CO_3 solution, and water, and then dried with $MgSO_4$. The solution was evaporated in vacuo to leave the residue which was recrystallized from ethanol to give **2** as colorless prisms; yield: 11 g (90%); mp 82—83 °C. IR (KBr): 1260 cm^{-1} (t-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.42 (18H, s, t-C_4H_9×2), 3.82 (2H, s, CH_2), 7.35 (2H, dd, J=8 and 2 Hz, 2- and 7-H), 7.48 (2H, d, J=8 Hz, 1- and 8-H), and 7.82 (2H, d, J=2 Hz, 4- and 5-H). Found: C, 90.34; H, 9.39%. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41%.

2,7-Dibromo-3,6-di-*t*-butylfluorene (8a). a) To a solution of **2** (1.1 g, 4 mmol) in dry propylene carbonate (26 ml) was added NBS (1.4 g, 8 mmol) and the mixture was heated for 6 h at 70—75 °C under stirring. The reaction mixture was poured into water, and the precipitated solid was filtered, washed with water and recrystallized from ethanol; yield: 1.6 g (92%); colorless prisms; mp 177—180 °C. b) To a solution of **2** (0.28 g, 1 mmol) in carbon tetrachloride (4 ml) with a small amount of iron powder was added the solution of bromine (0.48 g, 3 mmol) in carbon tetrachloride (2 ml) dropwised for 20 min at 35—40 °C and the reaction mixture was stirred for more 30 min at the same temperature. After the mixture was poured into water, it was extracted with ether, washed with 10% NaOH solution and then water, dried with $MgSO_4$ and concentrated in vacuo to give **8a** as colorless prisms; yield: 0.35 g (80%); mp 177—180 °C. IR (KBr): 1240 cm^{-1} (t-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.60 (18H, s, t-C_4H_9×2), 3.74 (2H, s, CH_2), 7.67 and 7.75 (each 2H, s, 1,8- and 4,5-H). Found: C, 57.63; H, 5.56%. Calcd for $C_{21}H_{24}Br_2$: C, 57.82; H, 5.55%.

2,7-Dichloro-3,6-di-*t*-butylfluorene (8b). Into a solution of **2** (0.56 g, 2 mmol) in carbon tetrachloride (8 ml) with a small amount of iron powder was bubbled chlorine gas for 30 min at 30 °C. After the reaction mixture was poured into water, it was extracted with ether, washed with 10% NaOH solution and water, and dried with $MgSO_4$. The ether solution was concentrated in vacuo to give **8b** as colorless prisms; yield: 0.58 g (84%); mp 155—157 °C (from ethanol). IR (KBr): 1240 cm^{-1} (t-C_4H_9); ^1H NMR ($CDCl_3$) δ=1.53 (18H, s, t-C_4H_9×2), 3.70 (2H, s, CH_2), 7.43 and 7.76 (each 2H, s, 1,8- and 4,5-H). Found: C, 72.42; H, 6.97%. Calcd for $C_{21}H_{24}Cl_2$: C, 72.62; H, 6.97%.

2,7-Dinitro-3,6-di-*t*-butylfluorene (8c). To a solution of **2** (1.4 g, 5 mmol) in acetic anhydride (26 ml) was added the mixture of fuming nitric acid (1.3 g, 20 mmol) and concd sulfuric acid (1.3 g) dropwised for 2 h at 15—20 °C. The precipitated solid as filtered, washed with water and then ether, and recrystallized from petroleum benzine to give **8c** as slight yellow crystals; yield: 0.8 g (45%); mp 246—247 °C. IR (KBr): 1240 (t-C_4H_9), 1350, 1515 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$) δ=1.51 (18H, s, t-C_4H_9×2), 3.90 (2H, s, CH_2), 7.48 and 7.91 (each 2H, s, 1,8- and 4,5-H). Found: C, 68.55; H, 6.63; N, 7.44%. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60%.

2,7-Diamino-3,6-di-*t*-butylfluorene (8d). To a solution of **8c** (1.2 g, 3.3 mmol) in ethanol (78%, 50 ml) was added $CaCl_2$ aqueous solution (0.5 g, 0.7 ml) and zinc powder (14 g, 0.2 mol). After the mixture was refluxed for 2 h, zinc powder was filtered off. The filtrate was concentrated in vacuo to give **8d** as white crystals. This crystals were washed with water and dried under reduced pressure; yield: 1.0 g (98%); mp 185—188 °C (decomp). IR (KBr): 1240 (t-C_4H_9), 3360, 3470 cm^{-1} (NH_2); ^1H NMR ($CDCl_3$) δ=1.44 (18H, s, t-C_4H_9×2), 3.48 (4H, br.s, NH_2×2), 3.60 (2H, s, CH_2), 6.54 and 7.32 (each 2H, s, 1,8- and 4,5-H). This product was unstable in atmosphere so that it was analyzed as the acetyl compound (**8e**).

2,7-Bis(acetylamino)-3,6-di-*t*-butylfluorene (8e). To a solution of **8d** (0.8 g, 2.5 mmol) in benzene (10 ml) was added acetic anhydride (0.3 g, 2.8 mmol), and the mixture was stirred for 20 min at 40—50 °C. The precipitation solid was filtered and washed with benzene to give **8e** as white crystals; yield: 0.9 g (93%); mp 333—336 °C (decomp) (from chloroform). IR (KBr): 1240 (t-C_4H_9), 1650 (CO), 3240 cm^{-1} (NH); ^1H NMR (CF_3COOH) δ=1.56 (18H, s, t-C_4H_9×2), 2.30, 2.66 (total 6H, br.s, $COCH_3$), 3.94, 3.98 (total 2H, br.s, CH_2), 7.40, 8.16 (each 2H, br.s, 1,8- and 4,5-H), 9.23, 9.37, and 9.95 (total 2H, br.s, NH). Found: C, 76.41; H, 8.16; N, 7.13%. Calcd for $C_{25}H_{32}N_2O_2$: C, 76.49; H, 8.22; N, 7.14%.

Trans-*t*-butylation of 8. A solution of **8** (3 mmol) and $AlCl_3$ (8 mg, 0.6 mmol) in benzene (15 ml) was stirred at 50 °C for 30 min, and then the mixture was quenched with water. The organic layer was extracted with ether, washed with water, dried with $MgSO_4$, and evaporated in vacuo at 100 °C to leave t-butylbenzene.

2,7-Dibromofluorene (9a). Yield: 43%; colorless prisms mp 166—168 °C (from ethanol) (lit,[10] 167—168 °C). ^1H NMR ($CDCl_3$) δ=3.72 (2H, s, CH_2), 7.34, 7.42 (each 2H, d, J=9 Hz, 3,6- and 4,5-H), and 7.49 (2H, s, 1- and 8-H).

2,7-Dichlorofluorene (9b). Yield: 37%; colorless prisms mp 122—125.5 °C (from ethanol) (lit,[10] 126 °C). ^1H NMR ($CDCl_3$) δ=3.86 (2H, s, CH_2), 7.36 (2H, dd, J=2 and 8 Hz, 3- and 6-H), 7.51 (2H, d, J=2 Hz, 1- and 8-H), and 7.63 (2H, d, J=8 Hz, 4- and 5-H).

2,7-Bis(acetylamino)fluorene (9e). Yield: 56%; white crystals mp 285—286 °C (from ethanol) (lit,[11] mp 281 °C). IR (KBr): 1360 ($COCH_3$), 1650 (CO), 3040, 3220 cm^{-1} (NH); ^1H NMR (CF_3COOH) δ=2.40, 2.65 (total 6H, br.s, $COCH_3$), 3.98, 4.04 (total 2H, br.s, CH_2), 7.40 (2H, br.d, J=8 Hz, 3- and 6-H), 7.62 (2H, br.s, 1- and 8-H), and 7.77 (2H, br.d, J=8 Hz, 4- and 5-H).

The authors wish to thank Drs. Shigeki Nagai, Yoshiaki Ishida, and Mr. Tsuyoshi Arai, Ube Research Laboratory, Ube Industries LTD., for the elemental analyses.

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