Clemmensen Reduction of 2-Acetylfluorene. Pathways for the Formation of 2,3-Di(2-fluorenyl)butane and Its Homologues

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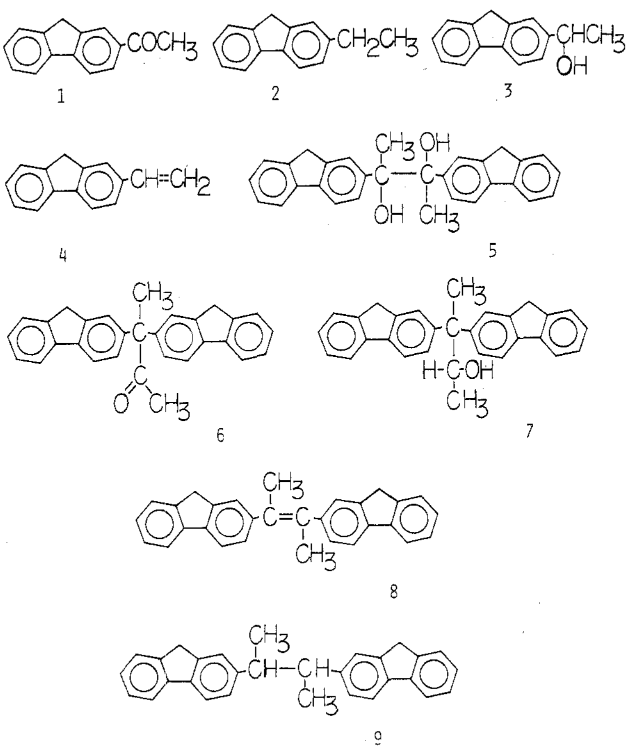
The Clemmensen reduction of 2-acetylfluorene gave not only 2-ethylfluorene but also 2-(α-hydroxyethyl)fluorene, 2-vinylfluorene, *cis-* and *trans*-2,3-di(2-fluorenyl)-2-butene, *meso-* and *dl*-2,3-di(2-fluorenyl)butane, 2,3-di(2-fluorenyl)-2,3-butanediol, 3,3-di(2-fluorenyl)-2-butanone, and 3,3-di(2-fluorenyl)-2-butanol. The confirmation of these compounds was achieved by established syntheses. The Clemmensen reduction of 2-acetylfluorene may proceed through the corresponding carbinol, 2-(α-hydroxyethyl)fluorene, to the normal reduction product, 2-ethylfluorene.

The Clemmensen reduction of 2-acetylfluorene (1)[1,2] has been reported by Campbell and Wang[3] to yield only 2-ethylfluorene (2)[4–6] in 45% yield.

The present paper deals with the reinvestigation of this reduction and 1 was found to form not only 2 (76%) but also intermediary compounds, 2-(α-hydroxyethyl)fluorene (3)[7] and 2-vinylfluorene (4),[6–8] and the related dimeric products, namely 2,3-di(2-fluorenyl)-2,3-butanediol (5), 3,3-di(2-fluorenyl)-2-butanone (6), 3,3-di(2-fluorenyl)-2-butanol (7), *cis*-(8a) and *trans*-2,3-di(2-fluorenyl)-2-butene (8b), and *meso*-(9a) and *dl*-2,3-di(2-fluorenyl)butane (9b). The structural proof for these compounds was confirmed by authorized syntheses.

Scheme I



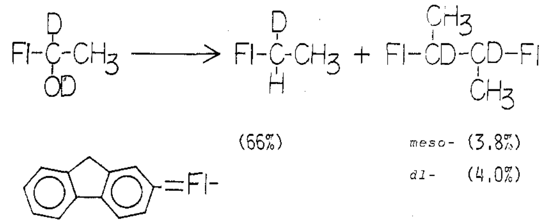
These results suggest, on the grounds of the formation of intermediaries 3 and 4, that the reduction sequence of 1 may differ somewhat from the conventional concept of the Clemmensen reduction;[9] generally, the reaction cannot proceed through the corresponding carbinol since the carbinol itself is not reduced.

The reduction of 1 gave, in addition to 2, a pair of cis, trans isomers, **8a** and **8b**, and diastereomers of **9a** and **9b**. The formation of these isomers provides some interesting stereochemical information, because the recent studies of the Clemmensen reduction have rarely observed such abnormal products as these stereoisomers.

Sequence of the Formation of 2-Ethylfluorene (2) by the Clemmensen Reduction of 2-Acetylfluorene (1). The reduction of 1 and its homologues was carried out in xylene using amalgamated zinc and hydrochloric acid according to the method described in *Organic Reactions.*[9] These results are summarized in Table I.

At an initial stage of the reduction, 1 yielded **2, 3, 4, 5, 6, 9a,** and **9b.** Carbinol **3** was also reduced to **2** accompanied by small amounts of **9a** and **9b** as easily as in the case of **1.** The Clemmensen reduction of olefin **4** afforded **2,** but the yield of **2** was smaller than that from **1.** Additionally, the deuteriocarbinol, 2-(α-hydroxyethyl)fluorene-C_α,O-d_2, was converted into 2-ethylfluorene-C_α-d and *meso-* and *dl*-2,3-di(2-fluorenyl)butane-C_2,C_3-d_2 under similar reaction conditions, as Scheme II shows.

Scheme II



These findings are explained by assuming that the carbinol **3** is one of the important intermediates in the Clemmensen reduction of **1.** The sequence of the formation of **2, 3, 4,** and **9** is presumed as Scheme III. Carbinol **3** may be formed from

Scheme III

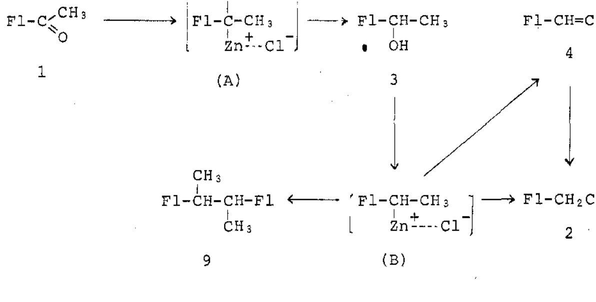


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Table I. Clemmensen Reductions of 2-Acetylfluorene (1) and Its Homologues

Reactant	Reaction time, h	Products, % 2	5	6	8a	8b	9a	9b	Recovd, %
1[a]	0.5	55.2	12.2				0.9	0.7	24.3
1	48	76.3		0.5	1.5	1.2	6.1	5.8	
2	48								97.5
3[b]	48	75.3					4.4	3.6	
4[c]	48	27.5							35.6
5	48	0.8		30.5	18.5	4.2	1.1	2.3	24.8
6[d]	30				2.7	5.4			85.0
7	48				0.6	1.3	0.8	0.7	89.5
8a	48					1.0	1.0		93.4
8b	48				1.9			3.1	93.1
9a	48								92.9
9b	48								95.8

[a] Trace amounts of **3**, **4**, and **6** were confirmed by ir and VPC. [b] A trace amount of **4** was confirmed by VPC. [c] Low quantity of **2** may be due to the formation of polymeric products.[8] [d] A trace amount of **7** was confirmed by LPC.

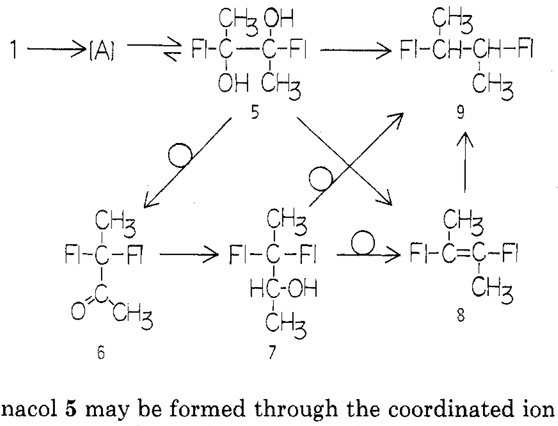
1 through the coordinated ion (A)[10] and **3** is converted easily via another intermediate ion (B) to **2** and **9**. An experiment using the deuterio compound would negate the equilibrium between A and B. A part of **2** can be obtained from **4** which is produced via β-hydride transfer of B to **1**.

Nakabayashi described,[11] supporting the concept of Brewster,[12] that phenyl methyl carbinol and styrene were not intermediates to ethylbenzene by the Clemmensen reduction of acetophenone, because both were not reduced under the similar conditions. On the other hand, fluorenol and its homologues have been reported[13] to be obtained by the same reduction of the corresponding fluorenones.

The high stability of fluorenol may be due to the steric hindrance of the 1 and 8 positions in fluorenol and the conjugation effects in such a rigid structure, which are much different from those of the mobile structure such as phenyl methyl carbinol. The effects in **3** would be between those of fluorenol and phenyl methyl carbinol.[14]

Dimeric Products by the Clemmensen Reduction of 2-Acetylfluorene (1). The Clemmensen reduction of **1** afforded **5**, **6**, **7**, **8**, and **9** as minor products, as shown in Scheme IV.

Scheme IV



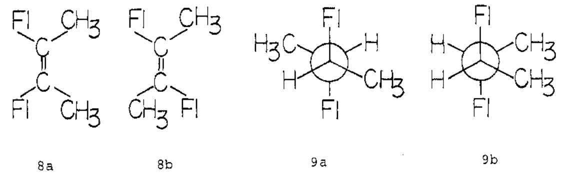
Pinacol **5** may be formed through the coordinated ion A. There is an equilibrium between A and **5** which lies nearly to **5**, because a small amount of **2** has been confirmed in the reduction of **5**. The pinacol **5** would yield **9**, **8**, and **6** by reduction, by dehydroxylation, and by pinacol-type transformation with the 2-fluorenyl migration, respectively. Pinacolone **6** is hydrogenated to alcohol **7**; **7** gives **8** and **9** by the Wagner–Meerwein (or retropinacol) rearrangement.

The dimeric final product **9** is afforded by reduction of **5** and **8**, by the Wagner–Meerwein transformation of **7**, and by coupling of the intermediate ion (B) with ion Fl–CH(CH_3)-OH_2^+ and/or with 2-(α-chloroethyl)fluorene[15] (Scheme III).

Formations and Reactions of the Dimeric Compounds. A pair of diastereomers with mp 306–308 °C (**9a**) and with mp 234–235 °C (**9b**) were obtained by the Clemmensen reduction of **1**. Both isomers were also formed by the reactions of 2-(α-bromoethyl)fluorene (**10**) with Mg and with $LiAlH_4$ and by treatment of **6** with hydriodic acid in acetic acid. Hydrogenations of **8a** and **8b** gave **9a** and **9b**, respectively, by cis addition, analogous to the formation of *meso*- and *dl*-diphenylbutane.[16] The chemical shifts of the methine and methyl protons in the NMR spectrum of **9a** are observed at higher fields than those of the isomeric **9b**. These findings are consistent with the assignment of **9a** to the meso isomer and **9b** to *dl*-2,3-di(2-fluorenyl)butane, by similar consideration to diphenylbutane isomers.[17]

Compounds of mp 144–145 °C dec (**8a**) and of mp 287–288 °C dec (**8b**) were obtained by reduction of **1** with $TiCl_4$–Zn in dry tetrahydrofuran (THF).[18] Maximum absorption in the uv spectrum of **8b** shifts to longer wavelength and the intensity increases compared to **8a**. The NMR chemical shift of the methyl groups in **8b** appears at higher field than that of **8a**. Photochemical isomerization of **8a** afforded isomeric **8b**. From this evidence, the isomers are assigned to be *cis*- (**8a**) and *trans*-2,3-di(2-fluorenyl)-2-butene (**8b**), similar to the case of dimethylstilbene,[19] as shown in Scheme V.

Scheme V



The oxidation of **8a** with osmic acid afforded **5** which has also been obtained under a short reduction period of **1** (Table I). The pinacol **5** was obtained by the reaction of di(2-fluorenyl)glyoxal with MeMgI, by photoreduction of **1** in Et_3N–ethanol, and by reductions of **1** with NaOH–Zn and with $TiCl_4$–Zn.[18] Further, **5** gave **1** by $Pb(OAc)_4$ oxidation.

The corresponding pinacolone **6** was given by the reaction of **5** with polyphosphoric acid or H_2SO_4 in acetic acid. The oxidation of **6** yielded 3,3-di(2-fluorenoyl)-2-butanone, di(2-fluorenoyl) ketone,[20] and fluorenone-2-carboxylic acid.[21] Consequently, the pinacolone **6** is established as the compound formed by the migration of the 2-fluorenyl group in **5**; the isomer due to methyl group migration is shown to be absent in these experiments.

The hydrogenation of **6** afforded **7**, which gave, of course, **9a** and **9b** by reaction with hydriodic acid.

Experimental Section

All the melting points are uncorrected.

The ir spectra were recorded on a IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.), as KBr pellets. The LPC data were obtained on a FLC-150 liquid-phase chromatograph (Jasco) attached a column JASCOSIL WC-01, using a 1:1 mixture of methylene chloride and isooctane as carrier. The measurements of uv spectra were run with a ORD/UV-5 optical rotatory dispersion recorder (Jasco) at scanning speed of 1.8 s/nm in isooctane.

The NMR spectra were obtained with a JNM-C60HL spectrometer (Japan Electron Optics Laboratory Co., Ltd.), using Me_4Si as internal reference. The VPC analyses were run with a JGC-1100FP gas chromatograph (JEOL), using a 1-m column containing 10% Silicone SE-30 on Chromosorb WAW (80–100 mesh) for dimeric products or a 20-cm column containing 10% PEGA on Diasolid M (80–100 mesh) for monomeric compounds. The mass spectra were measured with a RMU-6E apparatus (Hitachi, Ltd.) by means of a direct inlet system.

Clemmensen Reduction of 2-Acetylfluorene (1) and Its Homologues. General Procedure. Amalgamated zinc was prepared just before its use according to the procedure of Martin[9] from 10 g of zinc turnings, 14 ml of 10% aqueous mercuric chloride, and 1 ml of concentrated hydrochloric acid.

A solution of 0.01 mol of reactant and 200 ml of xylene was refluxed with the foregoing amalgamated zinc and 20 ml of 6 N hydrochloric acid. A 5-ml portion of concentrated hydrochloric acid was added every 6 h during the heating period.

After the mixture was allowed to cool to room temperature, the solution was decanted from any unchanged amalgam, and the residue was washed with a small amount of xylene. The washings and the reaction solutions were combined, and the organic layer was separated from the aqueous layer, washed with water until neutral, dried over calcium chloride (a trace part of it was analyzed by means of VPC and LPC), and evaporated to dryness.

The residue after evaporation was separated and purified by combination of vacuum sublimation, alumina-column chromatography, and recrystallization.

Clemmensen Reduction of 2-(α-Hydroxyethyl)fluorene-*C_α,O-d_2*. Deuteriocarbinol (100 mg) obtained by $LiAlD_4$ reduction of **1** was treated in the manner described above to give 2-(α-deuterioethyl)fluorene (66%) and trace amounts of *meso*- and *dl*-2,3-dideuterio-2,3-di(2-fluorenyl)butane.

2-Acetylfluorene (1) was synthesized by a method similar to that of Bachmann and Sheehan:[1] yield 92%; mp 131–132 °C (recrystallized from ethanol); ir ($\nu_{C=O}$) 1672 cm^{-1}; NMR (CCl_4) δ 2.50 (s, $-CH_3$), 3.77 (s, $>CH_2$), and 7.12–7.91 ppm (m, aromatic H).

The alcoholic mother liquor gave 2,7-diacetylfluorene:[22] yield 1%; mp 179.5–180 °C; ir ($\nu_{C=O}$) 1672 and 1662 cm^{-1}; mass spectrum *m/e* 250 (M^+), 235, 207, 192, and 165; NMR (benzene-d_6) δ 2.23 (s, 2-CH_3), 3.34 (s, $>CH_2$), and 7.12–7.90 ppm (m, aromatic H).

2-(α-Hydroxyethyl)fluorene (3).[7] The foregoing **1** (25 g) was hydrogenated in benzene (500 ml) using Raney nickel (W-7, 30 g) as a catalyst at room temperature: yield 94%; mp 140–141 °C (from cyclohexane); ir (ν_{OH}) 3320 cm.$^{-1}$

The same carbinol was also obtained by reduction of **1** (5 g) with sodium amalgam (50 g) in ethanol (500 ml), yield 4.4 g (88%).

2-Vinylfluorene (4). A. A finely powdered mixture of 13.9 g of **3**, 3.0 g of $KHSO_4$, and 1.5 g of copper powder was sublimed in vacuo at 180–190 °C, according to the method of Berkovic:[23] yield 5.7 g (45%); mp 137–139 °C; mass spectrum *m/e* 192 (M^+) and 165; NMR[8] (CCl_4) δ 3.64 (s, $>CH_2$), 5.12 (d, *trans*-Fl-C=CH), 5.61 (d, *cis*-Fl-C=CH), 6.63 (q, FlHC=), and 7.00–7.60 ppm (m, aromatic H).

B. A 2.7-g portion of **10** in 40 ml of freshly distilled *N,N*-dimethylformamide was refluxed with 1.3 g of KCN and 1.79 g of CuCN for 24 h, yield 74%.

2-(α-Bromoethyl)fluorene (10). Alcohol **3** (6.3 g) was treated with dry HBr in acetic acid (180 ml) at 20 °C. The deposited material was filtered, washed with water, dried, and recrystallized from hexane to give **10**: yield 6.2 g (76%); mp 99–100 °C dec; NMR (CCl_4) δ 1.98 (d, $-CH_3$), 3.64 (s, $>CH_2$), 5.13 (q, $>CH-$), and 7.09–7.64 ppm (m, aromatic H).

Anal. Calcd for $C_{15}H_{13}Br$: C, 65.95; H, 4.80. Found: C, 66.12; H, 4.84.

***meso*- and *dl*-2,3-Di(2-fluorenyl)butane (9). A. Grignard Reaction of 10.** A solution of bromide **10** (5.46 g) in 120 ml of THF was added dropwise for 20 min into 80 ml of THF containing magnesium (2.2 g), and the mixture was refluxed for 2 h. The resulting solution was evaporated to dryness and decomposed with dilute hydrochloric acid. The precipitate was sublimed in vacuo at 100 °C to afford 0.50 g (13%) of **2**, mp 99–100°. The unsublimable part was recrystallized from pyridine to give 1.28 g (33%) of **9a**, mp 306–308 °C, and 0.60 g (16%) of **9b**, mp 234–235 °C.

Mass spectrum of **9a** *m/e* 386 (M^+), 369, 205, 193 (base peak), 178, and 165; NMR (pyridine-d_5) δ 1.18 (d, 2-CH_3, *J* = 6 Hz), 2.98 (m,[24] 2 $>CH-$), 3.88 (s, 2 $>CH_2$), and 7.12–7.98 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.27; H, 6.53.

Mass spectrum of **9b** *m/e* 386 (M^+), 352, 193 (base peak), 178, and 165; NMR (pyridine-d_5) δ 1.35 (d, 2-CH_3), 3.09 (m,[24] 2 $>CH-$), 3.71 (s, 2 $>CH_2$), and 7.21–7.98 ppm (m, aromatic H). Anal. Found: C, 93.04; H, 6.90.

B. Reduction of 10 with $LiAlH_4$. Lithium aluminum hydride (0.57 g) suspended in THF (150 ml) was added to a solution of **10** (5.46 g) in THF (100 ml), and the resulting solution was refluxed for 9 h; 0.62 g (16%) of **9a**, 0.93 g (24%) of **9b**, and 0.71 g (18%) of **2** were isolated.

C. Rearrangement of 6. A mixture of **6** (2.0 g), hydriodic acid (1.5 ml), and red phosphorus (1.0 g) in acetic acid (50 ml) was heated for 24 h to give **9a** (0.89 g, 46%), **9b** (0.21 g, 11%), and **6** (0.26 g, 13%). In addition, a trace amount of **7** was confirmed by means of LPC.

2,3-Di(2-fluorenyl)-2,3-butanediol (5). A. Reduction of 1 with Zn–NaOH. A mixture of **1** (10.4 g), ethanol (300 ml), zinc dust (30 g), water (9 ml), and NaOH (20 g) was refluxed for 7 h. The reaction mixture was poured into 2000 ml of water and the organic precipitate was recrystallized from pyridine to afford 5.4 g (52%) of **5**: mp 278–279 °C dec (picrate mp 163–164 °C dec); ir (ν_{OH}) 3550 cm^{-1}; mass spectrum *m/e* 418 (M^+), 384, 369, 357 (base peak), 208, 193, and 165; NMR (Me_2SO-d_6) δ 1.41 (s, 2-CH_3), 3.77 (s, 2 $>CH_2$), 4.85 (s, 2-OH), and 7.07–8.55 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.34; H, 6.26.

Complex with 2,4,7-trinitrofluorenone, mp 224–226 °C dec. Anal. Calcd for $C_{30}H_{26}O_2 \cdot 2(C_{13}H_5O_7N_3)$: C, 64.12; H, 3.46; N, 8.01. Found: C, 63.83; H, 3.49; N, 8.03.

A mixture of **1** (3.5 g), zinc dust (10 g), NH_4Cl (0.7 g), and water (12 ml) in ethanol (100 ml) was treated in a manner similar to that described above to give **5** (2.2 g, 61%).

B. Reduction of 1 with $TiCl_4$–Zn. Ketone **1** (2.1 g) was reduced according to the direction of Mukaiyama et al.,[18] and gave **5** (1.6 g, 78%).

C. Photoreduction of 1 in Et_3N–Ethanol. Ketone **1** (6.3 g) in a mixture of ethanol (300 ml) and Et_3N (54 ml) was irradiated using a 100-W high-pressure mercury lamp at 53 °C for 2 h in an atmosphere of nitrogen according to the method of Davidson et al.;[25] 4.1 g (65%) of **5** was obtained.

D. Reaction of MeMgI with Di(2-fluorenyl)glyoxal. MeMgI (prepared from 0.25 g of Mg and 1.42 g of MeI in dry ether) was allowed to react with di(2-fluorenyl)glyoxal (300 mg) in dry benzene (60 ml) to yield pinacol **5** (233 mg, 72%).

E. Oxidation of 8a with Osmic Acid. A mixture of **8a** (384 mg), OsO_4 (300 mg), pyridine (0.4 ml), and ether (50 ml) was left for 45 h at room temperature under an inert atmosphere, evaporated to dryness, and chromatographed in benzene on alumina. The black adsorption band on the column was extracted with pyridine. The filtrate was treated with aqueous sodium sulfite to give 0.15 g (36%) of **5**.

Reaction of 5 with $Pb(OAc)_4$. A solution of **5** (0.88 g) and $Pb(OAc)_4$ (1.2 g) in absolute acetic acid (200 ml) was stirred at 29 °C for 3.5 h; 0.71 g (86%) of **1** and 0.07 g (8%) of **5** were obtained.

3,3-Di(2-fluorenyl)-2-butanone (6). A 100-ml portion of acetic acid containing 0.53 g of **5** and 1.3 g of polyphosphoric acid was refluxed for 6 h. After cooling, the reaction mixture was poured into 500 ml of water and the precipitate was purified by means of alumina-column chromatography in benzene and recrystallization from ethanol to afford 0.43 g (86%) of **6**: mp 156–157 °C dec; ir ($\nu_{C=O}$) 1705 cm^{-1}; mass spectrum *m/e* 400 (M^+), 357, 342, 191, 178, 165, and 43; NMR ($CDCl_3$) δ 2.00 (s, $-CH_3$), 2.20 (s, $-COCH_3$), 3.87 (s, 2 $>CH_2$), and 7.08–7.90 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 90.25; H, 5.89.

The residue of the filtration of the hot ethanolic solution gave 2,3-di(2-fluorenyl)-1,3-butadiene in 1.5% yield: mp 272–274 °C; mass spectrum *m/e* 382 (M^+), 368, 352, 191, and 165. Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.31; H, 5.74.

Oxidation of 3,3-Di(2-fluorenyl)-2-butanone (6). A mixture of **6** (1.0 g) and $KMnO_4$ (11 g) in acetone (70 ml) was refluxed for 2 h to yield 1.04 g (97%) of 3,3-di(2-fluorenoyl)-2-butanone: mp 195–196 °C; ir ($\nu_{C=O}$) 1717 and 1705 cm^{-1}; mass spectrum *m/e* 428 (M^+), 385, 370, and 179; NMR (Me_2SO-d_6) δ 2.05 (s, $-CH_3$), 2.20 (s, $-COCH_3$), and 7.20–7.75 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.09; H, 4.70. Found: C, 84.20; H, 4.69.

A solution of **6** (2.0 g), sodium dichromate (20 g), a few drops of H_2SO_4, and acetic acid (60 ml) was refluxed for 3.5 h; 0.68 g (35%) of di(2-fluorenoyl) ketone,[20] mp 298–299 °C, 0.13 g (6%) of 3,3-di(2-fluorenoyl)-2-butanone, mp 195–196 °C, and 0.05 g (2%) of fluorenone-2-carboxylic acid,[21] mp 338 °C dec, were separated.

3,3-Di(2-fluorenyl)-2-butanol (7). Butanone **6** (15.3 g) in benzene (250 ml) was hydrogenated under an atmospheric pressure of hydrogen using Raney nickel catalyst (W-7, 15 g) at room temperature. The reaction mixture was filtered, the filtrate was evaporated to dryness, the residue was recrystallized from cyclohexane, and the crystal was dried in vacuo at 95–105 °C for 10 h to afford 13.5 g (88%) of **7**: mp 134–135 °C dec; ir (ν_{OH}) 3570 cm^{-1}; mass spectrum *m/e* 402 (M^+), 384, 357, 341, and 165; NMR (pyridine-d_5) δ 1.35 (d, $-CH_3$), 1.98 (s, $-CH_3$), 3.75 (s, 2 $>CH_2$), 5.04 (quintet, $>CH-$), 6.05 (d, $-OH$), and 7.13–7.92 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.31; H, 6.41.

***cis*- and *trans*-2,3-Di(2-fluorenyl)-2-butene (8). A. Reduction of 1 with $TiCl_4$–Zn.** Ketone **1** (2.1 g) was reduced with $TiCl_4$ (2.8 g) and zinc (2.0 g) in THF (100 ml);[18] 1.48 g (76%) of **8a**, mp 144–145 °C dec (from ethanol), and 0.28 g (15%) of **8b**, mp 287–288 °C dec (from pyridine), were obtained.

Mass spectrum of **8a:** *m/e* 384 (M^+, base peak), 369, 354, 218, 203, 193, 191, 179, and 165; NMR (pyridine-d_5) δ 2.23 (s, 2-CH_3), 3.62 (s, 2 $>CH_2$), and 7.02–7.79 ppm (m, aromatic H); uv λ_{max} 271 nm (log ϵ 4.658). Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.89; H, 6.19.

Mass spectrum of **8b:** *m/e* 384 (M^+), 369, 354, 192, and 165; NMR (pyridine-d_5) δ 2.11 (s, 2-CH_3), 3.93 (s, 2 $>CH_2$), and 7.07–8.02 ppm (m, aromatic H); uv λ_{max} 278 nm (log ϵ 4.671). Anal. Found: C, 93.84; H, 5.99.

B. Reaction of 7 with H_2SO_4. Carbinol **7** (3.2 g) in benzene (25 ml) containing a few drops of H_2SO_4 was refluxed for 1 h to afford **8b** (2.22 g, 73%).

Hydrogenation of 2,3-Di(2-fluorenyl)-2-butene (8). Cis butene **8a** (100 mg) in benzene (100 ml) was stirred with Raney nickel (W-4, 10 g) at 50 °C for 3 h to give 87.4 mg (87%) of **9a.**

Trans isomer **8b** (500 mg) was treated with Raney nickel (25 g) in the manner described above to yield **9b** (196 mg, 39%) and recovery of **8b** (166 mg, 33%).

Photoisomerization of *cis*-2,3-Di(2-fluorenyl)-2-butene (8a). Cis butene **8a** (226 mg) in benzene (100 ml) was irradiated using a 100-W high-pressure mercury lamp for 18 h; 169 mg (75%) of **8b** was isolated.

Oxidation of *trans*-2,3-Di(2-fluorenyl)-2-butene (8b). A suspension of **8b** (384 mg) in acetone (20 ml) was refluxed with $KMnO_4$ (1.4 g) for 30 h. The reaction mixture was worked up as usual to give 2-acetylfluorenone[26] (186 mg, 41%), mp 160–161.5 °C, 2-(2-fluorenoyl)-3-(2-fluorenyl)-2-butene (9.5 mg, 2%), mp 244–245 °C, 2,3-di(2-fluorenoyl)-2-butene (14 mg, 4%), mp 280–281 °C, and recovery (113 mg, 30%) of **8b.**

Ir of 2-(2-fluorenoyl)-3-(2-fluorenyl)-2-butene ($\nu_{C=O}$) 1706 cm^{-1}; NMR (benzene-d_6) δ 1.90 (s, 2-CH_3), 3.52 (s, $>CH_2$), and 6.96–7.74 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.27; H, 5.82.

Ir of 2,3-di(2-fluorenoyl)-2-butene ($\nu_{C=O}$) 1710 cm^{-1}; NMR (benzene-d_6) δ 1.70 (s, 2-CH_3) and 7.01–7.62 ppm (m, aromatic H). Anal. Calcd for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.56; H, 4.91.

Friedel–Crafts Reaction of Fluorene with Oxalyl Chloride. A 1.5-g portion of oxalyl chloride was added dropwise to a mixture of fluorene (3.32 g) and $AlCl_3$ (2.0 g) in carbon disulfide (40 ml), and the resulting mixture was refluxed for 1 h.

Upon treatment in an usual manner, the reaction mixture was evaporated to dryness and chromatographed in benzene–ethanol (9:1) on alumina; di(2-fluorenyl)glyoxal (0.47 g, 12%), mp 262.5–263 °C, di(2-fluorenyl) ketone (0.57 g, 16%), mp 281–281.5 °C, and ethyl fluorene-2-carboxylate (0.47 g, 10%), mp 86–87 °C, were isolated.

Ir of di(2-fluorenyl)glyoxal ($\nu_{C=O}$) 1653 cm^{-1}. Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 87.04; H, 4.42.

Ir of di(2-fluorenyl) ketone ($\nu_{C=O}$) 1642 cm^{-1}; mass spectrum *m/e* 358 (M^+), 193, and 165. Anal. Calcd for $C_{27}H_{18}O$: C, 90.47; H, 5.06. Found: C, 90.52; H, 5.07.

Ir of ethyl fluorene-2-carboxylate ($\nu_{C=O}$) 1692 cm^{-1}; mass spectrum *m/e* 238 (M^+), 223, 210, 209, 193, and 165; NMR (CCl_4) δ 1.40 (t, $-CH_3$), 3.82 (s, $>CH_2$), 4.32 (q, $-CH_2-$), and 7.16–8.10 ppm (m, aromatic H). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.34; H, 5.94.

Di(2-fluorenyl) Ketone. The Friedel–Crafts reaction of fluorene (3.2 g) with fluorene-2-carbonyl chloride (4.3 g) using $AlCl_3$ (6.5 g) in carbon disulfide (80 ml) afforded di(2-fluorenyl) ketone, yield 6.4 g (97%), mp 281–281.5 °C.

Oxidation of the ketone with $KMnO_4$ gave di(2-fluorenoyl) ketone[20] (88%), mp 298–299 °C, mass spectrum *m/e* 386 (M^+).

Registry No.—**1,** 781-73-7; **2,** 1207-20-1; **3,** 20371-86-2; **4,** 10473-10-6; **5,** 58473-47-5; **5** complex with 2,4,7-trinitrofluorenone, 58473-48-6; **6,** 58473-49-7; **7,** 58473-50-0; **8a,** 58473-51-1; **8b,** 58473-52-2; **9a,** 58473-53-3; **9b,** 58473-54-4; **10,** 42914-77-2; 2,7-diacetylfluorene, 961-27-3; 2,3-di(2-fluorenyl)-1,3-butadiene, 58473-55-5; 3,3-di(2-fluorenoyl)-2-butanone, 58473-56-6; di(2-fluorenyl) ketone, 55341-69-0; fluorenone-2-carboxylic acid, 784-50-9; 2-acetylfluorenone, 42136-05-0; 2-(2-fluorenoyl)-3-(2-fluorenyl)-2-butene, 58473-57-7; 2,3-di(2-fluorenoyl)-2-butene, 58473-58-8; di(2-fluorenyl)glyoxal, 58473-59-9; di(2-fluorenyl) ketone, 55341-67-8; ethyl fluorene-2-carboxylate, 58473-60-2.

References and Notes

(1) W. E. Bachmann and I. C. Sheehan, *J. Am. Chem. Soc.*, **62,** 2687 (1940).
(2) E. F. Ray and G. Rieveschl, Jr., "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 23.
(3) N. Campbell and H. Wang, *J. Chem. Soc.*, 1513 (1949).
(4) E. Sawicki, *J. Am. Chem. Soc.*, **76,** 2269 (1954).
(5) J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 2337 (1959).
(6) J. F. Cairns and W. J. Hickinbottom, *J. Chem. Soc.*, 867 (1962).
(7) D. T. Mowry, M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68,** 1105 (1946).
(8) J. F. Yanus and J. M. Pearson, *Macromolecules*, **7,** 716 (1974).
(9) E. L. Martin, *Org. React.*, **1,** 155 (1942).
(10) T. Nakabayashi, *J. Am. Chem. Soc.*, **82,** 3900 (1960).
(11) T. Nakabayashi, *J. Am. Chem. Soc.*, **82,** 3906, 3909 (1960).
(12) J. H. Brewster, *J. Am. Chem. Soc.*, **76,** 6361, 6364, 6368 (1954).
(13) A. S. Harris, E. N. White, and D. McNeil, *J. Chem. Soc.*, 4216 (1955); K. Suzuki, *Bull. Chem. Soc. Jpn.*, **35,** 735 (1962); K. Suzuki, T. Maeda, N. Nawa, and Y. Soda, *ibid.*, **35,** 1299 (1962); K. Suzuki, M. Fujimoto, M. Murakami, and M. Minabe, *ibid.*, **40,** 1259 (1967).
(14) M. Poutsma and F. Wolthuis, *J. Org. Chem.*, **24,** 875 (1959).
(15) 2-(α-Chloroethyl)fluorene may be formed in the Clemmensen reduction (see ref 14) and **9** is obtained by the coupling reaction of the chloride and B. However, the presence of the chloride could not be established.
(16) F. von Wessely and H. Welleba, *Ber.*, **74,** 777 (1941).
(17) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84,** 743 (1962).
(18) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, 1041 (1973).
(19) N. Inamoto, S. Masuda, Y. Nagai, and O. Simamura, *J. Chem. Soc.*, 1433 (1963).
(20) K. Dziewonski and M. Panek, *Bull. Int. Acad. Pol. Sci. Lett., Cl. Sci. Math. Nat., Ser. A*, 745 (1927); *Chem. Abstr.*, **23,** 3888 (1928).
(21) F. E. Ray and G. Rieveschl, *J. Am. Chem. Soc.*, **65,** 836 (1943).
(22) N. Ishikawa and T. Ozawa, *J. Synth. Org. Chem. Jpn.*, **17,** 553 (1959).
(23) S. Berkovic, *Isr. J. Chem.*, **1,** 1 (1963).
(24) Since these compounds were slightly soluble in most organic solvents, the spin pattern of these methine protons could not be clarified.
(25) R. S. Davidson, P. F. Lambath, and F. A. Younis, *J. Chem. Soc. C*, 2203 (1969).
(26) T. Sulzberg and R. J. Cotter, *J. Org. Chem.*, **35,** 2762 (1970).