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Formation of 1,3-Di(2-fluorenyl)-1-butene from 2-(1-Bromoethyl)fluorene with Silver Powder

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An unexpected compound, 1,3-di(2-fluorenyl)-1-butene, was formed as the major product, accompanied by *meso*- and *dl*-2,3-di(2-fluorenyl)butane as the minor products, in the reaction of 2-(1-bromoethyl)fluorene with silver powder. The structure of the butene was confirmed to be the *E* form by a comparison of the UV spectra of the related compounds.

The Wurtz-Fittig-type reaction of 2-(1-bromoethyl)fluorene (**1**)1) afforded the unexpected 1,3-di(2-fluorenyl)-1-butene (**2**) as the major product in addition to the expected diastereomers, *meso*-(**3a**) and *dl*-2,3-di(2-fluorenyl)butane (**3b**),1) as minor products. The present paper is concerned with the formation, the stepwise synthesis, and the configurational assignment of **2**.

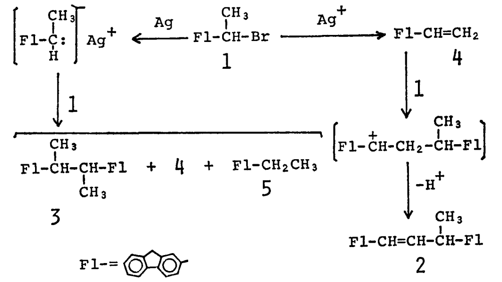
Results and Discussion

The reaction of **1** with silver powder in benzene gave **2** as the main product, and **3a**, **3b**, 2-vinylfluorene (**4**), and 2-ethylfluorene (**5**) as by-products accompanied by a considerable amount of resinous material. An appreciable quantity of hydrogen bromide was produced in this system.

The yield of **2** is higher than that of **3**, which may be formed by the usual Wurtz-Fittig reaction (Scheme 1). This finding is due to the fact that the unstable **1** is decomposed into **4** *via* 1-(2-fluorenyl)ethyl cation instead of 1-(2-fluorenyl)ethanide anion, and presumably to the smaller extent of the ionization of silver compared with that of sodium.

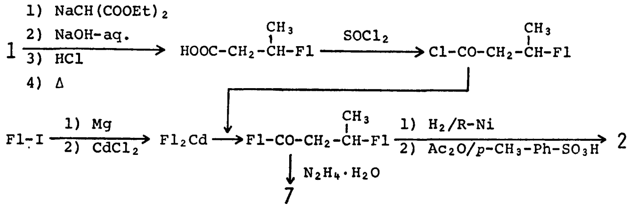
The reactive **1** is cleft easily into the olefin **4**, with elimination of hydrogen bromide, in the presence of the silver ions which are formed. The electrophilic attack of the α-carbon atom on the alkyl group of **1** to the methylidene carbon of **4** would form **2** through 1,3-di(2-fluorenyl)butyl cation.

The compound **2** (17%) was obtained by the reaction1) of 1-(2-fluorenyl)ethanol (**6**) with potassium hydrogensulfate. Moreover, **2** was isolated by the Friedel-Crafts reaction between **1** and **4** (11%), and by treatment of **6** with polyphosphoric acid (2%).



Scheme 1.

Hydrogenation of **2** yielded 1,3-di(2-fluorenyl)butane (**7**) and oxidation of **2** with potassium permanganate gave 2-acetyl-9-fluorenone and 9-oxofluorene-2-carboxylic acid. The structural proof of **2** was established by the independent synthesis using a procedure similar to that of Ela and Cram2) (Scheme 2).



Scheme 2.

Geometrical isomers of **2** can, in principle, exist in analogy with the case of 1,3-diphenyl-1-butene.2) The UV spectrum of **2** is strikingly similar to that of **4** (I in Fig. 1). A solution of **2** in cyclohexane was irradiated by ultraviolet light and the progress of the isomerization was traced by UV spectra, as shown in Fig. 1. After a short irradiation (for example, 3 min), the absorption maximum shifted to a shorter wavelength and showed some resemblance to that of **7** (II in Fig. 1). The spectrum obtained after a longer period (60 min) irradiation showed a further shift to a shorter wave-

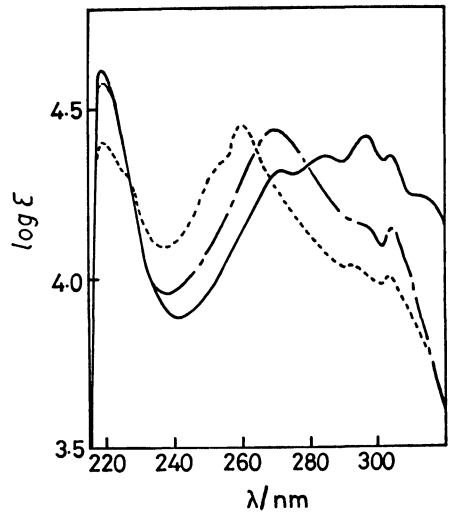


Fig. 1. UV spectra of **2** under ultraviolet irradiation. ——: Original (I), —·—: 3 min (II), ----: 60 min (III).

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length and was like that of the parent fluorene (III in Fig. 1).

The consideration of molecular models indicates that the vinylene bond of the *E* configuration in **2** can be situated on the same plane with respect to the adjacent 2-fluorenyl group. The absorption maximum of this conjugated system shifts to a bathochromic region, as in the case of **4**. However, the *Z* form of **2** can not be situated in the same plane as that of the *E* form, due to the steric interference between the two bulky fluorenyl rings at the 1- and 3-positions or between the fluorenyl ring at the 1-position and the methyl group at the 3-position in **2**. Therefore, the vinylene and fluorenyl π-electron systems might exist independently of each other and give spectra similar to that of fluorene. Accordingly, the configuration of the isolated **2** can be assigned to be the *E* form, and the compound having the UV spectrum of III may be the *Z*-isomer.

The compound obtained by a long irradiation (14 h) was first separated by silica gel column chromatography and dried *in vacuo* at 120 °C. The NMR spectrum shows that the resulting mixture consists of *E*- (**2**-*E*) and *Z*-isomers (**2**-*Z*) in a ratio of *ca.* 1 : 1. The UV spectrum of the mixture has a shape similar to that of II. Repeated recrystallization of the mixture afforded only **2**-*E*, whose spectrum was identical with that of I. Consequently, the attempt to isolate pure **2**-*Z* failed. These findings suggest that **2**-*E* can be isomerized to **2**-*Z* by ultraviolet irradiation and that the **2**-*Z* is converted gradually to **2**-*E* upon heating and/or standing in solution.

Experimental[3)]

The instruments used in this experiment were the same as those described elsewhere.[1)] UV spectra were recorded at a scanning speed of 0.76 s/nm in cyclohexane.

*Reaction of **1** with Silver Powder.* A solution of 8.19 g of **1** in 140 ml of dry benzene was refluxed with 3.24 g of silver powder for 40 h. A considerable amount of hydrogen bromide evolved during this period.

After cooling, the precipitate was filtered and extracted with benzene. The combined benzene solution was evaporated to dryness and the residue was distilled with steam. The distillate was recrystallized fractionally from hexane to give 0.005 g (0.09%) of **4**, mp 135—137 °C, and 0.015 g (0.26%) of **5**, mp 99—100 °C. The sticky residue was recrystallized fractionally from ethyl acetate to give 0.18 g (3.3%) of **3a**, mp 306—308 °C, and 0.08 g (1.4%) of **3b**, mp 234—235 °C. The mother liquor was evaporated to dryness and the residual solid was recrystallized from benzene–cyclohexane (1 : 1) to yield 2.20 g (38%) of **2**: mp 176—178 °C; NMR (pyridine-d_5) δ=1.54 (3H, d, J=6.9 Hz), 3.79 (1H, m), 3.83 (4H, s), 6.67 (2H, d, J=2.4 Hz), and 7.18—7.97 (14H, m); MS, *m/e*, 384 (M$^+$), 369, 353, 339, 218, 203, 192, 179, 165, and 152.

Complex of **2** with 2,4,7-trinitro-9-fluorenone (mole ratio= 1/2): mp 142—143 °C (dec); IR 1732 cm^{-1} ($>$C=O).

*Photo-irradiation of **2**.* A sample of **2** was prepared with the density of 9.54×10^{-6} mol per 1000 ml solution. The solution (5 ml) was sealed in a quartz cell and irradiated using a 100-W high-pressure mercury lamp. After each time interval, the UV spectrum was recorded immediately without any treatment.

A second irradiation of **2** (0.50 g) in cyclohexane (400 ml) was carried out for 14 h under an atmosphere of nitrogen. The mixture was concentrated to 100 ml and chromatographed on a silica gel column. The colorless eluate was evaporated *in vacuo* at 120 °C during a period of 5 h to leave a powder (0.40 g), which was found to be pure by means of thin layer chromatography and gas chromatography. NMR (benzene-d_6) δ=1.46 (–CH$_3$ of 2-*Z*, J=7.0 Hz, 45%) and 1.52 (–CH$_3$ of 2-*E*, J=7.0 Hz, 55%).

The materials gave 0.26 g of **2**-*E*, mp 176—178 °C, by repeated recrystallization from cyclohexane, cyclohexane–hexane, and cyclohexane–benzene.

*Reaction of **6** with Copper Powder and Potassium Hydrogensulfate.* A powdered mixture of 12.6 g of **6**, 2.73 g of potassium hydrogensulfate, and 1.36 g of copper powder was sublimed at 180—200 °C under reduced pressure for 30 min; the sublimate gave 3.61 g of **4**. The residual part was recrystallized from cyclohexane–benzene (1 : 1) to yield 2.01 g (17%) of **2**.

*Friedel-Crafts Reaction of **4** with **1**.* A mixture of 1.37 g of **1**, 0.96 g of **4**, and 0.035 g of fused zinc chloride in 60 ml of carbon disulfide was refluxed for 2.5 h to give 0.216 g (11%) of **2**.

*Hydrogenation of **2**.* Butene **2** (1.00 g) was hydrogenated with hydrogen, using 10 g of Raney nickel (W-4) as catalyst in benzene (70 ml); 0.72 g (72%) of **7**, mp 161—163 °C, was obtained. UV$_{\text{max}}$ 219 (log ε 4.70), 264 (4.48), 268 (4.50), 293 (4.01), and 304 nm (4.06); NMR (pyridine-d_5) δ=1.35 (3H, d, J=6.9 Hz), 2.07 (2H, t), 2.45—2.93 (3H, m), 3.86 (4H, s), and 7.23—8.05 (14H, m); MS, *m/e*, 386 (M$^+$).

*Oxidation of **2**.* A mixture of 0.38 g of **2**, 2.0 g of potassium permanganate, and 100 ml of acetone was stirred at room temperature for 2 h; 0.27 g (61%) of 9-oxofluorene-2-carboxylic acid, mp 336 °C (dec), and 0.04 g (18%) of 2-acetyl-9-fluorenone, mp 159—161 °C, were isolated.

3-(2-Fluorenyl)butanoic Acid. Dry ether (10 ml) containing diethyl malonate (6.4 g) was added to an ice-cooled solution of sodium ethoxide (2.7 g) in ether (30 ml) over a 10 min period with stirring under an atmosphere of nitrogen. To this was added a solution of 10.9 g of **1** in 50 ml of dry benzene, and the reaction mixture was stirred for an additional hour. After standing overnight at room temperature, the mixture was refluxed for 5.5 h and filtered, and the filtrate was evaporated to dryness to give diethyl 2-(2-fluorenyl)-1,1-propanedicarboxylate: mp 71—72 °C; IR 1740 and 1714 cm^{-1} ($>$C=O); NMR (CCl$_4$) δ=0.95 (3H, t), 1.21 (6H, t), 3.78 (2H, s), 3.43—4.33 (6H, m), and 7.05—7.70 (7H, m); MS, *m/e*, 352 (M$^+$).

The diester was refluxed with 12.8 g of sodium hydroxide in 100 ml of water for 4 h. After filtration, the filtrate was neutralized with hydrochloric acid to yield dicarboxylic acid: mp 195—196 °C (dec); IR 1723 cm^{-1} ($>$C=O).

The dibasic acid was heated at 150—160 °C for 1 h and the residue was sublimed *in vacuo* at 180 °C; the sublimate was recrystallized from benzene to give 7.63 g (76% based on **1**) of 3-(2-fluorenyl)butanoic acid: mp 155.5—157.0 °C; IR 2900 (–OH) and 1692 cm^{-1} ($>$C=O); NMR (benzene-d_6) δ=1.13 (3H, d, J=7.2 Hz), 2.43 (2H, d), 3.15 (1H, sex), 3.45 (2H, s), 6.93—7.73 (7H, m), and 11.55 (1H, s); MS, *m/e*, 252 (M$^+$).

Acid chloride (92% yield); mp 68—70 °C (dec); IR 1796 cm^{-1} ($>$C=O).

Methyl ester (93% yield): mp 86.5—87.0 °C; IR 1732 cm^{-1} ($>$C=O); NMR (CCl$_4$) δ=1.30 (3H, d), 2.48 (2H, d), 3.26 (1H, sex), 3.53 (3H, s), 3.76 (2H, s), and 6.97—7.68 (7H, m); MS, *m/e*, 266 (M$^+$).

3-(2-Fluorenyl)-1-butanol. The above methyl ester was reduced to the alcohol (98%): mp 82—83 °C; IR 3326 cm^{-1} (–OH); MS, *m/e*, 238 (M$^+$).

Corresponding acetate: mp 51.5—52.5 °C; IR 1732 cm^{-1} ($>$C=O); NMR (benzene-d_6) δ=1.15 (3H, d, J=6.9 Hz), 1.65 (3H, s), 1.77 (2H, q), 2.71 (1H, sex), 3.49 (2H, s), 3.96 (2H, t), and 6.92—7.67 (7H, m); MS, *m/e*, 280 (M$^+$).

1,3-Di(2-fluorenyl)-1-butanone. To the active magnesium prepared from 2.04 g of anhydrous magnesium chloride according to the literature,[4] there was added 4.38 g of 2-iodofluorene in 70 ml of dry tetrahydrofuran (THF) for 30 min at room temperature, and the reaction mixture was stirred for 1.5 h. Anhydrous cadmium chloride (1.4 g) was added all at once and the mixture was stirred for 2 h. To the solution of difluorenylcadmium, there was added the foregoing butanoyl chloride (prepared from 1.76 g of acid) in 20 ml of THF for 10 min at room temperature. The mixture was refluxed for 1 h and allowed to stand overnight at room temperature. This provided 0.50 g (18%) of 1,3-di(2-fluorenyl)-1-butanone: mp 175—176 °C; IR 1668 cm^{-1} ($>$C=O); MS, *m/e*, 400 (M$^+$).

Wolff-Kishner Reduction of 1,3-Di(2-fluorenyl)-1-butanone. A mixture of 0.10 g of the above ketone, 0.03 g of potassium hydroxide, 0.10 ml of hydrazine hydrate (90%), and 20 ml of diethylene glycol was treated in the usual manner to give 0.088 g (91%) of **7**: mp 161—163 °C.

1,3-Di(2-fluorenyl)-1-buthanol. The ketone (0.86 g) was reduced over Raney nickel (3.0 g) under an atmosphere of hydrogen at room temperature to afford 0.70 g (81%) of the alcohol: mp 151—153 °C; IR 3585 cm^{-1} (–OH); MS, *m/e*, 402 (M$^+$).

Dehydration of 1,3-Di(2-fluorenyl)-1-butanol. A solution of 0.30 g of the alcohol, 0.3 ml of acetic anhydride, 0.03 g of *p*-toluenesulfonic acid monohydrate, and 80 ml of acetic acid was refluxed for 4 h to yield 0.254 g (89%) of **2**: mp 176—178 °C.

References

1) M. Minabe, M. Yoshida, M. Fujimoto, and K. Suzuki, *J. Org. Chem.*, **41**, 1935 (1976).

2) S. W. Ela and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5777 (1966).

3) All the melting points are uncorrected. All new compounds gave satisfactorily elemental analyses.

4) R. D. Rieke and S. E. Bales, *J. Chem. Soc., Chem. Commun.*, **1973**, 879.