The Clemmensen Reduction of 3-Bromofluorenone[1]

Kazuo SUZUKI,* Minoru FUJIMOTO,** Mitsumasa MURAKAMI** and Masahiro MINABE*

* *Department of Industrial Chemistry, Faculty of Technology, Utsunomiya University, Ishii-cho, Utsunomiya*

** *Department of Industrial Chemistry, Faculty of Technology, Yamaguchi University, Tokiwadai, Ube*

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In our previous paper, we reported that the Clemmensen reduction of 2-bromofluorenone[2] afforded 2-bromo-fluorene, 2-bromo-9-fluorenol, 2, 2′-dibromo-9, 9′-bifluorenylidene, 2, 2′-dibromo-9,9′-bifluorenyl, 2,2′-dibromo-9,9′-dihydroxy-9, 9′-bifluorenyl, and a trace of spiro[2-bromofluorene-9, 9′(10′)-2′-bromophenanthrone]. In order to observe the effect of the bromine atom on the reaction sequences, 3-bromofluorenone (I) was reduced under the same conditions. It was found that the reduction proceeded in a manner similar to that observed with 2-bromofluorenone.

3-Bromofluorenone (I), prepared by the deamination of 2-amino-3-bromofluorenone,[3] was reduced by the procedure employed with fluorenone and 2-bromofluorenone, using toluene as the solvent.

From the reaction products, 3-bromofluorenol (II),[4] 3-bromofluorene (III),[4] 3, 3′-dibromo-9, 9′-dihydroxy-9, 9′-bifluorenyl (IV), 3, 3′-dibromo-9-hydroxy-9, 9′-bifluorenyl (V), 3, 3′-dibromo-9, 9′-bifluorenyl (VI),[4] and an unknown compound with a melting point of 225°C (VII) were isolated by means of a combination of recrystallization and column chromatography.

The experimental results are summarized in Table 1. The formation of IV reached a maximum after 4—5 hr. reaction. The yields of compounds III and VI[4] gradually increased during this time.

The IR spectra of IV and V were very similar to those of 2, 2′-dibromo-9, 9′-dihydroxy-9, 9′-bifluorenyl and 2, 2′-dibromo-9-hydroxy-9, 9′-bifluorenyl respectively. The reduction of IV (Run 7) also gave V, which was converted to a red 3, 3′-dibromo-9, 9′-bifluorenylidene (X) by alkali. Although VI and VII gave the same elementary analyses and very similar IR and NMR

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[1] Studies on Fluorene Derivatives. XXIV. Part XXIII: K. Suzuki and M. Fujimoto, This Bulletin, **37**, 1833 (1964).

[2] K. Suzuki, T. Maeda, N. Nawa and Y. Sōda, *ibid.*, **35**, 1299 (1962).

[3] K. Suzuki and M. Momoi, *ibid.*, **36**, 1693 (1963). In this synthesis, a small amount of a compound (mp 267—268°C) was isolated during the course of the deamination process. From the infrared spectrum (1705 cm^{-1} (C=O), 1510, 1340 cm^{-1} (NO$_2$)) and the analytical results (C, 51.25; H, 1.95%), this compound was identified as the 2-nitro-6-bromofluorenone (mp 267—268°C) reported by M. V. Bhatt (*Tetrahedron,* **20**, 803 (1964)).

[4] K. Suzuki, S. Kajigaeshi and M. Sano, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem. Japan)*, **16**, 82 (1958).

Table 1. Reduction products of I or derivatives under various conditions

Run	I g	React. time hr	II g	III g	IV g	V g	VI g	VII g	Recovd. I g
1	10	1	0.2	0.1	—	—	—	—	8.4
2	10	5	2.0	0.9	2.4	0.08	0.01	—	2.8
3	10	15	1.6	1.6	2.0	0.01	0.01	0.017	2.0
4	10	24	1.4	2.0	1.4	—	0.03	0.002	2.0
5	10	72	0.1	3.0	1.5	—	0.4	0.3	1.3
6*	8	2	0.1	1.5	2.0	—	0.4	0.3	1.6
7**	5.0(IV)	24				0.5	0.03	0.03	3.6(IV)

* Concentrated hydrochloric acid was used.
** I (0.2 g) was isolated from the reduction products.

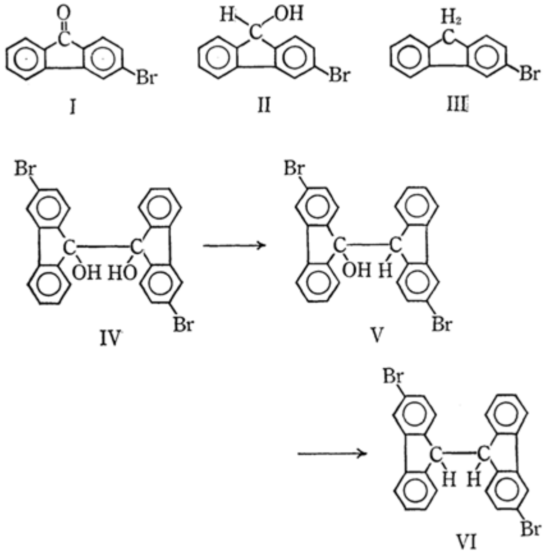

Chart 1

spectra, the structure of VII is not clear at present. When IV was heated with sulfuric acid in acetic acid, it afforded spiro[3-bromofluorene-9, 9′(10′)-3′-bromophenanthrene]-10′-one (VIII) by pinacol rearrangement; this was then reduced to 3, 3′-dibromophenanthreno[9′, 10′ : 9, 10]phenanthrene (IX), as is illustrated in Chart 2. The pinacol rearrangement of IV, however, did not occur during the reduction.

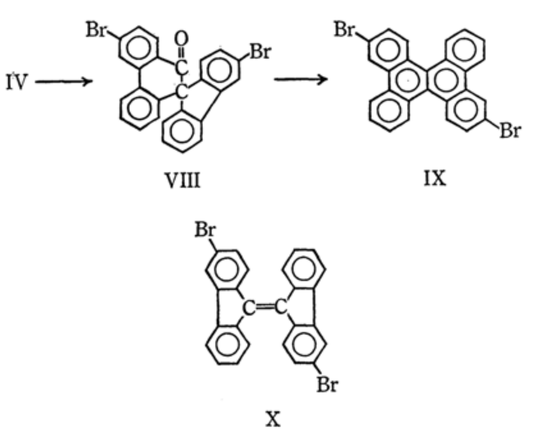

Chart 2

The IR spectra of VIII and IX were very similar to those of the corresponding 2-bromo substituted compounds.

Experimental[5)]

General Procedure for the Clemmensen Reduction of 3-Bromofluorenone (I). *Materials.* Amalgamated zinc filings were prepared by a method similar to that of Martin.[6)]

I (10 g), amalgamated zinc (20 g), concentrated hydrochloric acid (30 m*l*), toluene (50 m*l*), and water (15 m*l*) were refluxed for 15 hr, a 10-m*l* additional portion of concentrated hydrochloric acid being added every 6 hr during this period. The toluene layer developed an orange-yellow color after 15 hr.

The reaction mixture was then let stand overnight, and the product which coated the surface of the zinc was filtered out. This was then extracted with boiling benzene, and the precipitate which formed upon cooling was recrystallized from ethyl acetate to give IV (mp 205°C, 1.85 g).

Found: C, 60.60; H, 3.26%. Calcd for $C_{26}H_{16}O_2Br_2$: C, 60.03; H, 3.10%. IR, 3520 cm^{-1} (OH) (KBr-disk).

After the evaporation of the ethyl acetate mother liquor to a small volume, the precipitated material was recrystallized from ethyl acetate to give V (mp 140°C, 0.1 g).

Found: C, 62.24; H, 3.55%. Calcd for $C_{26}H_{16}$·OBr_2: C, 61.93; H, 3.20%. IR, 3320—3480 cm^{-1} (OH) (KBr-disk).

The original toluene mother liquor was dried and then evaporated under reduced pressure; the residue was dissolved in benzene and chromatographed on alumina. Three products, IV (0.15 g, mp 205°C (dec.)), V (1.0 g, mp 140°C), and II[4)] (1.6 g, mp 170—171°C; IR, 3120—3280 cm^{-1} (OH) KBr-disk), were isolated from the upper part of column. Confirmations of the products were made by mixed melting point determinations. I (2.0 g, mp 165—166°C; IR, 1705 cm^{-1}

[5)] All the melting points are uncorrected.

[6)] E. L. Martin, "Organic Reactions," Vol. I, Chapman and Hall, London (1942), p. 155.

(C=O) KBr-disk) was recovered from the yellow band of the column.

The colorless benzene solution of the material which was not absorbed on the column was evaporated to dryness, and the residue was heated with ethyl acetate. The insoluble part was recrystallized from benzene to yield VI (1.0 g, mp 248—250°C; IR, 3040 cm^{-1} (Ar.=C–H) KBr-disk; NMR ($\geqslant$CH), τ 5.27 ppm (singlet)). VII (0.17 g, mp 225°C) was isolated by the evaporation of the ethyl acetate mother liquor, followed by recrystallization.

Found: C, 64.03; H, 3.39%. Calcd for $C_{26}H_{16}Br_2$: C, 63.96; H, 3.30%. NMR, τ 5.29 ppm (singlet).

III was obtained by the evaporation of the ethyl acetate mother liquor and recrystallized from petroleum ether to give colorless crystals, mp 90—91°C, 1.6 g; NMR ($\rangle CH_2$), τ 6.23 ppm (quartet).

Pinacol Rearrangement of IV to VIII. IV (1.5 g) was dissolved in acetic acid (50 m*l*), and concentrated sulfuric acid (0.2 m*l*) was added; the mixture was then refluxed for 1 hr and then poured into cold water. The precipitate was filtered and washed well with water, then recrystallized from benzene to give VIII (0.8 g, mp 260—261°C, yield 75.5%).

Found: C, 62.32; H, 2.83%. Calcd for $C_{26}H_{14}OBr_2$: C, 62.18; H, 2.81%. IR, 1685 cm^{-1} (C=O) (KBr-disk).

I (0.05 g, mp 165—166°C) and IV (0.4 g, mp 205°C) were separated by a combination of recrystallization and column chromatography in benzene on alumina.

Reduction of VIII to IX. A mixture of amalgamated zinc (13.8 g), water (3.45 m*l*), toluene (23 m*l*), concentrated hydrochloric acid (11.5 m*l*), and VIII (2.3 g) was refluxed vigorously for 24 hr. A 2.3-m*l* portion of concentrated hydrochloric acid was added every 6 hr.

The product which coated the surface of the zinc was filtered, dried, and dissolved in benzene by heating; upon cooling, IX (0.15 g, mp 344—345°C) was obtained. When the toluene layer was steam-distilled, additional IX (0.15 g, mp 345°C) was isolated.

Found: C, 64.42; H, 2.82%. Calcd for $C_{26}H_{14}Br_2$: C, 64.22; H, 2.90%.

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