Studies on Fluorene Derivatives. XIX[1]. *The Clemmensen Reduction of 2-Bromofluorenone*

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Some interesting findings noted during the Clemmensen reduction of fluorenone were reported in a preceding paper[2] of this series. Thus, fluorene was obtained in a poor yield, but a great part of the fluorenone was converted abnormally into the related dimeric products, dibiphenylene-ethylene, -ethane, 10, 10-diphenylene-9-phenanthrone, 9, 10-diphenylenephenanthrene and other intermediates through 9, 9-dihydroxy-9, 9'-bifluorenyl (fluorenopinacol).

The present study deals with the effect on this reduction of an electron-attracting group such as bromine at the 2-position of fluorenone. This is of interest because the substituent influences may be transmitted to the carbonyl at the 9-position, both directly through the substituted ring and indirectly through the unsubstituted ring.

There is only one reference in the literature to the Clemmensen-Martin reduction of 2-bromofluorenone (I), that by Miller and Bachman[3], who reported a nearly quantitative yield of 2-bromofluorene (II).

In this study, I was submitted to the same procedure as was fluorenone[2]. I was refluxed vigorously for twenty-four hours with amalgamated zinc, water, concentrated hydrochloric acid and toluene or xylene, more acid being added at intervals of about six hours. From this reduction, II, 2-bromofluorenol (III) and

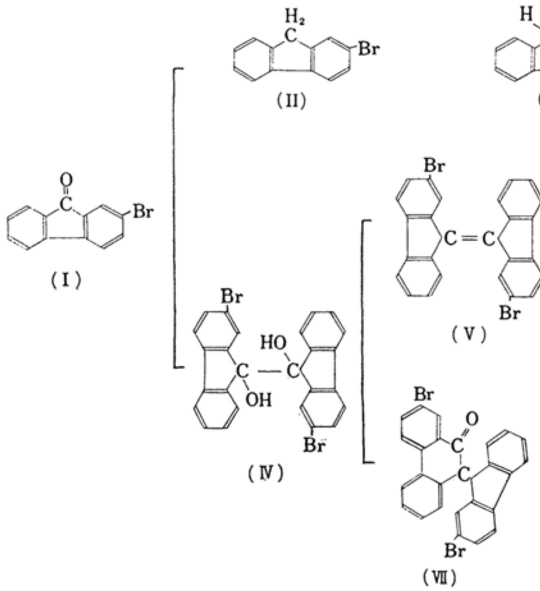

Chart 1.

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[1] XVIII of this series: K. Suzuki, *J. Org. Chem.*, 27 No. 6 (1962).

[2] XV of this series: K. Suzuki, This Bulletin, 35, 735 (1962).

[3] H. F. Miller and G. B. Bachman, *J. Am Chem. Soc.*, 57, 2447 (1935).

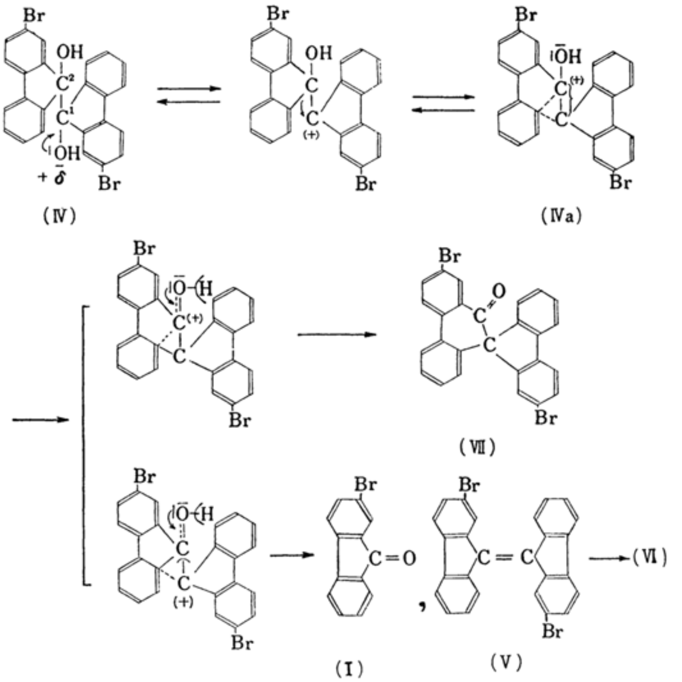

Chart 2.

several dimeric reaction products, namely 2, 2′-dibromo-9, 9-dihydroxy-9, 9′-bifluorenyl (2, 2′-dibromofluorenopinacol) (IV), 2, 2′-dibromodibiphenylene-ethylene (V)[4], -ethane (VI)[4] and a trace of spiro-[2-bromofluorene-9, 9′(10′)-2′-bromophenanthrone] (VII), were isolated by means of a combination of recrystallization and column chromatography.

These reaction products are shown in Chart 1.

The reduction of I is very slow; only 11% of it was recovered after 72 hr. On the other hand, III was isolated after just a 24 hr.-period, while fluorenol has the short reduction period of 2 hr. of fluorenone. The yield of IV is increased by the use of a more concentrated hydrochloric acid, as is shown in Table I (No. 4).

IX was, however, not isolated from this series, in contrast to the comparable reduction of fluorenone. The formation of IX is controlled by the formation of VII from IV. Actually, VII was obtained only in trace amounts by this reduction, as is described in the experimental section.

First, the results can mean that the oxygen atom of the hydroxyl group attached to the carbon, C^1, is positively charged by the electron-attracting bromine in IV. For this reason, the hydroxyl group is relatively more hindered for the elimination than it is in fluorenopinacol[2] owing to the electron-repelling effect on the protonation. Under these conditions, carbonium ion formation is unlikely.

A second possible explanation is that, due to being stabilized by the formation of the transition carbonium ion, IVa, by resonance, the hydroxyl group is dehydrated from the carbon, C^1. However, state IVa must cross a high energy barrier to reach stable state VII.

These sequences can be visualized, as in Chart 2.

It seems that the formation of I and V from IVa occurs preferentially to that of VII. This is indicated in view of the following experimental evidence.

Traces of VII, V and VI were also obtained by the Clemmensen reduction of I (Table I, No. 2). I, V and VI were isolated from IV by the same reduction procedure.

Therefore, IV was treated with hydrochloric acid in toluene under the same conditions but without amalgamated zinc; a small amount of I and V was isolated.

Subsequently the quantity of the reduced form of V and VI was gradually increased after 72 hr. (Table I, No. 3).

On the other hand, the fairly large amount of VII accompanying I and V was obtained from IV by pinacol rearrangement.

The following new compounds: VII, spiro-[2-bromofluorene-9, 9′-(10′)-2′-bromophenanethrol] (VIII), 2, 2′-dibromophenanthreno-9′,10′:

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[4] K. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 75, 714 (1954); J. Schmidt and H. Wagner, *Ann.*, 387, 155 (1912).

TABLE I. REDUCTION OF I UNDER VARIOUS CONDITIONS

Exp. No.	I g.	Solvent ml.	React. time hr.	II g.	III g.	IV g.	V g.	VI g.	Recvd. I g.	Other
1	20	Toluene 40	24	1.41	0.1	4.7	0.04	0.47	4.0	
2	20	Xylene 40	24	2.7	0.26	4.7	0.01	0.8	2.2	VII, 0.005 g.
3	20	Xylene 40	72	1.3			0.01	6.6	2.2	
4*	20	Toluene 40	24	1.21	1.7	10.0	0.01	1.35	1.4	m. p. >300°C Orange-red needles, trace

* In this case, 15 ml. of water and 85 ml. of concentrated hydrochloric acid were used.

9, 10-phenanthrene (IX) and 2, 11-dibromotetrabenzocyclodecane-9, 18-dione (X), were synthesized separately by the same procedure as that with which the corresponding compounds were obtained in the case of fluorenone[2].

VII was reduced to VIII by zinc and ammonium hydroxide in an alcoholic solution and then converted into IX by retropinacol rearrangement with hydrochloric acid in acetic acid. IX was also obtained directly by the Clemmensen reduction of VII in toluene, or by hydrogen iodide and red phosphorus in acetic acid.

IX was converted into X by sodium bichromate in acetic acid, and X was also reduced to IX by hydrogen iodide in acetic acid.

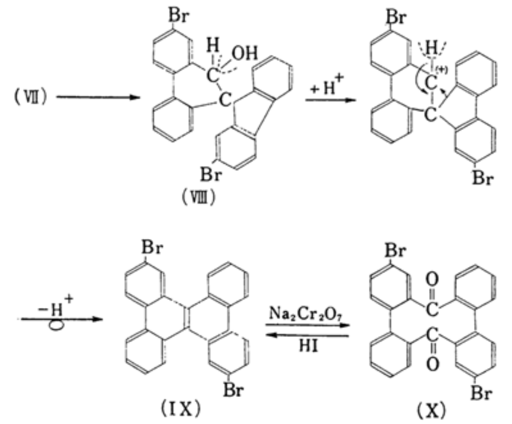

Chart 3.

Experimental*

General Procedure for the Clemmensen Reduction of 2-Bromofluorenone (I). — *Materials.* — Amalgamated zinc filings were prepared according to Martin's method[5].

2-Bromofluorene was obtained by the bromination of fluorene in chloroform; it was then oxidized to I[6] in over 80% yields.

About 0.077 mol. (20 g.) of the ketone I was refluxed vigorously for 24 hr. with 40 g. of amalgamated zinc, 30 ml. of water, 70 ml. of concentrated hydrochloric acid and 40 ml. of xylene in a 1000 ml. flask.

Concentrated hydrochloric acid (20 ml.) was added every six hours, according to Martin's method. The xylene layer turned an orange-red color after 24 hr.

When the mixture had been left standing, the crystals in the xylene layer were recrystallized from benzene, m. p. 195∼196°C (4.7 g.), identical with 2,2′-dibromofluorenopinacol (IV).

Found: C, 59.99; H, 3.13. Calcd. for $C_{26}H_{16}\cdot O_2Br_2$: C, 60.02; H, 3.10%. IR 3450 (OH) cm^{-1} (KBr-disk).

The products which coated the surface of the zinc were filtered, dried and dissolved in benzene by heating; upon cooling, VI (m. p. 274°C, 0.36 g.) was obtained and I (m. p. 140°C, 0.5 g.) was recovered from the benzene mother solution. The identity of both compounds was confirmed by mixed melting point determination.

The original xylene mother liquor was evaporated, and VI (m. p. 275°C, 0.05 g.), VII (m. p. 253∼254°C, 0.005 g.), and recovered I (m. p. 140°C, 0.35 g.) were isolated by fractional recrystallization. VII was identical with the material which had been prepared by the pinacol rearrangement of IV with sulfuric acid in acetic acid.

Found: C, 61.95; H, 2.70. Calcd. for $C_{26}H_{14}\cdot OBr_2$: C, 62.18; H, 2.81%.

The xylene mother solution was steam-distilled to remove the solvent, and II (m. p. 112°C, 2.7 g.) was obtained; this was confirmed by mixed melting point determination.

The orange residue was filtered and dried, and VI (m. p. 275°C, 0.38 g.), V (m. p. 264°C, 0.01 g.), I (m. p. 140°C, 1.3 g.) and III (m. p. 130°C, 0.26 g.) were separated by a combination of fractional recrystallization and chromatography in benzene on an alumina column. Mixed melting points established the nature of the products.

Clemmensen Reduction of IV. — A mixture of amalgamated zinc (11 g.), concentrated hydrochloric acid (18.2 ml.), water (6.5 ml.), toluene (13.4 ml.) and IV (4.2 g.) were refluxed for 24 hr. A 5 ml. portion of concentrated hydrochloric acid was added every six hours.

The toluene layer turned yellow after five minutes, and orange-yellow after 12 hr.

After the mixture had been left standing 24 hr., the deposited products were filtered and then recrystallized from benzene, whereupon (m. p. 195°C,

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* All the melting points are uncorrected.

[5] E. L. Martin, "Organic Reactins", Vol. 1, Chapman and Hall, London (1942), p. 155.

[6] J. Schmidt and K. Bauer, *Ber.*, 38, 3753 (1905).

1.2 g.) was recovered. Then V (m. p. 263°C, 0.2 g.) was isolated by evaporation and recrystallization from the mother liquor.

The last toluene mother liquor was subjected to steam distillation, and the yellow residue was filtered and recrystallized from benzene to yield VI (m. p. 273°C, 0.005 g.), then IV (m. p. 195°C, 0.8 g.) and I (m. p. 140°C, 0.51 g.) from the benzene mother solution. These compounds were confirmed by mixed melting point determinations.

Reaction of IV with Hydrochloric Acid. — IV (0.5 g.), toluene (2 ml.), water (0.8 ml.) and concentrated hydrochloric acid (1.8 ml.) were refluxed for 24 hr. A 0.5 ml. portion of hydrochloric acid was added every six hours.

The toluene layer turned an orange-yellow color after 20 hr. When the mixture had been left standing, the precipitate was filtered and recrystallized from benzene, m. p. 193°C (0.21 g.), identical with the recovered IV. The toluene mother liquor was steam-distilled to remove the solvent, yielding I (m. p. 140°C, 0.05 g.), which was recrystallized from alcohol.

The residual products were filtered; I (m. p. 142°C, 0.06 g.) and V (m. p. 263°C, 0.002 g.), obtained by means of chromatography in benzene on alumina, were confirmed by mixed melting point determinations.

Pinacol Rearrangement of IV to VII.—IV (5 g.) was dissolved in acetic acid (50 ml.), and concentrated sulfuric acid (0.5 ml.) was added; the mixture was then refluxed for 30 min. When the mixture had cooled, the deposited products were filtered and recrystallized from acetic acid to yield VII (m. p. 252°C, 3.0 g.) as colorless crystals. The mother liquor was poured into water, the precipitate was filtered, and additional VII (m. p. 252°C, 0.42 g.), recovered pinacol (IV) (m. p. 194°C, 0.06 g.) and I (m. p. 141°C, 0.11 g.) were separated by a combination of recrystallization and column chromatography in benzene on alumina. Moreover, a small amount of V (m. p. 264°C) was isolated from the mother liquor by recrystallization.

Reduction of VII to VIII.—Finely powdered VII (1 g.) was suspended in 600 ml. of ethyl alcohol, zinc dust (3 g.) and concentrated ammonium hydroxide (30 ml.) were added, and the mixture was refluxed for 10 hr. Concentrated ammonium hydroxide (30 ml.) was added every 3 hr. The reaction mixture was filtered, and the filtrate was evaporated to half volume. The white product deposited was filtered, then recrystallized from benzene to give unreacted VII (m. p. 253°C, 0.31 g.). The first mother liquor was evaporated to a small volume, and the precipitate was recrystallized from benzene to give crystals, m. p. 153~154°C (0.05 g); these were identical with VIII.

Found: C, 62.21; H, 3.32. Calcd. for $C_{26}H_{16}$·OBr_2: C, 61.93; H, 3.20%. IR 3484 (OH) cm^{-1} (KBr-disk).

Rearrangement of VIII to IX.—To a solution of VIII (0.2 g.) in acetic acid (10 ml.) there was added 1.5 ml. of concentrated hydrochloric acid, and the mixture was refluxed for 2 hr. When the mixture had cooled, the precipitate was filtered and recrystallized from benzene, m. p. 305°C, (0.05 g.); this was identical with IX.

Found: C, 64.11; H, 3.07. Calcd. for $C_{26}H_{14}$·Br_2: C, 64.22; H, 2.90%.

Rearrangement of VII to IX by Reduction.—A mixture of VII (1 g.), acetic acid (190 ml.), hydrogen iodide (10 ml.) and red phosphorus (1 g.) was refluxed for 9.5 hr. Upon cooling, the reaction mixture was filtered, and the filtrate was poured into water. The precipitate was then filtered and washed well with water. It was recrystallized from benzene to give IX (m. p. 305~307°C, 0.2 g.) as small colorless needles; unreacted ketone VII (m. p. 253°C, 0.4 g.) was also recovered.

Clemmensen Reduction of VII to IX.—A mixture of amalgamated zinc (6.0 g.), water (1.5 ml.), toluene (10 ml.), concentrated hydrochloric acid (5 ml.) and VII (1 g.) was refluxed vigorously for 24 hr. in a 100 ml., round-bottomed flask. A 1 ml. portion of concentrated hydrochloric acid was added every 6 hr. After reaction, the deposited material was filtered and recrystallized from benzene to yield IX (m. p. 305°C, 0.5 g.). Then VIII (m. p 150~152°C, 0.005 g.) and unreacted VII (m. p. 253°C, 0.66 g.) were also isolated from the mother liquor by fractional recrystallization.

Oxidation of IX to X.—IX (0.4 g.) in a mixture of acetic acid (700 ml.) and sodium bichromate (6 g.) was refluxed for 13 hr. Upon cooling, the reaction mixture was poured into water. The white amorphous product was recrystallized from benzene, m. p. 224~225°C (0.25 g.); this was identical with X.

Found: C, 60.53; H, 2.91. Calcd. for $C_{26}H_{14}$·O_2Br_2: C, 60.26; H, 2.72%. IR 1672 (C=O) cm^{-1} (KBr-disk).

Reduction of X to IX.—A mixture of X (0.1 g.), acetic acid (15 ml.), hydrogen iodide (1 ml.), and red phosphorus 0.1 g. was refluxed for 9 hr. Then the reaction mixture was filtered, and the filtrate was poured into water; the white precipitate was recrystallized from benzene, m. p. 305°C, (0.05 g.). This compound was identical with IX, as was shown by mixed melting point determination.

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