Studies on Fluorene Derivatives. XIII[1]. *The Formation of Tribiphenylenepropane by Self-condensation of Dibiphenyleneethylene*

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Certain halides possessing a relatively reactive α-hydrogen such as 9-halogenofluorenes or its derivatives are converted to dimeric olefines by the action of methanolic potassium hydroxide in acetone at room temperature. Thus, 9-bromo-(or chloro)-fluorene[2] gave dibiphenyleneethylene (I). The corresponding substituted I are obtained in good yields from 2-nitro-9-bromofluorene[3], 1-chloro-9-bromofluorene[4], 2,9-dibromofluorene[5], 3, 9-dibromofluorene[6a] and 4, 9-dibromofluorene[6b].

9-Chlorofluorene[7] and liquid ammonia also interact at room temperature to form I and fluorene.

In regard to the mechanisms[8] involved in the first reaction it has been postulated that a self-alkylation of the halides forms the corresponding dimeric halides which in turn give the dimeric olefines by a β-elimination.

In the present investigation different products were observed when 9-bromofluorene was refluxed for longer periods in methanolic potassium hydroxide-acetone. These were two isomers of tribiphenylenepropane (II)[9,10], m. p. 293°C and m. p. 257°C, dibiphenyleneethane (III)[11], fluorenone, a trace of fluorene, and a small amount of unidentified material, m. p. 90~92°C which analyzed correctly for 9-acetonylfluorene (Chart I).

Under the same conditions 3, 9-dibromofluorene and 4, 9-dibromofluorene furnished the corresponding 3, 3′, 3″-tribromotribiphenylenepropane(IV) and 4, 4′, 4″-tribromotribiphenylenepropane(V), respectively. Both propanes were identical with those obtained previously by the Michael condensation of 3, 3′-dibromodibiphenyleneethylene and 3-bromofluorene[5], or 4, 4′-dibromodibiphenyleneethylene and 4-bromofluorene[6b], respectively.

However, with 1, 9-dibromofluorene and with 2, 9-dibromofluorene the methanolic alkali in acetone yielded 1, 1′-dibibromodiphenyleneethan (XI) and 2, 2′-dibromodibiphenyleneethane (VI)[12], respectively, as reduction products, rather than the substituted tribromotribiphenylenepropanes. With the former compound this could be the result of steric hindrance due to the bromine at the 1-position. The Micheal condensation did not occur either between 1, 1′-dibromodibiphenyleneethylene and

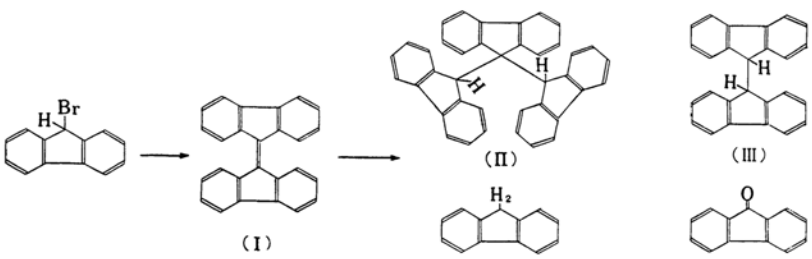


Chart 1.

1) Part XII S. Kajigaeshi, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **82**, 1397 (1961).
2) J. Thiele and A. Wansheidt, *Ann.*, **376**, 278 (1910).
3) E. Weisburger et al., *J. Org. Chem.*, **14**, 448 (1948).
4) S. Kajigaeshi, H. Tsuchida and K. Suzuki, *Mem. Fac. Eng. Yamaguchi Univ.*, **9**, 35 (1958).
5) E. Bergmann et al., *Bull. soc. chim. France*. **20**, 78 (1952).
6) a) K. Suzuki, S. Kajigaeshi and M. Sano, *J. Soc. Org. Synth. Chem. Japan* (*Yūki Gōsei Kagaku Kyōkaishi*), **16**, 82 (1958); b) K. Suzuki et al., ibid., **16**, 304 (1958).
7) L. A. Pinck et al., *J. Am. Chem. Soc.*, **68**, 379 (1946).
8) C. R. Hauser et al., ibid., **78**, 1653 (1956).
9) a) L. A. Pinck and G. E. Hilbert, ibid., **57**, 2398 (1935); b) L. A. Pinck and G. E. Hilbert, ibid., **68**, 2014 (1946); K. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **70**, 189 (1949); K. Suzuki, *Technol. Repts. Tōhoku Univ.*, **XIX**, 63 (1955).
10) L. A. Pinck first obtained II (m. p. 300°C, γ-form) by reaction of I and liquid ammonia. Later, in 1949, K. Suzuki also obtaind two kinds of II-isomer (m. p. 275°C, α-form, m. p. 257°C, β-form) by reaction of fluorene and sodium amide. The three compounds were inferred to be restricted free rotation isomers about a single bond and were given the names of α- β-, and γ-form respectively.
11) R. Weissgerber, *Ber.*, **46**, 2913 (1908).
12) J. Schmidt and H. Wagner, *Ann.*, **378**, 155 (1912).

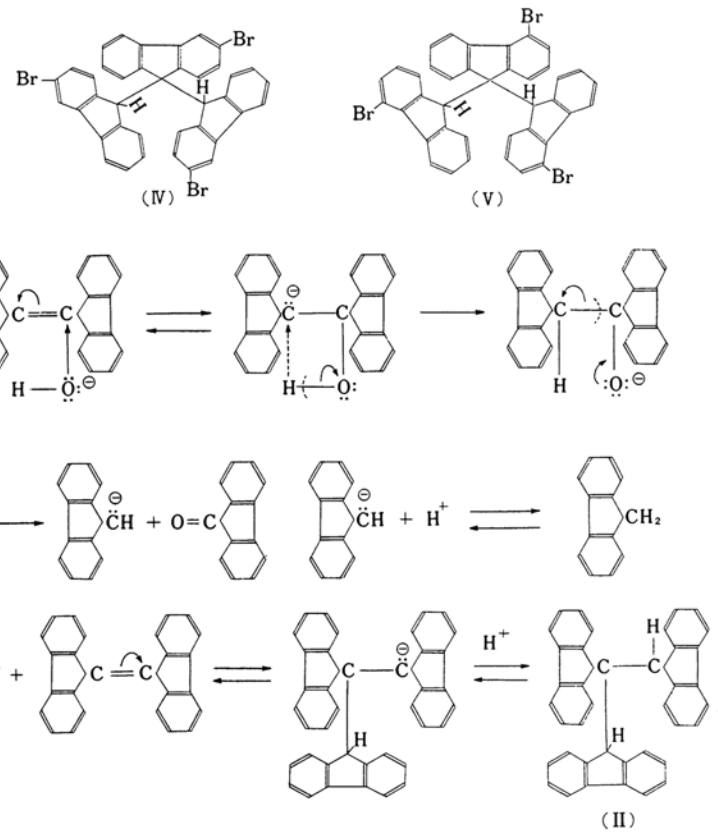


Chart 2.

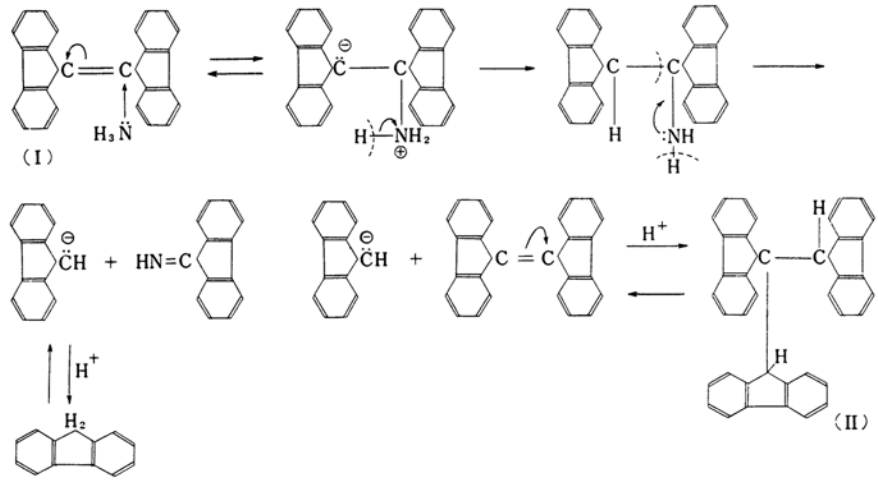


Chart 3.

1-bromofluorene. 2, 9-Dibromofluorene do not give rise to 2, 2′, 2″-tribromotribiphenylenepropane by methanolic alkali in acetone. This reason is not clear; it might be, however, that the formation of VI is the faster rather than the other leading to the 2-substituted propane from 2-substituted ethylene in the two competitive reaction sequences.

In any case, the conversion of 9-bromofluorene to II by the action of methanolic alkali and acetone probably proceeds via the intermediate formation of I. This concept is supported by the fact that practically the same products were obtained (Tables I and II) when the analogous reactions were performed using substituted I as the starting material. Here also,

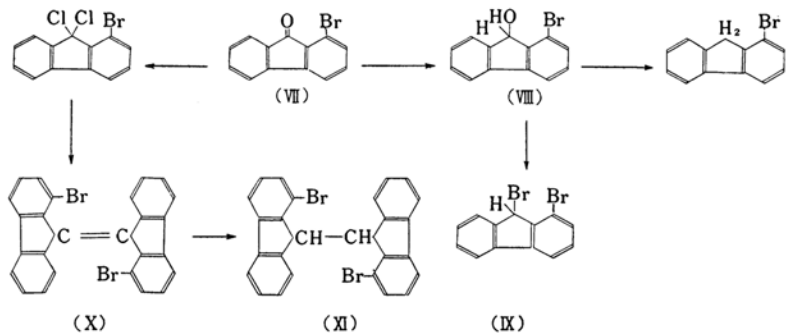


Chart 4.

both isomers of II, III, fluorene and fluorenone were the products.

Central π-electron pairs in I is less firmly held between the two carbon nuclei, and the approach of a negatively charged hydroxyl ion induces a charge separation. This high polarizability is greatly responsible for the reactivity of I for addition reaction.

The reactions accounting for the observed products is illustrated in Chart 2. It may be noted that they are analogous to the production of II from I and liquid ammonia (Chart 3).

The negatively charged fluorenyl ion and fluorenone were formed by addition of hydroxyl ion to I in methanolic alkali in acetone as a preliminary step. I is also reduced to III in the same solution as two competitive reactions. The required proton is obtained by interaction of acetone with alkali; thus these reactions do not proceed in the absence of acetone and alkali.

Moreover, in this case, the fluorenyl ion can not be formed by dissociation of III which is reduced from I in the same alkaline media as suggested by the observations of Weisburger and Grantham[13]. They could not isolate fluorene in any amount when subjecting III to a Wolff-Kischner reduction. On the other hand, they obtained 70% yields of fluorene (and 19% of III) which I as starting material[14].

In another analogous case, Pinck et al.[9a] isolated the γ-form of II, 9-fluorenylidene imine, and fluorene upon treating I with liquid ammonia for 21 days at 60°C. This is a direct addition of ammonia to the unsaturated grouping of I and is also an analogous behavior to that described above. And the mechanism of formation may be proposed as illustrated in Chart 3.

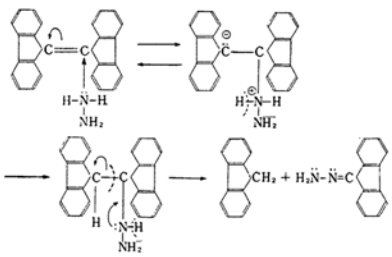
New intermediates required for these studies were prepared by conventional reactions. 1-Bromofluorenone (VII)[15] was obtained from 1-aminofluorenone by a Sandmeyer reaction, a method different from that used by Montagne[16]. The ketone was reduced to 1-bromo-9-fluorenol (VIII) by zinc dust and ammonium hydroxide. VIII was converted to 1, 9-dibromofluorene (IX) by the action of hydrogen bromide in acetic acid, or it was reduced to 1-bromofluorene by hydrogen iodide and red phosphorus. The reaction of phosphorus pentachloride on VII afforded 1-bromofluorene-9, 9-dichloride, which was dehalogenated by powdered copper to 1,1′-dibromodibiphenyleneethylene (X). This compound in turn was reduced to the ethane, XI as illustrated in Chart 4.

Experimental

Formation of Tribiphenylenepropanes.—*Reaction of 9-Bromofluorene and its Bromo-derivatives with Methanolic Potassium Hydroxide in Acetone.*—To a stirred solution of 2.9 g. of potassium hydroxide in 12 cc. of methanol 5 g. of 9-bromofluorene in 23 cc. of acetone was added in small portions at room temperature, and stirring was continued for 20 min. The red I precipitated immediately with heat evolution. The mixture was refluxed gently for 15 hr. during which the color changed from dark red to dark green, and small colorless crystals were deposited after 1/2 hr. The solids were filtered off, washed with water, and extracted with a large volume of ethanol. Colorless needles of III (0.13 g., m. p. and mixed m. p. 243°C) were isolated from the solution.

13) J. H. Weisburger et al., *J. Org. Chem.*, **21**, 1160 (1956).

14) The formation mechanisms of fluorene and hydrazone at the first stage of reaction between I and hydrazine hydrate may be presented as follows.



15) E. H. Huntress, K. Pfister and K. H. T. Pfister, *J. Am. Chem. Soc.*, **64**, 2847 (1942).

16) P. J. Montagne and J. M. Van Charante, *Rec. trav. Chim.*, **32**, 164 (1913); *Chem. Abstr.*, **7**, 3493 (1913).

TABLE I. CONDITIONS AND PRODUCTS WHEN THE SAME REACTIONS WERE PERFORMED ON SUBSTITUTED 9-BROMOFLUOROENES

Dibromo-fluorene g.	Acetone cc.	KOH g.	CH_3OH cc.	Time hr.	Product	Yield, g. (m. p., °C)
1,9-* 2.5	30	3	30	15	XI	0.6 (240~242)
2,9- 9.7	200	16.8	100	2	VI**	2.5 (283~285)
3,9- 0.5	10	0.8	3	7	IV	0.13 (273~275)
4,9- 1.3	20	2.3	10	1	V***	0.1 (254~257)

* 1,1'-Dibromodibiphenyleneethylene did not form at room temperature, but it does by heating.
** Found: Br, 33.08; mol. wt., 720.
*** Found: Br, 32.89; mol. wt., 718. Calcd. for $C_{39}H_{23}Br_3$: Br, 32.78%; mol. wt., 731.

TABLE II. CONDITIONS AND PRODUCTS WHEN THE SAME REACTIONS WERE PERFORMED ON SUBSTITUTED DIBIPHENYLENEETHYLENES

Dibromodibi-phenylene-ethylene, g.	Acetone cc.	KOH g.	CH_3OH cc.	Time hr.	Product	Yield, g. (m. p., °C)
1,1'-, 0.24	4	0.28	1	7	XI	0.04 (242)
2,2'-, 3.4	400	3.9	30	2	VI	0.3 (283)
3,3'-, 0.73	10	0.84	3	7	IV	0.1 (275)
4,4'-, 0.6	10	0.7	3	1	V	0.05 (256)

The ethanol-insoluble residue was fractionally crystallized from benzene to give two isomers of II, colorless tetragonal crystals, m. p. 293°C (decomp.), 0.2 g., and m. p. 257°C (decomp.), 0.25 g.

M. p. 293°C, Found: C, 94.69; H, 5.31; mol. wt., 490; m. p. 257°C, Found: C, 94.70; H, 5.30; mol. wt., 475. Calcd. for $C_{39}H_{26}$: C, 94.69; H, 5.31%; mol. wt., 494.

The mother liquor of the acetone-methanol reaction mixture, above, was steam-distilled. I (0.5 g., m. p. 187°C) was recovered from the brown residual product by crystallization from ethanol. Sublimation of this residue gave 0.01 g. of fluorene and 0.11 g. of fluorenone, m. p. 81°C. Colorless needless, m. p. 90~91°C, 0.1 g., which could be 9-acetonylfluorene were isolated from the mother liquor after removal of I. (Found: C, 86.46; H, 6.14%).

Reaction of I and its Bromoderivatives with Methanolic Potassium Hydroxide in Acetone. — To a solution of 1.8 g. of potassium hydroxide in 7.8 cc. of methanol 3 g. of I in 20 cc. of acetone was added and refluxed gently for 10 hr. The brown color noted during the addition turned dark brown after 1 hr. and dark green after 3 hr. The water-washed precipitate (1.6 g.) was extracted with 300 cc. of boiling ethanol. Colorless needles of III, m. p. 244°C, 0.01 g., crystallized from the solution. The insoluble residue was fractionally crystallized from benzene to yield 0.35 g. of colorless tetragonal II, m. p. 257°C. A further 0.25 g. of II, m. p. 257°C, 0.4 g. of the isomeric II, m. p. 293°C and 0.15 g. of fluorenone, m. p. 81°C were isolated from the mother liquor by chromatography in benzene on alumina.

The mother liquor from the reaction mixture was steam-distilled. The distillate contained 0.15 g. of fluorene, m. p. 113°C. In addition, 0.35 g. of I was recovered from the residue by chromatography in benzene on alumina.

Preparation of Intermediate Products.—*1-Bromofluorenone (VII).*—1-Aminofluorenone (8 g.) in 40 cc. of 40% hydrobromic acid was diazotized with 3 g. of sodium nitrite in 3 cc. of water below 10°C. The diazonium solution was added to a boiling mixture of 10 g. of cuprous bromide in 250 cc. of 40% hydrobromic acid and refluxing continued for 30 min. Upon cooling the product was filtered, washed with sodium hydroxide solution, and recrystallized from ethyl acetate 3 g. (28%), m. p. 132~134°C.

1-Bromo-9-fluorenol (VIII).—A mixture of 2 g. of VII, 6 g. of zinc dust, ammonium hydroxide and 60 cc. of ethanol was refluxed for 1 hr. and filtered hot. VIII (1.5 g., 75%, m. p. 140~141°C, colorless needles from benzene) was isolated upon concentration.

Found: C, 59.56; H, 3.41; Br, 30.38. Calcd. for $C_{13}H_9OBr$: C, 59.79; H, 3.47; Br, 30.61%.

1-Bromofluorene.—A mixture of 0.05 g. VIII, 0.4 g. red phosphorus, 2 cc. of hydroiodic acid (d=1.7) and 10 cc. of acetic acid was refluxed for 9 hr., cooled, filtered and poured into water: Colorless plates (0.39 g., 64%, m. p. 59~60°C from ethanol).

Found: C, 63.73; H, 3.83; Br, 32.76. Calcd. for $C_{13}H_9Br$: C, 63.70; H, 3.70; Br, 32.60%.

1,9-Dibromofluorene (IX).—VIII (2 g.) in 40 cc. of acetic acid and 3 cc. of hydrobromic acid (47%) was heated on a water bath for 3 hr. The crystals isolated upon cooling weighed 1.5 g. (60%), m. p. 137~138°C, from ethanol.

Found: C, 48.13; H, 2.72; Br, 49.51. Calcd. for $C_{13}H_8Br_2$: C, 48.18; H, 2.49; Br, 49.33%.

1,1'-Dibromodibiphenyleneethylene (X).—A mixture of 5 g. of VII and 25 g. of phosphorus pentachloride in a 100 cc. flask was placed in an oil bath preheated to 160°C. The temperature was raised to 185~190°C, and maintained for 1/2 hr. The cool mixture was added to water and the gradually solidifying 9,9-dichloro-1-bromofluorene was filtered: 4.5 g., 74%, m. p. 132~135°C, from benzene.

This material in 70 cc. of absolute xylene was refluxed for 15 hr. with 10 g. of powdered copper. After filtration and concentration, 2 g. (58%) of X (m. p. 230~231°C, dark red from acetone) was obtained.

Found: Br, 32.63; mol. wt., 490. Calcd. for $C_{26}H_{14}Br_2$: Br, 32.87%; mol. wt., 486.

1,1'-Dibromodibiphenyleneethane (XI).—A mixture of 0.5 g. of X in 30 cc. of benzene, 2 g. of zinc dust, and 12 cc. of concentrated ammonium hydroxide was refluxed for 3 hr. After filtration and concentration 0.2 g. (40%) of colorless needles, m. p. 240~242°C from benzene, were isolated.

Found: C, 64.06; H, 3.52; Br, 32.88. Calcd. for $C_{26}H_{16}Br_2$: C, 63.96; H, 3.30; Br, 32.74%.

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