Studies on Fluorene Derivatives. XXIII. The Synthesis of 2′-Bromotribiphenylenepropane and Some Related Observations*

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2′-Bromotribiphenylenepropane (I) was first obtained by the Michael condensation of dibiphenyleneethylene (II) with 2-bromofluorene. The thermal decomposition of such tribiphenylenepropane hydrocarbons is invariably accompanied by the formation of the 9-fluorenyl free radical species. Thus two tribiphenylenepropane isomers (m. p. 291∼293°C (decomp.), m. p. 257°C (decomp.)), 2,2′-dibromodibiphenyleneethane, II and dibiphenyleneethane can be obtained by the decomposition of I, as has previously been reported in this series.[1]

The present investigation will deal with the synthesis of I by the use of 9-fluorenyllithiums, and will reexamine the side reaction in the Michael condensation of II with 2-bromofluorene. The origin of the by-products can be understood on the basis of a sequence of condensation and disproportionation steps.

By refluxing II and 2-bromofluorene in pyridine in the presence of one percent of potassium hydroxide or sodium carbonate, I, a small

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* XXII of this series: K. Suzuki and M. Momoi, This Bulletin, 36, 1693 (1963).

[1] K. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 75, 711 (1954).

TABLE I. REACTION PRODUCTS OF DIBIPHENYLENEETHYLENE (II) AND 2-BROMOFLUORENE

Starting material g.		Solvent		Reaction time	Reaction product, g.						Recvd. g.
II	2-Br-fluorene	Pyridine ml.	Aqeous alkali ml.	hr.	I	Tri-biphenylenepropane	Fluorenone	2-Br-fluorenone	2, 7-diBr-fluorenone	IV	II
3.3	2.5	20	10% KOH 2	40	1.6	m. p. 289～291°C 0.2	0.02	0.2	0.05	—	0.3
3.3	2.5	20	10% Na_2CO_3 2	35	3.9	—	0.02	0.2	—	Trace	0.2

TABLE II. ALKALINE CLEAVAGE OF 2′-BROMOTRIBIPHENYLENEPROPANE (I) IN PYRIDINE SOLUTION

Material g.	Solvent		Reaction time	Reaction product, g.						Recvd. g.
2′-Br-tribiphenylenepropane	Pyridine ml.	10% Aq. KOH ml.	hr.	Fluorene	Fluorenone	2-Br-fluorenone	2, 7-diBr-fluorenone	II	IV	I
1.0	20	2	40	0.03	0.01	0.15	—	0.01	—	0.52
3.0	30	3	40	0.095	0.04	0.2	—	0.05	Trace	1.65
2-Br-fluorene 1.0	20	2	20	—	—	0.2	0.15	—	—	2-Br-fluorene 0.5

amount of tribiphenylenepropane (m. p. 289～291°C),²⁾ fluorenone, 2-bromofluorenone and 2′-bromodibiphenyleneethylene (IV)³⁾ were obtained; they were then characterized by a combination of column chromatography, sublimation and recrystallization. I was obtained in a good yield (79%) by the use of one percent sodium carbonate. These results are summarized in Table I.

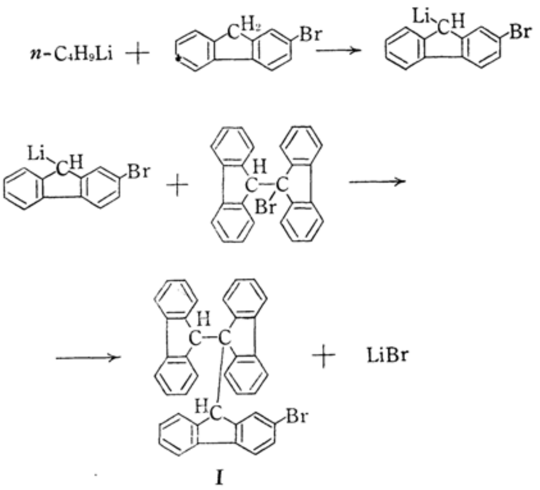
Moreover, a highly substituted I might lead to II and 2-bromo-9-fluorenyl anions or IV and 9-fluorenyl anions by the elimination of the protons in the 9′- or 9′′-positions of I in the pyridine-base solution. On the other hand, a minor portion of III, by means of a proton transfer, could form IV and fluorenyl ions. Then, tribiphenylenepropane (m. p. 289～291°C) could be formed by the addition of fluorenyl ions to II. This compound is identical with that of Suzuki,²⁾ as is shown by the fact that they have the same infrared absorption spectra and by mixed melting point determination. Figure 1. illustrates these reaction sequences.

I was then refluxed in pyridine with one percent potassium hydroxide under the same conditions for forty hours. Small amounts of fluorene, fluorenone, 2-bromofluorenone and dibiphenyleneethylenes were isolated from the reaction mixture. These results are summarized in Table II. Fluorenone and 2-bromofluorenone might be formed by the oxidation of fluorene and 2-bromofluorene respectively. 2, 7-Dibromofluorenone was obtained when 2-bromofluorene was treated similarly (see Table II), but it seems difficult to explain the formation of this compound.

These compounds were identified by mixed melting points, elementary analyses and infrared absorption spectra.

Aromatic hydrocarbons like fluorene and 9-phenylfluorene⁴⁾ have been successfully metalated by organo-lithium compounds. I was

$$n\text{-}C_4H_9Br + 2Li \longrightarrow n\text{-}C_4H_9Li + LiBr$$



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2) K. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*) **70**, 189 (1949); K. Suzuki, *Technol. Repts. Tôhoku Univ.*, **XIX**, 63 (1955).

3) S. Kajigaeshi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 102 (1962)

4) H. Gilman and R. D. Gorsich, *J. Org. Chem.*, 33, 550 (1958).

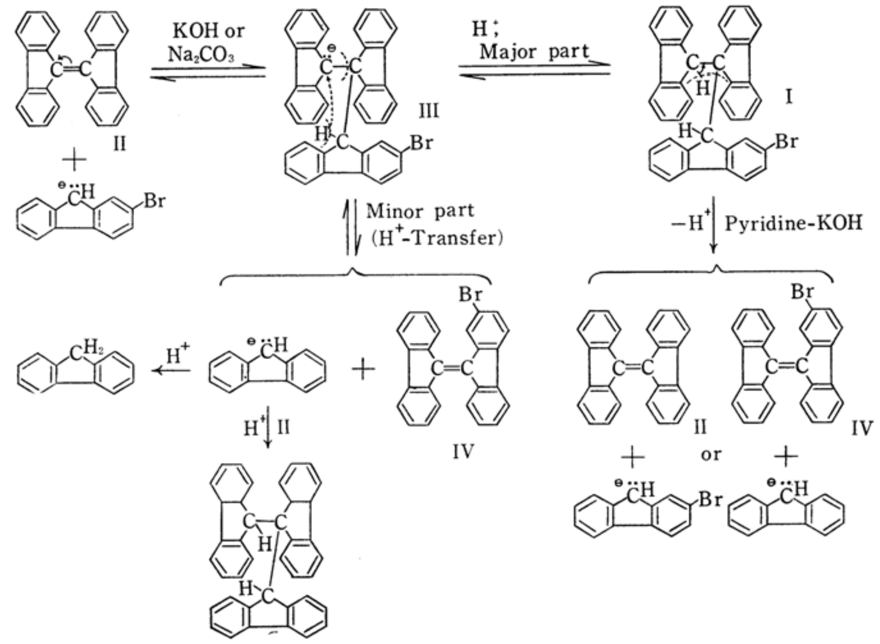

Fig. 1.

prepared by the following combinations of 9-fluorenyllithiums under similar conditions: 9-bromodibiphenyleneethane and 2-bromo-9-fluorenyllithium, 9-lithiodibiphenyleneethane and 2,9-dibromofluorene, 2′,9-dibromodibiphenyleneethane and 9-fluorenyllithium and 2′-bromo-9-lithiodibiphenyleneethane and 9-bromofluorene; the yields were 41.3%, 26.1%, 42.6% and 4.0% respectively. The identity of these compounds was confirmed by a comparison of their infrared absorption spectra with those of authentic compounds.

Dibiphenyleneethanes did not react so satisfactorily with metallic lithium to form 9-lithiodibiphenyleneethanes.

The generalized reaction scheme is shown in Fig. 2.

Experimental*

The Michael Condensation of Dibiphenylene-ethylene (II) with 2-Bromofluorene.—A solution of 3.3 g. of II, 2.5 g. of 2-bromofluorene and 2 ml. of a 10% aqueous solution of potassium hydroxide in 20 ml. of pyridine was refluxed for 40 hr., during which time the red color turned dark. After cooling, the reaction mixture was poured into water, and the orange-red precipitate was filtered. The crude product was extracted with hot benzene. The benzene solution was washed with water, dried over anhydrous calcium chloride, and then chromatographed on alumina.

Fluorenone (m. p. 83°C, 0.02 g.) and 2-bromofluorenone (m. p. 143∼144°C, 0.2 g.) were isolated from the yellow band in the column and fractionally recrystallized from alcohol. Their identity was confirmed by mixed melting points with authentic samples.

Upon the evaporation of the first two fractions, a red solution, a crystalline material, was deposited. This was separated into yellow crystals and a red benzene solution by filtration. The yellow crystals were digested several times with ethyl acetate; this solution, upon evaporation, gave a small amount of an unknown colorless compound, which melted with bubbling at 120°C, and then gradually solidified and melted again at 255°C (decomp.). The mixed melting point with I was not depressed (254°C (decomp.)). The infrared absorption spectrum was partly different from that of I and did show absorptions at 1730, 1368, 1250 and 1050 cm^{-1} not as did I.

UV: $\lambda_{max}^{CHCl_3}$ mμ (log ε): 304 (4.22) and 272 (4.73).

The residue was extracted with hot ethyl acetate, and I was obtained from the extracts (m. p. 255°C (decomp.); 1.6 g.).

UV: $\lambda_{max}^{CHCl_3}$ mμ (log ε): 304 (4.06) and 272 (4.60).

The last insoluble part was recrystallized from benzene and gave tribiphenylenepropane, m. p. 289∼291°C (0.2 g.), which did not react to a Beilstein test.

The red benzene mother solution was chromatographed again on alumina. II (0.3 g.) was recovered from the first fraction. The second and third fractions, upon evaporation, left a yellow solid which was recrystallized from ethanol to yield 0.05 g. of 2,7-dibromofluorenone, m. p. 200∼202°C;

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* All melting points are uncorrected.

(reported[5] m. p. 202∼203°C). (Found: Br, 47.33. Calcd. for $C_{13}H_6OBr_2$: Br, 47.28%; IR; 1714 cm^{-1} (ν C=O) (KBr-disk). This compound was identified by the melting point and the mixed melting point determination and by comparing its infrared absorption spectrum with that of an authentic sample of 2, 7-dibromofluorenone.

The Reaction of 2′-Bromotribiphenylenepropane (I) in a Pyridine-Potassium Hydroxide Solution.—A mixture of 3.0 g. of I and 3 ml. of a 10% aqueous solution of potassium hydroxide in 30 ml. of pyridine was refluxed for 40 hr., giving a dark red solution. The reaction mixture was then poured into water to yield an orange-red precipitate. The work-up of the products by column chromatography (benzene), sublimation and recrystallization gave fluorene (m. p. 114°C, 0.095 g.), fluorenone (m. p. 83°C, 0.04 g.), 2-bromofluorenone (m. p. 143∼145°C, 0.2 g.), II (m. p. 187°C, 0.05 g.), IV (m. p. 150∼152°C, trace) and the recovered starting material (1.65 g.). All compounds were identified by mixed melting point. These results are presented in Table II.

The Synthesis of 2′-Bromotribiphenylenepropane (I).—1) *n*-Butyl lithium was prepared from 2.0 g. (0.015 mol.) of *n*-butyl bromide in 20 ml. of anhydrous ether and 0.2 g. (0.03 g. atom) of lithium in 20 ml. of anhydrous ether. Then, 2-bromo-9-fluorenyl lithium was prepared by adding 2.9 g. (0.012 mol.) of 2-bromofluorene in 30 ml. of anhydrous xylene to the *n*-butyl lithium solution. Into this mixture there was added slowly with stirring a solution of anhydrous xylene containing 4.9 g. of 9-bromodipiphenyleneethane. After the reaction mixture had stood at room temperature overnight, the precipitate was filtered and then hydrolyzed with dilute ammonium chloride and recrystallized from benzene to give 2.4 g. of I (m. p. 257°C, decomp.; 41.3% (Balance yield); identical by mixed melting point and infrared absorption spectra with the authentic sample).

In addition, 0.6 g. of 9-hydroxydibiphenyleneethane[6] (m. p. 191∼193°C) and 0.2 g. of dibiphenyleneethylene (m. p. 187°C) were isolated by chromatography in benzene on alumina.

2) I was obtained by the reaction of 9-fluorenyl lithium with 2′, 9-dibromodibiphenyleneethane in a 42.6% yield.

3) A solution of 0.015 mol. of *n*-butyl lithium in 20 ml. of ether was added to a solution of 4.1 g. (0.01 mol.) of 9-bromodibiphenyleneethane in 30 ml. of xylene under the same conditions as in the first method. The wine-red color turned to brown-red, and a yellowish brown precipitate was formed. To this resulting solution there was added 10 ml. of anhydrous xylene containing 3.2 g. (0.01 mol.) of 2, 9-dibromofluorene.

The product was filtered off, hydrolyzed, and then recrystallized from benzene to give I (m. p. 257°C, decomp.; 0.6 g., 26.1%). This propane was identical with the authentic sample of I as shown by mixed melting point determination and infrared absorption spectrum. The xylene mother solution was evaporated to dryness under reduced pressure, and 2, 9-dibromofluorene (1.2 g.) was recovered by chromatography in benzene on alumina.

4) I was also obtained in a 4.0% yield by the reaction between 2′-bromo-9-lithiodibiphenyleneethane and 9-bromofluorene.

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[5] J. Schmidt and K. Bauer, *Ber.*, 38, 3737 (1905).

[6] This compound might arise from the hydrolysis of 9-bromodibiphenyleneethane as a result of the effect of alumina.