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Studies on Fluorene Derivatives. XXV.[1] Abnormal Products, Tribiphenylenepropanes, of the Michael Addition of 9,9'-Bifluorenylidenes and Fluorenes, and Syntheses of Related Compounds

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A normal compound, 2',7'-dibromotribiphenylenepropane (IV), and an abnormal compound, 2',7',2'',7''-tetrabromotribiphenylenepropane (VI), were obtained by the Michael addition of 9,9'-bifluorenylidene (I) and 2,7-dibromofluorene (III). In addition, another normal compound, 2,7,2',7'-tetrabromotribiphenylenepropane (VIII) and three abnormal compounds, IV, VI, and tribiphenylenepropane (VII), were isolated by the Michael addition of 2,7,2',7'-tetrabromo-9,9'-bifluorenylidene (IX) and fluorene (II). In both cases, the normal compounds were obtained in the presence of sodium ethoxide in ethanol. The abnormal compounds might be formed by the further condensation of 2,7-dibromo-9,9'-bifluorenylidene (V) and III or II in the presence of alkali. The related compounds, 2,7-dibromotribiphenylenepropane (X), IV, VI, VIII, and 2,7,2',7',2'',7''-hexabromotribiphenylenepropane, were synthesized by the reaction of substituted 9-fluorenyllithium and substituted 9-bromo-9,9'-bifluorenyl in an absolute xylene solution. The thermal decomposition of X and VIII afforded bromosubstituted or non-bromosubstituted-9,9'-bifluorenylidenes, 9,9'-bifluorenyls, fluorenones, and fluorenes. The ethanolysis of 2,7-dibromo-9'-hydroxy-9,9'-bifluorenyl gave fluorenone and III.

The formation of an abnormal addition product, 2',7',2'',7'' - tetrabromotribiphenylenepropane(VI), together with a normal addition product, 2',7'-dibromotribiphenylenepropane (IV), by a Michael addition reaction between 2, 7-dibromofluorene (III) and 9,9'-bifluorenylidene (I) has been previously reported in this series.[2] The reactions of 2,7,2',7'-tertabromo-9,9'-bifluorenylidene (IX) and fluorene (II) have also been investigated by Pinck and Hilbert,[3] but they isolated no specific compound except tribiphenylenepropane (VII).

In view of the interest in the formation of abnormal addition products, we have sought to clarify the mechanism of this addition reaction.

The present study has been primarily concerned with a re-examination of the formation of several compounds, including IV, VI, and VII,[3,4] by reactions between I and III, IX and II under various base conditions.

A Michael addition between I[5] and III was carried out in ethanol using sodium ethoxide (15%) as the catalyst; it gave a good yield of IV. In the case of potassium hydroxide (1%) in a pyridine solution, VI was obtained as the major product, while II, IV, VII, fluorenone, and 2,7-dibromofluorenone were the minor products. These results are summarized in Table 1.

In other observations of the Michael addition between IX and II, the normal compound VIII was obtained exclusively with sodium carbonate (5%) in a pyridine solution, or VIII and 2,7-dibromo-α, δ-dibiphenylenebutadiene were obtained with sodium ethoxide (5.8%) in an alcoholic solution. A compound (mp 303—304°C (dec)), three abnormal products, IV, VI and VII, and two elimination products, III and 2,7-dibromofluorenone, were also isolated using potassium hydroxide (0.5—5%) in a pyridine solution. These results are summarized in Table 2.

A transitory carbanion (A) is formed in the initial step by an attack of the 2,7-dibromo-9-fluorenyl carbanion (III') on the highly-polarized acceptor

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1) Part XXIV: K. Suzuki, M. Fujimoto, M. Murakami and M. Minabe, This Bulletin, **40**, 1259 (1967).

2) K. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **72**, 825 (1951).

3) L. A. Pinck and G. E. Hilbert, *J. Am. Chem. Soc.*, **68**, 2014 (1946).

4) K. Suzuki, *Nippon Kakagu Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **70**, 189 (1949).

5) R. C. Fuson and H. D. Porter, *J. Am. Chem. Soc.*, **70**, 895 (1948); J. Thiele and A. Wansheidt, *Ann.*, **376**, 278 (1910).

TABLE 1. REACTION PRODUCTS OF I AND III UNDER VARIED CONDITIONS

Run	Starting materials			Reaction conditions			Reaction products						Recvd.	
	I g	III g	Mol ratio of I/III	Solvent m*l*	Catalyst (base concn.) %	Time hr	IV g (%)	VI g	VII g	II g	Fluorenone g	2,7-Dibromo-fluorenone	I g	III g
1	3.3	3.2	1/1	Py 30	KOH 0.05	12	3.6 (55)	0.8	0.01		0.07	0.3	0.3	0.2
2	3.3	3.2	1/1	Py 30	KOH 0.1	2	1.0	3.5	0.2	0.25	0.18	0.25	0.01	
3	3.3	3.2	1/1	Py 30	KOH 1	2	0.6	4.0	0.25	0.2	0.2	0.3		0.03
4	3.3	3.9	1/1.2	Py 30	KOH 1	2	0.47	4.3	0.18	0.28	0.1	0.35		0.2
5	3.3	6.4	1/2	Py 30	KOH 1	2	0.3	6.55	0.05	0.35	0.08	0.4		0.85
6	6.6	3.2	2/1	Py 30	KOH 1	12	0.6	4.0	1.25	0.52	2.4	0.1	0.1	
7	3.3	3.2	1/1	EtOH 30	NaOEt 2.5	2.5	4.0 (61)	Trace					0.4	0.9
8	3.3	3.2	1/1	EtOH 30	NaOEt 15	2.5	5.72 (89)	0.08			0.02			

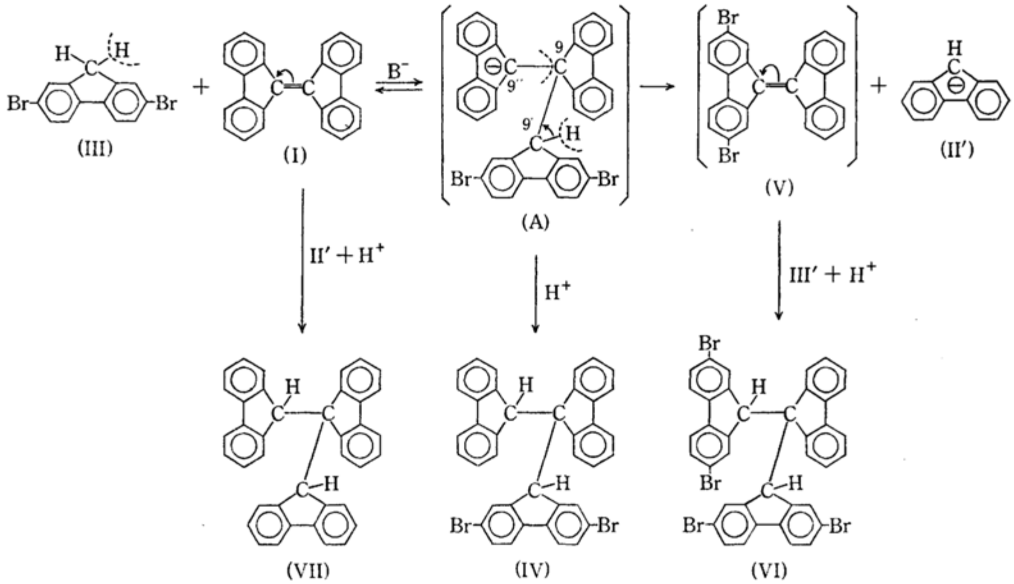
a) Py=Pyridine, EtOH=Ethanol, NaOEt=Sodium ethoxide.

b) Run 8: 9,9′-Bifluorenyl (0.06 g) and 2,7-dibromo-α, δ-dibiphenylenebutadiene (0.09 g) were also isolated.

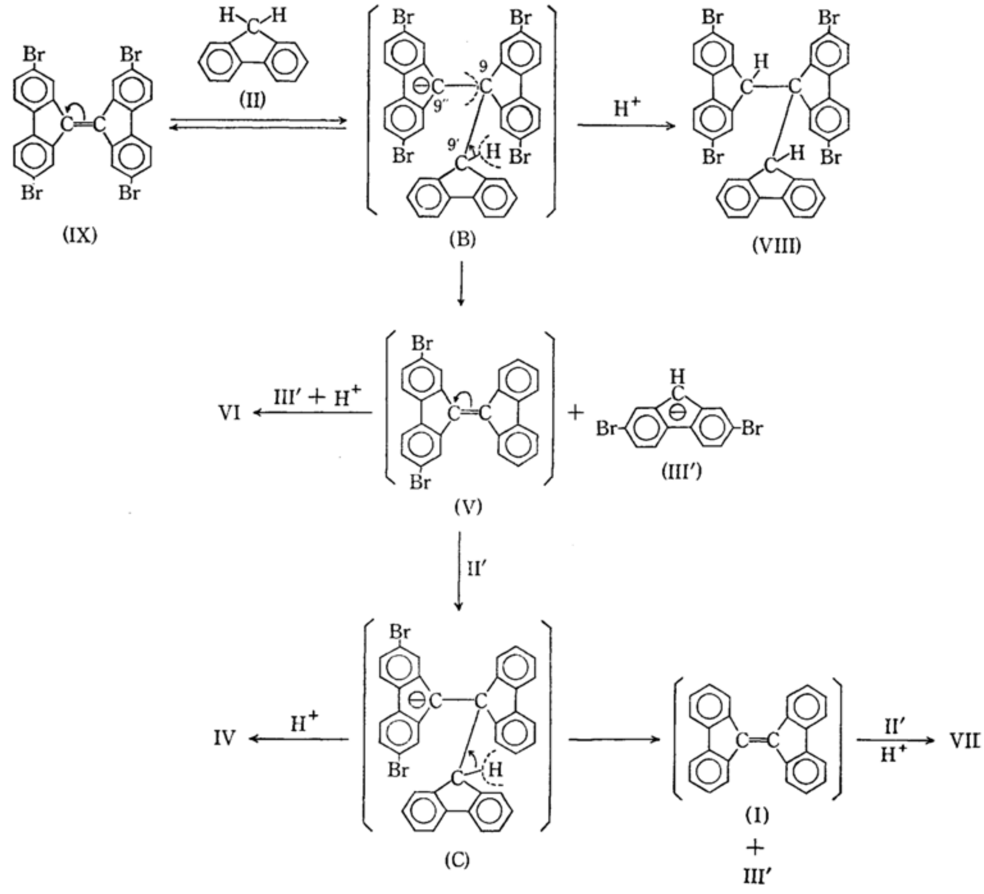
Table 2. Reaction products of IX and II under varied conditions

Run	Substrates			Reaction conditions			Products							Recvd.	
	IX	II	Mol ratio of IX/II	Solvent ml	Catalyst (base conc.) %	Time hr	VIII g	VI g	IV g	VII g	III g	2,7-Dibromo-fluorenone g	Fluorenone g	IX g	II g
1	2.00	1.55	1/3	Py 20	—	200							trace	1.95	1.46
2	2.00	1.55	1/3	EtOH 30	NaOEt 5.8	13	1.31						0.43	0.30	0.26
3	2.00	1.55	1/3	EtOH 30	NaOEt 15	19.5	0.16*	0.54	0.33		0.08	0.01	0.08		0.73
4	2.00	1.55	1/3	Py 30	Na_2CO_3 5	100	1.85		0.02		trace	0.02	0.08	0.05	0.85
5	2.00	1.55	1/3	Py 30	KOH 0.5	10	0.58*	0.64	0.57	0.10	0.40	0.05	trace	trace	0.64
6	2.00	1.55	1/3	Py 30	KOH 3	5.7	0.20*	0.86	0.55	0.04	0.40	0.15	trace	trace	0.59
7	2.00	1.55	1/3	Py 30	KOH 5	4.3	0.34*	0.55	0.69	0.04	0.28	0.19	trace	trace	0.35
8	2.00	1.55	1/3	Py 30	KOH 5	12	0.06*	0.94	0.61	0.03	0.19	0.51	0.04		0.48
9	2.00	0.52	1/1	Py 30	KOH 3	5.7		1.04	0.08		0.06	0.30	0.06	0.65	trace
10	1.50 (V)	1.55	1/3	Py 30	KOH 3	1/6			1.57			trace			0.99
11	1.50 (V)	3.03 (III)	1/3	Py 30	KOH 3	1/6		2.42			1.44 (recvd.)				

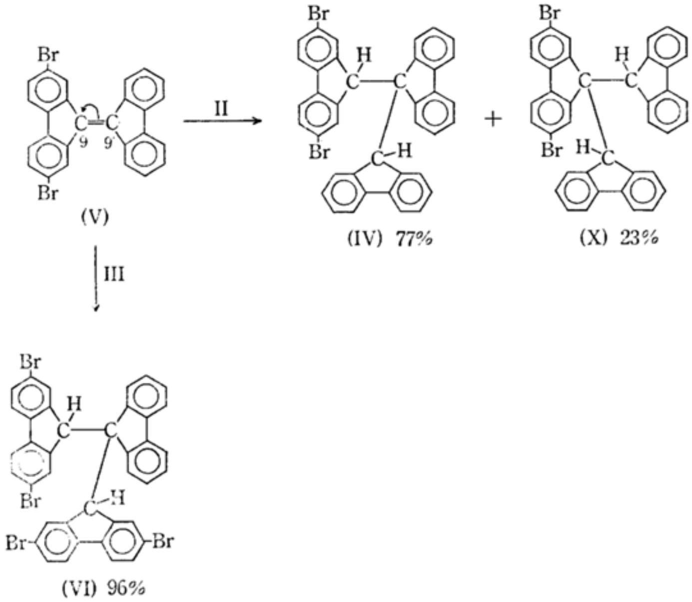
a) Py=Pyridine, EtOH=Ethanol, NaOEt=Sodium ethoxide.
b) *=mp 303—304°C.
c) Reactions were carried out in sealed tube at 93—95°C (Runs 1—9) or 97—98°C (Runs 10, 11).
d) Run 2: The reaction was carried out in nitrogen medium at boiling point. 2,7-Dibromo-α, δ-dibiphenylenebutadiene was also obtained (0.56 g).
e) Run 3: 2,7-Dibromo-α, δ-dibiphenylenebutadiene (0.46 g) was also isolated.
f) Run 10: X (0.46 g) was also isolated.



Scheme I



Scheme II



Scheme III

I in the presence of the base. (A) may then be transformed to the normal compound IV by protonation. The 9'-methine proton in (A) is reactive, and the fission of the 9—9'' carbon-carbon bond is accelerated when 2,7-dibromo-9,9'-bifluorenylidene (V) and 9-fluorenyl carbanion (II') are formed upon an increase in the alkali concentration. The abnormal VI is formed by a second Michael addition of III' and V. In this case, the yield of the secondary product, VI, is also increased if the amount of the donor, III, is raised (see Table 1, Run 5). The isomeric VIII was not formed. The unexpected formation of VII can be explained in terms of the interaction of I with II' which was eliminated from (A). The sequence of steps is shown in Scheme I.

A second transitory carbanion (B) is also formed by the interaction of IX with II. The formation of normal, abnormal, and elimination products is also conceivable as in the case of Scheme I. This sequence of steps is shown in Scheme II.

(A) and (B) are very crowded ions, and so the formation of II', III', or the stable V by an elimination reaction is perhaps favored over the protonation of (A) or (B) because there is sufficient space to release steric compression upon an increase in the alkali concentration.

The reactions of V and II or III were also carried out separately (see Table 2, Scheme III). The former reaction gave the two isomers in the ratio of 77% (IV) to 23% (X). The latter afforded a 96% yield of VI.

The 9'-carbon is more electro-positive than the 9-carbon for such highly-polarized acceptors as V because of the inductive effect of the two bromines. Also, the active methylene in the 9-position of III is greatly activated by the same means. Thus, IV and VI were formed exclusively in both reactions through, respectively, addition and protonation.

Thus, the yield of VI was higher than that of IV, while X was not isolated from the reaction products *via* the intermediate V during the interaction between IX and II. The tertiary product VII might be formed by the reaction of II and the I is eliminated from the carbanion (C).

Five related bromosubstituted tribiphenylenepropanes, IV, VI, VIII, X, and 2,7,2',7',2'',7''-hexabromotribiphenylenepropane,⁶⁾ were synthesized in order to confirm the reaction products from the interaction between substituted-9-bromo-9,9'-bifluorenyl and 9-lithiofluorenes by the halogen-lithium interconversion reaction shown in Table 3.

The thermal decomposition products of bromosubstituted tribiphenylenepropanes are interesting from the standpoint of free radical reaction. The thermal decomposition of X at 320°C led to 2, 7-dibromo-9,9'-bifluorenyl,⁷⁾ IX, V, 9,9'-bifluorenyl,⁸⁾ II, fluorenone, and 2,7-dibromofluorenone. Also, the thermal decomposition of VIII at 320—330°C led to IX, 2,7,2',7'-tetrabromo-9,9'-bifluorenyl,⁶⁾ V, 2,7-dibromo-9,9'-bifluorenyl, I, 9,9'-bifluorenyl, 2,7-dibromofluorenone, fluorenone, III, and II. These compounds were probably obtained by means of the formation and interaction of substituted

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6) K. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 795 (1954).

7) A. Sieglitz, *Ber.*, **53**, 2249 (1920); K. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **72**, 828 (1951).

8) R. Weissgerber, *Ber.*, **46**, 2913 (1908).

TABLE 3. SYNTHESES OF RELATED BROMOSUBSTITUTED TRIBIPHENYLENEPROPANES BY HALOGEN-LITHIUM INTERCONVERSION REACTION

Run	n-C_4H_9Br g	Li g	Fluorenes g	9,9′-Bifluorenyls g	Tribiphenylenepropanes	mp °C	g (%)	Anal Found C(%)	Anal Found H(%)	Anal Calcd C(%)	Anal Calcd H(%)
1	4.2	0.4	2,7-Dibromo- 10.0	9-Bromo-[d)] 6.3	2′,7′-Dibromo- (IV)	284—285	3.45 (34.4)	Mixture mp test			
2	2.8	0.28	Fluorene 5.0	2,7,9′-Tribromo-[5)] 5.7	2′,7′-Dibromo- (IV)	285—287	3.85 (58.7)				
3	2.8	0.28	2,7-Dibromo- 3.5	2,7,9′-Tribromo-[5)] 7.3	2′,7′,2′′,7′′- Tetrabromo- (VI)	313—314	5.75 (55.2)				
4	2.8	0.28	Fluorene 3.8	2,7,9-Tribromo-[5)] 5.8	2,7-Dibromo- (X)	303—303.5	4.6 (70.1)	71.84	3.83	$C_{39}H_{24}Br_2$ 71.79	3.68
5	2.8	0.28	2,7-Dibromo- 10.0	2,7,9-Tribromo-[5)] 5.8	2,7,2′,7′- Tetrabromo- (VIII)	293—294	3.14 (7.9)	58.05	2.88	$C_{39}H_{22}Br_4$ 57.79	2.74
6	1.0	0.1	2,7-Dibromo- 2.3	2,7,2′,7′,9- Pentabromo- 5.1	2,7,2′,7′2′′,7′′- Hexabromo-	332	1.45 (1.3)	48.82	2.39	$C_{39}H_{20}Br_6$ 48.39	2.08

a) All reactions were carried out in dry xylene medium.

b) Run 1: I (0.3 g), 9-hydroxy-9,9′-bifluorenyl (1.1 g) and III (1.55 g) were also isolated.

c) Run 6: 2,7,2′,7′,9-Pentabromo-9,9′-bifluorenyl (mp 420°C, 0.34 g), IX (0.04 g), 2,7,2′,7′-tetrabromo-9-hydroxy-9,9′-bifluorenyl (0.5 g), 2,7,2′,7′-tetrabromo-9,9′-bifluorenyl (0.26 g), III (0.6 g), and 2,7-dibromofluorenone (0.9 g) were also isolated.

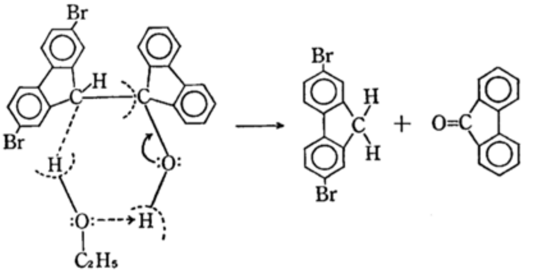
2,7,2′,7′-Tetrabromo-9-hydroxy-9,9′-bifluorenyl (mp 255—256°C, Found: C, 47.41; H, 2.39%. Calcd for $C_{26}H_{14}OBr_4$: C, 47.17; H, 2.13%). 2,7,2′,7′,9-Pentabromo-9,9′-bifluorenyl (mp>416°C, 79%) was obtained from the corresponding hydroxy compound by the action of hydrogen bromide in acetic acid.

d) cf). S. Kajigaeshi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 1712 (1961).

9-fluorenyl free radical species.

When 2,7-dibromo-9′-hydroxy-9,9′-bifluorenyl[9], one of the intermediates in the preparation of 2,7,9′-tribromo-9,9′-bifluorenyl,[9] was refluxed in ethyl alcohol for 25 min, fluorenone (89%) and III (78%) were formed. However, no reaction occured under the same conditions in a benzene solution. In two similar compounds, 9-hydroxy-9,9′-bifluorenyl[10] and 2,7-dibromo-9-hydroxy-9,9′-bifluorenyl[9], the same reaction did not occur in an ethyl alcohol solution.

In such a case, the reaction is presumably affected by an electron-attracting group, which makes the elimination of the two bromines easier. Ethanolysis can proceed through the hydrogen-bonded complex by means of the interaction of the substrate and a molecule of ethanol, as is indicated in Scheme IV.



Scheme IV

Experimental[11]

The Michael Reaction of 9,9′-Bifluorenylidene (I) with 2,7-Dibromofluorene (III). *General Procedure.* A mixture of 3.3g (0.01mol) of I, 3.2g (0.01 mol) of III, and 3m*l* of a 10% aqueous potassium hydroxide solution in 30m*l* of pyridine was heated in a sealed tube for 2hr. The mixture turned dark after 1.5hr, and precipitates were formed. Upon the filtration of the hot solution, a light yellow product was obtained.

The resulting product was extracted several times with ethyl acetate; the evaporation of the solvent from this extract afforded 0.1g of colorless fluffy crystals of IV; mp 285—287°C (dec). Found: C. 71.92; H, 3.68%. Calcd for $C_{39}H_{24}Br_2$: C, 71.78; H, 3.68%. The residue was recrystallized from benzene to yield 3.1g of colorless VI; mp 312—314°C (dec). Found: C, 57.86; H, 22.7%. Calcd for $C_{39}H_{22}Br_4$: C, 57.79; H, 2.74%.

After the orange yellow pyridine mother liquor had been allowed to cool, a light yellow deposit was collected and extracted with hot cyclohexane. Upon the cooling of the cyclohexane extract, 0.05g of 2,7-dibromofluorenone, mp 198—200°C, was isolated. The residue was extracted by refluxing it with ethyl acetate to afford 0.4g of IV, mp 286°C (dec). The last residual part was recrystallized from benzene to yield 0.2g of VI, mp 313—314°C (dec).

The original pyridine mother liquor was poured into water; the yellowish-orange material thus precipitated was collected by filtration, dried, and purified by fractional vacuum sublimation at 100—160°C to afford 0.15g of fluorenone, mp 82—84°C, 0.2g of II, mp 112—114°C, and 0.1g of 2,7-dibromofluorenone, mp 197—200°C. The work-up of the residual part by column chromatography (benzene) and fractional recrystallization from ethyl acetate gave 0.15g of 2,7-dibromofluorenone, mp 198—200°C, 0.05g of fluorenone, mp 83°C, 0.25g of VII, mp 291—293°C (dec), (no halogen), 0.7g of VI, mp 313—314°C (dec), 0.1g of IV, mp 286°C (dec), and 0.03 g of III, mp 163—164°C

The Michael Reaction of 2,7,2′,7′-Tetrabromo-9,9′-bifluorenylidene (IX) with Fluorene (II). *Materials.* IX was prepared according to a method in the literature,[12] but the product remained impure. Found: C, 51.20; H, 1.79%. Calcd for $C_{26}H_{12}Br_4$: C, 48.49; H, 1.88%. IX was then oxidized by means of sodium bichromate in acetic acid; the oxidation products, 2,7-dibromofluorenone and a small amount of 2-bromo-7-chlorofluorenone[13] as an impurity, were confirmed by gas chromatography. Pure IX, mp 429°C (dec), (Found: C, 48.55; H, 1.79%) was prepared by the reaction of 2,7,9-tribromofluorene[9] with methanolic potassium hydroxide in acetone under conditions similar to those used in the preparation of I.[5]

General Procedure. A mixture of 2.00g (0.0031 mol) of IX, 1.55g (0.0093 mol) of II, 0.9g of potassium hydroxide in 5m*l* of water, and 25m*l* of pyridine was heated in a sealed tube at 93—95°C for 5.7hr. During this period, the mixture turned from red to dark, and colorless crystals were formed.

Upon cooling, the deposited crystals were filtered, to this filtrate was added 25m*l* of methanol with stirring and the precipitated material was filtered again. The pyridine-methanol mother liquor was poured into water, and the precipitate was filtered, washed with water, dried, and sublimed *in vacuo* at 80—200°C.

The crops of the first and second portions were combined, washed with water, and dried, and then the residue of the sublimation was added. There were subsequently isolated 0.55g of IV, mp 285—286°C (dec), 0.86g of VI, mp 313—314°C (dec), 0.04g of VII, mp 292—293°C (dec), (no halogen), 0.20g of a material with a mp of 303—304°C (dec) (Found: C, 57.78; H, 2.53%. Calcd for $C_{39}H_{22}Br_4$: C, 57.79; H, 2.74%), and a trace of recovered IX, mp 429°C (dec) by means of fractional recrystallization from ethanol, ethyl acetate, and benzene. The material with a mp of 303—304°C (dec) (see Table 2) contained a small percentage VI in VIII. This contamination with VI could not be removed. It seems to be the reason for these solubilities lying close together; the IR and UV absorption spectra and the R_f-values obtained by thin layer chromatography are also similar. A phase diagram plotting the melting points *versus* the compositions of synthetic mixtures of authentic VIII and VI indicates that a material with a melting point o 303—304°C (dec) would correspond to about 4—5% VI in 96—95% VIII. The small amount of VI causes only a small elevation in the melting point of VIII.

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[9] K. Suzuki and M. Fujimoto, This Bulletin, **36**, 1654 (1963).

[10] V. Grignard and C. Courtot, *Compt. rend.*, **152**, 1493 (1911); C. Courtot, *Ann. Chem.*, **4**, 84 (1915).

[11] All melting points are uncorrected.

[12] J. Schmidt and H. Wagner, *Ann.*, **387**, 147 (1912).

[13] K. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 714 (1954).

The cyclohexane solution of the sublimed product was chromatographed on alumina. Further fractional recrystallization from ethanol gave 0.40g of III, mp 162—164°C, 0.15g of 2,7-dibromofluorenone, mp 200—202°C, and a trace of fluorenone, mp 82—84°C, while 0.59g of the II of the starting material, mp 112°C was also separated.

When sodium ethoxide was the catalyst, an unknown compound, mp 364°C (dec) was isolated as red needles (Table 2, Runs 2 and 3 or Table 1, Run 8). On oxidation with sodium bichromate in acetic acid, this material gave 73% of 2,7-dibromofluorenone and 41% of fluorenone, while the analytical results agreed with the value calculated for $C_{28}H_{16}Br_2$. The IR and UV absorption spectra of the compound with a mp of 364°C (dec) were very similar to those of α,δ-dibiphenylenebutadiene[14] and 2,7,2′,7′-tetrabromo-α,δ-dibiphenylenebutadiene[15] respectively. Thus, the structure of the unknown compound is presumably 2,7-dibromo-α,δ-dibiphenylenebutadiene, which has not been described hitherto.

All the compounds in this reaction series were identified by mixed-melting-point determinations and by comparing their IR and UV absorption spectra with those of authentic samples.

The Michael Reactions of 2,7-Dibromo-9,-9-′bifluorenylidene (V) with Fluorene (II) or 2,7-Dibromofluorene (III). The reaction was performed in a similar manner, 1.5g (0.0031 mol) of V,[7] mp 242-243°C, 1.55g (0.0093 mol) of II, 0.9g of potassium hydroxide in 5m*l* of water, and 25m*l* of pyridine in a sealed tube were heated at 97—98°C for 10min.

The precipitate which formed upon cooling was fractionally recrystallized from ethyl acetate and benzene to afford 1.57g (77%) of IV, mp 285—286°C (dec) and 0.46g (23%) of X, mp 303°C (dec). Found (for X): C, 71.55; H, 3.59%. Calcd for $C_{39}H_{24}Br_2$: C, 71.78; H, 3.68%. In addition, 0.99g of II, mp 112—115°C, and a trace of 2,7-dibromofluorenone, mp 198°C, were isolated from the mother liquor and were purified by a combination of vacuum sublimation and column chromatography.

The product, 2.42 g of VI, mp 314°C (dec), was obtained in a good yield (96%) from 1.50 g of V and 3.03 g (0.0093 mol) of III under the reaction conditions described above.

The identities were confirmed by mixed-melting-point determinations and by a comparison of the IR and UV absorption spectra with those of authentic samples.

The Synthesis of 2′,7′-Dibromotribiphenylenepropane (IV). *1) General Procedure.* The reaction of *n*-butyllithium and III in xylene led to 2,7-dibromo-9-fluorenyllithium, which then, upon treatment with carbon dioxide, gave 2,7-dibromofluorene-9-carboxylic acid, mp 208—209°C. Found: C, 45.49; H, 2.23%. Calcd for $C_{14}H_8O_2Br_2$: C, 45.69; H, 2.19%. IR: 1705 cm^{-1} (ν C–O) (KBr–disk).

2) *n*-Butyllithium was prepared from 2.8g (0.04 mol) of *n*-butyl bromide in 25 m*l* of anhydrous ether and 0.28g (0.04g atom) of lithium in 20m*l* of anhydrous ether. Then 9-fluorenyllithium was formed by adding 5g (0.03 mol) of fluorene in 50m*l* of anhydrous xylene to the *n*-butyllithium solution. To this mixture was added slowly 130m*l* of anhydrous xylene containing 5.7g (0.01 mol) of 2,7,9′-tribromo-9,9′-bifluorenyl with stirring.

After the reaction mixture had been allowed to stand overnight at room temperature, the precipitate was filtered, hydrolyzed with a dilute ammonium chloride solution, and recrystallized from ethyl acetate to give 3.8g (58.7%) of IV, mp 285—286°C (dec). mol wt: 658. Calcd for $C_{39}H_{24}Br_2$: 652.

Thermal Decomposition of 2,7-Dibromotribiphenylenepropane (X). Powdered X (5.0g; 0.0077 mol) was placed in a 100m*l* Erlenmeyer flask and then decomposed at 320°C in a preheated salt bath.

The red molten product was ground and extracted with boiling benzene, which had been filtered while hot. The orange colored residue was recrystallized form a large volume of benzene to yield 0.04g (2%) of IX, mp 430°C (dec).

The mother solution from this recrystallization was evaporated to dryness under reduced pressure. The fractional recrystallization of the residue from a mixture (1 : 1) of benzene and ethyl acetate gave 1.3g (35%) of 2,7-dibromo-9,9′-bifluorenyl, mp 268—270°C, 0.1g (4%) of 9,9′-bifluorenyl, mp 242—244°C, and 0.3g (6%) of of the starting material X, mp 303°C (dec).

When the product of the first benzene extraction was left to stand, red crystals (0.7g) of V, mp 240—242°C, separated out. This mother liquor was then evaporated to dryness under reduced pressure, and the residue was dissolved in benzene and chromatographed on alumina. A 0.7-g portion (27%) of 2,7-dibromofluorenone, mp 198—200°C, and 0.2g (7%) of fluorenone, mp 83°C, were isolated from the yellow band on the column. The colorless benzene eluate, upon evaporation and vacuum sublimation at 100°C, gave 0.05g (2%) of fluorene, mp 114°C. The residue from the sublimation was recrystallized from ethyl acetate to yield 0.15g of V, mp 240—242 °C (total; 0.85g, 23%).

Thermal Decomposition of 2,7,2′,7′-Tetrabromotribiphenylenepropane (VIII). Finely powdered VIII (3.24g; 0.004 mol) was decomposed at 320—330°C in a preheated metal bath. The red molten product was then ground and extracted with boiling benzene. The insoluble red part was recrystallized from pyridine to yield 0.35g (14%) of IX (mp 429—430°C (dec)).

After the benzene mother liquor had been evaporated to a small volume, 0.59g (23%) of 2,7,2′,7′-tetrabromo-9,9′-bifluorenyl,[3,5,7] mp 317—318°C, 0.68g (35%) of 2,7-dibromo-9,9′-bifluorenyl, mp 269—270°C, 0.25g (13%) of V, mp 241—242°C and the recovered VIII (0.02g; 1%) were separated by fractional recrystallization from ethyl acetate or benzene.

When the residual benzene solution was chromatographed on alumina, 0.03g (5%) of I, mp 182—184°C, 0.02g (3%) of 9.9′-bifluorenyl, mp 241—243°C, 0.01g (2%) of II (mp 114°C), and a trace of III were isolated. Moreover, 0.15g (6%) of 2,7-dibromofluorenone, mp 197—198°C, and 0.07g (10%) of fluorenone, mp 78—80°C, were separated from the two yellow bands.

The Reaction of 2,7-Dibromo-9′-hydroxy-9,9′-bifluorenyl in Ethanol. A mixture of 1.0g (0.002 mol) of 2,7-dibromo-9′-hydroxy-9,9′-bifluorenyl and 25m*l* of absolute ethanol was refluxed for 25min; the mixture turned yellow during this period. After half the volume

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[14] a) K. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 711 (1954); W. Wislicenus, *Ber.*, **48**, 617 (1915); R. Kuhn and A. Weinterstein, *Helv. Chim. Acta*, **11**, 119 (1928). b) M. K. Starfass, *Bull. Soc. Chim.*, [4] **29**, 145 (1921).

[15] See Refs. 2 and 14 b; E. Bergmann, H. Hoffman and D. Winter, *Ber.*, **66**, 46 (1933).

of the original alcohol had then been removed, pure crystals (0.5g;78%) of III, mp 165°C, were deposited.

The mother liquor was evaporated to dryness under reduced pressure, and the benzene solution of the residual part was chromatographed on alumina. Moreover, 0.32g (89%) of fluorenone, mp 81°C, was isolated from the yellow band and recrystallized from alcohol.

On the other hand, when 1.0g (0.002 mol) of 2,7-dibromo-9-hydroxy-9,9′-bifluorenyl was refluxed in absolute ethanol (45m*l*) for 3hr, 0.89g (89%) of the starting material was recovered.

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