The Michael Reactions of Substituted 9,9′-Bifluorenylidenes with 2-Iodo- and 2,7-Diiodofluorene, and Some Other Reactions of Iodofluorenes[1,2]

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The Michael-addition reaction between 2-iodofluorene and 9,9′-bifluorenylidene gave exclusively the normal addition product. The same reaction of fluorene with 2,2′-diiodo-9,9′-bifluorenylidene, of 2,7-diiodofluorene with 9,9′-bifluorenylidene, and of fluorene with 2,7,2′,7′-tetraiodo-9,9′-bifluorenylidene afforded not only the normal adducts, but also some abnormal compounds. Some new iodo-substituted fluorenes, -9,9′-bifluorenylidenes, -9,9-bifluorenyls, and -1,4-bis(2,2′-biphenylylene)-1,3-butadienes, were synthesized. The hydrogenolyses of 2- or 2,7-di-iodofluorene with lithium aluminum hydride, Raney nickel, and hydriodic acid were performed relatively smoothly to give fluorene. The Grignard and the Ullmann reactions of 2- or 2,7-di-iodofluorene gave the usual, expected compounds, accompanied by some unusual products. The cyano-substituted fluorenes were prepared by the reaction of 2- or 2,7-diiodofluorene with potassium cyanide–cupric cyanide in *N,N*-dimethylformamide.

The Michael reaction[3] of 9,9′-bifluorenylidene (**7**) with 2,7-dibromofluorene gave an abnormal product, 2,7,2″,7″-tetrabromo-9,9′,9′,9″-terfluorenyl, as the main product, and the normal addition product, 2,7-dibromo-9,9′,9′,9″-terfluorenyl, as a by-product. The similar addition of fluorene (**1**) to 2,7,2′,7′-tetrabromo-9,9′-bifluorenylidene afforded three abnormal products, 2,7-dibromo-9,9′,9′,9″-terfluorenyl and 2,7,2″,7″-tetrabromo-9,9′,9′,9″-terfluorenyl, as the main products, and 9,9′,9′,9″-terfluorenyl (**22**), and the normal addition product, 2,7,2′,7′-tetrabromo-9,9′,9′,9″-terfluorenyl, as by-products.

An analogous reaction[2] of 2-fluorofluorene with **7** in the presence of a sodium hydroxide–pyridine solution or sodium ethoxide in ethanol gave exclusively the normal addition product, 2-fluoro-9,9′,9′,9″-terfluorenyl. Also, 2,2′-difluoro-9,9′,9′,9″-terfluorenyl, 2,7-difluoro-9,9′,9′,9″-terfluorenyl, and 2,7,2′,7′-tetrafluoro-9,9′,9′,9″-terfluorenyl were obtained as normal main products by similar reactions of **1** with 2,2′-difluoro-9,9′-bifluorenylidene, of 2,7-difluorofluorene with **7**, and of **1** with 2,7,2′,7′-tetrafluoro-9,9′-bifluo-renylidene respectively.

The present paper will deal with the Michael reaction of iodo-substituted 9,9′-bifluorenylidenes with fluorenes and will attempt to elucidate some effects due to the difference between iodo-substitutions. It will also compare a few reactions in 2-iodofluorene (**2**)[4] or 2,7-diiodofluorene (**3**)[4b,4c,4e,5] with other, corresponding halogeno derivatives.

The Michael reaction of **7** with **2** in the presence of potassium hydroxide–pyridine gave 2-iodo-9,9′,9′,9″-terfluorenyl (**15**), 2-iodofluorenone (**5**)[4a,4d,4e,4f] and fluorenone (**4**). The yield of **15** increased with the increase in the base concentration, as is shown in Table 1.

The same reaction of 2,2′-diiodo-9,9′-bifluorenylidene (**8**)[6] with **1** afforded 2,2′-diiodo-9,9′,9′,9″-terfluorenyl (**16**), 2,2″-diiodo-9,9′,9′,9″-terfluorenyl (**17**), **4**, and **5**. The yield of **17** increased as the base concentration increased, while, on the contrary, the yield of **16** decreased, as is shown in Table 2. Compounds **16** and **17** are isomeric, and their structures were estimated by comparing the fragmentation peaks in the mass spectra.

An analogous reaction between **7** and **3** yielded 2,7-diiodo-9,9′,9′,9″-terfluorenyl (**19**), 2,7,2″,7″-tetraiodo-9,9′,9′,9″-terfluorenyl (**21**), and **22** as both normal and abnormal addition products, and 2,7-diiodofluorenone (**6**)[4e,5] and **4** as elimination products, as is shown in Table 3. The yields of these reaction products are closely related with the base concentration and with the molar ratio of the reactants.

2,2′,2″-Triiodo-9,9′,9′,9″-terfluorenyl (**18**) and 2,7,2′,7′,2″,7″-hexaiodo-9,9′,9′,9″-terfluorenyl (**23**) were obtained by the reactions of **2** with **8**, and of **3** with 2,7,2′,7′-tetraiodo-9,9′-bifluorenylidene (**9**). These products could be obtained as normal products, but the stereoisomeric 9,9′,9′,9″-terfluorenyls[7] were not isolated.

In the reaction of **9** with **1**, 2,7,2′,7′-tetraiodo-9,9′,9′,9″-terfluorenyl (**20**), **19**, **21**, **22**, **3**, **4**, and **6** were separated.

The sequences for the formation of the compounds in these Michael reactions can be represented by the typical reaction of **9** with **1** as is illustrated in Scheme 1. A transitory carbanion (D) is formed by the nucleophilic attack of the fluorenyl carbanion (**1′**) generated from **1** on the highly-polarized ethylenic carbons of **9** in the presence of the base. Subsequently, D may be transformed to the normal addition product, **20**, by protonation, but then, the D dis-

1) Studies on Fluorene Derivatives. XXVIII. A part of this paper was presented at the 23rd Meeting of the Chemical Society of Japan, Tokyo, April, 1970; Preprints, III, p. 1739.

2) Part XXVII of this series: M. Minabe, A. Tanaka, M. Wakui, and K. Suzuki, This Bulletin, **44**, 1614 (1971).

3) K. Suzuki, M. Minabe, M. Fujimoto, and N. Nohara, *ibid.*, **42**, 1609 (1969).

4) a) L. Chardonnens and L. Avar, *Helv. Chim. Acta*, **52**, 1091 (1969). b) Y. Ogata and I. Urasaki, *J. Chem. Soc., C*, **1970**, 1689. c) P. S. Varma and V. S. Rao, *J. Indian Chem. Soc.*, **15**, 72 (1938). d) M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, *J. Amer. Chem. Soc.*, **81**, 4583 (1959). e) F. Dewhurst and P. K. J. Shak, *J. Chem. Soc., C*, **1969**, 1503. f) Ch. Courtot, *Ann. Chem.*, **14**, 5 (1930).

5) T. Stauner, L. Avar, and L. Chardonnens, *Helv. Chim. Acta*, **53**, 1311 (1970).

6) This compound is not clear in respect to *cis-trans* isomerism.

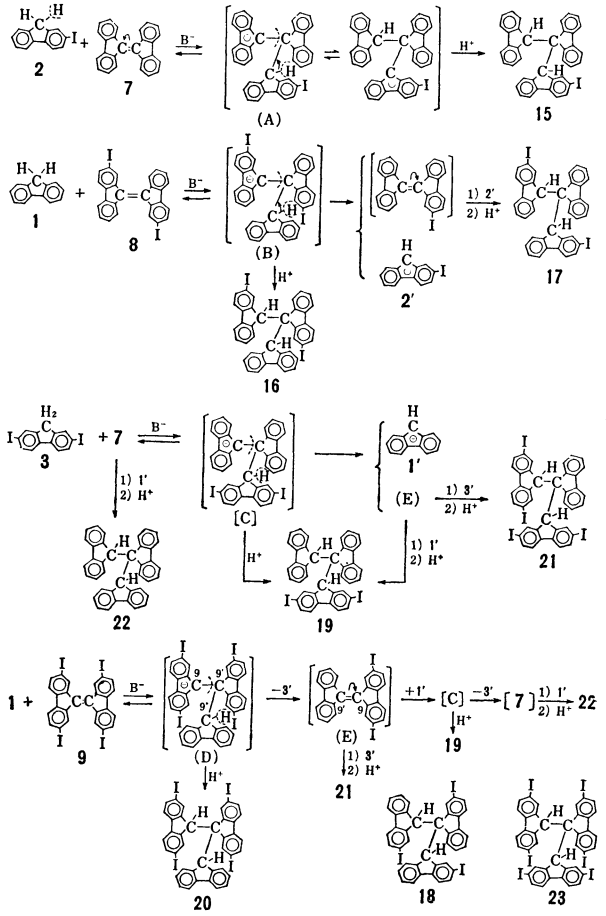
7) K. Suzuki, *Nippon Kagaku Zasshi*, **70**, 189 (1949); *ibid.*, **75**, 795 (1954); K. Suzuki, *Technol. Repts. Tohoku Univ.*, **19**, 63 (1955).

sociates into **3'** and the intermediate 2,7-diiodo-9,9'-bifluorenylidene (E)[8] by the fission of the 9-9' carbon-carbon bond, with the elimination of the 9''-proton. Therefore, the anomalous formation of **21** can be explained by a secondary Michael reaction of **3'** with (E), followed by protonation.

The reaction of E with **1'** gives the carbanion (C), which then yields an abnormal product, **19**. Further, the complete process of formation to the iodine-free compound, **22**, involves three additions and two eliminations through the two intermediates, (D and C), under consideration. Moreover, **3**, **4**, and **6** were also isolated by elimination or oxidation reactions in the process.[9]

Meanwhile, the 9-methylene hydrogen in 2-halo- or 2,7-dihalo-fluorenes are more reactive in forming fluorenyl carbanions than that in the parent fluorene in the Michael reaction. For this reason, the electron-withdrawing effect[10] of these substituents may operate on the 9-carbon atom in fluorenes. Moreover, the base concentration seems to be an important factor in the 9-methylene hydrogen.

In view of this effect, the ethylenic 9-carbon in E, for example, is more electronegative than the 9'-carbon,

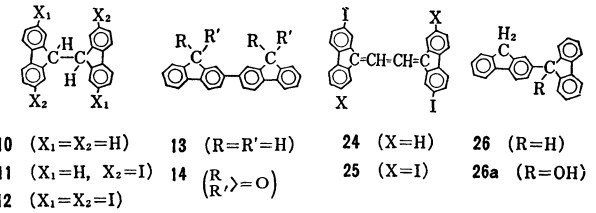


Scheme 1.

and the addition of **3'** is preferential in forming the 9'-carbon leading to **21** than the other possible way. These effects were supported experimentally by the corresponding bromo derivatives[3] in the analogous Michael reaction. The crowded carbanions, for example, C and D, which contain bulky iodine atoms, might be reactive because of the steric compression. Therefore, under reasonably mild reaction conditions, the addition products are chiefly normal compounds. However, the reaction is accelerated toward elimination upon an increase in the alkali concentration.

Because there is more active iodine than any other halogen on the 2- or 2,7-positions of fluorene, attempts at the step-by-step syntheses of iodine-substituted 9,9',9',9''-terfluorenyls were unsuccessful. However, we are able to estimate the positions of iodine by comparing the melting points and the mass and IR spectra of iodo-9,9',9',9''-terfluorenyls with those of the bromo-[3] and chloro-[11] analogues.

Barnett and others[4d] reported that 2,2'-bifluorenyl-9,9'-dione (**14**) was obtained by the Ullmann reaction of **5**, even though no 2,2'-bifluorenyl (**13**) was formed from **2**. The syntheses of these compounds were re-investigated by the Ullmann reaction; 42% of **14** was obtained from **5**, and 9% of **13** from **2**. In addition, a considerable amount of **1** was formed from **2**. The same reaction of **3** gave 15% of **1** instead of a polymeric substance upon dehalogenation.



10 ($X_1=X_2=H$) **11** ($X_1=H$, $X_2=I$) **12** ($X_1=X_2=I$) **13** ($R=R'=H$) **14** ($R_2C=O$) **24** ($X=H$) **25** ($X=I$) **26** ($R=H$) **26a** ($R=OH$)

Scheme 2.

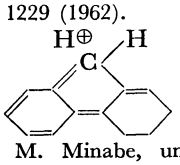
The iodine atoms in **2** and **3** were completely removed by reaction with Raney nickel, lithium aluminum hydride, or hydriodic acid. However, no reaction occurred at all for 2-bromofluorene and 2,7-dibromofluorene[12] under the same conditions.

The reaction of **2** with ethylmagnesium bromide afforded **1**, 2-ethylfluorene, and **13**. The yield of the anticipated compound, 2-ethylfluorene, was, however, very low, and **1** and **13** were unexpectedly ob-

8) The Michael reaction of **7** with 2-bromofluorene afforded a trace amount of 2-bromo-9,9'-bifluorenylidene. And therefore, (E) or 2-iodo-9,9'-bifluorenylidene can be regarded as intermediates in this series. See K. Suzuki and M. Fujimoto, This Bulletin, **37**, 1833 (1964).

9) A small amount of **3** can be oxidized to **6** under these reaction conditions.

10) The high reactivity of fluorene is due to the coplanarity enforced by the 9-methylene bridge. And the activation of 9-methylene group is attributable to enhanced hyperconjugation between the aromatic rings. See for example, P. B. D. de la Mare, D. M. Hall, M. M. Harris, and M. Hassan, *Chem. Ind.* (London), **1958**, 1086; H. C. Brown, M. Bubeck, and G. Goldman, *J. Amer. Chem. Soc.*, **84**, 1229 (1962).



11) K. Suzuki and M. Minabe, unpublished.

12) 2,7-Dibromofluorene, however, was reduced to **1** by refluxing with Raney nickel in xylene; see A. Schoenberg, K. H. Brosowski, and E. Singer, *Chem. Ber.*, **95**, 2984 (1962).

Table 1. The Michael reaction of **7** with **2**

Reactants g			Reaction conditions			Products g(%)			Recovered g(%)	
7	**2**	Mole ratio	Pyridine(m*l*)	KOH(%)	Time(hr)	**15**	**5**	**4**	**7**	**2**
2.19	1.95	1/1	30	0.1	22	0.96(23)	0.03 (2)	0.24(10)	1.03(53)	1.26(65)
2.19	1.95	1/1	30	1	11	2.06(50)	0.02 (2)			
2.19	1.95	1/1	30	10	7	3.06(74)	0.10 (5)	0.08 (3)		
2.19	2.92	1/1.5	30	1	9	3.31(79)	0.43(14)			0.93(32)
3.28	1.95	1.5/1	30	1	11	2.92(71)	0.04 (2)	0.15 (8)	0.36(11)	

Table 2. The Michael reaction of **8** with **1**

Reactants g			Reaction conditions			Products g(%)				Recovered g(%)	
8	**1**	Mole ratio	Pyridine(m*l*)	KOH(%)	Time(hr)	**16**	**17**	**5**	**4**	**8**	**1**
2.32	0.83	4/5	30	0.1	40	1.19(40)	0.56(19)	0.10(4)	0.02(2)	0.49(21)	0.37(45)
2.32	0.83	4/5	30	10	8	0.90(30)	1.10(37)	0.15(6)			0.08(10)
2.90	0.50	5/3	30	10	8	0.30(13)	0.84(37)	0.05(2)	0.02(4)	0.45(16)	

Table 3. The Michael reaction of **7** with **3**

Reactants g			Reaction conditions			Products g(%)						Recovered g(%)	
7	**3**	Mole ratio	Pyridine(m*l*)	KOH(%)	Time(hr)	**19**	**21**	**22**	**6**	**4**	**1**	**7**	**3**
2.2	2.8	1/1	30	0.05	24	0.48(10)			0.05			1.58	2.29
2.2	2.8	1/1	30	0.1	18.5	1.28(26)						0.004	0.98
2.2	2.8	1/1	30	1	2.5	3.69(74)	0.10 (3)		0.12	0.01		0.13	0.08
2.2	2.8	1/1	30	5	2.5	3.55(71)	0.36(11)		0.13	0.015		0.01	0.02
2.2	2.8	1/1	30	10	2.5	3.72(75)	0.38(11)		0.01	0.01	0.02	0.03	0.02
1.1	2.8	1/2	30	5	2.5	1.67(67)	0.53(16)		0.04	0.01	0.19		0.69
3.3	2.8	3/2	30	5	2.5	4.08(82)		0.002	0.04	trace	0.005	1.01	

tained in relatively high yields. The formation of **1** and **13** can be regarded as occurring by means of the reaction between **2** and magnesium, which was activated by ethyl bromide, followed by hydrolysis or alkylation. **1** was obtained in a 60% yield from **2** following the procedure of Morrison.[13]

The synthesis of 2,9′-bifluorenyl (**26**)[14] was examined by interaction between 2-fluorenylmagnesium iodide and 9-bromofluorene, but 9,9′-bifluorenyl (**10**), **13**, and **1** were afforded. These results can be explained in terms of the reactions of 9-fluorenylmagnesium bromide with 9-bromofluorene and of 2-fluorenylmagnesium iodide with **2** respectively. The reaction of 2-fluorenylmagnesium iodide with **4** afforded **26**, but not 9′-hydroxy-2,9′-bifluorenyl (**26a**). The interpretation of the unusual formation is not yet clear.

The synthesis of α-cyanonaphthalene, as has been reported by House and Fischer,[15] was adapted to the syntheses of 2-cyanofluorene derivatives. The reaction of **2** with potassium cyanide–cupric cyanide gave 2-cyanofluorene[16] and a small amount of 2-cyanofluorenone. Similarly, 2,7-dicyanofluorene and 2,7-dicyanofluorenone were obtained from **3**. The melting point of 2-cyanofluorene was 91—92°C,[16a] slightly different from that of the literature;[16b,16c] the structure of this compound was assigned by elemental analysis and by means of the IR and mass spectra. If 2-cyanofluorene is contaminated by a small amount of impurities, **1** and/or **2**, the mass spectra can be expected to be 166 and 292 *m/e*. However, neither fragmentation was observed.

Experimental[17]

The IR spectra were recorded on KBr pellets using a JASCO model IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.). The gas chromatograms were obtained by means of GCG-550T gas chromatograph (Yanagimoto Mfg. Co., Ltd.), using a column containing 5% of Silicone SE-30 on Celite 545-AW. The mass spectra were measured with a model RMU-6E apparatus (Hitachi, Ltd.) by means of the direct inlet system. The sample evaporating temper-

13) D. C. Morrison, *J. Amer. Chem. Soc.*, **74**, 3430 (1952).
14) K. Suzuki, *J. Org. Chem.*, **27**, 2224 (1962).
15) H. O. House and W. F. Fischer, *ibid.*, **34**, 3626 (1969).
16) a) M. Fortner, *Monatsh. Chem.*, **25**, 443 (1904). b) N. Ishikawa and T. Ozawa, *Yuki Gosei Kagaku Kyokai Shi*, **17**, 553 (1959). c) F. E. Ray and P. Quinlin, *J. Org. Chem.*, **13**, 652 (1948). d) J. V. Braun and H. Engel, *Ber.*, **57**, 191 (1923).
17) All the melting points are uncorrected. The identities of the compounds in this series were confirmed by mixed-melting-point determinations and by comparison of IR absorption spectra with those of authentic samples.

ature, chamber volt, total emission, and target current were maintained at 200°C, 80 V, 80 μA, and 50 μA respectively.

3 (mp 215—216.5°C) was synthesized in a 75% yield from **2** in a manner similar to that used for **2**[4a]; it was then converted to the corresponding ketone, **6** (80%); mp 207—208°C; IR (>C=O): 1716 cm^{-1}.

2-Iodofluorenol. A mixture of 5.2 g of **5**, 53 g of zinc dust, 220 m*l* of ethanol, and 5 g of calcium chloride in 10 m*l* of water was refluxed for 1 hr. The reaction mixture was then filtered, and the filtrate was poured into water. The precipitate was recrystallized from benzene-cyclohexane (1 : 1). Colorless needles; mp 121—123°C; yield 1.22 g (23%). IR (>OH): 3190 cm^{-1}. Found: C, 50.95; H, 2.88%. Calcd for $C_{13}H_9OI$: C, 50.68; H, 2.94%.

2,7-Diiodofluorenol. A 1.3-g portion of **6** was treated under the conditions described above to yield 1.02 g (78%) of 2,7-diiodofluorenol as fine, colorless needles; mp 201.5—203°C (decomp. to yellow). IR (-OH): 3270 cm^{-1}. Found: C, 36.13; H, 1.74%. Calcd for $C_{13}H_8OI_2$: C, 35.98; H, 1.86%.

2-Iodo-9-bromofluorene. a): A mixture of 8.76 g (0.03 mol) of **2**, 5.60 g of *N*-bromosuccinimide (NBS), and 50 m*l* of dry benzene was refluxed for 3 hr to afford 7.10 g (64%) of 2-iodo-9-bromofluorene; mp 126—127°C (from cyclohexane). Found: C, 42.36; H, 1.96%. Calcd for $C_{13}H_8BrI$: C, 42.09; H, 2.17%.

b): 2-Iodofluorenol (1.03 g) was brominated by hydrogen bromide in acetic acid to yield 0.75 g (53%) of the product; mp 126—127°C.

2,7-Diiodo-9-bromofluorene: a): A 2.1-g portion of **3** was worked up with NBS (1.0 g) to yield 1.6 g (64%) of 2,7-diiodo-9-bromofluorene; mp 204—205°C (from benzene and cyclohexane). Found: C, 31.43; H, 1.22%. Calcd for $C_{13}H_7BrI_2$: C, 31.42; H, 1.42%.

b): **3** (8.4 g; 0.02 mol) was dissolved in 150 m*l* of benzene, and then a trace amount of benzoyl peroxide was added. Into this boiling mixture there was stirred a solution of benzene containing 3.5 g (0.022 mol) of bromine under the irradiation with UV light for 15 min. After the mixture had been left standing to cool, 4.0 g of 2,7-diiodo-9-bromofluorene (mp 204—205°C) were collected by filtration. The mother solution was then treated as usual to afford an additional 2.3 g (total 6.3 g; 63%) of the product.

Furthermore, a small amount of 2,7-diiodo-9,9-dibromofluorene (mp 230—232°C) was isolated. Found: C, 27.30; H, 0.93%. Calcd for $C_{13}H_6Br_2I_2$: C, 27.56; H, 1.06%.

c): The bromination of 2,7-diiodofluorenol (15 g in 1 *l* of acetic acid) with hydrogen bromide yielded 7.7 g (45%) of the same compound; mp 204—205°C.

*1,4-Bis(4-iodo-2,2'-biphenylylene)-1,3-butadiene (**24**)*: A mixture of 1.46 g (0.005 mol) of **2**, 55 m*l* of ethanol, and 2.5 g of potassium hydroxide in 5 m*l* of water was refluxed under a gentle stream of air for 20 hr. The deposited product was then recrystallized from pyridine to yield 1.01 g (67%) of **24** (mp 405—405°C (decomp.)) as orange-red needles. Found: C, 55.50; H, 2.48%. Calcd for $C_{28}H_{16}I_2$: C, 55.47; H, 2.66%.

*1,4-Bis(4,4'-diiodo-2,2'-biphenylylene)-1,3-butadiene (**25**)*: The compound was prepared in a 54% yield by the same procedure; red needles; mp 455°C (decomp.). Found: C, 39.17; H, 1.25%. Calcd for $C_{28}H_{14}I_4$: C, 39.20; H, 1.64%.

*2,2'-Diiodo-9,9'-bifluorenylidene (**8**)*: An acetone solution (110 m*l*) containing 3.71 g (0.01 mol) of 2-iodo-9-bromofluorene was refluxed for 5 hr with potassium hydroxide-methanol (0.56 g/20 m*l*) to afford 1.91 g (66%) of red **8**; 262—263°C. Found: C, 53.48; H, 2.17%. Calcd for $C_{26}H_{14}I_2$: C, 53.82; H, 2.43%.

*2,7,2',7'-Tetraiodo-9,9'-bifluorenylidene (**9**)*: To a mixture of 10.0 g (0.02 mol) of 2,7-diiodo-9-bromofluorene and 3 *l* of methyl ethyl ketone, was added 30 m*l* of methanol containing equimolar sodium hydroxide at 5—8°C over a period of 15 min. Thereupon, the reaction mixture was worked up by the two following methods.

a) After stirring for 2 hr, the precipitate was filtered off, washed with water, dried, and washed with 50 m*l* of boiling benzene to afford 5.6 g (67%) of **9** (mp 425°C (decomp.)). Found: C, 37.51; H, 1.69%. Calcd for $C_{26}H_{12}I_4$: C, 37.54; H, 1.45%.

b) The other reaction mixture, which was prepared from 4.0 g of 2,7-diiodo-9-bromofluorene, was refluxed for 20 hr to yield 2.01 g (60%) of **9** (mp 423°C (decomp.)), 0.98 g (28%) of **6** (mp 206—207°C), and 0.01 g (0.3%) of **23** (mp 316—318°C (decomp.)).

*Reduction of **8**.* A mixture of 0.58 g (0.001 mol) of **8**, 700 m*l* of acetic acid, 10 g of zinc granule and 100 m*l* of concentrated hydrochloric acid was refluxed for 1.5 hr. The reaction mixture was evaporated to dryness, and the residue was recrystallized from ethyl acetate to afford 0.12 g (21%) of **8** (mp 260—262°C) and 0.18 g (31%) of 2,2'-diiodo-9,9'-bifluorenyl (**11**) (mp 287—288°C (decomp.) (from benzene)). Found: C, 53.77; H, 2.64%. Calcd for $C_{26}H_{16}I_2$: C, 53.64; H, 2.77%.

*The Michael Reaction of 9,9'-Bifluorenylidene (**7**) with 2-Iodofluorene (**2**).* A mixture of 2.19 g (1/150 mol) of **7**, 1.95 g (1/150 mol) of **2**, 28 m*l* of pyridine, and 3.0 g (10% for the solvent) of potassium hydroxide in 2 m*l* of water was placed in a sealed tube and heated at 97—100°C for 7 hr. The reaction mixture was then poured into 500 m*l* of water, and the precipitate was recrystallized from cyclohexane and then from benzene to give 3.02 g of **15** (mp 272—274°C (decomp.)). The analytical sample was recrystallized from *N,N*-dimethylformamide (DMF) and then from benzene. Found: C, 75.75; H, 3.90%. Calcd for $C_{39}H_{25}I$: C, 75.49; H, 4.06%.

The subsequent evaporation of the mother liquor *in vacuo* and chromatography on alumina in benzene gave an additional 0.04 g (total 3.06 g; 74%) of **15** (mp 271—274°C (decomp.)), 0.08 g (3%) of **4** (mp 81—82°C), and 0.10 g (5%) of **5** (mp 148—150°C).

*The Michael Reaction of 2,2'-Diiodo-9,9'-bifluorenylidene (**8**) with Fluorene (**1**).* A mixture of 2.32 g (0.004 mol) of **8**, 0.83 g (0.005 mol) of **1**, 28 m*l* of pyridine, and 3.0 g of potassium hydroxide in 2 m*l* of water was heated at 98—100°C for 8 hr in a sealed tube. The reaction mixture was then treated in a manner analogous to that described above to yield 0.90 g (30%) of **16** (mp 261—262°C (decomp.)) and 1.10 g (37%) of **17** (mp 281—282°C (decomp.)) from benzene and ethyl acetate. Anal for **16**. Found: C, 62.60; H, 3.07%. Calcd for $C_{39}H_{24}I_2$: C, 62.76; H, 3.24%. Mass (M^+): 746 *m/e*. For **17**. Found: C, 62.75; H, 3.47%. Calcd for $C_{39}H_{24}I_2$: C, 62.76; H, 3.24%. Mass (M^+): 746 *m/e*.

Although the compounds **16** and **17** are isomeric to each other, we have speculated on these structures by comparing the IR spectra, melting points, and relative intensities of the fragment ions in the mass spectra.

In addition, 0.08 g (10%) of **1** (mp 111—112.5°C) and 0.15 g (6%) of **5** (mp 149—150.5°C) were isolated by alumina column chromatography.

*The Michael Reaction of 2,2'-Diiodo-9,9'-bifluorenylidene (**8**) with 2-Iodofluorene (**2**).* A mixture of 2.32 g (0.004 mol) of **8**, 1.46 g (0.005 mol) of **2**, 28 m*l* of pyridine, and 1.5 g of potassium hydroxide in 2 m*l* of water was placed in a

sealed tube; then the mixture was heated in boiling water for 10 hr. The precipitate formed upon dilution with 400 ml of water was sublimed at 160°C. The sublimate afforded 0.15 g of **2** (mp 126—128°C) and 0.03 g of **5** (mp 146—147°C) by alumina-column chromatagraphy. The sublimation residue was recrystallized from ethyl acetate and then from benzene to afford 1.49 g (43%) of **18** (mp 281—282°C (decomp.)). Found: C, 54.06; H, 2.41%. Calcd for $C_{39}H_{23}I_3$: C, 53.70; H, 2.66%.

Further, 0.07 g of **8** (mp 258—261°C) was recovered from the mother solution.

*The Michael Reaction of 9,9'-Bifluorenylidene (**7**) with 2,7-Diiodofluorene (**3**).* A mixture of 2.2 g (1/150 mol) of **7**, 2.8 g (1/150 mol) of **3**, 28 ml of pyridine, and 0.3 g of potassium hydroxide in 2 ml of water was heated at 95—100°C for 2.5 hr. During this period, the reaction mixture turned dark and colorless crystals were deposited.

The crude product was recrystallized from benzene to afford 2.69 g of **19** (mp 286—288°C (decomp.)). The pyridine mother liquor was then poured into water, and the deposited product was separated by a combination of recrystallization, alumina-column chromatography, and vacuum sublimation to yield 1.00 g (total 3.69 g; 74%) of **19** (mp 287—288°C (decomp.)), 0.10 g (3%) of **21** (mp 307—307.5°C (decomp.)), 0.12 g of **6** (mp 205—207°C), 0.01 g of **4** (mp 81—82°C), 0.08 g of **3** (mp 213—214°C), and 0.13 g of **7** (mp 180—182°C). Anal for **19**. Found: C, 62.75; H, 3.15%. Calcd for $C_{39}H_{24}I_2$: C, 62.76; H, 3.24%. For **21**. Found: C, 46.86; H, 1.95%. Calcd for $C_{39}H_{22}I_4$: C, 46.93; H, 2.22%.

*The Michael Reaction of 2,7,2',7'-Tetraiodo-9,9'-bifluorenylidene (**9**) with Fluorene (**1**).* **1** (4.2 g, 0.025 mol) also underwent a similar reaction with **9** (4.2 g, 0.005 mol) in 112 ml of pyridine in the presence of potassium hydroxide (1.2 g; 1% for the solvent) in 8 ml of water at 95—100°C for 20 hr.

The following compounds were thus obtained; 0.47 g of **19** (mp 286—287°C (decomp.)), 0.09 g of **20** (mp 299—300°C (decomp.)), 0.17 g of **21** (mp 312—314°C (decomp.)), 0.02 g of **22** (mp 290—292°C (decomp.)), 0.89 g of **3** (mp 213—215°C), 0.23 g of **6** (mp 205—207°C), and 0.04 g of **4** (mp 83—84°C). In addition, 1.73 g of **1** (mp 113—114°C) and 0.03 g of **9** (mp 423—424°C (decomp.)) were recovered. Anal for **20**. Found: C, 46.84; H, 2.03%. Calcd for $C_{39}H_{22}I_4$: C, 46.93; H, 2.22%. For **21**. Found: C, 46.89; H, 2.31%. Calcd for $C_{39}H_{22}I_4$: C, 46.93; H, 2.22%. For **19**. Found: C, 63.11; H, 3.29%. Calcd for $C_{39}H_{24}I_2$: C, 62.76; H, 3.24%.

The **20** and **21** compounds are isomeric, and we estimated their structures by comparing the mass and IR spectra and melting points.

*The Michael Reaction of 2,7,2',7'-Tetraiodo-9,9'-bifluorenylidene (**9**) with 2,7-Diiodofluorene (**3**).* A 2.9-g portion of **3** was allowed to react with 1.11 g of **9** (mol. ratio 5/1), using 0.3 g of potassium hydroxide as a catalyst in 30 ml of pyridine for 55 hr. The reaction mixture was then worked up as usual. Thus, 0.14 g (9%) of **23** (mp 318—319°C (decomp.) and 1.00 g (90%) of recovered **9** (mp 424°C (decomp.)) were isolated. Also, 0.31 g (10%) of **6** (mp 207—207.5°C) and 2.20 g (76%) of **3** (mp 216—217°C) were obtained from the mother solution by alumina-column chromatography. Found for **23**: C, 37.70; H, 1.50%. Calcd for $C_{39}H_{20}I_6$: C, 37.47; H, 1.61%.

Under other conditions, **3** (1.67 g) was allowed to react with **9** (1.11 g) (mole ratio 3/1), using sodium ethoxide (10% for the solvent) in absolute ethanol (30 ml) for 40 hr; 0.66 g of **9** (mp 424°C (decomp.)) and a compound (mp 323—324°C (decomp.) (0.23 g)) were thus isolated. Found for compound with mp 323—324°C (decomp.): C, 37.63; H, 1.45%. Calcd for $C_{26}H_{14}I_4$: C, 37.44; H, 1.69%.

The IR spectrum of this compound resembles that of halogen-substituted 9,9'-bifluorenyl; hence, the compound is presumably a reduction product, 2,7,2',7'-tetraiodo-9,9'-bifluorenyl (**12**).

*The Ullmann Reaction of 2-Iodofluorene (**2**) and 2,7-Diiodofluorene (**3**).* *a)*: A mixture of 3.0 g of **2** and 6.0 g of activated copper bronze[18] was heated in a sealed tube at 150°C for 20 hr to give 0.15 g (9%) of **13** (mp 316°C (lit,[4d] mp 316.5—318°C)) and 0.36 g (22%) of **1** (mp 110—112°C).

In another reaction, in which a mixture of 1.5 g of **2**, 10 g of zinc-copper couple,[19] and 30 ml of dry xylene was refluxed for 19 hr, 0.225 g (27%) of **1** (mp 111—112.5°C) was isolated.

b): A mixture of 4.0 g of **3** and 8.0 g of a zinc-copper couple was treated in a sealed tube at 230°C for 20 hr to afford 0.25 g (15%) of **1** (mp 113—114.5°C).

*Hydrogenolyses of 2-Iodofluorene (**2**) and 2,7-Diiodofluorene (**3**).* *a)*: A suspension of 5.0 g of Raney nickel (W-7)[20] in 150 ml of ethanol containing 1.46 g of **2** was shaken under an atmospheric pressure of hydrogen at room temperature for 2 hr. The reaction mixture was then filtered from Raney nickel, and the nickel was washed with 100 ml of ethanol. The combined filtrate was concentrated to dryness under reduced pressure, and the residue was washed with water, dried, and recrystallized from ethanol to yield 0.73 g (88%) of **1** (mp 112—113°C).

b) A mixture of 2.09 g of **3**, 50 ml of tetrahydrofuran, and 10 g of Raney nickel was worked up in a manner similar to Method a) to give 0.70 g (84%) of **1** (mp 111—113°C).

*Reduction of 2-Iodofluorene (**2**) and 2,7-Diiodofluorene (**3**) with Lithium Aluminum Hydride.* *a)* To the stirring mixture of 0.38 g of lithium aluminum hydride and 40 ml of dry dioxane, was added, drop by drop, 2.92 g (0.01 mol) of **2** in 60 ml of dry dioxane at room temperature; the resulting solution was then refluxed for 4 hr. Upon concentration, the precipitate was decomposed with 100 ml of 10% hydrochloric acid, washed with water, dried, and recrystallized from ethanol; 1.36 g (47%) of recovered **2** (mp 124—125°C) and 0.84 g (51%) of **1** (mp 110—112°C (no halogen)) were thus obtained.

b) A 4.18-g portion (0.01 mol) of **3** was treated with 0.76 g of lithium aluminum hydride in 160 ml of dry tetrahydrofuran by the same procedure as in Method a); this afforded 0.48 g (29%) of **1** (mp 111—112°C), 1.43 g (49%) of **2** (mp 123—125°C), and 0.64 g (15%) of recovered **3** (mp 215—216°C).

*Reduction of 2-Iodofluorene (**2**) and 2,7-Diiodofluorene (**3**) with Hydriodic Acid.* *a)*: A mixture of 2.92 g (0.01 mol) of **2**, 5 ml of hydriodic acid, 2 g of red phosphorus, and 50 ml of acetic acid was refluxed for 22 hr. The resulting mixture was filtered, the filtrate was poured into 500 ml of water, and the precipitate was recrystallized from cyclohexane. This compound was confirmed to be **1** (mp 112—114°C; 1.61 g 97%).

b) A 2.09-g portion (0.005 mol) of **3** in 150 ml of acetic acid was allowed to react with 5 ml of hydriodic acid and 2 g of red phosphorus for 22 hr to yield 0.41 g (49%) of **1** (mp 111—113°C), 0.15 g (10%) of **2** (mp 123—125°C), and 0.57 g (27%) of recovered **3** (mp 213—215°C).

18) R. C. Fuson and E. A. Cleveland, "Organic Syntheses", Coll. Vol. III, p. 339 (1955).
19) E. Legoff, *J. Org. Chem.*, **29**, 2048 (1964).
20) H. Adkins and A. A. Pavlic, *J. Amer. Chem. Soc.*, **68**, 1471 (1946).

A 3.24-g portion (0.01 mol) of 2,7-dibromofluorene was worked up as in the case of **3**, but only 3.16 g (98%) of the starting material was recovered.

*Reaction of 2-Iodofluorene (**2**) with Ethylmagnesium Bromide.* A solution of ethylmagnesium bromide (from 0.02 mol of ethyl bromide and 0.04 g atom of magnesium) in ether (40 m*l*) was added to a solution of 2.92 g (0.01 mol) of **2** in 25 m*l* of dry tetrahydrofuran, and the mixture was gently refluxed for 5 hr. The reaction mixture was then worked up as usual, and the crude product was recrystallized from ethanol to yield 0.09 g (6%) of **13** (mp 316—318°C (from benzene)) and 1.03 g of recovered **2** (mp 124—126°C). The ethanol mother liquor was analyzed by means of gas chromatography; 0.16 g (10%) of **1**, 0.04 g (2%) of 2-ethylfluorene, and 0.25 g (total 1.28 g; 44%) of **2** were confirmed.

Reaction of 2-Fluorenylmagnesium Iodide. a) With 9-bromofluorene: To magnesium, which had been activated by ethylmagnesium iodide, in dry tetrahydrofuran (25 m*l*) was added a solution of 25 m*l* of dry tetrahydrofuran containing 2.92 g of **2**; this mixture was refluxed by stirring for 23 hr. Then, a mixture of 2.45 g (0.01 mol) of 9-bromofluorene and 25 m*l* of dry tetrahydrofuran was added, drop by drop, to the foregoing Grignard solution, and the mixture was refluxed for 3 hr.

The reaction mixture was worked up as usual; consequently, 0.52 g (32%) of **10** (mp 242—243°C), 0.46 g (28%) of **13** (mp 312—314°C), and 0.25 g of **1** (mp 113—115°C) were isolated. Found for **13**: C, 94.34; H, 5.41%. Calcd for $C_{26}H_{18}$: C, 94.55; H, 5.45%.

The sodium bichromate oxidation of **13** gave **14** (mp 290—291°C; IR (>C=O): 1710 cm^{-1}; lit,[4d] mp 295—297°C); this compound was identical in all respects with the product obtained by the Ullmann reaction of **5**.

*b) With **4***: 2-Fluorenylmagnesium iodide was prepared in the same manner as has been described above. A 1.80-g portion of **4** in 20 m*l* of tetrahydrofuran was added to the resulting Grignard solution, and the mixture was refluxed for 2 hr to afford 0.13 g (8%) of **26** (mp 224—225°C). In addition, a trace amount of a compound (mp 252—254°C (decomp.)) was isolated, but its structure is not clear at present.

*Reaction of 2-Iodofluorene (**2**) and 2,7-Diiodofluorene (**3**) with Potassium Cyanide-Cupric Cyanide in DMF. a)*: A mixture of 2.92 g of **2**, 1.30 g of potassium cyanide, and 1.79 g of cupric cyanide in 40 m*l* of freshly-distilled DMF was refluxed for 25 hr. During the period, the reaction mixture turned from brown to dark green.

The mixture was then cooled and poured into 500 m*l* of cold water, and 50 m*l* of hydrochloric acid was added. The precipitate was collected and sublimed *in vacuo* at 120°C. The sublimate was recrystallized from 20 m*l* of cyclohexane to yield 1.15 g (60%) of pure 2-cyanofluorene (mp 91—92°C) as colorless needles. (Lit, mp 88°C,[16a] 100.5—101.5°C,[16b] 105°C[16c]). Found: C, 87.82; H, 4.65; N, 7.49%. Calcd for $C_{14}H_9N$: C, 87.93; H, 4.74; N, 7.33%. IR (-CN): 2245 cm^{-1}. Mass: 191 (M^+); 186; 149 *m/e*.

The residual part was further sublimed at 170°C; the sublimate yielded 0.03 g (1%) of 2-cyanofluorenone (mp 175—177°C) as yellow needles (from benzene). Found: C, 82.13; H, 3.38; N, 6.47%. Calcd for $C_{14}H_7NO$: C, 81.94; H, 3.44; N, 6.83%. IR: (-CN) 2245; (>C=O) 1715 cm^{-1}. Mass (M^+): 205 *m/e*.

b): A mixture of 2.09 g of **3**, 1.30 g of potassium cyanide, and 1.79 g of cupric cyanide in 50 m*l* of DMF was refluxed for 25 hr. When the reaction products were sublimed *in vacuo* at 200°C, the sublimate afforded 0.11 g of 2,7-dicyanofluorene (mp 285°C), upon recrystallization from benzene. Found: C, 83.07; H, 4.05; N, 12.70%. Calcd for $C_{15}H_8N_2$: C, 83.32; H, 3.73; N, 12.95%. IR (-CN): 2245 cm^{-1}. Mass (M^+): 216 *m/e*.

The residue of the sublimation was extracted with four 40-m*l* portions of benzene, and 0.12 g of 2,7-dicyanofluorenone (mp 340°C (decomp.)) was obtained from the benzene extract. Found: C, 78.36; H, 2.87%. Calcd for $C_{15}H_6N_2O$: C, 78.26; H, 2.63%. IR: (-CN) 2245; (>C=O) 1715 cm^{-1}.