The Michael Reactions of Chloro-substituted-9,9'-bifluorenylidenes with Fluorenes and a Comparison with Analogous Halogen Compounds[1)]

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The Michael reactions of 2-chloro- and 2,7-dichloro-9,9'-bifluorenylidenes with fluorenes were investigated. Structures of these products were confirmed by syntheses through the well-established reactions of 9-lithiofluorenes and 9-bromo-9,9'-bifluorenyls. The formation of some abnormal compounds is explained by intermediary formation of 2,7-dichloro-9,9'-bifluorenylidene from the reaction of 9,9'-bifluorenylidene with 2,7-dichlorofluorene as with the bromo-derivatives. The corresponding fluoro- and iodo-series gave predominantly normal addition products. These differences are explained in terms of the inductive and steric effects of the halogen substituents.

The Michael reactions of chloro-substituted-9,9'-bifluorenylidenes with fluorenes, and the syntheses of some new chloro-derivatives were investigated. 2,7-Dibromo-substituted substrates afforded a large amount of abnormal 2,7,2'',7''-tetrabromo-9,9' : 9',9''-terfluorenyl and a small amount of bromine-free 9,9' : 9',9''-terfluorenyl (mp 293 °C (dec), **24**).[2)] However, the fluoro-[3)] and iodo-[4)] derivatives underwent predominantly normal additions.

In the present paper, the substituent effect of chlorine atoms in these Michael reaction is examined and compared with the effects of other halogen atoms in the crowded molecule 9,9' : 9',9''-terfluorenyl.

The reaction of 9,9'-bifluorenylidene (**7**) with 2,7-dichlorofluorene (**5**) gave the expected 2,7-dichloro-9,9' : 9',9''-terfluorenyl (**19**) and abnormal compounds 2,7,2'',7''-tetrachloro-9,9' : 9',9''-terfluorenyl(**22**) and **24**. The pathway of the reaction may be similar to that of the bromo-derivatives in which 2,7-dibromo-9,9'-bifluorenylidene is one of the intermediates.

TABLE 1. MICHAEL REACTION OF 2-SUBSTITUTED 9,9'-BIFLUORENYLIDENES WITH FLUORENES

Reactants g		React. conditions			Products g(%)				Recovered g	
9,9'-Bifluorenylidene	Fluorene	Solvent ml	Catalyst g	Time hr					9,9'-Bifluorenylidene	Fluorene
7	**3**				**14**	**4**	**2**		**7**	**3**
3.28	2.01	EtOH 30	NaOEt 1.5	5	4.63 (88)	0.02			0.11	0.08
3.28	2.01	Py. 30	KOH 0.3	15	3.15 (60)	0.01	0.02		0.60	0.25
3.28	2.01	Py. 30	KOH 3.0	5	4.93 (93)	0.01	trace			
3.28	3.01	Py. 30	KOH 3.0	5	5.26 (99)	0.005				0.75
4.92	2.01	Py. 30	KOH 3.0	5	5.25 (99)		0.10		0.42	
8	**1**				**16**	**4**				**1**
3.97	1.66	Py. 30	KOH 0.3	5	5.00 (79)	0.03				0.02
3.97	1.66	Py. 30	KOH 3.0	5	5.22 (93)	0.02				0.02
3.97	3.32	Py. 30	KOH 3.0	5	5.35 (95)	0.03				1.60
8	**3**				**18**	**25**	**12**	**4**		
1.99	1.01	EtOH 30	NaOEt 1.5	5	1.77 (59)	0.14	0.30	0.02		
1.99	1.01	Py. 30	KOH 3.0	5	2.68 (89)			0.05		
9	**1**				**14**	**15**	**2**			**1**
1.45	0.83	Py. 15	KOH 0.15	5	1.17 (58)	0.73 (36)	0.02			0.13
9	**3**				**16**	**17**	**4**			**3**
1.45	1.00	Py. 15	KOH 0.15	5	0.45 (22)	0.69 (34)	0.03			0.08

a) Found for **14**: C, 88.29; H, 4.63%. For **15**: C, 88.75; H, 4.66%. For **16**: C, 82.91; H, 4.21%. For **17**: C, 83.44; H, 4.19%. For **18**: C, 78.48; H, 3.91%.

Results and Discussion

Various normal and abnormal chloro-substituted-9,9′ : 9′,9″-terfluorenyls and elimination products were obtained by the reaction of 9,9′-bifluorenylidenes with fluorenes, as shown in Tables 1 and 2.

These reactions of chloro-derivatives afforded exclusively normal products in the presence of sodium carbonate or sodium ethoxide, but the yield of abnormal products in the reactions of **7** with **5** and of 2,7,2′,7′-tetrachloro-9,9′-bifluorenylidene (**10**)[5] with fluorene (**1**) increased with increasing concentration of potassium hydroxide in pyridine.

Table 2. Michael reaction of 2,7-disubstituted 9,9′-bifluorenylidenes with fluorenes

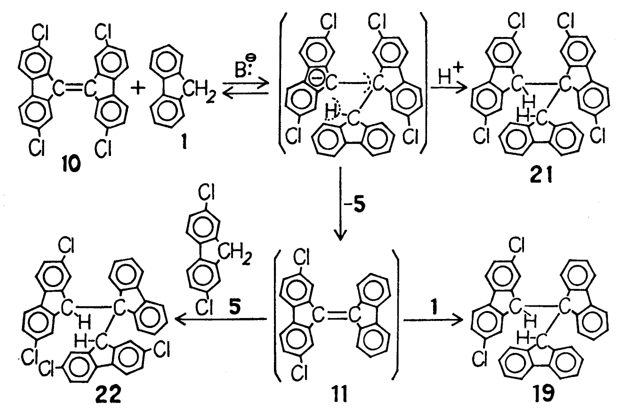
Reactants g		React. Conditions			Products g(%)						Recovered g	
9,9′-Bifluorenylidene	Fluorene	Solvent (30 ml)	Catalyst g	Time hr							9,9′-Bifluorenylidene	Fluorene
7	**5**				**19**	**22**	**24**	**1**	**2**	**6**	**7**	**5**
2.2	1.6	EtOH	NaOEt 0.3	4	2.31 (61)				trace			
2.2	1.6	Py.	KOH 0.015	40	0.27 (7)	0.17		0.09	0.05	0.03	0.97	0.16
2.2	1.6	Py.	KOH 0.3	3	0.57 (15)	1.35		0.21	0.09	0.16		
1.1	1.6	Py.	KOH 0.3	3	0.34 (18)	0.48		0.09	0.04	0.08		0.16
3.3	1.6	Py.	KOH 0.3	3	0.37 (10)	1.15	0.20	0.07	0.06	0.07	0.53	
10	**1**				**21**	**22**	**19**	**5**	**6**	**2**	**10**	**1**
2.33	2.49	Py.	Na_2CO_3 1.5	200	1.97 (62)				0.02	trace	0.32	1.85
2.33	2.49	Py.	KOH 0.15	9	1.54 (49)	0.23	0.40	0.26	0.03	0.01		1.74
2.33	2.49	Py.	KOH 0.9	7	0.19 (6)	0.67	0.55	0.39	0.01	trace		1.52
2.33	0.83	Py.	KOH 0.9	7		1.67	0.10	trace	0.07	trace	0.11	0.05
10	**5**				**23**	**26**	**6**				**10**	**5**
1.86	1.6	EtOH	NaOEt 1.5	50	2.39 (86)	0.19	0.01				0.03	0.60
1.86	1.6	Py.	KOH 1.5	3	2.64 (94)		0.12					0.49
11	**1**				**19**	**20**	**2**	**6**				**1**
2.4	1.13	Py.	KOH 0.3	1/4	2.33 (69)	0.79 (23)	0.04	0.06				0.10
11	**5**				**22**	**6**						**5**
2.4	1.6	Py.	KOH 0.3	1/4	3.56 (93)	0.03						0.08

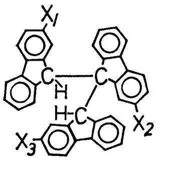
a) Found for **19**: C, 83.34; H, 4.22%. For **20**: C, 83.14; H, 4.06%. For **21**: C, 74.22; H, 3.63%. For **22**: C, 74.21; H, 3.39%. For **23**: C, 67.10; H, 3.13%. For **26**: C, 67.95; H, 2.56%.

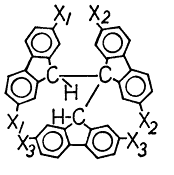
Table 3. Michael reaction of 9,9′-bifluorenylidene (**7**) with 2,7-dihalogenofluorene

Reactants (g)		9,9′ : 9′,9″-Terfluorenyls g(%); (mp) °C			1	2	2,7-Dihalogenofluorenone
7	Fluorene	2,7-Dihalogeno-	2,7,2″,7″-Tetrahalogeno	**24**	g	g	g
3.28	2,7-Difluoro- 2.02	5.01(95); 285—286 (dec)					0.07
3.28	2,7-Dichloro- 2.35	2.66(47); 285—287 (dec)	1.69; 314—315 (dec)	0.26; 292—293 (dec)	0.02	trace	
3.28	2,7-Dibromo- 3.24	2.30(35); 285—286 (dec)	2.60; 313—314 (dec)	0.77; 292—293 (dec)	0.05		0.01
3.28	2,7-Diiodo 4.18	6.40(86); 287—289 (dec)	0.10; 316—318 (dec)			0.04	0.10

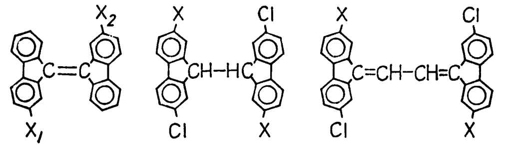
a) A mixture of 0.01 mol of reactants, 28 ml of pyridine, 0.3 g of KOH in 2 ml of water was heated in a sealed tube at 99—100 °C for 3 hr.







14 (X_1=Cl, X_2=X_3=H)
15 (X_2=Cl, X_1=X_3=H)
16 (X_1=X_2=Cl, X_3=H)
17 (X_1=X_3=Cl, X_2=H)
18 (X_1=X_2=X_3=Cl)
20 (X_2=Cl, X_1=X_3=H)
23 (X_1=X_2=X_3=Cl)
24 (X_1=X_2=X_3=H)



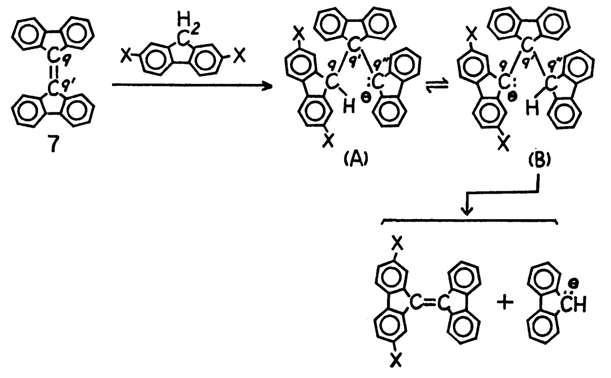
7 (X_1=X_2=H)
8 (X_1=X_2=Cl)
9 (X_1=Cl, X_2=H)
12 (X=H)
13 (X=Cl)
25 (X=H)
26 (X=Cl)

Scheme 1.

The structures of the new addition compounds were confirmed by syntheses through the interconversion reactions between 9-lithiofluorenes and 9-bromo-9,9′-bifluorenyls.

The Michael reaction of **7** with 2,7-dihalofluorene was carried out in order to examine the effects of different halogen substituents. It is noteworthy that the reaction of **7** with **5** gave significant amounts of abnormal compounds as with the corresponding bromo-derivative: however, 2,7-difluorofluorene gave only the expected compound, and the iodo-derivative afforded chiefly normal product. These irregular results are illustrated in Table 3.

In the primary addition, the overcrowded carbanion (A) (X=Cl) is formed by an attack of 2,7-dichloro-9-fluorenyl ion on the 9-position of the twisting central double bond in **7**. Carbanion (B) may be formed by intramolecular proton-transfer in (A), thus we propose the equilibrium shown in Scheme 2:

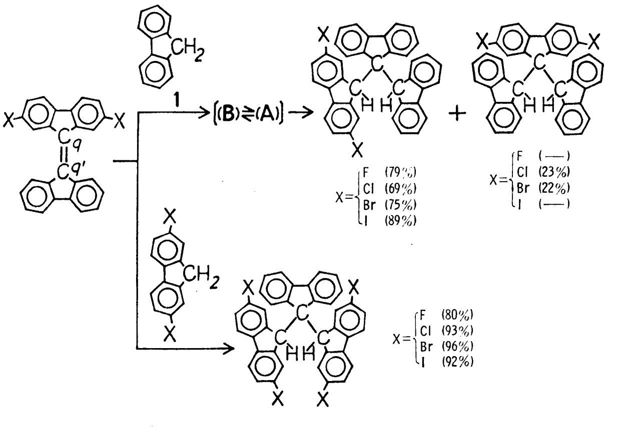


Scheme 2.

The ions (A) and/or (B) are transformed to the normal compound **19** by protonation.

The formation of the abnormal compounds can be explained by a series of reactions: elimination, re-addition, and protonation. Compound 2,7-dichloro-9,9′-bifluorenylidene (**11**) and 9-fluorenyl ion are probably formed by fission of the 9′-9″ carbon-carbon bond in ion (B). Subsequently, the secondary addition product **22** may be obtained by the nucleophilic attack of the 2,7-dichloro-9-fluorenyl ion on the highly-polarized **11**, followed by protonation. The tertiary product **24** could be formed by further reaction of **7** with a fragmentary 9-fluorenyl ion.

The stable abnormal compound **22** was obtained as one of the reaction products of three reactions: **7** with **5**, **10** with **1**, and also **11** with **5**. The reactive **11** which played an important role in the formation of **22** was not isolated in these experiments.[6] In this connection, Scheme 3 shows the reactions of halogen analogues of **11** with fluorenes.



Scheme 3.

From these findings, the 9-carbon atom on **11** is apparently more electronegative than the 9′-carbon due to the inductive effect of the two substituents.[7] The reaction of **11** with **5** gave exclusively **22** instead of 2,7,2′,7′-tetrachloro-9,9′ : 9′,9″-terfluorenyl (**21**). The formation of **22** can be explained by the steric effect in addition to the inductive effect: that is, the mutually repulsive 2,7- and 2″,7″-dichlorofluorenyl groups are placed as far from one another as possible. Therefore, the most stable compound, **22** is formed so as to minimize the steric hindrance.

Isomers **19** and 2′,7′-dichloro-9,9′ : 9′,9″-terfluorenyl (**20**) were obtained by the reaction of **11** with **1**, but no **20** was isolated by the reaction of **10** with **1**. This can be ascribed to the greater reactivity of **5** compared to **1** and to the low concentration of fragmentary **11** in the latter reaction.

The formation of the expected compound by reaction of **7** with 2,7-difluorofluorene can be explained as follows. The greater inductive effect of the two fluorine atoms will stabilize the ion (B) (X=F) (Scheme 2), and hence prevent the dissociation of the ion (B) into 2,7-difluoro-9,9′-bifluorenylidene and 9-fluorenyl ion. Consequently, protonation of ions (A) and/or (B) may occur readily (see Table 3). Actually, the expected fluoro compound was obtained by the reaction of 2,7-difluoro-9,9′-bifluorenylidene with **1** (Scheme 3).

The influence of the inductive effect of the two iodine atoms in the ion (A) (X=I) is smaller than those of other halogen atoms. Since, in addition to this effect, the 9-carbon atom of ion (A) cannot easily approach the 9″-carbanion on account of the steric repulsion of the bulky two iodine atoms attached to 9-fluorenyl group, intramolecular proton-transfer of (A) to (B) (X=I) is hindered (Scheme 2). Therefore, the normal iodo compound was formed with ease *via* the 9″-carbanion (A) (see Table 3).

The inductive influence of iodine atoms in 2,7-diiodo-9,9′-bifluorenylidene may be smaller than those of other halogen atoms. However, the reaction of 2,7-diiodo-9,9′-bifluorenylidene with **1** afforded predominantly 2,7-diiodo-9,9′ : 9′,9″-terfluorenyl. This indicates that no attack of 9-fluorenyl carbanion on the 9-position of the acceptor occurred due to the steric repulsion between the 9-fluorenyl group and the bulky 2,7-diiodo-9-fluorenylidene.

Consequently, the inductive effects and steric influences of chlorine and bromine atoms in (A) and (B) (X=Cl, Br) are intermediate between those of fluorine and iodine atoms (X=F, I). Thus, in the chloro- and bromo-substituted compounds, both normal and abnormal compounds could be formed in these crowded molecules.

Experimental[8]

*Syntheses of 9,9′-Bifluorenylidenes. 2-Chloro-9,9′-bifluorenylidene (**9**)*: **9** was produced from 2-chloro-9-bromo-9,9′-bifluorenyl or 2-chloro-9′-bromo-9,9′-bifluorenyl by the reaction with potassium hydroxide-methanol in acetone at 2—5 °C, with yields of 60% and 70%, respectively, mp 145—147 °C. Found: C, 85.79; H, 3.83%. Calcd for $C_{26}H_{15}Cl$: C, 86.06; H, 4.17%.

Complexes with 2,4,7-trinitrofluorenone, mp 219—220 °C. Found: C, 62.50; H, 2.32; N, 8.27%. Calcd for $C_{52}H_{25}N_6O_{14}Cl$: C, 62.88; H, 2.54; N, 8.46%.

Dehydration of 2-chloro-9′-hydroxy-9,9′-bifluorenyl by sulfuric acid in acetic acid afforded **9** in 25% yield, accompanied by 2-chloro-9′-acetoxy-9,9′-bifluorenyl (8%), mp 211—211.5 °C. Found: C, 79.37; H, 4.39%. Calcd for $C_{28}H_{19}O_2Cl$: C, 79.52; H, 4.53%. IR (>C=O): 1745 cm^{-1}.

*2,2′-Dichloro-9,9′-bifluorenylidene (**8**)*: 2-Chloro-9-bromofluorene was allowed to react with 1.1 mol equivalent of methanolic sodium hydroxide in acetone at 5—7 °C: red needles of **8** were formed (85%), mp 250 °C (Lit.,[9] mp 258—261 °C). Found: C, 78.64; H, 3.40%. Calcd for $C_{26}H_{14}Cl_2$: C, 78.60; H, 3.55%.

*2,7-Dichloro-9,9′-bifluorenylidene (**11**)*: A mixture of 4.1 g of 2,7-dichloro-9′-hydroxy-9,9′-bifluorenyl, 150 ml of acetic acid, and 2 ml of concentrated sulfuric acid was refluxed for 20 min. Red needles **11** were obtained in 94% yield after recrystallization from acetone, mp 227—228 °C. Found: C, 78.87; H, 3.61%.

*2,7,2′,7′-Tetrachloro-9,9′-bifluorenylidene (**10**)*: **10**, mp 426—428 °C (dec), was synthesized in 84% yield from 2,7-dichloro-9-bromofluorene in a similar manner to **8**. Found: C, 66.69; H, 2.65%. Calcd for $C_{26}H_{12}Cl_4$: C, 66.99; H, 2.59%.

In another method, the reaction mixture obtained as described above was heated for 20 min, and allowed to stand overnight. The resulting mixture was worked up to give **10** in 34% yield, mp 428 °C (dec), 3% of 2,7,2′,7′,2″,7″-hexachloro-9,9′ : 9′,9″-terfluorenyl (**23**), mp 319—320 °C (dec), and 26% of 2,7-dichlorofluorenone (**6**), mp 188—189 °C. Found for **23**: C, 66.92; H, 3.15%. Calcd for $C_{39}H_{20}Cl_6$: C, 66.79; H, 2.87%.

Synthesis of 2,7-Dichloro-9,9′-bifluorenyl. Four milliliters of concentrated hydrochloric acid was added to a boiling mixture of 0.2 g of **11**, 50 ml of acetic acid, and 1.0 g of zinc dust and the mixture was refluxed for 30 min. After filtration of the hot colorless reaction mixture, the dried precipitate was recrystallized from benzene to afford 0.19 g (95%) of colorless needles of 2,7-dichloro-9,9′-bifluorenyl, mp 263—264 °C. Found: C, 78.22; H, 4.01%. Calcd for $C_{26}H_{16}Cl_2$: C, 78.21; H, 4.04%.

*2,2′-Dichloro-9,9′-bifluorenyl (**12**)*:[10] This compound was synthesized from **8** under similar conditions to those for 2,7-dichloro-9,9′-bifluorenyl. Yield 99%, mp 275—276 °C. Found: C, 78.23; H, 3.89%.

2-Chloro-9,9′-bifluorenyl: **9** was reduced by the standard procedure. Yield 90%, mp 237—238 °C. Found: C, 85.82;, H, 4.37%. Calcd for $C_{26}H_{17}Cl$: C, 85.59; H, 4.70%.

*2,7,2′,7′-Tetrachloro-9,9′-bifluorenyl (**13**)*: The compound was obtained from **10**. Yield 90%, mp 300—301 °C. Found: C, 66.36; H, 2.92%. Calcd for $C_{26}H_{14}Cl_4$: C, 66.70; H, 3.01%.

*Syntheses of Bis(4-chloro-2,2′-biphenylylene)-1,3-butadiene (**25**) and Bis(4,4′-dichloro-2,2′-biphenylylene)-1,3-butadiene (**26**).*[11] A mixture of 1.00 g (5 mmol) of 2-chlorofluorene (**3**), 45 ml of ethanol, and 2.5 g of potassium hydroxide in 5 ml of water was refluxed under a gentle stream of air for 20 hr. The precipitate was recrystallized from pyridine to give 0.66 g (62%) of orange needles **25**, mp 386—388 °C (dec). Found: C, 79.75; H, 3.64%. Calcd for $C_{28}H_{16}Cl_2$: C, 79.44; H, 3.81%.

In addition, a small amount of 2-chlorofluorenone (**4**), mp 123—124 °C, was obtained from the ethanol mother solution.

Compound **26** was obtained from **5** in 55% yield, red needles, mp 392—393 °C (dec). Found: C, 68.23; H, 2.59%. Calcd for $C_{28}H_{14}Cl_4$: C, 68.32; H, 2.87%.

Syntheses of 9-Hydroxy-9,9′-bifluorenyls and 9-Bromo-9,9′-bifluorenyls. General procedure: 9-Hydroxy-9,9′-bifluorenyl was prepared under a slow stream of oxygen-free nitrogen in the usual way. To 9-lithiofluorene (obtained by the reaction of 0.035 mol of fluorene with *n*-butyl lithium) in xylene was added 0.03 mol of fluorenone (**2**), and the mixture was refluxed for 30 min. After cooling, the reaction mixture was hydrolyzed with aqueous ammonium chloride, washed with water, dried, and concentrated to dryness *in vacuo*. The precipitate was recrystallized from benzene, cyclohexane, or a mixture of both.

9-Bromo-9,9′-bifluorenyl was synthesized by the reaction of 9-hydroxy-9,9′-bifluorenyl with dry hydrogen bromide in acetic acid below 25 °C

1): 2-Chloro-9-hydroxy-9,9′-bifluorenyl, 97% yield, mp 184—186 °C. IR (-OH): 3540 cm^{-1} (sharp). Found: C, 81.97; H, 4.60%. Calcd for $C_{26}H_{17}OCl$: C, 81.99; H, 4.50%.

2-Chloro-9-bromo-9,9′-bifluorenyl, 86%. mp 180—182 °C (dec). Found: C, 70.57; H, 3.46%. Calcd for $C_{26}H_{16}ClBr$: C, 70.36; H, 3.64%.

2): 2-Chloro-9′-hydroxy-9,9′-bifluorenyl, 95%, mp 177—179 °C. IR (-OH): 3280 cm^{-1}. Found: C, 82.22; H, 4.49%.

2-Chloro-9′-bromo-9,9′-bifluorenyl, 94%, mp 153—155 °C (dec). Found: C, 70.51; H, 3.48%.

3): 2,2′-Dichloro-9-hydroxy-9,9′-bifluorenyl, 81%, mp 182—183 °C. IR (-OH): 3300 cm.$^{-1}$ Found: C, 75.44; H, 3.69%. Calcd for $C_{26}H_{16}OCl_2$: C, 75.19; H, 3.88%.

2,2′-Dichloro-9-bromo-9,9′-bifluorenyl, 83%, mp 184—185 °C (dec). Found: C, 65.67; H, 3.03%. Calcd for $C_{26}H_{15}Cl_2Br$: C, 65.30; H, 3.16%.

4): 2,7-Dichloro-9-hydroxy-9,9′-bifluorenyl, 59%, mp 197—198 °C. IR (-OH): 3265 cm^{-1}. Found: C, 74.85; H, 4.03%.

2,7-Dichloro-9-bromo-9,9′-bifluorenyl, 72%, mp 217—219 °C (dec). Found: C, 65.47; H, 3.32%.

5): 2,7-Dichloro-9′-hydroxy-9,9′-bifluorenyl, 44%, mp 189—191 °C. IR (-OH): 3550 cm^{-1} (sharp). Found: C, 75.39; H, 3.85%.

2,7-Dichloro-9′-bromo-9,9′-bifluorenyl, 83%, mp 201—202 °C (dec). Found: C, 65.76; H, 3.26%.

6): 2,7,2′,7′-Tetrachloro-9-hydroxy-9,9′-bifluorenyl, 51%, mp 227—229 °C. IR (-OH): 3555 cm^{-1} (sharp). Found: C, 64.37; H, 2.80%. Calcd for $C_{26}H_{14}OCl_4$: C, 64.49; H, 2.91%.

2,7,2′,7′-Tetrachloro-9-bromo-9,9′-bifluorenyl, 41%, mp 215—217 °C (dec). Found: C, 57.47; H, 2.35%. Calcd for $C_{26}H_{13}Cl_4Br$: C, 57.08; H, 2.40%.

Formation of 9,9′ : 9′,9″-Terfluorenyls by Lithium-Halogen Interconversion Reaction. General Procedure: To a 9-lithiofluorene solution (prepared from 0.014 g-atom of lithium chips, 7 mmol of *n*-butyl bromide, and 7 mmol of fluorene) was added 4 mmol of 9-bromo-9,9′-bifluorenyl in xylene at 5—10 °C over a period of about 1 hr. After refluxing for 1 hr, the reaction mixture was worked up as usual.

*2-Chloro-9,9′ : 9′,9″-terfluorenyl (**14**)*: This compound was synthesized from **3** and 9-bromo-9,9′-bifluorenyl, mp 255—257 °C (dec) (benzene-ethanol). Found: C, 88.64; H, 4.54%. Calcd for $C_{39}H_{25}Cl$: C, 88.54; H, 4.76%.

*2′-Chloro-9,9′ : 9′,9″-terfluorenyl (**15**)*: From **1** and 2-chloro-9-bromo-9,9′-bifluorenyl, mp 271—272 °C (dec) (ethyl acetate). Found: C, 88.66; H, 4.53%.

*2,2′-Dichloro-9,9′ : 9′,9″-terfluorenyl (**16**)*: From **3** and 2-chloro-9-bromo-9,9′-bifluorenyl, mp 253—254 °C (dec) (benzene-ethanol) Found: C, 83.01; H, 4.36%. Calcd for $C_{39}H_{24}Cl_2$: C, 83.13; H, 4.29%.

*2,2″-Dichloro-9,9′ : 9′,9″-terfluorenyl (**17**)*: From **3** and 2-chloro-9′-bromo-9,9′-bifluorenyl, mp 275—276 °C (dec) (ethyl acetate). Found: C, 83.43; H, 4.15%.

*2,2′,2″-Trichloro-9,9′ : 9′,9″-terfluorenyl (**18**)*: From **3** and 2,2′-dichloro-9-bromo-9,9′-bifluorenyl, mp 279—280 °C (dec) (ethyl acetate). Found: C, 78.02; H, 3.69%. Calcd for $C_{39}H_{23}Cl_3$: C, 78.34; H, 3.88%.

*2,7-Dichloro-9,9′ : 9′,9″-terfluorenyl (**19**)*: From **5** and 9-bromo-9,9′-bifluorenyl, mp 285—287 °C (dec) (ethyl acetate). Found: C, 83.10; H, 4.25%.

*2′,7′-Dichloro-9,9′ : 9′,9″-terfluorenyl (**20**)*: From **1** and 2,7-dichloro-9-bromo-9,9′-bifluorenyl, mp 305—306 °C (dec) (benzene). Found: C, 83.38; H, 4.47%.

*2,7,2′,7′-Tetrachloro-9,9′ : 9′,9″-terfluorenyl (**21**)*: From **5** and 2,7-dichloro-9-bromo-9,9′-bifluorenyl, mp 296—297 °C (dec) (ethyl acetate). Found:,C, 74.26; H, 3.46%. Calcd for $C_{39}H_{22}Cl_4$: C, 74.07; H, 3.51%.

*2,7,2″,7″-Tetrachloro-9,9′ : 9′,9″-terfluorenyl (**22**)*: From **5** and 2,7-dichloro-9′-bromo-9,9′-bifluorenyl, mp 314—315 °C (dec) (pyridine). Found: C, 74.38; H, 3.71%.

*2,7,2′,7′,2″,7″-Hexachloro-9,9′ : 9′,9″-terfluorenyl (**23**)*: From **5** and 2,7,2′,7′-tetrachloro-9-bromo-9,9′-bifluorenyl, mp 320 °C (dec) (benzene). Found: C, 66.91; H, 3.01%. Calcd for $C_{39}H_{20}Cl_6$: C, 66.79; H, 2.87%.

*Michael Reaction of 2,7-Dichloro-9,9′-bifluorenylidene (**11**) with 2,7-Dichlorofluorene (**5**). Typical Procedure*: A mixture of 2.4 g (6 mmol) of **11**, 1.6 g (6.6 mmol) of **5**, 28 ml of pyridine, and 0.3 g (1% for solvent) of potassium hydroxide in 2 ml of water was heated in a sealed tube at 98—100 °C for 15 min. During the heating, the color turned from red to dark green, and colorless crystalline was deposited.

Upon cooling, the reaction mixture was added to 400 ml of water, and the deposited material was filtered and sublimed at 160 °C *in vacuo*. The residual part after sublimation was recrystallized from pyridine to afford **22** in 3.56 g (93%), mp 314—315 °C (dec).

The sublimate was chromatographed on alumina with benzene solvent. The elute was concentrated under reduced pressure, and the residue was recrystallized from ethanol to give **5** in 0.08 g yield, mp 123—124 °C: 0.03 g of **6**, mp 186—187 °C (from ethanol), was isolated from the yellow band on the column.

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References

1) Studies on Fluorene Derivatives. XXX. Part XXIX of this series: M. Minabe and K. Suzuki, This Bulletin, **46**, 1573 (1973).

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

3) M. Minabe, A. Tanaka, M. Wakui and K. Suzuki, *ibid.*, **44**, 1614 (1971).

4) M. Minabe and K. Suzuki, *ibid.*, **45**, 3196 (1972).

5) J. Schmidt and H. Wagner, *Ann.*, **387**, 147 (1912).

6) The Michael reaction of **7** with 2-bromofluorene afforded a trace of 2-bromo-9,9′-bifluorenylidene. See K. Suzuki and M. Fujimoto, This Bulletin, **37**, 1833 (1964).

7) For example, the addition of hydrogen bromide to 2,7-dibromo-9,9′-bifluorenylidene gave exclusively 2,7,9′-tribromo-9,9′-bifluorenyl, but 2,7,9-tribromo- (63%) and 2,7,9′-tribromo-9,9′-bifluorenyl (14%) were obtained in the presence of peroxide.

8) All the melting points are uncorrected.

9) D. Bethell, A. F. Cockerill, and D. B. Frankham *J. Chem. Soc., B*, **1967**, 1287.

10) E. Bergmann, H. Hoffmann, and D. Winter, *Ber.*, **66B**, 46 (1933).

11) A Sieglitz and J. Schatzkes, *ibid.*, **54**, 2072 (1921).