The Michael Reaction of Fluoro-substituted-9,9′-Bifluorenylidenes and -Fluorenes, and the Syntheses of Some Related Compounds[1]

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The Michael reaction of fluoro-substituted 9,9′-bifluorenylidenes and fluorenes was carried out; the normal addition products, fluoro-substituted tribiphenylenepropanes, were obtained, but no abnormal product was isolated. Some new fluoro-substituted-fluorenes, -9,9′-bifluorenylidenes, -9,9′-bifluorenyls and -α,δ-dibiphenylenebutadienes, were synthesized. The structures of the fluoro-substituted tribiphenylenepropanes were confirmed by the lithium-halogen interconversion reaction of 9-lithiofluorenes and 9-bromo-9,9′-bifluorenyls. The pyrolyses of fluoro-substituted tribiphenylenepropanes afforded fluoro-substituted or nonfluoro-substituted-9,9′-bifluorenylidenes, -9,9′-bifluorenyls, -fluorenes, and -fluorenones. Differential scanning calorimetry was applied to fluoro-substituted-9,9′-bifluorenyls and -tribiphenylenepropanes.

The Michael reaction[2] of 9,9′-bifluorenylidene (**4**) with 2,7-dibromofluorene gave the normal product, 2′,7′-dibromotribiphenylenepropane, together with the abnormal 2′,7′,2″,7″-tetrabromotribiphenylenepropane and tribiphenylenepropane. Also, normal 2,7,2′,7′-tetrabromotribiphenylenepropane and the abnormal 2′,7′-dibromotribiphenylenepropane, 2′,7′,2″,7″-tetrabromotribiphenylenepropane and tribiphenylenepropane were similarly obtained from 2,7,2′,7′-tetrabromo-9,9′-bifluorenylidene and fluorene (**1**). The formation of these abnormal products was explained by a combination of addition, elimination, and protonation processes in the presence of sodium hydroxide-pyridine solution. The normal products were primarily obtained in the presence of sodium ethoxide, as has previously been reported in this series.[2,3]

The present paper will deal with another Michael reaction, that of fluoro-substituted 9,9′-bifluorenylidenes and fluorenes. The experiments were designed primarily to clarify any effects due to the difference between fluoro-substitution. Secondly, the new fluoro-substituted compounds were synthesized in order to compare their properties with those of other, corresponding halogeno compounds.

The Michael reaction of **4**[4] and 2-fluorofluorene (**2**)[5] with potassium hydroxide in pyridine or with sodium ethoxide in ethanol gave 2′-fluorotribiphenylenepropane (**12**), 2-fluorofluorenone (**10**),[5] and recovered materials. The yield of **12** increased with an increase in the base concentration (see Table 1, Runs 1—6.) When the reaction of 2,2′-difluoro-9,9′-bifluorenylidene (**6**)[5,6] with **1** was carried out under similar base conditions, 2,2′-difluorotribiphenylenepropane (**13**) and **10** were obtained (see Table 1, Runs 7—9).

An analogous reaction between **4** and 2,7-difluorofluorene (**3**)[7] yielded 2′,7′-difluorotribiphenylenepropane (**16**) exclusively (see Table 2, Runs 1—4). Further the condensation of 2,7,2′,7′-tetrafluoro-9,9′-bifluorenylidene (**8**) with **1** led to 2,7,2′,7′-tetrafluorotribiphenylenepropane (**17**) in a good yield (see Table 2, Runs 5—7).

The sequence for the formation of these addition products is shown in Scheme I. While a 9-fluorenyl carbanion (A′) is generated from (A) in the presence of a base, a new bond in carbanion (C′) can be formed by the attack of (A′) on the highly-polarized central double bond of (B). Then, (C′) may be transformed to the normal addition product (C) by protonation.

From 2- or 2,7-di-bromo-,[2] -iodo-, and -chloro-[8] derivatives, the normal and abnormal compounds were produced; however, in the corresponding fluoro derivatives, only the normal compounds were formed under the same conditions. These results can be explained in terms of the inductive effect of the fluorine atoms, which may operate on the 9′-methine carbon atom in the ion (C′); the 9′-hydrogen atom causes an increase in electron availability, and, consequently, the 9″-carbon is protonated in preference to the removal of a 9′-proton (*i.e.*, examples **12** and **16**). Likewise affected is the 9″-carbon (*i.e.*, examples **13** and **17**), so that the fission of the 9-9″ carbon-carbon bond is controlled; therefore, the 9″-carbon can be protonated with ease to form the normal compounds.

It can be assumed that the (C′) and (C″) ions could hardly attain equilibrium under such reaction conditions, so that the ions can be subjected to protonation with a fairly rapid formation of the corresponding tribiphenylenepropanes.

2,2′,2″-Trifluorotribiphenylenepropane (**15**) and 2,7,2′,7′,2″,7″-hexafluorotribiphenylenepropane (**19**) were obtained by the reaction of **6** and **2**, and by that

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Table 1. MICHAEL REACTION OF 2-FLUORO-SUBSTITUTED 9,9'-BIFLUORENYLIDENES AND FLUORENES

Run	Reactants g			React. conditions			Products g		Recovered g	
	9,9'-Bifluorenylidenes	Fluorenes	Mol. rate	Solvent (ml)	Base (%)	Time hr	Tribiphenylenepropanes (%)	Fluorenones	Acceptor	Donor
1	**4** 1.10	**2** 0.61	1/1	Py. 30	KOH 0.1	45	**12** 0.65 (38)	**10** 0.01	0.63	0.14
2	**4** 1.10	**2** 0.61	1/1	Py. 30	KOH 1	5.5	**12** 1.39 (81)	**10** 0.03	0.20	trace
3	**4** 1.10	**2** 0.61	1/1	Py. 30	KOH 15	0.75	**12** 1.52 (89)	**10** 0.02	0.08	trace
4	**4** 1.10	**2** 1.23	1/2	P . 30	KOH 10	0.75	**12** 1.64 (96)	**10** 0.33	0.02	0.17
5	**4** 1.10	**2** 0.61	1/1	EtOH 30	NaOEt 1	9	**12** 1.30 (76)	**10** trace	0.11	
6	**4** 1.10	**2** 0.61	1/1	EtOH 30	NaOEt 5	5	**12** 1.34 (78)	**10** trace	0.10	
7	**6** 1.21	**1** 0.55	1/1	Py. 30	KOH 0.1	75	**13** 1.19 (68)	**10** 0.03	0.19	0.16
8	**6** 1.21	**1** 0.55	1/1	Py. 30	KOH 10	2	**13** 1.55 (88)	**10** 0.02	trace	0.06
9	**6** 1.21	**1** 1.10	1/2	Py. 30	KOH 10	1.5	**13** 1.51 (86)	**10** 0.07	trace	0.65
10	**6** 1.21	**2** 0.61	1/1	Py. 30	KOH 10	2.5	**15** 1.63 (90)	**10** 0.01	0.06	0.04
11	**5** 1.15	**2** 0.61	1/1	Py. 30	KOH 10	2	**14** 1.54 (88)	**10** 0.02	0.02	0.02
12	**5** 1.15	**1** 0.55	1/1	Py. 30	KOH 10	4	**12** 1.33 (78)	**10** 0.016 **9** 0.02	0.06	0.04

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

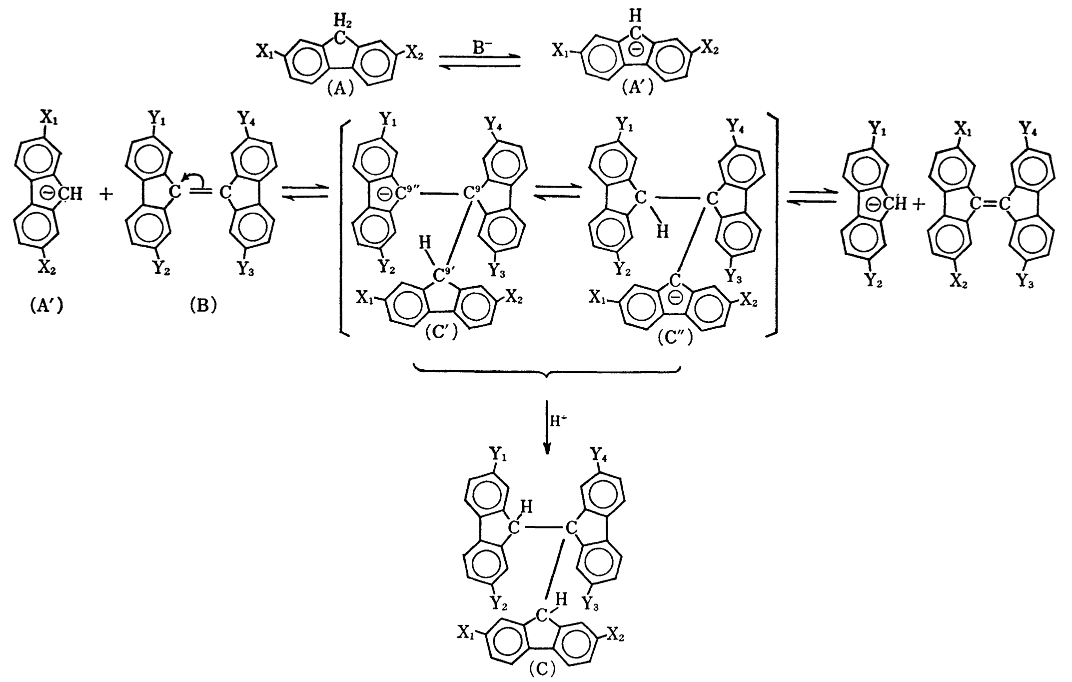
b) Found for **12**: C, 91.51; H, 4.71. For **13**: C, 88.29; H, 4.53. For **14**: C, 88.43; H, 4.43. For **15**: C, 85.16; H, 3.93%.

Table 2. MICHAEL REACTION OF 2,7-DIFLUORO-SUBSTITUTED 9,9'-BIFLUORENYLIDENES AND FLUORENES

Run	Reactants g			React. conditions			Products g		Recovered g	
	9,9'-Bifluorenylidenes	Fluorenes	Mol. rate	Solvent (ml)	Base (%)	Time hr	Tribiphenylenepropanes (%)	Fluorenones	Acceptor	Donor
1	**4** 1.10	**3** 0.67	1/1	Py. 30	KOH 0.1	60	**16** 0.61 (35)	**11** 0.05	0.56	0.31
2	**4** 1.10	**3** 0.67	1/1	Py. 30	KOH 10	1	**16** 1.30 (73)	**11** 0.21	0.10	trace
3	**4** 1.10	**3** 1.35	1/2	Py. 30	KOH 10	1	**16** 1.61 (91)	**11** 0.40	0.01	0.10
4	**4** 1.10	**3** 0.67	1/1	EtOH 30	NaOEt 10	2	**16** 1.57 (90)	**11** trace	trace	0.04
5	**8** 1.34	**1** 0.55	1/1	Py. 30	KOH 0.1	15	**17** 1.45 (77)	**11** 0.14	trace	0.10
6	**8** 1.34	**1** 0.55	1/1	Py. 30	KOH 10	2	**17** 1.41 (75)	**11** 0.06		0.05
7	**8** 1.34	**1** 1.11	1/2	Py. 30	KOH 10	2	**17** 1.60 (85)	**11** 0.10		0.58
8	**8** 1.34	**3** 0.67	1/1	Py. 30	KOH 10	2	**19** 1.77 (88)	**11** 0.14		trace
9	**7** 1.21	**3** 0.67	1/1	Py. 30	KOH 10	2	**18** 1.50 (80)	**11** 0.15		0.01
10	**7** 1.21	**1** 0.55	1/1	Py. 30	KOH 10	2	**16** 1.39 (79)	**11** 0.08 **9** 0.07	0.04	0.05

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

b) Found for **16**: C, 88.04; H, 4.73. For **17**: C, 82.84; H, 4.09. For **18**: C, 82.51; H, 3.79. For **19**: C, 77.61; H, 3.19%.



a). (A)=**1**($X_1=X_2=H$), **2**($X_1=F$; $X_2=H$) or **3**($X_1=X_2=F$).
b). (B)=**4**($Y_1=Y_2=Y_3=Y_4=H$), **5**($Y_1=F$; $Y_2=Y_3=Y_4=H$), **6**($Y_1=Y_4=F$; $Y_2=Y_3=H$), **7**($Y_1=Y_2=F$; $Y_3=Y_4=H$) or **8**($Y_1=Y_2=Y_3=Y_4=F$).
c). (C)=**12**($X_1=F$; $X_2=Y_1=Y_2=Y_3=Y_4=H$), **13**($Y_1=Y_3=F$; $X_1=X_2=Y_2=Y_4=H$), **14**($X_1=Y_1=F$; $X_2=Y_2=Y_3=Y_4=H$), **15**($X_1=Y_1=Y_3=F$; $X_2=Y_2=Y_4=H$), **16**($X_1=X_2=F$; $Y_1=Y_2=Y_3=Y_4=H$), **17**($X_1=X_2=H$; $Y_1=Y_2=Y_3=Y_4=F$), **18**($X_1=X_2=Y_1=Y_2=F$; $Y_3=Y_4=H$), **19**($X_1=X_2=Y_1=Y_2=Y_3=Y_4=F$), 2-Fluorotribiphenylenepropane($X_1=X_2=Y_1=Y_2=Y_3=H$; $Y_4=F$) or 2,7-Difluorotribiphenylenepropane ($X_1=X_2=Y_1=Y_2=H$; $Y_3=Y_4=F$).

Scheme 1.

TABLE 3. SYNTHESES AND ANALYTICAL DATA ON 9,9'-BIFLUORENYLS

9,9'-Bifluorenylidene g	9,9'-Bifluorenyl g	Mp °C	Formula	Found (%)		Calcd (%)	
				C	H	C	H
2-Fluoro- (**5**) 0.10	2-Fluoro- (**21**) 0.10	243—244	$C_{26}H_{17}F$	89.48	4.93	89.63	4.92
2,2'-Difluoro- (**6**) 0.10	2,2'-Difluoro- (**22**) 0.094	241—242	$C_{26}H_{16}F_2$	84.87	4.36	85.23	4.40
2,7-Difluoro- (**7**) 0.10	2,7-Difluoro- (**23**) 0.091	241.5—242.5	$C_{26}H_{16}F_2$	84.92	4.41	85.23	4.40
2,7,2',7'-Tetrafluoro- (**8**) 0.10	2,7,2',7'-Tetrafluoro- (**24**) 0.098	241—242	$C_{26}H_{14}F_4$	77.27	3.72	77.61	3.51

of **8** and **3**, respectively (see Table 1, Run 10 and Table 2, Run 8). These Michael products could be expected as normal products, but the stereoisomeric tribiphenylenepropanes[3b,9] were not isolated. The reactions of 2-fluoro-9,9'-bifluorenylidene (**5**) with **2** or **1** gave 2',2''-difluoro-9,9'-bifluorotribiphenylenepropane (**14**) or **12** (see Table 1, Runs 11 and 12). Similarly, the reactions of 2,7-difluoro-9,9'-bifluorenylidene (**7**) with **3** or **1** afforded 2',7',2'',7''-tetrafluorotribiphenylenepropane (**18**) or **16** respectively (see Table 2, Runs 9 and 10).

Four fluoro-substituted 9,9'-bifluorenyls, *i.e.*, 2-fluoro- (**21**) (mp 243—244°C), 2,2'-difluoro- (**22**)[5] (mp 241—242°C), 2,7-difluoro- (**23**) (mp 241.5—242.5°C), and 2,7,2',7'-tetrafluoro-9,9'-bifluorenyl (**24**) (mp 241—242°C), were obtained by the reduction of the corresponding 9,9'-bifluorenylidenes. Interestingly, these melting points are very close to that of 9,9'-bifluorenyl (**20**)[10] (mp 244—245°C).

The related fluoro-substituted 9-hydroxy-9,9'-bifluorenyls and 9-bromo-9,9'-bifluorenyls were synthesized in the usual way, as is shown in Table 4. Ten fluoro-substituted tribiphenylenepropanes were prepared and confirmed by the reaction of 9-lithiofluorenes and 9-bromo-9,9'-bifluorenyls, as is summarized in Table 5.

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Table 4. CHARACTERIZATION OF 9-HYDROXY-9,9'-BIFLUORENYLS AND 9-BROMO-9,9'-BIFLUORENYLS

Run	Reactants g Fluorene	Reactants g Fluorenone	9-Hydroxy-9,9'-bifluorenyl (mp) °C	Yield g (%)	IR spectra (−OH) cm^{-1}	Anal (%) Found C	Anal (%) Found H	Anal (%) Calcd C H (Formula)
1	**1** 2.0	**10** 2.3	2-Fluoro- (182—184)	3.8 (89)	3300	85.47	4.60	85.69 4.70 ($C_{26}H_{17}OF$)
2	**2** 5.9	**9** 5.4	2'-Fluoro- (184—186)	10.3 (95)	3300	85.68	4.96	85.69 4.70 ($C_{26}H_{17}OF$)
3	**2** 3.0	**10** 2.8	2,2'-Difluoro- (178—180)	4.9 (85)	3290	81.42	4.29	81.66 4.22 ($C_{26}H_{16}OF_2$)
4	**1** 1.4	**11** 1.5	2,7-Difluoro- (211—212)	2.5 (93)	3570 (sharp)	81.60	4.28	81.66 4.22 ($C_{26}H_{16}OF_2$)
5	**3** 4.5	**9** 3.6	2',7'-Difluoro- (199—200.5)	4.8 (63)	3280	82.01	4.44	81.66 4.22 ($C_{26}H_{16}OF_2$)
6	**3** 3.2	**11** 3.0	2,7,2',7'-Tetra-fluoro- (188—189)	5.3 (91)	3390	74.43	3.42	74.64 3.37 ($C_{26}H_{14}OF_4$)

Run	9-Bromo-9,9'-bifluorenyl (mp) °C	Yield %	Anal (%) Found C	Anal (%) Found H	Anal (%) Calcd C H (Formula)
1	2-Fluoro- (180—181; dec)	73	73.42	3.65	73.08 3.77 ($C_{26}H_{16}FBr$)
2	2'-Fluoro- (161—163; dec)	87	73.47	3.68	73.08 3.77 ($C_{26}H_{16}FBr$)
3	2,2'-Difluoro- (178—179; dec)	88	70.45	3.45	70.13 3.40 ($C_{26}H_{15}F_2Br$)
4	2,7-Difluoro- (173—174; dec)	73	70.33	3.66	70.13 3.40 ($C_{26}H_{15}F_2Br$)
5	2',7'-Difluoro- (176—177; dec)	99	70.40	3.44	70.13 3.40 ($C_{26}H_{15}F_2Br$)
6	2,7,2',7'-Tetrafluoro- (175—176; dec)	87	64.96	2.81	64.89 2.72 ($C_{26}H_{13}F_4Br$)

Table 5. FORMATION OF FLUORO-SUBSTITUTED TRIBIPHENYLENEPROPANES BY LITHIUM-HALOGEN INTERCONVERSION REACTION

Reactants g Fluorene	Reactants g 9-Bromo-9,9'-bifluorenyl	Tribiphenylenepropane (Yield) g (%); (mp) °C	Anal (%) Found C	Anal (%) Found H	Anal (%) Calcd C H (Formula)
1 0.66	2-Fluoro- 1.28	2-Fluoro- 0.12 (8); 283—284 (dec)	91.41	5.07	91.38 4.92 ($C_{39}H_{25}F$)
2 0.74	9-Bromo-9,9'-bifluorenyl 1.23	2'-Fluoro- (**12**) 0.20 (13); 279—280 (dec)	91.61	4.83	91.38 4.92 ($C_{39}H_{25}F$)
2 0.74	2-Fluoro- 1.28	2,2'-Difluoro- (**13**) 0.34 (21); 288—289 (dec)	88.01	4.35	88.28 4.56 ($C_{39}H_{24}F_2$)
2 0.74	2'-Fluoro- 1.28	2',2''-Difluoro- (**14**) 0.18 (12); 282—283 (dec)	88.36	4.29	88.28 4.56 ($C_{39}H_{24}F_2$)
2 0.74	2,2'-Difluoro- 1.34	2,2',2''-Trifluoro- (**15**) 0.17 (10); 298—300 (dec)	Mixed Mp Determination		
1 0.58	2,7-Difluoro- 1.38	2,7-Difluoro- 0.12 (8); 279—280 (dec)	88.19	4.43	88.28 4.56 ($C_{39}H_{24}F_2$)
1 0.58	2',7'-Difluoro- 1.38	2',7'-Difluoro- (**16**) 0.35 (22); 285—286 (dec)	88.56	4.75	88.28 4.56 ($C_{39}H_{24}F_2$)
3 0.71	2,7-Difluoro- 1.38	2,7,2',7'-Tetrafluoro- (**17**) 0.17 (10); 287—288 (dec)	82.95	3.82	82.67 3.91 ($C_{39}H_{22}F_4$)
3 0.71	2',7'-Difluoro- 1.38	2',7',2'',7''-Tetrafluoro- (**18**) 0.41 (24); 293—294 (dec)	82.53	3.78	82.67 3.91 ($C_{39}H_{22}F_4$)
3 0.71	2,7,2',7'-tetrafluoro- 1.49	2,7,2',7',2'',7''-Hexafluoro- (**19**) 0.21 (12); 303.5—304 (dec)	Mixed Mp Determination		

The pyrolyses of **19**, **17**, **13**, and **12** were also carried out. The carbon-fluorine bonds being stable under such thermal conditions, fluoro-substituted- or non-fluoro-substituted- 9,9′-bifluorenylidenes, -9,9′-bifluorenyls, -fluorenes, -fluorenones, and recovered tribiphenylenepropanes were obtained. The thermal behavior was analogous to that proposed previously.[1,3a)]

The thermal behavior of the 9,9′-bifluorenyls (**20**, **21**, **22**, **23**, and **24**) and the fluoro-substituted tribiphenylenepropanes (**12**, **13**, **15**, **16**, **17**, and **19**) was studied. Typical thermograms of **13** and **24** are shown in Fig. 1.

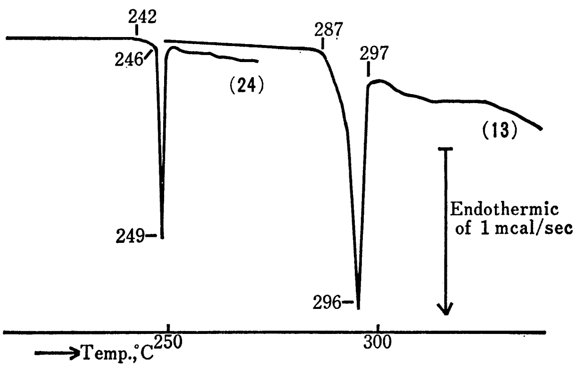

Fig. 1. Differential scanning calorimeter thermograms of **13** and **24**.

In the (**24**) thermogram, the sharp, first single peak curved slowly at 242°C and then steeply at 246°C to reach the inflection point, 249°C, of the melting endotherm, which corresponds to the melting point (241—242°C) of **24**. The peak indicates that **24** is thermally "unreactive."

The second major endothermic peak, centering at 287°C and 297°C in the thermogram (**13**), corresponds to the melting point (289—290°C (dec)), but it is relatively broader than that of **24**. This may be due to its being thermally "reactive" at the melting point. The further endothermal tendency of **13** after the melting peak indicates the formation of pyrolysates and their secondary pyrolyses. In addition, an analogous thermal behavior was observed for other compounds.

Experimental[11)]

The IR spectra were recorded on KBr pellets using a JASCO model IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.).

Measurements of DSC Thermograms. The instrument used in this series was a differential scanning calorimeter, Model DSC-1B (Perkin-Elmer Corp.). The experiments were run with a sensitivity of ±4 mcal/sec under an atmosphere of nitrogen, at a scan time of 8°C/min and a chart speed of 0.5 inch/min. Each sample, **24** (0.63 mg) and **13** (3.27 mg), was packed in aluminum pans with a volatile sample sealer.

Syntheses of 9-Bromofluorenes. *2-Fluoro-9-bromofluorene*: a) A mixture of 2.0 g of **2**, 2.0 g of *N*-bromosuccinimide (NBS), and 10 m*l* of anhydrous benzene was refluxed for 3 hr to afford 2.1 g (75%) of colorless 2-fluoro-9-bromofluorene (mp 112—113°C) from cyclohexane. Found: C, 59.33; H, 2.69. Calcd for $C_{13}H_8FBr$: C, 59.35; H, 3.06%.

b) 2-Fluorofluoren-9-ol[12)] (0.40 g; 0.002 mol) in 10 m*l* of acetic acid was saturated with hydrogen bromide at room temperature, after which the mixture was allowed to stand overnight. The removal of the solvent under reduced pressure, washing with water, and extraction with 10 m*l* of cyclohexane yielded 0.40 g (76%) of colorless needles, mp 113—114°C, identical in all respects with the product obtained by Method a.

2-Fluoro-7-nitrofluoren-9-one: A 0.92-g (0.004 mol) portion of 2-fluoro-7-nitrofluorene[7b),13)] was oxidized by sodium bichromate and recrystallized from benzene; 0.79 g (86%) of ketone was obtained as yellow needles, mp 201—202.5°C. IR (>C=O): 1716 cm^{-1}.

Found: C, 64.17; H, 2.52; N, 5.55%. Calcd for $C_{13}H_6NO_3F$: C, 64.21; H, 2.49; N, 5.76%.

2,7-Difluorofluoren-9-ol: The foregoing 2,7-difluorofluorenone (**11**)[14)] was subjected to reduction with zinc dust and aqueous ammonium hydroxide in ethanol, and recrystallized from aqueous methanol (25%); it gave a quantitative yield of 2,7-difluorofluoren-9-ol, mp 165.5—166°C, as fine, colorless needles. IR (-OH): 3190—3290 cm^{-1}.

2,7-Difluoro-9-bromofluorene: a) The bromination of 2,7-difluorofluoren-9-ol (5.0 g) with dry hydrogen bromide yielded 5.8 g (90%) of 2,7-difluoro-9-bromofluorene, mp 136—138°C. Found: C, 55.94; H, 2.34. Calcd for $C_{13}H_7F_2Br$: C, 55.55; H, 2.51%.

b) A 3.0-g portion of **3** was worked up with NBS; it formed 3.3 g (79%) of 2,7-difluoro-9-bromofluorene, identical in all respects with the product obtained by Method a.

Syntheses of 9,9′-Bifluorenylidenes. *2-Fluoro-9,9′-bifluorenylidene (5)*: A mixture of 10.2 g of 2-fluoro-9′-hydroxy-9,9′-bifluorenyl, 400 m*l* of acetic acid, and 5 m*l* of concentrated sulfuric acid was refluxed for 30 min. The reaction mixtures was then evaporated to 50 m*l* under reduced pressure, and the precipitate was filtered off, washed with water, and extracted with 100 m*l* of acetone. Red needles (4.1 g) of **5**, mp 208—209°C, formed, while the concentration of the mother liquor yielded an additional 2.6 g of **5** (total: 6.7 g, 69%). Found: C, 90.40; H, 4.20%. Calcd for $C_{26}H_{15}F$: C, 90.15; H, 4.36%.

2,7-Difluoro-9,9′-bifluorenylidene (7): A 0.8-g portion of 2,7-difluoro-9′-hydroxy-9,9′-bifluorenyl was worked up as in the synthesis of **5**; **7** was thus obtained (0.45 g; 59%) as red needles, mp 224—225°C.

Found: C, 86.00; H, 3.53%. Calcd for $C_{26}H_{14}F_2$: C, 85.70; H, 3.87%.

2,2′-Difluoro-9,9′-bifluorenylidene (6). a) **6** was prepared from 2-fluoro-9-bromofluorene (1.32 g; 0.005 mol), as in the case of **4**; 0.7 g (84%); mp 226—227°C.

Found: C, 86.04; H, 3.54%. Calcd for $C_{26}H_{14}F_2$: C, 85.70; H, 3.87%.

b) A benzene (20 m*l*) solution of 1.11 g (0.0025 mol) of 2,2′-difluoro-9-bromo-9,9′-bifluorenyl was percolated through an alumina column (45 g of activated alumina: for chromatography, 300 mesh, Wako Pure Chemical Ind. Ltd.; column: 1.8 cmϕ × 18 cm). The colorless solution immediately turned red over alumina, and the red band formed was eluted with benzene. The red solution was evaporated

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11) All the melting points are uncorrected.

12) G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962) (*Chem. Abstr.*, **57**, 8515 (1962)).

13) J. A. Miller, R. B. Sandin, E. C. Miller, and H. P. Rusch, *Cancer Res.*, **15**, 188 (1955) (*Chem. Abstr.*, **49**, 16178 (1955)).

14) H. L. Pan and T. L. Fletcher, *J. Med. Chem.*, **8**, 491 (1965).

to dryness under reduced pressure; subsequent recrystallization from acetic acid gave 0.78 g (86%) of **6** (mp 226.5—227°C).

*2,7,2′,7′-Tetrafluoro-9,9′-bifluorenylidene (**8**).* An acetone (34 m*l*) solution of 3.2 g of 2,7-difluoro-9-bromofluorene was treated with potassium hydroxide-methanol (0.64 g/14 m*l*) to give 2.1 g (92%) of red **8**, mp 337—338°C (dec). Found: C, 78.06; H, 3.10%. Calcd for $C_{26}H_{12}F_4$: C, 78.00; H, 3.02%.

Syntheses of 9,9′-Bifluorenyls. Typical Procedure: A mixture of 0.10 g of **5**, 20 m*l* of acetic acid, 1 g of zinc dust, and 1 m*l* of hydrochloric acid was refluxed for 2 hr. The reaction mixture was filtered, the filtrate was poured into cold water, and the preciptitate was recrystalized from a mixture of benzene and ethanol (1 : 1) to give 0.10 g of colorless needles, **21**, mp 243—244°C.

Formation of 2,2′-Difluoro-α,δ-dibiphenylenebutadiene and 2,7,2′,7′-Tetrafluoro-α,δ-dibiphenylenebutadiene. A mixture of 0.5 g of **2**, 45 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 24 hr. The precipitate was recrystallized from pyridine to give 0.14 g (26%) of 2,2′-difluoro-α,δ-dibiphenylenebutadiene as orange needles with a mp of 392—393°C (dec). Found: C, 86.21; H, 4.30%. Calcd for $C_{28}H_{16}F_2$: C, 86.14; H, 4.13%. In addition, 0.10 g (20%) of **2** and 0.21 g (39%) of **10** were isolated from the ethanol mother solution.

2,7,2′,7′-Tetrafluoro-α,δ-dibiphenylenebutadiene was prepared by the same procedure as before. Yield, 23% of fine orange-red needles, mp 398°C (dec). Found: C, 78.85; H, 3.23%. Calcd for $C_{28}H_{14}F_4$: C, 78.87; H, 3.31%.

The Michael Reaction of 9,9′-Bifluorenylidenes and Fluorenes. Typical Procedure: A Mixture of 1.34 g (1/300 mol) of **8**, 1.11 g (1/150 mol) of **1**, 28 m*l* of pyridine, and 3 g of potassium hydroxide in 2 m*l* of water was placed in a sealed tube and heated at 93—95°C for 2 hr. During this period, the color turned from red to dark green.

The reaction mixture was poured into 40 m*l* of methanol, and the precipitate was filtered off, washed with water, recrystallized from ethyl acetate, and from a mixture of benzene and ethanol to give 1.37 g of **17**, mp 286—287°C (dec.).

The pyridine-methanol mother solution was poured into 500 m*l* of water, and the precipitate was sublimed *in vacuo* at 150°C to yield an additional 0.23 g (total 1.60 g; 85%) of **17** from the sublimation residue.

The sublimed part was extracted with 50 m*l* of cyclohexane, and the extract was chromatographed on alumina; 0.58 g of **1**, mp 110—112°C, and 0.04 g of **11**, mp 200—201°C, were thus isolated. Further, 0.06 g (total 0.10 g) of **11** was obtained from the insoluble portion.

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

Syntheses of 9-Hydroxy-9,9′-bifluorenyls and 9-Bromo-9,9′-bifluorenyls. General Procedure: The reaction was carried out in the usual way. *n*-Butyllithium was prepared from 2.8 g of *n*-butyl bromide in 20 m*l* of anhydrous ether and 0.4 g of lithium chips in 40 m*l* of anhydrous ether. 2,7-Difluoro-9-lithiofluorene was prepared by adding 3.2 g of **3** in 40 m*l* of anhydrous benzene to the *n*-butyllithium solution. To this mixture we then added 150 m*l* of anhydrous benzene containing 3.0 g of **11**. Then, the reaction mixture was worked up as usual. 2,7,2′,7′-Tetrafluoro-9-hydroxy-9,9′-bifluorenyl was prepared in a good yield (5.3 g; 91%), mp 188—189°C, from cyclohexane.

A 4.6-g portion of 2,7,2′,7′-tetrafluoro-9-hydroxy-9,9′-bifluorenyl in 50 m*l* of acetic acid was saturated with dry hydrogen bromide at room temperature, after which the reaction mixture was allowed to stand overnight. Crystals of 2,7,2′,7′-tetrafluoro-9-bromo-9,9′-bifluorenyl (4.8 g) were thus obtained, mp 175—176°C (dec), from cyclohexane.

*Formation of 2′,2″-Difluorotribiphenylenepropane (**14**) by a Lithium-halogen Interconversion Reaction.* *n*-Butyllithium was prepared from 0.69 g of *n*-butyl bromide in 10 m*l* of anhydrous ether and 0.08 g of lithium chips in 20 m*l* of anhydrous ether. Then 2-fluoro-9-lithiofluorene was formed by adding 0.74 g of **2** in 15 m*l* of anhydrous benzene to the *n*-butyllithium solution. Into this resulting mixture there were slowly stirred 40 m*l* of anhydrous benzene containing 1.28 g of 2-fluoro-9′-bromo-9,9′-bifluorenyl. After standing overnight, the reaction mixture was treated as usual to give 0.18 g (12%) of **14** from ethyl acetate, mp 282—283°C (dec).

All the syntheses of this series were carried out in a similar manner.

*Pyrolysis of 2,7,2′,7′,2″,7″-Hexafluorotribiphenylenepropane (**19**).* Finely-powdered **19** (2.41 g; 0.004 mol) was heated at 310—320°C for 3.5 min in a 200-m*l* Erlenmeyer flask. The red molten product was extracted with 50 m*l* of boiling cyclohexane. The extract was allowed to stand overnight, and the deposit was combined with the insoluble portion. Upon fractional crystallization from benzene and ethyl acetate, 0.28 g of **8**, mp 336—338°C (dec), 0.76 g of **24**, mp 238—239°C, and 0.84 g of recovered **19**, mp 303—304°C (dec) were separated.

The cyclohexane mother solution was chromatographed on an alumina column; 0.02 g of **3**, mp 79—81°C, and 0.05 g of **11**, mp 203—205°C, were thus obtained.

*Pyrolysis of 2,7,2′,7′-Tetrafluorotribiphenylenepropane (**17**).* A 2.84-g portion of **17** was heated at 310°C for 3 min. The following compounds were separated: 0.02 g of **8**, mp 335°C (dec), 0.20 g of **24**, mp 239—241°C, 0.28 g of **23**, mp 238—240°C, 0.05 g of **11**, mp 199—201°C, and recovered **17**, mp 285—286°C (dec).

*Pyrolysis of 2,2′-Difluorotribiphenylenepropane (**13**).* A 2.66-g portion of **13** was heated at 310—320°C for 2 min. Consequently, 0.37 g of **22**, mp 239—241°C, 0.80 g of **21**, mp 240—241.5°C, 0.12 g of **20**, mp 241—243°C, 0.16 g of **6**, mp 224—226°C, 0.23 g of **5**, mp 206—207°C, 0.02 g of **4**, mp 181—182.5°C, 0.09 g of **10**, mp 112—114°C, and 0.03 g of fluorenone (**9**), mp 80—81°C, were obtained. Further, 0.15 g of **13**, mp 288—289.5°C (dec) was recovered.

*Pyrolysis of 2′-Fluorotribiphenylenepropane (**12**).* The heating of 5.13 g of **12** at 300—305°C for 3 min gave 0.48 g of **21**, mp 239—241°C, 0.80 g of **20**, mp 239—240°C, 0.02 g of **6**, mp 219—222°C, 0.26 g of **5**, mp 205—207°C, 0.23 g of **4**, mp 181—182°C, 0.004 g of **10**, mp 113—114°C, 0.02 g of **9**, mp 81—81.5°C, 0.01 g of **1**, mp 113—115°C, and 1.73 g of recovered **12**, mp 280—281.5°C (dec).

The identities of the compounds in this series were confirmed by a comparison of their melting points and IR spectra with those of authentic samples.

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