The Isomerization of the Stable Rotamers of 9,9′: 9′,9″-Terfluorenyls

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The conformational change of the *s-cis, s-trans*-9,9′: 9′,9″-terfluorenyl to the *s-cis, s-cis* form *via* the radical process was performed by means of a reaction with *N*-bromosuccinimide and with various oxidizing agents. A reverse change occurred on treatment with lithium aluminum hydride and with sodium bis(2-methoxyethoxy)-aluminum hydride.

Two stereoisomers (mp 293 °C (dec) and mp 257 °C (dec)) have hitherto been obtained by various reactions.[1] The conformational isomers of 9,9′: 9′,9″-terfluorenyls were inferred[2] from the results of restricted rotation around the $C_{9-9'-9''}$ single bonds: *s-cis, s-cis* (mp 293 °C (dec)) (**1**) and *s-cis, s-trans* (mp 257 °C (dec)) (**2**), both of which were stable at room temperature in solution.

1 was converted to **2** by a pyrolytic reaction[3] and by treatment with Raney nickel[2]; however, no isomer was obtained by the reverse change.

The present paper will deal with the isomerization from **1** to **2** or *vice versa.* The **2** rotamer was converted into **1** by reactions with molecular oxygen-benzyltrimethylammonium hydroxide (Triton B), with *N*-bromosuccinimide (NBS), and with such oxidants as manganese dioxide, selenium dioxide, and potassium permanganate.

Conversely, **1** was isomerized to **2** by treatment with lithium aluminum hydride. Both conformers were interconverted by refluxing with sodium bis(2-methoxyethoxy)aluminum hydride (SMAH) in benzene.

Results and Discussion

The hydrogen atoms on the 1,8, 1′,8′,1″,8″, 9, and 9″ positions are close in the overcrowded molecules, **1** and **2**. The conformation of the 9-hydrogen atom in **2** corresponds to that of *s-trans*-9,9′-bifluorenyl, and the other hydrogen on 9″-carbon is located on entering the back of the 9-fluorenyl plane, as the models indicate.[2] Therefore, the bulky 9-fluorenyl plane would tend to shield the 9″-carbon atom from an attack of approaching reagents, and it could be expected to facilitate the formation of a free radical at the less hindered 9-carbon atom.

Table 1 shows the results of the isomerization of **2** to **1** (maximum yield, 56%) by means of a reaction with NBS. 9,9′-Dibromo-9,9′-bifluorenyl,[4] 9-bromo-9,9′-bifluorenyl,[1a] fluorenone (**3**), and 9,9′-bifluorenylidene (**4**) were isolated as by-products.

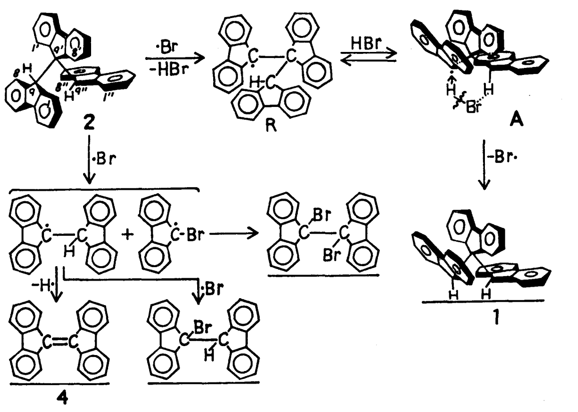
The reaction is initiated by the abstraction of the hydrogen atom from the tertiary 9-carbon of **2** by a bromine atom; 9,9′: 9′,9″-terfluorenyl 9-radical (R) and hydrogen bromide are formed in the main reaction. The radical (R) may abstract a hydrogen atom of hydrogen bromide to form the six-membered hydrogen-bonded intermediate (A), without any homolytic cleavage of the $C_{9-9'}$ or $C_{9'-9''}$ bond, as Scheme 1 shows. Moreover, the radical reaction can be conducted so as to form the *s-cis, s-cis* conformer **1**, with the loss of a bromine atom from (A).

This finding may be explained in terms of the bond energies of C–H and C–Br in the crowded molecule.

Table 1. The reaction of 9,9′: 9′,9″-terfluorenyls with NBS

Reaction conditions					Products g(%)				
Substrate (g)	NBS g	Benzene ml	Temp. °C	Time hr	**1**	9,9′-Dibromo-9,9′-bifluorenyl	9-Bromo-9,9′ bifluorenyl[a]	**4**	Recovered g(%)
2 (1.24)	0.49	150	Room Temp.	40 (days)	0.70 (56)	0.08 (4)	(25)	0.02 (2)	0.01 (1)
2 (1.24)	0.49	120	50	5	0.54 (44)	0.05 (3)	(35)	trace	
2[b] (1.24)	0.49	50	Refl.	3	0.58 (47)	0.09 (5)	(14)	0.11 (9)	
2[c] (1.24)	0.49	310 (CCl_4)	50	5	0.17 (14)		(8)	0.01 (1)	0.85 (69)
2 (1.24)	0.38 (NBA)	120	50	5	0.62 (50)	0.20 (11)	(15)	0.09 (7)	
1 (1.24)	0.49	120	50	5		trace			1.19 (96)
1[b,c] (1.24)	0.49	50	Refl.	3		0.01 (1)		0.02 (2)	1.12 (90)
1 (1.24)	0.38 (NBA)	120	50	5					1.20 (97)

a) Yield of 9-bromo-9,9′-bifluorenyl shows the total amounts of 9-bromo-9,9′-bifluorenyl and 9-hydroxy-9,9′-bifluorenyl.
b) A trace of benzoyl peroxide was used. c) A trace amount of **3** was additionally obtained. d) NBA=*N*-bromoacetamide.

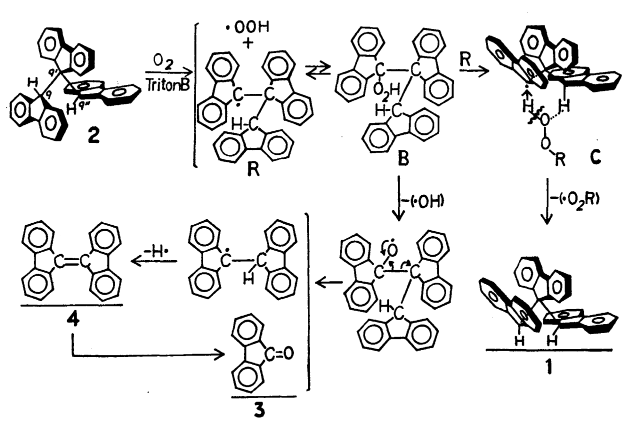


Scheme 1. (Underscored compounds were isolated.)

The molecular strain can be relieved when the radical is formed on the 9-position in **2**. Conversely, the steric compression may be increased when the crowed 9-position is occupied by a bulky bromine atom or when radical coupling takes place. Therefore, (A) is converted to **1**, or the $C_{9-9'}$ linkage in **2** dissociates partially into 9-bromofluorenyl and 9,9′-bifluorenyl radicals by an attack of the bromine atom to form stable dimerization and disproportionation products, without the formation of 9-bromoterfluorenyl.

The **2** isomerized to **1** (maximum yield, 42%) in pyridine upon treatment with molecular oxygen in the presence of a basic catalyst such as Triton B, as is shown in Table 2.

The initial radical (R) is formed along with hydroperoxide, and both species may recombine to form 9,9′:9′,9″-terfluorenyl-9-hydroperoxide (B). The **1** isomer is formed by the dissociation of the 9,9′:9′,9″-terfluorenyl-9-peroxide radical ($\cdot O_2R$) from the hydrogen-bonded intermediate (C) which is attributable to the reaction of (R) and (B), as Scheme 2 shows. The (R) and (B) intermediates can be reproduced by an attack of the radical ($\cdot O_2R$) on **2**.



Scheme 2. (Underscored compounds were isolated.)

The 9,9′-bifluorenyl radical and **3** may be formed from a part of (B) by the cleavage of the hydroxy radical. The 9,9′-bifluorenyl radical is converted into **4** by the splitting of the hydrogen atom, and **4** is oxidized finally to **3**.

The isomerization of **2** with bromine was performed under ultraviolet irradiation at room temperature; the **1** rotamer (29% yield) and 2-bromo-9,9′:9′,9″-terfluorenyl[1b)] (16% yield) were thus isolated. Compound **2** was isomerized to **1** by treatment with selenium dioxide (22% yield) and with potassium permanganate (61% yield). However, no reverse isomerization occurred under the same conditions. The formation of **1** is explicable in the same way as in the reaction using NBS.

Table 2. The reaction of 9,9′:9′,9″-terfluorenyls with Triton B

Reaction conditions				Products g(%)			Recovered g(%)
Substrate (g)	Triton B ml	Temp. °C	Time hr	1	4	3	
2 (1.24)	0.05	−2 −2→10	1 1	0.08 (7)	0.01 (1)	0.01 (1)	0.97 (77)
2 (1.24)	0.25	2→10	2	0.44 (36)	0.02 (2)	0.16 (11)	0.52 (42)
2 (1.24)	0.25	23	2	0.52 (42)	0.04 (3)	0.28 (19)	0.32 (26)
2[a)] (1.24)	0.25	25	2	0.06 (5)	0.02 (2)	0.01 (1)	0.96 (77)
2 (1.24)	None	115	4				1.21 (98)
1 (1.24)	0.25	22	2		0.05 (4)	0.10 (7)	1.00 (81)
1 (1.24)	1.00	23	2		0.24 (19)	0.27 (19)	0.46 (37)
1 (1.24)	12.0	115	2			1.13 (84)	
4[b)] (0.82)	1.00	20	2			0.33 (37)	0.48 (59)
Fluorenol (1.82)	8.00	25	2			1.70 (94)	
Fluorene (1.66)	8.00	24	2			1.29 (72)	0.25 (15)

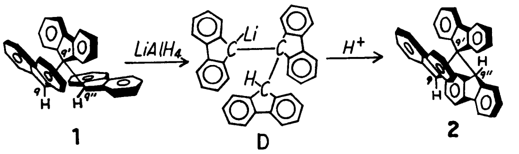
a) The reaction was carried out under nitrogen atmosphere. b) A 20 ml of pyridine was used as solvent.

The conformer **2**-9,9″-d_2[5] (or *s-cis*, *s-trans*-9,9′: 9′,9″-terfluorenyl-9,9″-dideuteride) was treated with suspended manganese(IV) dioxide in benzene to give **1**-9,9″-d_2[5] (58% yield). The deuterium contents of **1**-9,9″-d_2 and the recovered **2**-9,9″-d_2 are of the same order with that of the starting material.

It may be proposed that, under these conditions, the abstraction of 9-hydrogen in **2** by manganese dioxide may form a radical (R) and manganic oxyhydrate (HO-Mn^{III}=O). These are then converted to **1** and manganese dioxide through a six-membered hydrogen-bonded intermediate such as (A).

Conversely, **1** was isomerized to **2** by treatment with lithium aluminum hydride in dry tetrahydrofuran: **1**-9,9″-d_2 gave **2**-9-d[5] (36% yield) by being decomposed with ethanol and water. Moreover, **1** was allowed to react with the same reagent; subsequently it was decomposed with heavy water to give **2**-9″-d (50% yield). The **2** rotamer afforded only 9,9′-bifluorenyl (**5**) (0.3% yield) by the same reaction.

This isomerization presumably proceeds *via* 9-lithio-9,9′: 9′,9″-terfluorenyl (D), not through an intermediate such as (A) or (C), as Scheme 3 shows. Therefore, the conformation of (D) is considered to be *s-cis*, *s-trans* rather than *s-cis*, *s-cis*; (D) is then converted into **2**.



1 D 2

Scheme 3.

Furthermore, both rotamers were interconverted by means of a reaction with SMAH:[6] **1** into **2** (23% yield) and **2** into **1** (13% yield). The isomerization of **1** to **2** by a reducing agent may occur through 9-sodio-9,9′: 9′,9″-terfluorenyl in a way similar to that found for lithium aluminum hydride. The reverse change of **2** to **1** may be attributed to the strong basicity of SMAH, and the reaction may be proceed in analogy with the case of Triton B.

Experimental

All the melting points are uncorrected.

The compounds were confirmed by mixed-melting-point determinations and by a comparison of their IR spectra with those of authentic samples. The IR spectra were recorded as KBr-pellets using a IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.).

The NMR data were obtained in a C_6D_6 solution with a JNM-C60HL spectrometer (Japan Electron Optics Lab. Co., Ltd.).

The deuterium content was confirmed from the average value of five mass spectra recorded on a RMU-6E apparatus (Hitachi, Ltd.).

Isomerization of 2 to 1 by Treatment with NBS. Typical Procedure: A solution of 1.24 g (2.5 mmol) of **2** and 0.49 g (2.7 mmol) of NBS in 120 ml of dry benzene was maintained at 50 °C for 5 hr while being stirred. The dark-red benzene solution was then evaporated to dryness under reduced pressure, and the residue was washed with hot water, dried, and recrystallized from benzene (50 ml) to give 0.34 g of **1** (mp 290—292 °C (dec)).

When the benzene mother liquor was chromatographed on alumina, the elute gave the following compounds by recrystallization from cyclohexane, cyclohexane–benzene, or benzene–ligroin: 0.20 g (total 0.54 g, 44%) of **1** (mp 292—293 °C (dec)), 0.05 g (3%) of 9,9′-dibromo-9,9′-bifluorenyl (mp 239—240 °C (dec)), and a trace amount of **4** (mp 182—184 °C).

A 0.45-g portion (35%) of 9-hydroxy-9,9′-bifluorenyl (mp 193—194 °C) was isolated from the column.[7]

Isomerization of 2 by Treatment with Triton B and Oxygen. Typical Procedure: To a solution of 1.24 g of **2** and 0.25 g of Triton B (10% aqueous solution) in 50 ml of pyridine, oxygen was passed gently at 23 °C for 2 hr (the color changed to black).

The reaction mixture was then diluted with 500 ml of water, and the precipitate was sublimed *in vacuo* at 140 °C to give 0.28 g (19%) of **3** (mp 82—83 °C (ethanol)). The residue after sublimation afforded 0.52 g (42%) of **1** (mp 292.5—293 °C (dec)), 0.32 g (26%) of recovered **2** (mp 256—257 °C (dec)), and 0.04 g (3%) of **4** (mp 183—184.5 °C) by recrystallization from benzene.

With Manganese Dioxide. a): A solution of 0.5 g (1 mmol) of **2**-9,9″-d_2 in 25 ml of dry benzene was refluxed with 2.5 g of manganese dioxide (E. Merck, for synthesis) for 2 hr.

Upon cooling, the reaction mixture was filtered, and the manganese dioxide was extraced with a 150-ml portion of benzene. All of the benzene solution was chromatographed on alumina; 0.29 g (58%) of **1**-9,9″-d_2 (mp 292—293 °C (dec)), 0.02 g (4%) of **5** (mp 243—244 °C), 0.11 g (20%) of **3** (mp 81—83 °C), and 0.03 g (6%) of **2**-9,9″-d_2 (mp 255-257 °C (dec)) were thus obtained.

The deuterium contents in **1**-9,9″-d_2 and the recovered **2**-9,9″-d_2 were of the same order with that of the starting **2**-9,9″-d_2, as is shown by their mass spectra: m/e 494 (d_0, 1%), 495 (d_1, 12%), and 496 (d_2, 87%).

b): In a similar treatment, **1** gave only **3** (2%) and recovered **1** (90%).

With Potassium Permanganate. a): Compound **2** (1.0 g, 2 mmol) was refluxed with 3.5 g of potassium permanganate in 50 ml of dry pyridine for 5 hr. After cooling, the reaction mixture was decomposed with aqueous sodium bisulfite and hydrochloric acid, and the precipitate was sublimed *in vacuo* at 120 °C.

The sublimate gave 0.28 g (26%) of **3** (mp 83—84 °C), and the residue after sublimation yielded 0.61 g (61%) of **1** (mp 292—293 °C (dec)).

When **1** was treated in a similar manner, 97% of the starting material was recovered.

b): A mixture of **2** (1.0 g), potassium permanganate (6.5 g), and aluminum sulfate (6.8 g) in dry acetone (300 ml) was refluxed for 5 hr. The reaction mixture was then treated as has been described above to afford 0.58 g (58%) of **1** (mp 292—293 °C (dec)) and 0.41 g (38%) of **3** (mp 80—82 °C).

With Selenium Dioxide. a): A mixture of 1.0 g (2 mmol) of **2**, 0.5 g of selenium oxide, and 200 ml of dry acetic acid was refluxed for 10 hr. Upon cooling, the precipitate was filtered and then recrystallized from benzene to give 0.22 g (22%) of **1** (mp 292—293 °C (dec)).

The acetic acid solution was evaporated *in vacuo*, and the residue was extracted with a 50-ml portion of benzene to give 0.62 g (62%) of **2** (mp 255—257 °C (dec)). The benzene mother liquor was chromatographed on alumina to yield 0.01 g (1%) of **3** (mp 83—85 °C).

b): The **1** isomer (1.0 g) was treated with selenium oxide (0.5 g) in dry acetic acid (200 ml) for 5 hr. 98% of the **1** (mp 292—293 °C (dec)) was recovered, accompanied by a trace amount of **3**.

With Bromine. *a)*: A solution of 1.0 g of **2** and 0.32 g of bromine in 130 ml of chloroform was irradiated with a 100-W high-pressure mercury lamp for 4 hr at room temperature in an atmosphere of nitrogen. The reaction mixture was then washed with a 2% sodium hydroxide solution and with water and evaporated to dryness; the residue was recrystallized from ethyl acetate: 0.19 g (16%) of 2-bromo-9,9′:9′,9″-terfluorenyl (mp 255—257 °C (dec)) and 0.29 g (29%) of **1** (mp 291—293 °C (dec)) were isolated.

b): To a solution of 1.0 g (2 mmol) of **1** and 0.01 g of anhydrous ferric chloride in 90 ml of chloroform, a 0.32-g portion (2 mmol) of bromine in 10 ml of chloroform was added, drop by drop, over a period of 1 hr at room temperature under a nitrogen atmosphere in the dark, after which stirring was continued for an additional 23 hr.

Upon treatment as above, 0.63 g (54%) of 2-bromo-9,9′:9′,9″-terfluorenyl (mp 256—257 °C (dec)) and 0.30 g (30%) of **1** (mp 292—293 °C (dec)) were obtained.

Isomerization of 1 to 2 by Treatment with Lithium Aluminum Hydride. *a)*: The **1**-9,9″-d_2 rotamer (1.0 g, 2 mmol) was refluxed with 0.76 g (20 mmol) of lithium aluminum hydride in 70 ml of dry tetrahydrofuran for 5 hr. The reaction mixture was then evaporated to dryness under reduced pressure and decomposed with a 20-ml portion of ethanol and with a 100-ml portion of 1 M hydrochloric acid. The precipitate was filtered off, dried, and recrystallized from ethyl acetate; this afforded 0.36 g (36%) of **2**-9-*d* (mp 256—257 °C (dec)), 0.03 g of **5** (mp 242—243 °C), and 0.46 g (46%) of **1**-9,9″-d_2 (mp 291—293 °C (dec)).

The deuterium content of the recovered **1** was of the same order with that of the starting material. The NMR spectrum of **2**-9-*d* showed no peak at 5.36 ppm assigned to the 9-position.

Mass spectrum for recovered **1**-9,9″-d_2: *m/e* 494 (d_0, 1%), 495 (d_1, 8%), and 496 (d_2, 91%). For **2**-9-*d*: *m/e* 494 (d_0. 25%), 495 (d_1, 74%), and 496 (d_2, 1%).

b): A solution of 1.0 g of **1** in 70 ml of dry tetrahydrofuran was refluxed with 0.76 g lithium aluminum hydride for 5 hr, Upon cooling, 14 ml of deuterium oxide containing 4% of deuterium chloride was slowly added to the resulting mixture. The precipitate was recrystallized from ethyl acetate to give 0.50 g (50%) of **2**-9″-*d* (mp 256—257 °C (dec)) and 0.15 g of **5** (mp 242—243.5 °C). The mother liquor was then evaporated to dryness, and the residue was sublimed *in vacuo* at 120 °C; the sublimate gave 0.02 g of fluorene (mp 113—114.5 °C (recrystallized from *n*-hexane)).

The signal at 4.61 ppm (9″-position) was confirmed to decrease in the NMR spectrum of **2**-9″-*d*.

Deuterium content for **2**-9″-*d*: *m/e* 494 (d_0, 81%), 495 (d_1, 16%), and 496 (d_2, 3%).

c): Compound **2** (1.5 g) was treated with 1.1 g of lithium aluminum hydride in 100 ml of dry tetrahydrofuran for 9 hr. The reaction mixture was then worked-up as has been described above to yield 1.36 g (91%) of **2** (mp 255—257 °C (dec)) and 0.004 g of **5** (mp 242—244 °C).

Interconvertion Reactions of 1 and 2 by Treatment with SMAH. *a)*: A solution of 1.0 g (2 mmol) of **1** and 8 ml of SMAH (70% benzene solution) in 50 ml of dry benzene was refluxed for 15 hr (it turned dark).

Upon cooling, the reaction mixture was washed successively with a 100-ml portion of 10% hydrochloric acid and with two 100-ml portions of water and dried over calcium chloride to yield, after the removal of the solvent, 0.23 g (23%) of **2** (mp 254—256 °C (dec)) and 0.38 g (38%) of **1** (mp 291—293 °C (dec)). Additionally, 0.17 g of **4** (mp 183—185 °C), 0.05 g of fluorene (mp 112—114 °C), and 0.04 g of **3** (mp 82—83.5 °C) were obtained.

b): The **2** isomer (1.0 g) was treated with 4 ml of SMAH in 50 ml of dry benzene for 15 hr; 0.13 g (13%) of **1** (mp 292—293 °C (dec)), 0.68 g (68%) of **2** (mp 256—257 °C (dec)), 0.18 g of **4** (mp 182—184 °C), 0.01 g of fluorene (mp 112—115 °C), and 0.07 g of **3** (mp 81—83 °C) were thus isolated.

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6) Fluorenol was treated with SMAH and gave **3** (20%), **5** (0.7%), fluorene (0.06%), and recovered fluorenol (73%). This indicates that SMAH acts as oxidizing and reducing agent.

7) It is already known that 9-bromo-9,9′-bifluorenyl was converted to 9-hydroxy-9,9′-bifluorenyl by percolating through alumina. See Ref. 1a.