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Hydrogenolyses of Halo-9,9′: 9′,9″-terfluorenyls with the Raney Nickel Catalyst

Masahiro Minabe and Kazuo Suzuki

Department of Industrial Chemistry, Faculty of Technology, Utsunomiya University, Ishii-cho, Utsunomiya 321-31

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2,7-Di- and 2- halo-9,9′ : 9′,9″-terfluorenyls were treated with the Raney nickel catalyst to give 9,9′: 9′,9″-terfluorenyl isomers (mp 293 °C (dec) (I) and mp 257 °C (dec) (II)), fluorene (III), 9,9′-bifluorenyl (IV), halofluorene, and/or 1,2,3,4,4a,9a-hexahydrofluorene (V). The conformation around the C_9–$C_{9'}$ –$C_{9''}$ single bonds of these halo-9,9′: 9′,9″-terfluorenyls were concluded to be *s-cis*, *s-cis*, identical with those of the parent hydrocarbon I. These assignments were confirmed by hydrogenolyzing 9,9″-dideuterio-2,7-dihalo-9,9′ : 9′,9″-terfluorenyls. The chemical shifts of the 9- and 9″-methine protons in these haloterfluorenyls were explained in terms of the torsional conformations of the molecules.

The conformations of the two stereoisomers for 9,9′: 9′,9″-terfluorenyls (mp 293 °C (dec) (I) and mp 257 °C (dec) (II)) were proposed to be *s-cis*, *s-cis* and *s-cis*, *s-trans* respectively, based on the restriction of rotation around the C_9–$C_{9'}$–$C_{9''}$ single bonds.[1] These isomers were obtained simultaneously by the Michael reaction[2] of 9,9′-bifluorenylidene with fluorene (III) and by other reactions.[3]

I was converted into II by treatment with the Raney nickel catalyst (R-Ni), while II gave 9,9′-bifluorenyl (IV), III, and 1,2,3,4,4a,9a-hexahydrofluorene (V) under the same reaction conditions.[2] On the contrary, II was isomerized to I by a reaction with potassium permanganate, triton B, or other reagents.[4]

Halo-9,9′: 9′,9″-terfluorenyls were obtained in the absence of their stereoisomers by the Michael addition[5] of the corresponding fluorene to 9,9′-bifluorenylidene, by the reaction[5a–c] of the corresponding 9-lithiofluorene with 9-bromo-9,9′-bifluorenyl, and by other reactions.[6]

The present paper will describe the treatment of several halo-9,9′: 9′,9″-terfluorenyls with R-Ni; the experiments were undertaken in order to relate the conformations of these haloterfluorenyls to the conformation of I or II. In addition, 2- and 2,7-di-halofluorene and some related compounds were treated with R-Ni.

Results and Discussion

The 2,7-di- and 2-halo-9,9′: 9′,9″-terfluorenyls were treated with R-Ni at 60 °C in toluene under a dry atmosphere, as is shown in Table 1.

2,7-Diiodo-9,9′: 9′,9″-terfluorenyl[5d] produced I in a good yield, along with small quantities of III and V. Similarly, the 2-iodo analog[5d] afforded I as the main product, accompanied by small amounts of II, III, and V. 2′,7′-Dibromo-9,9′: 9′,9″-terfluorenyl[5a] gave 2′-bromo-9,9′: 9′,9″-terfluorenyl,[5e] I, II, 2-bromofluorene, III, and V.

The hydrogenolysis of 2,7-dibromo-9,9′: 9′,9″-terfluorenyl[5a] yielded 2-bromo-9,9′: 9′,9″-terfluorenyl,[6] I, II, III, IV, V, and 2-bromo- and 2,7-dibromo-fluorene. The 2-bromo-9,9′: 9′,9″-terfluorenyl separated from the products was further treated with R-Ni to produce I, II, III, IV, and V. The corresponding chloro derivatives[5c] gave results similar to those of the bromo analogs.

TABLE 1. HYDROGENOLYSES OF HALO-9, 9′: 9′, 9″-TERFLUORENYLS OVER RANEY NICKEL CATALYST

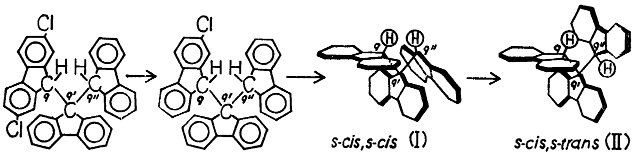
Reactant	React. condns.			Products (mol%)			Reactant recovered mol%
	R-Ni g	Et_3N g	Time hr	Monohalo-terfluorenyl	I	II	
2,7-F_2-[a]	20	0.6	3		22		12
2-F-[b]	10	0.6	1.5		6	29	5
2,7-Cl_2-	10	0.6	1.5	76			5
2,7-Cl_2-	10	0.6	3	45	14	4	3
2,7-Cl_2-	20	0.6	3	30	17	15	5
2-Cl-	10	0.6	1.5 (Room Temp.)				95
2-Cl-	5	0.6	1.5		37	7	37
2-Cl-	10	0.6	1.5		21	43	11
2,7-Br_2-	10	0.6	1.5	55	31		4
2,7-Br_2-	10	0.6	3	33	41	7	trace
2,7-Br_2-[c]	20	1.2	3	2	68	11	
2-Br-[c]	10	0.6	1.5		75	5	
2′,7′-Br_2-	10	0.6	3	49	26	3	6
2,7-I_2-	20	0.6	3		93		
2-I-	10	0.6	1.5		86	3	

a) In addition, 2,7-difluoro-9,9′-bifluorenyl (15%) was isolated. b) 2-Fluoro-9,9′-bifluorenyl (44%) was additionally obtained. c) Further, a small amount of IV was isolated.

2,7-Dichloro-9,9″-dideuterio-9,9′: 9′,9″-terfluorenyl afforded 2-chloro-9,9′ : 9′,9″-terfluorenyl, I, and II. The deuterium contents in 2,7-dichloroterfluorenyl, 2-chloroterfluorenyl, and I were of the same order: the deuterium was held at C-9 in II, but was exchanged with hydrogen at C-9″. Further, two deuterium atoms were held in I and 2-bromoterfluorenyl, which had been obtained by the treatment of 2,7-dibromo (and -iodo)-9,9″-dideuterio-9,9′: 9′,9″-terfluorenyl with R-Ni.

Accordingly, the conformations of these halo-9,9′:-9′,9″-terfluorenyls may be concluded to be identical with that of I, *i.e.* *s-cis*, *s-cis* around the central $C_{9-9'-9''}$ single bonds.

Thus, the hydrogenolysis of the aromatic carbon-halogen bonds in 2,7-dihalo-9,9′: 9′,9″-terfluorenyls occurs to form I without affecting the conformation at C-9 and C-9″ over R-Ni. For example, the reaction of 2,7-dichloro-9,9′: 9′,9″-terfluorenyl with R-Ni proceeds *via* 2-chloro-9,9′: 9′,9″-terfluorenyl to give I, which then isomerizes to II with an inversion of the conformation,[1] as is shown in Scheme 1. Small amounts of III, IV, 2,7-dichloro-, and 2-chloro-fluorene are formed by the reductive cleavage of the central $C_{9-9'}$ and/or $C_{9'-9''}$ bonds of terfluorenyls, and III is reduced to V.2)



Scheme 1.

In general, in the dehalogenation of organic compounds by catalytic hydrogenation, the order of reactivity is: iodine>bromine>chlorine. The halide ions thus formed inhibit the halogen-hydrogen exchange.7) In the hydrogenolysis of iodo derivatives, the further reaction of the I thus formed seems to be inhibited by the poisoning action of the iodine ion produced. On the other hand, the isomerization of I to II may follow the hydrogenolysis in the cases of chloro and bromo derivatives.

2,7-Difluoro-9,9′: 9′,9″-terfluorenyl5b) gave I, 2,7-difluoro-9,9′-bifluorenyl (15% yield), 2,7-difluorofluorene, III, and V. Further, 2-fluoro-9,9′: 9′,9″-terfluorenyl5b) afforded 2-fluoro-9,9′-bifluorenyl (44% yield), I, II, 2-fluorofluorene, III, and V by the same treatment.

The formations of 2,7-di- and 2-fluoro-9,9′-bifluorenyl indicate more resistance of the carbon-fluorine bond toward the hydrogenolysis, which may be attributed to the lesser polarizability of the carbon-fluorine bond and to its relatively weak affinity for the catalyst. The conformations of both fluoro-9,9′: 9′,9″-terfluorenyls can be identified as *s-cis, s-cis*, by analogy with other halo derivatives.

The hydrogenolysis of IV gave III and V, and 9,9′-bifluorenylidene yielded III, IV, and V.8) 2,7-Di- and 2-halofluorene were treated with R-Ni to give III and V, as Table 2 shows. The tendency of these hydrogenations is similar to that of halo-9,9′: 9′,9″-terfluorenyls.

Table 2. Hydrogenolyses of halofluorenes with Raney nickel catalyst

Fluorene	Components of reaction mixture (mol%) 15 mina)				60 mina)			
	V	III	2-Halo-fluorene	2,7-Dihalo-fluorene	V	III	2-Halo-fluorene	2,7-Dihalo fluorene
Fluorene	40	60			51	49		
2-F-	22	9	69		31	15	54	
2-Cl-	28	27	45		41	33	26	
2-Br-	16	40	44		29	45	26	
2-I-	17	47	36		25	46	29	
2,7-F_2-	12	0	1	87	16	1	0	83
2,7-Cl_2-	13	13	23	51	18	17	22	43
2,7-Br_2-	16	17	15	52	21	23	16	40
2,7-I_2-	20	23	14	43	20	26	20	34

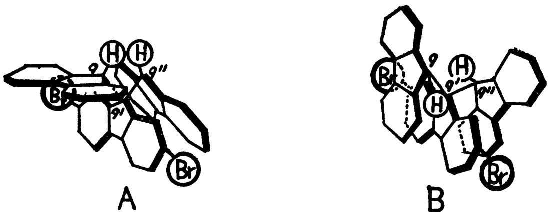
a) Reaction time.

Table 3. The chemical shifts of the 9- and 9″-methine protons in halo-9,9′: 9′,9″-terfluorenyls

9,9′: 9′,9″-Terfluorenyl	Chemical shift (δ) ppm 9-Hydrogen	9″-Hydrogen
I1)	5.36	5.36
II1)	5.36	4.61
2′,7′-Br_2-	5.14	5.14
2,7-F_2-	5.14	5.14
2,7-Cl_2-	5.14	5.21
2,7-Br_2-	5.14	5.23
2,7-I_2-	5.11	5.26
2-F-	5.22	5.22
2-Cl-	5.22	5.26
2-Br-	5.20	5.26
2-I-	5.16	5.25

Table 3 shows the chemical shifts of the 9- and 9″-methine protons in halo-9,9′: 9′,9″-terfluorenyls.

The conformations of these halo-9,9′: 9′,9″-terfluorenyls are presumed to be *s-cis, s-cis* forms at the ground state, by analogy with the parent hydrocarbon, I.1,2) However, the actual halomolecules are torsional conformers about the $C_{9-9'}$ and $C_{9'-9''}$ sp^3-sp^3 bonds, so that the 9- and 9″-fluorenyl rings are both twisted out from the 9′-fluorenylidene plane to release the strain within the range of the restricted degree, in the same way as with *o,o′*-substituted biphenyl. For example, *s-cis, s-cis*-2′,7′-dibromo-9,9′: 9′,9″-terfluorenyl (A) may be sketched as (B) in Scheme 2.



Scheme 2.

In addition, the equal torsion of each 9- and 9″-fluorenyl plane with respect to the central dibromo-9′-fluorenylidene may be more increased than in the case of I as a result of the greater steric repulsion by the bulky dibromo-9′-fluorenylidene group. Thus, two 9- and 9″-methine protons in 2′,7′-dibromoterfluorenyl are located in the shielding zone of the π electron cloud on the central 9′-fluorenylidene ring, which shifts the signal to a higher field (5.14 ppm).

However, the 9- and 9″-methine proton should be oriented differently in 2-halo- and 2,7-dihalo-9,9′: 9′,9″-terfluorenyls because of the different degrees of torsional and repulsive effects of the 9- and 9″-fluorenyl groups with respect to the central 9′-fluorenylidene ring. The spatial situation of the 2,7-dibromo-9-fluorenyl plane with regard to 9′-fluorenylidene in 2,7-dibromoterfluorenyl may be similar to that of the 2′,7′-dibromo analog: therefore, the 9-methine proton on the 2,7-dibromo derivative appears at 5.14 ppm. At the 9″-fluorenyl group in 2,7-dibromoterfluorenyl, the degree of twisting and repulsion is probably less than that of the 2′,7′-dibromo system. Thus, the 9″-methine proton signal is observed between those of the 9-methine protons of the 2,7-dibromo system and I.

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 melting points of the deuterio-compounds in this series are identical with those of the parent compounds.

The gc analyses were run with a JGC-1100FP gas chromatograph (Japan Electron Optics Lab. Co., Ltd.), using a 1 m Sus-27 column containing 3% Silicone DC QF-1 on Chromosorb WAW (60—80 mesh). Nitrogen gas, used as a carrier, was made to flow through at an inlet pressure of 1.0 kg/cm^2; the injector and detector temperatures were maintained at 290 and 265 °C respectively. The column temperature was 95 °C (for III and fluorofluorene), 125 °C (for chloro-derivatives), and 140 °C (for bromo- and iodo-analogies). The content of each component was calculated from the average value of five chromatograms.

The IR spectra were obtained as KBr pellets (4000—400 cm^{-1}) or as suspensions in hexachlorobutadiene (3000—2800 cm^{-1}) using a IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.).

The mass spectra were recorded on a RMU-6E apparatus (Hitachi, Ltd.) by means of the direct-inlet system. The chamber voltage, total emission, and target current were maintained at 80 V, 80 μA, and 23 μA respectively. The sample was evaporated at 170 °C. The number of the deuterium in the compounds was calculated from the average value of five spectra.

The NMR spectra were measured by means of a JNM-C60-HL spectrometer (JEOL) in benzene-d_6, using TMS as the internal reference.

Treatment of 2,7-Dibromo-9,9′: 9′,9″-terfluorenyl with R-Ni. Typical Procedure: A solution of 2.00 g (3 mmol) of 2,7-dibromo-9,9′: 9′,9″-terfluorenyl and 0.6 g of triethylamine in 110 ml of toluene was stirred with 10 g of R-Ni (W-4) at 60 °C for 1.5 hr. The reaction mixture was then filtered, and the catalyst was extracted with four 40-ml portions of toluene. All the toluene solution was then evaporated under reduced pressure. The residue was extracted with a 30-ml portion of boiling ethanol: the insoluble parts were recrystallized from ethyl acetate to give 0.46 g (31%) of I (mp 291—293 °C (dec)), 0.89 g of 2-bromo-9,9′: 9′,9″-terfluorenyl (mp 252—253 °C (dec)), and 0.07 g (4%) of the starting material (mp 286—287 °C (dec)).

Upon standing, the alcohol extract gave 0.06 g (total 0.95 g, 55%) of 2-bromo-9,9′: 9′,9″-terfluorenyl (mp 252—254 °C (dec)). The mother liquor was evaporated to dryness, and the residue was sublimed *in vacuo* at 180 °C. The sublimate (0.01 g) proved by means of gas chromatography to be a mixture of V (*ca.* 2.6 mg), III (*ca.* 5.7 mg), 2-bromo- (*ca.* 0.8 mg), and 2,7-dibromo-fluorene (*ca.* 0.9 mg).

Hydrogenolyses of 9,9′-Bifluorenyl (IV) and 9,9′-Bifluorenylidene. A solution of 1.32 g (4 mmol) of IV and 0.3 g of triethylamine in 110 ml of toluene was refluxed with 10.0 g of R-Ni for 3 hr.

Upon treatment in a manner similar to that described above, the residue was recrystallized from 50 ml of ethyl acetate to afford 0.69 g of IV (mp 242—243 °C). The mother liquor was evaporated to dryness, and the residue was extracted with petroleum ether. The insoluble parts yielded IV (0.02 g; total 0.71 g, 54%); mp 242—244 °C. The extract was analyzed by means of gc; the presence of 0.17 g (13%) of III and 0.33 g (24%) of V was thus confirmed.

9,9′-Bifluorenylidene (1.32 g, 4 mmol) was submitted in the same way as above: 0.85 g (64%) of IV, 0.10 g (7%) of III, and 0.35 g (25%) of V were obtained.

Hydrogenolyses of Halofluorenes. A solution of 2.5 mmol of the substrate in 15 ml of toluene was refluxed with 2.0 g of R-Ni. After each time interval, a small amount of the reaction mixture was taken out and the supernatant was examined by means of gc.

Synthesis of 2-Bromo-9,9″-dideuterio-9,9′: 9′,9″-terfluorenyl. Typical Procedure: 2-Bromo-9,9-dideuteriofluorene was prepared in a 93% yield by the method of Cram and Kollmeyer.[9] The extent of deuterium incorporation was 97%, as determined by means of the NMR spectrum.

A solution of 1.64 g of 9,9′-bifluorenylidene, 1.35 g of 2-bromo-9,9-dideuteriofluorene, and a 1-ml portion of D_2O containing 0.3 g of sodium carbonate in 14 ml of dry pyridine was placed in a sealed tube and heated at 97—100 °C for 50 hr. Upon an usual treatment,[5a] the reaction mixture afforded 0.82 g (44% yield) of 2-bromo-9,9″-dideuterio-9,9′: 9′,9″-terfluorenyl. The deuterium incorporation was calculated by means of the mass spectrum to be as follows: d_0, 1%; d_1, 12%; d_2, 87%.

Treatments of 2,7-Dihalo-9,9″-dideuterio-9,9′: 9′,9″-terfluorenyls with R-Ni. Some deuterio-compounds were treated with R-Ni in a manner analogous to those used for the parent haloterfluorenyls. The deuterium contents of the substrates and products were determined by means of the mass spectra to be as follows:

a): 2,7-Dichloro-9,9′: 9′,9″-terfluorenyl (d_0, 1%; d_1, 12%; d_2, 87%) gave a 2-chloro analog (d_0, 1%; d_1, 12%; d_2, 87%), I (d_0, 2%; d_1, 13%; d_2, 85%), and II (d_0, 12%; d_1, 88%; d_2, 0%).

b): 2,7-Dibromo derivative (d_0, 0%; d_1, 13%; d_2, 87%) yielded 2-bromo-9,9′: 9′,9″-terfluorenyl (d_0, 0%; d_1, 14%; d_2, 86%) and I (d_0, 0%; d_1, 18%; d_2, 82%).

c): I (d_0, 0%; d_1, 22%; d_2, 78%) was obtained from 2,7-diiodo-9,9′: 9′,9″-terfluorenyl (d_0, 1%; d_1, 22%; d_2, 77%).

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