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Reduction of *gem*-Bromofluorocyclopropanes with Organosilicon Hydrides

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7-Bromo-7-fluoronorcarane, 1-bromo-1-fluoro-2-phenylcyclopropane, and 7-bromo-7-fluoro-2-oxanorcarane were reduced with tri-*n*-butylsilane or di-*n*-butylsilane at 100—145 °C in the presence of a small amount of radical initiator, to afford the corresponding monofluorocyclopropanes. It has been found, by examining the stereochemistry of the reduction, that the extent of stereospecificity is dependent on the reaction temperature as well as on the kind of the silicon hydride used. Comparison of these results with those of the tri-*n*-butyltin hydride reduction shows that the reactivity of metal hydrides as a reducing agent of *gem*-dihalocyclopropanes is in the order $Bu_3SnH > Bu_2SiH_2 > Bu_3SiH$. These observations are well explained by postulating that the α-fluorocyclopropyl radical has a pyramidal configuration and that the extent of stereospecificity is determined by the relative rates of its inversion of configuration and its hydrogen abstraction from the tin or silicon hydride. The reduction of 7,7-dibromonoracrane with tri-*n*-butylsilane or di-*n*-butylsilane gave a mixture of the two geometrical isomers of 7-bromonoracrane, whose composition (*endo*-Br/*exo*-Br≒3.0) was nearly identical irrespective of the reaction temperature and of the reactivity of silicon hydride.

It has been known that organosilicon hydrides are capable of reducing organic halides.[1] Thus, the reduction of chloro- or bromoalkanes has been effected with triethylsilane in the presence of aluminum chloride,[2,3] and with trichlorosilane under irradiation of light.[4] Palladium-catalyzed reactions of tri-substituted organosilanes with halocarbons including aromatic halides are also known to result in halogen-hydrogen exchange, to afford a good yield of organosilicon halides.[5] It has been suggested that the reduction of aliphatic halides with organosilicon hydrides proceeds by an ionic mechanism in the presence of aluminum chloride,[2] and by a free-radical chain mechanism under irradiation of light.[4]

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[1] C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London (1960).

[2] F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *J. Amer. Chem. Soc.*, **69**, 2108 (1947).

[3] B. N. Dolgov, S. N. Borisov, and M. G. Voronkov, *Zh. Obshch. Khim.*, **27**, 716 (1957); *Chem. Abstr.*, **51**, 16282 (1957).

[4] J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *J. Chem. Soc., A*, **1968**, 510.

[5] J. D. Citron, J. E. Lyons, and L. H. Sommer, *J. Org. Chem.*, **34**, 638 (1969).

Nagai and his collaborators[6] have found that the reduction with organosilicon hydrides in the liquid phase can be effected by use of radical initiator such as benzoyl peroxide, and proposed the following mechanism:

$$\text{Initiator} \longrightarrow \text{In}\cdot$$

$$\text{In}\cdot + R_3SiH \longrightarrow InH + R_3Si\cdot$$

$$R_3Si\cdot + R'X \longrightarrow R_3SiX + R'\cdot$$

$$R'\cdot + R_3SiH \longrightarrow R'H + R_3Si\cdot$$

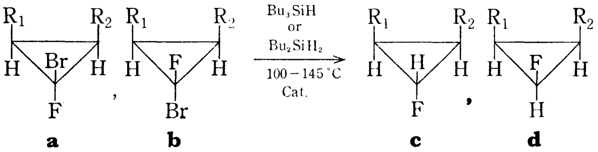
The mechanism shown above is very similar to the one proposed for the reduction of organic halides with organotin hydrides,[7] which have been found to reduce *gem*-halofluorocyclopropanes in an essentially stereospecific manner to yield the corresponding monofluorocyclopropanes.[8]

This paper describes the results of the reduction of some *gem*-bromofluorocyclopropanes with tri-*n*-butyl- and di-*n*-butylsilane, with emphasis directed upon the stereochemistry of the reaction as compared with that of the organotin hydride reduction.

Results

The *gem*-bromofluorocyclopropanes employed for the present study were 7-bromo-7-fluoronorcarane (**1**), 1-bromo-1-fluoro-2-phenylcyclopropane (**2**), and 7-bromo-7-fluoro-2-oxanorcrane (**3**). They were prepared, as a mixture of two geometrical isomers (**a** and **b**), by the reaction of bromofluorocarbene with cyclohexene, styrene, and 2,3-dihydro-4*H*-pyran, respectively.[9,10]

The reduction of these *gem*-bromofluorocyclopropanes was effected by use of 1.4—3 equivalents of tri-*n*-butyl- or di-*n*-butylsilane at 100—145 °C in the presence of a small amount of azobisisobutyronitrile (AIBN) or di-*t*-butyl peroxide (DTBP), to afford the corresponding monofluorocyclopropanes (**c** and **d**).



1 : $R_1, R_2 = -(CH_2)_4-$
2 : $R_1 = Ph, R_2 = H$
3 : $R_1, R_2 = -O-(CH_2)_3-$

The monofluorocyclopropanes thus formed were identified by comparison of their glpc retention times and infrared absorption spectra with those of authentic samples obtained by the reduction with tri-*n*-butyltin hydride.[8]

Table 1 summarizes the results of the reduction of 7-bromo-7-fluoronorcarane (**1**). As is shown in the table (run 1), the reduction of a mixture of the *exo*-F (**1a**) and the *endo*-F isomer (**1b**) with tri-*n*-butylsila neat 140—145 °C gave a mixture of 7-*exo*-fluoro- (**1c**) and 7-*endo*-fluoronorcarane (**1d**). Analysis by glpc showed the isomer ratio of the product (*exo*-F/*endo*-F=1.22) was not identical with the one of the starting material (*exo*-F/*endo*-F=1.67). This result is in sharp contrast with that of the organotin hydride reduction, where complete stereospecificity has been observed.[8] In order to obtain more detailed information about the stereochemistry of the reaction, the two isomers (**1a** and **1b**) were separated from each other by preparative glpc, and were reduced separately (runs 2—9).

When tri-*n*-butylsilane was used at 100 °C, a mixture of **1c** and **1d** was obtained either from **1a** or from **1b** (runs 2 and 6); the isomer ratio of the product was

TABLE 1. REDUCTION OF 7-BROMO-7-FLUORONORCARANE (**1**)

Run	**1** (m mol)		Silane (mmol)	Catalyst	Reaction condition		Yield (%)	Isomer ratio of product (*exo*-F/*endo*-F)
	exo-F	*endo*-F			Temp. (°C)	Time (hr)		
1	52.3[a]		Bu_3SiH (73.5)	DTBP	140—145	9.5	42	55/45
2	12.6	0	〃 (33.3)	AIBN	100	7	49	78/22
3	13.4	0	〃 (39.8)	DTBP	140	7		61/39
4	15.7	0	Bu_2SiH_2 (41.6)	AIBN	100	3.5	68	100/0
5	10.9	0	〃 (29.4)	DTBP	140	2		95/5
6	0	12.5	Bu_3SiH (32.8)	AIBN	100	7	33	15/85
7	0	25.5	〃 (41.0)	DTBP	140	7	36	32/68
8	0	10.2	Bu_2SiH_2 (27.2)	AIBN	100	3.5	51	0/100
9	0	7.5	〃 (20.6)	DTBP	140	2		4/96

a) An isomeric mixture (*exo*-F/*endo*-F=1.67).

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[6] Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori, and M. Hayashi, *J. Organometal. Chem.*, **9**, 21 (1967). b) Y. Nagai, K. Yamazaki, and I. Shiojima, *ibid.*, **9**, 25 (1967). c) Y. Nagai, K. Yamazaki, I. Shiojima, H. Matsumoto, and S. Nakaido, *Yuki Gosei Kagaku Kyokai-shi*, **26**, 884 (1968). d) Y. Nagai, I. Shiojima, K. Nishijima, and H. Matsumoto, *ibid.*, **26**, 999 (1968). e) Y. Nagai, K. Yamazaki, I. Shiojima, M. Hayashi, and H. Matsumoto, *ibid.*, **26**, 1004 (1968).

[7] L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

[8] a) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *ibid.*, **89**, 5719 (1967). b) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970).

[9] a) W. Funasaka, T. Ando, H. Yamanaka, H. Kanehira, and Y. Shimokawa, Abstracts of Symposium on Organic Halogen Compounds, p. 25, Tokyo (1967). b) H. Yamanaka, T. Yagi, K. Teramura, and T. Ando, *Chem. Commun.*, **1971**, 380.

[10] The reaction of bromofluorocarbene with 2,3-dihydro-4*H*-pyran did give a mixture of the *exo*-F (**3a**) and the *endo*-F isomer (**3b**) of **3**, but **3a** was so susceptible to ring expansion[11] that the distillation of the reaction mixture resulted in the decomposition of **3a**. The pure **3b** employed for the present study was obtained by treating the reaction mixture with hot quinoline followed by vacuum distillation.

[11] T. Ando, H. Hosaka, H. Yamanaka, and W. Funasaka, This Bulletin, **42**, 2013 (1969).

Table 2. Reduction of 1-bromo-1-fluoro-2-phenylcyclopropane (**2**)

Run	**2** (mmol)		Silane (mmol)	Catalyst	Reaction condition		Yield (%)	Isomer ratio of product (*anti*-F/*syn*-F)
	anti-F	*syn*-F			Temp. (°C)	Time (hr)		
10	15.8	0	Bu_3SiH (39.3)	AIBN	100	7	69	81/19
11	8.5	0	Bu_2SiH_2 (21.7)	AIBN	100	3.5	60	97/3
12	0	14.6	Bu_3SiH (37.4)	AIBN	100	7	61	16/84
13	0	9.3	Bu_2SiH_2 (23.4)	AIBN	100	3.5	68	2/98

Table 3. Reduction of 7-*exo*-bromo-7-*endo*-fluoro-2-oxanorcarane (**3b**)

Run	**3b** (mmol)	Silane (mmol)	Catalyst	Reaction Condition		Isomer Ratio of Product (*exo*-F/*endo*-F)
				Temp. (°C)	Time (hr)	
14	10.0	Bu_2SiH_2 (25.6)	AIBN	100	3	27/73
15	7.6	Bu_2SiH_2 (19.7)	AIBN	125	1	37/63
16	6.8	Bu_3SiH (17.5)	AIBN	100	7	61/39
17	6.7	Bu_3SiH (17.0)	AIBN	125	5	69/31

Table 4. Reduction of 7,7-Dibromonorcarane (**4**)

Run	Silane	Catalyst	Reaction condition		Isomer ratio of product (*endo*-Br/*exo*-Br)
			Temp. (°C)	Time (hr)	
18	Bu_3SiH	AIBN	100	2	75/25
19	Bu_3SiH	DTBP	140	1	76/24
20	Bu_2SiH_2	AIBN	100	2	75/25
21	Bu_2SiH_2	DTBP	140	1	75/25

78/22 or 15/85, respectively, indicating 22 or 15% inversion had occurred during the reaction. The increase of the reaction temperature to 140 °C increased the relative amount of the inversion product to 39 or 32%, respectively (runs 3 and 7).

The use of di-*n*-butyl-, in place of tri-*n*-butylsilane at 100 °C gave only one isomer of 7-fluoronorcarane with complete retention of configuration (runs 4 and 8), but at 140 °C a small amount (4—5%) of the inversion product was formed (runs 5 and 9).

Similar stereochemical results were obtained in the reduction of the *anti*-F (**2a**) and the *syn*-F isomer (**2b**) of 1-bromo-1-fluoro-2-phenylcyclopropane (**2**) at 100 °C; the reduction with di-*n*-butylsilane occurred in a more stereospecific manner than with tri-*n*-butylsilane. The experimental data are shown in Table 2.

In the reduction of the pure *endo*-F isomer (**3b**) of 7-bromo-7-fluoro-2-oxanorcarane (**3**) with di-*n*-butylsilane, a mixture of the *exo*-F (**3c**) and the *endo*-F isomer (**3d**) of 7-fluoro-2-oxanorcarane was formed even at 100 °C. Here again, it was observed that the use of tri-*n*-butylsilane or the increase of the reaction temperature caused the increase of the relative amount of the inversion product (**3c**). The data are given in Table 3.

In Table 4 are shown the results of the reduction of 7,7-dibromonorcarane (**4**). It proceeded much more readily than that of its bromofluoro analogue (**1**), and gave a mixture of 7-*exo*-bromo- (**5c**) and 7-*endo*-bromonorcarane (**5d**). The isomer ratio of the product (*endo*-Br/*exo*-Br=3.0), which was not affected appreciably either by the reaction temperature or by the kind of silicon hydride, was not very different from the one observed in the reduction with tri-*n*-butyltin hydride.[12]

Discussion

Tri-*n*-butyltin hydride has been shown to reduce *gem*-chlorofluorocyclopropanes at 80 °C in the presence of an appropriate radical initiator such as AIBN, and *gem*-bromofluorocyclopropanes at room temperature in the absence of catalyst, to afford the corresponding monofluorocyclopropanes.[8,9] Since neither tri-*n*-butyl- nor di-*n*-butylsilane could reduce *gem*-chlorofluorocyclopropanes even at 140 °C in the presence of radical initiator, and since the reduction of *gem*-bromofluorocyclopropanes with di-*n*-butylsilane occurred under milder conditions than with tri-*n*-butylsilane, it may be concluded that the reactivity of these hydrides increases in the order $Bu_3SiH < Bu_2SiH_2 < Bu_3SnH$. This order of reactivity is in good agreement with the recent work of Kaplan,[13] who compared the hydrogen-transfer ability of some group IV hydrides and found the order $Ph_3SiH < Ph_2SiH_2 < Ph_3GeH < Ph_3SnH$.

The fact that the reduction with organosilicon hydrides could not be effected in the absence of radical initiator strongly suggests that the reaction follows a free-radical chain mechanism similar to the one already proposed for the reduction of aliphatic halides.[4,6] Very probably it involves the intermediate formation of the α-fluorocyclopropyl radical as one of the chain-

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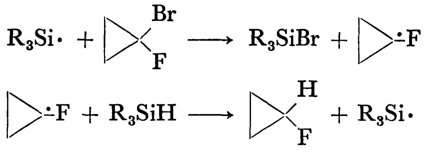
[12] D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

[13] L. Kaplan, *Chem. Commun.*, **1969**, 106.

propagating steps, and may be formulated as follows:

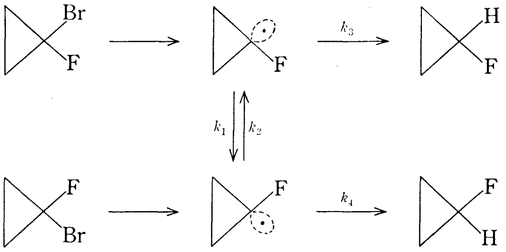
$$\text{Initiator} \longrightarrow \text{In}\cdot$$

$$\text{In}\cdot + R_3SiH \longrightarrow \text{InH} + R_3Si\cdot$$



As was described in the preceding section, the reduction of *gem*-bromofluorocyclopropanes with organosilicon hydrides is essentially less stereospecific than that with organotin hydrides under similar conditions. Moreover, the isomer ratio of the product, *i.e.*, the extent of stereospecificity, is dependent on the reaction temperature as well as on the kind of silicon hydride used.

These observations are well explained by postulating that the α-fluorocyclopropyl radical has a pyramidal structure and that the extent of stereospecificity is determined by the relative rates of its hydrogen abstraction from the silicon or tin hydride (k_3 or k_4), and of its inversion of configuration (k_1 or k_2).



If the reduction is effected with organotin hydrides, which possess an extremely high reactivity toward radicals,[14] the hydrogen transfer from the hydride to the α-fluorocyclopropyl radical should occur at a much faster rate than the inversion of configuration. If the reduction is effected with the less reactive organosilicon hydrides, however, the rate of hydrogen transfer should become slower, and the extent of stereospecificity should be decreased. The experimental results are in good agreement with these expectations. The higher stereospecificity associated with di-*n*-butyl- than tri-*n*-butylsilane may be attributed to the higher reactivity of di-*n*-butyl- than tri-*n*-butylsilane toward radicals.

The low stereospecificity in the reduction of 7-bromo-7-fluoro-2-oxanorcarane (**3**), relative to 7-bromo-7-fluoronorcarane (**1**), is another problem of interest. As analogous effect of ring oxygen has been noted in the reduction of 7-chloro-7-fluoro-2-oxanorcarane with tri-*n*-butyltin hydride,[8] although the origin of the effect is not yet clear at present.

Experimental

Materials. *gem*-Bromofluorocyclopropanes **1**, **2**, and **3** were prepared by the addition reaction of bromofluorocarbene, generated from dibromofluoromethane and potassium *t*-butoxide, to the corresponding olefin.[9] The separation of isomers **1a** and **1b**, and of **2a** and **2b**, was performed by preparative glpc (7.5% TCP on 60/80 Celite 545 at 100 °C and at 80 °C, respectively). The isolation of pure **3b** was accomplished by treating the reaction mixture, containing both **3a** and **3b**, with quinoline at 140 °C for 2 hr, followed by vacuum distillation. Tri-*n*-butylsilane, bp 102—104°/21 mmHg (lit,[15] 215—220 °C), was prepared by the reaction of trichlorosilane with an excess of *n*-butylmagnesium bromide in ether; yield 77%. Di-*n*-butylsilane, bp 63 °C/28 mmHg (lit,[16] 160 °C/773 mmHg), was prepared by the reduction of di-*n*-butylchlorosilane, obtained from trichlorosilane and two equivalents of *n*-butylmagnesium bromide, with lithium aluminum hydride; yield 62%.

7,7-Dibromonorcarane (**4**) was prepared by the addition reaction of dibromocarbene to cyclohexene.

General Procedure for Reduction of gem-*Bromofluorocyclopropane* (**1**, **2**, and **3b**). In a 30 ml, three-necked flask fitted with a thermometer, a magnetic stirrer, an inlet tube for nitrogen, and a reflux condenser was placed a mixture of a *gem*-bromofluorocyclopropane (1.3—3.2 g), 1.4—3 equivalents of tri- or di-*n*-butylsilane, and a small amount of radical initiator (AIBN or DTBP). It was stirred under nitrogen under the condition shown in Table I, II, or III. The isomer ratio of the products was determined by glpc (5% Apiezon Grease L on 60/80 Celite 545 at 80—100 °C) before distillation. In general, the *exo*- or *anti*-F isomer (**1c**, **2c**, or **3c**) had a shorter retention time than the *endo*- or *syn*-F isomer (**1d**, **2d** or **3d**). The yields were calculated by glpc analysis with mesitylene or *n*-dodecane as internal reference. The identification of the products was made by comparing their glpc retention times and infrared absorption spectra with those of authentic specimens.[8] In the reduction of **2** and **3b**, some unidentified by-products were formed.

Reduction of 7,7-Dibromonorcarane (4). The procedure was essentially the same as the one described above. The reaction conditions listed in Table IV were sufficient for 100% conversion. In glpc the *exo*-Br isomer (**5c**) had a shorter retention time than the *endo*-Br isomer (**5b**). The products were identified by comparison with authentic specimens.[12]

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[14] L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

[15] H. Gilman, D. H. Miles, L. D. Moore, and G. W. Gerow, *J. Org. Chem.*, **24**, 219 (1959).

[16] R. West and E. G. Rochow, *ibid.*, **18**, 203 (1953).