Reduction of *gem*-Halofluorocyclopropanes with Tri-*n*-butyltin Hydride

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Some monocyclic and bicyclic *gem*-halofluorocyclopropanes, *viz.*, 1-chloro-1-fluoro-2,2,3,3-tetramethylcyclopropane, 1-chloro-1-fluoro-2,2,3-trimethylcyclopropane, 1-chloro-1-fluoro-2-phenylcyclopropane, 1-chloro-1-fluoro-2-methyl-2-phenylcyclopropane, 1-chloro-1-fluoro-2-ethoxycyclopropane, 7-chloro-7-fluoronorcarane, 6-chloro-6-fluorobicyclo[3.1.0]hexane, 7-chloro-7-fluoro-2-oxanorcarane, 6-chloro-6-fluoro-3-oxabicyclo[3.1.0]hexane, and 7-bromo-7-fluoro-2-oxanorcarane, were reduced with tri-*n*-butyltin hydride at 20–175° to yield the corresponding monofluorocyclopropanes. It has been found, by isolating the geometrical isomers of each substrate and reducing them separately, that in most cases the configuration of the starting material is retained during the reduction, but the stereospecificity tends to be decreased by the increase of the reaction temperature, the decrease of the hydride concentration, and the presence of ring oxygen in bicyclic structure. These results are reasonably explained by postulating a pyramidal structure for the cyclopropyl radical.

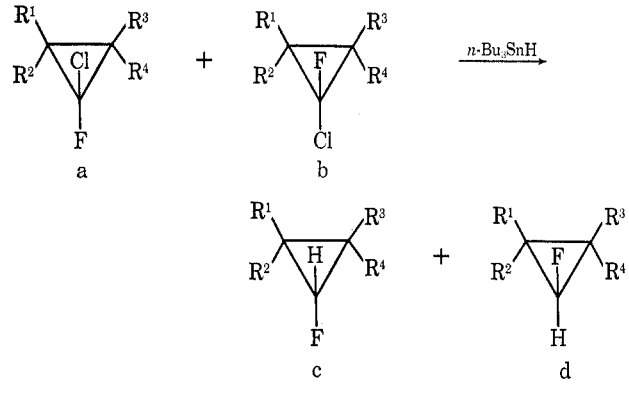
Since the discovery by van der Kerk, *et al.*,[1] that organotin hydrides are capable of reducing organic halides to the corresponding hydrocarbons, much study has been made on the reaction,[2] and it has been found that not only alkyl, allyl, aryl, and vinyl halides but also cyclopropyl halides may be reduced by organotin hydrides. Thus, Seyferth and collaborators[3] have succeeded in preparing some monohalocyclopropanes by use of tri-*n*-butyltin hydride, and Oliver, *et al.*,[4] have reported on the reduction of 1-chloro-1-fluoro-2,2-dimethylcyclopropane[4a] and of 1,1-diiodocyclopropane[4b] by use of tri-*n*-butyltin hydride or a mixture of tri-*n*-butyltin chloride and lithium aluminum hydride. The reduction of 7-chloro-7-phenylnorcarane with triphenyltin hydride in monoglyme has been reported by Jensen and Patterson[5] to yield 7-phenylnorcarane (50–60%) together with a small amount of an olefinic product.

In none of these studies, however, has the stereochemistry of the reaction ever been fully elucidated; even in cases where the *gem*-dihalo- or monohalocyclopropane to be reduced was a mixture of geometrical isomers, *e.g.*, 7-bromo-7-chloronorcarane or 7-chloro-7-phenylnorcarane, no attempt has been made to separate the isomers and reduce them separately. The available data are only the isomer ratios in the starting material and the product.

The present paper will describe the preparation of some new mono- and bicyclic fluorocyclopropanes by reducing the corresponding *gem*-chlorofluorocyclopropanes with tri-*n*-butyltin hydride, as well as the stereochemistry of the reaction.[6]

Results

Reduction of Monocyclic *gem*-Chlorofluorocyclopropanes.—The monocyclic *gem*-chlorofluorocyclopropanes employed for the present study were 1-chloro-1-fluoro-2,2,3,3-tetramethylcyclopropane (Ia), 1-chloro-1-fluoro-2,2,3-trimethylcyclopropane (IIa and IIb), 1-chloro-1-fluoro-2-phenylcyclopropane (IIIa and IIIb), 1-chloro-1-fluoro-2-methyl-2-phenylcyclopropane (IVa and IVb), and 1-chloro-1-fluoro-2-ethoxycyclopropane (Va and Vb). Except for Ia, they were composed of two possible geometrical isomers (a and b), the ratio of which is given in Table I. The reduction was effected by treating them with a slight excess of tri-*n*-butyltin hydride either at 80–90° in the presence of azobisisobutyronitrile (AIBN) or at 130–140° in the presence of di-*t*-butyl peroxide (DTBP). The results are summarized in Table I (runs 1–6). In the absence of AIBN or DTBP, the reduction occurred to little or no extent.



I, $R^1 = R^2 = R^3 = R^4 = Me$ II, $R^1 = R^2 = R^3 = Me$; $R^4 = H$
III, $R^1 = Ph$; $R^2 = R^3 = R^4 = H$ IV, $R^1 = Ph$; $R^2 = Me$; $R^3 = R^4 = H$
V, $R^1 = EtO$; $R^2 = R^3 = R^4 = H$

The structure assignments for the products were made by their proton and fluorine nmr spectra, based on the generalizations that in fluorocyclopropanes the ring hydrogen[7] and fluorine[8] are more strongly coupled with *cis* hydrogen than with *trans* hydrogen, and that in alkyl-, aryl-, or alkoxy-substituted cyclopropanes the ring hydrogen[7,9] and fluorine[10] are shielded by *cis* and deshielded by *trans* substituents. The parameters of the nmr spectra are listed in Table II.

As is shown in Table I, the isomer ratio of the monofluorocyclopropanes thus formed is generally very close to that of the starting chlorofluorocyclopropanes, suggesting the stereospecific nature of the reduction. In order to examine this possibility, IIIa and IIIb were separated from each other by preparative gas chromatography, and each was reduced separately with tri-

(1) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

(2) For review, see (a) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); (b) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

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

(4) (a) J. P. Oliver, U. V. Rao, and M. T. Emerson, *Tetrahedron Lett.*, 3419 (1964); (b) J. P. Oliver and U. V. Rao, *J. Org. Chem.*, **31**, 2699 (1966).

(5) F. R. Jensen and D. B. Patterson, *Tetrahedron Lett.*, 3837 (1966).

(6) A part of the present work has been reported as a preliminary communication: T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Amer. Chem. Soc.*, **89**, 5719 (1967).

(7) (a) J. D. Graham and H. T. Rogers, *ibid.*, **84**, 2249 (1962); (b) W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).

(8) K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, **90**, 6717 (1968).

(9) D. T. Lougone and A. H. Miller, *Chem. Commun.*, 447 (1967).

(10) R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

TABLE I

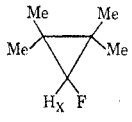
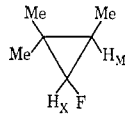
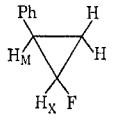
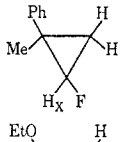
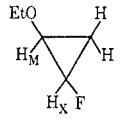
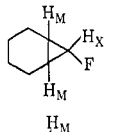
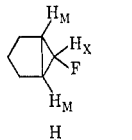
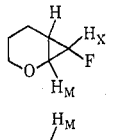
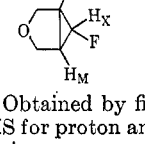
REDUCTION OF MONOCYCLIC *gem*-CHLOROFLUOROCYCLOPROPANES

Run	Compd reduced: Structure	Compd reduced: Isomer ratio, a/b[a]	Reaction condition: Temp, °C	Reaction condition: Catalyst	Product: Structure	Product: Isomer ratio, c/d[a]	Yield, %
1	Ia		80	AIBN	Ic		66
2	IIa + IIb	66:34[b]	90	AIBN	IIc + IId	67:33	53
3	IIIa + IIIb	55:45	90	AIBN	IIIc + IIId	57:43	52
4	IIIa + IIIb	55:45	135	DTBP	IIIc + IIId	55:45	75
5	IVa + IVb	52:48	135	DTBP	IVc + IVd	53:47	78
6	Va + Vb	60:40[b]	85	AIBN	Vc + Vd	61:39	50

[a] Determined by glpc, unless otherwise stated. [b] Determined by fluorine nmr.

TABLE II

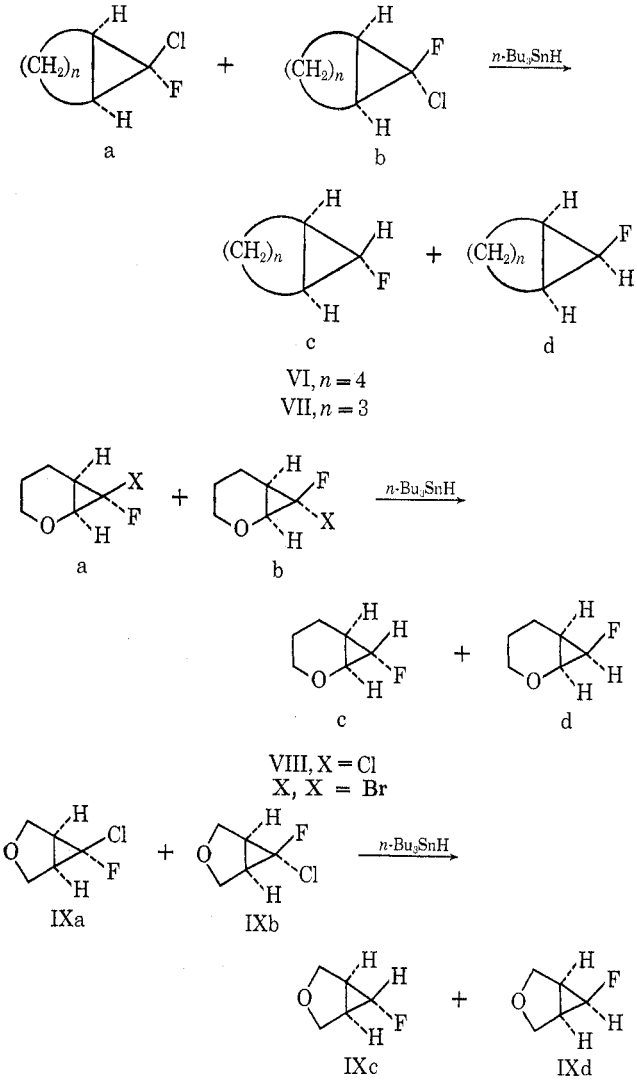
PARAMETERS OF NMR SPECTRA OF FLUOROCYCLOPROPANES[a]

Compd	No.	Chemical shift, ppm[b]: H_X	Chemical shift, ppm[b]: F	Coupling constant, Hz: J_{H_XF}	Coupling constant, Hz: $J_{H_MH_X}$	Coupling constant, Hz: J_{H_MF}
	Ic	3.76	139	65.7		
	IIc	3.92	136	65.0	3.0	22.5
	IId	4.15	153	66.5	7.5	12.0
	IIIc	4.49	121	64.1	2.4	
	IIId	4.58	141	65.9	6.8	
	IVc	4.49	128	65.5		
	IVd	4.55	135	65.9		
	Vc	4.43	134	63.0	0	
	Vd	4.32	154	63.0	4.5	
	VIc	4.25	126	65.0	2.0	18.0
	VId	4.47	156	68.0	6.3	9.0
	VIIc	4.23	137	64.3	1.0	21.0
	VIId	4.62	158	66.3	6.5	10.0
	VIIIc	4.34	135	60.0	0	11.4
	VIIId	4.29	165	63.3	4.3	0
	IXc	5.80	136	69.0	1.0	18.5
	IXd	5.30	157	66.0	6.0	8.0

[a] Obtained by first-order analysis. [b] Downfield from internal TMS for proton and upfield from external trifluoroacetic acid for fluorine.

n-butyltin hydride at 135° in the presence of DTBP. The gas chromatograms and the nmr spectra of the products proved that only one isomer (IIIc) was formed from IIIa, and the other isomer (IIId) was formed from IIIb. A similar stereospecificity was observed also in the reduction of Va at 85° (AIBN). These results are summarized in Table III (runs 7–9).

Reduction of Bicyclic *gem*-Chlorofluorocyclopropanes.—The *gem*-chlorofluorocyclopropanes employed



were 7-chloro-7-fluoronorcarane (VIa and VIb), 6-chloro-6-fluorobicyclo[3.1.0]hexane (VIIa and VIIb), 7-chloro-7-fluoro-2-oxanorcarane (VIIIa and VIIIb), and 6-chloro-6-fluoro-3-oxabicyclo[3.1.0]hexane (IXa and IXb). They were reduced, as a mixture of geometrical isomers, with tri-*n*-butyltin hydride to give the results shown in Table IV (runs 22–28).

To examine the stereochemistry of the reaction, VIa, VIb, VIIb, VIIIb, and IXb were isolated pure and reduced separately. The results are shown in Table III (runs 10–19).

As is evident from Table III, the reduction of VIa, VIb, or VIIb at 80–130° occurred essentially stereospecifically, but that of the corresponding oxa compounds, VIIIb or IXb, did not. Moreover, the isomer ratio of the product obtained from VIIIb or IXb is strongly temperature dependent; the reaction becomes

TABLE III

STEREOCHEMISTRY OF REDUCTION OF *gem*-HALOFLUOROCYCLOPROPANES

Run	Isomer reduced	Reaction condition		Product	
		Temp, °C	Catalyst	Structure	Isomer ratio, c/d[a]
7	IIIa	135	DTBP	IIIc	100:0
8	IIIb	135	DTBP	IIId	0:100
9	Va	85	AIBN	Vc	100:0
10	VIa	130	DTBP	VIc	100:0
11	VIa	165	DTBP	VIc + VId	92:8
12	VIb	130	DTBP	VId	0:100
13	VIb	165	DTBP	VIc + VId	5:95
14	VIIb	80	AIBN	VIId	0:100
15	VIIIb	80	AIBN	VIIIc + VIIId	16:84
16	VIIIb	130	DTBP	VIIIc + VIIId	35:65
17	VIIIb	165	DTBP	VIIIc + VIIId	95:5
18	IXb	90	AIBN	IXc + IXd	24:76
19	IXb	130–135	DTBP	IXc + IXd	58:42
20	Xb	20	None	Xd	0:100
21	Xb	80–90	None	Xc + Vd	28:72

[a] Determined by glpc.

TABLE IV

REDUCTION OF BICYCLIC *gem*-CHLOROFLUOROCYCLOPROPANES

Run	Compd reduced		Reaction condition		Product		
	Structure	Isomer ratio, a/b[a]	Temp, °C	Catalyst	Structure	Isomer ratio, c/d[a]	Yield, %
22	VIa + VIb	58:42	90	AIBN	VIc + VId	58:42	40
23	VIa + VIb	58:42	135–140	DTBP	VIc + VId	58:42	78
24	VIIa + VIIb	70:30[b]	80	AIBN	VIIc + VIId	71:29	30
25	VIIIa + VIIIb	61:39[b]	80	AIBN	VIIIc + VIIId	65:35	33
26	VIIIa + VIIIb	61:39[b]	120–130	DTBP	VIIIc + VIIId	71:29	60
27	VIIIa + VIIIb	61:39[b]	170–175	DTBP	VIIIc + VIIId	98:2	60
28	IXa + IXb	75:25[c]	90	AIBN	IXc + IXd	70:30	36

[a] Determined by glpc, unless otherwise stated. [b] Determined by fluorine nmr. [c] Determined by proton nmr.

less stereospecific the higher the temperature. Based on these data, it was expected that the reduction of VIIIb at a lower temperature, although actually impossible because of the low reactivity of VIIIb toward organotin hydride, would proceed with more enhanced stereospecificity. The validity of this expectation was tested by reducing one isomer (Xb) of structurally analogous but more reactive[11] 7-bromo-7-fluoro-2-oxanorcarane. It gave only VIIId at 20° (run 20), whereas a mixture of VIIIc and VIIId was obtained at 80–90° (run 21).

A similar effect of reaction temperature was noted in the reduction of VIa or VIb, although to a lesser extent; the reduction occurred quite stereospecifically at 130° (runs 10 and 12), but gave a mixture of isomers at 165° (runs 11 and 13).

The extent of stereospecificity of the reduction of VIIIb was also dependent on the concentration of tri-*n*-butyltin hydride; the increase of concentration of the hydride generally caused the increase of the relative amount of VIIId. The results of some typical experiments are shown in Table V.

TABLE V

EFFECT OF HYDRIDE CONCENTRATION ON ISOMER RATIO

Run	Molar ratio, VIIIb/Bu_3SnH	Catalyst	Reaction Temp, °C	Isomer ratio, VIIIc/VIIId[a]
29	1:1	AIBN	90	26:74
30	1:3	AIBN	90	15:85
31	1:6	AIBN	90	14:86
32	1:1	DTBP	135–140	53:47
33	1:3	DTBP	135–140	33:67
34	1:6	DTBP	135–140	32:68

[a] Determined by glpc.

Discussion

The reduction of organic halides with organotin hydrides has been rationalized primarily as a free-radical chain reaction,[11–14] except in the case of hydrogenolysis of aromatic halides, in which a four-center reaction mechanism has been proposed.[15]

The catalytic action of AIBN and DTBP, especially the relationship between their effectiveness and their half-lives at the reaction temperature,[16] suggests that the reduction of the *gem*-chlorofluorocyclopropanes employed in the present study is a radical chain reaction which involves intermediate formation of a fluorocyclopropyl radical as one of the chain-propagating steps. The intermediacy of a cyclopropyl radical has already been postulated in the reduction of some 7,7-dihalonorcaranes[3] and of 7-chloro-7-phenylnorcarane.[5]

If the above assumption is valid, the stereospecificity observed in the reductions of IIIa and IIIb at 135° (runs 7 and 8) must be ascribed to the pyramidal structure of the intermediate 1-fluorocyclopropyl radical and to the much faster rate of its hydrogen ab-

(11) Organic bromides are known to be more reactive toward organotin hydrides than the corresponding chlorides: H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Amer. Chem. Soc.* **84**, 3584 (1962).

(12) L. W. Menapace and H. G. Kuivila, *ibid.*, **86**, 3047 (1964).

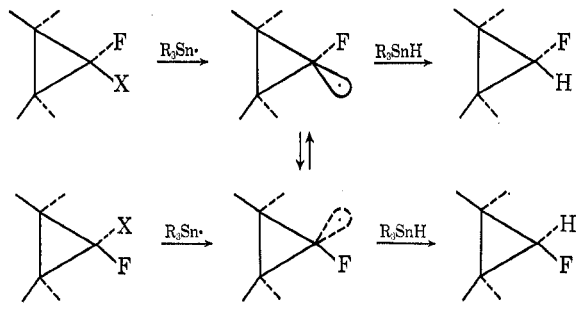
(13) (a) E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 764 (1964); (b) E. J. Kupchik and R. J. Kiesel, *ibid.*, **29**, 3960 (1964).

(14) F. D. Greene and N. N. Lowry, *ibid.*, **32**, 882 (1967).

(15) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *ibid.*, **28**, 703 (1963).

(16) See ref 6, footnote 17.

straction from the organotin hydride, relative to its inversion of configuration; if the radical is planar or if the inversion occurs before hydrogen abstraction, a mixture of two isomeric fluorocyclopropanes in the same composition must be formed from either of the starting materials irrespective of their geometry. The stereospecific reduction of Va (run 9), VIa and VIb (at 130°, runs 10 and 12), VIIb (run 14), and Xb (run 20) can be best explained on the same ground.[17]



The hypothesis advanced above may seem to be inconsistent with the experimental data reported so far, particularly with the finding by Kuivila, *et al.*,[11] and by Sisido, *et al.*,[18] that optically active halides lose their activity when reduced with organotin hydride. This apparent discrepancy may be explained, however, by the substituent effect of fluorine to stabilize the pyramidal structure of radicals. There is good esr and ir spectroscopic evidence that a fluorine substituent can force a normally planar (or very rapidly inverting) radical to become preferentially pyramidal.[19,20] This view is strongly substantiated by the fact that the reduction of 7-*exo*-bromo-7-*endo*-chloronorcarane with tri-*n*-butyltin hydride at 0° gives an isomeric mixture of 7-chloronorcarane (*endo*-Cl/*exo*-Cl = 76:24),[21] indicating a much faster rate of inversion for 7-chloronorcar-7-yl than for 7-fluoronorcar-7-yl radical. It should be noted, in this connection, that in the 1-halo-2-phenylvinyl system the increase of electronegativity of the halogen has been found to increase the extent of stereospecificity.[22]

For the reduction to proceed stereospecifically, the very fast rate of hydrogen transfer from the hydride to the intermediate radical is an essential requirement. A support for this view is given by the fact that the use of less reactive reducing agents, organosilyl hydrides,[23] had the effect of decreasing the extent of stereospecificity;[24] the reduction of 7-*exo*-bromo-7-*endo*-fluoronorcarane with tri-*n*-butylsilyl hydride at 140° in the presence of DTBP gave a mixture of VIc and VId (VIc/VId = 32:68),[25] while that of the 7-*exo*-chloro analog (VIb) with tri-*n*-butyltin hydride gave only VId under similar conditions (run 12). The extremely high reactivity of organotin hydrides toward radicals has already been pointed out by Greene, *et al.*,[14] as well as by Kaplan,[26] who also suggested their potential use to trap configurationally labile radicals.

Another factor which affects the extent of stereospecificity is the reaction temperature; the increase of the temperature generally tends to decrease the stereospecificity. Thus, as is shown in Table III (runs 10–13), VIa and VIb are reduced completely stereospecifically at 135°, but not at 165°. It indicates that at higher temperatures the inversion of configuration of the intermediate 1-fluorocyclopropyl radical is accelerated more pronouncedly than the hydrogen abstraction from organotin hydride. A similar effect of temperature was experienced with other substrates, as shown in runs 15–17, 18 and 19, and 20 and 21, as well as in Table V.

The reduction of VIIIb reveals another feature, the effect of ring oxygen. In contrast to structurally analogous VIb, which is reduced stereospecifically at 130° (run 12), VIIIb gives a mixture of isomers even at 80° (run 15). Moreover, the ratio of VIIIc/VIIId increases as the temperature is raised, reaching as high as 95:5 at 165° (runs 15–17). The difference in the behavior of IXb and VIIb (comparison of runs 18 and 19 with run 14) also suggests a similar effect of ring oxygen.

Since it is very unlikely that an essentially different mechanism operates in the reductions of VIIIb and IXb, these results must be interpreted as showing that the inversion of 7-*endo*-fluoro-2-oxanorcar-7-yl or 6-*endo*-fluoro-3-oxabicyclo[3.1.0]hex-6-yl radical occurs at a rate comparable with, or faster than, their hydrogen abstraction, at least in the temperature range examined. This view is supported by the results shown in Table V; the increase of the concentration of the hydride increases the rate of hydrogen abstraction and thereby increases the extent of stereospecificity.

In addition, the results obtained in runs 15–17 (compared with runs 25–27) and in run 18 (compared with run 28) suggest that the effect of ring oxygen of increasing the rate of inversion (or of decreasing the rate of hydrogen abstraction) of the *exo*-fluoro radicals

(17) Comparison of run 9 with run 6, and of run 14 with run 24, suggests that the reduction of Vb and of VIIa also proceeds essentially stereospecifically, because, if it is not stereospecific and gives a mixture of isomers, the isomer ratio in the product of run 6 or 24 must have been different from that in the starting material.

(18) K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, 3551 (1964).

(19) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); (b) G. A. Carlson and G. C. Pimentel, *ibid.*, **44**, 4053 (1966); (c) D. E. Milligan, M. E. Jacox, and J. J. Comeford, *ibid.*, **44**, 4058 (1966).

(20) It has recently been found that the thermal decomposition of optically active 2,2-diphenyl-1-fluorocyclopropanecarbonyl peroxide in chloroform affords the corresponding cyclopropane of very high specific rotation: J. C. Chen, private communication. It suggests that the slow inversion rate of the 1-fluorocyclopropyl radical is better explained as being due to the effect of fluorine itself, rather than to the complex formation with organotin compounds.[6]

(21) T. Ando, K. Kushima, H. Yamanaka, and W. Funasaka, unpublished results.

(22) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **89**, 5251 (1967).

(23) Y. Nagai, K. Yamazaki, and I. Shiojima, *Bull. Chem. Soc. Jap.*, **40**, 2210 (1967).

(24) The relative hydrogen-transfer ability of organotin, -germanium, and -silicon hydrides has recently been reported on by L. Kaplan [*Chem. Commun.*, 106 (1969)], who pointed out the general utility of the group IV hydrides as selective radical-trapping agents and the possibility of studying configurational and structural isomerization of radicals by choice of one or a series of such hydrides. J. Osugi, S. Hirayama, and S. Kusuhara [*Nippon Kagaku Zasshi*, **88**, 810 (1967); *Rev. Phys. Chem. Jap.*, **36**, 93 (1967)] also reported on the relative ability of silicon and tin hydrides to trap "radical-like" excited states of ketones.

(25) T. Ando, H. Hosaka, H. Yamanaka, and W. Funasaka, unpublished results.

(26) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

is not so pronounced as with the corresponding *endo*-fluoro radicals.[27]

The origin of such an effect of ring oxygen is not clear at present, but it may be explained as follows: a factor such as electrostatic repulsion between unshared electron pairs of F and O,[28] or increased steric strain in the bicyclic structure caused by the presence of ring oxygen, destabilizes the oxygen-containing *endo*-fluoro radicals to a greater extent than the corresponding *exo*-fluoro radicals, with a net effect of lowering the energy barrier for their inversion of configuration, particularly for inversion of the *endo*-fluoro radicals.

Experimental Section

Infrared spectra were obtained with a Shimadzu IR-27 Infracord spectrophotometer. Proton nmr spectra were obtained with a Varian Associates A-60 or H-100 or a Jeolco H-60 spectrometer in carbon tetrachloride or deuteriochloroform with tetramethylsilane (TMS) as internal reference. Fluorine nmr spectra were obtained with a Jeolco C-60 or a Hitachi H-60 spectrometer (56.4 MHz) in carbon tetrachloride with trifluoroacetic acid as external reference. Gas chromatographic (glpc) analyses and preparative separations were performed with a Shimadzu GC-2C or a Yanagimoto 5DH gas chromatograph. For analytical purposes, a 0.3 mm × 3 mm column was used with 7.5% Apiezon L or 10% TCP on 60–80 or 80–100 Celite 545 or Chromosorb W. For preparative purposes, a 10 mm × 3 m column was used with 30% Apiezon L or 30% TCP on 60–80 Celite 545. As carrier gas, helium was used at a rate of 10–20 ml/min. Isomer distributions were calculated from peak areas in nmr spectra or gas chromatograms. The values of isomer ratio given in Tables I, III, IV, and V are accurate within ±2 for glpc analysis and ±5 for nmr analysis. All boiling points are uncorrected.

Materials.—The *gem*-chlorofluorocyclopropanes employed for the present study (I through IX) were prepared by the reaction of the corresponding olefins with chlorofluorocarbene, generated by gradual addition of methanol to a mixture of sodium hydride and methyl dichlorofluoroacetate.[29] 7-Bromo-7-fluoro-2-oxanorcarane (X) was obtained by the reaction of 2,3-dihydro-4H-pyran with bromofluorocarbene, generated by basic decomposition of dibromofluoromethane.[30] Tri-*n*-butyltin hydride was synthesized by the reduction of tri-*n*-butyltin bromide with lithium aluminum hydride[31] or by the reaction of tri-*n*-butyltin oxide with polymethylhydrosiloxane.[32]

Separation of IIIa and IIIb, and of VIa and VIb, was performed by preparative glpc. Isolation of pure Va, VIIb, VIIIb, IXb, and Xb was achieved by heating an isomeric mixture of Va and Vb, VIIa and VIIb, VIIIa and VIIIb, IXa and IXb, and Xa and Xb, respectively, with an excess of quinoline, followed by vacuum distillation. This treatment resulted in the decomposition of only one of the isomers, the other isomer being recovered unchanged.[33]

General Procedure for Preparation of Fluorocyclopropanes from *gem*-Chlorofluorocyclopropanes.—In a 100-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 0.2 mol of a *gem*-chlorofluorocyclopropane, 66.7 g (0.23 mol) of tri-*n*-butyltin hydride, and a small amount of azobisisobutyronitrile (AIBN) or di-*t*-butyl peroxide (DTBP).[34] The mixture was stirred at a specified temperature (see Tables I and IV) until an aliquot from the reaction mixture showed no absorption due to SnH stretching (near 1820 cm^{-1}), which took 3–10 hr. The product was isolated by distillation at reduced pressure or by preparative glpc.

1-Fluoro-2,2,3,3-tetramethylcyclopropane (Ic).—The reduction was conducted at 80–85° (AIBN) for 10 hr to yield 66% Ic, bp 80–82°, $n^{22}D$ 1.3955, together with 7% recovered Ia: ir 2955 (s), 2902 (m), 1483 (s), 1460 (s), 1415 (m), 1382 (m), 1125 (m), 1090 (s), 1013 (m), 940 (s), and 720 cm^{-1} (m).

Anal. Calcd for $C_7H_{13}F$: C, 72.37; H, 11.28. Found: C, 72.26; H, 11.36.

When the reaction was carried out at 95–100° for 7 hr, an olefin estimated to be 3-fluoro-2,4-dimethyl-2,4-pentadiene [ir 1690 and 1638 cm^{-1}; nmr δ 5.0 (2 H, multiplet) and 8.2–8.3 (9 H, multiplet)] was obtained in 10% yield, in addition to 23% Ic and a small amount of unchanged Ia.

1-Fluoro-2,2,3-trimethylcyclopropane (IIc and IId) was obtained in 53% yield (90°, AIBN): bp 40–45° (165 mm); $n^{22}D$ 1.3795; ir 2950 (s), 2880 (s), 1475 (m), 1460 (m), 1382 (m), 1150 (m), 1070 (s), 1030 (m), 964 (m), and 785 cm^{-1} (m).

Anal. Calcd for $C_6H_{11}F$: C, 70.55; H, 10.85. Found: C, 70.82; H, 10.99.

1-Fluoro-2-phenylcyclopropane (IIIc and IIId) was obtained in 75% (135°, DTBP) or 52% yield (90°, AIBN): bp 76–80° (14 mm); $n^{20}D$ 1.5120; ir 3050 (s), 2930 (m), 1603 (s), 1502 (s), 1460 (s), 1438 (s), 1378 (s), 1355 (s), 1222 (s), 1180 (vs), 1143 (vs), 1028 (s), 978 (s), 832 (m), 765 (s), and 699 cm^{-1} (s).

Anal. Calcd for C_9H_9F: C, 79.39; H, 6.66. Found: C, 79.28; H, 6.80.

IIIa and IIIb were separated by preparative glpc (Apiezon L, 110°) and were reduced separately (135°, DTBP). Glpc analysis (Apiezon L, 80°) of the products showed the formation of only one isomer from each of the isomers (IIIc from IIIa, and IIId from IIIb).

1-Fluoro-2-methyl-2-phenylcyclopropane (IVc and IVd) was obtained in 78% yield (135°, DTBP): bp 71–72° (20 mm); $n^{19}D$ 1.5030; ir 3065 (m), 3026 (s), 2970 (s), 2875 (m), 1603 (m), 1502 (s), 1440 (s), 1368 (s), 1133 (s), 1080 (vs), 1042 (s), 1029 (s), 1016 (m), 941 (s), 860 (s), 748 (s), and 700 cm^{-1} (s).

Anal. Calcd for $C_{10}H_{11}F$: C, 79.97; H, 7.38. Found: C, 79.84; H, 7.32.

1-Fluoro-2-ethoxycyclopropane (Vc and Vd) was obtained in 50% yield (80–90°, AIBN): bp 45–48° (110 mm); $n^{24}D$ 1.3740 (Vc) or 1.3859 (Vd); ir 2995 (s), 2890 (s), 1452 (s), 1396 (m), 1378 (m), 1338 (m), 1295 (s), 1225 (s), 1180 (vs), 1142 (vs), 1120 (s), 1078 (vs), 1048 (s), 1000 (m), 972 (s), 952 (m), 910 (m), 843 (m), and 879 cm^{-1} (m).

Anal. Calcd for C_5H_9OF: C, 57.68; H, 8.71. Found: C, 57.85; H, 8.66.

Pure Va was isolated and reduced (85°, AIBN) to give only Vc, as confirmed by glpc (Apiezon L, 90°).

7-Fluoronorcarane (VIc and VId) was obtained in 78% (135°, DTBP) or 40% yield (90°, AIBN): bp 130–133°; $n^{20}D$ 1.4403; ir 3002 (m), 2924 (s), 2875 (s), 1452 (s), 1430 (s), 1345 (m), 1080 (vs), 1018 (m), 940 (m), 870 (m), 857 (m), 752 (m), and 736 cm^{-1} (m).

Anal. Calcd for $C_7H_{11}F$: C, 73.65; H, 9.71. Found: C, 74.96; H, 9.70.

VIa and VIb were separated by glpc (TCP, 100°) and reduced separately (135°, DTBP). Glpc (Apiezon L, 70°) of the products confirmed that only one isomer was formed from each of the isomers (VIc from VIa, and VId from VIb). When the reduction was effected at 165° (DTBP, 3 hr), glpc of the products showed the presence of two components, the ratio of which (VIc/VId) was 92:8 (from VIa) or 5:95 (from VIb).

6-Fluorobicyclo[3.1.0]hexane (VIIc and VIId) was obtained in 30% yield (80°, AIBN): bp 55–56° (166 mm); $n^{21}D$ 1.4234; ir 3024 (m), 2948 (s), 2884 (s), 1475 (m), 1452 (m), 1404 (s),

(27) For example, simple calculation using the data of runs 28 and 18 leads to the prediction that the reduction of pure IXa at 90° should give a mixture of IXc and IXd in the ratio of $(70 - 25 \times 0.24)/(30 - 25 \times 0.76) = 85:15$. Similarly, based on the data of runs 25 and 15, the reduction of pure VIIIa is expected to yield a mixture of VIIIc and VIIId in the ratio of $(65 - 39 \times 0.16)/(35 - 39 \times 0.84) = 96:4$. These calculations are only qualitative, but are sufficient to conclude that the reduction of *exo*-fluoro isomers proceeds with greater stereospecificity than the reduction of *endo*-fluoro isomers.

(28) Interactions between F and O cannot be neglected even in IXa and IXb, if they exist in a quasiboat form as their parent compound, bicyclo[3.1.0]hexane, does. See (a) S. Winstein, E. C. Friedlich, R. Backer, and Y.- I. Lin, *Tetrahedron Lett.*, 621 (1966); (b) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindlay, *J. Org. Chem.*, **33**, 1448 (1968).

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(34) Neither dibenzoyl peroxide nor *t*-butyl perbenzoate was effective in accelerating the reduction.

1306 (m), 1295 (m), 1197 (m), 1110 (vs), 1080 (s), 1010 (s), 915 (s), 878 (m), 860 (m), and 770 cm^{-1} (m).

Anal. Calcd for C_6H_9F: C, 71.97; H, 9.06. Found: C, 72.01; H, 9.25.

The formation of only one isomer (VIId) from VIIb was confirmed by isolation and reduction (80°, AIBN) of pure VIIb, followed by glpc (Apiezon L, 65°).

7-Fluoro-2-oxanorcarane (VIIIc and VIIId) was obtained in 33% (80°, AIBN), 60% (120–130°, DTBP), or 60% yield (170–175°, DTBP): bp 45–52° (30 mm); $n^{20}D$ 1.4352 (VIIIc) or 1.4433 (VIIId); ir 2934 (vs), 2880 (s), 1454 (m), 1439 (m), 1403 (m), 1280 (m), 1238 (vs), 1208 (s), 1148 (s), 1085 (vs), 1035 (s), 912 (s), 880 (s), 820 (s), and 735 cm^{-1} (s).

Anal. Calcd for C_6H_9OF: C, 62.05; H, 7.81. Found: C, 62.19; H, 7.98.

The isomer distributions in the products were determined by glpc (Apiezon L, 80°) and are shown in Table IV.

6-Fluoro-3-oxabicyclo[3.1.0]hexane (IXc and IXd) was obtained in 36% yield (90°, AIBN): bp 51.5–52.5° (20 mm); $n^{20}D$ 1.4168 (IXc) or 1.4329 (IXd); ir 3055 (m), 2950 (s), 2895 (vs), 1483 (m), 1420 (s), 1358 (s), 1200 (m), 1182 (vs), 1110 (vs), 1078 (vs), 1020 (s), 1000 (s), 983 (vs), 900 (s), 840 (s), 815 (s), 779 (s), 719 (s), and 705 cm^{-1} (m).

Anal. Calcd for C_5H_7OF: C, 58.82; H, 6.91. Found: C, 58.80; H, 6.82.

The reduction of pure IXb at 90° (AIBN) or at 130–135° (DTBP) gave a mixture of IXc and IXd, the ratio of which (see Table III) was determined by glpc (Apiezon L, 60°).

The Reduction of 7-*exo*-Chloro-7-*endo*-fluoro-2-oxanorcarane (VIIIb) under Various Conditions. A. Change in Reaction Temperature.—A mixture of 6 g (0.04 mol) of VIIIb, 12.8 g (0.05 mol) of tri-*n*-butyltin hydride, and a small amount of AIBN was heated at 80° for 10 hr. The reaction mixture was submitted to glpc before distillation and the ratio of VIIIc/VIIId was determined. The reductions at 130 and at 165° in the presence of DTBP were carried out similarly. The results are shown in Table III.

B. Change in Tri-*n*-butyltin Hydride Concentration.—A mixture of 6 g (0.04 mol) of VIIIb, 10.3 g (0.04 mol) of tri-*n*-butyltin hydride, and a small amount of AIBN (or DTBP) was heated at 90° (or at 135–140°) for 5 hr. The isomer ratio (VIIIc/VIIId) in the product was determined by glpc before distillation. The reductions using a three- or sixfold amount of tri-*n*-butyltin hydride were carried out similarly. The results are shown in Table V.

The Reduction of 7-*exo*-Bromo-7-*endo*-fluoro-2-oxanorcarane (Xb).—A mixture of 9.8 g (0.05 mol) of Xb and 15.4 g (0.06 mol) of tri-*n*-butyltin hydride was stirred at 20° for 10 hr, in the absence of catalyst. Distillation of the reaction mixture gave 4.6 g (80%) of 7-*endo*-fluoro-2-oxanorcarane (VIIId), with no sign of the *exo*-fluoro isomer (VIIIc) being formed (glpc). The reduction at 80–90° in the absence of catalyst gave a 95% yield of a mixture of VIIIc and VIIId, in the ratio 28:72 (glpc).

Registry No.—Tributyltin hydride, 688-73-3; Ic, 17370-50-2; IIc, 22140-48-3; IId, 22140-49-4; IIIc, 22140-50-7; IIId, 22140-51-8; IVc, 22140-52-9; IVd, 22140-53-0; Vc, 22140-54-1; Vd, 22140-55-2; VIc, 16646-98-3; VId, 16646-97-2; VIIc, 19144-92-4; VIId, 19144-93-5; VIIIc, 22140-60-9; VIIId, 22140-61-0; IXc, 22140-62-1; IXd, 22140-63-2.

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A Nuclear Magnetic Resonance Analysis of Several Photodimers Containing Cyclobutane Rings

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The nmr spectra of the cyclobutane protons of the head-to-head *syn* dimer of coumarin and the head-to-head *anti* dimer of N-methylcarbostyril have been analyzed. The analysis has demonstrated that it is possible to correlate the structure and stereochemistry of these photodimers with the coupling constants. A similar analysis of the photodimers of 6-chloro- and 6-methylcarbostyril has been performed and their structure and stereochemistry have been assigned.

Although dimerization was one of the first observed photochemical reactions, the difficulties involved in determining the exact structures of these dimers have handicapped progress in understanding the mode and mechanism of their formation. To develop procedures that would aid and simplify the structure elucidation of photodimers containing cyclobutane rings, the nmr spectra of several such dimers have been examined. Fleming and Williams[1] have summarized the known coupling constants between protons on cyclobutane rings and their summary indicates that *cis* couplings are generally larger than *trans* couplings. However, the coupling constants vary over a sufficient range so that some overlap between the values occurs. Therefore knowledge of a single coupling constant between protons in a cyclobutane ring is frequently insufficient to establish the stereochemistry of the protons in question. We have examined the nmr spectra of several dimers of coumarin[2] as well as those of dimers of carbostyrils.[3] The structures of the coumarin dimers I–III and the carbostyril dimers IVa and IVb previously have been rigorously established and it was found that each of the dimers contains four cyclobutane protons which are held in a rigid configuration by their fused six–four ring junctions.

Previous attempts to analyze the nmr spectra of the cyclobutane coumarin dimers[2] I, II, and III have been unsuccessful owing to their very poor solubility and because in the solvents commonly employed for nmr spectroscopy the four cyclobutane protons were found to be essentially magnetically equivalent. We have found that liquid sulfur dioxide is a good solvent for these compounds and that the previously magnetically

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