[2.2.1]heptane (**13**) and *endo*-2-hydroxymethylbicyclo-[2.2.1]heptane (**15**) are very close, there is a considerable difference in their limiting slopes. The steric environments of the hydroxyl groups are similar and, therefore, the larger slope for the oxa compound must be the result of two acceptor sites within the same molecule.

Registry No.—**1**, 2566-48-5; **2**, 694-70-2; **3**, 13118-70-2; **4**, 497-37-0; **5**, 13118-71-3; **6**, 13118-72-4; **7**, 13143-81-2; **8**, 6196-84-5; **9**, 497-36-9; **10**, 13118-75-7; **11**, 13118-76-8; **12**, 13118-77-9; **13**, 13118-78-0; **14**, 13118-79-1; **15**, 13137-31-0.

Acknowledgment.—The authors wish to thank Dr. Paul G. Gassman, The Ohio State University, for samples of compounds **5**, **6**, **7**, **10**, and **11** used in this study.

A Novel 1,4-Elimination Reaction of 1-Chloro-2-alkylperfluorocycloalkenes with Alkoxide Ion

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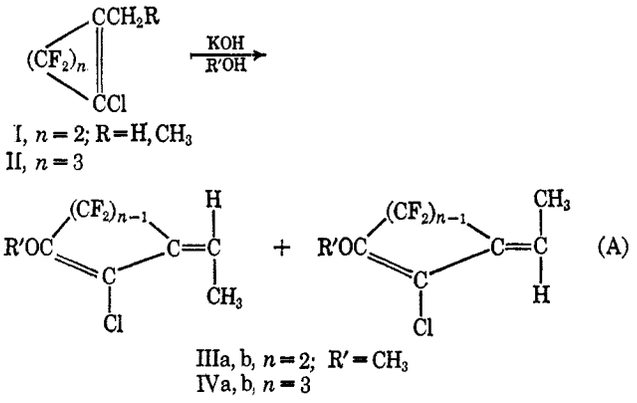
The nucleophilic attack by alkoxide ion on 1-chloro-2-alkylperfluorocyclobutene and -pentene brought about a novel 1,4-elimination reaction which yielded the corresponding 1-alkoxy-2-chloro-3-methyleneperfluorocyclobutene and 1-alkoxy-2-chloro-3-ethylideneperfluorocyclopentene. The physical properties of these compounds along with their nmr data are also presented.

In the course of our studies of nucleophilic attack by alkoxide ion on alicyclic polyfluoro olefins, a novel 1,4-elimination reaction was encountered when 1-chloro-2-alkyltetrafluorocyclobutene-1 (I) and 1-chloro-2-alkylhexafluorocyclopentene-1 (II), respectively, were treated with alcoholic potassium hydroxide (reaction A). A mixture of geometrical isomers of the corresponding 1-alkoxy-2-chloro-3-alkylideneperfluorocycloalkene-1 and 1-alkoxy-2-chloro-3-methyleneperfluorocycloalkene-1 was obtained in high yield. Thus, ab-

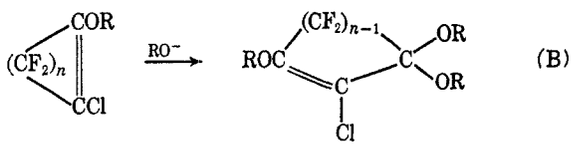


I, $n = 2$; R = H, CH_3
II, $n = 3$

(A)

IIIa, b, $n = 2$; R' = CH_3
IVa, b, $n = 3$

straction of an α hydrogen from the alkyl group by alkoxide ion is apparently preferred to the "normal" nucleophilic displacement of vinylic allylic halogen (reaction B). The acidity of these protons (reaction



(B)

A) can be attributed both to the allylic nature of the protons on the α carbon and their proximity to a highly fluorinated ring structure.[2]

(1) This paper represents part of a Ph.D. thesis submitted to the Graduate School, University of Colorado, 1967.

Although no other example of an analogous 1,4-elimination of hydrogen fluoride involving proton abstraction from a carbon atom has been reported to the best of our knowledge, a similar mechanism may be involved in the reaction of alicyclic polyfluoro olefins with an excess of amines,[3] hydroxylamine,[4] or potassium hydroxide in polar aprotic solvents.[5]

McBee[4] reported that both 1,2-dichlorohexafluorocyclopentene-1 (V) and octafluorocyclopentene-1 (VI) gave 1,3-iminoamines upon treatment with hydroxylamine. Two competitive reaction paths are available to initially formed 1-halo-2-hydroxylaminohexafluorocyclopentene-1 in this reaction: elimination of hydrogen fluoride or additional attack by hydroxylamine (Scheme I). The isolation of the 1,3-iminoamine from VI was cited as evidence against the latter possibility since all previous studies in these systems indicated that the remaining vinylic fluorine would be displaced preferentially.[6]

A similar conclusion has recently been suggested by Stockel and co-workers[5] concerning the hydrolysis of polyhalo olefins with potassium hydroxide in polar aprotic solvents. Two plausible reaction paths were advanced and are illustrated in Scheme II. Path B is capable of explaining why the reaction of VI with hydroxide ion differs from that with alkoxide ion[6] since the formation of enolate ion is not possible in the latter case. The over-all similarity of these reactions is apparent if the heteroatom in the previously mentioned examples is equated with the α carbon of the ethyl group in I and II.

Failure of recovered I to exhibit deuterium incorporation in the allylic position when methanol-OD was

(2) The inductive effect of the γ-carbon fluorines in this example may be relatively unimportant. However, the acidity of a proton with adjacent β-difluoro groups is well documented: A. Streitwieser, Jr., and D. Holtz, Abstracts, 152nd National Meeting of the American Chemical Society, Sept 1966, New York, N. Y., p K-30.

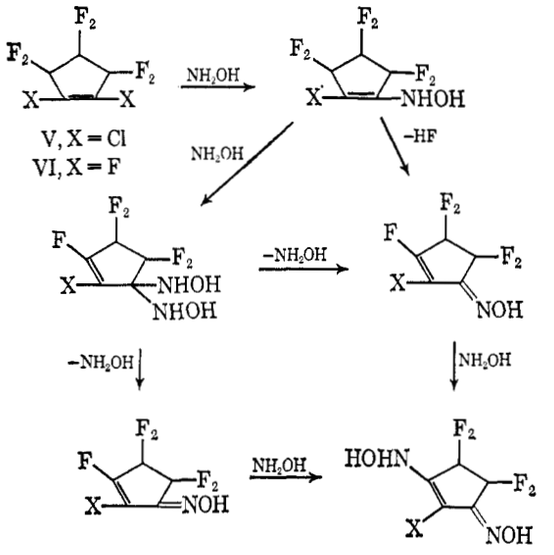
(3) R. L. Pruett, J. T. Barr, *et al.*, *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(4) E. T. McBee, J. J. Turner, C. J. Morton, and A. P. Stefani, *J. Org. Chem.*, **30**, 3698 (1965).

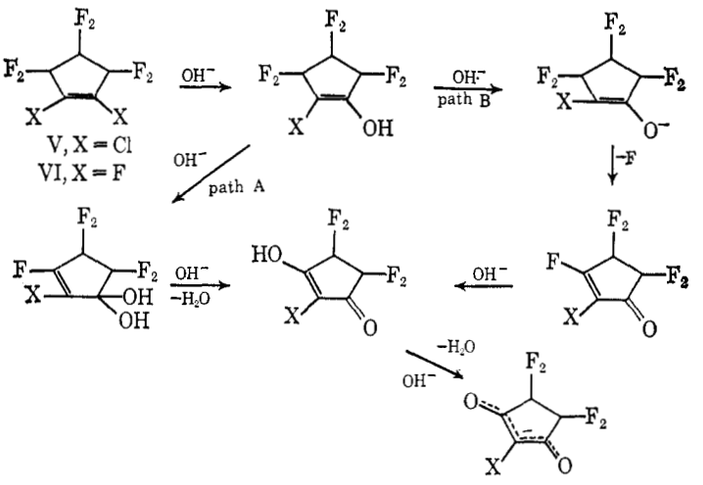
(5) R. F. Stockel, M. T. Beachem, and F. H. Megson, *ibid.*, **30**, 1629 (1965).

(6) R. D. Chambers and R. H. Mobbs, *Advan. Fluorine Chem.*, **4**, 50 (1965).

SCHEME I

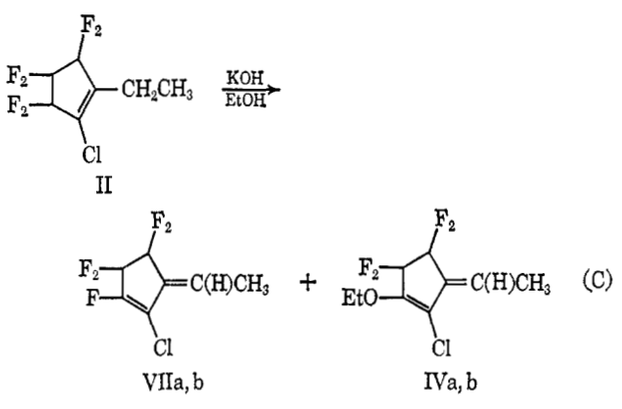


SCHEME II



employed suggests that either the loss of hydrogen fluoride occurs in a concerted manner or that proton abstraction is the rate-determining step if a discrete allylic carbanion is involved in this reaction.

The isolation of trace amounts of 2-chloro-3-ethylidenepentafluorocyclopentene-1 (VIIa, b)[7] in the reaction of II with a deficiency of potassium hydroxide (reaction C) indicates that these reactions proceed *via*



the discrete formation of 2-chloro-3-alkylideneperfluorocycloalkenes which then undergo facile nucleophilic displacement of vinylic fluorine by additional alkoxide ion. Treatment of the corresponding methyl compounds, 1-chloro-2-methyltetrafluorocyclobutene-1 (VIII) and 1-chloro-2-methylhexafluorocyclopentene-1 (IX), with ethanolic potassium hydroxide yielded 1-ethoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X) and 1-ethoxy-2-chloro-3-methylenetetrafluorocyclopentene-1 (XI). These compounds, particularly X, were found to polymerize far more readily than the analogous ethylidene cyclo olefins, presumably because of the removal of the bulky methyl group from the α carbon of the side chain.

The question of absolute assignment of geometrical structure to the ethylidene derivatives is unresolved at the present time. It is apparent from the data in Table I that differences do exist in the proton nmr spectra of these compounds. However, it is particularly disconcerting to note that, although both the cyclobutenyl and cyclopentenyl derivatives exhibit a downfield shift in the proton nmr spectrum of the isomer with the longer glpc retention time (arbitrarily assigned the "b" isomer designation), the relative magnitudes of the differences in allylic and vinylic proton signals are reversed in the two ring systems: $\Delta H^{a}_{IIIa,b} = \tau\ 0.32$; $\Delta H^{b}_{IIIa,b} = \tau\ 0.05$; $\Delta H^{b}_{IVa,b} = \tau\ 0.12$. Thus, the deshielding of the protons of the ethylidene group is apparently dependent on ring structure as well as position relative to the ring substituents and renders a structural assignment based solely on this data highly suspect at present.

Another consequence of ring size is the ratio of geometrical somers, a:b, observed: 40% a to 60% b (1-methoxy-2-chloro-3-ethylidenedifluorocyclobutene, IIIa, b) *vs.* 75% a to 25% b (1-methoxy-2-chloro-3-ethylidenetetrafluorocyclopentene-1, IVa, b).

Although potassium fluoride has been demonstrated to effect isomerization in similar systems,[8] the origin of the isomer ratio a:b is believed to reflect kinetic control rather than an equilibration of initially formed products since IIIa was found to undergo no detectable isomerization when refluxed in methanol containing the inorganic salts present in the reaction mixture.

When I and II were treated with a variety of alkoxides derived from primary and secondary alcohols, the corresponding alkoxydienes formed readily in all cases studied, although the dienes derived from higher molecular weight alcohols were more difficult to separate into pure component isomers and were more sensitive to thermal decomposition. The isomer ratio was essentially constant, within experimental error, for the ethylidenecyclobutenyl compounds although a slight but reproducible shift to the "b" isomer was observed with secondary alkoxides. Similar results were observed with the ethylidenecyclopentenes derived from II.

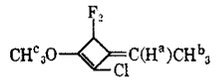
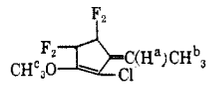
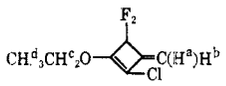
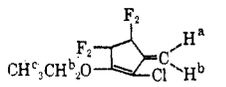
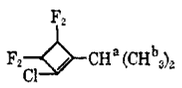
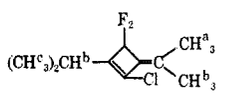
The data seem to be most consistent with a relatively free rotation of the ethyl side chain with minor differences in ground-state energy between the possible rotamers. Assuming that an allylic carbanionic intermediate formed in a nonconcerted elimination would be

(7) J. D. Park and R. J. McMurtry, *Tetrahedron Letters*, 1301 (1967).

(8) D. H. Burton and D. J. Herkes, *ibid.*, 4509 (1965).

TABLE I

SPECTRAL DATA OF NEW COMPOUNDS

Structure	Compd	Nmr signal	τ	J, cps	Integrated area	Assignment	ν (>C=C<), cm^{-1}
	IIIa	Quartet	5.08	7.0	1	H^a	1655
		Singlet	5.94	...	3	H^c	1740
		Doublet	8.23	7.0	3	H^b	
	IIIb	Quartet	4.76	7.0	1	H^a	1645
		Singlet	5.96	...	3	H^c	1735
		Doublet	8.18	7.0	3	H^b	
	IVa	Quartet	4.09	7.6	1	H^a	1645
		Singlet	5.93	...	3	H^c	1680
		Doublet	8.01	7.6	3	H^b	
	IVb	Quartet	4.05	7.6	1	H^a	1640
		Singlet	5.93	...	3	H^c	1680
		Doublet	7.89	7.6	3	H^b	
	X	Doublet	5.18	2.0	1	H^a	1635
		Doublet	5.39	2.0	1	H^b	1705
		Quartet	5.56	7.2	2	H^c	
		Triplet	7.58	7.2	3	H^d	
	XI	Singlet	4.54	...	2	H^a	1640
		Quartet	5.55	7.0	2	H^b	1655
		Triplet	8.60	7.0	3	H^c	
	XIII	Heptet	7.23	7.0	1	H^a	1645
		Doublet	8.74	7.0	6	H^b	
	XIV	Heptet	7.27	7.0	1	H^b	1605
		Singlet	8.17	...	3	H^a	1725
		Singlet	8.21	...	3	$H^{a'}$	
		Doublet	8.78	7.0	6	H^c	

geometrically stable,[9] incorporation of geometrical identity would occur with proton abstraction by the attacking base irregardless of whether the reaction proceeded *via* a concerted or stepwise loss of hydrogen fluoride.

That this reaction may well be quite general in scope is illustrated by the reaction of 1-chloro-2-isopropyltetrafluorocyclobutene-1 (XIII) with excess isopropylmagnesium bromide. Instead of products resulting from nucleophilic displacement of chloride or fluoride ion, treatment of XIII with a 3 *M* excess of isopropylmagnesium bromide led to a 34% yield of 1-isopropyl-2-chloro-3-isopropylidenedifluorocyclobutene-1 (XIV) along with unreacted XIII. The proton nmr spectrum of XIV was consistent only with the assigned structure and, along with the infrared spectrum and elemental analysis obtained, established the diene structure.

That a delicate balance exists between this course of reaction and nucleophilic displacement of halide ion is evidenced by the observation that only products resulting from the latter pathways were detected in the reaction of 1-chloro-2-ethyltetrafluorocyclobutene-1 with excess ethylmagnesium bromide.[10] Preference for one route over the other is probably dependent on both the acidity of the hydrogen in question and the bulk of the attacking Grignard species.

(9) D. J. Cram and D. H. Hunter, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

(10) J. D. Park, R. Sullivan, and R. J. McMurtry, *Tetrahedron Letters*, 173 (1967).

Experimental Section

Preparation of the Cyclopentenes.—Two general synthetic methods were employed in the preparation of the new halogenated alicyclic olefins. The first involved a catalytic replacement of vinylic halogen by bromine in the preparation of 1-bromo-2-chlorohexafluorocyclopentene and 1,2-dibromohexafluorocyclopentene from the commercially available 1,2-dichlorohexafluorocyclopentene and anhydrous hydrogen bromide. Displacement of vinylic halide by lithium halide in polar aprotic solvents was utilized to obtain the other desired olefins. All boiling points were taken by the Siwoloboff method.[11] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Infracord, while nmr spectra were obtained using a Varian A-60 analytical spectrometer.

1-Bromo-2-chlorohexafluorocyclopentene-1 and 1,2-Dibromohexafluorocyclopentene-1.—A mixture of 1,2-dichlorohexafluorocyclopentene and hydrogen bromide was passed through a 100 cm × 2.5 cm Pyrex glass tube packed with a 25:75 $BaSO_4$–C catalyst heated to *ca.* 225°. The catalyst was prepared in the manner of Sharrah.[12] In a typical run, 500 g (2.04 mole) of 1,2-dichlorohexafluorocyclopentene was swept through the tube with *ca.* 3.7 *M* excess of anhydrous hydrogen bromide. The crude reaction products were washed with aqueous sodium bicarbonate and ice water. The aqueous extracts were extracted with ether and the combined organic layers dried over anhydrous magnesium sulfate. Fractional distillation yielded 275 g of unreacted olefin, 128 g (22% of theory) of 1-bromo-2-chlorohexafluorocyclopentene, bp 101° (629 mm), and 106 g (16% of theory) of 1,2-dibromohexafluorocyclopentene, bp 119° (629 mm).

(11) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p 86.

(12) J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2339 (1949).

Anal. Calcd for C_5BrClF_6: C, 20.82; Cl, 12.30; Br, 27.71; F, 39.52. Found: C, 20.60; Br, 27.44; Cl, 12.36; F, 39.21. *Anal.* Calcd for $C_5Br_2F_6$: C, 17.98; Br, 47.87; F, 34.14. Found: C, 17.95; Br, 47.63; F, 34.02.

1-Chloro-2-alkyltetrafluorofluorocyclobutene-1 (where alkyl is CH_3 or C_2H_5) was prepared according to the method of Park and Fontanelli[13] from the reaction of 1,2-dichlorotetrafluorocyclobutene and the Grignard reagent.

1-Chloro-2-ethylhexafluorocyclopentene-1 (II).—Into a 500-ml three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, 50 g (0.204 mole) of 1,2-dichlorohexafluorocyclopentene in 250 ml of tetrahydrofuran was introduced and cooled to 0°. With rapid stirring, 80 ml of a 3 *M* solution of ethylmagnesium bromide in tetrahydrofuran was added dropwise for 1.0 hr. The contents of the flask were allowed to reach room temperature and then gently heated to *ca.* 50° for an additional 2.0 hr. After cooling, unreacted Grignard reagent was destroyed by the cautious addition of 25 ml of dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with ether. The extracts and product layer were dried over anhydrous magnesium sulfate. Distillation yielded 40.6 g (83% of theory) of II, bp 112.5° (629 mm), $n^{28}D$ 1.3644.

Anal. Calcd for $C_7H_5ClF_6$: C, 35.23; H, 2.12; Cl, 14.87; F, 47.78. Found: C, 35.50; H, 2.18; Cl, 15.02; F, 47.73.

The nmr spectrum contained a quartet centered at τ 7.52 and a triplet at τ 8.80 with $J_{H^1H^2}$ = 7.5 cps.[10]

1-Methoxy-2-chloro-3-ethylidenedifluorocyclobutene-1 (IIIa, b).—In a 250-ml three-neck flask equipped with stirrer, condenser, and addition funnel was placed 10.0 g (0.053 mole) of 1-chloro-2-ethyltetrafluorocyclobutene-1 (I) in 15 ml of absolute methanol. The flask was cooled in an ice–water bath and 6.2 g (0.11 mole) of potassium hydroxide dissolved in 15 ml of absolute methanol was added dropwise with rapid stirring for 1 hr. The reaction mixture was then stirred for an additional 2 hr, then poured through a filter into a separating funnel half filled with ice water. The flask and filter were washed with methylene chloride which was added to the funnel. The organic layer was drawn off and the aqueous layer extracted twice with methylene chloride. The methylene chloride and product mixture was dried over anhydrous magnesium sulfate and fractionally distilled under vacuum to yield 7.4 g (78% of theory) of crude IIIa, b. Analysis by glpc showed this material to consist of two components in a 40:60 ratio. Preparative-scale glpc yielded pure IIIa and IIIb (spectral data in Table I).

Anal. Calcd for $C_7H_7ClF_2O$ (IIIa): C, 46.55; H, 3.91; Cl, 19.64; F, 21.04. Found: C, 46.53; H, 4.01; Cl, 15.94; F, 16.87. *Anal.* Calcd for $C_7H_7ClF_2O$ (IIIb): C, 46.55; H, 3.91; Cl, 19.64; F, 21.04. Found: C, 44.24; H, 3.79; Cl, 16.75; F, 21.90.

1-Methoxy-2-chloro-3-ethylidenetetrafluorocyclopentene-1 (IVa, b).—The reaction of 1-chloro-2-ethylhexafluorocyclopentene-1 (10 g, 0.042 mole) with methanolic potassium hydroxide (4.8 g, 0.086 mole in 10 ml methanol) was carried out according to the previously described procedure for alkoxide attack of alkyl halo olefins to yield 8.0 g (83% of theory) of a 74:26 mixture of IVa and IVb. Separation of the geometrical isomers IVa and IVb was effected by preparative-scale glpc on an 18 ft × 0.25 in. Carbowax 20 M column at 140° (spectral data in Table I).

Anal. Calcd for $C_8H_7ClF_4O$ (IVa): C, 41.66; H, 3.06; Cl, 15.38; F, 32.94. Found: C, 41.60; H, 3.07; Cl, 15.52; F, 33.13. *Anal.* Calcd for $C_8H_7ClF_4O$ (IVb): C, 41.66; H, 3.06; Cl, 15.38; F, 32.95. Found: C, 41.70; H, 3.01; Cl, 15.50; F, 32.98.

1-Chloro-2-ethylhexafluorocyclopentene-1 (II).—Into a 500-ml three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, 50 g (0.204 mole) of 1,2-dichlorohexafluorocyclopentene in 250 ml of tetrahydrofuran was introduced and cooled to 0°. With rapid stirring, 80 ml of a 3 *M* solution of ethylmagnesium bromide in tetrahydrofuran was added dropwise for 1.0 hr. The contents of the flask were allowed to reach room temperature and then were gently heated to *ca.* 50° for an additional 2.0 hr. After cooling, unreacted Grignard reagent was destroyed by the cautious addition of 25 ml of dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with ether. The extracts and product layer were dried over anhydrous magnesium sulfate. Distillation yielded 40.6 g (83% of theory) of II, bp 112.5° (629 mm), $n^{28}D$ 1.3644.

Anal. Calcd for $C_7H_5ClF_6$: C, 35.23; H, 2.12; Cl, 14.87; F, 47.78. Found: C, 35.50; H, 2.18; Cl, 15.02; F, 47.73.

The nmr spectrum contained a quartet centered at τ 7.52 and a triplet at τ 8.80 with $J_{H^1H^2}$ = 7.5 cps.

1-Ethoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X).—1-Chloro-2-methyltetrafluorocyclobutene-1 (VIII) (10.0 g, 0.057 mole) was treated according to the previously described procedure for an alkoxide reaction with 6.0 g (0.107 mole) of potassium hydroxide in 15 ml of absolute ethanol to effect an *ca.* 40% conversion to 1-ethoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X), which was shown by glpc to consist of 98% or better of the reaction products. The minor component, of longer glpc retention time, was tentatively identified as 1-methyl-2-chloro-3,3-diethoxydifluorocyclobutene-1 (XIIa) (spectral data in Table I).

Anal. Calcd for $C_7H_7ClF_2O$ (X): C, 46.55; H, 3.91; Cl, 19.64; F, 21.04. Found (polymeric material): C, 42.76; H, 3.88; Cl, 21.08; F, 19.67. *Anal.* Calcd for $C_9H_{13}ClF_2O_2$ (XIIa): C, 47.68; H, 5.77; Cl, 15.65. Found: C, 47.69; H, 5.86; Cl, 15.92.

The infrared ν(>C=C<) frequency of 1670 cm^{-1} corresponded to the expected value for a chloromethyl-substituted cyclobutene. The proton nmr spectrum contained a quartet centered at τ 6.22 (J_{HH} = 7.2 cps) and triplets at τ 7.20 (J_{HH} = 7.2 cps) and τ 8.19 with J_{HF} = 1.5 cps. Preference for the proposed structure over 1-chloro-2-methyl-3,3-diethoxy difluorocyclobutene was based on the magnitude of the J_{HF}, a value consistent with fluorines β to the methyl group.

1-Ethoxy-2-chloro-3-methylenetetrafluorocyclopentene-1 (XI).—1-Chloro-2-methylhexafluorocyclopentene-1 (5.0 g, 0.022 mole) was treated according to the previously described procedure for an alkoxide reaction with 3.0 g (0.054 mole) of potassium hydroxide in 10 ml of absolute ethanol. Work-up yielded 3.4 g (64% of theory) of crude XI. Preparative-scale glpc on a 10 ft × 0.25 in. Ucon LB 550X column yielded pure XI, $n^{28}D$ 1.4391 (spectral data in Table I).

Anal. Calcd for $C_8H_7ClF_4O$: C, 41.66; H, 3.06; Cl, 15.38; F, 32.95. Found: C, 41.80; H, 3.05; Cl, 15.18; F, 32.92.

1-Chloro-2-isopropyltetrafluorocyclobutene-1 (XIII).—1,2-Dichlorotetrafluorocyclobutene (25 g, 0.128 mole) was treated with an *ca.* 2 *M* solution of isopropylmagnesium bromide in tetrahydrofuran (70 ml, *ca.* 0.14 mole) according to the previously described procedure. Work-up of the reaction products in the previously described manner yielded 11.7 g (45% of theory) of XII, bp 122° (630 mm), $n^{28}D$ 1.3746.

Anal. Calcd for $C_8H_7ClF_6$: C, 37.59; H, 2.76; Cl, 13.88; F, 44.60. Found: C, 38.24; H, 2.93; Cl, 13.99; F, 45.19.

Reaction of 1-chloro-2-isopropyltetrafluorocyclobutene-1 (XIII) with isopropylmagnesium bromide was carried out according to the previously described procedure utilizing 5.0 g (0.02 mole) of XIII and 60 ml of an *ca.* 2 *M* solution of isopropylmagnesium bromide in tetrahydrofuran to yield 3.2 g of unreacted XIII and 1.6 g (34% of theory) of 1-isopropyl-2-chloro-3-isopropylidenedifluorocyclobutene-1 (XIV), bp 180° (629 mm) dec, d^{28}_4 1.00, $n^{28}D$ 1.4591.

Anal. Calcd for $C_{10}H_{13}ClF_2$: C, 58.11; H, 6.34; Cl, 17.17; F, 18.39. Found: C, 58.05; H, 6.33; Cl, 17.04; F, 18.22.

Registry No.—II, 13169-07-8; IIIa, 13169-08-9; IIIb, 13169-09-0; IVa, 13169-10-3; IVb, 13169-11-4; X, 13169-12-5; XI, 13169-13-6; XIIa, 13169-14-7; XIII, 13169-15-8; XIV, 13169-16-9; 1-bromo-2-chlorohexafluorocyclopentene, 13169-17-0; 1,2-dibromohexafluorocyclopentene, 13169-18-1.

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