tion can be written either as a synchronous displacement on phosphorus, or as a prior addition followed by elimination; however, inversion has been observed in nucleophilic displacements on phosphorus.[25] There is an electrolyte effect upon this reaction (Table V), and tetramethyl ammonium hydroxide is a more effective reagent than the alkali metal hydroxides. These observations suggest that cations of low charge density assist this reaction in which the initial state, a neutral substrate, and the hydroxide ion, which has a high charge density, go to an anionic transition state of low charge density. A similar salt order has been observed for reactions between alkoxide ions and chloronitrobenzenes, generally in solvents which favor ion pairing.[26]

However, the attack of lyate ions upon 2,4-dinitrochlorobenzene in water or aqueous methanol is assisted by tetraalkyl ammonium ions, and hindered by lithium, sodium, and potassium ions, as is the reaction between thiosulfate ion and *n*-pentyl bromide in aqueous ethanol,[27] suggesting that these specific electrolyte effects may be general for these classes of nucleophilic displacements.

The reaction with hydroxide is approximately twice as fast in dioxane–water, 5:95 v/v, than in dioxane–water, 60:40 v/v, although one might have expected the hydroxide ion to be more nucleophilic in the less aqueous solvent,[28] and the results do not fit the qualitative Hughes–Ingold solvent theory.[16] These observations suggest that the transition state for the alkaline as well as the acid hydrolysis is strongly hydrated, consistent with the low activation energy and very negative activation entropy for the alkaline hydrolysis of these triaryl phosphates, and a similar solvent effect is observed with triphenyl phosphate in going from dioxane–water, 60:40 v/v to 75:25 v/v.[5]

Strong interactions between water and the transition states for both the acid and alkaline hydrolyses of these phosphate triesters are to be expected in terms of the preferred model for bimolecular substitution at a phosphoryl phosphorus atom,[2,29] because any factor which increases the electrophilicity of the phosphoryl phosphorus atom, and hence lowers the activation energy for substitution, will also increase the polarity of the transition state and hence increase its solvation. The net effect will therefore be a further lowering of the activation energy for substitution, at the cost of very negative entropy of activation arising from the ordering of the solvent about the transition state.

Registry No.—*p*-Nitrophenyl diphenyl phosphate, 10359-36-1; $HClO_4$, 7601-90-3; H_2SO_4, 7664-93-9; HCl, 7647-01-0; NaOH, 1310-73-2; KOH, 1310-58-3; LiOH, 1310-65-2; $(CH_3)_4N \cdot OH$, 75-59-2.

Acknowledgments.—We thank Julia M. Bunton for technical assistance with the distribution experiments.

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[25] R. F. Hudson and M. Green, *Angew. Chem. Intern. Ed. Engl.*, **2**, 11 (1963).

[26] J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran, and E. W. Barr, *J. Am. Chem. Soc.*, **80**, 164 (1958); J. D. Reinheimer, J. T. Gerig, and J. C. Cochran, *ibid.*, **83**, 2873 (1961).

[27] L. Robinson, unpublished results.

[28] J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961); A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

[29] G. Aksnes, *Acta Chem. Scand.*, **14**, 1515 (1960).

The Reactions of Some Alicyclic 1,2-Dihalopolyfluoro Olefins with Ethanolic Potassium Hydroxide. The Effect of Ring Size on Product Distribution

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Received May 31, 1967

A series of 1,2-dihalotetrafluorocyclobutenes and corresponding cyclopentenes was synthesized, and their reactions with alkoxide ion are reported and these results interpreted on the basis of carbanion formation.

Nucleophilic substitution reactions of fluoro olefins, particularly displacement of halogen by alkoxide ion, constitute one of the most thoroughly studied aspects of fluorocarbon chemistry. Mechanistic interpretations concerning these reactions have generally been based on the pioneering work of Miller[2] who first rationalized the base-catalyzed addition of alcohols to chlorotrifluoroethylene on the basis of a rate-determining carbanion formation. Alicyclic polyfluorinated olefins (I) were subsequently found to yield unsaturated products of structure II, and the mechanism illustrated in Scheme I has been advanced as a compromise between a concerted displacement[3] of vinylic halide and an addition–elimination of hydrogen halide, the differentiation between which cannot be made on the basis of presently available data.

The continuing program concerned with the synthesis of new polyhalo olefins in this laboratory has given rise to a new series of 1,2-dihaloperfluorocyclobutenes and -pentenes which serve as convenient systems to evaluate nucleophilic attack on alicyclic olefins with respect to two points: initial attack to form a monoether and direction of the subsequent attack.

A series of 1,2-dihalotetrafluorocyclobutenes and 1,2-dihalohexafluorocyclopentenes was prepared in which the vinylic halogens were the three possible combinations of chlorine, bromine, and iodine. The addition of an equivalent amount of ethanolic potassium

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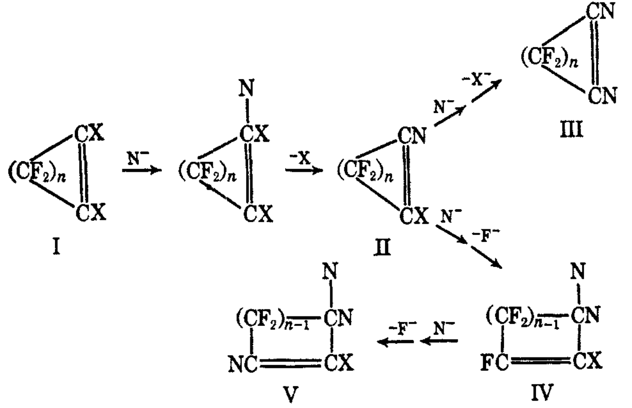
[1] This paper represents parts of Ph.D. Theses submitted to the Graduate School, University of Colorado, Boulder, Colo., by R. J. McMurtry, 1965, and by R. Sullivan, 1964.

[2] W. T. Miller, E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

[3] It is generally recognized that the transition states for reactions at unsaturated centers of low electron density such as carbonyl[4a] and phosphoryl[4b] resemble the corresponding addition intermediates. Thus, although a discrete carbanion may not be involved, as implied above, the transition state leading to a concerted displacement of halide would presumably possess considerable bond formation between the attacking nucleophile and the relatively slight bond cleavage between the carbon and the leaving halogen.

[4] (a) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960); (b) R. F. Hudson, *Advan. Inorg. Radiochem.*, **5**, 362 (1963).

SCHEME I

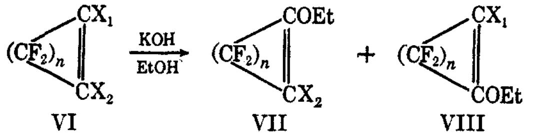


hydroxide to a solution of the perhalo alicyclic olefin in ethanol gave the two possible monoethers in a reaction free of competing side reactions. No products resulting from displacement with rearrangement were detected.

For use in verification of the structure, the new bromo and iodo ethers were also prepared by treatment of the corresponding 1,2-dibromo- or 1,2-diiodoperfluorocycloalkene with equivalent amounts of ethanolic potassium hydroxide. The proposed structures for the new monoethers were substantiated by their elemental analysis, infrared spectra, and proton nmr spectra. The assumptions were made on the basis of previously presented arguments[5] that (1) an inductively stabilized anion occurs as a reaction intermediate and (2) the formation of this intermediate is rate determining. Thus, the ratio of monoethers formed should reflect on the relative rates of formation of the respective carbanionic intermediates, or more generally, the energy requirements of the transition states leading to these intermediates (or products in a concerted displacement).

The ratios of monoethers obtained is tabulated in Table I. The close agreement between the two ring systems and the relative labilities of the vinylic halogens are of particular interest. If these reactions do proceed *via* the formation of a discrete carbanionic intermediate whose relative rate of formation is governed by the stability of the intermediate formed,[5] the relative order of α stabilization of the incipient carbanion derived from this data is I > Br > Cl. Since the rate of carbanion formation has been found to vary with the α substituent in the same order by Hine[6] in studies on the exchange of deuterated haloforms with light water and by Bergman[7] in studies concerning the exchange of various haloforms with deuterium oxide and nucleophilic attack on pentafluorobenzenes[8] this data lends credence to the postulation of a transition state resembling a carbanionic intermediate in the reaction of halocycloalkenes with alkoxide ion. It should be noted, however, that attack at the more electron-deficient carbon, presumably the carbon carrying the more electronegative halogen, would also lead to a similar order of reactivity, the assumption being made that the transition state leading to the postulated intermediate more closely resembles the cycloalkene in question than the negatively charged species. The importance of both the relative ground-state and transition-state stabilities in the rationalization of halide displacement patterns in fluoroaromatics has recently been suggested by Burdon[8] in similar arguments.

TABLE I
PRODUCTS ARISING FROM ALKOXIDE ATTACK ON 1,2-DIHALOPERFLUOROCYCLO OLEFINS



n	X_1	X_2	% VII	% VIII	VII/VIII
2	Cl	Br	75	25	3
2	Br	I	90	10	9
2	Cl	I	97.5	2.5	39
3	Cl	Br	77	23	3.3
3	Br	I	89	11	8.1
3	Cl	I	97	3	32

The possibility of differences in steric bulk of the respective halogens preferentially influencing attack at one site is unlikely in the light of recent work by Coates.[9] In any event, similar factors appear to influence the direction of attack regardless of differences in ring strain or conformation between the cyclobutenyl and cyclopentenyl systems.

Since completion of this work, a report[10] has appeared indicating that the reaction of perfluorocyclopentene gives, in addition to the previously reported[11] displacement of vinylic fluorine, 4% of a product identified as 3-methoxyheptafluorocyclopentene. Although no ethers resulting from loss of fluoride ion were detected in this work, their presence in trace amounts cannot be rigorously excluded since a monoether of the type 3-alkoxy-2,3-dihalopentafluorocyclopentane would almost certainly have reacted with additional alkoxide to form a 1,3-dialkoxy-2,3-dihalotetrafluorocyclopentene which would have escaped detection under the conditions employed in the separation using gas chromatographic techniques. It should be noted, however, that the more electronically favorable loss of halogen from the $>$C(X)OR grouping (X = Cl, Br, I) is contrasted to the loss of F from the relatively stable $>CF_2$ group in this work while, in the case of octafluorocyclopentene, loss of F from $>CF_2$ and $>$C(F)OR groups is compared.[10]

Olefins containing vinylic fluorine were avoided in this work because of the extreme susceptibility of a fluorine-carrying trigonal carbon toward attack by nucleophiles,[12] both with respect to initial attack on perhalo compounds and 1-substituted perfluoro olefins.

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[5] J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, **31**, 1116 (1966).

[6] J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

[7] L. H. Slaugh and E. Bergman, *J. Org. Chem.*, **26**, 3158 (1961).

[8] J. Burdon, *Tetrahedron*, **21**, 3373 (1965).

[9] (a) J. S. Coates, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1966. (b) This work does not necessarily exclude the presence of a steric effect at the carbon atom attacked if the assumption is made that the effective bulk of the two halogens at the two trigonal carbon atoms is similar; *e.g.*, unequal solvation of the two halogens occurs and/or the interatomic C-X distance increases at a rate equal to, or faster than, the increase in Van der Waals radius of X.[9c] (c) H. C. Brown and R. L. Klimisch, *J. Am. Chem. Soc.*, **88**, 1425 (1966).

[10] A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 7358 (1965).

[11] R. F. Stockel, M. T. Beachem, and F. H. Megson, *Can. J. Chem.*, **42**, 2880 (1964).

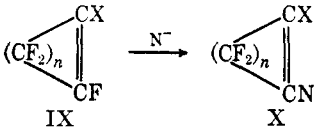
[12] That the relative receptiveness of the trigonal carbons to nucleophilic attack cannot be directly equated with lability of the vinylic fluorine has been clearly demonstrated[10] in the cyclohexenyl series where it was found that, although methoxide attack on 1-hydro-, 1-methoxy-, and 1-methylnonafluorocyclohexene led to 51.5, 62, and 46%, respectively, of products resulting from expulsion of fluorine from a $>CF_2$ group, nucleophilic attack occurred exclusively at the fluorine-carrying trigonal carbon.

This "abnormally high" reactivity has been variously attributed to a mesomeric drift of electron density to the π system by a nonbonded electron pair, an effect which could be manifested in either the ground state or the transition state,[2] an α fluorine being an ineffectual stabilizer of the negative charge developing in a carbanionic intermediate[4] or attack at the more electropositive (fluorine-carrying) carbon.

Several recent reports[13,14] have indicated that certain nucleophiles exhibit a dependence on ring size in the mode of subsequent attack on 1-chloro-2-substituted perfluorocycloalkenes, a result seemingly inconsistent with a common carbanionic intermediate and suggesting that the mechanistic pathway of the halide displacement may be influenced by structural features of the ring system in question. The reaction of sodium borohydride with 1-chloro-2-hydrotetrafluorocyclobutene, for example, was found to yield products arising from the displacement of the vinylic chlorine (37.5%) and displacement with rearrangement (62.5%) while the corresponding cyclopentene was found to yield products arising from vinylic displacement and displacement with rearrangement in the ratio of 8.31 to 91.7 (1:11). Similar results have been reported with sodium borohydride[13a] and Grignard reagents[15], although alkoxide attack on 1-chloro-2-alkoxyperhalocycloalkenes has been reported to yield only products resulting from displacement with rearrangement (IV,[16] V).[17] The product distribution arising from nucleophilic attack on 1-fluorocycloalkanes is given in Table II.

TABLE II

PRODUCT DISTRIBUTION ARISING FROM NUCLEOPHILIC ATTACK ON 1-FLUOROCYCLOALKENES

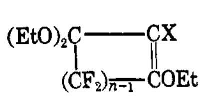


IX X

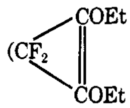
n	X	N	% X	Ref
2	Cl	OEt	100	*a*
2	OEt	OEt	100	*b*
2	H	BH_4, AlH_4	100	*c*
2	Et	EtMgBr	100	*d*
3	Cl	OMe	100	*e*
3	Cl	BH_4	100	*f*
3	Et	EtMgBr	100	*g*
3	OMe	OMe	96	*h*

[a] F. J. Lorenzi, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1954. [b] J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949). [c] See ref 13a. [d] See ref 15. [e] N. A. Edelson, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1962. [f] D. J. Burton and R. L. Johnson, *J. Am. Chem. Soc.*, **86**, 5361 (1964). [g] See ref 14. [h] See ref 10.

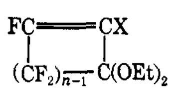
The subsequent path of reaction of the monoethers reported here toward additional nucleophile was studied by treating the various monosubstituted ethers with additional ethanolic potassium hydroxide. In all instances, the triethers of structure XI formed smoothly with no detectable side reactions. No diethers of the 1,2-diethoxyperfluorocycloalkene (XII) class were detected in any of the reactions. Likewise, no diethers of the 1-halo-5,5-diethoxyperfluorocycloalkene structure (XIII) were detected in the reaction products although this may be a result of the reaction conditions employed, particularly in the light of McBee's reported[17b] isolation of minor amounts of 1-chloro-5,5-dimethoxypentafluorocyclopentene from the reaction of 1-chloro-2-methoxyhexafluorocyclopentene with additional methanolic potassium hydroxide. Subsequent attack by alkoxide, thus apparently occurs in a manner analogous to that of alkoxide attack on mono chloro ethers.[16,17] An unanswered question remains concerning the direction of attack by other nucleophilic species on these compounds. Grignard reagents, the other nucleophilic species studied in this laboratory with regard to fluoroalicyclicolefins, gave rise to a competing "halogen exchange" with the perhalocyclobutenes[18] and complete destruction of the olefin accompanied by formation of intractable oils with the cyclopentenes.[19]



XI



XII



XIII

The above data on alkoxide attack may be regarded as being fully consistent with a general mechanistic approach to nucleophilic attack on polyfluorocycloolefins subject to electronic control determined in these instances by the relative stability of the carbanionic intermediate formed. The similarity in data concerning halocyclobutenes and pentenes suggests that differences in geometric constraint of the two ring systems and/or possible differences in relief of strain in intermediates are not instrumental in determining the direction of nucleophilic attack by alkoxide.

Experimental Section

The preparation of 1-bromo-2-chloro-3,3,4,4-tetrafluorocyclobutene-1 (VIa), 1-bromo-2-iodo-3,3,4,4-tetrafluorocyclobutene-1 (VIb), and 1-chloro-2-iodo-3,3,4,4-tetrafluorocyclobutene-1 (VIc) were carried out according to procedure[18] of Sullivan, Lacher, and Park. 1-Bromo-2-chlorohexafluorocyclopentene-1 (VId) and 1,2-dibromohexafluorocyclopentene-1 (IIa) were prepared according to the method[20] of Park and McMurtry.

All boiling points were taken by the Siwoloboff method.[21] 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.

Preparation of 1-Chloro-2-ethoxy-3,3,4,4-tetrafluorocyclobutene-1 (VIIc) and 1-Bromo-2-ethoxy-3,3,4,4-tetrafluorocyclobutene-1 (VIIa). Reaction of 1-Bromo-2-chloro-3,3,4,4-tetrafluorocyclobutene (VIa) with Alcoholic Potassium Hydroxide.— To a solution of 241 g (1.01 mole) of VIa in 150 ml of ethanol in a 1-l., three-neck flask (that was cooled in an ice bath) was added dropwise 57.5 g (1.01 mole) of potassium hydroxide dissolved in 100 ml of ethanol. A white solid formed immediately. The

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(13) (a) D. J. Burton and R. L. Johnson, *Tetrahedron Letters*, 2681 (1966); (b) W. J. Feast, D. R. A. Perry, and R. Stephens, *Tetrahedron*, **22**, 433 (1966).

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

(15) J. D. Park and R. Fontanelli, *J. Org. Chem.*, **28**, 258 (1963).

(16) (a) J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 2342 (1951); (b) J. D. Park, J. R. Dick, and J. R. Lacher, *J. Org. Chem.*, **28**, 1154 (1963).

(17) (a) R. A. Shepard, H. Lessoff, J. D. Domijan, D. B. Hilton, and T. F. Finnegan, *ibid.*, **23**, 2011 (1958); (b) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlov, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962).

(18) R. Sullivan, J. R. Lacher, and J. D. Park, *J. Org. Chem.*, **29**, 3664 (1964).

(19) Unpublished results, this laboratory.

(20) J. D. Park and R. J. McMurtry, *J. Org. Chem.*, **32**, 2397 (1967).

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

addition took 2 hr and stirring was continued for an additional 3 hr. A large volume of water was then added to remove the solid and the ethanol solvent. The water layer was extracted with ether; the ether extracts were dried over magnesium sulfate and distilled. Glpc analysis before distillation showed the presence of monoethers in a 3.1 to 1 ratio with the 1-bromo-2-ethoxy-3,3,4,4-tetrafluorocyclobuten-1 (VIIa) predominating. No other products were detected. Distillation gave 16.5 g of recovered starting material, 29.8 g of 1-chloro-2-ethoxy-3,3,4,4-tetrafluorocyclobutene (VIIc) (16.1% conversion), bp 46° (20 mm), which was identified by comparison of the infrared spectrum with that from an authentic sample, and 115.3 g (51.8% conversion) of compound VIIa: bp 144.5° (614 mm); $n^{25}_{\rm D}$ 1.4062; d^{25}_{25} 1.620. The calculated molar refraction was 37.72 and that observed was 37.65. The nmr spectrum of VIIa showed a methylene quartet with a τ value of 5.50 and a methyl triplet at 8.60. The infrared spectra of the two ethers were similar. A double-bond absorption of VIIc was at 1680 and that for VIIa at 1670 cm^{-1}.

Anal. Calcd for $C_6H_5BrF_4O$: C, 28.94; H, 2.02; Br, 32.09; F, 30.52. Found: C, 29.01; H, 2.19; Br, 32.30; F, 30.69.

1-Iodo-2-ethoxy-3,3,4,4-tetrafluorocyclobutene (VIIb).—To a solution of 4.1 g (0.014 mole) of 1-iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene (VIc) in 5 ml of ethanol kept at 0° was added dropwise 0.8 g (0.014 mole) of potassium hydroxide in ethanol. A white precipitate formed immediately. Stirring was continued for 1.5 hr until the solution was neutral to Hydrion paper. Work-up was performed as described above for the preparation of VIa. Glpc of the ether solution before distillation showed the molar ratio of VIIb to VIIc to be 35 to 1. Separation of VIIb was accomplished on a preparative-scale glpc column at 125° (Dow Corning FS 1265 fluid) to yield 1.50 g (36.6% yield) of the iodo ether: bp 166–167° (613 mm); mp 10–11°; $n^{25}_{\rm D}$ 1.4432; d^{25}_{25} 1.835. The calculated molar refraction was 42.56 and that observed was 42.80. The nmr spectrum showed a methylene quartet at τ 5.0 and a methyl triplet at 8.0. The infrared spectrum is nearly identical with that of VIIa, with the double-bond absorption at 1655 cm^{-1}.

Anal. Calcd for $C_6H_5IF_4O$: C, 24.35; H, 1.71; I, 42.90; F, 25.68. Found: C, 24.50; H, 1.88; I, 43.05; F, 25.40.

Reaction of 1-Iodo-2-bromo-3,3,4,4-tetrafluorocyclobutene (VIb) with Alcoholic Potassium Hydroxide.—The reaction was performed as described above for VIIb with 2.03 g (0.006 mole) of potassium hydroxide in ethanol. Glpc analysis of the ether solution showed the molar ratio of VIIb to VIIa to be 9.0 to 1. The products were separated by preparative-scale vpc and identified by analysis of their infrared spectra.

1-Bromo-2,4,4-triethoxy-3,3-difluorocyclobutene (XI, n = 2, X = Br).—A 2.8-g (0.05 mole) potassium hydroxide in ethanol solution was added dropwise to 6.0 g (0.624 mole) of VIIa in 10 ml of ethanol at room temperature. The mixture was stirred for 3 hr, washed with water, and the product extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and distilled to yield 5.3 g (74% conversion) of XI: bp 78–79° (2 mm); d^{25}_{25} 1.360; $n^{25}_{\rm D}$ 1.4450. The calculated molar refraction was 59.08 and that observed was 59.07. The nmr spectrum showed a single vinyl ethoxy group with τ values as follows: methylene quartet centered at 5.70 and the methyl triplet at 8.65. There are also two equivalent ethoxy groups with τ values centered at 6.20 and 8.80.

Anal. Calcd for $C_{10}H_{15}BrF_2O_3$: C, 39.88; H, 5.02; Br, 26.53; F, 12.62. Found: C, 39.74; H, 4.99; Br, 26.58; F, 12.88.

1-Iodo-2,4,4-triethoxy-3,3-difluorocyclobutene (XI).—The procedure followed was the same as that for the preparation of X with 1.33 g (0.0044 mole) of VIIb and 0.84 g (0.015 mole) of potassium hydroxide in ethanol. Distillation on a semimicro column gave 1.12 g (73.2% yield) of XI: d^{25}_{25} 1.5045; $n^{25}_{\rm D}$ 1.4733. The calculated molar refraction was 64.11 and that observed was 63.81. The nmr spectrum is nearly identical with that for VI with the respective τ values as follows: 5.65, 8.65, 6.20, 8.75.

Anal. Calcd for $C_{10}H_{15}IF_2O_3$: C, 34.50; H, 4.34; I, 36.46; F, 10.87. Found: C, 34.33; H, 4.37; I, 36.63; F, 10.74.

1-Chloro-2-iodohexafluorocyclopentene-1 (VIf). 1.—A mixture of 70 g (0.271 mole) of 1,2-dichlorohexafluorocyclopentene-1 (Ia), 112 g (0.677 mole) of potassium iodide, and 125 ml of diglyme was refluxed for 14 days to give a highly discolored solution containing diglyme, unreacted Ia, 1-chloro-2-iodohexafluorocyclopentene-1 (VIf), and traces of several unidentified materials. Fractional distillation yielded 54.6 g of 1,2-dichlorohexafluorocyclopentene-1 (Ia) and 6.8 g of crude 1-chloro-2-iodohexafluorocyclopentene-1 (VIf) (7.4% of theory). Removal of the 5% diglyme impurity on F.S. 1265 (125) gave pure VIf, a colorless liquid: bp 128° (628 mm); d^{28}_{4} 2.13; $n^{28}_{\rm D}$ 1.4268.

Anal. Calcd for C_5ClF_6I: C, 17.85; Cl, 10.55; F, 33.88; I, 37.72. Found: C, 18.90; Cl, 8.85; F, 33.74; I, 36.27.

The infrared spectrum contained a sharp absorption at 1600 cm^{-1} corresponding to the $>$C=C$<$ stretching frequency.

2. A mixture of 25 g (0.102 mole) of 1-bromo-2-chlorohexafluorocyclopentene-1 (VId), 50 g (0.301 mole) of potassium iodide, and 75 ml of diglyme were refluxed for 14 days. Distillation yielded 14.1 g of unreacted VId and 7.3 g (22% of theory) of slightly impure VIf.

1-Bromo-2-iodohexafluorocyclopentene-1 (VIe) and 1,2-Diiodohexafluorocyclopentene-1 (IIIa).—A mixture of 9.8 g of 1,2-dibromohexafluorocyclopentene-1 (IIa), 18.2 g of anhydrous potassium iodide, and 50 ml of diglyme were refluxed for 3 days. Addition of water forced out 11.3 g of organic product. Extraction of the aqueous layer with methylene chloride and distillation of the combined organic layers gave 3.1 g of unreacted (IIa), 4.6 g of 1-bromo-2-iodohexafluorocyclopentene-1 (VIe), and 3.8 g of crude 1,2-diiodohexafluorocyclopentene-1 (IIIa).

1-Bromo-2-iodohexafluorocyclopentene-1 (VIe) had bp 142° (628 mm); $n^{28}_{\rm D}$ 1.4488.

Anal. Calcd for C_5BrF_6I: C, 15.77; Br, 20.98; F, 29.93; I, 33.32. Found: C, 15.86; Br, 21.06; F, 29.85; I, 34.0.

The infrared spectrum of VIe contained a sharp absorption at 1590 cm^{-1} corresponding to the $>$C=C$<$ stretching frequency.

1,2-Diiodohexafluorocyclopentene-1 (IIIa) had bp 172° (631 mm); d^{20}_{4} 2.50; $n^{28}_{\rm D}$ 1.4848.

Anal. Calcd for $C_5F_6I_2$: C, 14.03; F, 26.64; I, 59.32. Found: C, 15.28; F, 25.16; I, 58.93.

The infrared spectrum of IIIa contained a sharp absorption at 1560 cm^{-1} corresponding to the $>$C=C$<$ stretching frequency.

Reaction of 1,2-Dichlorohexafluorocyclopentene-1 (Ia) with Ethanolic Potassium Hydroxide.—In a 25-ml, three-neck, round-bottom flask, fitted with condenser, pressure equalizing addition funnel, and magnetic stir bar, was placed 10.0 g (0.0366 mole) of 1,2-dichlorohexafluorocyclopentene-1 (Ia) in 10 ml of absolute ethanol. After cooling to 0°, 2.24 g (0.040 mole) of potassium hydroxide in 10 ml of absolute ethanol were added dropwise with rapid stirring. After addition of the KOH–EtOH solution, the reaction mixture was stirred for an additional 2 hr at room temperature, and then poured into a separatory funnel half filled with ice water. The reaction flask and filter were washed with methylene chloride which was added to the funnel. The organic layer was drawn off first and washed with water, followed by a wash with saturated sodium chloride solution. The washings and aqueous layer were then extracted with low-boiling petroleum ether (30–60°). The organic layer and petroleum ether extracts were combined and dried over anhydrous magnesium sulfate. Fractional distillation yielded 8.1 g of 1-chloro-2-ethoxyhexafluorocyclopentene-1 (VIIf): bp 137° (628 mm); $n^{28}_{\rm D}$ 1.3754 (lit.[17a] bp 143–144° (750 mm); $n^{20}_{\rm D}$ 1.3774).

Reaction of 1,2-Dibromohexafluorocyclopentene-1 (IIa) with Ethanolic Potassium Hydroxide.—In a 25-ml, three-neck, round-bottom flask, fitted with condenser, addition funnel, and magnetic stir bar, was placed 5.0 g (0.0144 mole) of 1,2-dibromohexafluorocyclopentene-1 (IIa) in 5 ml of absolute ethanol. After cooling to 0°, 0.84 g (0.015 mole) of potassium hydroxide in 3.0 ml of absolute ethanol were added dropwise with constant stirring. The reaction mixture was stirred for an additional 2 hr at room temperature. Distillation yielded 3.8 g of crude bromo ether. Pure 1-bromo-2-ethoxyhexafluorocyclopentene-1 (VIId) was isolated *via* glpc (10-ft FS 1265 at 140°): bp 150° (629 mm); d^{28}_{4} 1.72; $n^{28}_{\rm D}$ 1.3958.

Anal. Calcd for $C_7H_5F_6BrO$: C, 28.11; H, 1.69; Br, 26.73; F, 38.12. Found: C, 28.28; H, 1.82; Br, 26.49; F, 37.79.

The infrared spectrum of VIId contained a sharp absorption at 1655 cm^{-1} corresponding to the $>$C=C$<$ stretching frequency.

The proton nmr of VIId exhibited a quartet at τ 5.42 with J = 7.0 cps and a triplet at 8.60 with J = 7.0 cps (integrated areas 2:3) corresponding to the methylene and methyl protons of a vinylic ethoxy group.

Reaction of 1,2-Diiodohexafluorocyclopentene-1 (IIIa) with Ethanolic Potassium Hydroxide.—In a 25-ml, three-neck, round-bottom flask, fitted with a dropping funnel, condenser, and magnetic stir bar, was placed 1.5 g (0.0034 mole) of 1,2-diiodohexafluorocyclopentene-1 (IIIa) in 2 ml of ethanol. After cooling to 0°, 0.20 g (0.0036 moles) of potassium hydroxide in

2 ml of absolute ethanol was added dropwise with constant stirring. After addition of the KOH–EtOH solution, the reaction mixture was stirred for an additional 2 hr at room temperature. Work-up in the previously described manner for an alkoxide reaction yielded 1.1 g of crude 1-iodo-2-ethoxyhexafluorocyclopentene-1 (VIIe). Pure VIIe was isolated *via* preparative-scale glpc (18 ft × 0.25 in. Ucon 550X at 150°): bp 172.5° (628 mm); $d^{28}{}_4$ 1.4371.

Anal. Calcd for $C_7H_5F_6IO$: C, 24.30; H, 1.46; F, 32.95; I, 36.68. Found: C, 25.52; H, 2.36; F, 28.58; I, 36.7.

The infrared spectrum of VIIe contained a $>C{=}C<$ absorption at 1635 cm^{-1}.

The proton nmr spectrum of VIIe contained a quartet at τ 5.43 with $J = 7.1$ cps and a triplet at 8.53 with $J = 7.1$ cps corresponding to the methylene and methyl protons of a vinylic ethoxy group.

Reaction of 1-Bromo-2-ethoxyhexafluorocyclopentene-1 (VIId) with Ethanolic Potassium Hydroxide.—A solution of 3.0 g (0.010 moles) of 1-bromo-2-ethoxyhexafluorocyclopentene-1 (VIId) and 10 ml of absolute ethanol was introduced into a 50-ml, three-neck, round-bottom flask, fitted with condenser, addition funnel, and mechanical stirrer. After cooling to 0°, 1.57 g (0.028 mole) of potassium hydroxide in 5 ml of absolute ethanol was added dropwise with rapid stirring. The reaction mixture was stirred for an additional 2 hr at *ca.* 50°. Work-up in the previously described manner for an alkoxide reaction (see compound VIIc) yielded 2.7 g of 1,3,3-triethoxy-2-bromotetrafluorocyclopentene-1 (XI, $n = 3$, X = Br): bp 229° (627 mm); $d^{28}{}_4$ 1.49; $n^{28}{}_D$ 1.4326.

Anal. Calcd for $C_{11}H_{15}BrF_4O_3$: C, 37.62; H, 4.31; Br, 22.76; F, 21.64. Found: C, 37.74; H, 4.32; Br, 22.56; F, 21.90.

The infrared spectrum of Xa contained strong absorptions at 3020 (C–H) and 1660 cm^{-1} ($>C{=}C<$).

The proton nmr Xa contained a triplet at τ 8.59 with $J = 7.2$ cps and a quartet at 5.60 with $J = 7.2$ cps corresponding to the methyl and methylene protons of a vinylic ethoxy group. Signals at τ 6.22 (quartet with $J = 7.2$ cps) and 8.74 (quartet with $J = 7.2$ cps) corresponding to an allylic ethoxy group were also observed. The integrated areas were consistent with the structural assignment.

Reaction of 1-Iodo-2-ethoxyhexafluorocyclopentene-1 (VIIe) with Ethanolic Potassium Hydroxide.—This reaction was carried out according to the previously described procedure described for an alkoxide reaction (see compound VIIc) and afforded pure 1,3,3-triethoxy-2-iodotetrafluorocyclopentene-1 (XIa): bp 240° (627 mm); $d^{28}{}_4$ 1.61; $n^{28}{}_D$ 1.4561.

Anal. Calcd for $C_{11}H_{15}F_4IO_3$: C, 33.18; H, 3.80; F, 19.09; I, 31.88. Found: C, 33.40; H, 3.88; F, 19.27; I, 31.76.

The infrared spectrum of XIa contained strong absorptions at 3020 and 1640 cm^{-1}.

The proton nmr spectrum contained quartets at τ 5.64 and 6.21 and triplets at 8.58 and 8.75. Integrated areas were consistent with the proposed triether structure. All splitting patterns exhibited $J = 7.2$ cps.

Reaction of 1-Bromo-2-chlorohexafluorocyclopentene-1 (VId) with Ethanolic Potassium Hydroxide.—In a 25-ml, three-neck, round-bottom flask, fitted with a condenser, addition funnel, and magnetic stir bar, was placed 4.6 g (0.0158 mole) of 1-bromo-2-chlorohexafluorocyclopentene-1 (VId) in 5 ml of absolute ethanol. After cooling to 0°, 0.94 g (0.0175 mole) of potassium hydroxide in 4 ml of absolute ethanol was added dropwise with rapid stirring. The reaction mixture was stirred for an additional 2 hr at room temperature and worked up according to the previously described procedure used for VIIc.

Analysis of the methylene chloride solution was made on 10 ft × 0.25 in. FS 1265 at 125° and 20 ft × 0.25 in. Ucon 550X at 135° columns using a disk integrator equipped recorder. Integration of peak areas gave 23% of chloro ether (VIIIf) and 77% of bromo ether (VIId). Analytical samples of the respective ethers were obtained by preparative-scale glpc. The respective ethers were identified by comparison of boiling points, glpc retention times, and infrared spectra with those obtained from an authentic sample.

Reaction of 1-Bromo-2-iodohexafluorocyclopentene-1 (VIe) with Ethanolic Potassium Hydroxide.—The reaction was performed (as described above for VId) with 3.0 g (0.0079 mole) of 1-bromo-2-iodohexafluorocyclopentene-1 (VIe) in 5 ml of ethanol and 0.45 g (0.0081 mole) of potassium hydroxide in 3 ml of ethanol. Glpc analysis of the methylene chloride solution showed the molar ratio of the bromo and iodo ethers to be 9% (VIId) to 91% (VIIe). Analytical samples were obtained by preparative-scale glpc and identified by their infrared spectra.

Reaction of 1-Chloro-2-iodohexafluorocyclopentene-1 (VIf) with Ethanolic Potassium Hydroxide.—The reaction was performed as described above (see compound VId) utilizing 2.7 g (0.0080 mole) of 1-chloro-2-iodohexafluorocyclopentene-1 (VIf) in 5 ml of ethanol and 0.47 g (0.0084 mole) of potassium hydroxide in 3 ml of ethanol. Glpc analysis of the methylene chloride solution showed the molar ratio of the chloro and iodo ethers to be 3 (VIIIf) to 97 (VIIe). Analytical samples were obtained by preparative-scale glpc and identified by their infrared spectra.

Registry No.—III ($n = 3$, N = I), 14627-43-1; VI ($n = 3$, X_1 = Br, X_2 = I), 14627-44-2; VI ($n = 3$, X_1 = Cl, X_2 = I), 14627-45-3; VII ($n = 2$, X_2 = Br), 14856-66-7; VII ($n = 2$, X_2 = I), 14627-46-4; VII ($n = 3$, X_2 = Br), 14627-47-5; VII ($n = 3$, X_2 = I), 14627-48-6; VIII ($n = 2$, X_1 = Cl), 360-13-4; VIII ($n = 3$, X_1 = Cl), 715-02-6; XI ($n = 2$, X = Br), 14856-68-9; XI ($n = 2$, X = I), 14856-70-3; XI ($n = 3$, X = Br), 14627-51-1; XI ($n = 3$, X = I), 14627-52-2; potassium hydroxide, 1310-58-3.

Acknowledgment.—The authors wish to express their appreciation to the Minnesota Mining and Manufacturing Co., St. Paul, Minn., and the U. S. Army Natick Laboratories, Natick, Mass., under Scientific Project officer Dr. Malcolm Henry, for their partial support of this work.