2-Chloropropyl Methyl Sulfite and Isomer. The product was obtained according to the above procedure. To determine the isomer distribution, the reaction products were isolated by preparative GLC: ir ν_{max} S=O 1192, S–O 690, 735 cm^{-1}; NMR δ 4.69 (sextet, $-OCH(CH_3)CH_2Cl$), 4.04 (AA′X, $-OCH_2CH(CH_3)Cl$).

Anal. Calcd for $C_4H_9ClO_3S$: C, 27.83; H, 5.52; S, 18.52. Found: C, 27.55; H, 4.97; S, 18.72.

2-Chloro-3-methoxypropyl Methyl Sulfite and Isomer. The results of elementary analyses were satisfactorily consistent with calculated values without further preparative GLC: ir ν_{max} S=O 1200, S–O 710 cm^{-1}; NMR δ 4.58 [q, $-O(CH_2Cl)CH(CH_2OCH_3)$], 4.10 [m, $-OCH_2CH(Cl)-$].

Anal. Calcd for $C_5H_{11}ClO_4S$: C, 29.63; H, 5.43; S, 15.80. Found: C, 29.69; H, 5.59; S, 15.36.

2-Chloromethyl-2-chloroethyl Methyl Sulfite and Isomer. Methyl chlorosulfinate was added to epichlorohydrin as described in the general procedure. The reaction mixture slowly darkened in 10 hr at 30°. An appreciable by-product was isolated by the use of GLC at this stage. Crude product was purified by preparative GLC: ir ν_{max} S=O 1190, S–O 705, 730 cm^{-1}; NMR δ 4.73 [q, $-OCH(CH_2Cl)_2$], 4.20 [m, $-OCH_2CH(CH_2Cl)Cl$].

Anal. Calcd for $C_4H_8Cl_2O_3S$: C, 23.18; H, 3.86; S, 15.46. Found: C, 23.01; H, 4.33; S, 15.26.

Reaction of Alkyl Chlorosulfites with THF. To excess THF alkyl chlorosulfinates were added. After reflux had continued for 4–5 hr, the corresponding 4-chlorobutyl alkyl ethers were isolated by distillation at atmospheric pressure after treating the reaction mixture with 10% aqueous sodium hydroxide solution and dehydrating by anhydrous sodium sulfate. Boiling points and elementary analyses of individual products are summarized in Table VIII. The structures of all of the compounds were confirmed by infrared and NMR spectra: for $CH_3CH(CH_3)CH_2O(CH_2)_4Cl$ ir ν_{max} ether bond 1112 cm^{-1}; NMR δ 0.89 [d, 6 H, $(CH_3)_2CH-$], 3.12 (d, 2 H, $-CHCH_2O-$), 3.30–3.70 (m, 4 H, $-OCH_2CH_2-$, $-CH_2Cl$), 1.60–2.10 (m, 5 H, $-CH_2CH_2-$, $-CHCH_2-$).

Time Dependence of 4-Chlorobutyl Methyl Ether and Methyl Chlorosulfinate. An equimolar mixture of methyl chlorosulfinate and THF was allowed to react in carbon tetrachloride, and the progress of the reaction was followed by means of NMR spectroscopy. The amounts of the products and methyl chlorosulfinate were determined from the integrated values on NMR spectra by using dichloromethane as the internal standard: NMR δ 4.08 [$CH_3OS(O)Cl$], 3.28 [$CH_3O(CH_2)_4Cl$], 3.05 (CH_3Cl).

Registry No.—Methyl chlorosulfinate, 13165-72-5; 1,4-dichlorobutane, 110-56-5; methyl acetoxysulfinate, 5308-06-5.

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Fluoro Olefins. VI. Ring Size Effects in Cyclic Fluoro Olefins with Alkoxide Nucleophiles

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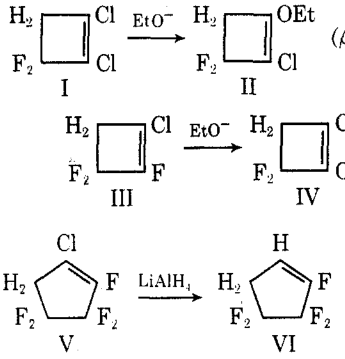
In contrast to 1,2-dichloro-3,3-difluorocyclobutene (I), which undergoes almost exclusive displacement of chloride ion when reacted with ethoxide, the five-membered analog, 1-chloro-5,5-dihydropentafluorocyclopentene (V), undergoes facile allylic rearrangement. Similarly, the six-membered analog undergoes facile dehydrohalogenation. These results show that the conformational changes, as the ring size changes, dominate the reactions of these cyclic fluoro olefins containing *gem*-dihydro groups, and that the "carbanion stabilization" theory of Park cannot be applied indiscrimately to the larger ring system.

The susceptibility of fluorinated olefins to nucleophilic attack is well documented.[2] Park and coworkers theorized the kinetic control of intermediate carbanion formation by α- and β-position substituents.[3] However, a report by Burton and Johnson suggested that the carbanion stabilization theory did not completely explain the reactions of metal hydrides with cyclic polyfluoro olefins.[4] They suggested that steric effects (between entering nucleophile and the leaving group) might be contributing to the different mixtures of products obtained from the reactions of sodium borohydride or lithium aluminum hydride with cyclic fluoro olefins. In addition to this apparent discrepancy between alkoxides and complex metal hydrides, both Burton and Park have observed that the ring size of the cyclic fluoro olefins can have an effect upon product ratios.[4,5] Since most of Park's kinetic control theory has been obtained with cyclobutene systems, it suggested to us that these discrepancies between alkoxides and hydrides might be another example of ring size effects. Accordingly, this paper presents the results of our study into this problem with respect to alkoxides. A later paper will report results obtained with these substrates and their reaction with complex metal hydrides.

The experimentally determined order of α-stabilization was reported to be I > Br > Cl > H > OR > F.[6] To a lesser extent, these intermediates are stabilized by substituents in the β position to the negative charge. The experimentally determined order of β-stabilization was reported to be *gem*-Cl_2 > *gem*-ORCl > *gem*-FCl > *gem*-F_2 > *gem*-$(OR)_2$ > *gem*-H_2.[7]

Examples of the discrepancies between alkoxide and metal hydride reaction products are shown below. Park has reported that the reactions of 1,2-dichloro-3,3-difluorocyclobutene (I) and 1-chloro-2,3,3-trifluorocyclobutene (III) with ethoxide ion give ether products which would be expected from the α- and β-carbanion stabilization theory.[8] Feast and coworkers have reported that the reaction of 1-chloro-5,5-dihydropentafluorocyclopentene (V) with lithium aluminum hydride gives the chloride displaced product.[9] This cyclopentene reaction product is not that expected by application of the carbanion stabilization theory, which would predict fluoride displacement. Park concluded that this latter reaction was evidence that complex metal hydrides might proceed by a different reaction mechanism than that of the alkoxides.[8]



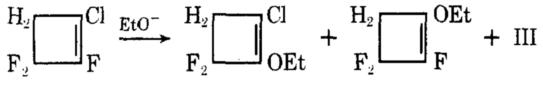
I II (β-*gem*-F_2 > β-*gem*-H_2)

III IV (α-Cl > α-F)

V VI (α-F > α-Cl?) (β-*gem*-F_2 > β-*gem*-H_2)

Results

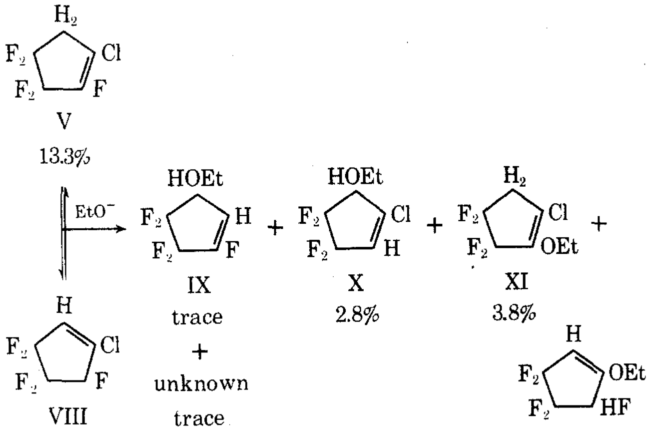
The reaction of III with potassium hydroxide in ethanol was repeated. The results observed by Park were essentially verified.[8] The main product, 1-chloro-2-ethoxy-3,3-difluorocyclobutene (IV), resulted from fluoride displacement; however, a small amount of chloride displaced product, 1-ethoxy-2,3,3-trifluorocyclobutene (VII), was also observed.



III IV VII

77.3% 2.7% 20%

The reaction of V with potassium ethoxide in ethanol gave five new products plus one trace unknown. Here the main product, 1-ethoxy-2,5-dihydropentafluorocyclopentene (XII), resulted from chloride displacement. The reaction of 1-chloro-6,6-dihydroheptafluorocyclohexene (XIII) with potassium ethoxide in ethanol produced two new cyclohexadienes and six unidentified ether products. The listed product ratios (in this reaction) represent the relative integrated areas of GLC chromatograms of the respective final product solutions.



V 13.3%

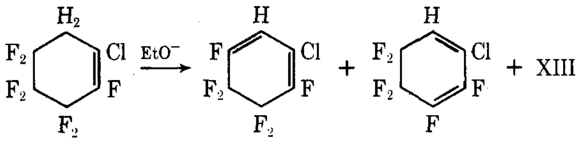
IX trace + unknown trace

X 2.8%

XI 3.8%

VIII 20.2%

XII 59.9%

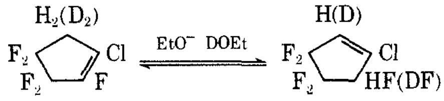


XIII XIV XV

30% 3% 12%

+ six ethers (not isolated)

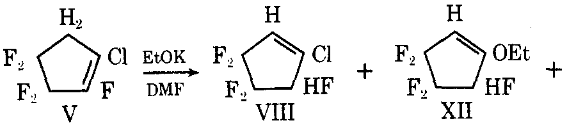
When it became apparent that an allylic rearrangement was contributing to the major product in the cyclopentene case, both the cyclobutene and cyclopentene reactions were repeated using potassium ethoxide in ethanol-*O*-*d*. The potassium ethoxide was pregenerated by reaction of potassium metal with ethanol-*O*-*d*. Previous reactions had shown that potassium metal or potassium hydroxide gave the same reaction products when premixed in ethanol. When III was treated at −10° for 11 days in ethanol-*O*-*d* the same relative ratio of products was observed and no deuterium incorporation into the ring protons was found.[10] When the reaction of V with ethoxide in ethanol-*O*-*d* was carried out, considerable deuterium incorporation in isolated XI and XII was found. In a separate reaction, pure XII was mixed with 0.1 equiv of potassium ethoxide in ethanol-*O*-*d*. Reisolation of XII showed by ^1H NMR that no exchange or additional reaction had taken place. The allylic isomer equilibrium was studied in two ways. One reaction was carried out in ethanol-*O*-*d* (5–10°) but quenched with water after 35 min. Only a trace of ether products was present, but the ratio of allylic isomers V:VIII was 62:38. The isolated compounds showed considerable deuterium incorporation as shown below. A second reaction used previously isolated VIII to demonstrate that the isomerization was reversible and gave V plus ether products.



V (62%) VIII (38%)

	Analysis method	
14.4% D (of H is D)	Mass spectrum	67.3 D (sum of 2- and 5-H)
14.2% D (of H is D)	D elemental	70.5% D
	^{19}F NMR integration	82.9% of 5-H is D

The reaction of V with potassium ethoxide was also studied in dimethylformamide solvent. While the rearrangement of V to VIII did occur in DMF, the reaction mixture turned very black and a GLC chromatogram of the reaction mixture showed many broad unresolved peaks which were assumed to be polymers of cyclopentadienes.



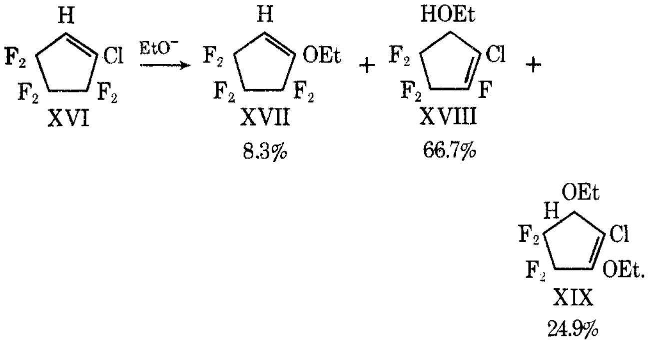
V VIII XII

small amounts

polymers + V

major products

The ratio of nucleophilic attack at chloride compared to attack at hydrogen in the allylic isomer, VIII, appears to be about 20:1 (60%:3%). This isomer has the same olefinic substitution as 1-chloro-2-hydrohexafluorocyclopentene (XVI). The reaction was carried out because we believed that attack would occur mainly at hydrogen (as predicted by both steric and carbanion stabilities). A GLC analysis of the final reaction showed that, indeed, attack at hydrogen was favored by about 10:1.



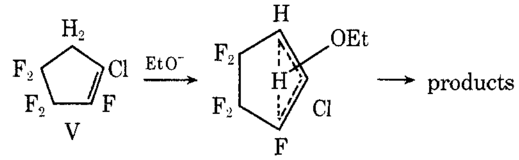
Discussion

The kinetic carbanion theory of Park and steric effects would both predict that fluoride should be the major displacement product in all cases. The results, however, show that fluoride is the major displacement product for the cyclobutene III, but that chloride displacement is preferred with ethoxide and the cyclopentene V. Neither the carbanion theory nor steric effects adequately suggest a means of rationalization of products.

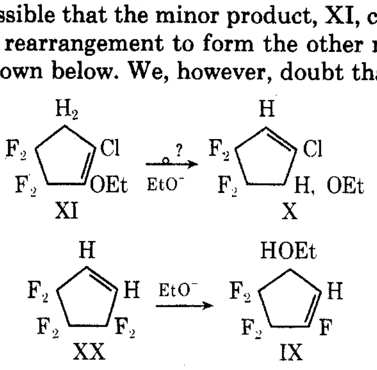
A third alternative, that of ethanol addition across the double bond and a subsequent elimination of either HCl or HF, also does not suggest an explanation for the results. However, elimination of HX cannot be entirely ruled out as making a contribution to some of the products observed. A recent paper reports the observation of small amounts of saturated compounds in alkoxide reactions with 1,2-dihydropolyfluorocyclobutenes, -pentenes, and -hexenes.[11] This paper did, however, state that the reaction path involved addition of alkoxide ion to generate a carbanionic species. Only a minor portion of the carbanion protonated to form the saturated ether; the main product was formed by rearrangement of the carbanion to eliminate fluoride ion (SN2′) and form a new ether olefin. In addition, separate reaction of the saturated ether with alkoxide did not give olefins, showing that the olefin generated was by rearrangement and not HX elimination. Koch has observed a saturated ether product in the reaction of 2-phenylperfluoropropene with ethoxide ion.[12] It was pointed out that even in this noncyclic fluoro ether the rate of dehydrofluorination (to form olefin) was at least six orders of magnitude slower than the rate of reaction of the original olefin with ethoxide.

It therefore seems most reasonable to us to explain these reactions as being due to ring size effects. The deuterium exchange studies clearly show that the cyclobutene III is not acidic enough to form an allylic carbanion system or even exchange any of the ring protons for deuterium under these conditions. Similar deuterium studies on the cyclopentene V show that it is acidic enough to enter into a reversible and mobile equilibrium to form the allylic isomer VIII. Furthermore, from the ^{19}F NMR integration of the 5 position of VIII it can be seen that a fair amount of hydrogen (17%) of V migrates without exchange for deuterium. Such an intramolecular transfer is common in allylic rearrangements and has been described as the "conducted tour" or "internal return" by Cram and others.[13] The cyclohexene system, XIII, also has an acidic, allylic hydrogen pair and in the presence of a strong base (alkoxide) reacts to form 1,2- and 1,4-cyclohexadiene elimination products. The cyclohexene is more acidic than either the cyclopentene or the cyclobutene, probably because conformational effects of the larger ring allow it to more easily orient itself for trans elimination of HF. Overall, then, the switch from major fluoride displacement between the cyclobutene and cyclopentene with alkoxides is due to ring size effects.

Park's original conclusion of alkoxide and hydride mechanism[8] differences was based on the switch from fluoride to chloride displacement as stated in the introduction. While we have shown that alkoxides also show this product switch and we attribute it to ring size effects, there is a mechanism change between the alkoxide reactions on III and V. We feel, as does Park, that the cyclobutene reaction is under kinetic control of the most stable carbanion. However, the cyclopentene case differs by the proton shift and the intramolecular nature of this shift. In addition, we know that VIII undergoes preferential displacement of chloride (to form XII) (20:1). In contrast, attack at the vinyl hydrogen in the model compound, XVI, which carries the same vinyl substitution as VIII, is favored by 10:1.[14] This information allows us to suggest that an acid–base-like alkoxide bridged intermediate is kinetically favored. This intermediate, shown below, explains the intramolecular nature of the allylic rearrangement and positions the ethoxide above the vinyl chloride to make it inherently more probable that nucleophilic displacement take place at that site. This intermediate is highly solvated by the alcoholic solvent. The solvent impedes the reactivity of the alkoxide ion as shown by the DMF solvent reaction. In that solvent the alkoxide is not strongly hydrogen bonded to alcoholic solvent molecules and apparently the increased basicity of the ethoxide is enough to favor complete removal of a proton from the substrate. This removal, we speculate, makes elimination to form cyclopentadienes favored over allylic rearrangement. The DMF reaction did prematurely stop as would be expected from HX neutralization of potassium ethoxide. Some fluorocyclopentadienes have been known to polymerize easily.



We have shown that the main cyclopentene product, XII, does not undergo exchange with deuterium or further reaction. It is possible that the minor product, XI, could undergo an allylic rearrangement to form the other minor product, X, as shown below. We, however, doubt that this rearrangement takes place, as our experience and that of others[5] has shown that once ether substitution has taken place the protons are no longer very acidic. As stated before, X was probably formed by ethoxide attack on VIII. We have no rationale for the formation of the trace product, IX, from either V or VIII. It would most easily be formed from an impurity, 1,2-dihydrohexafluorocyclopentene (XX), in our starting material.[4] We cannot, however, detect any of



this in our starting material. The trace unknown was not identified because it eluted next to the main product (by GLC) and we were unable to isolate it.

The cyclohexene (XIII) reaction was undertaken in order to better investigate possible ring size effects. The reaction, as observed by gas chromatography, was fairly rapid. We were unable to resolve the ether products well enough to use preparative gas chromatography. Nevertheless, isolation of the dienes and recovered starting material was possible by distillation from the relatively nonvolatile ether products and their identification does allow us to say that again there is a mechanism change when the ring size is increased. Identification of the ether products will be undertaken as part of a study of the nucleophilic displacement reactions of alkoxides on cyclohexadienes.

In summary, ring size effects caused by conformational changes dominate the reactions of these cyclic fluoro olefins containing allylic *gem*-dihydro groups with potassium ethoxide. While the kinetic carbanion theory of Park correctly predicts the reaction products of the cyclobutene III, other reaction paths become kinetically favored for larger ring systems. The reader is also referred to a recent paper on the parent hydrocarbon systems of cyclopentene and cyclohexene for more examples of ring size effects.[15]

Experimental Section

Gas–liquid chromatography analyses were obtained on a Hewlett-Packard Model 5752 gas chromatograph. Preparative GLC was carried out on a Varian Aerograph Model 700 instrument. For product ratios the peak areas were determined by a disk integrator and the areas obtained were normalized to 100%. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer. The spectra were calibrated by use of a standard polystyrene peak at 6.238 μm. Proton magnetic resonance spectra were obtained on either a Varian A-60 or HA-100 instrument. Chemical shifts are reported in δ values downfield from tetramethylsilane. Fluorine spectra were obtained on the HA-100 retuned to 94.075 MHz and were calibrated by the audio side-band technique. Fluorine chemical shifts are reported as ϕ units upfield from trichlorofluoromethane internal standard.

Preparation of Starting Materials. 1-Chloro-5,5-dihydropentafluorocyclopentene (V). Commercially available 1,2-dichlorohexafluorocyclopentene was reduced with 2 equiv of sodium borohydride in diglyme in the presence of water. The major product, V, was isolated by steam distillation of the diglyme final solution and spin band distillation of the volatile organic layer. The major fraction (~85%) boiled at 89–90° and was shown by ir and NMR to be V (lit. bp 89.5°).[16]

1-Chloro-2,3,3-trifluorocyclobutene (III). Commercially available 1,1,2,2-tetrachlorotetrafluorocyclobutane was dechlorinated with metallic zinc using the procedure of Rapp.[17] The product formed was 1,2-dichlorotetrafluorocyclobutene. This olefin was reduced with 2 equiv of sodium borohydride as above to give a solution containing III (~50%) and other fluorocarbons (~50%). Spin band distillation gave pure III, bp 52.5° (745 mm) (lit. bp 53°).[17b]

1,2-Dichloro-3,3-difluorocyclobutene (I). Commercially available 1,1-dichloroethene was cyclodimerized with 1,1-dichlorodifluoroethyene according to a procedure reported by Dick.[18] The dimerization products were dissolved in dioxane and dechlorinated with metallic zinc. A fraction boiling at 80–90° was collected and spin band distilled to give a 7.8% yield of I, bp 89–90° (750 mm), ^{1}H NMR δ_{CH_2} 3.17 (triplet, J_{HF} = 3.0 Hz) (lit. δ 3.15, J = 3.0 Hz).[19]

1-Chloro-6,6-dihydroheptafluorocyclohexene (XIII). Commercially available 1,2-dichlorooctafluorocyclohexene was reduced with 2 equiv of sodium borohydride in diglyme. The reaction mixture was hydrolized with dilute nitric acid and diluted with water, and the lower, fluorocarbon layer separated. This material was distilled at 115° (750 mm) to give a 67% yield of XIII. The compound gave n^{20}D 1.3606, ir 1706 cm^{-1} (FC=CCl) (lit. 116°, 1705 cm^{-1}).[9]

Reaction of 1-Chloro-2,3,3-trifluorocyclobutene (III) with Ethoxide. The reaction was carried out once using potassium hydroxide in ethanol and once using potassium metal in ethanol-*O-d*. In a 100-ml three-necked flask equipped with a condenser, Teflon stopcock, dropping funnel, and magnetic stirrer were placed 2.85 g (0.02 mol) of III and 10 ml of absolute ethanol. To the flask was rapidly added 10 ml of absolute ethanol in which 1.45 g (0.022 mol) of potassium hydroxide had previously been dissolved. The reaction mixture was stirred overnight at 25°. A GLC analysis (QF-1, 10%, 10 ft, 70–150°) of the final mixture gave, in order of elution, III (20%), minor product (2.7%), and major product (77.3%).

The reaction was repeated at temperatures of −9 to −13° utilizing a thermocouple-cooled bath. In the flask was placed 0.78 g (0.02 mol) of potassium metal while a slow nitrogen gas stream was maintained through the flask. Ten milliliters of ethanol-*O-d* (C_2H_5OD) was dropped onto the metal. Once addition was completed the flask was immersed in the cold bath and a magnetic stirrer and 2.85 g (0.02 mol) of precooled III was added. The progress of the reaction was followed by periodically removing 0.05 ml of reaction solution, dilution with water, and injecting the lower, fluorocarbon layer into the GLC. After some 50 hr an additional 0.01 mol of potassium dissolved in 5 ml of ethanol-*O-d* was added. The reaction was quenched with water after 11 days, although 13% starting material remained. The two reaction products were isolated by preparative GLC (QF-1, 3, 140°) to give a minor component with ir 1754 cm^{-1} (FC=COR) assumed to be 1-ethoxy-4,4-dihydrotrifluorocyclobutene (VII) (lit. ir 1750 cm^{-1}),[4] and a major component, 1-chloro-2-ethoxy-3,3-difluorocyclobutene (IV): ir 1690 cm^{-1} (ClC=COR); ^{1}H NMR δ_{CH_3} 1.30 (t, 7.0), δ_{CH_2} 4.20 (q, 7.0) and 2.77 (t, J_{HF} = 3.0 Hz) [lit. ir 1680 cm^{-1}; ^{1}H NMR δ 1.30, 4.20, and 2.77 (J = 3.0 Hz)].[8] The ^{1}H NMR integration (2:2:3) showed that *no* deuterium exchange had taken place. The ether products were present in the approximate ratio of 3:97 (VII:IV).

Reaction of 1-Chloro-5,5-dihydropentafluorocyclopentene (V) with Ethoxide. In a 100-ml flask equipped as above was placed 2.15 g (0.055 mol) of potassium. Dry nitrogen was slowly swept through the flask as 45 ml of absolute ethanol was slowly dropped onto the potassium. When the reaction was completed, 9.63 g (0.05 mol) of 1-chloro-5,5-dihydropentafluorocyclopentene (V, precooled) was added rapidly. The reaction mixture was maintained at 0–3° for 23 hr, after which time it was quenched with water. The reaction was periodically monitored by removing a 0.1-ml sample, diluting it with water, and injecting the lower layer into the gas chromatograph (QF-1, 10%, 10 ft, 90–165° at 15°/min). A peak (which eluted just after the starting material) was observed to grow rapidly with time and slowly decay during the reaction as other materials of greater retention times grew in proportion. After the reaction was quenched GLC analysis gave starting material (V, 13.3%); starting material isomer, 1-chloro-2,5-dihydropentafluorocyclopentene (VIII, 20.2%); 1,5-dihydro-5-ethoxypentafluorocyclopentene (IX, trace); 1,3-dihydro-2-chloro-3-ethoxytetrafluorocyclopentene (X, 2.8%); a trace unknown not isolated because it could not be separated from main product; and 1,3-dihydro-2-ethoxypentafluorocyclopentene (XII, 59.9%). Products from a number of these reactions were combined and isolated by preparative GLC (QF-1, 30%, 165°) for product identification and characterization. The starting material isomer (VIII) gave ir 1630 cm^{-1} (HC=CCl); ^{1}H NMR δ_{5H} 5.7 (J_{HF} = 52.4 Hz), 8.5, 5.0, 2.3, 2.2, δ_{2H} 6.30 (m); ^{19}F NMR ϕ_{3F} 104.8 and 109.6 (m of AB pattern, J_{FF} = 265 Hz), ϕ_{4F} 121.6 and 129.3 (m of AB pattern, J_{FF} = 251 Hz), and ϕ_{5F} 193.8 (d of m, J_{HF} = 52.5 Hz). The ether products respectively: IX gave ir 1695 cm^{-1} (HC=CF); ^{1}H NMR δ_{CH_3} 1.24 (t), δ_{CH_2} 3.68 (ABX$_3$ pattern, J_{AB} = 9.1, J_{AX} = 7.0, J_{BX} = 6.9 Hz), δ_{5H} 4.34 (m), δ_{1H} 5.69 (m); X gave bp 151.5° (743 mm); n^{20}D 1.3943, ir 1630 cm^{-1} (HC=CCl); ^{1}H NMR δ_{CH_3} 1.24 (t, J = 7.0 Hz), δ_{CH_2} 3.78 (ABX$_3$ pattern, J_{AB} = 9.2, $J_{A,BX}$ = 7.0 Hz), δ_{1H} 6.05 (m), δ_{3H} 4.30 (m); XI gave bp 38° (3 mm); n^{20}D 1.3789; ir 1673 cm^{-1} (ClC=COR); ^{1}H NMR δ_{CH_3} 1.34 (t, J_{HH} = 7.0 Hz), δ_{CH_2O} 4.30 (q, 7.0), δ_{CH_2} 3.20 (t of t, J_{4F5H} = 11.2, J_{3F5H} = 3.4 Hz); ^{19}F NMR ϕ_{3F} 115.5, ϕ_{4F} 115.1; XII gave bp 50° (3 mm), 106° (100 mm); n^{20}D 1.3770; ir 1647 cm^{-1} (HC=COR); ^{1}H NMR δ_{CH_3} 1.38 (t, J_{HH} = 7.0 Hz), δ_{CH_2} 4.02 (q, 7.0), δ_{1H} 5.13 (m), δ_{3H} 5.15 (m, J_{HF} = 53.1 Hz, 9.15, 4.85, 1.65, 1.65); ^{19}F NMR ϕ_{5F} (AB pattern at 97.8 and 105.7, J_{FF} = 251 Hz), ϕ_{4F} (AB pattern at 121.7 and 128.8, J_{FF} = 250 Hz), ϕ_{3F} 195.6 (m, J_{HF} = 53.5 Hz, and others). Anal. Calcd for $C_7H_7F_5O$: C, 41.60; H, 3.49. Found: C, 41.33; H, 3.40.

A similar 0.05-mol reaction was carried to 98.7% completion and the GLC showed that the major product, XII, was 91.1% of the final mixture. After dilution with water and separation of the organic layer the water layer was acidified with nitric acid and treated with silver nitrate. A total of 6.21 g of a possible 7.09 g of silver chloride was isolated. This 87.6% yield of chloride compares favorably with the 91.1% GLC assay for the chloride displaced product, XII.

Reactions of 1-Chloro-5,5-dihydropentafluorocyclopentene

(V) in Ethanol-*O-d*. A duplication of the above reactions using potassium ethanol-*O-d*-[20] from 0° to room temperature showed that considerable deuterium incorporation occurred. The ring proton positions of 1-chloro-5,5-dihydrodeuteriotetrafluorocyclopentene (XI) showed 78% D. The major product, 1,3-dihydrodeuterio-2-ethoxypentafluorocyclopentene (XII), showed 83 and 87% D, 1 and 3 positions, respectively. These values were taken from integration of the respective ^1H NMR spectra and subsequent comparison of ring proton to side chain proton count (which was always 2:3).

In a separate experiment 6.2 ml of ethanol-*O-d* and 1.9 g (0.01 mol) of V were stirred together for 44 hr at room temperature. An infrared spectrum of the isolated fluorocarbon showed no bands in the fingerprint region which could be assigned to deuterium incorporation when compared to an authentic sample of V.

Rearrangement of 1-Chloro-5,5-dihydropentafluorocyclopentene (V). In a 100-ml three-necked flask equipped with a magnetic stirrer, condenser, dropping funnel, and nitrogen inlet was placed 2.15 g (0.055 mol) of potassium. To the flask was carefully added 35 ml of ethanol-*O-d*. Subsequently 10 ml of ethanol-*O-d* containing 9.63 g (0.05 mol) of V was added. Over a 35-min period the reaction temperature varied from 4 to 9°. The reaction was quenched at this time with dilute nitric acid. A GLC (QF-1, 85°) of the fluorocarbon layer gave starting material (V, 62%) and isomer, 1-chloro-2,5-dihydropentafluorocyclopentene (VIII, 38%) with a trace of ether products. The two compounds were isolated by preparative GLC (TCEP, 30%, 100°). The amounts of deuterium incorporation as determined by elemental analysis[21] and mass spectral analysis (20 eV),[22] respectively, for each compound were found to be as follows: V, 14.2 and 14.4%, and VIII, 70.5 and 67.3%. In addition, VIII was selectively assayed for D incorporation at the 2 position by ^{19}F NMR. The high-field peak (ϕ 194 ppm) doublet collapsed to a singlet (with concurrent 0.65 ppm upfield shift) with D substitution. The ^{19}F integration of the singlet and doublet showed 82.9% D at the 2 position.

Reaction of 1-Chloro-2,5-dihydropentafluorocyclopentene (VIII) with Ethoxide. In a 100-ml three-necked flask equipped as above were placed 3.3 g (0.017 mol) of VIII and 6.3 ml of ethanol-*O-d*. To the flask with stirring was added 5 ml of ethanol-*O-d* which had previously been treated with 0.4 g (0.01 mol) of potassium. A GLC analysis after 45 min showed all the products observed from the reaction of ethoxide with V. The reaction mixture was allowed to warm to 25° and quenched with water after 5 hr. A GLC analysis at this time showed V (10%), starting material (VIII, 33%), four very minor peaks (5%), and XII (52%). Identifications were made by retention times. This reaction showed that the isomerization of V to VIII was reversible and suggested that VIII was the thermodynamically preferred isomer.

Reaction of 1-Chloro-5,5-dihydropentafluorocyclopentene (V) with Ethoxide (DMF). In a 100-ml three-necked flask equipped as above was placed 1.08 g (0.028 mol) of potassium. While nitrogen was being swept through the flask 10 ml of ethanol was slowly added. After the reaction was completed, unreacted ethanol was removed under vacuum while warming the flask with an infrared lamp. To the flask and contents was added 25 ml of dry DMF. The solution was cooled with the aid of an ice bath and 5 ml of DMF which contained 4.82 g (0.025 mol) of V was added. An immediate blackening of the reaction mixture was observed. A GLC analysis (QF-1, 10%, 100–200°, 15°/min) within 30 min showed starting material (V), a small amount of VIII, and mainly one ether product surrounded by broad unresolved peaks. A GLC analysis showed very little change, indicating almost no additional reaction. A ^1H NMR of the steam-distilled reaction mixture showed that the main product was 1,3-dihydro-2-ethoxypentafluorocyclopentene (XII). It was suspected that dehydrofluorination had occurred. This side reaction removed ethoxide and caused low conversion to products. The cyclopentadiene, which resulted, probably polymerized to give the black reaction mixture and high-boiling components observed on the GLC.

Reaction of 1-Chloro-2-hydrohexafluorocyclopentene (XVI) with Ethoxide. In a 250-ml flask equipped as above was placed 9.0 g (0.23 mol) of potassium. To the flask was carefully added 100 ml of absolute ethanol. This solution was added to another 200-ml flask containing 25 ml of absolute ethanol and 42 g (0.199 mol) of XVI.[13] The reaction was carried out at −10° overnight. Subsequently the reaction mixture was poured into water and separated, and the water layer was acidified with nitric acid and treated with silver nitrate in the usual manner. A total of 3.25 g of a theoretical 25.4 g of silver chloride was isolated (89% completed reaction by GLC), indicating that 12.8% of the product resulted from chloride displacement. A GLC (Carbowax 20M, 10%, 120–200°, 15°/min) of the reaction products showed (excluding recovered XVI) 1-chloro-5-ethoxy-5-hydropentafluorocyclopentene (XVIII, 66.7%), 1-ethoxy-2-hydrohexafluorocyclopentene (XVII, 8.3%), and 1-chloro-2,5-diethoxy-5-hydrotetrafluorocyclopentene (XIX, 24.9%). The products gave XVIII, bp 134° (743 mm); $n^{20}D$ 1.3796; ir 1704 cm^{-1} (ClC=CF); XVII, ir 1660 cm^{-1} (HC=COR); ^1H NMR δ_{CH_3} 1.41 (t, J_{HH} = 7.0 Hz), δ_{CH_2} 4.42 (q, 7.0), δ_{2H} 5.19 (m); XIX, ir 1669 cm^{-1} (ClC=COR), ^1H NMR (acetone-d_6) δ_{2CH_3} 1.34 (t, J_{HH} = 7.0 Hz), δ_{2CH_2} 4.43 (q, 7.0), δ_{5CH_3} 1.22 (t), δ_{5CH_2} ~ 3.81 (ABX_3 pattern, J_{AX} = 7.0, J_{BX} = 6.9, J_{AB} = 9.4 Hz), δ_{5H} 4.58 (m, J_{HF} 11.3 Hz, 6.5, 2.3, 1.5).

Registry No.—I, 14851-11-7; III, 694-62-2; IV, 14851-13-9; V, 5239-60-1; VII, 55871-52-8; VIII, 55871-53-9; IX, 55871-54-0; X, 55871-55-1; XI, 55871-56-2; XII, 55871-57-3; XIII, 5239-63-4; XVI, 3761-95-3; XVII, 55871-58-4; XVIII, 55871-59-5; XIX, 55871-60-8; 1,2-dichlorohexafluorocyclopentene, 706-79-6; 1,2-dichlorooctafluorocyclohexene, 336-19-6; ethoxide, 16331-64-9.

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(22) A typical mass spectra of parent ion (20 eV) showed *m/e* 192 to 196 peaks. The percent D incorporated was determined by the change in total area percent of *m/e* 193 and greater mass peaks when compared to authentic materials.