TECHNICAL REPORT
69-17-CM

THE SYNTHESIS OF SPECIAL FLUORINE-CONTAINING MONOMERS

by
J.D. Park and J.R. Lacher

University of Colorado
Boulder, Colorado

Contract No. DA-19-129-AMC-869 (N)

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UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing and Organic Materials Laboratory
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FOREWORD

This report was prepared by J. D. Park of the University of Colorado under U. S. Army Contract DA-19-129-AMC-869 (N) (Project No. 1CO. 24 401A 329) with Dr. Malcolm Henry as project supervisor. This report covers work conducted from 1 December, 1965 to 15 March, 1968. The work was supervised by Dr. Joseph D. Park and Dr. John R. Lacher. Other contributors to all or part of the program included:

- Sam Kwon Choi
- George G. I. Moore
- Thomas S. Croft
- Robert Rhodes
- Richard O. Michael
- Randolph McMurtry
- Richard Bennett
- Otto Furuta
- Clarence Bertino
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- Michael Riley

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ABSTRACT

A large number of fluorine-containing intermediates were synthesized and shipped for further polymer studies. Among the organic fluorine compounds synthesized were: (a) various bicyclobutenyl derivatives; (b) Grignard reaction products; (c) perhalocycloalkenes containing vinylic halogens (I, Br, Cl, F); and (d) vinylic mono- and di-carboxylic acids of perhalocycloalkenes.

THE SYNTHESIS OF SPECIAL FLUORINE-CONTAINING MONOMERS

I. Introduction

The purpose of this project is to carry out a basic chemistry research program to synthesize new, potentially useful monomers containing fluorine. Monomers synthesized will consist of compounds both partially and completely fluorinated. In addition, these fluorine-containing monomers will have active sites of suitable activity for participation in homo-, co-, and terpolymerizations.

Olefinic and acetylenic fluorine compounds containing both conjugated or unconjugated unsaturation will be considered. In addition, or as alternative sites of potential activity, other organic functional groups may be substituted, as for example, carbonyl, nitroso, carboxylic or sulfone.

Methods of preparation of desired monomers may vary depending on the compound in question. Typical methods will include, for example, dehydrohalogenations, dehalogenations, pyrolysis, decarboxylations, disproportionations and dimerizations.

This research is authorized under U. S. Army Contract DA-19-129-AMC-869(N) and is the Final Report for the period 1 December 1965 to 15 March 1968 under this project with Dr. Malcolm Henry as project officer. Three semiannual reports covering the periods from 1 December 1965 to 1 June 1967 are previous publications to be read in conjunction with this final report. Previously, similar researches authorized under Contract No. DA-129-QM-1926 (01 6028-62), under Dr. Malcolm Henry as project officer, were summarized in three semiannual reports and a final report, covering the period 1 October 1963 to 1 October 1965.

These prior reports should be used in conjunction with the present series to bring the historical portion up to date.

II. Summary of Current Progress

Intermediate for Polymer Studies

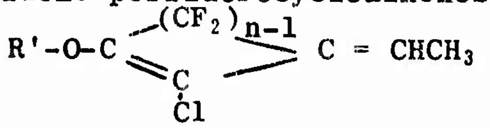
The synthesis of a series of new olefins and diolefins is still in progress. These are possible candidates for polymer evaluation as well as basic intermediates for the synthesis of other monomers containing a hetero-atom or atoms. Some of the above types of compounds will be used to prepare highly sterically hindered nitroso monomers for evaluation as a possible candidate for polymerization.

A large number of fluorine-containing intermediates were synthesized and shipped for further polymer studies.

Among the organic fluorine compounds synthesized were:

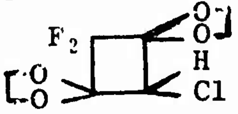
(a) a variety of bicyclobutenyl derivatives.

(b) alkylidene perfluorocycloalkenes of the type



where n = 2,3
R'= CH_3

(c) the reaction products of ethylene glycol and perhalocyclobutenes



(d) various new perhalocyclobutenes obtained by boron trifluoride catalyzed rearrangements.

(e) the preparation and reactions of 1,2-diiodo-perfluorocycloalkenes.

(f) Grignard reaction products obtained by reaction of Grignard reagent with perhalocycloalkenes.

(g) Synthesis of H-containing cyclofluoroalkenes by catalytic hydrogenation.

(h) The reaction of perhalocycloalkenes with certain nucleophiles, i.e., Na_2S.

III. Monomer Synthesis

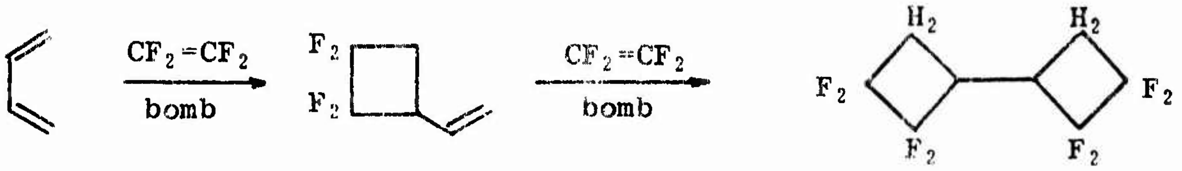
Investigations of the Synthesis and Reactions of Perhalobicyclobutenyl Compounds.

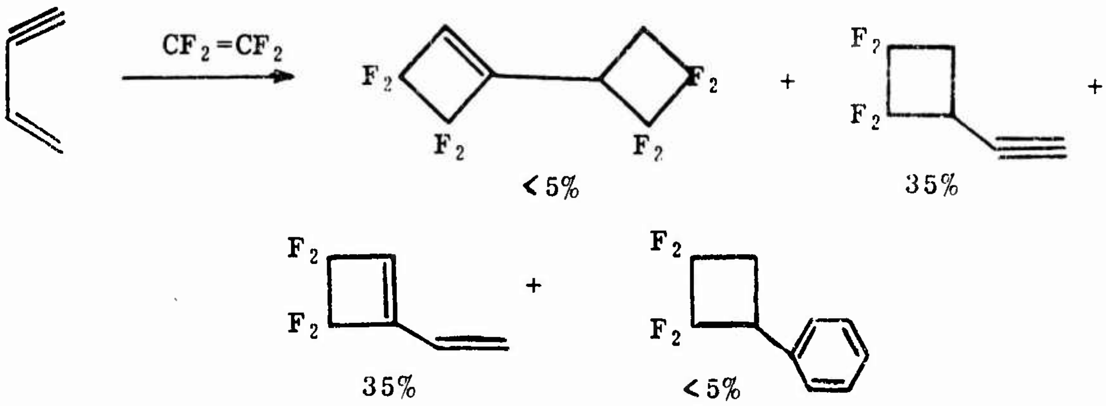
Part A: Synthesis Pathways

1. Object. To develop a useful synthetic pathway to perhalobicyclobutenyl compounds which should be important intermediates in the syntheses of diketodicarboxylic acids.

2. Historical. There are relatively few syntheses of bicyclobutyl or bicyclobutenyl compounds (hereinafter referred to as dibox compounds) reported in the literature. An adequate review of earlier work in this area has been compiled by Frank.(1)

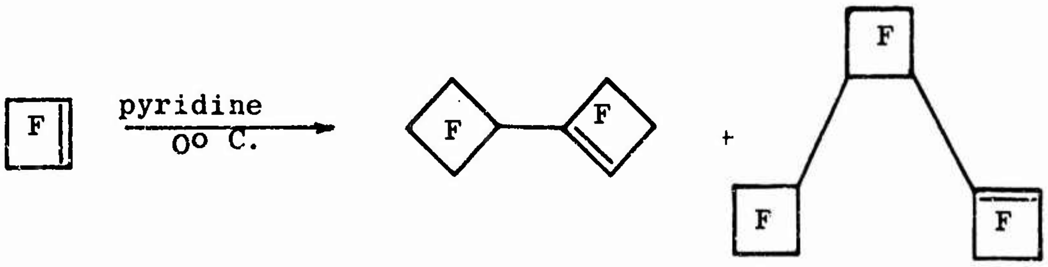
Prior to Frank's work, no general pattern for the synthesis of halogenated dibox compounds had been developed. Coffman, Barrick et al.(2) were the first to apply thermal cycloalkylation reactions to this end by reacting butadiene with excess tetrafluoroethylene in a bomb under autogenous pressure to obtain a 10-15 percent yield of 2,2,2',2',3,3,3',3'-octafluorobicyclobutyl. In addition, they treated vinylacetylene with tetrafluoroethylene to give the products indicated below.



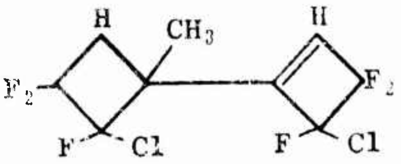


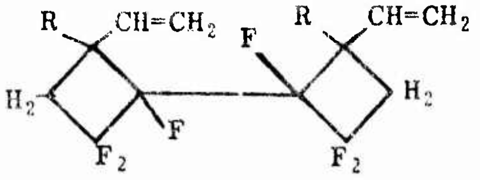
Shortly thereafter, Miller$^{(3)}$ accomplished a coupling of two perfluorobicyclobutene units in liquid fluorine at -78°C to yield perfluorobicyclobutyl. The product was an inert liquid at 86-87°C.

Pruett *et al.*$^{(4)}$ prepared a mixture of the dimer and trimer of perfluorocyclobutene by the treatment of the monomer with pyridine at 0°C.



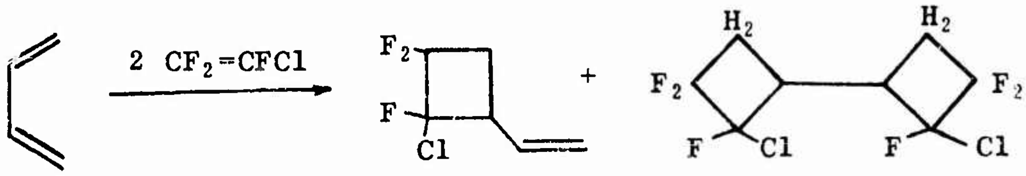
Sharts and Roberts(5) again applied thermal alkylation reactions in treating isopropenylacetylene with chlorotrifluoroethylene to give the two expected 1:1 adducts and less than 5 percent of a dibox derivative. Similarly, Ryananova(6) et al. reported 10-15 percent yields of 2:1 adducts from the thermal addition of 1,3-butadiene to perfluorobutadiene.



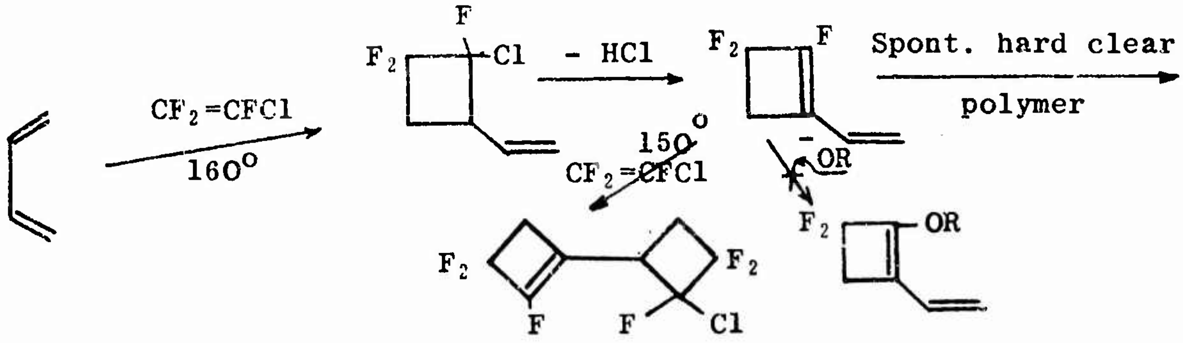


R = H, CH$_3$

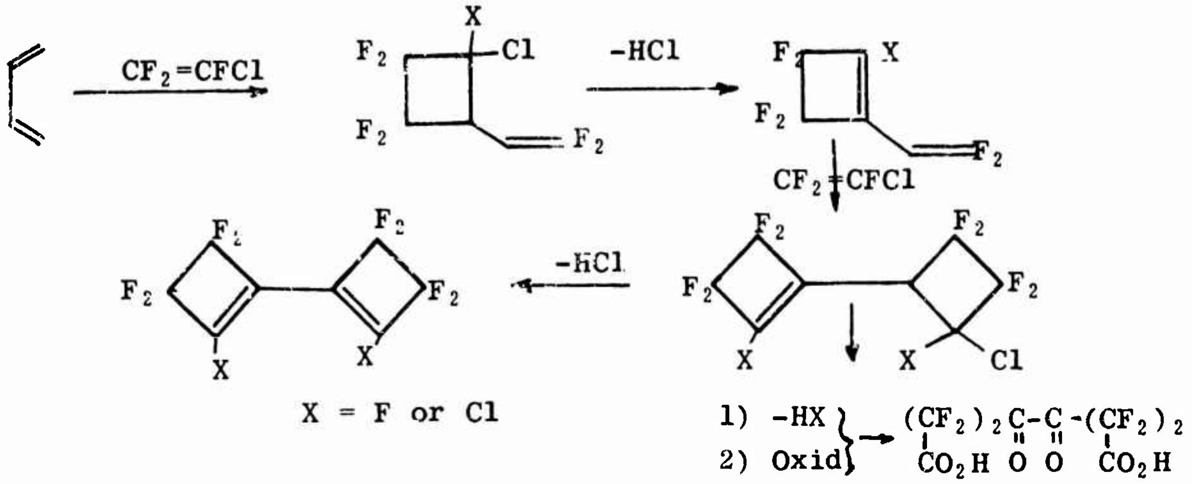
Frank of this laboratory extended the knowledge of thermal cycloalkylation reactions of haloethylenes in preparing cyclobutanes (several reviews have recently been published(2,7) to the synthesis of dibox derivatives. In reacting 1,3-butadiene with trifluorochloroethylene in an autoclave, he isolated 5-10 percent of a 1:2 adduct, 2,2'-dichloro-2,2',3,3,3'3'-hexafluoro-bicyclobutyl, in addition to the normal 1:1 adduct. An increase in the molar ratio of trifluorochloroethylene did not improve the yield of diadduct significantly.



The following synthetic pathway ultimately proved most useful in the synthesis of dibox compounds.

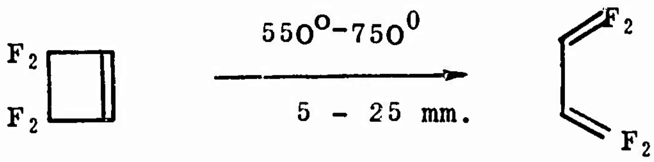


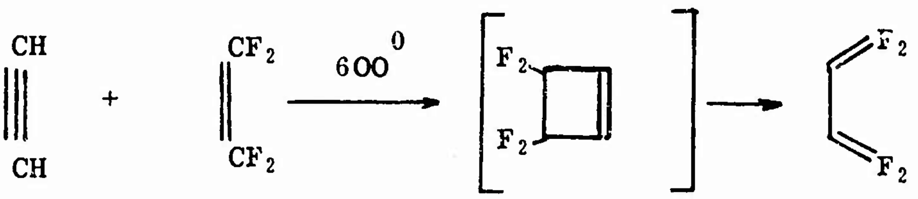
3. Results and Discussion. It is apparent that a logical pathway to perhalobicyclobutenyl compounds would involve thermal addition of haloethylenes to 1,1,4,4-tetrafluorobutadiene followed by dehydrohalogenation.



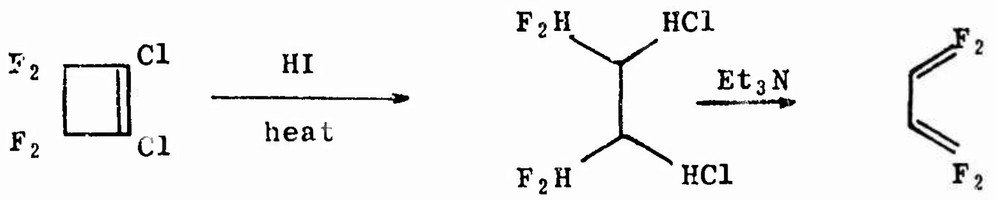
The initial step in developing such a synthesis involves preparation of the butadiene. Two syntheses of 1,1,4,4-tetrafluorobutadiene have been reported to give reasonable yields from available starting materials.

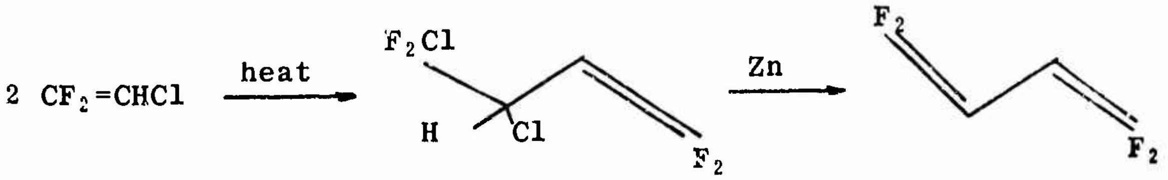
Anderson, Putnam, and Sharkey(8) report the thermal scission of 3,3,4,4-tetrafluorocyclobutene at 550-750° and 5-25 mm to give the desired butadiene quantitatively. In the same paper they report preparation of the butadiene by copyrolizing equimolar amounts of acetylene and tetrafluoroethylene at 600°C and 1 atm. This reaction is postulated to proceed via the cyclobutene.



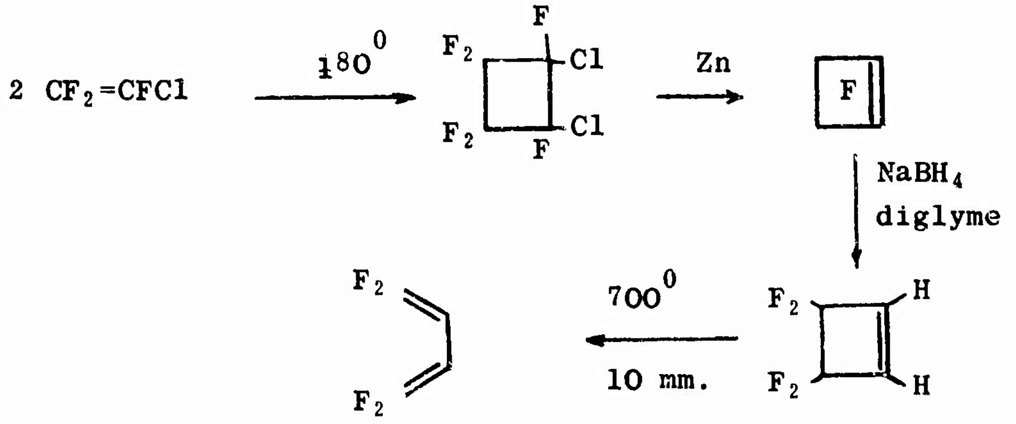


Two further syntheses of the diene logically develop from the work of Haszeldine and Osborne.(9) They are outlined below:

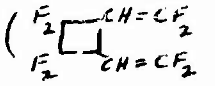




Currently, the following route has been successfully used to prepare the desired diene:

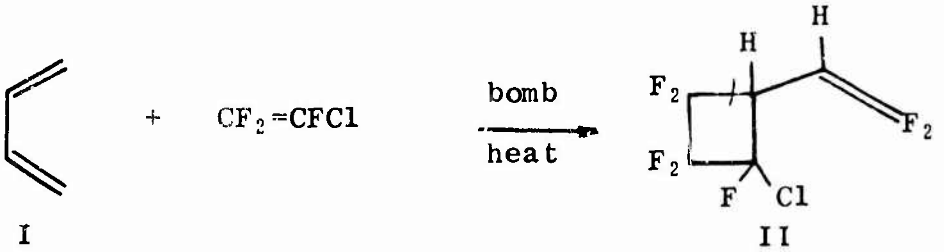


The first two steps of this sequence proceed in excellent yield to afford perfluorocyclobutene. Reduction of this cyclobutene with sodium borohydride in diglyme, however, has been accomplished only in $\sim$35 percent yield. Burton(10) reports this reaction to proceed in 55 percent yield. No reason for this discrepancy is apparent. Pyrolysis of 1,2-dihydrotetrafluorocyclobutene proceeds quantitatively.

Reaction of the diene in a heated autoclave with four mole-equivalents of chlorotrifluoroethylene gave 1-(β,β-difluoro)-vinyl-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (I) in 70 percent yield along with the expected 1,2-dichlorohexafluorocyclobutane and a small higher boiling fraction. The high boiling residue was separated by GLC in the hope of obtaining some diadduct. The major fraction (75%) of the residue, however, was identified as 1,2-(β,β-difluorodivinyl-tetrafluorocyclobutane () by comparison with the properties reported for this compound by Putnam, Anderson and Sharkey(11), reported H_D^{25} 1.3458; found, 1.3456 at 25°. IR-reported and found peaks at: 3080 (vin-H), 2950 (allyl H), 1755 (CF_2=CH), 1405, 1350, 1305, 1255, 1165, 1080, 922, 906, 814, 759.

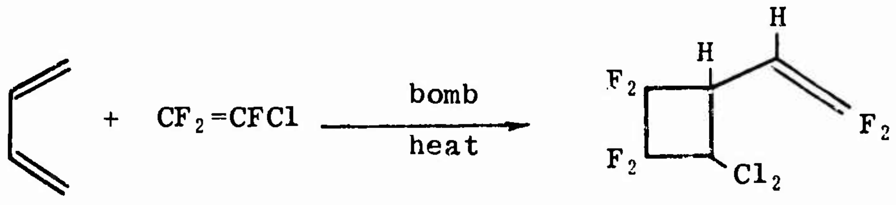
Failure of any diadduct to result from this reaction is surprising in view of Frank's work cited earlier. (I) is surely more activated to cycloalkylation than the analogous vinyl compound due to the CF_2 moiety. It remains possible, though, that the temperature of the reaction was not sufficient to initiate the second addition.

As reported previously, 1-chloro-1,2,2-trifluoroethylene (F1113) adds to 1,1,4,4-tetrafluorobutadiene (I) in good yield to form 1-(β,β-difluorovinyl)-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (II). No diadduct was obtained in this reaction at 160° or 220° C.



I II

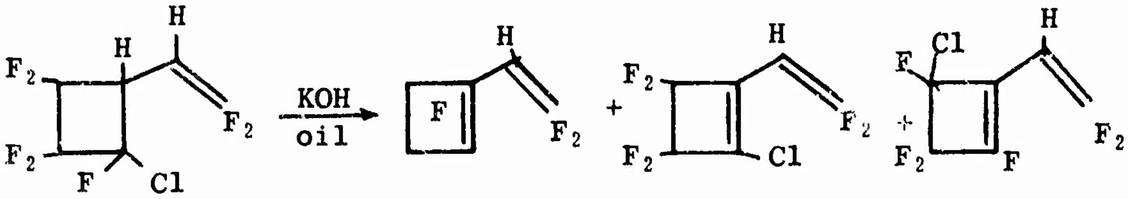
Similarly, 1,1-dichloro-2,2-difluoroethylene (F112A) codimerizes with I to afford 1-(β,β-difluorovinyl)-2,2-dichloro-3,3,4,4-tetrafluorocyclobutane (III) in varying yields. The yield of III was 39 per cent when the reaction was conducted at 205°C but rose to 93 percent at 220°. In addition to III and 1112A dimer, a



III

substantial high boiling fraction (137-160°) is obtained in this experiment. Three components were isolated from this fraction whose structures cannot be determined. The hoped-for diadduct of 1112A and I was not present in the mixture.

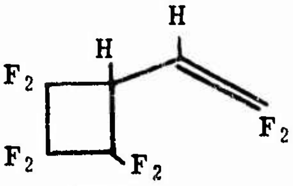
Dehydrohalogenation of the vinylcyclobutanes, II and III, has been the subject of extensive investigation. As reported previously, both compounds react with KOH in mineral oil but



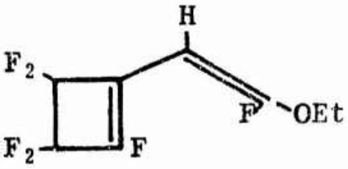
II IV V VI

yields are uncertain with considerable polymerization or decomposition and loss of both HF and HCl occurs to give a mixture of products (IV, V, VI).

The reaction of II with KOH in ethanol gives a very complex mixture of the three possible dienes (IV, V, VI) (HF and HCl elimination) (~35%) and at least 10 ethers (~65%). Although a complete analysis of this complex mixture was impossible, some components were identified. An interesting major product (11%) was assigned the structure VII on the basis of its IR and mass spectra. It might arise from F^- attack on II or addition of HF to IV.



VII



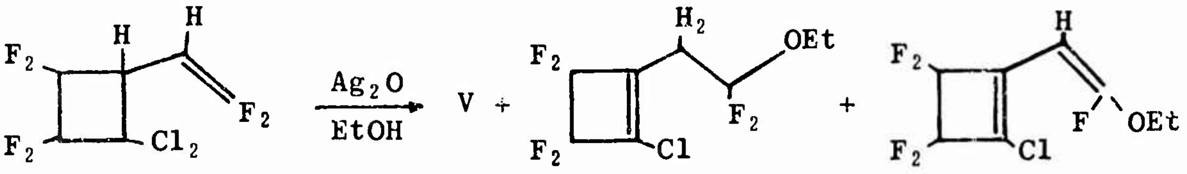
VIII

The major ether product (~17%) has tentatively been assigned structure VIII. This is based largely on the IR spectrum as a molecular ion is absent in the mass spectrum. Most of the products are highly reactive diene ethers and are unsuitable for analysis.

Reaction of III with KOH and ethanol similarly gives a mixture of products. Two unsaturated ethers and one saturated ether were isolated in addition to the diene, V. Data collected on these ethers have not yet allowed structure assignments.

Several other dehydrohalogenation mediums were investigated in hopes of obtaining exclusive dehydrochlorination in good yield. Triethylamine reacts violently with III even if highly diluted and at -76°C. Pyridine and aniline react less violently but with appreciable discoloration or polymerization. Aniline might react suitably in cold dilute solutions. Dilute aqueous KOH again gave HF and HCl elimination in a slow reaction. Hydrolysis or degradation caused rapid base depletion and a poor recovery of fluorocarbons. Silver oxide in DMF and diglyme gave mixtures of products in low conversion.

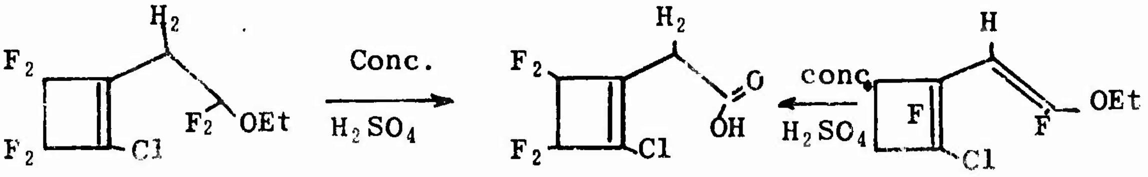
Silver oxide in ethanol is the best reagent yet discovered for the dehydrohalogenation of III. The reaction is complete under mild conditions and affords the diene, V, in 55 percent yield and 1-(β,β-difluoro-β-ethoxyethyl)-2-chlorotetrafluorocyclobutene (IX) and 1-(β-fluoro-β-ethoxyvinyl)-2-chlorotetrafluorocyclobutene (X) in 25 and 20 percent yields, respectively. X has



III IX X

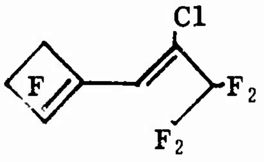
been shown to be the trans (H-F) isomer by proton NMR. No cis isomer is produced. Since IX is stable with respect to X under the reaction conditions, it must be concluded that X results from nucleophilic attack on the diene, V. This is confirmed qualitatively by monitoring the ratio of the two products as the reaction progresses. The reason for such an attack giving rise to trans X exclusively is unclear.

Investigations on the hydrolysis of the ethers IX and X were conducted. Treatment of either compound with concentrated sulfuric acid results in a rapid and quantitative conversion to 1-carboxymethyl-2-chloro-3,3,4,4-tetrafluorocyclobutene (XI).

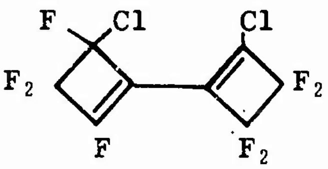


XI

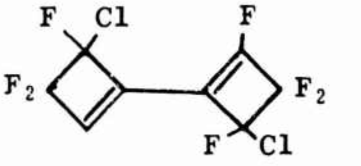
A codimerization of the mixed dienes obtained from dehydrohalogenation of II with Genetron 1113 led to a complex mixture as anticipated. A substantial portion of the dienes was recovered unreacted and no cyclobutenylcyclobutanes were observed. Two bicyclobutenes were in the product mixture resulting from thermal dehydrofluorination of the missing adducts. Other products may be present and further investigations are in progress. The lowest boiling adduct has been assigned structure XII.



XII



XIII

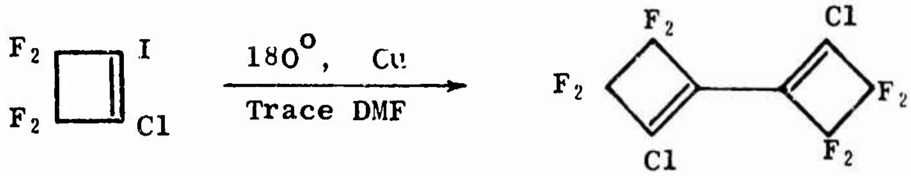


XIV

This is supported by the mass spectrum (m/e = 302 with one Cl), partial analysis and an IR spectrum showing a strongly conjugated unsymmetrical diene system. The second adduct collected has been assigned the structure 2,2'-dichlorooctafluorobicyclobutene. A third isomeric component has been isolated. Its IR spectrum and melting point distinguish it from the preceding compound. Consideration of possible products leads to the conclusion that the compound has structure XIII or XIV. Fluorine NMR will serve to distinguish between these possibilities.

A codimerization between Genetron 1112A and the diene, III, was also carried out but has not yet been worked up. Considerable unreacted diene was recovered.

A significant advance in the synthesis of the title compounds has been accomplished by Sam Choi[*] in a reaction in which 1-iodo-2-chlorotetrafluorocyclobutene has been coupled on passing over hot copper. Studies have indicated the need for a long contact time and a trace of DMF as a catalyst. Yields are nearly quantitative with complete conversion with sufficient contact time over copper powder. The 2,2'-dichlorooctafluorobicyclobutene (XV) obtained has been the subject of numerous additional studies in part B of this report.



XV

Further studies on the synthesis of 2,2'-diiodooctafluorobicyclobutene by a photochemical coupling of 1,2-diiodotetrafluorocyclobutene are discussed elsewhere in this report.

B. Reactions

1. Object. To investigate the reactions and prepare important derivatives of the title compounds.

2. Historical. The work which follows is entirely new but certain generalizations based on known reactions of the corresponding cyclobutenes can be made. The compounds can be expected to behave as alkyl substituted cyclobutenes or as vinylogues of 1,2-dihalocyclobutenes. Therefore, it is the degree of conjugation between the rings which should dominate the chemistry at the vinyl positions.

3. Results and Discussion. 2,2'-Dichlorooctafluorobicyclobutene (XV) reacts readily with KOEt to give a mixture of ethers. Two equivalents of ethoxide react to give nearly a 50:50 mixture of 2-ethoxy-2'-chlorooctafluorobicyclobutene (XVI) and 2,4,4-tri-

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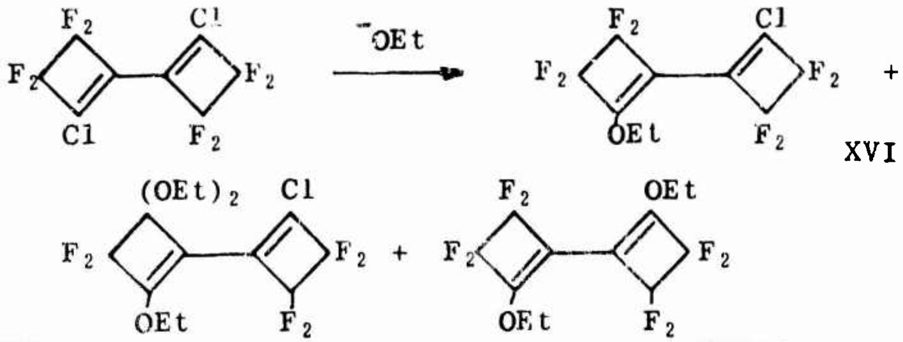
[*] University of Colorado



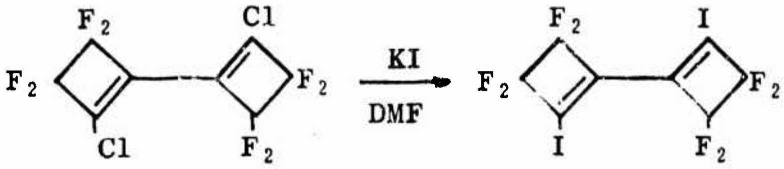
XV XVI

XVII XVIII

ethoxy-2'-chlorohexafluorobicyclobutene (XVII). 2,2'-Diethoxyoctafluorobicyclobutene (XVIII) was obtained in less than 5 percent yield. Further treatment with ethoxide gives higher ethers. A tetraether, two pentaethers and a hexaether were identified by their GLPC retention times on an SE 30 column. Exhaustive ethoxide treatment gives the postulated hexaether exclusively.

Sulfuric acid hydrolysis of thepostulated hexaether has been accomplished giving a bright orange, water-soluble solid in fair yield. Aqueous solutions are neutral, inferring that the compound is not the long-sought disquaric acid. The infrared spectrum shows little except strong carbonyl absorptions and an NMR spectrum indicates the total absence of hydrogens. Further work on characterizing this substance is now in progress.

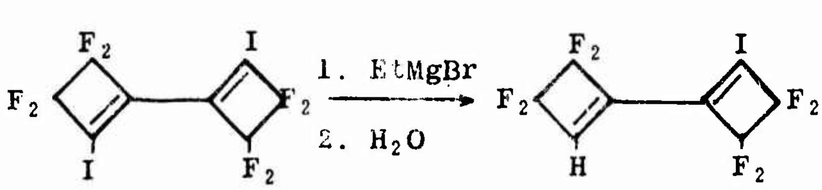
XV has been shown to react spontaneously and quantitatively to 2,2'-diiodooctafluorobicyclobutene (XIX) on brief treatment with KI in diglyme. This reaction suggests a far greater ability of these diene systems to stabilize a carbanion due to delocalization in ad-



XV XIX

dition to the α-effects which act through their vinylogs. The delocalization allows β-effects to play a greater role in these systems and may stabilize the carbanion enough to permit trapping experiments. Synthetically, this reaction is important since XIX is a more reactive starting material for a number of important reactions.

The diiodo compound, XIX, reacts readily with excess EtMgBr



XIX XX

at 0° to form a mono Grignard reagent. This on hydrolysis gives 2-hydro-2'-iodooctafluorobicyclobutene (XX).

4. Experimental

Synthesis of 1-(β,β-difluorovinyl)-3,3,4,4-tetrafluoro-2,2-dichlorocyclobutane (III).

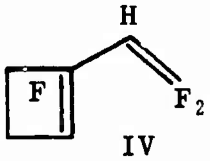
A 500-ml stainless steel autoclave was charged with 67.8 gm (0.54 m) of 1,1,4,4-tetrafluorobutadiene, 225 gm (1.70 m) of G-1112A, and 2.0 ml of d -limonene. The mixture was heated at 220°C for 36 hours. After cooling for six hours the dark liquid contents were collected. Fractional distillation gave 126.7 gm (93%) of III, a clear colorless liquid, b.p. 105-107°C, identical to III prepared in moderate yield previously.

Continued distillation afforded a substantial yield of G 1112A dimer and a major liquid fraction b.p. 137-160°C. Separation of this fraction on an SE30 column afforded three unidentified components.

Dehydrohalogentation of 1-(β,β-difluorovinyl)-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (II).

A. Reaction with KOH in mineral oil. A three-necked, 30-ml round bottom flask was fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. A mixture of 10 ml light mineral oil and 2.8 gm (0.05 m) of KOH was prepared in the flask. To this was added 8.10 gm (0.033 m) of II during 90 minutes, the reaction mixture being kept below 120°C. Some difficulty in controlling the temperature was experienced. Stirring and heating (~75°C) was continued for eight hours after which the mixture was vacuum distilled to give about 60 percent recovery of crude fluoro carbons. Chromatographic analysis and separation revealed the presence of reactant, II, and three diene products, IV, V, and VI in the ratio of 5:2:3, respectively.

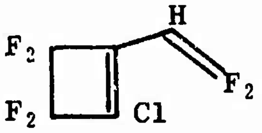
IV is the expected product by loss of HCl from II. It is a colorless liquid which polymerizes and decomposes readily. n_D^{27} = 1.3453, ρ at 27°C = 1.62. IR: characteristic absorptions at 3150, 1750, and 1700 cm^{-1}. The mass spectrum shows an intense molecular ion at m/3 = 206 (no chlorine). Intense peaks at 187 (-F), 156 ($-CF_2:$), and 137 ($-CF_3$) are present.



IV

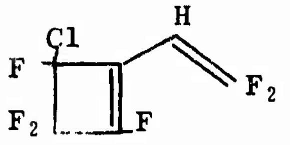
Molar refraction: calcd., 26.56; obsd., 27.0.
Anal. calcd. for C_6HF_7: C, 35.0: H, 0.5; F, 64.5
Found: C, 33.03; H, 0.49; F, 64.01

V is identical to the diene prepared previously from dehydrochlorination of II. Its mass spectra reveals an intense molecular ion at m/e = 222 (one chlorine) with major fragments from loss of F or Cl.



V

VI is another dehydrofluorination product of II. It is an unstable colorless liquid. IR: principal absorptions at 3130, 1750, and 1700 cm^{-1}. Mass spectrum: molecular ion at m/e = 222 (one chlorine) with peaks at 203 (-F) and 187 (-Cl).

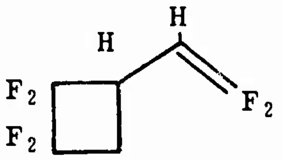

VI

Anal. calcd. for C_6HClF_6: C, 32.4; H, 0.5; Cl, 15.9; F, 51.2.
Found: C, 31.31; H, 0.52; Cl, 15.65; F, 52.35.

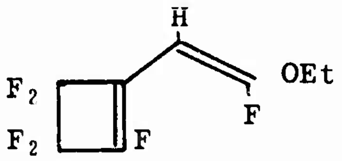
B. Reaction with KOH in 95 percent ethanol. A three-necked, 50-ml round bottom flask was fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. A solution of 2.8 gm (0.05 m) of KOH in 15 ml of 95 percent ethanol was prepared in the flask. Addition of 8.05 gm (0.033 m) of II was carried out during 90 minutes with some cooling with an ice bath. The mixture became yellow and finally brown with some solid formation. Stirring at room temperature was continued another 90 minutes by which time GLPC analysis revealed complete consumption of II. The mixture was quenched with water and the organic fraction was washed with water and dried over sodium sulfate.

GLPC analysis of the product revealed the presence of the three possible dienes, IV, V and VI, plus a large number of ethers. Data were collected on manopreped samples of many of these ethers.

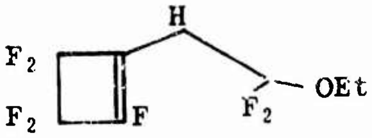
The only major new non-ether product ($\sim$11%) is a stable colorless liquid. Its IR shows a strong olefinic band at 1745 cm^{-1} indicative of $-CH = CF_2$. No C-H stretching frequencies are seen, but an intense -HF peak is seen in the mass spectrum, showing the presence of hydrogen. The mass spectrum also shows an intense molecular ion at m/e = 226 with fragments at 207 (-F), 187 ($-HF_2$), 175 ($-CF_2$) and 175 ($-CHF_2$).


VII

The major ether product constitutes about 17 percent of the total reaction mixture. Its IR spectrum shows a strong conjugated diene absorption at 1600 and 1650 cm^{-1}. The mass spectrum reveals no molecular ion or closely related fragments, but chlorine is absent in all fragments. ρ at 26° = 1.23, n_D^{26}= 1.4010. Further work is in progress to confirm the proposed structure.


VIII

Another ether product ($\sim$5%) has been assigned the structure



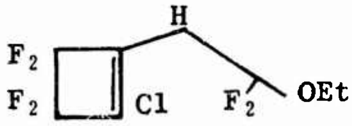
indicated. An intense olefinic absorption occurs at 1650 cm^{-1} in the IR while no evidence for chlorine is seen. The mass spectrum gives a weak molecular ion at m/e = 252. Fragments appear at 233 (-F), 232 (-HF), 224 ($-C_2H_4$), 223 ($-C_2H_5$) and 204 ($-C_2FH_5$). The compound must therefore be an isomer of $C_8F_7H_7$.

Molar refraction: calcd., 39.9; obsd., 41.8.

Further studies on this mixture are in progress.

Dehydrohalogentation of III with Ag_2O in 95 percent ethanol. A three-necked, 50-ml round bottom flask was fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. A mixture of 2.32 gm (0.01 m) of Ag_2O in 10 ml of 95 percent ethanol was prepared in the flask. To this was added during 10 minutes with rapid stirring a solution of 5.18 gm (0.02 m) of III in 10 ml of 95 percent ethanol. The mixture became warm and considerable AgCl was produced during 17 hours of stirring without heat. On quenching with water, a pale yellow oil separated. This was washed with water and dried over sodium sulfate. Analysis of the product revealed four components, of which the major peak is the diene, V (55%).

The major ether product, IX, results from addition of ethanol across the terminal double bond. It accounts for 22 percent of the product mixture and is a colorless liquid. n_D^{25} = 1.3777, ρ at 25° = 1.46. IR: characteristic absorptions at 3070, 1670, 948, 860 and 837 cm^{-1}. NMR: 8 = 1.27, triplet with J_{HH} = 7.0 cps from CH_3; δ= 2.98, broad triplet with J_{HF} = 9.5 cps from allylic CH_2; δ= 3.94, quartet with J_{HH} = 7.0 cps from ether CH_2.

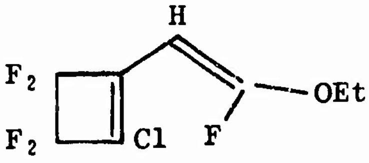


(IX)

Molar refraction: calcd., 42.17; obsd., 42.23.

An intermediate ether mixture of 0-6 percent is observed, but it has not been possible to separate or analyze this mixture.

X is a major product constituting 18% of the product. It is an opaque colorless wax. mp = 38.1 - 39.7°C. IR: characteristic absorptions at 3050, 1695, 1640, 1490, 1125, 1000, 948, and 863 cm^{-1}. NMR: δ= 1.43, triplet with J_{HH} = 7.0 cps for CH_3; δ= 4.13, quartet with J_{HH} = 7.0 for CH_2; δ= 4.52, doublet with J_{HF} = 31.0 cps for CH.

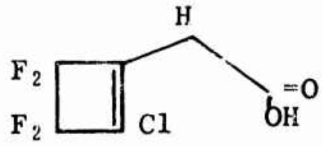


X

Sulfuric acid hydrolysis of X.

A mixture of 1.5 ml of the ether, X, and 5.0 ml of concentrated H_2SO_4 was prepared in a six-inch test tube. Gas was evolved and some heating and darkening of the solution occured on mixing. Agitation with a stirring rod was continued as long as gas was being evolved (about 15 minutes). The mixture was carefully quenched with 8 ml of ice water while immersed in an ice bath. Quantitative chromatography of the dark oily product indicated a 94 percent yield of the new colorless liquid acid, XI. n_D^{29} = 1.3968, ρ at 28°C = 1.40.

IR: characteristic absorptions at 3030, 1760, 1670, 1350, 1030, 955 and 860 cm^{-1}. The mass spectrum lacks a molecular ion but intense peaks occur at m/e = 201 (-OH), 173 (-COOH), 154 (-COOH, F), 123 (-COOH, CF_2) and 119 (_COOH, F, Cl).



XI

Molar refraction: calcd., 36.35; obsd., 33.25.

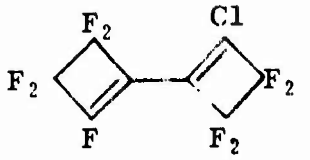
Sulfuric acid hydrolysis of IX.

A mixture of 1.5 ml of the ether, IX, and 7.0 ml of concentrated H_2SO_4 was prepared in a six-inch test tube. Gas was rapidly evolved as the solution darkened and became hot. Agitation with a stirring rod was continued for 15 minutes by which time gas evolution had ceased. The mixture was cooled and carefully quenched with water to give 1.3 ml of dark oil. The major component of this oil (94%) was identified as identical to the acid, XI, prepared previously.

Codimerization of mixed vinyl cyclobutenes with Genetron 113.

A 1/2 l. stainless steel autoclave was charged with 3.0 ml of d-limonene, 19 ml of crude vinylcyclobutanes and vinylcyclobutenes, and 210 gm. of G1113. The mixture was headed at 185°C for 42 hours with shaking. On cooling, a light liquid product was collected. Fractional distillation afforded 18 ml of crude tan liquid product after removal of the 113 dimer. Vacuum disseparated 5-ml fractions. The highest boiling fraction was found to contain several new substances which were collected by preparative scale gas chromatography. Considerable unreacted starting material constitutes the two lower boiling fractions.

The major new product is the unsymmetrical dibox diene, XII, obtained in a yield of 1.8 ml. It must result from a thermal dehydrohalogenation of one or more of several possible adducts. The infrared spectrum of XII shows a strongly conjugated unsymmetrical diene system at 1740, 1670 and 1610 cm^{-1}. Other major infrared absorptions occur at 1420, 1325, 1260, 1140, 975, 885, 855, and 770 cm^{-1}. The mass spectrum shows an intense molecular ion at m/e = 302 (one chlorine) with principal fragments at 283 (-F), 267 (-Cl), 233 ($-CF_3$) and 217 ($-CF_2Cl$). n_D^{26} = 1.3721, d at 26° = 1.75.

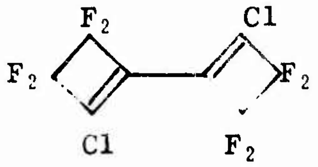


XII

Molar refraction: calcd., 37.66; obsd., 39.3.

Anal. calcd. for C_8F_9Cl: C, 31.7; Cl, 11.7.
Found: C, 29.72; Cl, 12.43.

A white, waxy solid, mp = 67.8 - 69.1°C. constitutes 30 percent of the high boiling fraction. It has been assigned structure XV on the basis of spectral data. The infrared spectrum shows a weak symmetrical olefinic stretch at 1570 cm^{-1} with other absorptions at 1320, 1250, 1145 and 870 cm^{-1}. The mass spectrum gives a molecular ion at m/e = 318 (two chlorines) with principal fragments at 299 (-F), 283 (-Cl), 248 ($-CF_3$), 247 ($-Cl_2$) and 233 ($-CF_2Cl$). A third solid component was obtained in low yield and was not characterized.



Thermal coupling of 1-iodo-2-chlorotetrafluorocyclobutene over copper.

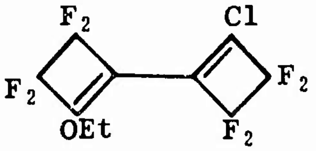
A 1-inch i.d. pyrex tube was packed with alternating 3-inch bands of fine copper turnings and fine powdered copper metal along a 12-inch length. The tube was suspended vertically in a tube furnace and a 4-inch condenser and a dropping funnel were mounted above the tube. A closed receiver was placed at the bottom of the tube to collect product and supply back pressure to increase contact time. The cyclobutene, to which a trace of dimethylformamide catalyst had been added, was released at a rate of 2 cc per hour into the 180°C tube. A single white crystalline product emerged from the bottom of the tube in 83 percent yield, mp = 68.2 - 69.8°C. The product is identical spectrally to compound XV prepared previously.

Analysis calcd. for $C_8F_8Cl_2$: C, 30.0; F, 47.7; Cl, 22.2.
Found: C, 29.84; F, 47.88; Cl, 21.97.

Ethoxide attack on XV.

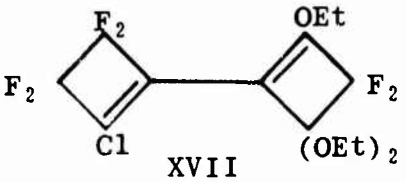
A. Reaction with two moles of ethoxide. A mixture of 3.2 gm (0.01 m) of XV in 5.0 ml of 95 percent ethanol was prepared in a 50-ml, three-necked round bottom flask equipped with a reflux condenser, addition funnel, and a mechanical stirrer. Chromatographic analysis indicated a 25 percent conversion before ethoxide addition to a new compound, XVI, identified later as a monoether. During 50 minutes, a solution of 10 ml of 95 percent ethanol and 1.12 gm (0.02 m) of KOH was added with stirring. The reaction was moderately exothermic but occured smoothly. After another hour of stirring the reaction mixture was poured into 100 ml of water and extracted twice with methylene chloride. Preparative gas chromatography revealed a 50:50 mixture of two new compounds and a trace of a third.

Compound XVI is obtained in 50 percent yield and has been identified as a monoether. Its infrared spectrum exhibits characteristic absorptions at 3000, 1700 and 1600 (strong conjugated unsymmetrical diene), 1260, 1030, 897, 861 and 765 cm^{-1}. The mass spectrum confirms the assigned structure with a molecular ion at m/e = 328 (one chlorine) and principal fragments at 309 (-F), 300 $(-C_2H_4)$, 281 $(-C_2H_4F)$ and 280 $(-C_2H_5F)$.



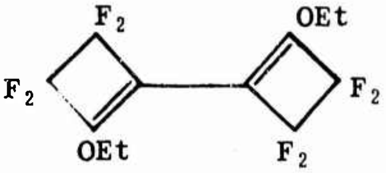
XVI

Compound XVII constitutes the remainder of the reaction product with the exception of a trace of compound XVIII. XVII is a colorless liquid which rapidly turns yellow on standing. The infrared spectrum is complex below 1500 cm^{-1}, but a strong CH stretch at 3000 cm^{-1} and two strong conjugated diene absorptions at 1600 and 1680 cm^{-1} support the assigned structure. The mass spectrum gives a molecular ion at m/3 = 381 (one chlorine) with principal fragments at 335 $(-C_2H_6O)$, 307 $(-C_4H_{10}O)$, 306 $(-C_4H_{11}O)$ and 278 $(-C_6H_{15}O)$. Numerous intense lower peaks can be attributed to loss of halogen or HX from the 278 peak. Although the major argument for the assigned structure over other possible triethers is mechanistic, spectral evidence is also compelling. The strong tendency to lose one oxygen on electron bombardment is a general characteristic of diethers.



XVII

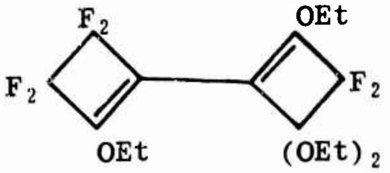
Traces of a third ether, XVIII, were found in the reaction mixture. Identification of this compound is based strongly on its mass spectrum, showing an intense molecular ion at m/e = 338 (no chlorine) with major fragments at 319 (-F), 310 (-C_2H_4), 306 (-CHF), 282 (-C_4H_8), 234 (-$C_2H_4F_4$), 230 (-CHF_5), 206 (-$C_4H_8F_4$), etc. The infrared spectrum has characteristic absorptions at 303, 1640, 1600, 865, and 765 cm^{-1} with strong bands from 950 to 1400 cm^{-1}.



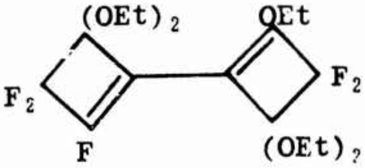
B. Reaction with five moles of ethoxide. The reaction was carried out exactly as in part A except that 2.80 gm (0.05 m) of KOH in 20 ml of 95 percent ethanol was added to 3.2 gm (0.01 m) of the fluorocarbon.

Since the object of this experiment was to gain insight on the course of ethoxide attack and not to prepare the unstable higher ethers, the product was analyzed only by gas chromatography. By their retention times on an SE 30 column, the following were identified: the tetraether, A, 70 percent; the pentaethers, B and C, 15 percent; and the hexaether, D, 10 percent.

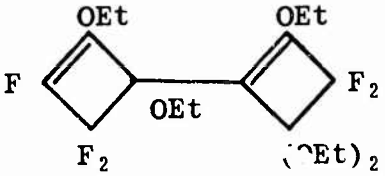
A.



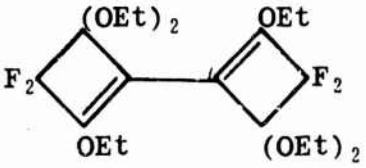
B.



C.



D.



Sulfuric acid hydrolysis of the hexaether of compound XV.

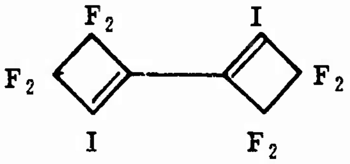
A reaction between 3.2 gm (0.01 m) of compound XV and 4.48 gm (0.08 m) of KOH was carried out as in part A of the preceding reaction except that the mixture was heated to 70°C and allowed to stir two hours after completion of the addition. GLPC analysis indicated complete conversion to a single new compound by this time.

The crude dark oil obtained from the quenched ethoxide reaction (1.16 ml) was mixed with 4.8 ml of concentrated sulfuric acid in a six-inch test tube. The mixture was heated at 100°C and agitated periodically for two hours during which time a white curdy precipitate developed. The mixture was carefully diluted with 10 ml of water. Cooling in an ice bath afforded 0.4 gm of pale orange, grainy crystals. Recrystallization from water gave 0.3 gm of bright orange needles of the new compound.

The infrared spectrum of the orange crystals in either a nujol mull or a CCl_4 slurry shows strong carbonyl absorptions at 2040, 1850, 1760, 1710 and 1600 cm^{-1}. Absorption also occurs at 1250, 1100 and 1010 cm^{-1} with no other observable peaks. an NMR spectrum taken at a 5 percent solution in D_2O gives no proton signal for the compound under conditions which give a full-scale signal for the 0.2 percent hydrogen in the solvent. The compound is stable up to at least 300°C but loses water of hydration rapidly above 100°C. Analysis and mass spectral data are pending.

Reaction of XV with potassium iodide in diglyme.

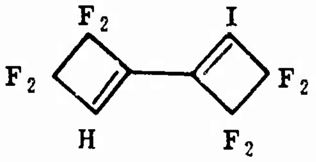
A 50-ml, three-necked round bottom flask was equipped with a reflux condenser, a mechanical stirrer and a stopper. A slurry of 3.2 gm (0.01 m) of XV in 10 ml of diglyme was prepared in the flask. To this was added in two portions, 6.8 gm (0.04 m) of KI. On addition, the cyclobutene rapidly dissolved and the solution became warm. Little discoloration occurred and chormatographic analysis indicated complete reaction to a single new compound, XIX, within five minutes. The mixture was poured into 100 ml of cold water and the crude brown solid which dropped out was collected by vacuum filtration. Recrystallization from 95 percent ethanol gave 4.38 gm (87%) of white crystalline product. Due to some ether formation on heating in ethanol, hexane is now used for recrystallization and 97 percent yield of pure crystalline product can be obtained.



Reaction of XIX with ethyl magnesium bromide followed by water.

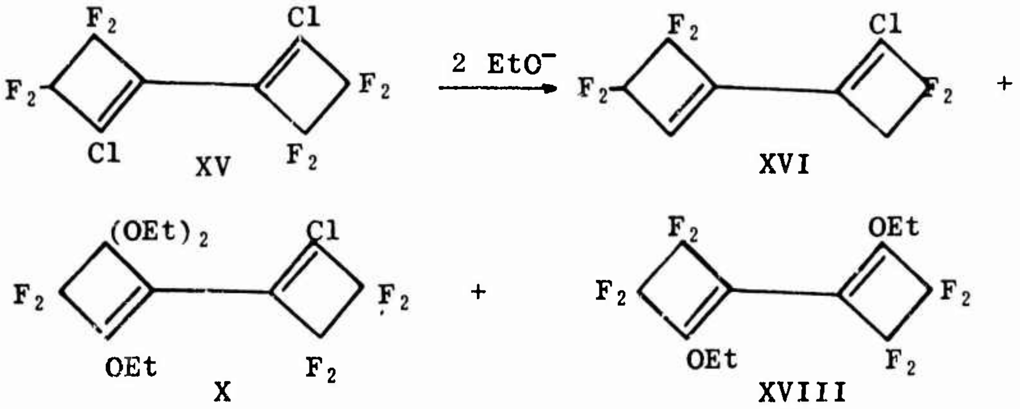
A 50-ml, three-necked round bottom flask equipped with a reflux condenser, mechanical stirrer, and an addition funnel was purged with dry nitrogen for six hours. A solution of 2.50 gm (0.005 m) of XIX in 15 ml of anhydrous diethyl ether was pipetted into the flask. The mixture was maintained at 0° with slow stirring while 2.5 ml of 2M EtMgBr was added during 10 minutes. After stirring for 20 minutes the mixture was quenched carefully with 20 ml of water. The mixture was extracted with ether and the solvent evaporated to give a tan solid.

Chromatographic analysis indicated a 93 percent yield of a new compound, XX, m.p. = 99.8 - 100.5°C. Its infrared spectrum shows weak but sharp peaks at 3180 cm^{-1} (vinyl CH) and 1770 and 1550 cm^{-1} (unsymmetrical diene system). The mass spectrum gives a molecular ion at m/3 = 376 with major fragments at 357 (-F), 307 ($-CF_3$), 249 (-I), 230 (-FI) and 199 ($-CF_2I$).



C. Results

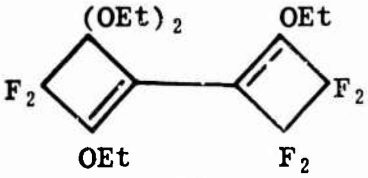
As expected, 2,2'-dichlorooctafluorodicyclobutene (XV) reacts readily with KOEt in ethanol to give mixtures of ethers. Two equivalents of ethoxide react exothermically to give nearly a 50:50 mixture of 2-ethoxy-2'-chlorooctafluorodicyclobutene (XVI) and 2,4,4-triethoxy-2'-chlorohexafluorodicyclobutene (X).



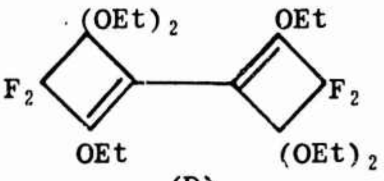
XV XVI X XVIII

2,2'-Diethoxyoctafluorodicyclobutene (XVIII) was obtained in less than 5 percent yield.

Treatment with four equivalents of ethoxide gives a more complex mixture consisting of X (50%), 2,2'4,4-tetraethoxyhexafluorodicyclobutene (A, 20%), and 2,2',4,4,4',4'-hexaethoxytetrafluorodicyclobutene (D, 25%). The remaining 15 percent of the mixture was divided between several minor components.



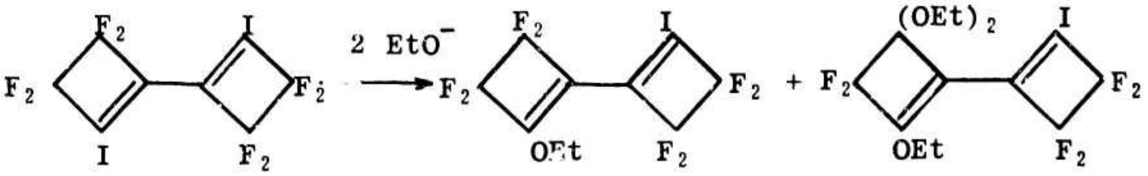
(A)



(D)

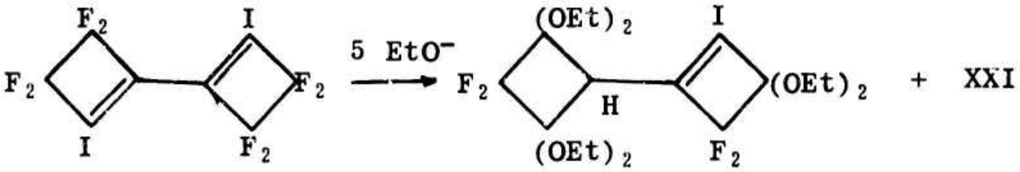
Exhaustive treatment with eight equivalents of ethoxide gave a four-component mixture consisting of 70 percent of D. An isomeric hexa-ether (15%) was identified by its mass spectrum but the sample is too unstable to permit structural analysis. Since the final reaction mixture was observed to contain considerable excess ethoxide, it is clear that D is a stable terminal product of ethoxide attack on XV. Mechanistically, the methodical stepwise nature of the reaction along a single dominant pathway is of paramount importance.

Ethoxide attack on 2,2'-diiodooctafluorodicyclobutene (XIX) occurred very readily. Attempts to recrystallize IX from hot 95 percent ethanol result in partial conversion to 2-ethoxy-2'-iodooctafluorodicyclobutene (XX). Treatment with two equivalents of ethoxide gives a rapid exothermic reaction to a 50:50 mixture of XX and 2,4,4-triethoxy-2'-iodohexafluorodicyclobutene (XXI).



(XIX) (XX) (XXI)

Reaction with five equivalents of ethoxide is also rapid and exothermic, leading to a mixture of XXI (30%) and 1-hydro-2,2,4,4-tetraethoxy-3,3-difluorocyclobutane-2-iodo-3,3-diethoxy-4,4-difluorocyclobutene (XXII, 60%), a stable, colorless, crystalline solid. Only traces of other ethers were present.

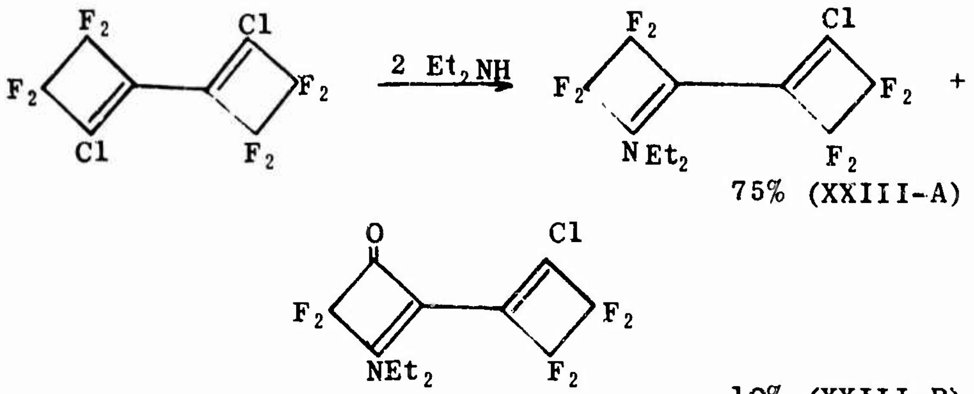


(XXII)

The failure of XXI to lose iodide is a marked contrast to the behavior of X, a fact which will be discussed at length when the mechanism of alkoxide attack is considered.

The facile reaction of XX with alkoxide suggests a high degree of susceptibility to all nucleophiles. This postulate was borne out when, by accident, it was discovered that XV reacts exothermically with triethylamine in a variety of solvents. Unfortunately the initial product reacts rapidly with solvent or water, giving a complex mixture of products. In diglyme, acetone, or dichloromethane, an immediate precipitate of triethylamine hydrochloride forms in the reaction mixture, representing a proton abstraction from solvent. The complex nature of this reaction and the large number of products observed led to the study of the reaction of primary and secondary amines with XV.

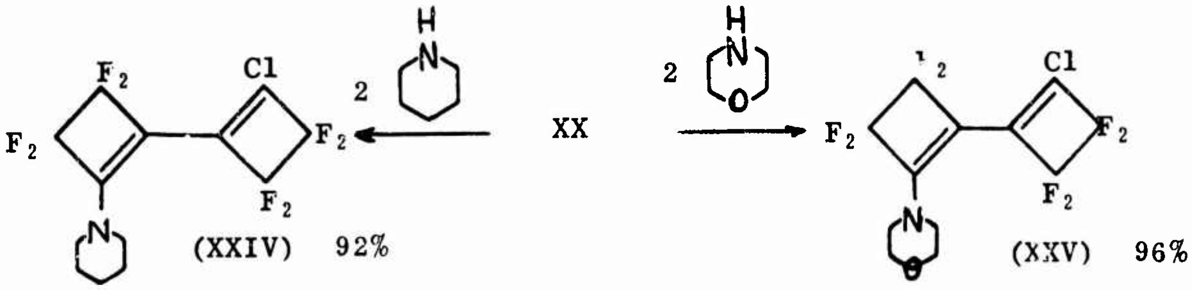
Two equivalents of diethylamine react readily with XV to form 2-N, N-diethylamino-2'-chlorooctafluorodicyclobutene (XXIIIA), (80%) and 2-N,N-diethylamino-2'-chloro-4-ketohexafluorodicyclobutene (XXIIIB, 10%). Both compounds are white solids but rapidly discolor on standing. In an analogous manner to the reaction



75% (XXIII-A)

10% (XXIII-B)

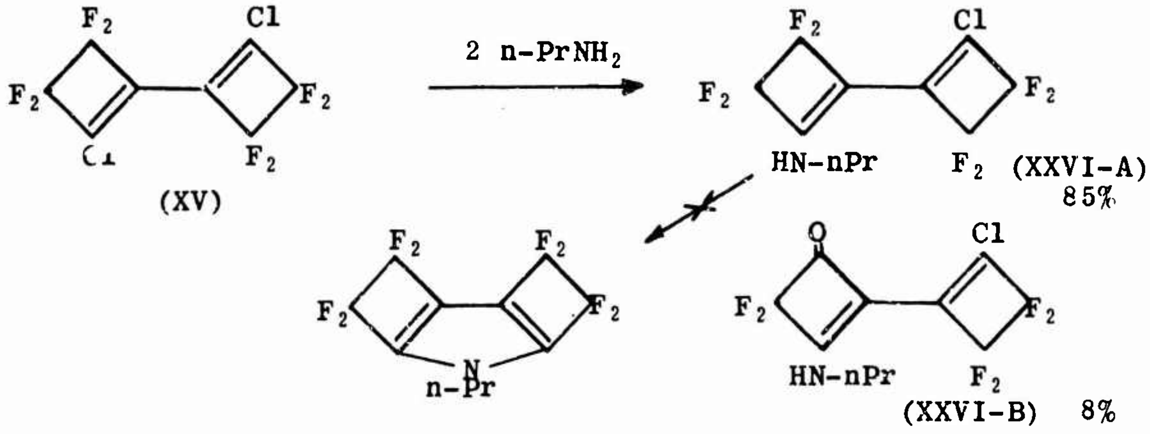
with diethylamine, XV reacts with piperidine to give 2-N-piperidino-2'-chlorooctafluorodicyclobutene (XXIV) or with morpholine to give 2-N-morpholino-2'-chlorooctafluorodicyclobutene (XXV) in excellent yields.



(XXIV) 92%

(XXV) 96%

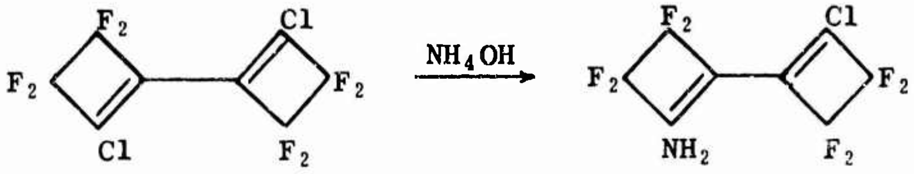
n-Propylamine reacts with XV in a similar manner to give 2-N-n-propylamino-2'-chlorooctafluorodicyclobutene (XXVIA 85%) and 2-N-n-propylamino-4-keto-2'-chlorohexafluorodicyclobutene (XXVIB, 8%). A variety of conditions were studied which might lead to an intramolecular reaction of XXVIA to a pyrrole structure. Prolonged heating of the compound neat, in acetone, and in diglyme gave no reaction except decomposition.



(XXVI-A) 85%

(XXVI-B) 8%

Of greater interest synthetically than the foregoing amine reactions is the facile reaction of XV with concentrated ammonium hydroxide in acetone to afford 2-amino-2'-chlorooctafluorodicyclobutene (XXVII) in 92 percent yield (60% conversion).

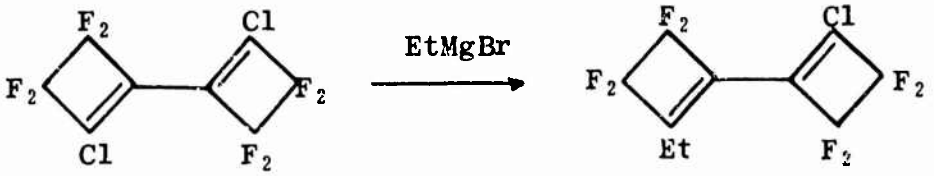


(XXVII)

The vinyl amine is a white volatile solid which discolors slowly and shows no tendency to cyclize to a pyrrole or isomerize to an imine structure. Intermolecular reactions were not observed but further study of this compound's chemistry is certainly suggested.

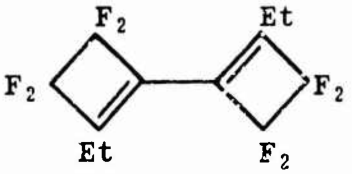
To further elucidate the chemistry of the dicyclobutenes, the reaction of Grignard reagents with XV and XIX was investigated.

A slow addition of one equivalent of ethyl magnesium bromide to XV results in a purely statistical ratio of recovered XV (25%), 2-ethyl-2'-chlorooctafluorodicyclobutene (XXVIII, 50%)



(XXVIII) 50%

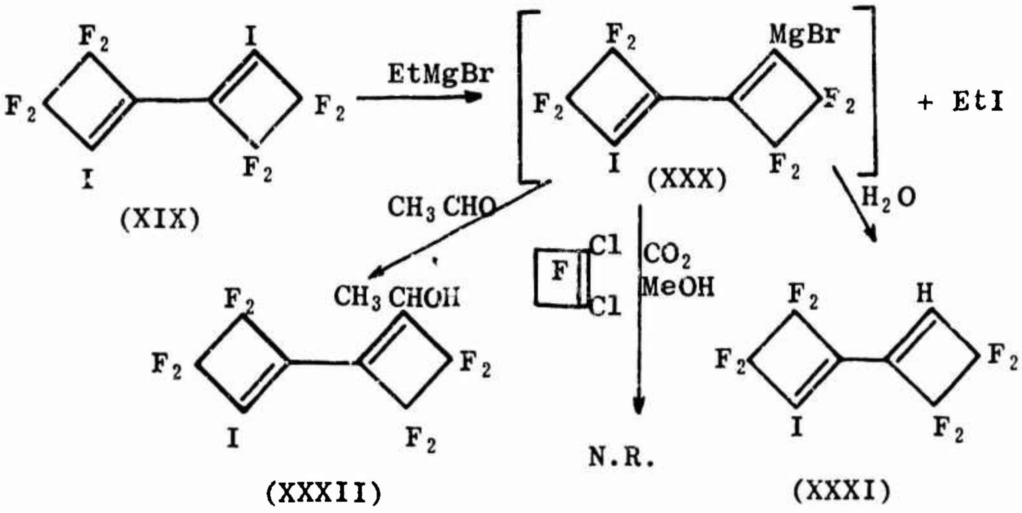
XV +
25%



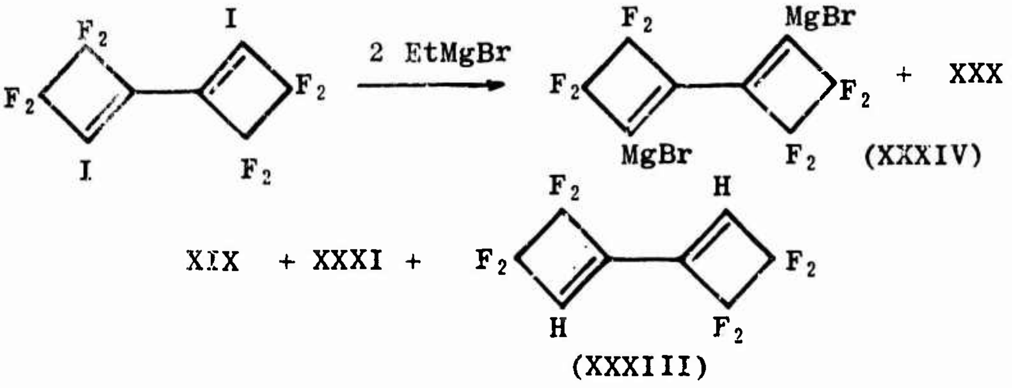
(XXIX) 25%

and 2,2'-diethyloctafluorodicyclobutene (XXIX, 25%).

In contrast to the foregoing reaction, but in agreement with cyclobutene studies, XIX reacts with one equivalent of ethyl magnesium bromide to give ethyl iodide and 2-magnesium bromide-2'-iodocotafluorodicyclobutene (XXX). The Grignard reagent was, of course, not isolated but products of its reactions prove its presence. XXX reacts with water to give 2-hydro-2'-iodooctafluorodicyclobutene (XXXI) in 82 percent overall yield. XXX does not react with carbon dioxide, 1,2-dichlorocyclobutene or methanol at 0°C. It does, however, react with acetaldehyde slowly to give 2-(1-hydroxyethyl)-2'-iodooctafluro-dicyclobutene in fair yield. Lesser amounts of XIX, XXXI and 2,2'-dihydrooctafluorodicyclobutene (XXXIII) were also produced.

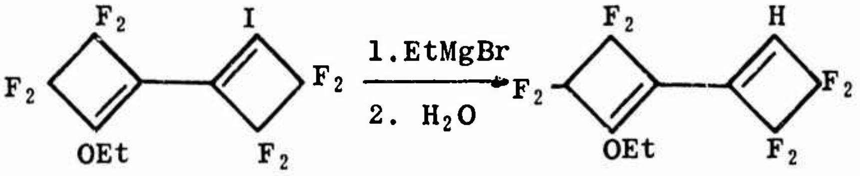


The observation of XXXIII in the foregoing reaction suggested the possibility of preparing a di-Grignard of XIX. Treatment with



two equivalents of ethyl magnesium bromide resulted in separation of a dense dark oily phase from the ether solution but little apparent decomposition. Hydrolysis gave XXXIII in 65 percent yield, the remaining product being equally divided between XIX and XXXI.

To further study the generality of the Grignard exchange reaction in dibox compounds, XVI was treated with one equivalent of ethyl magnesium bromide. Hydrolysis of the intermediate vinyl Grignard afforded 2-hydro-2'-ethoxyoctafluorodicyclobutene (XXXV) in 86 percent yield. Some starting material was again recovered.



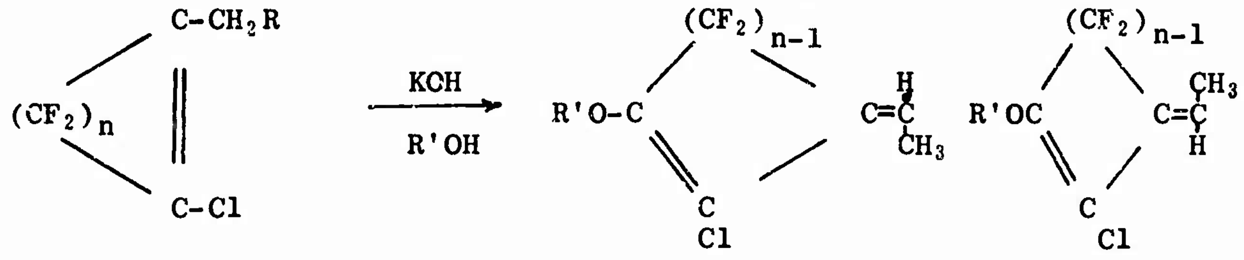
(XXXV)

The success in preparing stable Grignard reagents led to the study of the reaction of XIX with methyl lithium. Three attempts to prepare lithium reagents in diethyl ether led to one fire, a fair deposit of carbon in each case and a good recovery of starting material. Despite these discouraging results, further efforts to prepare dibox lithium reagents, possibly by other methods, will be undertaken in the future.

IV. A Novel 1,4-Elimination Reaction of 1-Chloro-2-Alkyl Perfluorocycloalkenes with Alkoxide Ion.

Abstract: The nucleophilic attack by alkoxide ion on 1-chloro-2-alkylperfluorocyclo-butene and -pentene brought about a novel 1,4-elimination reaction which yielded the corresponding 1-alkoxy-2-chloro-3-methylene perfluorocyclobutene and 1-alkoxy-2-chloro-3-ethylideneperfluorocyclopentene. The physical properties of these compounds along with their NMR data are also presented. These compounds are of potential interest as reactive monomers and possibly as intermediates for the synthesis of reactive polyfunctional derivatives.

In the course of our studies of nucleophilic attack by alkoxide ion on alicyclic polyfluoroolefins, 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. 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, abstraction of an α-hydrogen from the alkyl group by alkoxide ion is apparently preferred to the

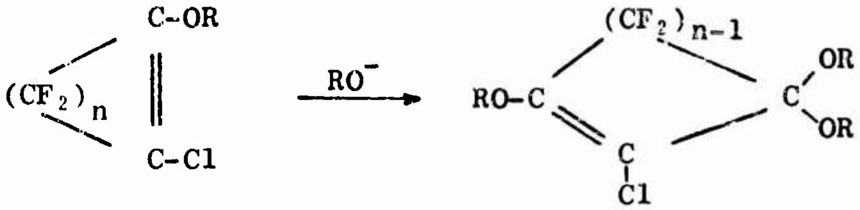


n=2 I
R=H,CH$_3$. n=3 II

n=2 IIIa,b.
R' =CH$_3$. n=3 IVa,b.

"normal" nucleophilic displacement of vinylic or allylic halogen.

B.

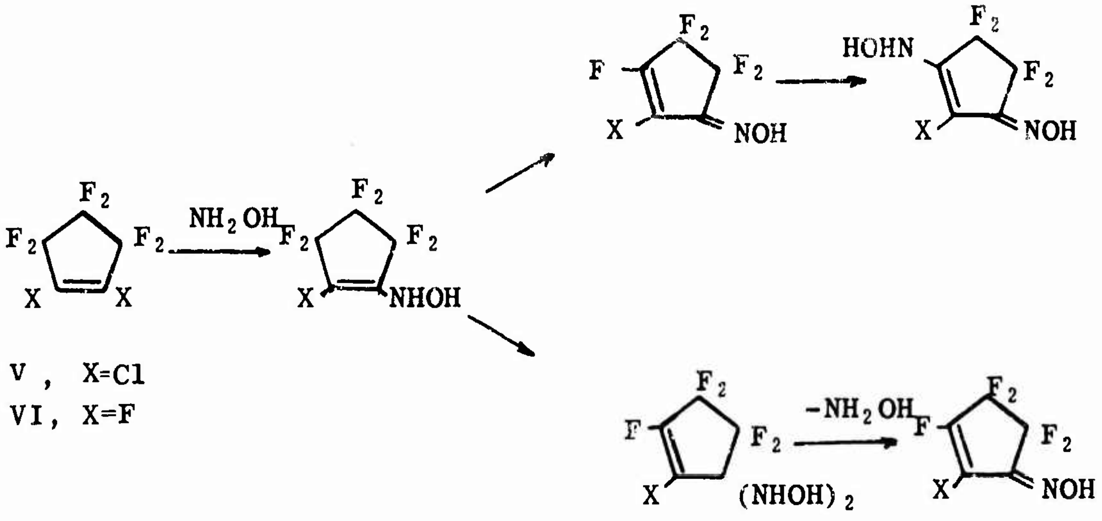


The acidity of these protons (Reaction A) can be attributed both to the allylic nature of the protons on the α-carbon and their proximity to a highly fluorinated ring structure.*

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 polyfluoroölefins with an excess of amines,(12) hydroxylamine,(13) or potassium hydroxide in polar aprotic solvents.(14)

McBee(13) 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.

The isolation of the 1,3-iminoamine from VI was cited as



V , X=Cl

VI, X=F

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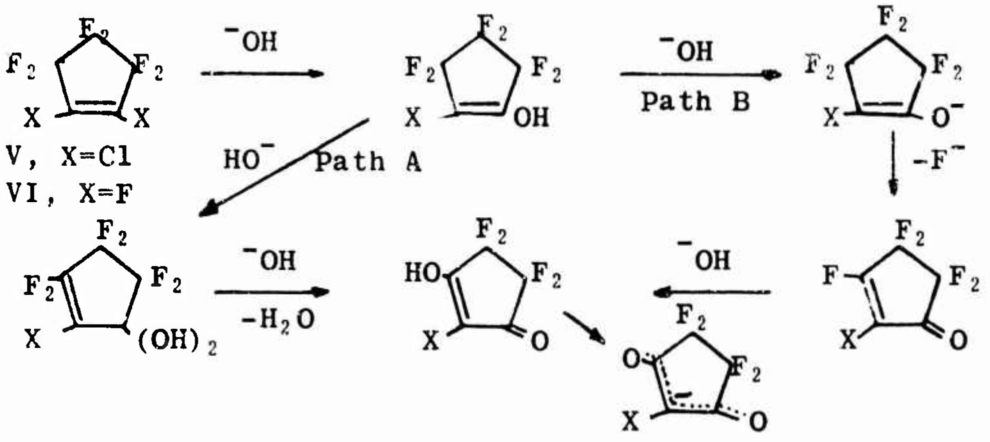
*The inductive effect of the α-carbon fluorines in this example may be relatively unimportant. However, the acidity of a proton with adjacent β-difluorogroups is well documented.(13)

evidence against the latter possibility since all previous studies in these systems indicated that the remaining vinylic fluorine would be displaced preferentially.(15)

A similar conclusion has recently been suggested by Stockel and co-workers(14) concerning the hydrolysis of polyhaloölefins with potassium hydroxide in polar aprotic solvents. Two plausible reaction paths were advanced and are illustrated below:

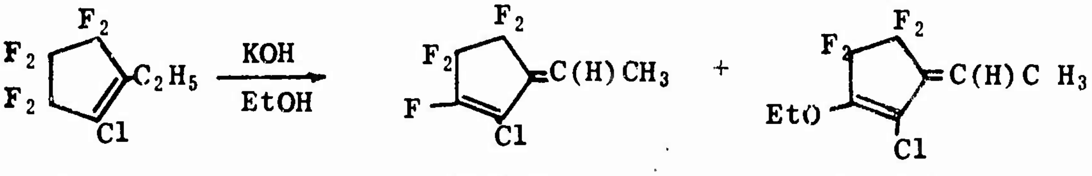


Path B is capable of explaining why the reaction of VI with hydroxide ion differs from that with alkoxide ion (15) since the formation of enolate ion is not possible in the latter case.

The overall similarity of these reactions is apparent, if the hetero-atom 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 D-O-methanol was 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)(16) in the reaction of II with a deficiency of potassium hydroxide indicates that these reactions



II VII a, b. IV a,b.

proceed via the discrete formation of 2-chloro-3-alkylideneperfluorocycloalkenes which then undergo facile nucleophilic displacement of vinylic fluorine by additional alkoxide ion.

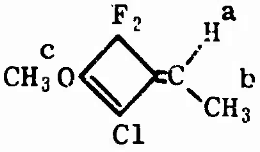
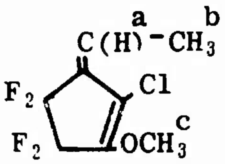
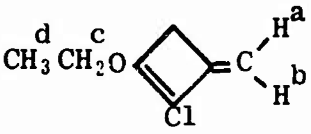
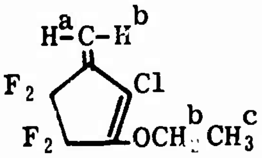
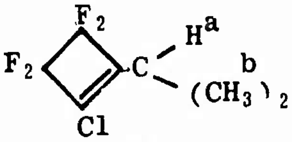
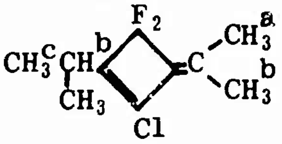
Treatment of the corresponding methyl compounds, 1-chloro-2-methyltetrafluorocyclobutene-1 (VIII) and 1-chloro-2-methylhexafluorocyclopentene-1 (IX) with ethanolic potassium hydroxide yielded 1-ethyoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X) and 1-ethoxy-2-chloro-3-methylenetetrafluorocyclopentene-1 (XI).

These compounds, particularly X, were found to polymerize far more readily than the analogous ethylidenecycloolefins, 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 g.l.c. 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: $\Delta H^{a}_{IIIa,b} = 0.32\tau$; $\Delta H^{b}_{IIIa,b} = 0.05\tau$; $\Delta H^{b}_{IVa,b} = 0.12\tau$. 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 these data highly suspect at present.

TABLE I

SPECTRAL DATA OF NEW COMPOUNDS

Compound		NMR signal	τ	J(cps)	integrated area	assignment	$\nu(>C=C<)$
	IIIa	Quartet	5.08	7.0	1	H^a	1655 cm^{-1}
		Singlet	5.94	-	3	H^c	1740 cm^{-1}
		Doublet	8.23	7.0	3	H^b	
	IIIb	Quartet	4.76	7.0	1	H^a	1645 cm^{-1}
		Singlet	5.96	-	3	H^c	1735 cm^{-1}
		Doublet	8.18	7.0	3	H^b	
	IVa	Quartet	4.09	7.6	1	H^a	1645 cm^{-1}
		Singlet	5.93	-	3	H^c	1680 cm^{-1}
		Doublet	8.01	7.6	3	H^b	
	IVb	Quartet	4.05	7.6	1	H^a	1640 cm^{-1}
		Singlet	5.93	-	3	H^c	1680 cm^{-1}
		Doublet	7.89	7.6	3	H^b	
	X	Doublet	5.18	2.0	1	H^a	1635 cm^{-1}
		Doublet	5.39	2.0	1	H^b	1705 cm^{-1}
		Quartet	5.56	7.2	2	H^c	
		Triplet	8.57	7.2	3	H^d	
	XI	Singlet	4.54	-	2	H^a	1640 cm^{-1}
		Quartet	5.55	7.0	2	H^b	1655 cm^{-1}
		Triplet	8.60	7.0	3	H^c	
	XIII	Heptet	7.23	7.0	1	H^a	1645 cm^{-1}
		Doublet	8.74	7.0	6	H^b	
	XIV	Heptet	7.27	7.0	1	H^b	1605 cm^{-1}
		Singlet	8.17	-	3	H^a	1725 cm^{-1}
		Singlet	8.21	-	3	H^a	
		Doublet	8.78	7.0	6	H^c	

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

Although potassium fluoride has been demonstrated to effect isomerization in similar systems(17), 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 non-concerted elimination would be geometrically stable(18), incorporation of geometrical identity would occur with proton abstraction by the attacking base regardless of whether the reaction proceeded via a concerted or stepwise loss of hydrogen fluoride.

This reaction may well be quite general in scope and it 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 three molar excess of isopropylmagnesium bromide, led to a 34 percent 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.

The fact 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(19). 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.

Experimental:

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 halogent 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(20). Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. 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,2-dichlorohexafluorocyclopentene and hydrogen bromide was passed through a 100 cm 2.5 cm pyrex glass tube packed with at 25/75 $BaSO_4$/carbon catalyst heated to ca. 225°C. The catalyst was prepared in the manner of Sharrah.(21) In a typical run, 500 g (2.04 mole) 1,2-dichlorohexafluorocyclopentene was swept through the tube with ca. 3.7 molar 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°C (629 mm), and 106g (16% of theory) of 1,2-dibromohexafluorocyclopentene, bp 119°C (629 mm).

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.

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-ethylhexafluorocyclopentene-1 (II). - In a 500-ml, three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, 50g (0.204 mole) of 1,2-dichlorohexafluorocyclopentene in 250 ml of tetrahydrofuran was introduced and cooled to 0°C. With rapid stirring, 80 ml of a 3M solution of ethylmagnesium bromide in tetrahydrofuran was added dropwise over a 1.0 hour period. The contents of the flask were allowed to reach room temperature and then gently heated to ca. 50°C for an additional 2.0 hours. 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^{o}/ 629 mm., n_D^{28} 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 c.p.s.^{9}

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 one hour.

The reaction mixture was then stirred for an additional two hours, 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 g.l.c. showed this material to consist of two components in a 40:60 ratio. Preparative scale g.l.c. yielded pure IIIa and IIIb.

IIIa: Anal. Calcd. for $C_7H_7ClF_2O$ = 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.

Spectral data in Table I

IIIb: Anal. Calcd. for $C_7H_7ClF_2O$: 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.

Spectral data in Table I

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 alkyhaloölefins 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 g.l.c. on an 18 foot x 1/4 inch Carbowax 20 M column at 140^{o}.

IVa: Anal. Calcd. for $C_8H_7ClF_4O$: C, 41.66; H, 3.06; Cl, 15.38; F, 32.95. Found: C, 4160; H, 3.07; Cl, 15.52: F, 33.13.

Spectral data in Table I

IVb: Anal. Calcd. for $C_8H_7ClF_4O$ = 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.

Spectral data in Table I

1-Chloro-2-ethylhexafluorocyclopentene-1 (II). - In a 500-ml, three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, 50g (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 3M solution of ethylmagnesium bromide in tetrahydrofuran was added dropwise over a 1.0 hour period. The contents of the flask were allowed to reach room temperature and then gently heated to ca. 50° for an additional 2.0 hours. 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 113.5°/629 mm., n_D^{28} 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 τ7.52 and a triplet at τ8.80 with J_{H,H_2} = 7.5 c.p.s.

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 absolute ethanol to effect an ca. 40 percent conversion to 1-ethoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X), which was shown by g.l.c. to consist of 98 percent or better of the reaction products. The minor component, of longer g.l.c. retention time, was tentatively identified as 1-methyl-2-chloro-3,3-diethoxydifluorocyclobutene-1 (XIIa).

X. Anal. Calcd. for $C_7H_7ClF_2O$: 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.

Spectral data in Table 1

XIIa. Anal. Calcd. for $C_9H_{13}ClF_2O_2$: C, 47.68; H, 5.77; Cl, 15.65. Found: C, 47.69; H, 5.86; Cl, 15.92. The infrared V c=c frequency at 1670 cm^{-1} correspond to the expected value for a chloro, methyl substituted cyclobutene. The proton NMR spectrum contained a quartet centered at τ 6.22 (J_{HH} = 7.2 c.p.s.) and triplets at τ 7.20 (J_{HH} = 7.2 c.p.s.) and τ 8.19 with J_{HF}= 1.5 c.p.s. Preference for the proposed structure over 1-chloro-2-methyl-3,3- iethoxydifluorocyclobutene 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-methylexafluorocyclopentene-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. Workup yielded 3.4 g (64% of theory) of crude XI. Preparative scale g.l.c. on a 10 foot x 1/4 inch Ucon LB 550X column yielded pure XI, n_D^{28} 1.4391; d_4^{28}1.39; bp. 163°/621 mm (decompn).

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.

Spectral data in Table I

1-Chloro-2-isopropyltetrafluorocyclobutene-1 (XIII). - 1,2-Dichlorotetrafluorocyclobutene (25 g, 0.128 mole) was treated with an ca. 2M solution of isopropylmagnesium bromide in tetrahydrofuran (70 ml, ca. 0.14 mole) according to the previously described procedure.(22) Workup of the reaction products in the previously described manner yielded 11.7 g (45% of theory) of XII, bp 122°C (630 mm), n_D^{28}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. The reaction of XIII with isopropyl magnesium 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. 2M 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°C (629 mm) (decomposition): d_4^{28} 1.00; n_D^{28}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.

V. The Base-Catalyzed Reaction of Ethylene Glycol with Perfluorocyclobutene and 1,2-Dichloro-3,3,4,4-Tetrafluorocyclobutene.

Object of the Study

To develop methods of synthesis of new fluorinated alcohol derivatives of cyclobutene which would be potential sources for reactive monomers as well as cyclobutyl derivatives possessing polyfunctionality.

Experimental

I. Reaction of ethylene glycol with perfluorocyclobutene.

About 230 grams of 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane was dechlorinated with zinc dust using n-butanol as solvent and the dechlorinated product was bubbled directly into a 500-ml., 3-neck flask containing ethylene glycol and KOH. The flask was fitted with a mechanical stirrer and a Dewar-type condensor containing dry ice.

It was found that in previous runs of this type that decomposition took place if the glycol solution was not kept at a moderate temperature. Therefore, the 500-ml. flask was occasionally cooled in an ice bath. If, however, the solution began to freeze, moderate heat was applied. After complete addition of perfluorocyclobutene, stirring was continued for an hour.

The reaction product was neutralized with 15 percent HCl and excess water was added to dissolve the KF and extract unreacted glycol. The dense organic layer was separated. This organic material was kept under refrigeration. (After storage for about two weeks under refrigeration, evolution of HF can be detected). Fractional distillation of 25 ml. of the liquid was attempted at 10 mm. pressure. Decomposition with evolution of HF took place as expected. VPC analysis of the reaction products using a 20-foot carbowax column at 165°C showed the presence of at least five components. Two components were separated by VPC which were not identified.

II. Reaction of ethylene glycol with 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene.

To 100 ml. of ethylene glycol was added 50 grams of KOH. This solution was then placed in a 500-ml., 3-neck flask fitted with a mechanical stirrer and dry ice condenser. 25 ml. of (I) was added slowly to the flask. The addition took one hour and stirring was continued for an additional one and a half hours. Crystal formation occurred as long as (I) was dropped into the flask. Upon completion of the reaction, a large volume of water was added. The white solid was filtered and dried. A Beilstein test indicated that the solid contained halogen. The glycol-water solution was neutralized and tested with 5 percent $AgNO_3$ solution. A white precipitate formed, indicating the presence of chloride ion.

Recrystallization of the product was effected from ethylene glycol and water. However, it was found that after repeated washings with water, some ethylene glycol remained as an impurity in the crystals. Therefore, vacuum sublimation of the product was effected.

Properties of the sublimate:

1. IR (mull) no hydroxide or double bond reaction

2. melting point - 131 degrees C.

			ratio
3. NMR:	complex absorption at 5.8	$-CH_2-$	8
	doublet at 5.5, J_{HF} 7_{HF} c.p.s.	-CHCl	1

4. Elemental Analysis, %

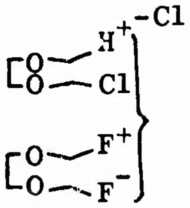
	Experimental Results	Calculated (based on structure III)
C	39.51	39.60
H	3.73	3.74
Cl	14.40	14.61
F	15.79	15.66
O	26.47	26.38

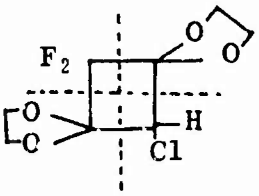
5. Mass Spectra: no molecular ion

m/e
207

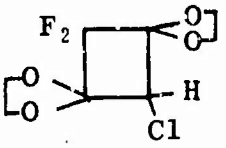
120

122

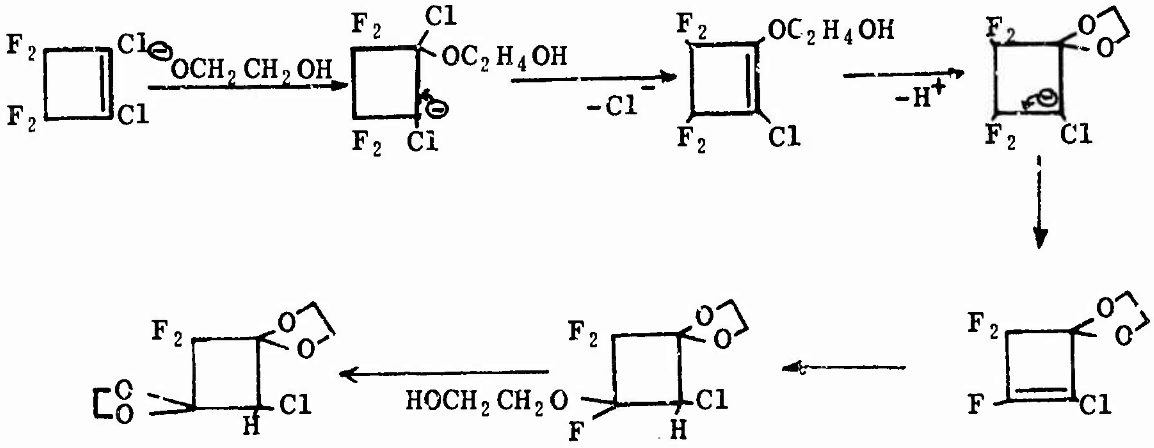




Structure of Compound:

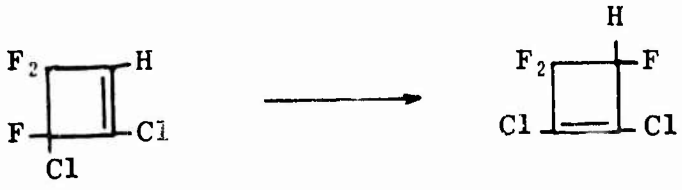


The mechanism of the reaction can be explained in accordance with a carbanion intermediate.



VI. Boron Trifluoride Catalyzed Rearrangements of Fluorinated Halocyclobutenes

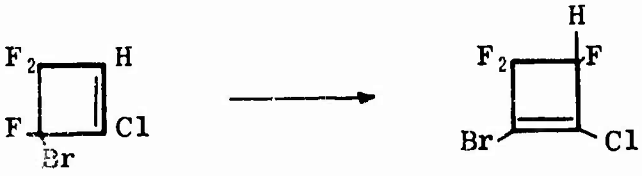
A novel and heretofore unknown rearrangement of certain fluorinated halocyclobutenes has been discovered in which a 1,3-shift of fluorine occurred in the presence of anhydrous boron trifluoride at elevated temperatures and pressures. This rearrangement was discovered while attempting to add hydrogen fluoride across the double bond of 2,3-dichloro-3,4,4-trifluorocyclobutene (I). Henne and Arnold(23) found that addition of hydrogen fluoride to olefins such as R-CH=CHX and R-CH=CX_2 (where X is any halogen) proceeded easily with anhydrous boron trifluoride as the catalyst. Thus, it was somewhat surprising that when I was treated with a mixture of hydrogen fluoride and boton trifluoride in a steel autoclave at 225°C for 72 hours, no addition of HF or substitution of chlorine occurred. Instead, an isomerization occurred in which the allyl fluorine underwent a 1,3-shift to give 1,2-dichloro-3,3,4-trifluorocyclobutene (II) as indicated below:



I II

By repeating the reaction using hydrogen fluoride alone and anhydrous boron trifluoride alone, it was determined that boron trifluoride was solely responsible for the observed isomerization.

Under similar conditions two other compounds were found to isomerize. Isomerization of 3-bromo-2-chloro-3,4,4-trifluorocyclobutene (III) proceeded smoothly under milder conditions than did I to give 2-bromo-1-chloro-3,3,4-trifluorocyclobutene (IV) as given below:(26)

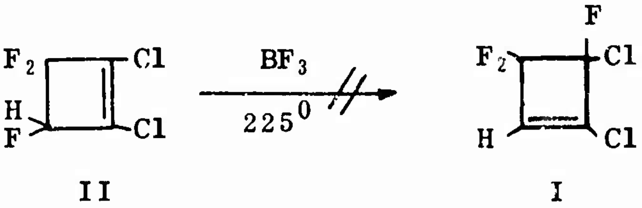


III IV

Considerable decomposition occurred in the isomerization of 3-chloro-3,4,4-trifluorocyclobutene (V), but a small amount of 2-chloro-3,3,4-trifluorocyclobutene (VI) was formed as shown below:

No isomerization occurred, even under more drastic conditions, with the following compounds: 1-chloro-3,3,4,4-tetrafluorocyclobutene (VII); 2-fluoro-3-chloro-3,4,4-trifluorocyclobutene (VIII); 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (IX).

From the observations that none of the reactions proceeded completely to the isomerized product, that the concentration of boron trifluoride was unimportant, and that several repetitions of a reaction at the same temperature but for different lengths of time gave essentially the same percentage of product, the possibility that these reactions may involve thermal equilibria was considered. To determine if these reactions were indeed equilibrium reactions, II was treated with boron trifluoride under the same conditions as the isomerization of I which was discussed previously. If an equilibrium is involved, some isomerization to I should occur as follows:



The fact that no isomerization did occur is good evidence that these isomerizations are not equilibrium reactions.

The structures of new compounds described in this communication were determined by elemental analysis and infrared and nuclear magnetic resonance (NMR) spectroscopy. Proton NMR was particularly useful in this study since the coupling constants, J_{HF}, for the gem-hydrofluoro group were in the range of 60-64 Hz. All other coupling constants were under 20 Hz.

Table II

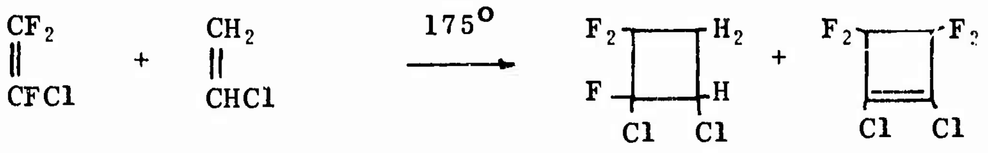
PROPERTIES OF VARIOUS CYCLOBUTENES

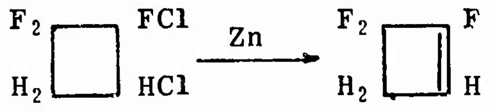
Compounds	B.P. °C/mm.Hg.	n_D^{25}
I(24)	91-92°/763	1.3942
II	84-85°/630	1.4053
III	108°/628	1.4272
IV	103°/629	1.4331
V(25)	76.5°/630	1.3270
VI	77°/628	1.3681

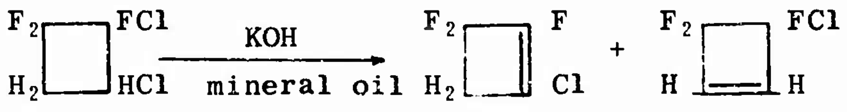
VII. Preparation and Reactions of Various Fluorocycloalkenes

1. Historical

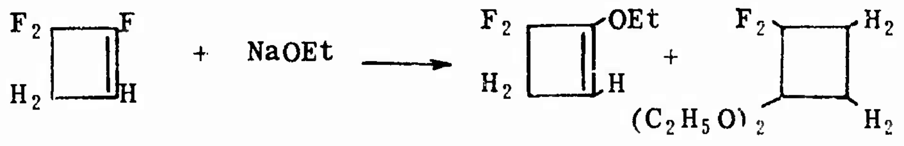
In 1962, Groppelli(25) studied the chemistry of various derivatives of 1,2-dichloro-2,3,3-trifluorocyclobutane, including 2,3,3-trifluorobutane, 1-chloro-2,3,3-trifluoroethylene, and 2-chloro-3,4,4-trifluorocyclobutane.

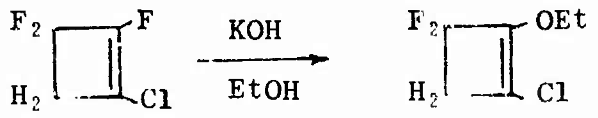


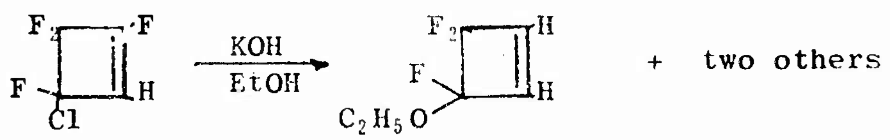




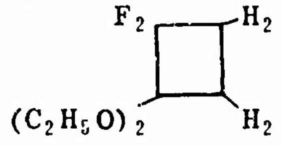
The following nucleophilic substitutions were then run.(25)





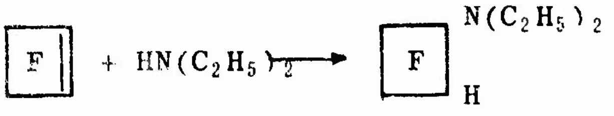


All these reactions have now been repeated and verified, with the exception that no was found.

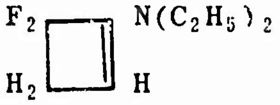


The physical data of the products obtained agree very well with those of Groppelli.(25)

In 1950,(29) Rapp, Pruett, Barr, Bahner, Gibson, and Lafferty studied the reaction of chlorotrifluoroethylene and of hexafluorocyclobutene with diethylamine. With hexafluorocyclobutene, the following reaction occurred:



The reaction of 2,3,3-trifluorocyclobutene with diethylamine has now been run, and appears to give , as indicated by the infrared and mass spectra of the product. Not enough has been isolated to obtain physical constants.

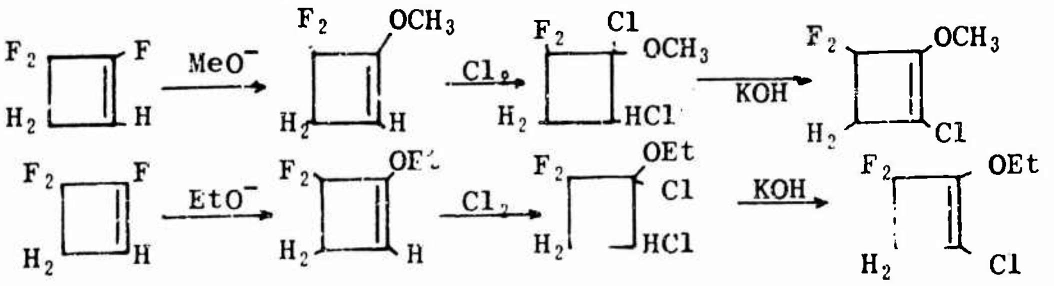


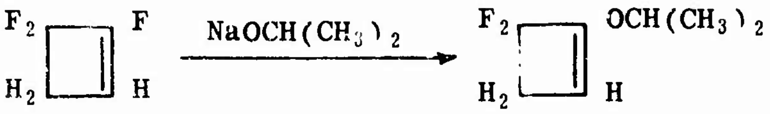
2. Discussion and Results

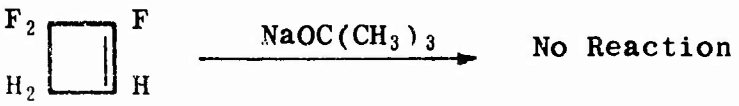
The various reactions that Groppelli ran were repeated and verified, with the exception mentioned above. In addition, 2,3,3-trifluorocyclobutene was reacted with methoxide and isopropoxide to give the ethers by substitution of the vinylic fluorine. No ether resulted with tertiary butoxide.

The methoxy and ethoxy compounds were chlorinated to give the saturated 1,2-dichlorocyclobutanes. These were then dehydrohalogenated with potassium hydroxide in mineral oil. Each gave only one product, the cyclobutene with vinylic chlorine.

When 2-methoxy-3,3-difluorocyclobutene was reacted with excess sodium methoxide for 24 hours at reflux, no further substitution product could be isolated, and the starting material seemed to have decomposed.





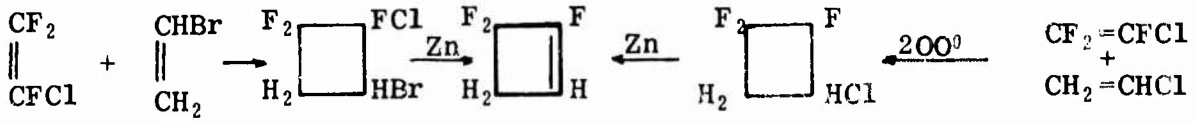


Nucleophilic substitution of the vinylic fluorine in 2,3,3-trifluorocyclobutene occurs only under much more vigorous conditions than substitution of the vinylic fluorines of hexafluorocyclobutene. Anhydrous conditions and temperatures around $100^{\circ}C$ are required for ether formation in contrast to hexafluorocyclobutane which gives the diether with KOH in ROH at room temperature.

Although basicity increases in the direction $Me<Et<i\text{-}Pr<t\text{-}Bu$, the yield of ether was in the opposite direction in this system. The yields were 70 percent methoxy, 31 percent ethoxy, 18 percent isopropoxy, and 0 percent tertiary butoxy. Apparently the effect is steric, the smaller nucleophiles being better able to approach the reaction site.

The results of the dehydrohalogen experiments can be explained by stating that the hydrogen geminal to chlorine should be much more acidic than the hydrogen vicinal to two fluorines and one chlorine.

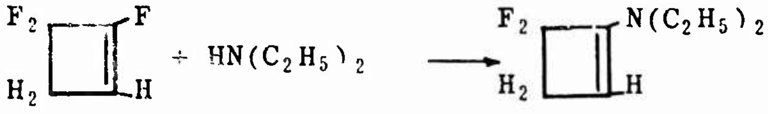
2,3,3-trifluorocyclobutene was obtained either by dehalogenating 1,2-dichloro-2,3,3-trifluorocyclobutane or 1-bromo-2-chloro-2,3,3-trifluorocyclobutane. These were prepared either by thermally codimerization of chlorotrifluoroethylene with vinyl chloride or with vinyl bromide.



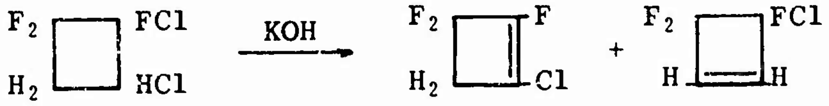
Contrary to the results of Gini(28) and Croft(27), the codimer of chlorotrifluoroethylene and vinyl bromide was never obtained in better than 11 percent yield, due to the formation of large quantities of tar. This occurred even when the bomb was rinsed with 15 molar ammonia and dried before use, calcium carbonate was added to the reaction mixture, and the temperature was significantly below that reported by Gini and Croft.

On the other hand, chlorotrifluoroethylene and vinyl chloride gave practically a quantitative yield of clear, water-white product, which was distilled to give 45 percent yield of 1,2-dichlorohexafluorocyclobutane and 47 percent yield of 1,2-dichloro-2,3,3-trifluorocyclobutane. In both cases, 1 - 10 ml. of dilimonene was added as a polymerization inhibitor, and care was taken to exclude air from the system.

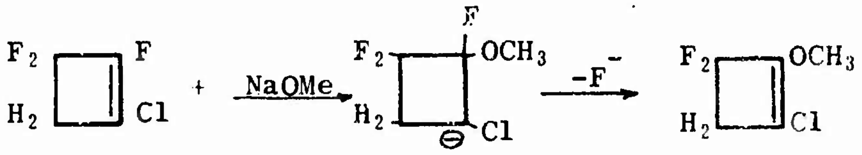
A reaction occurred upon mixing 2,3,3-trifluorocyclobutene and diethylamine. Only enough product was isolated to obtain a mass spectrum, which indicated a molecular ion of m/e 161. Further study on this system is in progress.



1-Chloro-2,3,3-trifluorocyclobutene and 3-chloro-3,4,4-trifluorocyclobutene were prepared by reacting 1,2-dichloro-2,3,3-trifluorocyclobutane with powdered potassium hydroxide in mineral oil.



When 1-chloro-2,3,3-trifluorocyclobutene was reacted with a threefold excess of sodium methoxide under anhydrous conditions at reflux, only one product resulted, 1-chloro-2-methoxy-3,3-trifluorocyclobutene. This is in accordance with the theory of carbanion stabilization which predicts that the major intermediate will be that with the negative charge on carbon bonded to chlorine.(27)



However, a different mechanism operates when 3-chlor-3,4,4-trifluorocyclobutene is reacted with ethoxide, which goes thus, and which goes much more vigorously than the reaction with 2,3,3-trifluorocyclobutene.

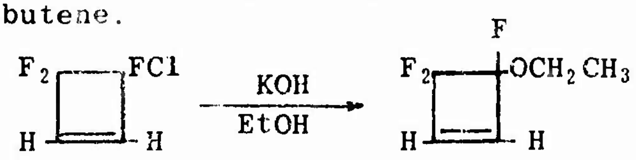
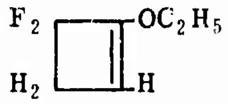
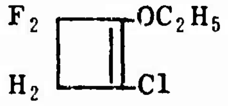
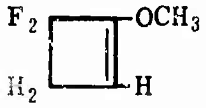
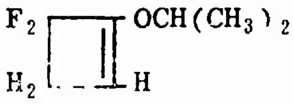
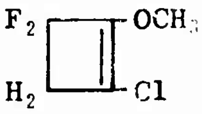
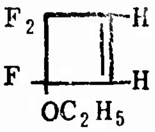


Table III

NUCLEAR MAGNETIC RESONANCE DATA FOR DERIVATIVES OF 2,3,3-TRIFLUOROCYCLOBUTENE

	Area	τ	
	3H Triplet	8.66	J = 7 cps
	2H Triplet of Doublets	7.40	J = 2 cps J = 1 cps
	2H Quartet	6.06	J = 7 cps
	1H Triplet of triplets	4.92	J = 13 cps J = 1 cps
	3H Triplet	8.62	J = 7 cps
	2H Triplet	7.25	J = 2.5 cps
	2H Quartet	5.88	J = 7 cps
	2H Poorly resolved triplet	7.43	J = 3 cps
	3H Singlet	6.32	
	1H Triplet of triplets	4.98	J = 13 cps
	6H Doublet	8.82	J = 6 cps
	2H Triplet	7.62	J = 3 cps
	1H Heptet	6.02	J = 6 cps
	1H Triplet	5.32	J = 13 cps
	2H Triplet	7.19	J = 2 cps
	3H Singlet	6.08	
	3H Triplet	8.80	J = 7 cps
	2H Quartet	6.46	J = 7 cps
	1H Doublet	5.71	
	1H Multiplet	4.38	J = 1 cps

3. Experimental

1-Bromo-2-chloro-2,3,3-trifluorocyclobutane

The 0.5-liter bomb was rinsed with 15 molar ammonia and dried, then one gram of calcium carbonate and one ml of d-limonene were placed inside. The bomb was sealed and evacuated while being cooled to -80°C in a dry ice acetone bath. Chlorotrifluoroethylene, 126 g, and 149 g of vinylic bromide were distilled in. Heating at 128° for 62 hours gave 140 g of crude product (51% yield). This was distilled to give 28.6 g of 1-bromo-2-chloro-2,3,3-trifluorocyclobutane.

1,2-Dichloro-2,3,3-trifluorocyclobutane

Five ml of d-limonene was placed inside the 1.5-liter bomb, which was then sealed and cooled, and evacuated. Vinyl chlorine, 459 g (7.4 moles) and 723 g 22 moles) of chlorotrifluoroethylene were distilled in. Heating at about 200°C for about 24 hours yielded 1,103 g (93.5% yield) of crude product. Fractional distillation yielded 328 g (45% yield) of 1,2-dichlorohexafluorocyclobutane, bp. 52-54.5°; and 410 g (48% yield) of 1,2-dichloro-2,3,3-trifluorocyclobutane, bp 98-100°C.

2,3,3-Trifluorocyclobutane from 1-bromo-2-chloro-2,3,3-trifluoroethylene

n-Butanol, 65 ml, and 24 g of zinc dust were placed in a 100-ml., three-neck flask equipped with a dropping funnel, stirrer, and reflux condenser connected to a dry ice-acetone trap. About one ml of 37 percent hydrochloric acid was added as a catalyst and a trace of t-butylcatechol and diphenylamine was added to both the flask and the gas trap as a polymerization inhibitor. 1-Bromo-2-chloro-2,3,3-cyclobutane, 55.9 g, was added dropwise over about five hours while the zinc-butanol was gently refluxed. 2,3,3-Trifluorocyclobutene, 23.8 g, (88.2% yield) were collected and identified by its infrared spectrum.

2,3,3-Trifluorocyclobutene from 1,2-dichloro-2,3,3-trifluorocyclobutane

Exactly the same setup as the foregoing was used, except that a 1,000-ml. three-neck flask was used, instead of a 100-ml. flask. t-Butylcatechol and diphenylamine were used as before and about 1 ml. of 37 percent HCl as a catalyst. 1,2-Dichloro-2,3,3-trifluorocyclobutane, 253 g, were added to 106.5 g of zinc dust in 300 ml. of n-butanol. After about 24 hours, 139.3 g (87.5% yield) of 2,3,3-trifluorocyclobutene were obtained. This proceeds much slower than the above reaction; only about one third of the product had appeared after the initial addition of 1,2-dichloro-2,3,3-trifluorocyclobutane.

A slight flow of nitrogen through the entire set-up accelerates the collection of the product, as otherwise it tends to reflux back into the reaction flask, bp 26°.

2-Ethoxy-3,3-difluorocyclobutene

A 500-ml., three-neck flask equipped with a stirrer, dropping funnel, and refluxed condenser connected to a dry ice trap was used. Sodium, 15.6 g, was dissolved in 200 ml. of absolute ethanol under nitrogen. 2,3,3-Trifluorocyclobutene, 58.2, was added dropwise to the refluxing sodium ethoxide solution over two hours, then refluxed for seven hours. The reaction mixture was cooled and diluted with about 1,250 ml. of water. A heavy oily layer, 58.9 g, (81% yield) settled to the bottom. This was dried over anhydrous $MgSO_4$ at -30°C and then distilled to give 22.3 g (30.8% yield) of 2-ethoxy-3,3,-difluorocyclobutene. Vapor phase chromatography showed it to be greater than 90 percent pure.

d^{25} =1.0758 g/ml Groppelli's data d^{25} = 1.07g/ml

d^{25} =1.3869 g/ml n^{22} = 1.3865

M_d calculated = 29.33

M_d experimental = 29.319

2-Methoxy-3,3-difluorocyclobutene

Exactly the same procedure as the foregoing was used as for the ethoxy compound. Sodium, 35.9 g, was dissolved in 200 ml. of methanol under nitrogen. A trace of t-butylcatechol and diphenyamine were added. While the solution was refluxed in an oil bath at 135-150°C, 63.5 g of 2,3,3-trifluorocyclobutene was added dropwise over about two hours, then refluxed for an additional two hours. The original became cloudy with sodium fluoride as the reaction progressed. The cooled reaction mixture was poured into about one liter of cold water and 3.7 percent HCl was added to just neutralize the aqueous layer (color changed from red to light yellow-orange). Crude product, 106.5 g (151% yield), settled to the bottom, which was dried and distilled to give 49.5 g (70% yield) of 2-methoxy-3,3-difluorocyclobutene. Vapor phase chromatography on a five foot Uconn column at 100°C indicated the product to be greater than 99 percent pure.

Boiling point 91°C at 630 mm. Hg with decomposition

d^{26} = 1.1196 g/ml

n^{26} = 1.3779

M_d calculated = 24.71

M_d experimental = 24.758

2-Isopropoxy-3,3-difluorocyclobutene

The same procedure as the foregoing was used. Sodium, 26.6 g, was dissolved in 300 ml of isopropanol under nitrogen. About 0.5 g of t-butylcatechol and 0.5 g of dipenlyamine were added. 2,3,3-Trifluorocyclobutene, 72.3 g, was added over about an hour while the reaction was stirred and refluxed on a mineral oil bath at 135-165°C. The cooled reaction mixture was dissolved in about 1,050 ml of water, and extracted with three 100-ml portions of dichloromethane. Short path distillation yielded an imhomogeneous fraction boiling about 75°C, that appeared to contain water plus the desired product. The crude product was extracted with a 2:1 volume of water and dried over $MgSO_4$ at -30°. Yield 17.7 g (17.7% yield). It was shown to be about 95 percent pure on a ten foot x 1/8 inch FS 1265 column.

d^{28} = 1.0181 g/ml/

n^{28} = 1.3931

M_d calculated = 33.95

M_d experimental = 34.74

Attempted Synthesis of 2-t-butoxy-3,3-difluorocyclobutene

The procedure was similar to the foregoing. Sodium, 17.1 g, was dissolved in 200 ml of tertiary butanol under nitrogen. Trifluorocyclobutene, 54 g, was added dropwise over about 20 minutes to the refluxing solution, which was then refluxed for four hours. Dilution by water caused a nonaqueous layer to rise to the top, yield 80.8 g (99.7% yield), which was stored overnight over anhydrous $MgSO_4$ at -30°C. Distillation yielded only water plus t-butanol, identified by its retention on an $SE_{3}0$ column.

Reaction of 2-Methoxy-3,3-difluorocyclobutene with Excess Sodium Methoxide.

Under the same conditions as before with a 100-ml, three-neck flask, 5.2 g of sodium was dissolved in 43 ml of methanol under nitrogen. 2-Methoxy-3,3-difluorocyclobutene, 13.1 g, was added, and the solution was heated in an oil bath at about 130° for 24 hours. The reaction mixture immediately turned dark brown upon the initial addition. A few drops of the reaction mixture were mixed with water, a lower layer separated which contained starting material according its infrared spectrum. No definite evidence for any new cyclobutene compound was found.

The mixture was refluxed for another 24 hours, then the cooled reaction was poured into about 500 ml of cold water. Only a single yellow liquid and a heavier brown solid formed.

1,2-Dichloro-2-methoxy-3,3-difluorocyclobutane

The apparatus consisted of a 100-ml, three-neck flask equipped with a gas bubbler and reflux condenser connected to a dry ice trap.

An open-ended mercury manometer was placed in the inlet line and a capillary tube was placed in the outlet from the dry ice trap. 2-Methoxy-3,3-difluorocyclobutene, 33 g, was placed in the flask and nitrogen bubbled through for 10 minutes. Chlorine was then bubbled through at about 10 mm Hg pressure above atmospheric pressure (630 mm Hg) for f ur hours, then nitrogen was bubbled through for 10 minutes. The initially clear starting material immediately turned intensely black as soon as the chlorine flow was started, then soon became clear again with a yellow brown color, due to dissolved chlorine, and remained so for the duration of the reaction.

The crude product was washed with sodium carbonate solution and with water until no more chlorine odor was detectable and the aqueous and organic layers were nearly colorless. Crude product, 42.9 g, (81% yield) was obtained and stored over $MgSO_4$ at -30°C. Short path distillation gave 30 g (57% yield) of 1,2-dichloro-2-methoxy-3,3-difluorocyclobutane.

This was shown to be 90-95 percent pure on a five-foot Uconn column at 150°.

Boiling Point 76° 49 mm.

d^{27} = 1.3955 g/ml
n^{27} = 1.4225
M_d calculated = 34.90
M_d experimental = 34.816

1,2-Dichloro-2-ethoxy-3,3-difluorocyclobutane

Exactly the same apparatus and procedure was used as above. 2-Ethoxy-3,3-diflurocyclobutene, 37 g, yielded 33 g (84% yield) of crude product which was distilled to give 22.6 g of 1,2-dichloro-2-ethoxy-3-,3-difluorocyclobutane. It was shown to be about 80 percent pure on a 20 foot SE_{30} column at 104°C.

Approximate boiling point 75°C at 24 mm
Physical constants have not been determined.

1-Chloro-2-methoxy-3,3-difluorocyclobutane

The apparatus consisted of a 250-ml, three-neck flask equipped with a dropping funnel, stirrer, reflux condenser, and dry ice trap. Nitrogen was passed through a T-tube at the outlet to prevent the influx of air. 1,2-Dichloro-2-methoxy-3,3-difluorocyclobutane, 30 g, was added dropwise over 43 minutes to 42 g of powdered potassium hydroxide in 100 ml of heavy white mineral oil in an oil bath at 58°C. As the reaction progressed, the infrared spectrum of the reaction mixture showed an increasing c=c peak at 1700 cm^{-1} and the development of a new fingerprint pattern. After 272 minutes, the reaction mixture was filtered to give a clear yellow liquid. Short path distillation yielded 10.7 g (83.5% yield). This was manopreped on a 20 foot x 3/8 inch 30 percent SE column at

140°C to give a product pure by vapor phase chromatography. Estimated yield 10.7 g 0.8 = 8.6 g (67% yield).

d^{27} = 1.2725 g/ml

d^{27} = 1.4075

M_d calculated = 29.57

M_d experimental = 29.822

1-Chloro-2-ethoxy-3,3-difluorocyclobutane

Exactly the same apparatus and procedure was used as above. 1,2-Dichloro-2-ethoxy-3,3-difluorocyclobutane, 15.9 g, was added dropwise to 8.1 g of powdered potassium hydroxide in 25 ml of heavy white mineral oil heated to 80°C on a mineral oil bath. As the original KOH seemed to clump together, 11.9 g additional KOH was added. The dark brown reaction mixture boiled vigorously and filled the condenser with foam. After 20 hours, the reaction mixture was chilled and washed with 200 ml water and 250 ml of 3.7 percent HCl. Distillation yielded what appeared to be 1-chloro-2-ethoxy-3,3-difluorocyclobutene plus carbon tetrachloride. Vapor phase chromatography confirmed the presence of CCl_4, and the nuclear magnetic resonance spectrum indicated the presence of 1-chloro-2-ethoxy-3,3-difluorocyclobutene.

2H Quartet	5.38 τ	J = 7 cps
2H Triplet	5.27 τ	J = 2.5 cps
3H Triplet	8.62 τ	J = 7 cps

The presence of carbon tetrachloride in the product cannot be accounted for.

2-Diethylamino-3,3-difluorocyclobutene

2,3,3-Trifluorocyclobutene, 12.5 g, and 34.1 g of diethyl amine were mixed in a 125-ml, ground glass, stoppered flask. After 11 hours at 25°C, the reaction mixture had frozen to a reddish brown solid. It was mixed with about 100 ml of 1 N NaOH and a light organic layer appeared. This was washed with another portion of 1 N NaOH, then with 100 ml of 1 N HCl, upon which a heavy lower layer settled out. Tertiary cyclobutylamines are insoluble in acid. The lower layer was washed again with acid and collected. Crude product, 5.6 g, was dried over $MgSO_4$. Vapor phase chromatography on the 20 foot x 3/8 inch 30 percent SE_{30} column showed the product to be about 10 percent 2-diethylamino-3,3-difluorocyclobutene and 90 percent diethylamine. A little of the cyclobutane peak was collected and its mass spectrum indicated a molecular ion at m/3 161.

1-Chloro-2,3,3-trifluorocyclobutene and 3-chloro-3,4.4-trifluorobutene

The apparatus consisted of a 1,000-ml, three-neck flask equipped with a dropping funnel, stirrer, reflux condenser connected to a dry ice trap, and a Y tube for nitrogen flushing.

1,2-Dichloro-2,3,3-trifluorocyclobutane, 303 g, was added dropwise over about three hours to 232 g of powdered potassium hydroxide in 300 ml of white mineral oil maintained at 28-63°. This was refluxed for 63 hours, then fractionally distilled to 48.4 g (16% yield) of 1-chloro-2,3,3-trifluorocyclobutene, bp 46.5-49°C, and 42.9 g (14% yield) of 3-chloro-3,4,4-trifluorocyclobutene, bp 74-78°C. Vapor phase chromatography indicated both samples to be greater than 95 percent pure.

1-Chloro-2-methoxy-3,3-difluorocyclobutene from 1-Chloro-2,3,3-trifluorocyclobutene

The apparatus consisted of a 500-ml, three-neck flask. Sodium, 24 g, was dissolved in 200 ml of methanol under nitrogen, and heated to gentle reflux on an oil bath at 91.5-102°C. 1-Chloro-2,3,3-trifluorocyclobutene, 42.1 g, was added dropwise over 24 minutes, and the reaction mixture turned from clear to milky. It was refluxed for seven more hours, during which time the reaction mixture became even more opaque. The cooled reaction mixture was diluted with about 1,250 ml of cold water, and a heavy oily layer settled out. This was distilled to give a product greater than 95 percent pure by vapor phase chromatography on 305 SE_{30} at 150. The product was shown to be 1-chloro-2-methoxy-3,3-difluorocyclobutene.

Yield 15.4 g 33 percent yield

d^{21} = 1.2748 g/ml

n^{21} = 1.4100

M_d calculated = 29.57

M_d experimental = 29.891

2-Ethoxy-3,4,4-trifluorocyclobutene

The apparatus consisted of a 100-ml, three-neck flask equipped with a dropping funnel, stirrer, and reflux condenser connected to a dry ice trap. KOH, 17.9 g, was dissolved in 37 ml of 95 percent ethanol. 3-Chloro-3,4,4-trifluorocyclobutene, 16.3 g, was added dropwise over about one hour. The reaction mixture immediately became cloudy and so warm that it had to be cooled with ice water. After three hours, the reaction was diluted with 100 ml of water and a dark brown liquid settled to the bottom, yield 20.4 g (133% yield). This was stored over $MgSo_4$ and manopreped on a 20 foot x 3/8 inch 30 percent SE_{30} column at 85-95°C. The second peak was collected and appeared to be 2-ethoxy-3,4,4-trifluorocyclobutene. The mass spectrum gave a molecular ion at m/3 152. The nuclear magnetic resonance gave the following peaks:

3H	Triplet	8.80 τ	J = 7 cps
2H	Quartet	6.46 τ	J = 7 cps
1H	Doublet	5.71 τ	
1H	Multiplet	4.38 τ	J = 1 cps

VIII. Studies on the Preparation and Reactions of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene (I)

Part A. Synthesis of I

1 Object. To develop the best conditions for reacting potassium iodide and diglyme with 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (II) to yield I and to effect the complete removal of solvent I.

2. Historical Background. Studies on the halide exchange reaction for these compounds were initiated by George Moore in the University of Colorado laboratories. His studies employed KI and acetone and led him to conclude that the exchange approached equilibrium.

Randy McMurtry, also of the University of Colorado, has within the past year concluded studies indicating glyme and diglyme are superior solvents for this reaction. His studies show considerable enhancement of the rate and higher conversion of II to I.

Studies on the reactions of I comprise a new and interesting field. It was decided to begin these reactions by attempting an Ullmann-type condensation. The Ullmann reaction is a coupling reaction resulting from the heating of aryl halogen compounds in the presence of finely divided copper. The reaction is usually attempted in the absence of solvent. However, high boiling solvents such as resorcinol have been used.(30)

3. Results and Discussion. II was reacted with excess potassium iodide in diglyme by heating a mixture of the three under reflux for nine days. Runs were made with pot temperatures maintained at 115°C, 135°C, and 155°C. The latter was the temperature of slowly refluxing diglyme. The progress of each reaction was followed by VPC analysis. Considerable tar and carbon was formed in each reaction but the amounts were greatest at higher temperature. The halogen exchange reaction proceeded toward an apparent equilibrium in all cases but with a slightly higher percentage of I after nine days at 115°C. This is probably not meaningful. Large differences were observed in the rate of attainment of equilibrium. At 115°C there was an appreciable difference between the relative ratios of II, I, and the intermediate 1-chloro-2-iodo-3,3,4,4-tetrafluorocyclobutene (III) between the fourth and ninth day. At 155°C the reaction reached equilibrium by the fourth day with the percent I being twice that of the percent I obtained at 115°C after four days. The run at 135°C showed intermediate behavior. It was thus concluded that a higher reflux temperature is best since it greatly speeds the halide exchange reaction without significantly reducing the yield of I.

Complete removal of diglyme from the product, I, has been a source of considerable difficulty. Although the ether solvent is soluble in water, repeated extractions are unable to remove the last five percent. For this reason the product mixture from the reaction was added to twice its volume of water and the resultant mixture steam distilled. The organic layer was found to still contain around 10 percent ether. This product, however, when steam distilled again with a twentyfold volume of water afforded a nearly ether-free organic layer. A slight modification of this procedure in which the organic layer was washed by decantation several times with water before the first steam distillation ultimately led to material which contained no ether.

Distillation of the organic residue gave rise to compounds I, II, and III. I still contained a contaminant of unknown origin in small amounts. On cooling to -20°C, a fractional crystallization was effected. Upon repeating this twice, a VPC pure sample of I could be obtained. The impure fraction from the fractional crystallization contained nearly 30 percent of the total I and was thus reserved for further investigation.

4. Experimental. A. This group of experiments on the preparation of I deals with different solvents for the halogen exchange reaction. Twenty gm of II, 43 gm of KI, 50 ml of water, and 50 ml of acetone were combined in a flask and refluxed for 20 days. Discoloration was slight. The mixture was heterogeneous with an organic layer on top separating whenever the mixture was cooled. A GPC analysis of the organic layer showed only 15 percent conversion to 1-chloro-2-iodo-3,3,4,4-tetrafluorocyclobutene (III) and no I.

Sealed in a Carius tube were 83 gm of KI and 40 gm of II and heated until the pressure reached 114 psig. The mixture refluxed at this pressure for five days. GPC analysis revealed a 25 percent conversion to III and a 5 percent conversion to I.

Another experiment employed 75 ml of glyme and 42 gm of KI to which was added 20 gm of II. The solvent was discolored by KI on mixing. The mixture was allowed to reflux for five days before quenching with water and extracting with methylene chloride. Distillation gave a poor yield of II and only traces of I. Analysis of samples taken during the reaction indicated, however, good conversion to III. It is felt that much product was lost during the separations and the method may be useful if this difficulty can be overcome.

A third preparative method in current use now involves refluxing a mixture of II and diglyme over excess KI for about 48 hours. This method gives mainly I as a product with yields approaching 60 percent. Degradation of II appears not to exceed 25 percent although there is considerable degradation of the solvent. This method has only one serious drawback and that is the difficulty in removing the solvent from the product. Boiling points are nearly the same and although the ether is water soluble, repeated extractions will not remove the last 5-10 percent.

(B) Ullmann Reaction In a test tube was placed 250μl of I. While stirring, a small amount of red powdered copper was added. No reaction was observed for this mixture either at room temperature or under reflux. Zinc metal was then added to the cooled system and the heating process repeated. No reaction was observed and GPC analysis indicated that I was recovered unchanged.

A second attempt at coupling reactions was run employing Zn in glacial acetic acid. Upon mixing, the solution became milky and an exothermic reaction took place. The mixture was kept at 60°C with some heating for several minutes after the exothermic reaction had subsided. Cooling and filtering gave a clear solution and a white solid identified as zinc iodide. The solution was analyzed and separated showing only traces of I and a good yield of a new compound, IV. This new compound has been identified as 1-iodo-3,3,4,4-tetrafluorocyclobutene and has the following physical constants: bp 97°C at 623 mm, $\rho = 2.11$; $n_D^{25.2} = 1.4295$ and MR calc. = 30.48, observed 30.7.

Anal. Calcd. for C_4HF_4I = 19.5% C, 0.40% H, 50.4% I, 29.7% F. Found = 19.37% C, 0.61% H, 49.85% I, 30.29% F.

Investigation of this reaction and its product will be continued as soon as more starting material is available.

Recently a series of reactions was begun to study the stability of I to hv irradiation and to Ag and $AgNO_3$. Although no conclusions are possible at this time, it can be said that $AgNO_3$ and Ag react slowly with I in the presence or absence of light to produce AgI. No new fluorocarbon products have been observed and quantitative studies are now underway to determine the extent of the reaction. When irradiated in the absence of solvent or other reagents, I liberates I_2 and clear, brittle crystals slowly separate from the liquid. Current efforts are being focused on identification of these crystals.

Part B: UV Catalyzed Reactions of I

1. Object To study the photochemical reactions of I with particular interest addrssed to coupling products.

2. Historical It is well known that the normal carbon-iodine bond is cleaved by UV irradiation to yield the respective carbon and iodine radicals. In normal alkyl iodides, wavelengths on the order of 3100A^0 or shorter are required to effect this cleavage. The products of such reactions can be predicted by examination of the probable fates of the radicals formed.

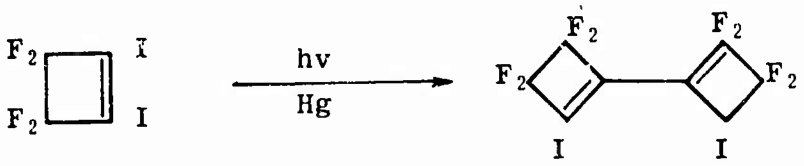
Haszeldine(31) has studied the UV absorption spectra of a number of halogen-containing alphatic iodo compounds and has correlated the broad absorption maximum in the 2500-3500A^0 region to structure. In particular, the presence of halogens in the β-position and the tertiary nature of the carbon to which iodine is attached will be expected to cause a distinct bathochromic shift and an increase in the extinction coefficient of the absorption. Conversely, the vinyl nature of the carboniodine bond will result in a dramatic shift to shorter wavelength. This is illustrated in studies by Park, Seffl, and Lacher(32) on $CF_2 = CFI$ vapor. They observed λ_{max} to occur at 2580A^0. This is nearly identical to ethyl iodide vapor have λ_{max} at 2580A^0 with an extinction coefficient of 310.

3. Results and Discussion Interest in photochemical reactions of I originated when it was observed that a freshly distilled sample discolored markedly on standing in a clear bottle exposed to sunlight. Samples turn pink within a few minutes and then rapidly progress to eep maroon or brown. A sample in a corked pyrex flask, however, showed no new peaks by GLC analysis after several days despite this discoloration. After one month, numerous clear colorless rhombic crystals separated from the liquid. There was insufficient sample for characterization beyond a melting point and infrared spectrum on the crude solid.

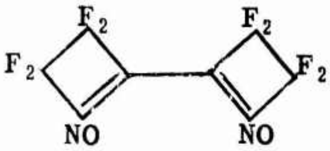
An ultraviolet spectrum of I was obtained in an effort to seek optimum conditions for photochemical reaction. The compound exhibits a broad absorption band with λ_{max} at 2400A^0 and ε =2080. The upper limit of the band occurs at 2970A^0 where zero absorbence is found.

The observed spectra is in good general agreement with that predicted for I. The somewhat large extinction coefficient explains the observed high light sensitivity. The sensitivity in Pyrex glassware, however, is not explained since Pyrex affords near zero transmittance below 3650A^0. It is hoped that this matter will soon be resolved.

Irradiation of I over mercury with a high intensity ultraviolet source gave interesting and unexpected results. Several products were evident by GLC analysis but only one, a solid, was isolated. This solid was purified and identified as 2,2'-diiodo-3,3,4,4,3',3',4',4'-octafluorobicyclobutene (IV).



Compound IV will be used to obtain the corresponding dinitrosoderivative. IV, however, does not agree either as to chemical or physical



properties with the solid obtained earlier by irradiation in a Pyrex vessel. This reaction over mercury is now being repeated in an effort to isolate more IV and to characterize the other products. The rate of the reaction with the different ultraviolet sources will also be studied in a crude effort to correlate reactivity to wavelength.

4. Experimental

Sunlight Irradiation of I.

In a 25-ml Pyrex erlenmeyer flask fitted with a cork was placed 0.2 ml of I having 4 percent diglyme as an impurity. The sample became pink within a few minutes. After 33 days the sample was deep pink and a few small crystals were evident in the liquid. The cork was badly stained with iodine. After 85 days the sample was largely converted to several clear colorless brittle rhombic crystals, mp 78-87°C. A poor IR in mineral oil on the crude crystals gave bands at 3500, 1700, 1150, and 770 cm^{-1}. There was insufficient sample for analysis or further characterization.

Preparation of 2,2'-diiodo-3,3,3',3',4,4,4',4'-octafluorobicyclobutene (IV). In a quartz U tube fitted with a condenser was placed 2.0 ml of Hg and 3.0 ml of I containing three percent diglyme impurity. The reaction vessel was suspended inside a Rayonet Photochemical Chamber Reactor equipped with four RPR-3500A° "black light" lamps and five RPR-2537A° clear lamps, at an average distance of two and one-half inches. Within the first few hours the liquid turned deep brown and I_2 crystals formed above the liquid. During succeeding days, the liquid level dropped slightly and bright mercuric iodide crystals developed. After 24 days numerous tan crystals were filtered from the mixture. They were recrystallized from CCl_4, and ethanol-water. Finally they were sublimed at 135-145° in a vacuum to yield 61 mg of white grainy crystals, mp 143-145°. The crystals turn pale yellow on standing. An IR (mineral oil) was obtained showing peaks at 1530, 1300, 1240, 1120, 820, and 760 cm^{-1}.

Anal. Calcd. for $C_8F_8I_2$: C, 19.1; F, 30.3; I, 50.5; H, 0.0.
Found: C, 18.85; F, 30.91; I, 50.02; H, 0.0.

Part C: Nitroso Derivatives of I

1. Object To prepare 1,2-dinitroso-3,3,4,4-tetrafluorocyclobutene (V).

2. Historical Perfluoroalkylnitroso compounds have been synthesized in several laboratories in recent years. They have been shown to form dimers and polymers with perhalo olefins(33,34,35). The polymers thus formed can be oils, waxes, or elastomers depending on the reactants used and the conditions of polymerization. The synthesis of V would make available an important and versatile new starting material for the development of such polymers.

Previous syntheses of perfluoroalkylnitroso compounds can be roughly divided into two categories. The first category makes use of perfluorocarboxylic acid derivatives. Haszeldine(36) was the first to react the silver salt of trifluoroacetic acid with nitrosyl chloride to obtain trifluoronitrosomethane in low yield. Rosser(37) extended this reaction to get good yields of perfluoronitrosoalkanes and isolated the intermediate perfluoroacyl nitrites. His work also shed some light on the nature of the Hunsdiecker reaction occuring during decarboxylation of the intermediate. This decarboxylation can occur with explosive violence if R_f contains less than three carbon atoms.

$$R_fCOOAg \xrightarrow{NOCl} R_fCOONO \xrightarrow{Heat} R_fNO + CO_2$$

The second general method of preparation of these nitroso derivatives employs the corresponding perfluoroalkylidodo compounds. Iodine in these compounds is replaced by NO in a photochemically induced free radical reaction in the presence of mercury to remove nitrogen dioxide and iodine(33,34). This method has been proved useful with compounds containing vinylic iodine(33) and thus seems most adaptable to the proposed synthesis.

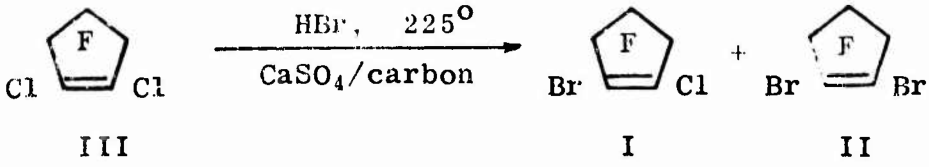
$$R_fI \xrightarrow[hv,\ Hg]{NO} R_fNO$$

Detailed experimental plans for the synthesis have not yet been worked out.

IX. Preparation of the Cyclopentenes

Two general synthetic methods were employed in the preparation of the halogenated cycloölefins.

The first involved a catalytic replacement of vinylic chlorine by bromine in the preparation of 1-bromo-2chlorohexafluorocyclopentene-1 (I) and 1,2-dibromohexafluorocyclopentene-1 (II) from the readily available 1,2-dichlorohexafluorocyclopentene-1 (III). This highly unusual reaction has little precedent in literature.

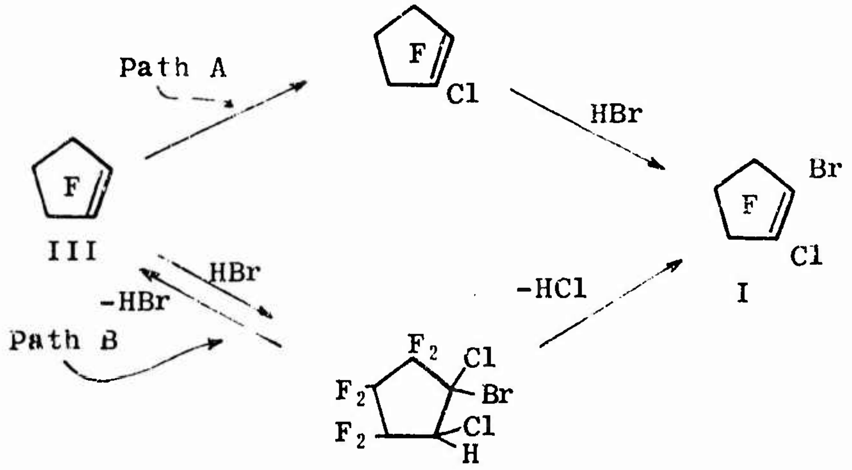


Sharrah(38) reported the addition of hydrogen bromide to chlorotrifluoroethylene ("Freon-1113") yielded 1-chloro-2-bromo-1,2,3-trifluoroethane. Subsequent work in this laboratory has shown that the formation of several more highly brominated products was rationalized by Park and McClure(39) in terms of the formation of vinylic free radicals derived from the initially formed addition product.

The only report of the addition of hydrogen bromide to a halocycloölefin was that of Sharrah who found that hydrogen bromide added to perfluorocyclobutene yielded 1-bromo-2-hydrohexafluorocyclobutane.

When this reaction was extended to 1,2-dichlorotetrafluorobutene (IV), only unreacted starting material and compounds identified as 1-bromo-2-chlorotetrafluorocyclobutene-1 and 1,2-dibromotetrafluorocyclobutene-1 were isolated under the reaction conditions employed. Similar vinylic substitution was observed with the analogous 1,2-dichlorohexafluorocyclopentene-1 (III). However, the yield was much higher, presumably due to the inherently greater stability of the cyclopentenyl ring to the reaction conditions.

Two mechanistic interpretations are apparent for this reaction.



Path A would involve the formation of a vinylic free radical followed by abstraction of bromine from HBr. A second, and more energetically feasible pathway, would require addition of hydrogen bromide to the olefin followed by loss of halogen halide to give either starting material (loss of HBr), or product (loss of HCl). Since an excess of hydrogen bromide was employed, the law of mass action would favor the formation of the product.

Under identical conditions, molecular bromine and (III) did not react.

Baranauckas and Carr(40) have recently reported the isolation of 1,2-dichlorohexafluorocyclopentene from the reaction of 1-chloroheptafluorocyclopentene-1 and hydrogen chloride, a reaction which may be similar in nature.

Halide Ion Attack

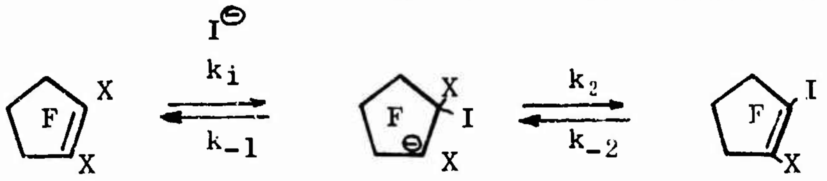
The concept of reversible carbanion formation in halocyclobutenes by halide ion attack was developed by Moore in this laboratory. No attempt will be made to cover the fine points inherent to this hypothesis other than to explain the source of some of the synthetic difficulties encountered.

In contrast to the cyclobutenes, acetone was found to be unsuitable as a solvent for halide attack on halocyclopentenes and halocyclohexenes. Either no reaction occured, or yields of products were low. However, the use of diglyme as a solvent was found to accelerate the conversion to the desired products. It is uncertain, at present, whether the use of diglyme as a solvent favorably alters the equilibrium between reactants and products, or merely serves to kinetically accelerate the reaction because of the higher reaction temperature obtainable with this solvent. Preliminary finds indicate both factors may be involved in the effectiveness of diglyme as a solvent in these reactions.*

The chief difficulty inherent in the use of this solvent is in the separation of the halocyclobutene from the diglyme. In several instances, the boiling point of solvent and product are almost identical and combined distillation and aqueous extractions were necessary to isolate a relatively pure product.

Although not actively investigated, the use of similar solvents with somewhat different boiling points, in such cases, would probably be advantageous.

Moore(41) reported the isolation of 1-chloro-2-idotetrafluorocyclobutene-1 and 1,2-diiodotetrafluorocyclobutene-1 from the reaction of potassium iodide and 1,2-dichlorotetrafluorocyclobutene-1. Unfortunately, the cyclopentenes are not as receptive toward attack by the iodide ion. This was circumvented by employing a starting material with a vinylic halogen more similar in "leaving group ability" to the iodide ion. That is, if $k_{-1} \gg k_2$ for X=Cl, little conversion to the monoiodo-compound would be expected and even less to the diiodo-compound. If the magnitude of k_{-1} and k_2 are more nearly equal when X=Br, the increased conversion to the iodo-compounds should be affected. Use of 1,2-dibromohexafluorocyclopentene-1 (II) afforded the bromo-, iodo- and diiodo-products in appreciable yields. When large-scale preparative runs were initiated, minor amounts of unidentified higher boiling compounds were also detected. The identity and source of these compounds are not known at present. Although the bromochloro- and dibromohexafluorocyclopentenes could also be synthesized through this method using lithium bromide in diglyme, the hydrogen bromide addition-elimination reaction was preferred because of its high yield, freedom from side reactions, and ease of work-up.



3. Experimental Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were taken using a Perkin-Elmer Infracord. NMR spectra were obtained using a Varian A-60 analytical spectrometer and pure liquid samples with tetramethylsilane as an internal reference except where otherwise indicated.

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* These findings have recently been verified by Dr. G.G.I. Moore(41) who, working independently, has arrived at very similar results.

Preparation of 1-bromo-2-chlorohexafluorocyclopentene-1 (I) and 1,2-dibromohexafluorocyclopentene-1 (II). The reaction was carried out by passing a mixture of the olefin and hydrogen bromide through a 1--cm x 2.5-cm Pyrex glass tube packed with a 25/75 $BaSO_4$/activated carbon catalyst heated to ca. 225°C. The catalyst was prepared in the manner described by Sharrah. In a typical run, 500 gm (2.04 moles) of 1,2-dichlorohexafluorocyclopentene-1 (X) was swept through the tube with about 3.7 molar excess of hydrogen bromide. The crude reaction products were washed with an aqueous sodium bicarbonate solution and twice with 50 ml portions of ice water. The aqueous layers were extracted with two 25 ml portions of diethyl ether and the combined organic layer and ether extracts dried over anhydrous magnesium sulfate. Fractional distillation yielded 275 gm of unreacted X; 128 gm (22% of theory) of 1-bromo-2-chlorohexafluorocyclopentene-1 (I); bp, 101°C/629 mm; d_4^{28}=1.92; n_D^{25}= 1.3890.

Anal. Calculated for C_5ClBrF_6: C, 20.82; Cl, 12.30; Br, 27.71; F, 39.52. Found: C, 20.60; Cl, 12.36; Br, 27.44; F, 39.21 and 106 gm (16% of theory) of 1,2-dibromohexafluorocyclopentene-1 (V); bp 119°/629mm; d_4^{28}= 2.17; n_D^{25} = 1.4114.

Anal. Calculated for $C_5Br_2F_6$: C, 17.98; Br, 47.87; F, 34.14. Found: C, 17.95; Br, 47.63; F, 34.02.

The infrared spectra of I and II contained sharp absorption in the olefinic stretching region at 1610 cm^{-1} and 1605 cm^{-1}, respectively.

Preparation of 1-chloro-2-iodohexafluorocyclopentene-1 (V).
1. A mixture of 70 gm (0.271 mole) of 1,2-dichlorohexafluorocyclopentene-1 (III), 112 gm (0.677 moles) of potassium iodide, and 125 ml of diglyme was refluxed for 14 days to give a highly discolored solution containing diglyme, unreacted III, 1-chloro-2-iodohexafluorocyclopentene-1 (V) and traces of several unidentified materials. Fractional distillation yielded 54.6 gm of 1,2-dichlorohexafluorocyclopentene-1 (III) and 6.8 gm of crude 1-chloro-2-iodohexafluorocyclopentene-1 (V) (7.4% of theory). Removal of the 5 percent diglyme impurity on F. S. 1265 (125) gave pure V, a colorless liquid, bp 128°C/628 mm; d_4^{28}= 2.13; n_D^{28} = 1.4268.

Anal. Calculated for C_5ClF_6I: C, 17.85; Cl, 10.55; F, 33.88; I, 37.72. Found: C, 1890; 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 gm (0.[illegible]2 moles) of 1-bromo-2-chlorohexafluorocyclopentene-1 (I), 50 gm (0.301 moles) of potassium iodide, and 75 ml of diglyme were refluxed for 14 days. Distillation yielded 14.1 gm of unreacted I and 7.3 gm (22% of theory) of slightly impure VI.

Preparation of 1-bromo-2-iodohexafluorocyclopentene-1 (VI) and 1,2-diiodohexafluorocyclopentene-1 (VII). A mixture of 9.8 gm of 1,2-dibromohexafluorocyclopentene-1 (II), 18.2 gm of anhydrous potassium iodide, and 50 ml of diglyme were refluxed for three days. Addition of water forced out 11.3 gm of organic product. Extraction of the aqueous layer with methylene chloride and distillation of the combined organic layers gave 3.1 gm unreacted II, 4.6 gm of 1-bromo-2-iodohexafluorocyclopentene-1 (VI) and 3.8 gm of crude 1,2-diiodohexafluorocyclopentene-1 (VIII).

1-Bromo-2-iodohexafluorocyclopentene-1 (VI), bp 142°C/628 mm; n_D^{28} = 1.4488.

Anal. Calculated 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 VI contained a sharp absorption at 1590 cm^{-1} corresponding to the (>C = C<) stretching frequency.

1,2-Diiodohexafluorocyclopentene-1 (VIII), bp 172°C/631 mm; d_4^{20} = 2.50; n_D^{28}= 1.4848.

Anal. Calculated 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 VIII contained a sharp absorption at 1560 cm^{-1} corresponding to the (>C = C<) stretching frequency.

Reaction of 1,2-dichlorohexafluorocyclopentene-1 (III) with Ethanolic Potassium Hydroxide. In a 25-ml, 3-neck, round-bottom flask, fitted with condenser, pressure equalizing addition funnel, and magnetic stir-bar, was placed 10.0 gm (0.0366 mole) of 1,2-dichlorohexafluorocyclopentene-1 (X) in 10 ml of absolute ethanol. After cooling of 0°C, 2.24 gm (0.040 mole) of potassium hydroxide in 10 ml of absolute thanol were added dropwise with rapid stirring. After addition of the KOH/EtOH solution, the reaction mixture was stirred for an additional two hours 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 methylene chloride. The organic layer and methylene chloride extracts were combined and dried over anhydrous magnesium sulfate. Fractional distillation yielded 8.1 gm of 1-chloro-2-ethoxyhexafluorocyclopentene-1 (IX). Found: bp 137°C/628 mm; n_D^{28} = 1.3754. Reported: bp 143-144°C/750 mm; n_D^{20} = 1.3774.

Reaction of 1,2-dibromohexafluorocyclopentene-1 (II) with Ethanolic Potassium Hydroxide. In a 25-ml, 3-neck, round-bottom flask, fitted with condenser, an addition funnel, and magnetic stir-bar, there was placed 5.0 gm (0.144 mole) of 1,2-dibromohexafluorocyclopentene-1 (XI) in 5 ml of absolute ethanol. After cooling to 0°C, 0.84 gm (0.015 mole) of potassium hydroxide in 3.0 ml of absolute thanol were added dropwise with constant stirring. The reaction mixture was stirred for an additional two hours at room temperature. Distillation yielded 3.8 gm of crude bromoether. Pure 1-bromo-2-ethoxyhexafluorocyclopentene-1 (X) was isolated via G.L.C. (10' FS 1265 at 140°C); b.p. 150°C/629 mm; $d_4^{28} = 1.72$; $n_D^{28} = 1.3958$.

Anal. Calculated 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 X contained a sharp absorption at 1655 cm^{-1} corresponding to the ($>C = C<$) stretching frequency.

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

Reaction of 1,2-diiodohexafluorocyclopentene-1 (VIII) with Ethanolic Potassium Hydroxide. In a 25-ml, 3-neck, round-bottom flask, fitted with dropping funnel, condenser and magnetic stir-bar, there was placed 1.5 gm (0.0034 mole) of 1,2-diiodohexafluorocyclopentene-1 (VIII) in 2 ml of ethanol. After cooling to 0°C, 0.20 gm (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 two hours at room temperature. Work-up in the previously described manner for an alkoxide reaction (see compound IX) yielded 1.1 gm of crude 1-iodo-2-ethoxyhexafluorocyclopentene-1 (XI). Pure XI was isolated via preparative scale G.L.C. (18 foot x 1/4 inch Ucon 550X at 150°C); b.p. 172.5°C/268 mm; $d_4^{28} = 1.78$; $n_D^{28} = 1.4371$.

Anal. Calculated 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 V contained a ($>C = C<$) absorption at 1635 cm^{-1}.

The proton NMR spectrum of XI contained a quartet at 5.43 τ with J = 7.1 c.p.s. and a triplet at 8.53 τ with J = 7.1 c.p.s. corresponding to the methylene and methyl protons of a vinylic ethoxy group.

X. Preparation of the Derivatives of α,ω-bis (1,1,2-trifluoro-2-chlorethoxy) Alkanes

1. <u>Historical Background</u> Abramo(42) has added trimethylene glycol to chlorotrifluoroethylene to obtain an azeotropic mixture of 3-(1,1,2-trifluoro-2-chloroethoxy) propanol and 1,3-bis (1,1,2-trifluoro-2-chloroethoxy) propane (I). Few other additions of glycols to polyfluorohaloethylenes have been carried out.(43)

Chlorination studies of compound I above with or without a solvent results in hard-to-separate mixtures of the mono-, the di- and more highly chlorinated products. The NMR spectra of the first two compounds, separated by V.P.C., show that the first two new chlorine atoms are attached to the two α-positions on the propane chain. Dehydrochlorination of these chlorinated products, run on the mixture, was quite difficult. It was hoped that this procedure would yield unsaturated glycol ethers which could prove useful in further polymerization studies.

2. <u>Experimental</u>: <u>Chlorination of bis-(1,1,2-trifluoro-2-chloroethoxy) propane.</u>

This was carried out by passing Cl_2 gas through a solution of the fluorinated ether in the presence of ultraviolet light. This resulted in a mixture of monochlorinated and more highly chlorinated products which could only be separated by V.P.C.

The mixture obtained from these chlorinations was treated with potassium hydroxide in mineral oil and stirred at 40° overnight. No dehydrohalogenation occured as shown by IR. Next, KOH in refluxing isopropanol was tried with the same results. (There was a very small peak in the carbon-carbon double bond region of the IR). KOH in refluxing n-butanol was tried next. IR indicated some olefin was produced. Sixty grams (.175 moles) of the chlorinated propane diether were treated with .2 moles of KOH in 110 ml of absolute alcohol at reflux for 10 hours. The V.P.C. chart of the liquid, after removal of the ethanol and inorganic compounds, showed no reaction had taken place. This liquid was refluxed with <u>n</u>-butanol and KOH for six hours, resulting in a mixture which showed slight carbon-carbon double bond absorption in the IR. V.P.C. showed a small amount of a new compound.

Thirty-four grams of the chloro-diether was heated to about 180°C (the liquid was turning brown) and KOH in n-butanol added dropwise. The mixture was refluxed vigorously for 24 hours. V.P.C. showed a new compound and the double bond absorption in the IR was stronger than before. Evidently it takes quite vigorous conditions to pull out HCl when the chlorine is <u>alpha</u> to the ether linkage. Treatment of the chloro-diether with sodium ethoxide in ethy alcohol gave a mixture of about 10 compounds whose IR spectrum showed absorption at 3030 cm^{-1} which was probably olefinic C-H stretching, in addition to several absorptions in the double bond region.

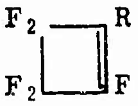
The preparations of β-(1,1,2-trifluoro-2-chloroethoxy) ethanol and 1,2-bis(1,1,2-trifluoro-2-chloroethoxy) ethane (A) were accomplished using the method of Park and Abramo.(42) The best yield of diether was obtained by using an excess of trifluorochloroethylene and a temperature of about 75°. Fifty-six grams (1 mole) of KOH were dissolved in 125g. (2 moles) ethylene glycol and this solution put into a 500 ml bomb with one ml of limonene. The bomb was cooled in a dry ice-acetone bath and 400g. (3.5 moles) of $CF_2=CFCl$ were pressured in. The mixture was rocked at 75° for 48 hours. Distillation of the products of two of these reactions resulted in 98g. of an azeotropic mixture of the ether-alcohol anddiether, containing 74 percent and 26 percent of each, respectively, and 110g. of the diether. These fractions distilled at 50°-$53^{\circ}C$ and 59°-$61^{\circ}C$ at 1 mm. respectively.

When $CF_2=CFCl$ was bubbled through a solution of 56g. of KOH in 125g. of theylene glycol warmed with an infrared lamp for 48 hours, no ether product resulted.

When chlorination of A was carried out, by bubbling chlorine through the pure liquid in the presence of ultraviolet light, until only 5-10 percent of the starting material was left, the product contained only about 10 percent dichlorinated diether. NMR showed the chlorine atoms to be on the two alpha-positions of the ethane chain.

Dehydrochlorination of this chloro-diether was easier than that of the propane homologue. Thirty-three grams (.1 mole) of the chloro-diether was heated to about $120^{\circ}C$ and a solution of 10g. of KOH in 50 ml. of absolute alcohol was added. This was refluxed for 24 hours and then 10g. more of KOH were added and refluxing continued for 24 hours more. The V.P.C. chart of the product showed about equal amounts of two new compounds, probably the cis and trans isomers, and only a little of the chloro-diether left. The IR spectrum showed a weak absorption at 1700 cm^{-1} and a very weak, sharp peak at 3180 cm^{-1} which could be olefinic C-H stretching. These haven't been separated yet.

Object of Investigation Synthesis of mono-and dialkyl cyclobutenes by use of the Grignard reaction on perfluoro cyclobutenes to obtain compounds of the types:



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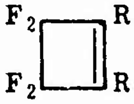
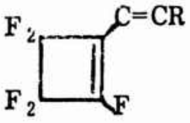


From these compounds, it is hoped to obtain compounds of the following type:



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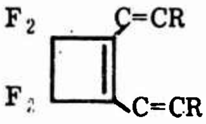


Experimental:

In the following reactions, the apparatus consisted of a 0.5-liter, three-neck flask fitted with an equalizing funnel, a stirrer, and a Friedrick condenser. The condenser was connected through a bubbler to a 2-liter, three-neck flask fitted with a stirrer and a dry-ice cooled condenser. To this was connected a second bubbler and a dry-ice cooled trap. The entire system is swept with dry nitrogen.

1,2-Di-n-butyl-3,3,4,4-tetrafluorocyclobutene and 1-n-butyl-2,3,3,4,4-pentafluorocyclobutene. A tetrahydrofuran solution, 500 ml of 2.2 molar n-butyl magnesium bromide was prepared and cooled in ice. In another set-up, 116 grams (0.5 moles) of 1,2-di-chloro-1,2,3,3,4,4-hexafluorocyclobutane was added to a heated solution of 37 grams (0.6 moles) of zinc in 150 ml of n-butyl alcohol to give a slow evolution and addition of perfluorocyclobutene to the Grignard. After addition was complete, the Grignard solution was refluxed slowly for five hours and then stirred at 25°C for 12 hours. The remaining Grignard reagent was destroyed by dilute hydrochloric acid and then extracted with THF. After drying with anhydrous magnesium sulfate, distillation gave: 29 gms (0.2 moles, 40% of theory) of 1-n-butyl-2,3,3,4,4-pentafluorocyclobutene, b.p. 106.5 - 108°/628 mm., n_D^{25}=1.3538, d^{24}=1.15(44) b.p.= 112°/760 mm.

Anal. Calcd. for $C_8H_9F_5$: C, 48.00; H, 4.50; F, 47.50; found C, 48.22; H, 4.48; F, 47.20.

About 65 gms (0.27 moles, 54% of theory) of 1,2-di-n-butyl-3,3,4,4-tetrafluorocyclobutene, b.p. = 198.5 - 199°/626 mm., n_D^{25}= 1.4130, d^{24} = 1.03(44), b.p. = 110°/20 mm.

Anal. Calcd. for $C_{12}H_{18}F_4$; C, 58.07; H, 7.27; F, 30.66; found C, 60.62; H, 7.63; F, 31.99.

Also, an impurity, thought to be n-octane, was isolated, (identical with IR of authentic sample), b.p. = 116.5 - 117°/634 mm.

1,2-Di-isobutyl-3,3,4,4-tetrafluorocyclobutene and 1-isobutyl-2,3,3,4,4-pentafluorocyclobutene. A 2.2 molar tetrahydrofuran solution, 500 ml, of isobutyl magnesium bromide was prepared and cooled in ice. Perfluorocyclobutene, prepared by the slow addition of 116 gms (0.5 moles) of 1113 dimer to a heated solution of 37 gms (0.6 moles) of An in n-butyl alcohol, was passed into the Grignard solution. After addition, the Grignard was reluxed slowly for three hours and then stirred for 10 hours at room temperature.

After destroying the remaining Grignard reagent with dilute hydrochloric acid, extracting with THF, and drying with anhydrous magnesium sulfate, distillation gave: 44 gms (o.42 moles, 94 % of theory) of 1-isobutyl-2,3,3,4,4-pentafluoro cyclobutene, b.p. = 101-101.5°/630 mm., n_D^{26}=1.3509, d^{26}= 1.19 gm/ml.

Anal. Calcd. for $C_8H_9F_5$: C, 48.00; H, 4.50; F, 47.50; found: C, 47.81; H, 4.57; F, 47.46.

Ten gms (0.04 moles, 8% of theory) of 1,2-di-isobutyl-3,3,4,4-tetra-flurocyclobutene, b.p. 187.5 - 188.5°/630 mm., n_D^{26}=1.3983, d^{26} = 1.08 gm/ml.

Anal. Calcd. for $C_{12}H_{18}F_4$: C, 58.07; H, 7.27; F, 30.66; found C, 60.72; H, 7.68; F, 32.21.

Also isolated was an impurity, 2,5-dimethyl hexane (identical with authentic IR), b.p. = 95°/624 mm.

1-Sec-butyl-2,3,3,4,4-pentafluorocyclobutene. After preparing 500 ml of a 2.2 molar sec-butyl magnesium bromide solution in tetrahydrofuran and cooling in ice, perfluorocyclobutene was slowly introduced. The cyclobutene was prepared by slowly adding 116 gms (0.5 moles) of 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutene to a heated mixture of 37 gms (0.6 moles) of zinc in n-butyl alcohol. After addition was complete, the Grignard solution was refluxed slowly for four hours, then at 25°C for 12 hours.

Dilute hydrochloric acid was used to destroy the remaining Grignard. After extraction with THF and drying with anhydrous magnesium sulfate, distillation gave: 24 gms (0.12 moles, 24% of theory) of 1-sec-butyl-2,3,3,4,4-pentafluorocyclobutene, b.p. = 97.5 - 99.5°/624 mm., n_D^{25}=1.3522, d^{25}=1.17 gm/ml.

Anal. Calcd. for $C_8H_9F_5$: C, 48.00; H, 4.50; F, 47.50; found: C, 47.96; H, 4.66; F, 47.26.

Also isolated was 3,4-dimethyl hexane (identical with authentic IR) b.p. = 106.5 - 107°/626 mm.

1-Isobutyl-2,3,3,4,4-pentafluorocyclobutene. A tetrahydrofuran solution, 500 ml of 2.2 molar isobutyl magnesium bromide was prepared and cooled in ice. Perfluorocyclobutene was slowly bled in from the slow addition of 116 gms (0.5 moles) of 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutene to a heated solution of 37 gms (0.6 moles) of zinc in n-butyl alcohol. After completion of the addition, the reaction mixture was refluxed for four hours, then held at 25°C for 10 hours.

The reaction product was worked up by destroying the excess Grignard reagent with dilute hydrochloric acid and extracting with THF. Anhydrous magnesium sulfate was used to dry the solution, after which distillation gave: 8.8 gms (0.05 moles, 10% of theory) of 1-isobutyl-2,3,3,4,4-pentafluorocyclobutene, b.p. = 77 - 79°/623 mm., n_D^{25}= 1.3433, d^{26}= 1.19 gm/ml.

Anal. Calcd. for $C_7H_7F_5$: C, 48.00; H, 4.50; F, 47.50; found: C, 47.81; H, 4.57; F, 47.46.

1-Isopropyl-2,3,3,4,4-pentafluorocyclobutene. After preparing 500 ml of a 1.4 molar isopropyl magnesium bromide solution in tetrahydrofuran and cooling in ice, perfluorocyclobutene (prepared by slowly adding 116 grams (0.5 moles) of 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutene to a heated mixture of 37 grams (0.6 moles) of Zn in n-butyl alcohol) was slowly introduced. The Grignard solution was reluxed for three hours after addition was complete and then stirred at 25°C for an additional 12 hours.

The remaining Grignard was destroyed with dilute hydrochloric acid and extracted with THF. After drying over anhydrous magnesium sulfate, distillation gave: 8.8 grams (0.05 moles, 10% of theory) of 1-isopropyl-2,3,3,4,4-pentafluorocyclobutene, b. p. = 77-79°/623 mm., n_D^{25} = 1.3433, d^{26} = 1.19 gm/ml.

Anal. Calcd. for $C_7H_7F_5$: C, 45.16; H, 3.72; F, 50.53; found: C, 45.46; H, 3.94; F, 50.74.

1,2-Di-isopropyl-3,3,4,4-tetrafluorocyclobutene. A 3.3 molar isopropyl magnesium chloride, 325 ml, in tetrahydrofuran solution was cooled in ice and perfluorocyclobutene, prepared from 116 gms (0.5 moles) of 113 dimer and 37 gms (0.6 mole) of zinc in n-butyl alcohol, introduced slowly. The solution was heated five hours at reflux and then stirred for 12 hours at 25°C.

Workup and distillation gave: 11 grams (0.05 moles, 10% of theory) of 1,2-di-isopropyl-3,3,4,4-tetrafluorocyclobutene, b.p.= 155 - 156°/622 mm., n_D^{26}= 1.3892, d^{25} = 1.05 gm/ml.

Anal. Calcd. for $C_{10}H_{14}F_4$: C, 57.37; H, 6.67; F, 36.19; found: C, 57.06; H, 6.75; F, 35.97.

1,2-Dimethyl-3,3,4,4-tetrafluorocyclobutene. In tetrahydrofuran, 800 ml of 2.4 molar methyl magnesium chloride was cooled in ice and cyclobutene slowly introduced. The cyclobutene was prepared by slowly adding 232 grams (1 mole) of 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutene to 72 grams (1.1 mole) of zinc in n-butyl alcohol. The solution was then heated to reflux for nine hours and finally stirred at 25°C for 10 hours.

After workup as usual, distillation gave: 32 grams (0.21 moles, 21% of theory) of 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene, b.p. = 98-98.5°/626 mm., n_D^{26}= 1.3475, d^{25} = 1.16 gm/ml(44) b.p. = 100 - 104°/760 mm. $n_D^{27.5}$ = 1.3478. (1) b.p. = 104°/760.(45)

Anal. Calcd. for $C_6H_6F_4$: C, 46.75; H, 3.90; F, 49.35; found: C, 47.02; H, 3.99; F, 49.21.

1-n-Propyl-2-isopropyl-3,3,4,4-tetrafluorocyclobutene. 1-n-Propyl-2,3,3,4,4-perfluorocyclobutene, 39 grams (0.21 moles) was added to a chilled solution of 200 ml of a 2 molar isopropyl magnesium chloride solution in tetrahydrofuran. After heating at reflux for five hours, and stirring at 25°C for 16 hours, the solution was worked up as usual and upon distillation yielded 41 grams (0.20 moles, 98% of theory) of 1-n-propyl-2-isopropyl-3,4,4-tetrafluorocyclobutene, b.p. = 158.5-160°/622 mm., n_D^{26} = 1.3894, d^{25} = 1.06 gm/ml.

Anal. Calcd. for $C_{10}H_{14}F_4$: C, 57.35; H, 6.67; F, 36.19; found: C, 56.98; H, 6.68; F, 36.25.

1-Ethyl-2-isopropyl-3,3,4,4-tetrafluorocyclobutene. To a 167 ml of a 1.8 molar isopropyl magnesium bromide solution in tetrahydrofuran was added 25 grams of 1-ethyl-2,3,3,4,4-pentafluorocyclobutene (0.15 moles). Then the solution was heated at reflux for five hours, and stirred at 25°C for 13 hours.

After workup, distillation gave: 12 grams (0.06 moles, 40% of theory) of 1-ethyl-2-isopropyl-3,3,4,4-tetrafluorocyclobutene, b.p. = 144-145°/622 mm., n_D^{26} = 1.3831, d^{25} = 1.08 gm/ml.

1-Ethyl-2-sec-butyl-3,3,4,4-tetrafluorocyclobutene. 1-Ethyl-2,3,3,4,4-pentafluorocyclobutene, 25 grams (0.15 moles), was added to a chilled solution of 167 ml of 1.8 molar sec-butyl magnesium bromide in tetrahydrofuran. Then the solution was heated for five hours at reflux and for 12 hours at 25°C. After workup as usual, distillation gave: 6 grams (0.03 moles, 20% of theory) of 1-ethyl-2-sec-butyl-3,3,4,4-tetrafluorocyclobutene, b.p. = 163-164°/627 mm., n_D^{25} = 1.3898, d^{25} = 1.04 gm/ml.

Anal. Calcd. for $C_{10}H_{14}F_4$: C, 57.35; H, 6.67; F, 36.19; found: C, 57.05; H, 6.89; F, 36.35.

1-Methyl-2-isopropyl-3,3,4,4-tetrafluorocyclobutene. To 100 ml of a 2.0 molar tetrahydrofuran solution of isopropyl magnesium chloride was added eight grams (0.05 moles) of 1-methyl-2,3,3,4,4-pentafluorocyclobutene. The solution was then heated for four hours at reflux, kept at room temperature for 13 hours and worked up as previously described. Separation by g.l.c. on a UCONNcolumn gave: 0.5 grams (0.003 moles, 4% of theory) of 1-methyl-2-isopropyl-3,3,4,4-tetrafluorocyclobutene, b.p. = 129.5-130°/629 mm., n_D^{25} = 1.3716, d^{25} = 1.11 gm/ml.

XI. SYNTHESIS OF HYDROGEN CONTAINING FLUOROÖLEFINS

1. Object of Investigation

The primary object of this investigation was to study a series of two and three carbon fluoroölefins of the general formula, RXC=CYZ (where $R=CF_3-$, F
X=F, Cl, Br, I, H
Y=F, Cl, Br, I, H
Z=F, Cl, Br, I, H were Y and Z are never both H or both F at the same time) under varying hydrogenation conditions in a flow system with resulting substitution of X, Y, Z (except F and H) by H without saturation of the double bond.

The secondary object was to determine if this is an addition-elimination reaction or an abstraction-substitution reaction.

2. Discussion

The study has been expanded (although not exhaustively) since the previous research report and probes into the reaction mechanism have been attempted.

The new catalyst, which was reported in the previous research report, was experimentally examined and found to work very satisfactorily. Since the new catalyst is granular, the problem of the catalyst drifting has been eliminated and reproducible results are now possible.

$CH_2=CHCl$ and $CF_2=CFBr$ were selected to test the newly prepared catalyst, since they are readily available, and were known to give relatively good conversion to product, $CF_2=CFH$. The reactions were run under similar conditions as previously reported and data correlations made. The new catalyst system gave at least comparable yields and conversions to the old system and was thus employed for the remainder of the experimental sequence.

To date, the olefins studied now include $CF_2=CFCl$, $CF_2=CFBr$, $CF_2=CCl_2$, $CF_2=CHCl$, $CF_2=CH_2$, $CH_2=CHCl$, and  the results of these studies will be discussed individually.

Since $CF_2=CFCl$ and $CF_2=CFBr$ were converted to an olefin containing one hydrogen, with fluorine seemingly irreplaceable under reaction conditions, an olefin containing two halogen atoms other than fluorine was studied to see the effect of geminal halogens under hydrogenation conditions. Thus, when $CF_2=CCl_2$ was subjected to reaction conditions, the expected product, $CF_2=CHCl$ was found, but, in only 31 percent yield, and the somewhat unexpected olefin, resulting from replacement of two geminal chlorines, $CF_2=CH_2$ was found in 69 percent yield.

Since $CF_2=CHCl$ was found in the reaction mixture, it appeared quite possible that the $CF_2=CH_2$ resulted from initial conversion to $CF_2=CHCl$ which then underwent further reaction to give the final product. Attempts were made to find reaction conditions under which only one of the olefins was formed and which would shed some light into the reaction mechanism, i.e., whether conversion to $CF_2=CH_2$ is a one or two-step process. The reactions studied are summarized in the following table:

Starting Material	Run No.	T°C	Flow Rate(cc/min) C=C	Flow Rate(cc/min) H_2	%Product $CF_2=CH_2$	%Product $CF_2=CHCl$
$CF_2=CCl_2$ (1112A)	8	200→250(a)	75	110	69	31
1112A	9	200→250	75	110	87	13
1112A	10	152→159	82	115	90	10
1112A	11	272→285	150	100	70	30
1112A	12	310	125	93	66	34
1112A	13	410	120	100	60	40
1112A	17	170	100	1500	65	35

(a) Arrow indicates exotherm to highest temperature during reaction.

From these runs, it appeared that the % conversion to the two products was essentially independent of temperature when above 150°, but favoring formation of $CF_2=CH_2$, (runs 8-13), and possibly dependent on the ratio of olefin to H_2 (runs 11-13).

A series of reactions was conducted at temperatures below 100°C in an attempt to get formation of $CF_2=CHCl$ since, as noted above, high T appeared to cause preferential formation of $CF_2=CH_2$. These reactions are summarized in the following table:

Starting Material	Run No.	T°C	Flow Rate(cc/min) C=C	Flow Rate(cc/min) H_2	%Product $CF_2=CH_2$	%Product $CF_2=CHCl$
$CF_2=CCl_2$, 1112A	15	50→80(a)	100	100	49	51
1112A	16	50→60	100	750	25	75
1112A	18	60	20	500	20	80

The above data indicate that conversion to $CF_2=CHCl$ is again not wholly temperature-dependent but appears quite dependent on the olefin /H_2 ratio. More important is that at lower temperatures, increasing the ratio of H_2/ olefin causes preferential formation of $CF_2=CHCl$ which is the reversal of that observed when compared to this same ratio at higher temperatures and somewhat contrary to what one might expect, i.e., more hydrogen should favor CF_2-CH_2 formation. This seemingly indicates that different reaction mechanisms are operating at various temperatures and it would seem, almost impossible to be able to distinguish between them. I feel it is safe to say that this reaction is not proceeding via radical mechanism at low temperatures since at these temperatures it seems quite unreasonable that one could generate molecular hydrogen or break a C-X bond. One might be tempted to postulate complex formation of X with the Pd at low temperatures in light of the above data. To show that Pd is somehow entering into the reaction mechanism, $CF_2=CCl_2$ was subjected to the same reaction conditions with Pd being absent. GLC showed only starting material recovered. It is noteworthy that under all the reaction conditions employed, there was never any evidence for a saturated product being formed.

Since $CF_2=CHCl$ was being formed as a reaction product, and since it also has a hydrogen on the carbon bearing the replaceable chlorine (the effects of hydrogen substitution being unknown), this olefin was also subjected to hydrogenation conditions. Its reactions are summarized below:

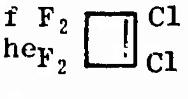
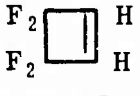
Starting Material	Run No.	T°C	Flow Rate(cc/min)		%Product	
			C=C	H_2	CF_2=CH_2	CF_2=CHCl
CF_2=CHCl	19	53	100	100	0	100
CF_2=CHCl	20	163→187	100	100	40	60
CF_2=CHCl	21	60	100	100	0	0

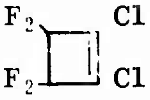
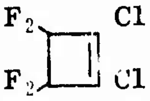
These data are very interesting. Whereas CF_2=CHCl can be formed from CF_2=CCl_2 at 60°C, at this same temperature, it itself is highly unreactive. Thus, the presence of a single H on a C bearing halogen grossly affects the reactivity of the olefin and possibly lends some credence to the formation of CF_2=CHCl as an intermediate.

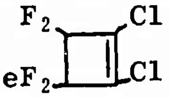
Run 20 in the above table does show that CF_2=CHCl can be converted to CF_2=CH_2 but that this is also accompanied by saturation. It will be recalled that in the conversion of CF_2=CCl_2 to products no saturation was observed. This further supports the hypothesis that CF_2=CHCl is not an intermediate in $CF_2=CCl_2 \rightarrow CF_2=CH_2$.

Since CF_2=CHCl showed some tendency to saturate, CF_2=CH_2 was subjected to hydrogenation conditions, i.e., $T^{o}=170^{o}$, H_2 and C=C flow 100 cc/min, expecting a higher degree of saturation. The only product isolated from the reaction mixture was the saturated product CF_2HCH_3. This was the expected product since previous reactions have shown the reluctance of HF elimination.

A literature search showed that replacement of a vinylic halogen by a hydrogen without saturation of the double bond was not unique to fluoroölefins. To show this to be the case, CF_2=CHCl was subjected to hydrogenation conditions, i.e., $T=195^{o}$, H_2 and C=C flow at 100 cc/min. The reaction mixture was very messy compared to the fluoroölefins, as it contained nine components, all in approximately equal yield. Out of this mixture was isolated some CH_2=CH_2; the remainder of the reaction products were not identified. In light of the large number of products formed, this type of reaction does not appear very applicable to hydro-carbons, which is in direct contrast to the fluoroölefins studied.

The hydrogenation of  to give  seemed very interesting since the dihydro compound is now obtained in low yields by a very tedious process. For this process to be feasible, conversion to either the mono- or dihydro derivative would have to be almost quantitative since separation of these compounds by conventional techniques is not possible. Experimental results of this reaction are listed in the following table:

Starting Material	Run No.	T°C	Flow Rate (cc/min)		%Product	
			C=C	H_2	$CF_2=CH_2$	$CF_2=CHCl$
	25	233	60	60	50	50
	26	233	120	60	70	30

As seen from the table, the desired conversion was not obtained. Due to the higher boiling point of , which makes it difficult to handle in a gaseous flow system, plus its high cost, it appeared unreasonable to conduct studies to find optimum conditions for the desired quantitative conversion. A model for this compound would be CFCl=CFCl for which the starting material is now available. This system will be studied and optimal conditions for its conversion to either CHF=CHF or CFCl=CHF transferred to the cyclic system.

Since a radical mechanism is a possibility, the reaction of a fluoroölefin in the absence of H_2 should give products from the radicals formed. This was attempted with two olefins, $CF_2=CCl_2$ and $CF_2=CFCl$. $CF_2=CCl_2$ was a poor choice since the overall conversion to all products was only 3 percent. Thus, when the reaction products were examined by GLC, only very small peaks were found to elute, but the presence of compound formation supports the possibility of a mechanism involving radicals.

The reaction of $CF_2=CFCl$ was much more informative. Reaction conditions were 200°C and flow of 100 cc/min. The reaction was run for 15 minutes. A GLC of the reaction products showed the presence of six peaks with one peak accounting for 95 percent of all products. This peak was isolated and found to be $CF_2=CCl_2$. This would only arise from a radical disproportionation reaction as follows:

$$(1)\quad CF_2=CFCl \xrightarrow{\Delta} CF_2=CF\cdot + Cl\cdot$$

$$(2)\quad CF_2=CF\cdot + CF_2=CFCl \longrightarrow CF_2=CF_2 + CF_2=CCl\cdot$$

$$(3)\quad CF_2=CCl\cdot + CF_2=CFCl \longrightarrow CF_2=CCl_2 + CF_2=CF\cdot$$

(2), (3), (2), (3), ...

An attempt to isolate $CF_2=CF_2$ from the reaction products failed. This is not too surprising since $CF_2=CF_2$ would be expected to be very reactive under these conditions and could very easily be converted to Teflon which would not come out of the reaction vessel.

This reaction will have to be repeated and the reaction vessel purged at high temperature with M_2 to see if any $CF_2{=}CF_2$ can be isolated. Also, the reaction will have to be run for a long enough time to allow isolation and identification of all products formed. The fact that $CF_2{=}CCl_2$ is formed is definite evidence that a radical process can be operating and could lead to the observed products under normal reaction conditions.

A reaction has been devised which should show, if addition-elimination is operating, as a major reaction mechanism. This is shown below.

The following reaction is known to occur:

$$CF_2{=}CCl_2 \xrightarrow[\Delta,\,Pd/C]{H_2} CF_2{=}CH_2$$

The following reaction will be run:

$$CFCl{=}CCl_2 \xrightarrow[\Delta,\,Pd/C]{H_2} CFCl{=}CH_2$$

If this product can be made, then the following reaction will be run:

$$CFCl{=}CCl_2 \xrightarrow[\Delta,\,Pd/C]{D_2} CFCl{=}CD_2$$

If addition-elimination is operating, the following should occur:

$$CFCl{=}CF_2 \xrightarrow[\Delta,\,Pd/C]{H_2} CFHCl,\ \ CD_2H$$

$$CFHCl{=}CD_2H \xrightarrow{-HCl} CFH{=}CD_2\,(1)$$

$$CFHCl{=}CD_2H \xrightarrow{-OCl} CFH{=}CDH\,(2)$$

Product (1) can be differentiated from (2) by NMR.

Product (1) can be formed from a radical mechanism but product (2) cannot. Thus, any appearance of (2) would be definite evidence for the addition-elimination mechanism.

The preparation of $CF_2H{-}CCl_2H$ will have to be made and this subjected to various temperatures in an attempt to split out HX. If this cannot be done, then this is evidence against addition-elimination operating as a reaction mechanism.

In summary, the scope of the reaction has been expanded considerably. However, several olefins are left to be studied. It appears several mechanisms might be operative in this type of hydrogenation. Evidence is presented for a radical mechanism at elevated temperatures and possibly complex formation between chlorine and Pd at low temperatures.

XII. The Reaction of Perhalocycloalkenes with Certain Nucleophiles

A. The Synthesis of 2,3:5,6- Bis[perfluoro-n-methylene]-1,4-dithiins

The reaction of Na_2S with 1,2 dichloroperfluorocyclic olefins has led to the formation of a new class of compounds, the 2,3:5,6-Bis perfluoro-n-methylene -1,4-dithiins.

1. Historical Background Fluorocarbon sulfides have previously been prepared by heating perfluoroalkyl iodides with sulfur under pressure. This procedure generally results in a mixture of mono-di-trisulfides as evidenced by the work of Hauptschien and Grosse(46). Saunders and Stacey(47) and McCombie and Saunders(48) have prepared fluorine substituted ethane 1,2-disulfides by the reaction of alkyl halides with sodium mercaptides. More recently, Krespan and Langkammer(49) have prepared perfluoro 1,4-dithianes by the reaction of C_2F_4 and sulfur at elevated temperatures and pressure.

2. Discussion In our own group, extensive work has been conducted with attack of nucleophiles on 1,2-dichloroperfluoro cyclic olefins, but nowhere is there a report of attack by a doubly charged species. Therefore, this investigation was undertaken.

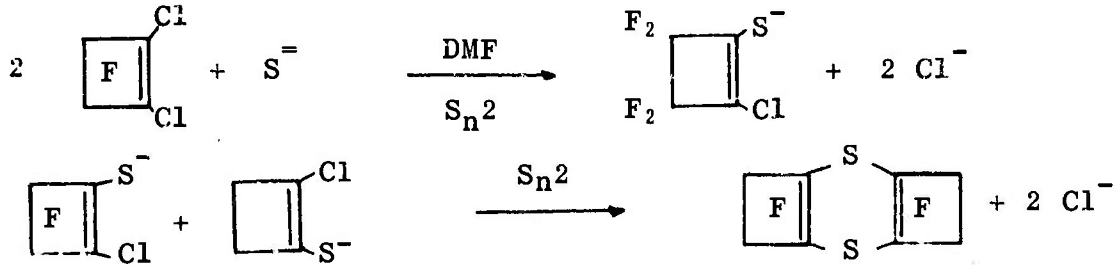
When Na_2S is dissolved in DMF, an emerald green solution results. The addition of a 1,2-dichloroperfluoro cycloölefin causes an immediate change in the color to bright yellow (when the olefin is C_4 or C_5) and red-brown when the olefin is C_6. The reactions are exothermic, with flocculent solids forming as the reaction proceeds. The reaction time is dependent on the olefin and the yields vary immensely. For C_4 olefins, the reaction is spontaneous and appears over in minutes; for the C_5 and C_6 olefins, the yields are lower and reaction times are much longer. As the reaction proceeds, the fluorocarbon, which is initially soluble in the DMF, separates, and, after filtration to remove the solid, can be easily isolated. Depending on the amount of solvent used, some of the reaction product also, under certain conditions, precipitates from solution and can be recovered by dumping all the solid into water, the organic sulfide being insoluble.

The sulfides of the C_4 and C_5 olefins are easily detected by their brilliant yellow color. Surprisingly, the sulfide of the C_6 olefin is colorless.

All of the sulfides are very easily sublimed and this technique can be used to isolate product as well as a means for purification of it.

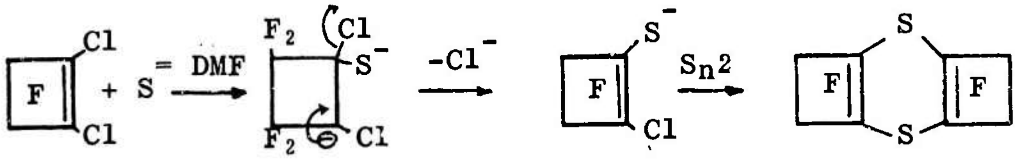
The order of reactivity is C_4, C_5, C_6 and yields are in the same direction. The overall reaction is very clean with only cyclic product being obtained. The C_6 olefin yields three such cyclic products while the C_4 and C_5 yield only one product respectively.

The order of reactivity of the olefins studied is the same direction as their reactivity toward S_N2 displacement, i.e., 4 5 6. Also, since DMF·is a good positive charge solvator, the possibility of the presence of doubly charged sulfide ion, $S^{=}$, is enhanced. In light of this, the following mechanism (A) is proposed as the dominant one for the C_4 and C_5 olefins. The C_4 olefin will be used to illustrate the mechanistic pathway.

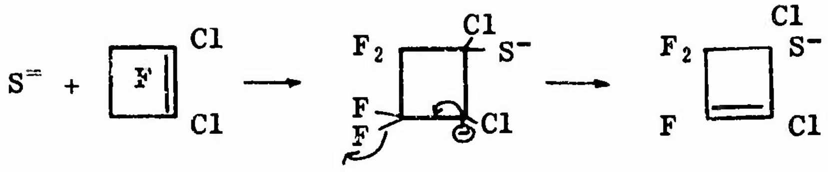


For an S_N2 mechanism to be operating would require front side attack on the carbon bearing halogen. While this type of attack is known, it is not common, but in light of experimental data, it must be postulated as occuring in the systems so far investigated.

Another possible mechanism (B) which may be operating is that of addition-elimination whereby a carbanion is formed:

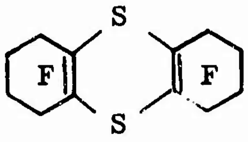


In either reaction mechanism, the intermediate anion formed can be the same. The straight S_N2 displacement mechanism, however, seems more plausible, since in mechanism B, the carbanion, in order to expel Cl^-, would have to be shifting negative charge in the direction of a carbon atom already bearing a negatively charged species, and this would appear energetically quite unfavorable. If mechanism B were operating, one might expect product from F^- being expelled, i. e.

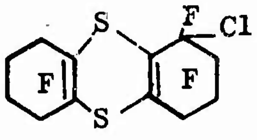


that none of this product is found is evidence that this mechanism is not operating in the C_4 and C_5 reaction sequence.

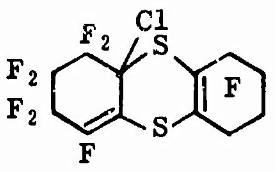
Mechanism (B) appears to be a definite possibility in the C_6 olefin reaction, since three cyclic products are obtained in approximately a 1:1:1 ratio. Structural assignments are based on mass spectral fragmentation products plus IR data and are as follows (a):



I



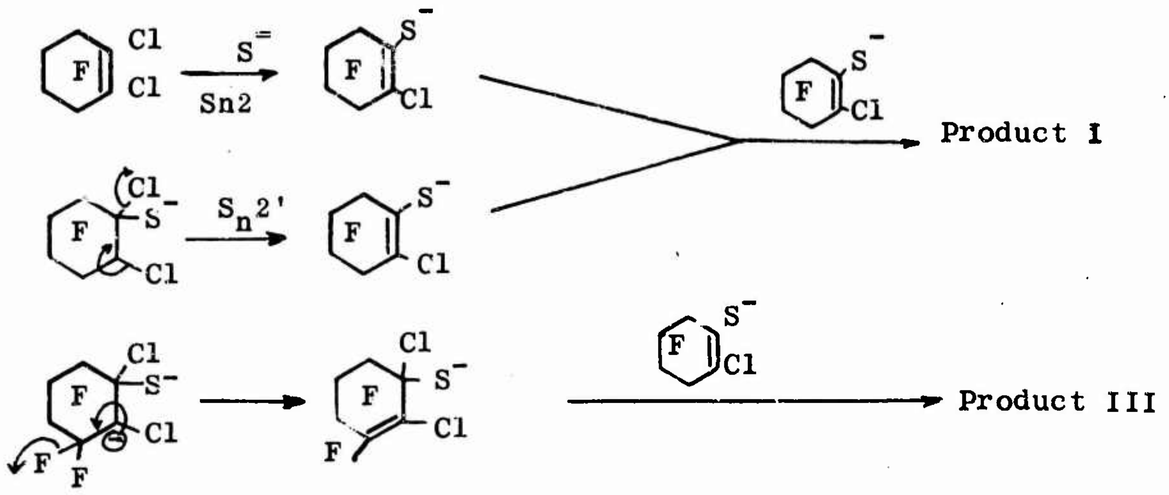
II



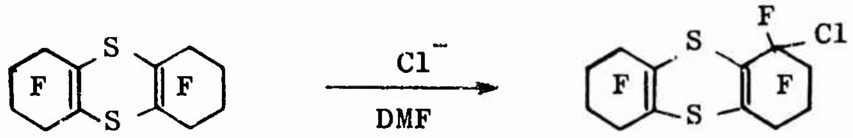
III

(a) Mass spectral data were used for all systems studied.

The following routes are possible to formation of I and III, with an apparent competition between S_N2 and S_N2' mechanisms occuring.

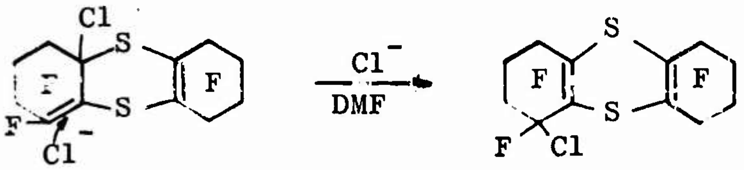


Product II could arise as follows:



Since the F^- being replaced is allylic to both the double bond and the sulfur, it should be very labile and might possibly be able to be displaced by chloride ion. This can be very easily proved by taking the symmetrical olefin, I, and placing it under reaction conditions in the presence of NaCl. If Cl^- displacement is occurring, the reaction product II will be formed.

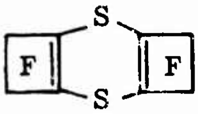
Another possible route to II would be an S_N2' on product III.



Again, this reaction mechanism can be readily proven or disproven by reaction with NaCl on product III in DMF.

As mentioned previously, structural assignments of the cyclic sulfides are based largely on mass spectral data. These data are presented in Tables IV-VII.

TABLE IV



MASS SPECTRAL DATA OF 2,3:5,6-Bis [perfluorodimethylene] -1,4-dithiin

Calc.M.Wt.			M.Wt. found	312
	C-8	96		
	F-8	152		
	S-2	64		
		312		

M/e	fragment
74	C_3F_2
88	C_2S_2 or CF_4
94	C_2F_2S
106	C_3F_2S
118	C_4F_2S
124	C_4F_4
130	C_5F_2S
137	C_4F_3S
156	C_4F_4S
193	$C_6F_3S_2$
200	$C_5F_4S_2$
212	$C_6F_4S_2$
218	C_6F_6S
230	C_7F_6S
243	$C_7F_5S_2$
262	$C_7F_6S_2$
293	$C_8F_7S_2$

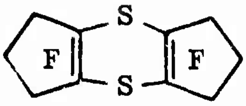


TABLE V

MASS SPECTRAL DATA OF 2,3:5,6-Bis [perfluorotrimethylene] -1,4-dithiin

Calc.M.Wt.	C-10	120	M.Wt. found	412
	F-12	228		
	S-2	64		
		412		

m/e	fragment
106	C_3F_2S
155	C_5F_5
206	C_5F_6S
262	$C_7F_6S_2$
293	$C_8F_7S_2$
312	$C_8F_8S_2$
343	$C_9F_9S_2$
362	$C_9F_{10}S_2$
393	$C_{10}F_{11}S_2$

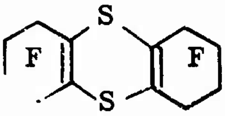


TABLE VI

MASS SPECTRAL DATA OF
2,3:5,6-Bix [perfluorotetramethylene] -1,4-dithiin

Calc.M.Wt.	C-12	144	M.Wt. found	512
	F-16	304		
	S-2	64		
		512		

m/e	fragment
88	C_2S_2 or CF_4
106	C_3F_2S
124	C_4F_4
125	C_3F_3S
156	C_4F_4S
312	$C_8F_8S_2$
331	$C_8F_9S_2$
343	$C_9F_9S_2$
362	$C_9F_{10}S_2$
393	$C_{10}F_{11}S_2$
412	$C_{10}F_{12}S_2$
443	$C_{11}F_{13}S_2$
462	$C_{11}F_{14}S_2$
493	$C_{12}F_{15}S_2$

As can be seen by the cracking pattern, these molecules tend to lose simple, low mass fragments in all cases, i.e., F, CF_2, CF_3, CF_4, C_2F_5, etc., thus setting up a pattern which might be used in determining structures of molecules substituted with other halogens. Using this basic pattern as a model, the structures of two cyclic isomers containing a single chlorine atom have been assigned as follows:

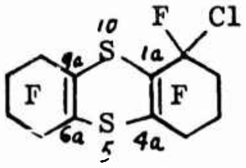


TABLE VII

MASS SPECTRAL DATA OF
1a,4a:6a,9a-Bis [1-monochloro-perfluorotetramethylene] -5,10-dithiin

Calc. M.Wt.	C-12	144	M.Wt.found	528.5
	F-15	285		
	Cl-1	35.5		
	S-2	64		
		528.5		

m/e	fragment	fragment lost
87	C_3FS	$C_9F_{14}SCl$
106	C_3F_2S	$C_9F_{13}SCl$
125	C_3F_3S	$C_9F_{12}SCl$
131	C_3F_5	$C_9F_{10}S_2Cl$
137	C_4F_3S	$C_8F_{12}SCl$
156	C_4F_4S	$C_8F_{11}SCl$
324	$C_9F_8S_2$	C_3F_7Cl
343	$C_9F_9S_2$	C_3F_6Cl
	$C_8F_{10}S_2$	C_4F_5Cl
374	$C_{10}F_{10}S_2$	C_2F_5Cl
393	$C_{10}F_{11}S_2$	C_2F_4Cl
424	$C_{11}F_{12}S_2$	CF_3Cl
443	$C_{11}F_{13}S_2$	CF_2Cl
461	$C_{11}F_{14}S_2$	CFCl
493	$C_{12}F_{15}S_2$	Cl
509	$C_{12}F_{14}Cl_1S_2$	F

As can be seen by comparing the cracking patterns, the perfluoro and the monochloro compound have essentially the same fragmentation pattern. The only structure which can plausibly fit this M.Wt. and cracking pattern is one in which a $-CF_2$ moiety is replaced by a $-CFCl$.

That compound III is an isomer of II is borne out by its mass spectrum and a comparison of IR's. The structure assigned to III is:

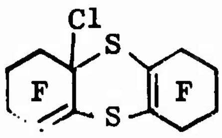


TABLE VIII

MASS SPECTRAL DATA OF 2,3:5,6-Bis[9a-monochloro-perfluorotetramethylene]-1,4-dithiin

Calc. M. Wt. 528.5 M. Wt. found 528

m/e	fragment	fragment lost	rel.size of common peaks in II vs III
87	C_3FS	$C_9F_{14}SCl$	1:1 (a)
106	C_3F_2S	$C_9F_{13}SCl$	1:1 (a)
125	C_3F_3S	$C_9F_{12}SCl$	1:1 (a)
131	C_3F_5	$C_9F_{10}S_2Cl$	1.5:1 (a)
137	C_4F_3S	$C_8F_{12}SCl$	1:1 (a)
156	C_4F_4S	$C_8F_{11}SCl$	1.5:1 (a)
343	$C_9F_9S_2$	C_3F_6Cl	1:6
374	$C_{10}F_{10}S_2$	C_2F_5Cl	2.5:1
393	$C_{10}F_{11}S_2$	C_2F_4Cl	5:1
428	$C_{10}F_{11}Cl_1S_2$	C_2F_4	1:50
443	$C_{11}F_{13}S_2$	CF_2Cl	4:1
461	$C_{11}F_{14}S_2$	$CFCl$	3:1
493	$C_{12}F_{15}S_2$	Cl	2:1
509	$C_{12}F_{14}Cl_1S_2$	F	1:1 (a)

(a) Note ratio is essentially the same when Cl is involved in fragment lost only when accompanied by loss of a single sulfur.

Note that when only Cl must be included in fragment lost, a large variation in the relative size of the peaks results. This indicates that Cl is not on a carbon bearing F which leaves only bridgehead carbons available, bonded directly to S.

The infrared spectrum of compound III shows three distinct carbon-carbon double bond stretches; one at 1615 cm^{-1} which is attributed to the symmetrical C=C stretch (compared with 1595 cm^{-1} for compound I and 1590 cm^{-1} for compound II), one at 1660 cm^{-1}, which is attributed to a binylic fluorine and is a shift of approximately 30 cm^{-1} from that of the C=C stretch in the cyclic starting material, and the other stretch at 1580 cm^{-1}.

The overall shift and positions, plus the presence of three C=C stretching frequencies, are evidence of destroyed symmetry in the molecule and are also indicative of conjugation involving a vinylic halogen as evidenced in the cyclic "dibox" olefins.

Further correlation of IR data will be attempted at a later date when the structure has been further elucidated.

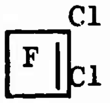
Since compound III has a vinylic fluorine, a F^{19} NMR should easily show whether or not the assigned structure is correct. However, due to extremely poor conversion and lack of availability of starting olefin, none is available for NMR studies at the time of this report.

Dreiding models of the cyclic sulfides show that all of the molecules are quite planar, the C_8 and C_{10} sulfides being more so than the C_{12} sulfides. The sulfides from the C4 and C_5 olefins are fairly rigid, the most significant motion coming from inversion of the sulfur atoms which should tend to give a time average position which would be planar. The C_{12} sulfide probably exists in a twist-boat conformation which would tend to relieve most of the eclipsing interactions. A full chair conformation is impossible for any of the six-membered rings.

The chemistry of these compounds has not yet been investigated and one can only speculate as to how broad the area might be. On the surface, it appears quite interesting.

3. <u>Experimental</u> The experimental approach is essentially the same for all the aforementioned compounds. Therefore, only one example will be discussed.

Into a 50-ml., round-bottom flask equipped with a Teflon stirring blade, dropping funnel and thermometer is added 25 ml of DMF. To this is added 7.8 g (0.1 moles) of Na_2S. The solution turns emerald green as some of the Na_2S goes into solution. This solution is stirred to get maximum dissolution and is then cooled to 0°C with an ice-water bath. Twenty grams (0.1 mole) of



in the dropping funnel is added slowly to the solution, (with stirring) the first few drops turning the solution bright yellow. This is accompanied immediately by solid formation. The olefin is added over a 15 minute period and the dropping funnel replaced with a water-cooled reflex condenser and the reaction is allowed to warm to room temperature. (Depending on the olefin, the reaction time is now varied.) After a suitable reaction time, the stirring is stopped and the hydrocarbon and fluorocarbon layers separate. The liquid is decanted from the reaction vessel to a funnel; the remaining liquid in the flask is removed from the solid via water aspirator. The liquid portions are combined in a separatory funnel and the lower fluorocarbon layer removed. The hydrocarbon layer is then poured into water and product is precipitated out.

Vaccum distillation at room temperature(through a -78° trap to collect unreacted olefin) causes separation of the solid sulfide from the fluorocarbon. Partial separation can be obtained by cooling the fluorocarbon to 0°C which causes precipitation of the solid.

GLC of the fluorocarbon on carbowax at 195°C also affords a means of separation of the products. Suprisingly, the solid sulfides elute very shortly after their respective starting olefins.

Maximum yields obtained have been in the range of 20-30 percent based on olefin.

B. The Synthesis of 2,3:5,6-Bis[perfluoro-n-methylene]-1,4-Diselenins

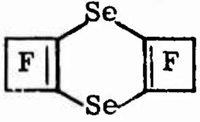
1. Historical Perfluoroselenium compounds have been prepared in a manner analogous to the previously discussed sulfides. Thus, reaction of CF_3I and selenium at 270°-295°C yields $(CF_3)_2Se$ and $(CF_3)_2SeSe(CF_3)_2$. These compounds have been briefly described by reviews by Emeleus(50, 51, 52). More recently, Krespan and Langkammer(49) revealed the preparation of perfluorodiselenanes from the reaction of C_2F_4 and selenium at elevated temperatures and pressures.

In this report, I would like to disclose the synthesis of the first of a new class of perfluoroselenium compounds, the 2,3:5,6-Bis perfluoro-n-methylene -1,4-Diselenins.

2. Discussion Since Na_2S afforded cyclic sulfides and since $S^=$ and $Se^=$ have very similar properties, i.e.,

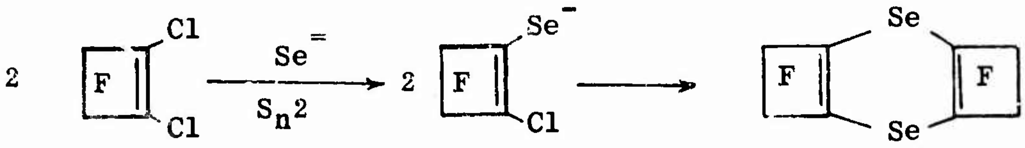
	Radius $X^=$	Covalent Radius-X-	Electronegativity
S	1.90	1.04	2.44
Se	2.02	1.17	2.48

The reaction of Na_2Se with 1,2-dichloroperfluorocyclobutene was attempted.

When Na_2Se was dissolved in DMF, a deep brown solution resulted. Addition of the cyclic butene caused immediate change in the color to red-brown and solid formation. After a reaction period of three hours, the liquid was separated and a few drops placed in H_2O. A yellow product proceeded to precipitate from solution and was later identified as  the cyclic diseleniin compound.

To date, only the 2,3:5,6-Bis[perfluorodimethylene]-1,4-Diseleniin has been prepared. There is no reason to expect, however, that the analogous selenium derivatives of the sulfides cannot be made, especially in light of the properties sited for the two anions.

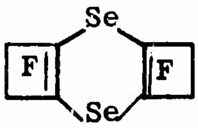
A mechanism analogous to that of sulfide formation is proposed for the preparation of the cyclic selenium compounds:



As mentioned, the C_8 selenide is also yellow in color, although not nearly as brilliant as its sulfur analog.

Structural assignment is based on IR and mass spectral data. The mass spectrum of the compound is presented below.

TABLE IX



MASS SPECTRAL DATA OF
2,3:5,6-Bix perfluorodimethylene -1,4-Diselenin

Calc.M.Wt.		
	C-8	96
	F-8	152
	Se^{79}-2	158
		406

M.Wt. found 406

Since Se^{80} is major isotope, this will be used in fragmentation pattern and M.Wt. becomes 408.

m/e	fragment
80	Se
93	C_3F_3
124	C_4F_4 (large)
135	C_3FSe (large
154	C_3F_2Se (large)
184	C_2Se_2 (large
284	$C_4F_4Se_2$
308	$C_6F_4Se_2$
328	C_8F_8Se (large)
358	$C_7F_6Se_2$
389	$C_8F_2Se_2$

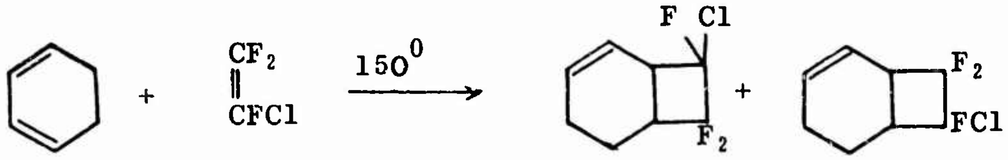
It is interesting to compare the mass spectrums of the C_8 sulfide and the above compound. The largest peak in the above pattern (328), due to loss of Se, has no counterpart in the sulfide. This seems quite surprising. Outside of this, the cracking patterns are quite similar.

The similarity between the sulfides and the selenide can also be seen in their IR spectrums, the only major difference being in the C-S vs. C-Se absorptions.

The chemistry of the selenide prepared has not been studied at the time of this report. The preparation of the C_{10} and C_{12} selenides has not yet been attempted.

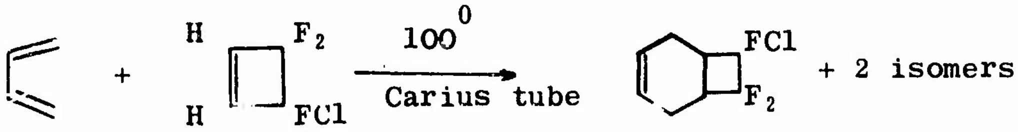
XIII. New Compounds and New Information

The previously reported reaction shown immediately below had not been completely characterized as to the ring system. Now, the products are assigned the bicyclo (4.2.0) octene-2 system:



#0 - 1 #0 - 2

The physical properties were previously reported.

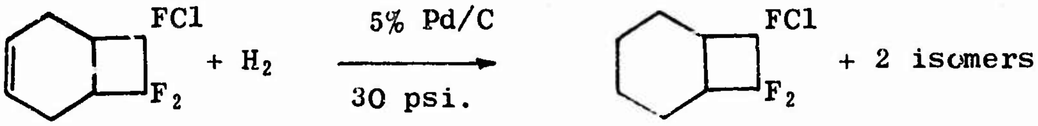


#0 - 4(a+b)

#0-04 (a and b)

d^{26} 1.31
n_D^{27} 1.4450
$M_{D(calc.)} = 39.8$
$M_{D(obs.)} = 39.8$

IR:		
	3060 cm^{-1}	vinylic hydrogen
	2980 cm^{-1}	sat'd carbon-hydrogen
	1650 cm^{-1}	vinylic carbon-carbon



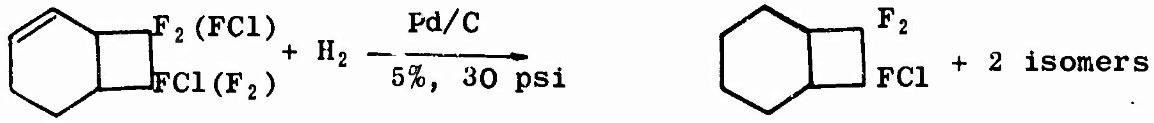
#0 - 5(a+b)

#0-05 (a and b)

IR: shows disappearance of peaks at 3060 and 1650 cm^{-1}

in parent compound. Otherwise IR spectrum is very similar.

GLC: both peaks in glc are shifted to higher retention time but retain rel. areas.

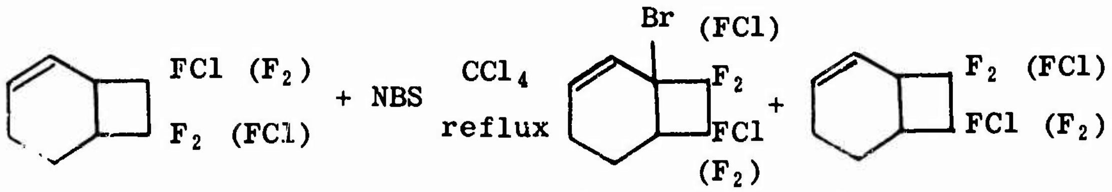


#0 - 5(a+c)

#0-05 (and and c)

GLC: retention time of peak for 0-05 a is the same in both this and previous reaction is the same.

IR: IR spectra are the same also.



#0-06(a+b) #0-06(c+d)

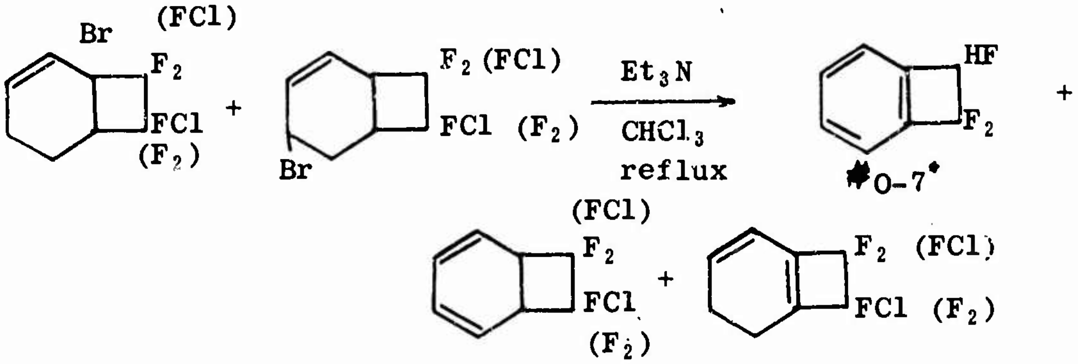
0-06

$n_D^{25.5} = 1.4927$

$d^{25.5} = 1.68$

Calc'd C: 35.00, H: 2.55, Cl=12.71, Br=29.10, F=20.70

Obs'd C=36.19, H=3.09, Cl=12.70, Br=28.28, F=20.39



#0-7*

#0-9(a+b) #0-8(a+b)

#0-7

Calc: C=60.18, H=3.16, F=36.10

Found: C=60.18, H=3.12, F=35.46

PNMR: m/e=158

2.6 τ (4H)

3.6 τ, 4.5 τ (two doublets) (1H)

IR:

2990 cm^{-1}	C-H
3102 cm^{-1}	Aromatic C-H

UV:

λ max (EtOH) = 258.5, 264, 270, 279.5 mμ

#0-8

$d^{26} = 1.34$ bp 155°/627mm

$n_D^{26} = 1.4506$

$M_D^{obs} = 38,9$

$M_D^{calc} = 39.2$

calc: C= 49.3, H=30.8,
F=29.3, Cl=18.20

found: C=49.16; H=3.26,
F=29.52, Cl=18.23

PNMR

4.2 τ (2 protons)
7.0 τ (4 protons)

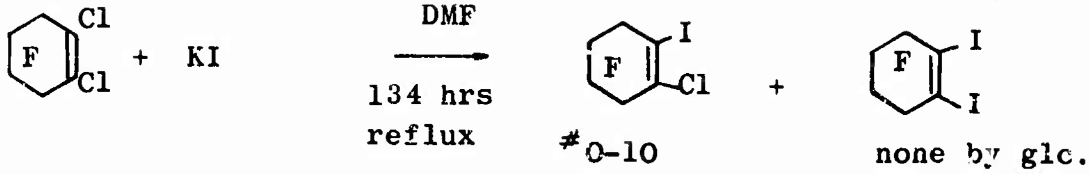
F^{19}NMR

shows probably assigned structure

#0-9

IR:

2930 cm^{-1}	C-H
3060 cm^{-1}	vinylic C-H
1670 cm^{-1}	conjugated
1600 cm^{-1}	diene similar to 



#0-10

none by glc.

#0-10

IR: 1610 cm^{-1} C=C
870 cm^{-1} C-Cl

n_D^{26}= 1.4213
$d^{26.5}$= 2.12

m/e = 386
bp = 144.5/632.1mm

#0-11

#0-11

IR: 1560 cm^{-1} C=C

#0-12

 # 0-12

IR: no C=C obs.

Analysis:				
	Calc'd	C=30.7	H=0	F=48.7
	Obs'd	C=30.05	H=0.13	F=50.39

FNMR: singlet (consistent with structure)

mp=123-133
m/e=312

XIV. 1-Carboxy-2-haloperfluorocycloalkenes and 1,2-Dicarboxyperfluorocycloalkenes

1. Introduction Specific studies* aimed at the introduction of functionalities other than halogen at the vinylic position in perhalocycloalkenes have received but meager attention. As a consequence, many salient areas remain unexplored.

The present undertaking was initiated in light of these considerations.

2. Historical Although lithium halogen interchange reactions have been known since publication of the classic work of Gilman and Jacoby(53) in 1938, applications to polyfluoronated hydrocarbons were unknown until 1953 when McBee and coworkers reported the successful preparation of perfluoro-n-propyllithium(54). Subsequent to this paper, reports of the generation of perfluro-i-propyllithium and perfluoro-n-heptyllithium were published(55, 56) and shown, in addition to perfluoro-n-propyllithium(57), to be useful synthetic intermediates - despite their limited stabilities.

Employment of polyfluorinated olefins as substrates was not investigated until 1963 when Tarrant and coworkers reported the preparation and several reactions of trifluoro-vinyllithium(58). The organometallic was generated by means of lithium halogen exchange.

Dilithioperfluoroalkanes were without precedent until 1966 when Johncock published the preparation of 1,4-dilithioperfluorobutane in 18 percent yield using 1,4-diiodoperfluorobutane as substrate(59).

For this work, a series of 1,2-dihaloperfluorocycloalkenes was prepared in which the relative ability of various vinylic halogens to undergo metal halogen interchange could be studied. The present report describes the *in-situ* generation of a number of fluorinated cycloalkenyl lithium reagents and their characterization as carbonation products.

3. Results and Discussion Two rather different synthetic methods were employed in the preparation of the requisite 1,2-dihaloperfluorocycloalkenes.

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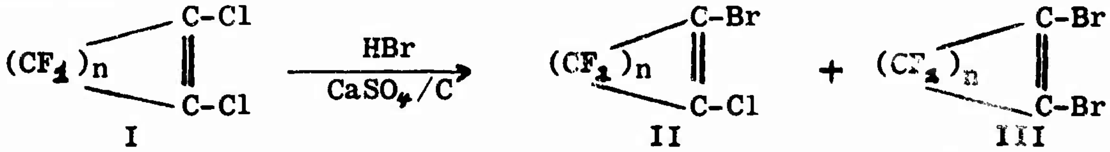
*These independent studies were made by Mr. Bruce Nakata under a fellowship grant not supported by this Army Contract but was tied into this program as far as long range objectives were concerned.

The first involved a catalytic thermal displacement of vinylic chlorine by bromine in the preparation of the monobromo and dibromo derivatives from the commercially available 1, 2-dichloroperfluorocycloalkenes. As pointed out by McMurtry,(60) this reaction has little precedent in the published chemical literature.



The product distribution from the three starting 1,2-dichlorocycloölefins employed is depicted in Table X.

TABLE X

PRODUCT DISTRIBUTION OF THE HBr ADDITION TO CYCLOÖLEFINS

Olefin (I)	Ref.	%Yield (II)	%Yield (III)
n=0; @ 290°		25.4	39.2
n=1; @ 225°	60	22	16
n=2; @ 290°		30.1	21.5

The mechanistic implications of this reaction is under active investigation at the present and will be reported forthwith.

Nucleophilic attack by halide ion, a reaction studied in depth by Moore(61) and extended somewhat by McMurtry(60) in this laboratory, constituted the second general route to the desired 1,2-dihaloperfluorocycloalkenes; in particular to monoiodo and diiodo derivatives - where nucleophile = iodide ion. The use of dimethylformamide (DMF) as a suitable reaction medium, (initially discovered by Park and Nakata) instead of the more customary acetone and diglyme, afforded realization of drastically reduced reaction times and greater product yields in the case of cyclobutenyl and cyclopentyl homologs. This fortuitous circumstance is due, in all probability, to the lesser degree of solvation about the attacking nucleophile in DMF relative to the degree of solvation experienced in diglyme or acetone.(62) The lack of solvation may have sufficiently raised the ground state to make the reaction energetically more favorable.

The cyclohexenes, unfortunately, are not as receptive toward iodide attack and even DMF was found to be less effective as a solvent; the yields realized in the case of 1,2-dichlorooctafluorocyclohexene were either none or, under extreme reaction conditions, low(63). This reluctance was partially circumvented by employing a starting material with a vinylic halogen more similar in leaving group ability to the attacking nucleophile, iodide. Use of 1,2-dibromooctafluorocyclohexene-1 afforded the bromoiodo species in appreciable yield (51.9%) and the diiodo derivative in moderate yield (6.5%).

The preparation of cyclic vinyllithium reagents was accomplished by treating either 1-iodo-2-haloperfluorocycloalkenes or the 1,2-dihalo derivatives (where X_1=X_2=Br or X_1=X_2=I) with methyllithium in ether at -78°. Subsequent treatment with either dry ice or, more preferably, with gaseous carbon dioxide gave up the organolithio specie, in varying yields, as their carboxy derivatives.

Not surprisingly, lithium halogen exchanges were confined exclusively to the vinylic iodo and bromo substituents. Indeed, the chemical literature is bereft of any references to fluoro or chloro substituents entering into halogen metal interchanges except in highly specialized instances(64). Treatment of the 1,2-diiodocycloölefins with two equivalents of methyllithium in ether at -78°C afforded, interestingly, the dilithio specie - characterized by their conversion to the corresponding diacid derivatives. Apparently, the basicity of the fluorodianion is of such a magnitude that it can more than successfully compete with the methide ion for the gegen lithyl cation. In contrast, treatment of 1,2-dibromotetrafluorocyclobutene-1 with excess ethylmagnesium bromide in ether reportedly yields none of the analogous di-Grignard reagent(65).

4. *Experimental* All boiling points were taken by the Siwoloboff method(20). Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were taken on a Perkin-Elmer Infracord. All melting points are uncorrected and were taken on a Thomas-Hoover UniMelt melting point apparatus.

Reaction of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene-1; with Hydrogen Bromide: *The reaction was accomplished by sweeping a mixture of the* olefin and excess hydrogen bromide through a 100 cm. x 2.5 cm. Pyrex tube packed with a 25:75/calcium sulfate: activated carbon catalyst heated to approximately 290°. The products were collected in traps maintained at 0°C. The catalyst was prepared in the manner reported by Park and Sharrah(38). In a typical run, 100 gm. (0.513 mole) of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene-1 was passed through the heated tube together with a fourfold excess of hydrogen bromide. The crude reaction products were washed with an aqueous sodium bicarbonate solution, then with water, and, finally, dried over anhydrous magnesium sulfate. Subsequent distillation at atmospheric pressure afforded 31.2 gm. (25.4% of theory) of 1-bromo-2-chloro-3,3,4,4-tetrafluorocyclobutene-1, b.p. 81°/630 mm. (lit.(65) b.p. 79.4°/626 mm.) and 56.9% (39.2% of theory) of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene-1, b.p. 96°/630 mm. (lit.(65) b.p. 95-96°/626 mm.).

Reaction of 1,2-Dichloro-3,3,4,4,5,5,6,6-octafluorocyclohexene-1 with Hydrogen Bromide: The reaction was accomplished in the manner described above. Thus, 108 gm (0.366 mole) of 1,2-dichloro3,3,4,4,5,5,6,6-octafluorocyclohexene-1 yielded, on work up and distillation, 37.3 gm (30.1% of theory) of 1-bromo-2-chloro-3,3,4,4,5,5,6,6-octafluorocyclohexene-1 and 30.1 gm. (21.5% of theory) of 1,2-dibromo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1.

1-bromo-2-chloro-3,3,4,4,5,5,6,6-octafluorocyclohexene-1; b.p. 122°/631 mm; n_D^{27}=1.3865.

Anal. Calcd. for C F BrCl: C, 21.2; F, 44.7; Br, 23.2; Cl, 10.4. Found: C, 21.01; F, 44.90; Br, 23.18.

The infrared spectrum contained a sharp absorption at 1620 cm^{-1} corresponding to olefin stretch.

1,2-dibromo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1: b. p. 140°/631 mm. (lit.(66) b.p. 149-150°); n_D^{27}= 1.4063.

The infrared spectrum contained a sharp olefinic absorption centered at 1610 cm^{-1}.

Reaction of 1,2-Dibromo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1 with Potassium Iodide: 1,2-Dibromooctafluorocyclohexene-1, 21.5 gm. (0.056 mole) and 30 gm. of potassium iodide were refluxed together for 34 hours with stirring. At the end of this time, the reaction mixture was cooled, poured into water, and the resulting organic layer washed repeatedly with water. There was obtained 18.6 gm of organic residue. G.l.c. analysis of the residue on F.S. 1265 (176°) indicated the presence of 12.5 gm (51.9% of theory) of 1-iodo-2-bromo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1 and 1.73 gm. of 1,2-diiodo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1 (6.5% of theory). Analytical samples were obtained through preparative g.l.c.

1-iodo-2-bromo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1: n_D^{27} = 1.4416; ν_{max}1600 cm^{-1}.

Anal. Calcd. for C_6F_8BrI: C, 16.72; F, 35.28; Br, 18.45; I, 29.45. Found: C, 1679; F, 35.00; Br, 18.25; I, 29.19.

1,2-diiodo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1: v_{max} 1580 cm^{-1} corresponding to olefinic stretching.

Anal. Calcd. for $C_6F_8I_2$: C, 15.08; F, 53.11; I, 31.81. Found: C, 14.87; F, 52.98; I, 31.67.

1-Iodo-2-chlorohexafluorocyclopentene-1: A mixture of 122 bm. (0.50 mole) of 1,2-dichlorohexafluorocyclopentene-1, 200 gm. (1.20 mole) of potassium iodide, and 125 ml. of dimethylformamide (DMF) was refluxed for 19 hours. At the end of this time, the reaction mixture was poured into water and the resulting organic phase drawn off, washed well with water, and dried over anhydrous magnesium sulfate. Fractional distillation afforded 42.9 gm. of unreacted 1,2-dichlorohexafluorocyclopentene-1 and 75.5 gm. (44.9% of theory) of 1-iodo-2-chlorohexafluorocyclopentene-1, b.p. 128°/628 mm. (lit.(60) 128°/628 mm).

The infrared spectrum contained a sharp absorption at 1600 cm^{-1} corresponding to the (c=c) stretching frequency.

1-Iodoheptafluorocyclopentene-1: A mixture of 45.7 gm. (0.20 mole) of 1-chloroheptafluorocyclopentene-1, 66.4 gm. (0.40 mole) of potassium iodide, and 75 ml. of DMF was refluxed for three days. At the end of this time, the reaction mixture was worked up in the manner described above to yield 19.7 gm. of unreacted starting olefin and 12.5 gm. (19.5% of theory) of 1-iodoheptafluorocyclopentene-1, b.p. 114°/623 mm.

The infrared spectrum contained a sharp absorption at 1590 cm^{-1} corresponding to the (c=c) stretching frequency.

1-Iodo-2-chlorotetrafluorocyclobutene-1: A mixture of 39.0 gm. (0.20 mole) of 1,2-dichlorotetrafluorocyclobutene-1, 66.4 gm (0.40 mole) of potassium iodide, and 50 ml. of DMF was refluxed together for five hours. At the end of this time, the reaction mixture was worked up in the manner described above to yield 20.3 g. (35.6% of thoery) of 1-iodo-2-chlorotetrafluorocyclobutene-1, b.p. 48°/70 mm. (lit.(65) b.p. 48°/70 mm.) and 14.8 gm. of 1,2-diiodotetrafluorocyclobutene-1, b.p. 148°/623 mm. (lit.(61) b.p. 151.5°/632 mm.).

1,2-Diiodohexafluorocyclopentene-1: This compound was prepared according to the procedure described by McMurtry(60).

1-Iodo-2-chloro-3,3,4,4,5,5,6,6-octafluorocyclohexene-1: This compound was prepared by Mr. Otto Furuta of this laboratory.

1-Carboxy-2-chlorohexafluorocyclopentene-1: In a nitrogen swept, elongated, three-neck reaction vessel cooled in a dry ice acetone bath and containing 39.7 gm. (0.118 mole) of 1-iodo-2-chlorohexafluorocyclopentene-1 in 60 ml. of anhydrous diethyl was added 46 ml. of a 2.58 M ethereal solution of methyllithium. The resulting dark blue reaction mixture was stirred for 60 minutes at -78°C then carbonated with excess dry ice. The carbonation mixture was allowed to attain room temperature, whereupon it was hydrolyzed with water and treated with a dilute solution of sodium hydroxide. The basic aqueous phase was drawn off, washed with ether, warmed to expel any dissolved organic solvent, then acidified with 6N hydrochloric acid. The resulting oil was taken up in ether and dried over anhydrous magnesium sulfate. Removal of the ether at reduced pressure and subsequent vacuum sublimation of the residual solid afforded 18.5 gm. (61.5% of theory) of the pure acid, m.p. 62.5-64.0°.

Anal. Calcd. for $C_6HF_6ClO_2$; C, 28.31; H, 0.39; F, 44.79, Cl, 13.93. Found: C, 28.09; H, 0.18; F, 44.60; Cl, 13.71.

The infrared spectrum contained absorptions at 3000 cm^{-1} (broad), 1730 cm^{-1} (sharp), and 1640 cm^{-1} (sharp) corresponding to (-OH), (C=O), and (c=c) stretching frequencies, respectively.

1-Carboxy-2-bromohexafluorocyclopentene-1: In a nitrogen swept, elongated, three-neck reaction vessel cooled in a dry ice acetone bath and containing 16.7 gm. (0.050 mole) of 1,2-dibromohexafluorocyclopentene-1 in 60 ml. of anhydrous diethyl ether was added 40.8 ml. of a 2.45M ethereal solution of methyllithium. The resulting reaction mixture was stirred for 30 minutes at -78°C then carbonated with excess dry ice. The carbonation mixture was allowed to attain room temperature and worked up in the manner described above - affording 5.20 gm. of the pure acid, m.p. 71-72°.

Anal. Calcd. for $C_6HF_6BrO_2$: C, 24.10; H, 0.34; F, 38.13; Br, 26.73. Found: C, 2 .93; H, 0.40; F, 38.16; Br, 26.52.

The infrared spectrum contained absorptions at 3000 cm^{-1} (broad), 1730 cm^{-1} (sharp), and 1635 cm^{-1} (sharp) corresponding to (-OH), (C=O), and (C=C) stretching frequencies, respectively.

1-Carboxy-2-chloro-3,3,4,4-tetrafluorocyclobutene-1: In the manner described above, 10.0 gm. (0.035 mole) of 1-iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene-1 was treated with 20 ml. of a 2.45M ethereal solution of methyllithium. Workup in the manner described above afforded 2.89 gm. (40.6% of theory) of 1-carboxy-2-chloro-3,3,4,4-tetrafluorocyclobutene-1, m.p. 89-91.5°C.

Neutralization equivalent: Calcd., 204.5; Found, 203.7.

The infrared spectrum contained a carbonyl absorption at 1735 cm^{-1} and a sharp olefin stretching absorption at 1640 cm^{-1}.

1-Carboxyheptafluorocyclopentene-1: In the manner described above, 12.5 gm. (0.039 mole) of 1-iodoheptafluorocyclopentene-1 was treated with 16 ml. of a 2.45 M ethereal solution of methyllithium. Workup in the customary fashion afforded 2.70 gm. (28.4%

of theory) of 1-carboxyheptafluorocyclopentene-1, m.p. 56.6-58°C.

1-Carboxy-2-chloro-3,3,4,4,5,5,6,6-octafluorocyclohexene-1: In the manner described above, 4.97 gm. (0.0129 mole) of 1-chloro-2 iodo-3,3,4,4,5,5,6,6-octafluorocyclohexene-1, upon treatment with exactly one equivalent of methyllithium in ether, yielded 2.59 gm. of a residual solid (66.7% of theory); from which, through vacuum sublimation, white microcrystals of 1-carboxy-2-chloro-3,3,4,-4,5,5,6,6-octafluorocyclohexene-1, m.p. 55.5-55.7°C was obtained.

Anal. Calcd. for $C_6HClF_8O_2$: C, 27.61; H, 0.33; Cl, 11.64; F, 49.91. Found: C, 27.67, H, 0.43; Cl, 11.85; F, 49.66.

The infrared spectrum contained a strong absorption at 1740 cm^{-1} corresponding to the carbonyl stretching frequency and a sharp absorption at 1640 cm^{-1} corresponding to the olefinic stretching frequency.

1-2-Dicarboxy-3,3,4,4-tetrafluorocyclobutene-1: To a nitrogen swept, elongated, three-neck reaction vessel cooled in a dry ice acetone bath and containing 10.6 gm. (0.028 mole) of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene-1 in 50 ml. of anhydrous ethyl ether was added 24 ml. of a 2.32 M ethereal solution of methyllithium. The resulting reaction mixture was stirred for 30 minutes at -78°, then carbonated with gaseous carbon dioxide. Following carbonation, the flask contents were allowed to attain ambient temperature and hydrolyzed with water. The aqueous phase was drawn off, washed well with ether, warmed to expel any dissolved solvent, and, finally, acidified with 1N hydrochloric acid. The resulting oil was taken up in ether and dried over anhydrous magnesium sulfate. Removal of the ether and subsequent vacuum sublimation of the residual solid, 4.16 gm. (69.4% of theory), afforded finely divided crystals of 1,2-dicarboxy-3,3,4,4-tetrafluorocyclobutene-1, m.p. 175-175°C.

Anal. Calcd. for $C_6H_2F_4O_4$: C, 33.66; H, 0.94; F, 35.01; Found: C, 33.72; H, 0.98; F, 35.23.

The presence of two carboxyl functional moities was confirmed by titration in aqueous solution: 0.0636 gm. of the microcrystalline solid required 5.98 ml. of a 0.0994 N sodium hydroxide solution (100% of theory).

The infrared spectrum contained an olefinic absorption at 1660 cm^{-1} and two carbonyl bands at 1750 (free) and 1690 (associated) cm^{-1}.

1,2-Dicarboxy-3,3,4,4,5,5-hexafluorocyclopentene-1: Following the procedure above, 10.7 gm (0.025 mole) of 1,2-diiodo-3,3,4,4,5,-5-hexafluorocyclopentene-1 gave 4.77 gm. of a residual solid (72.3% of theory); from which finely divided crystals of 1,2-dicarboxy-3,-3,4,4,5,5-hexafluorocyclopentene-1, m.p. 157-159° were obtained.

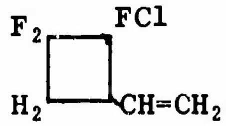
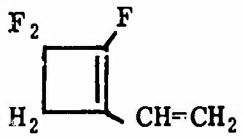
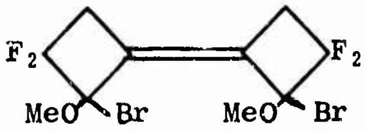
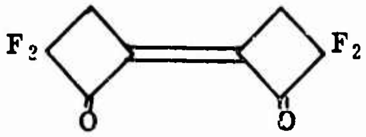
Anal. Calcd. for $C_7H_2F_6O_4$: C, 31.83; H, 0.76; F, 43.17. Found: C, 31.64; H, 0.74; F, 43.02.

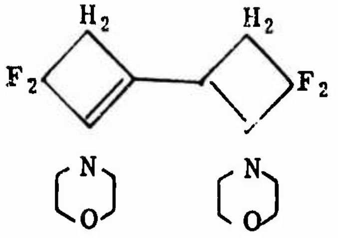
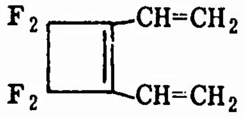
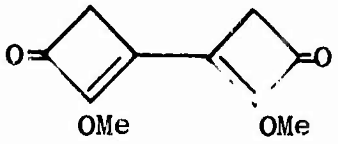
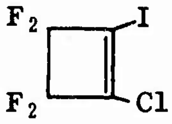
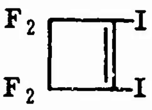
The presence of two carboxyl groups was confirmed by titration in aqueous medium: 0.0479 gm. of the white, crystalline solid required 3.68 ml. of a 0.0992 N sodium hydroxide solution (99.5% of theory).

The infrared spectrum contained an olefinic absorption at 1680 cm^{-1} and two carbonyl bands at 1750 (free) and 1725 (associated) cm^{-1}.

XV. Compounds for Evaluation

The following samples were prepared and sent to Dr. Douglas Relyea of the Uniroyal Company:

		grams
FC-300		50
FC-303		50
FC-312		112
FC-313		2

		grams
FC-314		22
FC-315	 (Polymer of)	2
FC-316	Disodium salt of 	7
FC-317		7
FC-318		7

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13. ABSTRACT

A large number of fluorine-containing intermediates were synthesized and submitted for further polymer studies. Among the organic fluorine compounds synthesized were a) various bicyclobutenyl derivatives, b) Grignard reaction products, c) perhalocycloalkenes containing vinylic halogens (I, Br, Cl, F.) and d) vinylic mono- and di-carboxylic acids of perhalocycloalkenes.

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Fluorochemicals	2,4					
Monomers	2					
Fluorine	2					
Polymerization	4					
Elastomers	4					

UNCLASSIFIED

Security Classification