TECHNICAL REPORT
66-54-CM

THE SYNTHESIS OF SPECIAL FLUORINE-CONTAINING MONOMERS

by

J. D. Park and J. R. Lacher

University of Colorado
Boulder, Colorado

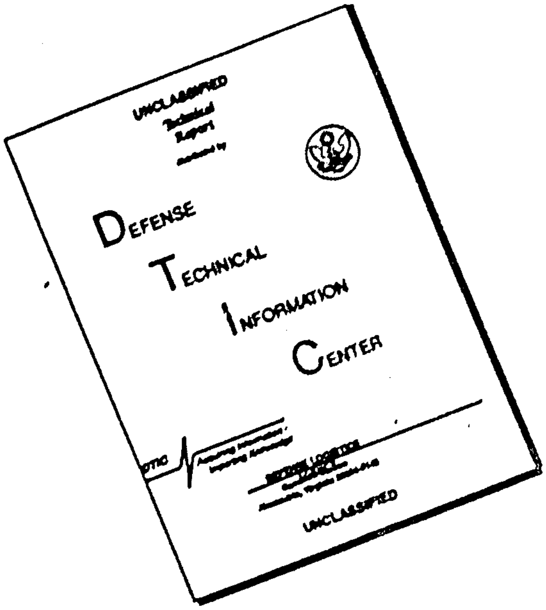
Contract No. DA-19-129-QM-1926
(01-6028-62)

January 1966

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

U.S. ARMY MATERIEL COMMAND

C&OM DIVISION
C&OM-17



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Clothing and Organic Materials Division
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts 01760

FOREWORD

This is a final report covering two years of research at the University of Colorado. The research described was conducted during the period October 1, 1963 to October 1, 1965.

The purpose of this project was to conduct studies and investigations on fluorine-containing compounds with a view towards developing techniques and processes of synthesizing special monomers from which elastomers could be obtained that were chemical and gasoline resistant and which also retain their flexibility at extremely low temperatures and thermal stability at high temperatures. Under this program numerous new fluorinated monomers have been synthesized. New syntheses have been perfected and new molecules characterized.

Under other Army contracts the monomers synthesized during the course of this contract have been subjected to polymerization studies.

This report was prepared by Dr. Joseph D. Park and Dr. John R. Lacher, both of the University of Colorado, under U. S. Army Contract DA-19-129-QM-1926, with Dr. Malcolm C. Henry as project supervisor.

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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 and pyrolysis materials obtained therefrom (c) unsaturated fluorine - containing halogenated (Br,Cl,I) cyclobutenes and (d) various α,ω-diolefins. Most of the above compounds were new to the arts.

The Synthesis of Special Fluorine-Containing Monomers

I. Introduction

The purpose of this project is to conduct studies and investigations on fluorine-containing compounds with a view toward developing techniques and processes of synthesizing special monomers from which to obtain elastomers which will be chemical and gasoline-resistant and will retain their flexibility at extremely low temperatures and thermal stability at high temperatures.

This research is authorized under U.S. Army Contract DA-19-129-QM-1926 (01 6028-62) and this report is the Final Report for the period October 1, 1963, to October 1, 1965, under this project with Dr. Malcolm Henry as project officer. Previously, similar researches authorized under Contract No. DA-19-129-QM-1263, QMC Project No. 7-93-15-004 under Dr. Juan Montermoso as project officer, were summarized in twelve quarterly reports. These reports should be used in conjunction with the present series to bring the historical portion up to date. Historical Background: See Quarterly Progress Reports 1,2,3,4,5,6,7,8, and 9.

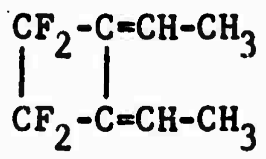
Summary of Current Progress

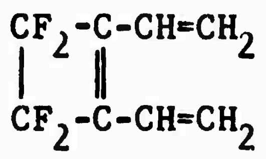
(A) Intermediate for Polymer Studies - The synthesis of a series of new olefins and non-conjugated diolefins were carried out. These are possible candiates for polymer evaluation as well as basic intermediates for the synthesis of other monomers containing a heteroatom or atoms.

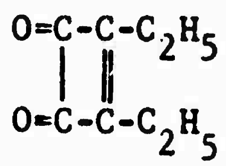
(B) The Chemistry of Bicyclobutenyl Derivatives - This program was embarked upon to find new and interesting intermediates for evaluation as monomers. A large number of interesting and heretofore unknown fluorinated bicyclobutenyl derivatives were synthesized and studied.

(B_1) Grignard Reactions and Pyrolysis Studies - A large number of new alkyl substituted tetrafluorocyclobutene of the type $CF_2\text{-}\underset{R}{C}=\underset{R}{C}\text{-}CF_2$ were synthesized and subjected to pyrolytic reaction conditions in hopes of obtaining dienes of the type $CF_2=\underset{R}{C}\text{-}\underset{R}{C}=CF_2$. However, conversions to the dienes were in order of less than 5% and seemed to be of equilibrium favoring the formation of the cyclic butene derivative. On the basis of this study, further work on this mode of attack was discontinued.

(B_{11}) Cyclobutene monomer intermediates were synthesized which may be of interest as polymer intermediates. Below are listed some of these compounds.







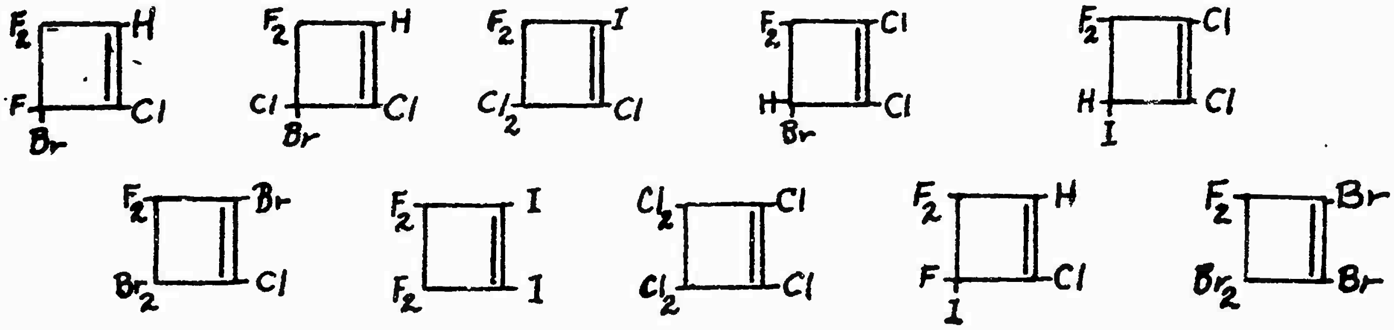
(C) Miscellaneous Studies

a) The epoxidation of hexafluorocyclobutene and of $CF_3CCl=CClCF_3$ were attempted in the presence of ultraviolet light and oxygen but thus far no epoxides were isolated. The only products thus far isolated were $(CF_2COOH)_2$ from hexafluorocyclobutene and CF_3COOH from $CF_3CCl=CClCF_3$.

b) The nucleophilic displacement by halide ion on fluorohalocyclobutenes were carried in order to develop a new and novel method of preparing heretofore unavailable fluorohalocyclobutenes of the following type: X_2C-C-X where X may be F, Cl, Br or I.

X_2C-CX

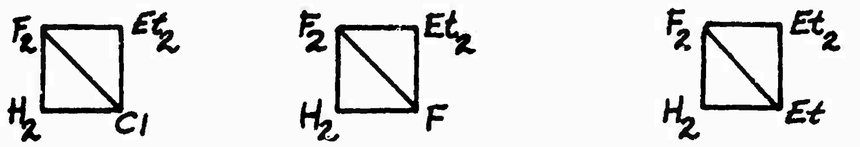
As examples of this technique, the following were prepared.

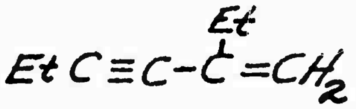


A probable mechanism is also proposed for the reactions of the halide ions with the fluorohalocyclobutenes based on the hypothesis of a carbanion intermediacy. Although as yet unproven, it provides a working rule for the prediction of the reaction products. Similar studies were carried out with the fluorinated halocyclopentenes.

c) Along similar lines and for similar reasons, the reaction of aluminum chloride with fluorohalocyclobutenes and with fluorohalocyclopentenes were carried out. Results similar to those with the cyclobutenes were achieved.

d) In the reaction of the ethyl Grignard reagent with $\overline{CF_2-CF=CCl-CH_2}$, a novel production of bicyclobutanes and aromatic compounds was achieved.





$EtC\equiv C-\overset{Et}{C}=CH_2$

NMR and mass spectrographic analyses were used in arriving at many of the structures of the complex reactions.

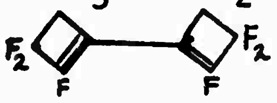
e) Some studies were carried out in attempts to prepare new fluorine containing monomers having the nitroso and nitro groups. The results of these studies are as yet inconclusive.

The following compounds were prepared and delivered:

F.C.-303	$CF_2{=}CF\text{-}CF_2\text{-}COOK$	5 g.	Dr. E. Stump - Peninsula
F.C.-304	$CF_2{=}CF(CF_2)_3COONa$	5 g.	Dr. E. Stump - Peninsula
F.C.-305	$(CF_2{=}CF\text{-}CF_2)_2$	16 g.	Dr. H. Garner - U. S. Rubber
F.C.-306	$CF_2{=}CH\text{-}CF_2CH_2CF_2CH{=}CF_2$	17 g.	" " " "
F.C.-307	$CF_2{=}CF\text{-}CF_2COOMe$	17 g.	" " " "
F.C.-308	$(CF_2{=}CF\text{-}CH_2\text{-}CF_2\text{-})_2$	11 g.	" " " "
F.C.-309	Light Fraction Fluorinated Oil (Montecatini)	28 g.	Mr. Charles B. Griffis - Natick
F.C.-310	Medium Fraction Fluorinated Oil (Montecatini)	28 g.	" " " "
F.C.-311	Heavy Fraction Fluorinated Oil (Montecatini)	2 g.	" " " "
F.C.-306	$(CF_2{=}CH\text{-}CF_2)_2\text{-}CH_2$	6 g.	Dr. D. Relyea - U. S. Rubber

Samples of polymer obtained from $\begin{array}{l}CF_2\text{-}C\text{-}CH{=}CH_2\\CF_2\text{-}C\text{-}CH{=}CH_2\end{array}$ were also delivered to Dr. Henry and Mr. Charles B. Griffis at our contractors' meeting held in Miami Beach on May 6, 1965.

The following compounds were also prepared and shipped.

1)	57.8 g.	$\begin{array}{l}CH_2\text{-}CH\text{-}CH{=}CH_2\\CF_2\text{-}CFCl\end{array}$	To: Dr. M. Fein, Thiokol Co.
2)	56. g.	"	To: Dr. B. Landrum, FMC Corp.
3)	98 g.	$CF_3\text{-}CH{=}CH_2$	To: " " " "
4)	13 g.		" " " " "
5)	23 g.	$CF_2{=}CF\text{-}CF_2\text{-}CFCl\text{-}CF_2\text{-}CF{=}CF_2$	" " " "

This latter compound, $CF_2{=}CF\text{-}CF_2\text{-}CFCl\text{-}CF_2CF{=}CF_2$ (b.p. 103°/630 mm.) was first reported by Park and Holler[1] (W.A.D.C. Technical Rept. 56-590, Part 1, pp. 21-22(1957). Subsequently Fearn and Wall of the national Bureau of Standards in an article[2] (SPE Transactions, July 1963, pp. 321-4) reported that the above diene (presumably) had a boiling point of 121°/760 mm. This is at great variance from ours. As shown in the "Experimental" section of our report, the data from our work is correct and those of Fearn and Wall incorrect. In light of this, the results of the latters' study on the "Polymers and Telomers of 4-Chloroperfluoroheptadiene-1,6" may now be in doubt.

A) Syntheses of α,ω-diolefins:

The object of this work is to synthesize some highly fluorinated non-conjugated dienes for polymer evaluation.

Utilizing the method of Holler[1] 4-chloroundecafluorohepta-1,6-diene (28 g.) was prepared and dispatched. Acid '8114', $Cl(CF_2-CFCl)_3CF_2CO_2H$, was neutralized with caustic soda and its salt was pyrolyzed at 250-300°C to give $Cl(CF_2=CFCl)_2CF_2-CF=CF_2$ in yields of 96%. This monoolefin was dehalogenated with HCl activated zinc to give mainly 4-chloroundecafluorohepta-1,6-diene in yields of 76%. The products were separated by fractional distillation and preparative-scale gas chromatography to give the diene in an overall yield of 30% (based on the amount of '8114' used). Examination of the other products showed that unchanged monoolefin was present in 1.5% yield. Four other components were present and separated in yields of 6,6,0,4 and 1%. Examination of these four compounds is still underway.

Tarrant et al.[3] claimed that the free-radical reaction between CF_2Br_2 and $CF_2=CH_2$ using benzoyl peroxide as initiator gave $CF_2BrCH_2CF_2Br$ and $CF_2BrCH_2CF_2CH_2CF_2Br$ in yields of 28 and 23% respectively. This method was used to prepare these two compounds as precursors of two dienes. Examination of the products by gas chromatography of CF_2Br_2 and $CF_2=CH_2$ showed six new components, two of which were present in heavy concentrations.

The first major component was separated by fractional distillation and treated with aqueous potassium hydroxide to proceed as shown: $CF_2BrCH_2CF_2Br \xrightarrow{aq.\ KOH} CF_2BrCH=CF_2$
Examination by gas chromatograph and infrared spectroscopy indicated the presence of a second compound, tetrafluoroallene. It is proposed to couple two molecules of 3-bromo-1,1,3,3-tetrafluoroprop-1-ene by the elimination of bromine with copper to give 1,1,3,3,4,4,5,5-octafluorohexa-1,5-diene.

When sufficient quantity of the second major component presumably, $CF_2BrCH_2CF_2CH_2CF_2Br$, has been separated by gas chromatography, it is proposed to dehydrobrominate it to give 1,1,3,3,4,4-hexafluoropenta-1,4-diene.

Attempts will be made to identify the other four products of the addition of CF_2Br_2 and $CH_2=CF_2$.

Tarrant et al[3] has also shown that the free radical addition of CF_2Br_2 and $CF_2=CH_2$ using benzoyl peroxide as initiator gave $CF_2BrCFHCF_2Br$ and $CF_2BrCFHCF_2CFHCF_2Br$ in yields of 9 and 18% respectively. Examination by gas chromatography of the products of such a reaction showed seven new components, two of which predominated in a ratio of roughly 1:2.

Separation of these products by fractional distillation and preparative scale gas chromatography is presently being done. It is proposed to identify as many of the seven components as possible and to use the above propane and pentane as precursors to two dienes, $CF_2{=}CFCF_2CF_2CF{=}CF_2$ and $CF_2{=}CFCF_2CF{=}CF_2$, by the same route as for the products of $CF_2Br_2 + CF_2 = CH_2$.

Tarrant[3] has shown that $CF_2ClCFClI$ adds to olefins in high yields in the presence of benzoyl peroxide. He claimed the formation of $CF_2ClCFClCHFCF_2I$ in yields of 79 [illegible] from $CHF{=}CF_2$. The work was repeated, but gas chromatography of [illegible] products displayed four new components. Two peaks close togethe[illegible]d of equal intensity predominated. This indicated random additio[illegible] to the olefin to give $CF_2ClCFClCHFCF_2I$ and $CF_2ClCFClCF_2CFHI$. It is proposed to verify this addition and then to couple each propane by the elimination of iodine by zinc in dioxan to give $(CF_2ClCFClCHFCF_2-)_2$ and $(CF_2ClCFClCF_2CFH-)_2$. These octanes will then be dechlorinated to give two octa-1, 7-dienes. Also by the dehydrochlorination of the former a octa-2,6-diene should be formed.

It is also proposed to use a similar sequence of reactions with $CF_2ClCFClI$ and $CF_2{=}CH_2$.

Synthesis of α,ω-diolefins

Experimental

Preparation of $CF_2{=}CF(CF_2CFCl)_2CF_2Cl$

$Cl(CF_2CFCl)_3CF_2CO_2H$ ["Kel-F acid 8114"] (154g. 0.32 mole) was mixed with ice and neutralized with cold sodium hydroxide solution using phenolphthalein as indicator. This salt solution was evaporated to dryness on a hot plate and the resulting salt cake was dried in a vacuum desiccator over two charges of calcium chloride and finally over phosphoric oxide. The salt cake was pulverized between changes in the drying agent. The dried salt was pyrolyzed at 250-300° and a liquid product was distilled into a trap cooled at -78°*. Redistillation of the crude product gave $CF_2{=}CF(CF_2CFCl)_2CF_2Cl$ (123 g., 96% yield), b.p. 66°/25 mm. Hg, n_D^{25} 1.3639; values quoted in the literature b.p. 65.9-66.3°/25 mm. Hg, n_D^{25} 1.3622[1]. The infrared spectrum was identical to that displayed in the literature.[1]

Preparation of $CF_2{=}CFCF_2CFClCF_2CF{=}CF_2$

$CF_2{=}CF(CF_2CFCl)_2CF_2Cl$ (123 g., 0.31 mole) was added dropwise to a stirred slurry of HCl-activated Zn dust (64 g., 1 mole) suspended in dibutoxytetraethyleneglycol (150 ml.) cooled with ice water to keep the temperature below 50°. The addition was completed after 6 hours and the reaction mixture was stirred at 60° for 2 hours. The crude products were distilled from the mixture, dried ($MgSO_4$) and fractionally distilled through a vacuum jacketed column (5" X 1/2") packed with glass helices giving the following fractions:

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* All the temperatures reported in this report are in degrees Centigrade.

1) -80° 19.5 g.; 2) 80-100° 23.5 g.;

3) 100-102° 26 g.; 4) 102-130° 8 g.

The fractions were examined by gas chromatography which showed that (1) and (2) contained $CF_2=CFCF_2CFClCF_2CF=CF_2$ and two components with lower retention times; fraction (3) contained $CF_2=CFCF_2CFClCF_2CF=CF_2$; and fraction (4) contained $CF_2=CFCF_2CFClCF_2CF=CF_2$ and three components with higher retention times, the latter of which was identified as unreacted $CF_2=CF(CF_2CFCl)_2CF_2Cl$. Separation of fractions (1), (2) and (4) by preparative gas chromatography gave:

(1) and (2) component (i) 6 g. component (ii) 5.6 g.
component (iii) 5.2 g.
(4) component (iii) 1.1 g. component (iv) 0.5 g.
component (v) 1.3 g. component (vi) 1.84 g.

The combined fractions (32 g.) of fraction (3) and component (iii) gave $CF_2=CFCF_2CFClCF_2CF=CF_2$ in a yield of 32%. Physical properties were b.p. 102°/627 mm. Hg., n_D^{25} 1.3312; values quoted in the literature b.p. 103°/633 mm. Hg., n_D^{25} 1.3310[1]. The infrared spectrum was identical to that displayed in the literature.[1]

Component (vi) was identified as unreacted $CF_2=CF(CF_2CFCl)_2CF_2Cl$ by infrared spectroscopy.

Components (i), (ii), (iv), and (v) have not yet been identified.

The Reaction between CF_2Br_2 and $CF_2=CH_2$

CF_2Br_2 (476 g., 2.3 mole), $CF_2=CH_2$ (59 g., 0.92 mole), and benzoyl peroxide (5g., 0.02 mole) were sealed in a 1-l. stainless steel bomb and shaken for 16 hours at 90°. The low boiling contents were bled off and collected in traps cooled to -78°. The higher boiling contents were poured out on opening the bomb. Upon fractional distillation, CF_2Br_2 (349 g.) and higher boiling products (119 g.) were recovered. The combined higher boiling products (535 g.) of five such reactions were washed with sodium bicarbonate solution and water, dried over magnesium sulphate, and fractionally distilled through a vacuum jacketed column (1' X 1/2"), packed with glass helices, giving the following fractions:

(1) 20-53° 65.5 g.; (2) 53-94° 32 g.; (3) 94-95° 193.5 g.;

(4) 95-150° 85.5g.; (5) 150° 65 g.; (6) 150-156° 37.4 g.

Examination of these fractions by gas chromatography showed that (1) was mainly CF_2Br_2; (2) contained component (i) and component (ii), $CF_2BrCH_2CF_2Br$; (3) contained only (ii), $CF_2BrCH_2CF_2Br$; (4) contained components (ii), (iii), (iv) and (v); (5) contained components (iv) and (v); (6) contained components (v) and (vi).

Separation of these fractions by preparative gas chromatography gave: (2) (i) 0.1 g., (ii) 15.2 g.; (4) (ii) 18.8 g. (iii) and (iv) 13.5 g. (v) 39.6 g.; (5) (iv) 1.5 g. (v) 40 g.

Physical properties of $CF_2BrCH_2CF_2Br$ (227.5 g.) from fraction (3) and component (ii) were b.p. 94-95°/630 mm. Hg. n_D^{25} 1.3975, d^{25} 2.0735, MR_D found 31.85, calculated 31.58 using F=1.100; values quoted in the literature b.p. 42°/85 mm. Hg., n_D^{25} 1.3974, d^{25} 2.0943[2].

Physical properties of $CF_2BrCH_2CF_2CH_2CF_2Br$ (80 g.) from component (v) were b.p. 150/630 mm. Hg., n_D^{25} 1.3981, d^{25} 2.0010, MR_D found 40.82 calculated 40.82 using F=1.100; values quoted in the literature b.p. 54°/14 mm. Hg., n_D^{25} 1.4032, d^{25} 2.003[2].

The Reaction between CF_2Br_2 and CF_2=CFH

CF_2Br_2 (480 g., 2.3 mole), CF_2=CFH (63 g., 0.77 mole) and benzoyl peroxide (7 g. 0.03 mole) were sealed in a 1/2 l. stainless steel bomb and shaken for 16 hours at 85°. The low boiling contents were bled off and collected in traps cooled to -78°. The higher boiling contents were poured out on opening the bomb. Fractional distillation of the products gave CF_2Br_2 (385 g.) and higher boiling products (109 g.). The combined products (472 g.) of several such reactions were washed with sodium bicarbonate solution and water, dried over magnesium sulphate, and fractionally distilled through a vacuum jacketed column (1' X 1/2"), packed with glass helices, giving the following fractions:

(1) 190 g. 24-29° (2) 42 g. 29-90°; (3) 45.6 g. 90-115°;
(4) 136.5 g. 115-163° (5) 45 g.

Examination of these fractions by gas chromatography showed the presence of eight principal peaks together with a number of minor peaks. Two of the principal peaks predominated. The fractions contained the following components: (1) mainly CF_2Br_2; (2) component (i), $CF_2BrCFHCF_2Br$, and component (ii); (3) Components (i), (ii), (iii), (iv), (v), and (vi); (4) contained components (i)-(viii); (5) contained mainly component (viii).

Separation of fractions (2) and (3) by preparative gas chromatography gave: (2) (i) 23.5 g., (ii) negligible; (3) (i) 21.2 g., (ii) 0.7 g., and others 0.5 g.

Physical properties of $CF_2BrCFHCF_2Br$(44.5 g.) from components (i) were b.p. 86.5°/621 mm. Hg., n_D^{25} 1.3819, d^{25} 2.1235, MR_D found 31.98 calculated 31.58 using F=1.100; values quoted in the literature b.p. 35°/78 mm. Hg., n_D^{25} 1.3816, d^{25} 2.1025[2]. The first component (i) was isolated in such a small quantity that its examination was not pursued. Component (iii) appeared to be a mixture from its infrared spectrum, but component (iv) appears to be a pure compound and its identity is being investigated. Component (vi) is probably the next telomer in the reaction sequence $CF_2Br(CH_2\text{-}CF_2)_3Br$.

CF_2=CH-CF_2Br was prepared in experimental quantities by the treatment of $CF_2BrCH_2CF_2Br$ with aqueous KOH. The presence of tetrafluoroallene was not detected this time, presumably because milder conditions were employed. The bromine of CF_2=CH-CF_2Br has been replaced with iodine by the action of potassium iodide in acetone, but the product which contains unreacted $CF_2=CH-CF_2Br$ has not been separated. It is intended to couple two molecules of $CF_2=CH-CF_2Br$ by an Ullmann reaction and to do the same with the iodide by the action of zinc in dioxan. These two reactions should both give 1,1,3,3,4,4,6,6-octafluorohexa-1,5-diene.

$CF_2BrCH_2CF_2CH_2CF_2Br$ was dehydrobrominated in aqueous potassium hydroxide. Early attempts with equimolar proportions at 50° gave no product. Likewise, the use of a threefold excess of potassium hydroxide failed. However, the use of reflux temperatures gave three products. Upon fractional distillation, two more products were discovered by analytical gas chromatography. The identity of these 5 new compounds is under way. From the physical properties it appears that the initial three compounds were two dienes and a monoene. The monoene was present in a large excess. The two new compounds seemed to be formed at the expense of the monoene and also appear to be monoenes.

The addition of ICl to $CF_2=CFCl$ at 0° should give 98% of $CF_2ClCFClI$ and 2% of CF_2ICFCl_2. However, it was found that this addition always gave at least 20% CF_2ICFCl_2. The separation of these isomers was difficult, so in reactions between $CF_2ClCFClI$ and $CF_2=CHF$, using benzoyl peroxide as initiator, the mixture was used. An examination of the mixture prior to the reaction and the unused mixture after the reaction by gas chromatography (Tri-m-tolyl phosphate on chromosorb) showed that $CF_2ClCFClI$ was preferentially, if not solely, consumed. The two major products from this reaction are being separated but both sets of the physical properties are almost identical with each other and with those that Tarrant found for this reaction. He gave the compound (probably the mixture) the structure $CF_2ClCFClCHFCF_2I$ on the grounds that dehydroiodination gave $CF_2=CFCFClCF_2Cl$ in 71%. Presumably the other 29% could have been $CF_2ClCFCLCF_2CFHI$. However, it must be noted that the new compounds have been obtained in almost equal quantities.

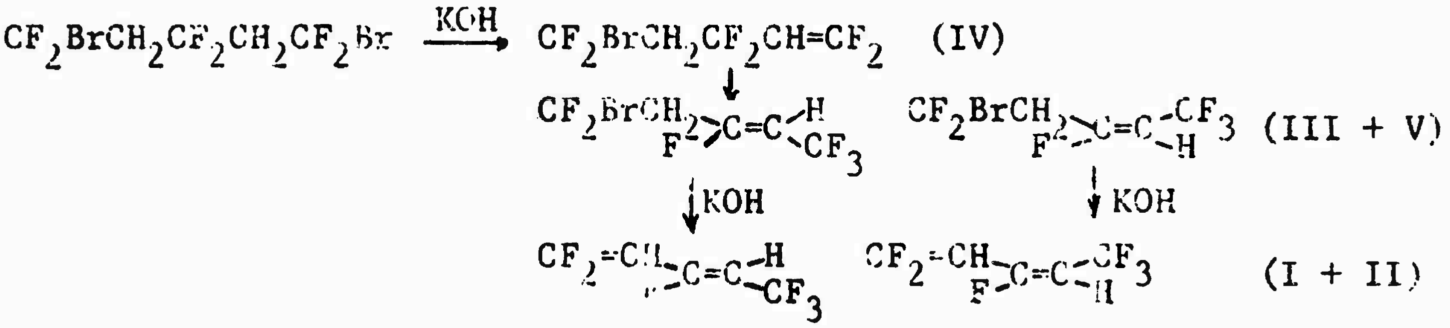
When sufficient quantities of $CF_2ClCFClCF_2CFHI$ and $CF_2ClCFCl$ $CFHCF_2I$ have been separated, it is proposed to identify the two structures and then to couple each butane by the elimination of iodine with zinc in dioxan to give $(CF_2ClCFClCF_2CFH-)_2$ and $(CF_2ClCFClCFHCF_2-)$. These octanes will then be dechlorinated to give two octa-1,7-dienes. Also, by the dehydrochlorination of the latter a octa-2,6-diene should be obtained.

<u>Dehydrobromination of $CF_2BrCH_2CF_2Br$.</u> - $CF_2BrCH_2CF_2Br$ (248 g., 0.9 mole) was added dropwise to a stirred solution of KOH (185 g., 3.3 mole) in water (400 ml.) during a period of 2 hours and the temperature of the solution was maintained at about 50°. The product (106 g.) was allowed to distill out of the mixture and was collected in a trap cooled to 0°. The dried ($MgSO_4$) product gave 1 peak on analytical gas chromatography.

Physical properties of $CF_2=CH-CF_2Br$ were n_D^{25} 1.3461; d^{25} 1.723; values quoted in the literature n_D^{25} 1.3463; d^{25} 1.747. The infrared spectrum displayed a peak at 3120 cm^{-1} which is indicative of vinylic C-H.

Preparation of $CF_2=CH-CF_2I$. - $CF_2=CF-CF_2Br$ (53 g., 0.28 mole), NaI (61 g., 0.4 mole), and acetone (130 ml.) were allowed to stand at room temperature for 30 days. The acetone was removed by washing with water and then the solution was washed with sodium bisulphate solution. The organic product (42 g.) was dried over phosphorous oxide and distilled to give a clean solution (25 g.). Analytical gas chromatography displayed two peaks indicating the presence of $CF_2=CF-CF_2Br$ and $CF_2=CF-CF_2I$. The latter appeared to be present in 60-70%.

Dehydrobromination of $CF_2BrCH_2CF_2CH_2CF_2Br$ was carried out and it was hoped to obtain $CF_2BrCH_2CF_2CH=CF_2$ and $CF_2=CHCF_2CH=CF_2$. However, three products (I, II and IV) were obtained. Upon fractional distillation (or reflux) product IV gave two further products III and V. Physical properties, element analysis, and ultraviolet spectroscopy indicated that I and II were conjugated dienes. The UV spectrum gave for I, λ 2195Å (13,900) and for II, λ 2185Å (14,710). Likewise, elemental analysis, physical properties, and the lack of strong absorption in the ultraviolet indicated that III, IV and V were monoenes. The separate dehydrobromination of III and V gave I and II, respectively. The dehydrobromination of IV is under investigation. It would appear that the following is the reaction scheme.



Upon refluxing separate quantities of III and V no rearrangement took place.

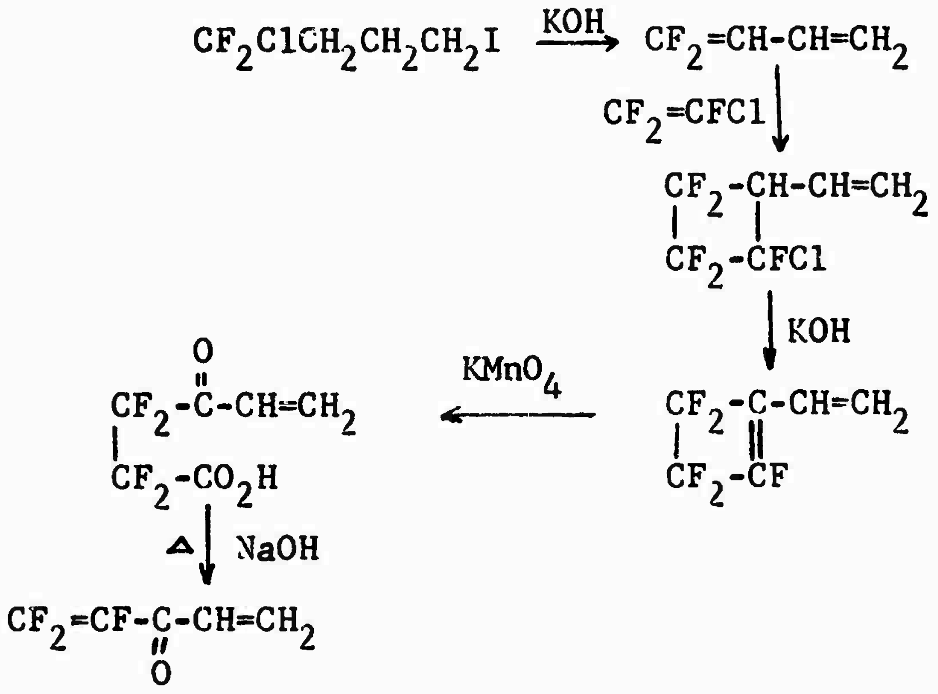
In the previous report it was shown that the addition of $CF_2ClCFClI$ to $CF_2=CFH$ gave principally two products $CF_2ClCFClCFHCF_2I$ (A) and $CF_2ClCFClCF_2CFHI$ (B). Ultraviolet spectroscopy gave similar absorptions, so it was not possible to identify the two products. Tarrant[3] had assigned the structure of the product of this reaction as solely (A), because dehydroiodination gave $CF_2ClCFClCF=CF_2$ in 79% yield. However, dehydroiodination of both products gave this same product. This can be rationalized by assuming that (B) dehydroiodinates to give a carbene, which rearranges to give $CF_2ClCFClCF=CF_2$. There is evidence for the abstraction of HI from the carbon of similar compounds.[2]

The addition of $CF_2ClCFClI$ to $CF_2=CH_2$ was shown to give $CF_2ClCFClCH_2CF_2I$, because dehydroiodination gave $CF_2ClCFClCH=CF_2$, which upon dechlorination gave the known $CF_2=CF-CH=CF_2$. The ultraviolet spectrum λ 2720Å (ε 253) was also consistent with a $-CF_2I$ group (CF_2I absorbs at 2710Å, R_fCH_2I absorbs at λ 2620Å.

The coupling of two molecules of $CF_2ClCFClCH_2CF_2I$ by zinc in acetic anhydride gave $(CF_2ClCFClCH_2CF_2-)_2$ in yields of 52%. However, the action of ultrviolet light upon the iodide and mercury gave yields of 67% and a product with fewer minor products. Dechlorination of the octane to give a diene is in progress.

$CF_2Cl(CH_2)_3I$ has been synthesized as the precursor to two fluorinated dienes. It is proposed to couple two molecules of this iodide to give $CF_2Cl(CH_2)_6CF_2Cl$. Dehydrochlorination should give $(CF_2{=}CH\text{-}CH_2CH_2\text{-})_2$.

The following is the proposed scheme to the second diene.



The synthesis of $CF_2Cl(CH_2)_3I$ was as follows:

$$ICl + CF_2 = CH_2 \rightarrow CF_2ClCH_2I \xrightarrow{\text{ethylene}} CF_2Cl(CH_2)_3I$$

Dehydrobromination of $CF_2BrCH_2CF_2CH_2CF_2Br$

$CF_2BrCH_2CF_2CH_2CF_2Br$ (170 g.; 0.5 mole) was added dropwise to a stirred solution of KOH (80 g.; 1.4 mole) in water (100 ml.) during a period of 2 hours and was heated at reflux temperature. The products (106 g.) were distilled from the mixture as the reaction proceeded, dried ($MgSO_4$), and fractionally distilled through a vacuum jacketed column (1' X 1/2") packed with glass helices. The following fractions were obtained:

(1) 42° 3.5 g.	(2) $42\text{-}64^\circ$ 6 g.	(3) 64° 3.2g.
(4) $64\text{-}92^\circ$ 6.5 g.	(5) 92° 12.5 g.	(6) $92\text{-}94^\circ$ 10 g.
(7) $94\text{-}110^\circ$ 30 g.	(8) 110° 7.1 g.	Residue 5 g.

Separation of these fractions by preparative gas chromatography gave:

(1) 3.5 g. of component (i) (2) (i) 0.7 g.; (ii) 3.5 g.; (3) (ii) 3.2 g.; (4) (ii) 1 g.; (iii) 1.5 g.; (v) 1.5 g. (5) (ii) 0.1 g.; (iii) 2. g.; (iv) 4.6 g.; (v) 0.1 g. (6) (iii) 2 g.; (iv) 2.8 g.; (v) 0.2 g. (7) (iv) 2 g.; (v) 20.3 g. (8) (v) 7.1 g.

Properties of these five components.

(i) b.p. 38°/627 mm. n_D^{26} 1.3301; d^{25} 1.3828; the infrared spectrum displayed peaks at 3120 (w), 1740 (s), and 1670 (w) cm^{-1}. Absorption in the ultraviolet region occurred at λ 2195Å (ε 13,900).
(ii) b.p. 65.5°/627 mm. n_D^{26} 1.3366; d^{25} 1.4076; the infrared spectrum displayed peaks at 3125, 1735 and 1680 cm^{-1}. Absorption in the ultraviolet region occurred at λ 2185Å (ε 14,710).
(iii) b.p. 89°630 mm.; n_D^{25} 1.3561; d^{25} 1.7068; the infrared displayed peaks at 3050 (s), 2990 (w), 1715 (s) cm^{-1}. Absorption in the ultraviolet region occurred at λ 1935Å (ε 1235) and λ 2750Å (ε 64.9).
(iv) b.p. 92°/629 mm.; n_D^{25} 1.3648; d^{25} 1.7347; the infrared displayed peaks at 3110 (s), 3000 (w), 1750 (s). Absorption in the ultraviolet region occurred at λ 1930Å (ε 705) and λ 2725Å (ε 38.5).
(v) b.p. 110°/629 mm.; n_D^{25} 1.3587; d^{25} 1.7201. The infrared displayed peaks at 3110 (s), 2990 (w), and 1720 cm^{-1}. Absorption in the ultraviolet region occurred at λ 1935Å (ε 1368).

Element analysis calculated for $CF_2{=}CHCF_2CH{=}CF_2$, $\begin{matrix}CF_2{=}CH\\F\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}H\\CF_3\end{matrix}$, and $\begin{matrix}CF_2{=}CH\\F\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}CF_3\\H\end{matrix}$, C, 34.11; H, 1.15; F, 64.74%.

Elemental analysis calculated for $CF_2BrCH_2CF_2CH{=}CF_2$, $\begin{matrix}CF_2BrCH\\F\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}H\\CF_3\end{matrix}$, and $\begin{matrix}CF_2BrCH\\F\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}CF_3\\H\end{matrix}$, C, 23.37; H, 1.18; Br, 31.09; F, 44.36%.

Found (i) C, 32.97; H, 1.56; Br, ---; F, 61.75%;
(ii) C, 34.36; H, 1.30; Br, ---; F, 64.51;
(iii) C, 23.33; H, 1.51; Br, 31.15; F, 44.04;
(iv) C, 23.48; H, 1.43; Br, 31.33; F, 44.75;
(v) C, 23.43; H, 1.68; Br, 30.14; F, 44.69;

Dehydrobromination of (v)

Component (v) (27 g.; 0.11 mole) from above, KOH (20 g., 0.36 mole), and water (40 ml.) were stirred and refluxed for 3 hours. The organic layer (13.2 g.) was separated, washed with water, and dried ($MgSO_4$). Examination of the product by vapor phase chromatography at 75° (Fluorosilicon packing upon chromasorb) showed one peak. Infrared spectroscopy showed that the product was identical to component (ii) obtained above.

Dehydrobromination of (iii)

Component (iii) (5.5 g. 0.02 mole) from above, KOH (5 g. 0.1 mole), and water (25 mol.) were stirred and refluxed for 10 hours. The organic layer was separated, washed with water, and dried ($MgSO_4$). Examination of the product (0.7 g.) by infrared spectroscopy showed that it was identical to component (i) obtained above.

Attempted isomerization of (v)

Component (v) (27.g.) was refluxed for 10 hours. Vapor phase chromatography of the product showed no change.

Attempted isomerization of (iii)

Component (iii) (5.5g.) was refluxed for 10 hours. Vapor phase chromatography of the product showed no change.

Addition of $CF_2ClCFClI$ to $CF_2=CFH$

The experimental details are recorded in the progress report for the period April 1 - October 1, 1964. Separation of the product (10 g.) by preparative gas chromatography (Fluorosilicon upon kieselguhr) gave two compounds.

1) b.p. 143°/630 mm.; $n_D^{23.5}$ 1.4224; d^{25}, 2.1095. Absorption in the ultraviolet region occurred at λ1945Å (ε 1412) and λ2715Å (ε 2715).
2) b.p. 146.5°/630 mm.; $n_D^{23.5}$ 1.4230; d^{25} 2.1125. Absorption in the ultraviolet region occurred at λ1945Å (ε 1240) and λ2720Å (ε 307).
Elemental analysis calculated for $CF_2ClCFClCFHCF_2I$ and $CF_2ClCFClCF_2CFHI$:

C, 13.31; H, 0.28; Cl, 19.65; F, 31.59; I, 35.17

Found Peak 1) C, 13.46; H, 0.19; Cl, 19.5; F, 31.47; I, 35.30.
Peak 2) C, 13.39; H, 0.29; Cl, 19.65; F, 31.71; I, 35.40.

Dehydroiodination of Peak 2

Component (2) (5.4 g.; 0.015 mole), KOH (3 g., 0.054 mole), and water (20 ml.) were stirred at 26° for 5 hours. The organic layer was separated, washed with water, and dried to give 2.8 g. of product. The product was separated by vapor phase chromatography (fluorosilicon upon chromosorb at 65°) giving 1) suspected $CF_2ClCFClCF=CF_2$ (1 g.); 2) other products negligible; 3) unreacted component (2) negligible.
Physical properties of $CF_2ClCFClCF=CF_2$: b.p. 59°/627 mm.; n_D^{25} 1.3412; d^{25} 1.6011. The infrared spectrum displayed peaks at 1780 (s), 1445 (s), and 1297 (s) cm^{-1}. Values quoted in the literature[1]: b.p. 65.5-67°; n_D^{22} 1.344; d^{22} 1.615. Infrared absorption 1780 cm^{-1}.

Dehydroiodination of Peak 1

Component (1) (7.3 g., 0.02 mole), KOH (4 g., 0.072 mole), and water were stirred at room temperature (24°) for 5 hours. The organic layer was separated, washed with water, dried ($MgSO_4$) to give 3.9 g. of product. The products were separated by vapor phase chromatography (fluorosilicon upon chromosorb at 65°) giving 1) suspected $CF_2ClCFClCF=CF_2$ (1 g.); 2) other product negligible; 3) unreacted component (1) 0.6 g.

The infrared spectrum of this suspected $CF_2ClCFClCF=CF_2$ was identical to that obtained from the product of the dehydroiodination of component (2).

Addition of $CF_2ClCFClI$ to $CF_2=CFH$. - $C_2Cl_2F_3I$ (284 g., 1 mole), $CF_2=CFH$ (50 g., 0.61 mole), and benzoyl peroxide (10 g., 0.04 mole) were sealed in a 1-L stainless steel bomb and shaken for 16 hrs. at 115°. The products (6 g.) were collected by bleeding the low-boiling products through a trap cooled at -78° and the remainder (304 g.) of the liquid contents were poured out. The combined products (310 g.) were washed with water, dried ($MgSO_4$), and fractionally distilled at 35°/120 mm. to give unreacted $C_2Cl_2F_3I$ (185 g.) and higher boiling products (89 g.).

Analytical gas chromatography (Fluorosilicon packing on chromosorb) of these higher boiling products showed the presence of two peaks very close together and much smaller amounts of other products.

Separation of 10 g. of these peaks by preparative gas chromatography gave pure specimens of these compounds. Physical properties of these compounds:

HI:

1) $n_D^{23.5}$ 1.4224; d^{25} 2.1095

2) $n_D^{23.5}$ 1.4230; d^{25} 2.1125

Values quoted in the literature for the presumably unresolved mixture were b.p. 56°/23 mm. Hg., n_D^{28} 1.4224, d^4 2.110, MR_D 43.49 (Calc. 43.21).

The reaction between $CF_2ClCFClI$ and $CF_2=CFH$ is described above. A similar reaction between $CF_2ClCFClI$ and $CF_2=CH_2$ has now been carried out. Only one major product was isolated this time and it is believed to be $CF_2ClCFClCH_2CF_2I$, because the addition of the radical, $CF_2ClCFCl$, would be expected to attack only the least hinder side of this olefin. Likewise, CF_2Br_2 was found to attack only this side. It is proposed to confirm the above addition by dehydroiodination and dechlorination, as the resulting $CF_2=CF-CH=CF_2$ is known. The $CF_2ClCFClI$ (70%) was used in a mixture of $C_2Cl_2F_3I$ isomers. The other 30% was CF_2ICFCl_2. However, the excess $C_2Cl_2F_3I$ only contained $CF_2ClCFClI$ in a 20% proportion. This indicated that $CF_2ClCFClI$ was probably the only isomer consumed.

$CF_2Cl-CFCl-CH_2-CF_2I$ was coupled by the elimination of iodine with zinc in acetic anhydride and methylene chloride. It is proposed to dechlorinate $(CF_2Cl-CFCl-CH_2-CF_2-)_2$ to give $(CF=CF-CH_2-CF_2)_2$ and dehydrochlorinate to give $(CF_2Cl-CF=CH-CF_2-)_2$.

A further sample (13.5 g.) of $(CF_2=CF-CF_2)_2$ CFCl was prepared and despatched. It was prepared from $Cl(CF_2-CFCl)_3CF_2CO_2H$ by essentially the same route given in the 10th Quarterly Report (1st Jan. 1964-1st April 1964).

Addition of $CF_2ClCFClI$ to $CF_2=CH_2$. - $C_2Cl_2F_3I$ (540 g., 1.93 mole; 70% $CF_2ClCFClI$ isomer), $CF_2=CH_2$ (159 g., 2.5 mole), and benzoyl peroxide for 16 hrs. at 98°. The bomb was permitted to cool to 25°. The unused $CF_2=CH_2$ and any low boiling products were bled off and collected in traps cooled at -78°. The higher boiling contents were poured out on opening the bomb. The $CF_2=CH_2$ was allowed to escape and the combined products (556 g.) were washed with a solution of sodium thiosulphate to remove traces of iodine, and then washed with water. The dried ($MgSO_4$) organic layer was fractionally distilled through a vacuum jacketed column (1' X 1/2") giving the following fractions:

1) 35°-90°/100 mm. 205 g.
2) 90°/100 mm. 251 g.
3) 90-130°/20 mm. 39 g.
Residue 6 g.

Examination of these fractions by gas chromatography showed that fraction (1) contained mainly unused $C_2Cl_2F_3I$, but only 20% was $CF_2ClCFClI$ isomer; fraction (2) contained two new components in a ratio of about 100:1; (3) contained the two components in fraction (2) and other high boiling points.

Separation of 10 g. of fraction (2) by preparative gas chromatography (Ucon on chromosorb) gave (i) 8.7 g. (ii) negligible.

Physical properties of the suspected $CF_2ClCFClCH_2CF_2I$ are b.p. 145°/627 mm., n_D^{25} 1.4332; d^{25} 2.0588. Absorption in the ultraviolet region occurred at λ1935Å(ε 798) and λ2720Å(ε 253). (This is consistant for a $-CF_2I$ group: $-CF_2I$ absorb at 2710Å and R_f-CH_2I absorb at 2620Å). Elemental analysis: calculated for $CF_2ClCFClCH_2CF_2I$; C, 14.02; H, 0.58; Cl, 20.68; F, 27.71; I, 37.03. Found: C, 13.87; H, 0.53; Cl, 20.38; F, 27.98; I, 37.19.

<u>Preparation of $(CF_2ClCFClCH_2CF_2-)_2$.</u> 1) Acetic anhydride (80 ml.), methylene chloride (80 ml.), and powdered zinc (16.3 g., 0.25 mole) were placed in a 500 ml. three-necked flask. $CF_2ClCFClCH_2CF_2I$ (85 g., 0.25 mole) was added to the stirred slurry during a period of one hour. The reaction mixture was stirred for 16 hrs., when analytical gas chromatography (fluorosilicon packing on chromosorb) showed that all the $CF_2ClCFClCH_2CF_2I$ had been consumed. Zinc and zinc iodide were removed by filtration. Cold 50% sulphuric acid was added to the cooled (0°) reaction mixture. The acetic acid was removed by washing with dilute sodium hydroxide and water. The organic layer was dried ($MgSO_4$) and then fractionally distilled through a column (6" X 1/2") packed with glass helices giving:

(1) methylene chloride 38° 60 g. (2) 38°-90°/100 mm. 4 g.
(3) 90°/100 - 140°/10 mm. (28 g.)

Analytical gas chromatography showed that fraction (2) contained methylene chloride and a new component (i); fraction (3) contained new component (i), (ii) and (iii).

8 g. of fraction (3) were separated by preparative gas chromatography giving (i) negligible, (ii) 6 g., (iii) negligible.

Physical properties of component (ii) identified as $(CF_2Cl-CFClCH_2CF_2-)_2$ were b.p. 198°/627 mm. n_D^{25} 1.3798.

2) The iodide (25 g.) and mercury were sealed under vacuum in a thin walled tube (6" X 1") and the tube was spun horizontally for 180 hours while being irradiated by ultraviolet light. Examination of the filtered product by v.p.c. showed that the main product 80% was $(CF_2ClCFClCH_2CF_2-)_2$. There were two other lower boiling products. The crude yield was 10.5 g., 67%.

Dehydrohalogenation of $CF_2ClCFClCH_2CF_2I$

The iodide (75 g., 0.22 mole), KOH (56 g., 1 mole) and water (50 ml.) were stirred for 1 hour; heat was evolved. Vapor phase chromatography (v.p.c.) showed that about 10% of the starting material had given a new product. The mixture was refluxed for 3 hours. The v.p.c. showed that the organic layer had still about 50% of starting material. The water layer had a thick precipitate present, so it was separated off and replaced with KOH (56 g.) in water (50 ml.). The mixture was refluxed for a further 3 hours. The organic layer (32 g.) was separated, washed with water, dried ($MgSO_4$). V.p.s. showed the organic layer to be overwhelmingly one product, i.e. $CF_2ClCFClCH{=}CF_2$.

Physical properties of $CF_2ClCFClCH{=}CF_2$ (a sample was purified by preparative v.p.c.) b.p. 68.5°/630 mm.; n_D^{25} 1.3524; d^{25} 1.5323. The infrared spectrum displayed peaks at 3100 (w), 1740 (s), 1450 (s) cm^{-1}. Elemental analysis calculated for $CF_2ClCFClCH{=}CF_2$: C, 22.35; H, 0.47; Cl, 32.99; F, 44.20. Found: C, 22.47; H, 0.56; Cl, 32.75; F, 44.49.

Dechlorination of $CF_2ClCFClCH{=}CF_2$

$CF_2ClCFClCH{=}CF_2$ (25 g., 0.12 mole), Zn dust (16 g., 0.025 mole), and dioxan (50 ml.) were stirred under gentle reflux conditions. The product (9 g.) was allowed to distill off. The infrared spectrum of the product was identical to one displayed in the literature[3] for $CF_2{=}CF{-}CH{=}CF_2$.

Addition of ICl to $CF_2{=}CH_2$

$CF_2{=}CH_2$ was bubbled slowly through a solution of ICl (500 g.) in CH_2Cl_2 (200 ml.) until no further uptake of the olefin took place. The solution was washed with sodium thiosulphate solution, water and dried ($MgSO_4$). Fractional distillation of the products gave (1) CH_2Cl_2; (2) mixture 22 g.; (3) b.p. 91°/629 mm. 511 g. of CF_2ClCH_2I; n_D^{25} 1.4613; d^{25} 2.1347. Absorption in the ultraviolet region occurred at λ2630Å(ε 543), which is consistent for a $-CH_2I$ group ($-CF_2I$ λ2710Å and $R_f{-}CH_2I$ λ 2620Å). Elemental analysis calculated for $C_2H_2ClF_2I$: C, 10.61; H, 0.89; Cl 15.66; F, 16.78; I, 56.05. Found: C, 10.75; H, 0.73; Cl, 14.15; F, 17.92; I, 52.64%.

Addition of CF_2ClCH_2I to $CH_2{=}CH_2$

CF_2ClCH_2I (276 g., 1.12 m.), $CH_2{=}CH_2$ (35 g., 1.25 m.) and benzoyl peroxide (9 g., 0.04 m.) were selaed in 1-l. stainless steel bomb and shaken for 24 hours at 150°. The contents of the bomb were poured out, washed with sodium thiosulphate solution and water, dried ($MgSO_4$), and were then fractionally distilled through a vacuum jacketed column (1' X 1/2") packed with helices. The following fractions were obtained:
(1) Unchanged CF_2CH_2I (71 g.); 90-91°; (2) mixture 20 g.; 90-152°;
(4) suspected $CF_2Cl(CH_2)_3I$ (87 g.); 110°/150 mm.; (5) $CF_2Cl(CH_2)_3I$ and high boilers (3 g.); 110-125°/150 mm.
Physical properties of $CF_2Cl(CH_2)_3I$ are b.p. 110°/150 mm.; n_D^{25} 1.4733; d^{25} 1.8650. Absorption in the ultraviolet region occurred at 2580Å(439) This is consistent for a $R{-}(CH_2)_2I$ group. A sample has been submitted for elemental analysis.

Dechlorination of $CF_2ClCFClCH_2CF_2CF_2CH_2CFClCF_2Cl$ with zinc in dioxan was carried out and $CF_2=CF-CH_2CF_2CF_2CH_2CF=CF_2$ and $CF_2ClCFClCH_2CF_2CF_2CH_2CF=CF_2$ were obtained in yields of 16.5 and 31.5%, respectively. Dechlorination of $CF_2ClCFClCH_2CF_2CF_2CH_2CF=CF_2$ also gave the diene, $CF_2=CFCH_2CF_2CF_2CH_2CF=CF_2$, in yields of 27.5%. A sample (12 g.) of this diene was sent for polymer evaluation.

It had been proposed to dehydrochlorinate $CF_2ClCFClCH_2CF_2CF_2CH_2CFClCF_2Cl$ to give the following compounds, $CF_2Cl-CF=CH-CF_2CF_2-CH=CF-CF_2Cl$ and $CF_2ClCFClCH_2CF_2CF_2-CH=CF-CF_2Cl$, but the reaction of $CF_2ClCFClCH_2CF_2CF_2CH_2CFClCF_2Cl$ with aqueous potassium hydroxide gave a black tar.

Earlier reports[1] described the preparation of $CF_2BrCH_2CF_2Br$ and $CF_2BrCH_2CF_2CH_2CF_2Br$ from the telomerization of CF_2Br_2 and $CF_2=CH_2$. Combination of the high-boiling products from a number of such telomerizations enabled the next telomer, $CF_2BrCH_2CF_2CH_2CF_2CH_2CF_2Br$, to be isolated. This heptane was dehydrobrominated with aqueous potassium hydroxide to give $CF_2=CHCF_2CH_2CF_2CH=CF_2$ and $CF_2=CHCF_2CH_2CF_2CH_2CF_2Br$ in yields of 27 and 20.5% respectively. Dehydrobromination of $CF_2=CHCF_2CH_2CF_2CH_2CF_2Br$ gave more of the diene, $CF_2=CHCF_2CH_2CF_2CH=CF_2$, in yields of 51%. Two samples of this diene were sent for polymer evaluation.

Earlier reports[2] described the preparation of $CF_2=CHCF_2Br$ from $CF_2BrCH_2CF_2Br$. The treatment of $CF_2=CH-CF_2Br$ with KI in acetone gave small yields of $CF_2=CHCF_2I$. A red treacle, formed in the reaction vessel, appeared to consume most of the product. Insufficient $CF_2=CHCF_2I$ was prepared to enable the coupling of two molecules by the elimination of iodine to give $CF_2=CHCF_2CF_2CH=CF_2$.

It was previously reported that the addition of $CF_2ClCFClI$ to $CF_2=CFH$ gave two products, $CF_2ClCFClCFHCF_2I$(A) and $CF_2ClCFClCF_2CFHI$(B). Tarrant[4] had earlier declared that the sole products of this reaction was (A) and on this basis it was proposed to use (A) to give $(CF_2ClCFClCFHCF_2-)_2$ by coupling two molecules of (A) with mercury and UV light. Dechlorination and dehydrochlorination of $(CF_2ClCFClCFHCF_2-)_2$ would both give a monoene and a diene. Unfortunately, the separation of the mixture (A) and (B) was difficult. Fractional distillation would not effect a separation and preparative gas chromatography required repeated separations to give small quantities of pure (A) and (B). This line of investigation was not pursued any further.

EXPERIMENTAL

Dechlorination of $(CF_2ClCFClCH_2CF_2-)_2$ - $CF_2ClCFClCH_2CF_2CF_2CH_2CFClCF_2Cl$ (100 g., 0.23 mole), zinc dust (40 g., 0.62 mole) and p-dioxan (75 ml.) were stirred at reflux temperatures for 2-1/2 days. The sludge of zinc and zinc chloride was filtered off and the filtrate was washed with water to remove the p-dioxan. However, an emulsion was formed with the filtrate, so the organic products were extracted with ether (100 ml. x 5). The emulsion of the aqueous layer was filtered off and an unidentified cream powder (1 g.) was obtained. The ethereal layer was dried ($MgSO_4$) and fractionally distilled through a column (6" X 1") packed with glass helices. The fractions were separated into 6 pure components by preparative gas chromatography: (1) ether; (2) trace of an unidentified compound; (3) $CF_2{=}CFCH_2CF_2CF_2CH_2CF{=}CF_2$ (8 g. 16.5% yield) b.p. 119°/617 mm. n_d^{25} 1.3281; d^{25} 1.5282. (Found: C, 33.01; H, 1.50; F, 62.26. Calc. for $C_8H_4F_{10}$: C, 33.13; H, 1.39; F, 65.51%.) Infrared spectroscopy showed peaks at 2970 (w), and 1804 (s) cm^{-1}; (4) Trace of p-dioxan; (5) $CF_2{=}CF\text{-}CH_2CF_2CF_2CH_2CFClCF_2Cl$ (19 g. 31.5% yield); b.p. 164.5°/623 mm. n_d^{25} 1.3569; d^{25} 1.6243 (Found: C, 26.42; H, 1.23; Cl, 19.44; F, 52.33. Calc. for $C_8H_4Cl_2F_{10}$: C, 26.63; H, 1.12; Cl, 19.64; F, 52.64%); Infrared spectroscopy displayed peaks at 3000 (w) and 1804 (s) cm^{-1}. (6) Unreacted starting material (28 g.)

Dechlorination of $CF_2{=}CFCH_2CF_2CF_2CH_2CFClCF_2Cl$. - $CF_2{=}CFCH_2CF_2CF_2CH_2$-$CFClCF_2Cl$ (33.5 g., 0.093 mole), zinc dust (16 g., 0.25 mole), zinc chloride (1 g.) and p-dioxan (100 ml.) were stirred at reflux temperatures for 3 days. The solid residue was filtered off and the filtrate was added to water (300 ml.). However, an emulsion was formed with the filtrate, so the organic products were extracted with ether (100 ml. x 5). The emulsion in the aqueous layer was filtered off and a cream-colored solid (0.2 g.) was obtained. The ethereal extracts were washed with water to remove more p-dioxan, dried ($MgSO_4$) and the ether was distilled off. The residue (18 g.) was separated by preparative gas chromatography to give: (1) $(CF_2{=}CF\text{-}CH_2CF_2\text{-})_2$ (6 g., 27.5% yield) identified by infrared spectroscopy; (2) p-dioxan (0.5 g.); (3) unreacted starting material (6.2 g.).

Attempted dehydrochlorination of $(CF_2ClCFClCH_2CF_2\text{-})_2$. - $CF_2ClCFCl$-$CH_2CF_2CF_2CH_2CFClCF_2Cl$ (51 g., 0.12 mole), KOH (30 g., 0.54 mole) and water (100 ml.) were stirred at reflux temperature for 16 hours. Analytical gas Chromatography after 2 hours of the organic layer showed the presence of a new compound in small yields. However, after the full 16 hours only a black tar remained below the aqueous layer.

Dehydrobromination of $CF_2BrCH_2CF_2CH_2CF_2CH_2CF_2Br$. - $CF_2BrCH_2CF_2$-$CH_2CF_2CH_2CF_2Br$ (96 g., 0.24 mole) was added to a solution of KOH (32 g., 0.57 mole) in water (100 ml.) and the mixture was stirred and refluxed for 12 hours. The organic layer was separated from the aqueous layer and a fresh solution of KOH (32 g.) in water (100 ml.) was used for a futher reflux of 16 hours. The products were distilled from the mixture, washed with water, dried ($MgSO_4$), and then they were fractionally distilled through a column (6" X 1") packed with glass helices giving the following fractions:

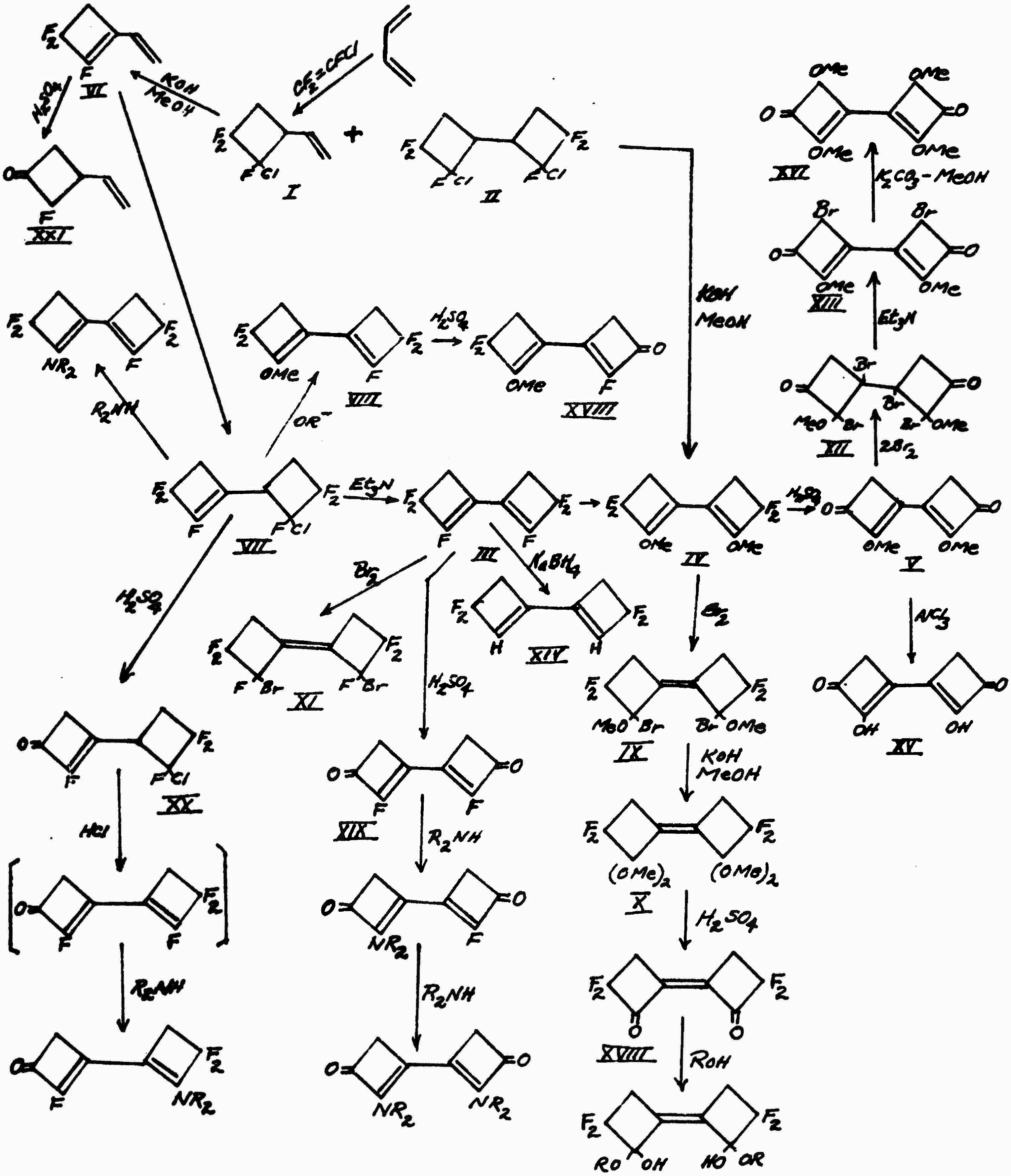
1) 80-104°/623 mm.	3 g.	peaks on v.p.c. (i) and (ii)
2) 105°/623 mm.	12 g.	peak (ii), $CF_2{=}CHCF_2CH_2CF_2CH{=}CF_2$
3) 105-152.5/623 mm.	4.2 g.	peaks (ii), (iii) and (iv)
4) 152.5/623 mm.	10 g.	peak (iv) $CF_2BrCH_2CF_2CH_2CF_2CH{=}CF_2$
5) Undistilled	10 g.	peak (iv) and unchanged starting material

Separation of fraction (1) and (3) by preparative gas chromatography gave 2 g. of peak (ii) and 3.8 g. of peak (iv).

B.) The Chemistry of Bicyclobutenyl Derivatives

Figure 1.

Synthetic Pathways in the Bicyclobutyl ("Dibox") Series



Combined fractions of peak (ii) $CF_2=CHCF_2CH_2CF_2CH=CF_2$, (14 g. 27% yield) had the following properties: b.p. 105°/623 mm., n_d^{25} 1.3334; d 1.4645. The infrared spectrum displayed peaks at 3100 (w), 2970 (w) and 1760 (s) cm^{-1}. Elemental analysis found: C, 34.80; H, 1.90; F, 63.45. Calc. for $C_7H_4F_8$: C, 35.02; H, 1.67; F, 63.30%.

Combined fractions of peaks (iv), $CF_2BrCH_2CF_2CH_2CF_2CH=CF_2$, (14 g., yield 29.5%) had the following properties, b.p. 152.5°/623 mm., n_d^{25} 1.3694; d^{25} 1.7297. The infrared spectrum displayed peaks at 3100 (w), 2970 (w), and 1745 (s) cm^{-1}. (Elemental analysis found: C, 25.95; H, 1.57; Br, 25.05; F, 47.46. Calc. for $C_7H_5BrF_8$: C, 26.19; H, 1.57; Br, 24.89; F, 47.33%).

Dehydrobromination of $CF_2BrCH_2CF_2CH_2CF_2CH=CF_2$. - $CF_2BrCH_2CF_2CH_2CF_2CH=CF_2$ (14 g., 0.045 mole) was added to a solution of KOH (30 g., 0.54 mole) in water (100 ml.) and the mixture was stirred under reflux for 2 days. The organic products were distilled from the mixture, washed with water, and dried ($MgSO_4$). Separation of the organic product by preparative gas chromatography gave:

(1) $CF_2=CHCF_2CH_2CF_2CH=CF_2$ (4.2 g., 51% yield)
(2) Unreacted $CF_2BrCH_2CF_2CH_2CF_2CH=CF_2$ (3.0 g.)

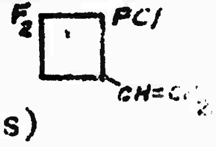
The product and the unchanged material were identified by infrared spectroscopy.

Attempted preparation of $CF_2=CHCF_2I$. - $CF_2=CFCF_2Br$ (42 g., 0.22 mole), KI (50 g., 0.33 mole) and acetone were refluxed for 7 days under a condenser cooled to -78°. The liquid contents were then poured into a flask containing more KI (50 g.) and were refluxed for a further 3 days. The products and the acetone were removed by distillation from the red-brown solution leaving behind a red treacle with the KI and KBr. The acetone was removed by washing with water and the organic layer (5 g.) was separated by a separating funnel. Analytic gas chromatography showed the presence of two compounds $CF_2=CH-CF_2Br$ and presumably $CF_2=CH-CF_2I$.

-The following section deals with the chemistry of the Bicyclobutenyl Derivatives.

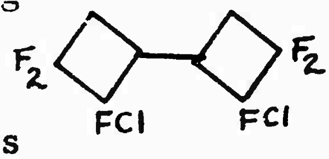
EXPERIMENTAL SECTION

Cycloaddition of 1,3-butadiene with trifluorochloroethylene (1 mole):



A two-liter steel bomb containing 5 ml. of limonene as inhibitor was cooled in a dry ice/acetone bath for several hours and then charged with 330 g. (2.9 moles) of trifluorochloroethylene and 150 g. (2.78 moles) of butadiene. This was heated under autogenous pressure in a shaker at 150° for 24 hours and at 175° for an additional 24 hours. On cooling, bleeding off excess gases, and opening, 412 g. of liquid product was obtained, plus a considerable amount of solid material. On distillation, 350 g. (75%) of the 1-vinyl-2,3,3-trifluoro-2-chlorocyclobutane (I) was obtained boiling 108.5-109.0°/630 mm. The distillation residue was placed in a refrigerator at -20° for two weeks, at which time 15 g. of colorless crystalline material was filtered in the cold (-15°). The crystals melted at 49-60° and were identified as 2,2-dichloro-2,2',3,3,3',3'-hexafluorobicyclobutyl (II). The product was dissolved in hot ethanol (50 ml), decolorized twice with charcoal and water added to the boiling solution. The clear solution on cooling yielded colorless needles m.p. range 57-67°.

Cycloaddition of butadiene with trifluorochloroethylene (2 moles):



A one-half liter stainless steel bomb containing 2 ml. limonene was chilled in a dry-ice/acetone bath and then charged with 270 g. (2.28 moles)of trifluorochloroethylene and 60 g. (1.1 mole) of butadiene. The bomb was then heated under autogenous pressure at 100° for 4 hours, 140° for 28 hours, and 170° for 28 hours. On cooling the bomb, bleeding off gases, and opening, 330 g. of crude liquid product were obtained. Distillation yielded 162.5 g. of 1,2,3,3,4,4-hexafluoro-1,2-dichlorocyclobutane, b.p. 54-55°/630 mm.; and about 75 g. of distillation residue. The residue was diluted with 20 ml. ethanol and cooled to -20° for two days at which time the solid which separated was filtered in the cold (-15°). About 60 g. of 2,2'-dichloro-2,2',3,3,3',3'-hexafluorobicyclobutyl (II) was thus obtained (17-20% yield). This was recrystallized from ethanol-water mixture, m.p. 65-67°. An analytical sample was prepared by two recrystallizations from an ethanol-water mixture.

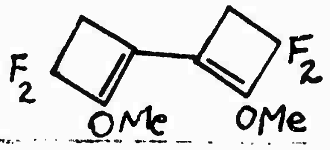
Anal. Calcd. from $C_8H_6F_6Cl_2$: C, 33.5; H, 2.09; Cl, 24.7; F, 39.7.
Found: C, 33.09; H, 2.06; Cl, 22.88; F, 38.38.

Vapor-phase chromatography of compound II on a highly polar adsorbent (Fluorocarbon FS on Firebrick R) gave three peaks in the ratios 1.0:1.3:1.0. These peaks correspond to the three types of stereoisomers: the cis-cis isomers (F with respect to adjacent H), the trans-cis isomers, and the trans-trans isomers. The compound gave distinctive infrared peaks at 2930 and 1420 cm^{-1}. Nuclear magnetic resonance showed a very complex splitting pattern.

Cycloaddition of 1-vinyl-2-chloro-2,3,3-trifluorocyclobutane (I) with trifluorochloroethylene.

A one-half liter stainless steel bomb containing 175 g. (1.12 moles) of I and 1 ml. of limonene was cooled and charged with 135 g. (1.16 moles) of trifluorochloroethylene. It was then heated at 160° for 25 hours. On cooling the bomb, bleeding off the gases, and opening, 267 g. of liquid product was obtained. The product was not worked up in the usual manner (see above), but rather analyzed by vapor phase chromatography, which showed 16 parts of trifluorochlorethylene dimer (50% of original CF_2:CFCl); 36 parts of I (86% recovery); 7 parts of II (10% yield); and 5 parts of an unidentified higher retention product.

2,2'-Dimethoxy-3,3,3'3'-tetrafluorobicyclobutenyl (IV).

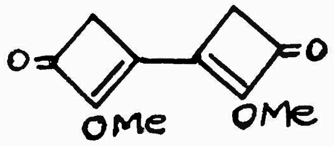


About 2.78 g. (.0097 mole) of 2,2'dichloro-2,2',3,3,3',3'-hexafluorobicyclobutyl (II) was dissolved in 20 ml. of methanol and to this

solution was added a solution of 3.0 g. (0.053 moles) of potassium hydroxide in 15 ml. of methanol. This was then heated over a steam bath to slow reflux for 15 minutes. The yellow-orange fluid was filtered hot and crystals which formed in the funnel were washed through with hot methanol. The solute was concentrated in vacuo and allowed to cool and crystallize. Pale yellowish needles (1.10 g.) m.p. $98-99^{\circ}$ were obtained. A second crop yielded 0.2 g. of IV making a yield of 56%. The diether IV was further purified by treatment with activated charcoal and recrystallization from an alcohol-water mixture to give colorless needles, m.p. 101°C. Ultraviolet spectrum: max= 2700 A(E=18,000). Infrared spectrum: bands at 1440, 1620, and 2990 cm^{-1}. The n.m.r. spectrum showed a $-CH_2$-split by an adjacent $-CF_2$- in addition to a $-OCH_3$ singlet.

Anal. Calcd. for $C_{10}H_{10}F_4O_2$: C, 50.4; H, 4.20; F, 31.9
Found: C, 50.20; H, 4.44; F, 31.62

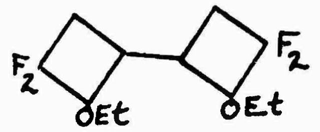
2,2'-Dimethoxy-3,3'-diketobicyclobutenyl (V).



Approximately 2.0 g. (0.0075 mole) of the diether IV as prepared above was added with stirring to 10 ml. of concentrated sulfuric acid. When the solid had dissolved, 5 ml. of cold water was added slowly dropwise with stirring, care being taken to avoid severe overheating. The resulting brownish solution was poured into 100 ml. of cold water. A yellow solid immediately precipitated. After the addition, the yellow solid was filtered off and washed with water. Typical yields of (V) were 1.2-1.5 g. (85-100% yield). The diketone was conveniently recrystallized from hot toluene or hot aqueous ethanol. The former was a better solvent. Yellow needles were thus obtained, m.p. 203°. Ultraviolet spectrum: max=3650 A(E=13,000). Infrared spectrum: bands at 1277, 1580, and 1730 cm^{-1}. The n.m.r. spectrum showed two single peaks for $-OCH_3$ and for $-CH_2-CO-$.

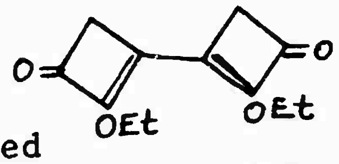
Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.9; H, 5.16
Found: C, 61.9; H, 5.40

2,2'-Diethoxy-3,3,3',3'-tetrafluorobicyclobutenyl (IVa).



Exactly 2.78 g. (0.0097 mole) of II was dissolved in 25 ml. absolute ethanol and to this was added a solution of 3.0 g. (0.053 mole) of potassium hydroxide in 20 ml. of ethanol. This mixture was heated to reflux for ten minutes and turned orange. It was then filtered to remove the salts. The filtrate was concentrated to half its original volume by heating under vacuum. The concentrated solution was poured into cold water (100 ml) and extracted with oen 25 ml. portion of the same solvent. The chloroform extracts were dried over anhydrous potassium carbonate and evaporated in vacuo. A red liquid (about 1.2 g.) (50 % yield) was obtained. This crystallized readily upon refrigeration and melted readily on warming. The material was heated in alcohol with activated charcoal, allowed to recrystallize at -20° and filtered in the cold. After two such recrystallizations, white crystals were obtained melting at 32.3°. The crude liquid product was of sufficient purity for subsequent steps. Infrared spectrum: bands at 1440, 1620, and 2960 cm^{-1}. No microanalysis was performed since the product darkened rapidly on standing.

2,2'-Diethoxy-3,3'-diketobicyclobutenyl (Va)



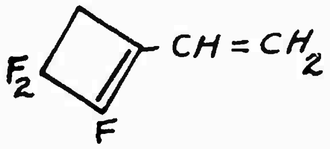
The diethoxy diketone (IVa) was prepared by the same procedure as the corresponding dimethoxy compound (IV). Recrystallization from hot alcohol/water yielded bright-yellow needles m.p. 118-119°. Typical yields were 80%. Ultraviolet spectrum: max 3650Å(E 12,670). Infrared spectrum: peaks at 1260, 1580, and 1730 cm^{-1}. The n.m.r. spectrum showed an unsplit methylene for-CH_2-CO and the expected series of peaks for -O-CH_2-CH_3.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.3.
Found: C, 65.23; H, 6.64.

Attempt to prepare the di-tert-butyl diether.

Two grams of lithium metal ribbon were dissolved in 10 mls. of hot tert-butyl alcohol. This solution was added at once to a solution of 2.87 g. 2,2',3,3,3',3'-hexafluoro-2,2'-dichlorobicyclobutyl (II) in 40 ml. tert-butyl alcohol. The resulting mixture was refluxed 20 hours and then cooled. Colorless crystals were observed but these seemed unfilterable (the solvent always froze in the filter funnel). The liquid was poured into water and extracted twice with chloroform. The extracts were dried over sodium sulfate and then evaporated *in vacuo*. The resulting red liquid gave an infrared spectrum similar to that of the dimethyl and diethyl ethers of IV and IVa. The material dissolved in concentrated sulfuric acid to give an intense red-orange color. No solid product was obtained on pouring the acid solution over ice, and the aqueous solution did not give a positive enol test with ferric chloride.

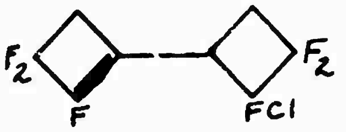
1-Vinyl-2,3,3-trifluoro-1-cyclobutene (VI).



About 34.0 g. (0.20 mole) of 1-vinyl-2,3,3-trifluoro-2-chlorocyclobutane (I) was dissolved in 50 ml. of absolute methanol. A solution of 13.0 g. of potassium hydroxide (0.23 mole) in 50 ml. methanol was added dropwise with stirring and cooling. The temperature was maintained at 10-20° throughout the addition. After the addition, the temperature was allowed to rise to 25-30° for one-half hour and then the mixture was heated to reflux for ten minutes. It was then poured into 500 ml. of cold water in a separatory funnel. After shaking, the product which separated to the bottom was removed. After drying over anhydrous calcium chloride, 20-25 g. (80-90%) of crude straw-colored liquid VI was obtained. (Additional small amounts could be obtained by extracting the aqueous phase with chloroform.) Fractional distillation under reduced pressure yielded 1-vinyl-2,3,3-trifluoro-1-cyclobutene (VI) boiling 44.0°/174 mm., n_D^{25} 1.3971. Freshly distilled samples were found to polymerize very readily to a hard, clear, and colorless solid. The crude material can be stored for several weeks at -20° in the presence of inhibitors (e.g., hydroquinone and t-butylcatechol). The infrared spectrum contained significant peaks at 1370, 1460, and 1720 cm^{-1}.

Anal. Calcd. for $C_6H_5F_3$: C, 53.5; H, 3.73; F, 42.5.
Found: C, 53.2; H, 4.06; F, 42.1.

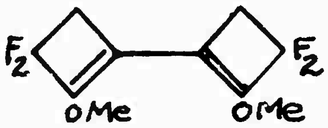
1-(2,3,3-Trifluoro-2-chlorocyclobutyl-)-2,3,3-trifluorocyclobutene (VII).



About 186 g. (1.37 mole) of 1-vinyl-2,3,3-trifluoro-2-cyclobutene (VI) (freshly prepared by the previous method, dried over magnisium sulfate, but not distilled) was placed in a one-half liter stainless steel bomb along with 1 g. of hydroquinone and about 2 ml. of limonene. The bomb was sealed, checked for leaks, chilled in dry ice, evacuated, and the 190 g. (1.63 moles) of trifluorochloroethylene bled in. It was then heated in a heater-shaker at 150° for 5 1/2 hours. On cooling and opening the bomb, 316 g. of an orange liquid was obtained. Vapor phase chromatography showed the absence of diolefin VI, the presence of a small amount of trifluorochloroethylene and its dimer, and a high proportion of the desired product VII. Distillation at atmospheric pressure gave 255 g. (75%) of a colorless liquid boiling at 160°/630 mm. D_{25}^{25}=1.4676, n_D^{25}= 1.3910. The infrared spectrum contained significant bands at 1440, 1650 (wk).), and 1720 cm^{-1}.

Anal. calcd. for $C_8H_5ClF_6$: C, 38.3; H, 2.00; F, 45.5
Found: C, 38.52; H, 1.83; F, 45.70.

2,2'-Dimethoxy-3,3,3',3'-tetrafluorobicyclobutenyl (IV) Best Method.

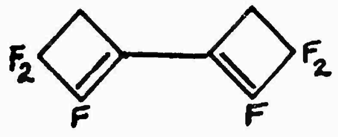


Potassium hydroxide 140 g. (2.5 moles) was dissolved in 500 ml. absolute methanol in a 1 liter 3-neck flask equipped with an ice bath, reflux condenser, thermometer and stirrer. To this was added slowly by means of an addition funnel 150 g. (.6 mole) of VII while the temperature was kept below 30° (the reaction is very exothermic). After the addition, heat was applied and the temperature allowed to rise slowly to 60°. It was then thrown into a large volume of ice water with vigorous stirring. The product precipitated and was filtered and washed with several large portions of cold water. After pumping the product dry and drying the solid overnight in a roto-vac 140 g. (approximately 98% yield) of diether IV (m.p. 99°) was obtained of sufficient purity for subsequent reactions. The infrared spectrum was identical with that of IV prepared from II. On hydrolysis with sulfuric acid, it yielded diketone Va identical to that described earlier.

2,2'-Diethoxy-3,3,3',3'-tetrafluorobicyclobutenyl (IVa) Method B.

To a solution of 3.16 g. of VII (0.0126 mole) in 10 ml. of ethanol was added dropwise 20 ml. of a 10% solution of potassium hydroxide in ethanol. The reaction was vigorous. After the initial reaction, the mixture was warmed slightly for five minutes. The solution was filtered and the filtrate concentrated to half its original volume. The solution was poured into water, extracted with two 15 ml. portions of dichloromethane. The extracts were dried over anhydrous magnesium sulfate and the solvent then stripped off *in vacuo* to yield 2.70 g. of straw-colored liquid (80%) yield). The infrared spectrum was identical to that prepared directly from II.

2,2'3,3,3',3'-Hexafluorobicyclobutenyl (III).

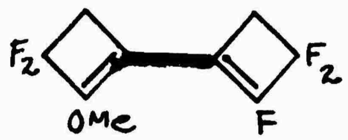


A. About 25 g. (0.10 mole) of VII was dissolved in 100 ml. of absolute ethanol, and the solution cooled in an ice-water bath. Slowly with stirring and cooling 56 ml. of 10 g./100 ml. solution of potassium hydroxide was added to this. Precipitation occurred immediately. After the addition, the solution was allowed to warm to 25°, and then poured into a separatory funnel with 500 ml. of water. On separation of the organic layer, much of the material solidified requiring a heat lamp to remove it. This material was allowed to solidify somewhat and then filtered with mild suction. This yielded 7.8 g. of crude III, melting 50-55°. The filtrate was also found to be very rich in III along with monoether VIII. The following method was found to be best for obtaining III.

B. Fifty ml. (36 g., 0.35 mole) of triethylamine were cooled to -20° and mixed with similarly chilled compound VII (50.0 g., 0.20 mole). The mixture was swirled several minutes and then allowed to set overnight in a refrigerator at 0°C. The solid was then broken up and washed with water. Hydrochloric acid (10 ml. 20%) was added to dissolve the excess amine. The solid was filtered off with gentle vacuum (caution--this material has a very high vapor pressure) and washed with a large volume of ice water. The crystalline solid was placed on filter paper and pressed to remove excess water. It was redissolved in hot Skellysolve B and the solution dried over anhydrous magnesium sulfate. The dried and filtered solution was then chilled overnight at -20°. The hexafluorobicyclobutenyl (III) separated as colorless, dense plates. The yield was 32.3 g. (76%), m.p. 57°. The ultraviolet spectrum consisted of one peak at 2375 A (E=8,330). The infrared spectrum contained significant peaks at 1340 and 1655 cm^{-1}. The n.m.r. spectrum was in accord with a $-CH_2-$split by cross ring $-CF-$; and resplit by adjacent $-CF_2-$.

Anal. Calcd. for $C_8H_4F_6$: C, 44.9; H, 1.87; F, 53.3.
Found: C, 44.51; H, 1.98; F, 53.02.

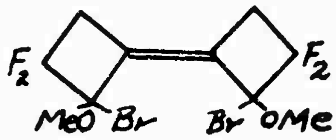
2-Methoxy-2'3,3,3',3'-pentafluorobicyclobutenyl (VIII).



A solution of VII 25.0 g. (0.10 mole) in 100 ml. absolute methanol was cooled to 0° and a solution of 12.0 g. (0.214 mole) potassium hydroxide in 100 ml. absolute methanol was added dropwise slowly with stirring and cooling (0.10°). After the addition, the ice bath was allowed to warm to room temperature and the following day the reaction was poured into 700 ml. ice water and the organic layer allowed to separate. The lower layer was dried over calcium sulfate. The crude monoether VIII amounted to 19.63 g. (87%) and was of relatively high purity according to the vapor phase chromatogram. The refractive index at 26° was 1.4270. The infrared spectrum contained significant peaks at 2980, 1710, 1640, and 1348 cm^{-1}.

Anal. Calcd. for $C_9H_7F_5O$: C, 47.7; H, 3.10; F, 42.0.
Found: C, 47.47; H, 3.10; F, 41.79.

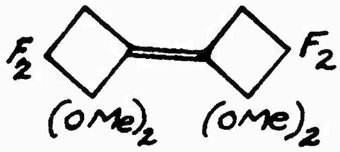
2,2'-Dibromo-2,2'-dimethoxy-3,3,3',3'-tetrafluorobicyclobutylidene (IX).



A solution of bromine, 26.4 g. (.165 mole) in 50 ml. glacial acetic acid, was added in portions with stirring to a solution of diether IV 36.5 g. (.155 mole) in 100 ml. glacial acetic acid and the mixture was stirred for ten minutes and then poured over 500 ml. ice in a large flask with vigorous shaking. A yellowish solid quickly separated. Sodium bisulfite solution was added to remove the bromine color. The solid (now white) was then filtered off, washed and pumped dry. White waxy powder IX 63 g. (c. 100%) was obtained. The product is purified sufficiently for the next step or can be recrystallized from hot Skellysolve C. The recrystallized product melted at 106-107°. The infrared spectrum contained strong characteristic peaks at 720, 812, 881, and 989 cm^{-1} and lacked peaks in the olefinic region as would be expected for a symmetrically tetrasubstituted olefin.

Anal. Calcd. for $C_{10}H_{10}Br_2F_4O_2$: C, 30.3; H, 2.53; Br, 40.0; F, 19.4.
Found: C, 30.50; H, 3.06; Br, 39.70; F, 20.62.

2,2,2',2'-Tetramethoxy-3,3,3',3'-tetrafluorobicyclobutylidene (X).



Dibromide IX (as prepared above) 63 g. (.155 mole) was dissolved in 150 ml. absolute methanol and to this was added slowly with stirring and cooling a solution of 17 g. (.30 mole) potassium hydroxide in 50 ml. absolute methanol. After the addition, stirring was continued for 10 minutes and the mixture poured over ice. A creamy white, fluffy precipitate formed which was filtered and washed with water. After pumping dry for 30 minutes, 37 g. crude tetra-ether X (ca. 80%) was obtained. This was purified further by recrystallization from hot Skellysolve C to give 30 g. of colorless plates m.p. 122°. The crude product can be used as is for the preparation of diketone XVII. The infrared spectrum had strong characteristic peaks at 716, 749, 878, 1007, and 1310 cm^{-1}. The proton n.m.r. spectrum showed a strong singlet for $-OCH_3-$ and two separate close triplets for $-CH_2-CF_2-$ in cis and trans configurations.

Anal. Calcd. for $C_{12}H_{16}F_4O_4$: C, 48.0; H, 5.33; F, 25.3.
Found: C, 47.78; H, 5.71; F, 26.39.

2,2'-Dimethoxy-1,1',2,2'-tetrabromo-3,3,3',3'-tetrafluorobicyclobutyl Attempt.

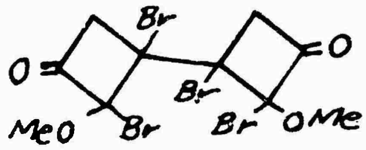
Crude 2,2'-dimethoxy-3,3,3',3'-tetrafluorobicyclobutenyl (IV) 12 g. (0.06 mole) was dissolved in 100 ml. methylene chloride and the solution dried over anhydrous magnesium sulfate. After filtering, bromine 22.5 g. (0.14 mole) diluted with methylene chloride was added at once and the mixture allowed to set overnight. The solvent and excess bromine was stripped *in vacuo* to give a yellowish viscous fluid which could not be crystallized. The material was quite unstable and darkened on standing. The infrared spectrum contained two olefinic peaks. The instability of the material limited full characterization.

Bromination of 2,2'3,3,3',3'-hexafluoro-bicyclobutenyl (III).

Bromine 39 g. (0.244 mole) and diene III 21.4 g. (0.1 mole) were dissolved in 100 ml. of methylene chloride and left in a stoppered flask for eight days at which time it was stripped in a roto-vac to give about 40 g. of pale yellowish viscous liquid. The infrared spectrum of the crude mixture showed an absorption at 1720 (vinylic fluorine). On standing several weeks colorless crystals had separated. These were filtered off and washed with cold Skellysolve F; the 2,2',-dibromo-2,2',3,3,3',3'-hexafluorobicyclobutilydene XI obtained amounted to 10 g. and melted at 97-98°. The infrared spectrum was quite similar to that of the crude material but lacked absorption in the olefinic region. Major significant peaks were at 1390, 1290, 1220, 900, and 717 cm^{-1}. The filtrate is considered to be a mixture of the two isomeric dibromides (1,2-dibromo and 2,2'-dibromo).

Anal. Calcd. for $C_8H_4Br_2F_6$: C, 25.7; H,1.07; Br, 42.5.
Found: C, 26.00; H, 1.00; Br, 41.17.

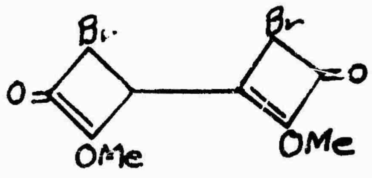
1,1',2,2'-Tetrabromo-2,2'-dimethoxy-3,3'-diketobicyclobutyl XII.



In a clean dry 500 ml. Erlenmeyer flask was placed 19.4 g. (0.1 mole) of 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (V) and 150 ml. methylene chloride with shaking to dissolve the solid. To this was added with swirling 40.0 g. (0.25 mole) of bromine diluted in methylene chloride. The mixture was shaken until solution was complete. It was then set near an ultraviolet lamp for two hours at which time colorless crystals of tetrabromide had formed. The solution was concentrated by stripping most of the solvent. Skellysolve F (300 ml.) was added and the white solid filtered and washed with Skellysolve. Forty-three grams of a white product XII, m.p. 145° dec., was thus obtained making the yield 85%. An analytical sample was prepared by recrystallization from methylene chloride-petroleum ether. The infrared spectrum had strong characteristic peaks at 1800, 1270, 1000, and 719 cm^{-1}. The material loses hydrogen bromide on standing in a bottle.

Anal. Calcd. for $C_{10}H_{10}Br_4O_4$: C, 23.4; H, 1.95; Br, 62.3.
Found: C, 23.42; H, 2.02; Br, 62.05.

2,2'-Dimethoxy-3,3'-diketo-4,4'-dibromobicyclobutenyl XIII.



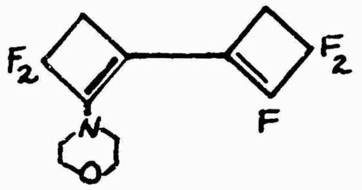
In a 250 ml. round-bottomed flask equipped with a mechanical stirrer, reflux condenser, thermometer and addition funnel, 10.0 g. (0.02 mole) of 1,1',2,2'-tetrabromo-2,2'-dimethoxy-3,3'-diketobicyclobutyl XII was dissolved in 200 ml. dry benzene. Triethylamine 4.0 g. (0.04 mole) in 20 ml. of benzene was added dropwise keeping the temperature below 40°. After the addition, the flask was warmed to reflux for 40 minutes, and then filtered hot to give 7.8 g. of dull gray salts. The salts were extracted to give 1.1 g. of black, water-insoluable solid. The filtrate was concentrated *in vacuo* to about 50 ml. Skellysolve F (150 ml.) was then added and the solution chilled to -15° for several hours. The product XIII was then filtered as a yellowish crystalline solid 6.5 g. (90%) melting at 130° dec. The infrared spectrum contained strong characteristic peaks at 1740, 1590, 1280, 993, and 727 cm^{-1}. (The spectrum was relatively simple and very similar to that of 2,2'-dimethoxy-3,3'-diketobicyclobutenyl).

Anal. Calcd. for $C_8H_8Br_2O_4$: C, 34.2; H, 2.37; Br, 45.4.
Found: C, 34.51; H, 2.40; Br, 45.14.

Addition of bromine (1 mole) to 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (V).

Bromine 4.95 g. (0.031 mole) and diketone V 6.0 g. (0.031 mole) were dissolved together in 100 ml. methylene chloride and allowed to set for two hours. The solvent was then stripped off and the solid washed with Skellysolve F. It was found to be a mixture of starting material and bromides. The infrared spectrum of the bromide mixture showed the major peaks of the tetrabromide along with strong peaks 1650, 1760 cm^{-1} consistnet with the assignment 1'-(1,2-dibromo-2,methoxy-3-keto-cyclobutyl)-2'methoxy-3'keto-cyclobutene. The material was very unstalbe quickly losing hydrogen-bromide on standing and reacting with moisture to give water soluble yellow tars.

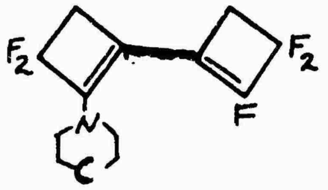
2-(N-Morpholino-)2',3,3,3',3'-pentafluorobicyclobutenyl.



In a 250 ml. flask equipped with a stirrer, reflux condenser, and addition funnel was placed 38.0 g. (0.43 mole) morpholine and 100 ml. dioxane. To this was added dropwise with cooling 25.0 g. (0.10 mole) 1-(2,3,3-trifluoro-2-chlorocyclobut-1-ene. The temperature was kept below 40°. After the addition, heat was applied and the mixture allowed to warm to 60-5° for five minutes. It was cooled and drowned in ice water with stirring. A yellowish solid separated which was filtered off and recrystallized from anhydrous methanol. The first crop amounted to 22.4 g. and melted at 88.5°. The infrared spectrum contained characteristic peaks at 1690, 1630, 1350, 913, 870, 753, and 708 cm^{-1}.

Anal. Calcd. for $C_{12}H_{12}NOF_5$: C, 51.2; H, 4.26; F, 33.8.
Found: C, 50.80; H, 4.16; F, 32.14.

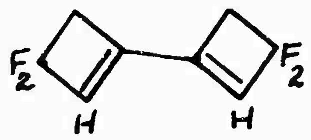
2-Piperidino-2',3,3,3',3'-pentafluorobicyclobutenyl



In 50 ml. of dioxane was dissolved 10 g. (0.04 mole) of 1(2,3,3-trifluoro-2-chlorocyclobutyl-)-2,3,3-trifluorocyclobutene. To this was added dropwise with cooling and stirring 8.5 g. (0.10 mole) of piperidine. After the addition the mixture was stirred at room temperature for an hour. The reaction was worked up by drowning in ice water with shaking and filtering off and washing the creamy-white solid. On drying the product 10 g. of yellowish solid was obtained. The infrared spectrum contained significant peaks at 1690, 1630, 1445 and 915 cm^{-1}. The product was recrystallized from Skellysolve F. It melted at 62.0-62.5°.

Anal. Calcd. for $C_{13}H_{14}NF_5$: C, 56.0; H, 5.02; F, 34.0
Found: C, 56.42; H, 5.25; F, 33.03.

3,3,3',3'-Tetrafluorobicyclobutenyl XIV.



In a 500 ml. round-bottom flask equipped with a mechanical stirrer, addition funnel, and ice-acetone bath was plac3d a solution of diene III 21.4 g. (0.1 mole) in 75 ml. diglyme (freshly distilled over lithium aluminum hydride.) When the solution temperature went below 0°C. a solution of sodium borohydride 2.4 g. (0.063 mole) was dropped in slowly, keeping the temperature below 0°C. After the addition, the solution was stirred at 0°-5° for 1 1/2 hours and then was allowed to rise slowly to room temperature. Ten ml. of water was added very cautiously followed by 5 ml. of 6N hydrochloric acid. Considerable foaming occurred. The mixture was poured over 700 ml. ice water and shaken vigorously. A fluffy white solid separated. Two hours later the solid was filtered with gentle vacuum (caution--product has high vapor pressure) and washed with cold water. About 18.0 g. of moist product was obtained which was dissolved in Skellysolve F. The solution was dried over anhydrous magnesium sulfate and then concentrated over a steam bath until saturated, then chilled to -20°. 16.5 g. of product was obtained; this was found by vapor phase chromatography to contain 1 part 2,3,3,3',3'-pentafluorobicyclobutenyl to 4 parts 3,3,3',3'-tetrafluorobicyclobutenyl. An analytical sample was prepared by vapor phase chromatography and melted at 85-86°. The infrared spectrum contained characteristic peaks at 1545, 1435, 910, and 692 cm^{-1}.

Anal. Calcd. for $C_8H_6F_4$: C, 53.9; H, 3.39; F, 42.5.
Found: C, 53.86; H, 3.69; F, 41.39.

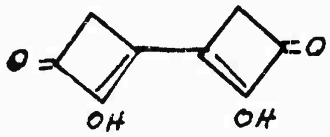
Attempted Diels-Alder Reactions of 2,2'-dimethoxy-3,3,3',3'-tetrafluorobicyclobutenyl (IV).

A. With Maleic Anhydride: 2.38 g. (0.01 mole) of the above "dibox" compound IVa and 1.5 g. (0.015 mole) of maleic anhydride were refluxed with 50 ml. toluene for 55 hrs. At the end of the reflux period, a small amount of black solid was filtered off. The filtrate, on cooling, yielded 0.45 g. of bright yellow needles. Infrared spectra showed this to be identical to 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (IV) prepared by sulfuric acid hydrolysis of the same starting material.

B. With Tetracyanoethylene: 2.38 (0.01 mole) of IV and 1.20 g. of Tetracyanoethylene (0.01 mole) were dissolved separately in 10 ml. portions of tetrahydrofuran and the two solutions were then mixed. No colored pi-complex was observed. A day later the solvent was evaporated *in vacuo*. The residual solid was found to be a mixture of the two starting materials. There was no indication of any reaction haveing occurred.

A similar unsuccessful attempt was made using hexafluorobicyclobutenyl (III) as a diene. No pi complex was observed, and after two days only starting materials were recovered.

2,2'-Dihydroxy-3,3'-diketobicyclobutenyl XV ("Diboxic Acid")



The best procedure found consisted of separately pulverizing 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (Va) 10.0 g. (0.05 mole) and 20 g. aluminum chloride (anhydrous). The two powders were then ground together. In a 250 ml.

round-bottom flask equipped with a reflux condenser and a mechanical stirrer, 150 ml. of tetrachloroethane was heated almost to reflux. The powder mixture was then added slowly in portions and after the addition the mixture was heated to reflux for one hours. The mixture was then allowed to cool and 250 ml. of Skellysolve B then added. The red-orange solid was filtered off and pumped dry. On standing in air the aluminum complex became bright yellow in color. The aluminum complex after setting in air for a few days was dissolved in a minimum amount of water and the unreacted dietherdiketone removed by filtration. The bright yellow filtrate was acidified with concentrated hydrochloric acid. On standing a yellow precipitate formed which on filtering amounted to 5-7 g. m.p. 220° dec. The infrared spectrum contained characteristic peaks at 3150, 1710, 1610, 1320, 1230, and 945 cm^{-1}. The infrared spectrum of the aluminum complex contained broad peaks at 2900-3400, 1100-1200, 840-850 cm^{-1} and sharper peaks at 2420, 1950, and 1640 cm^{-1}. Solutions of the complex dissolved silver nitrate without formation of silver chloride. Addition of a sodium chloride solution also failed to cause precipitation indicating that a stable soluble silver complex had formed.

Anal. Calcd. for $C_8H_6O_4$: C, 57.8; H, 3.62.
Found: C, 56.31; H, 3.83.

Reaction of V with morpholine.

In a small flask 2.0 g. of 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (v) was heated for 5 minutes to 85-90° in 20 ml. of morpholine. A dark red-orange solution was obtained. This was allowed to set for two days at room temperature. It was then poured into 80 ml. water and extracted with three 100 ml. portions of methylene chloride. The extracts were dried over anhydrous magnesium sulfate and evaporated in vacuo. A dark vixcous wax was thus obtained which could not be recrystallized. The infrared spectrum contained strong peaks at 1745, 1640, 1440, and 1115 cm^{-1}. A similar product was obtained on heating the diether V with piperidine. The consitution of these products is unclear.

Reaction of V with piperidine at room temperature.

Diketone V, 2.0 g., was allowed to dissolve slowly in 25 ml. of piperidine with frequent shaking. Quickly a bright red-orange color formed. When dissolution was complete (five hours) the solution was poured into 150 ml. of cold salt water and then extracted twice with methylene chloride. The extracts were dried over anhydrous magnesium sulfate and then stripped in vacuo. A brownish-yellow waxy solid was thus obtained. Attempts to crystallize this were unsuccessful. The infrared spectrum contained characteristic peaks at 1740, 1635, and 1600 cm^{-1}, and supported the assignment of 2-N-piperidino-2'-methoxy-3,3'-diketobicyclobutenyl for the product.

Reaction of Diketone V with Alkoxide.

Diketone V (5.0 g.) was dissolved with heating in 50 ml. of absolute ethanol. Potassium hydroxide pellets (3.0 g.) were then added with stirring. A deep reddish brown color quickly developed. The mixture was heated for five minutes and then diluted with 150 ml. cold water to give a dark orange solution. This was acidified with concentrated hydrochloric acid and then extracted with a 100 ml. and 50 ml. portions of dichloromethane. The extracts were dried over magnesium sulfate and then stripped in vacuo to give a dark yellow viscous liquid which reacted with bicarbonate to release carbon dioxide. The infrared spectrum of the liquid contained significant peaks at 3250, 2980, 1735, 1610, and 1445 cm^{-1}. Attempts to further characterize the reaction product were fruitless.

Attempted Selenium Dioxide Oxidation of V.

Several attempts to prepare esters of disquaric acid by the selenium dioxide oxidation of diketone V were made. The diketone was refluxed with freshly sublimed selenium dioxide in toluene, dioxane, and in dioxane for 24 hours. In each case only starting material was recovered and there was no sign of oxidation having occurred.

Reaction of 2,2'-dimethoxy-3,3'-diketo-4,4'dibromobicyclobutenyl with Water.

The dibromo derivative XIII (3.0 g.) was dissolved in 100 ml. of acetonitrile and 10 ml. of water was added with shaking. A dark brown color quickly developed. After allowing the mixture to set overnight, it was stripped in a roto-vac. A dark brown water soluble solid (2.0 g.) was thus obtained. The infrared spectrum consisted of three broad peaks centered at 3400, 1720, and 1200 cm^{-1}.

Anal. Found: C, 42.43; H, 3.97; Mol Wt./acetone=578. This analysis is in agreement with the composition $C_{20}H_{24}Br_2O_9$.

Reaction of Dibromo Derivative XIII with Silver Nitrate.

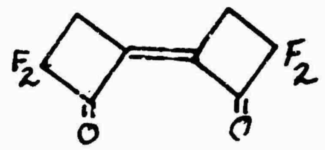
The dibromodiketone XIII (5.0 g., .014 mole) was dissolved in 200 ml. of acetonitrile and to this was added a solution of silver nitrate (4.85 g., 0.028 mole) in a minimum amount of acetonitrile. The reaction was quite exothermic and slight cooling was required. The mixture was stirred for several hours and then filtered. The filtrate was stripped *in vacuo* to dryness. The dark red-orange tarry solid was dissolved in methylene chloride. A white solid separated and was filtered but not identified. The methylene chloride solution was poured into Skellysolve F and then chilled. About 3 grams of a dark orange solid was obtained, which readily lost nitrogen oxides on standing. It yielded black polymeric material on treatment with triethylamine. The orange solid gave infrared peaks at 3400, 1730, 1600, 1420, and 1250 (v.broad). The white solid showed a carbonyl doublet at 1690 and 1730 along with peaks at 1610, 1050, and 883 cm^{-1}. The orange solid could not be purified further and was quite unstable.

Reaction of XIII with Alcoholic Potassium Carbonate.

The dibromoketone XIII (2.0 g.) was dissolved in 30 ml. of absolute methanol and 1.0 g. of anhydrous potassium carbonate added. The mixture was stirred at room temperature for two hours at which time the solids were filtered and the filtrate evaporated *in vacuo* to dryness to yield a reddish-brown tar. This was treated with concentrated hydrochloric acid which solidified the material somewhat. The acid was then decanted and the residue dissolved in a minimal amount (5-10 ml) of toluene with heating. The solution was treated with activated charcoal and then chilled to -20°. A small amount of bright yellow needles was obtained. The infrared spectrum of the product showed peaks at 1760, 1595, 1450, and 895 cm^{-1}. The n.m.r.

spectrum showed three separate singlets in the ratios 3:3:1 in accord with the assignment of the structure 2,2',4,4'-tetramethoxy-3,3'-diketobicyclobutenyl XVI which must be considered only tentative. This material failed to yield a tetraketone upon treatment with sulfuric acid.

2,2'-Diketo-3,3,3',3'-tetrafluorobicyclobutylidene (XVII).



Concentrated sulfuric acid (60 ml.) was placed in a beaker and 37 g. (.127 mole) of 2,2,2',2'-tetramethoxy-3,3,3',3'-tetrafluorobicyclobutylidene (X) was dissolved with stirring. To this was added 100 ml. of methylene chloride and 100 ml. of ice in portions, and the mixture shaken vigorously in a separatory funnel. The organic layer was removed and the acid layer extracted with two additional 100 ml. portions of methylene chloride. The extracts were combined and dried over anhydrous magnesium sulfate, and then concentrated over a steam bath until yellow crystals began to deposit. It was then chilled overnight. Yellow crystals of diketone XVIII, m.p. 157-9°, were then filtered off and amounted to 10.0 g. (Second crop 1.5 g.; total yield, 47%.) The infrared spectrum contained significant peaks at 1775, 1390, 1190, 1045, and 873 cm^{-1} and lacked olefinic absorption as would be expected for a symmetrically tetrasubstituted olefin. Diketone XVII was found to be very reactive to bases to give polymeric materials. In methylene chloride it reacted with triethylamine or with pyridine to give an intense purple solution.

Anal. Calcd. for $C_8H_4F_4O_2$: C, 46.1; H, 1.93; F, 36.5.
Found: C, 46.04; H, 2.18; F, 34.02.

This material slowly dissolves in water to form hydrates. In methanol it quite quickly forms a colorless hami-ketal.

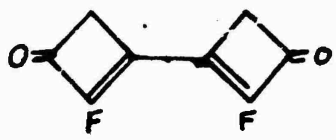
2-Methoxy-2',3,3,3-trifluoro-3'-ketobicyclobutenyl(XVIII).

Sulfuric acid, 100 ml. and 2-methoxy-2',3,3,3',3'-pentafluorobicyclobutenyl VIII (39.0 g., .174 mole) were stirred together for about 5 minutes until a single phase was obtained. The reaction was slightly exothermic and the temperature rose to about 40°. The mixture was poured over ice and then extracted with methylene chloride. The extract was dried over magnesium sulfate and then stripped in vacuo to yield about 20 g. of crude dark fluid. On distillation, a yellowish fluid, b.p. 92-6/.4-.5 mm. n_D^{28}=1.4866 was obtained. The material exhibited significant infrared absorptions at 1770, 1650, 1605, 1440, and 1320 cm^{-1} in agreement with the proposed structure. Hydrolysis at highter temperatures resulted in destruction of the material.

Hydrolysis of 2-morpholino-2',3',3,3',3'-pentafluorobicyclobutenyl.

Amine (5.g.) was dissolved slowly with stirring in cold sulfuric acid. A very pale yellow solution resulted. This was poured over ice and extracted with methylene chloride in the usual manner. On evaporating off the solvent, a straw-colored oil was obtained. The infrared spectrum gave significant peaks at 3400, 2950 1810, 1790, 1715, and 1440 cm^{-1}. A structure assignment could not be made with any confidence. Hydrolysis at higher temperature resulted in cleavage reactions.

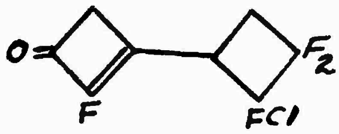
2,2'-Difluoro-3,3'-diketobicyclobutenyl (XIX).



In a tall test tube containing 20 ml. of concentrated sulfuric acid was placed 1.0 g. of 2,2',3,3,3',3'-hexafluorobicyclobutenyl (III). The mixture was heated with stirring over a steam bath for 25-30 minutes until a single phase was observed. It was then poured over 100 ml. ice with stirring. No solid separated for about ten minutes. Crystallization was completed by chilling the solution for several hours. On recrystallization from Skellysolve C the product was obtained as colorless needles, m.p. 96.5-97.0°. The infrared spectrum contained significant peaks at 1775, 1610, 1422, 1260 and 925 cm^{-1}, and was completely in accord with the proposed structure.

Anal. Calcd. for $C_8H_4F_2O_2$: C, 56.5; H, 2.36; F, 22.4.
Found: C, 56.46; H, 2.50; F, 22.60.

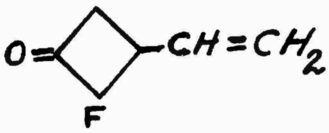
1-(2,3,3-Trifluoro-2-chlorocyclobutyl)-2-fluoro-3-ketocyclobutene. (XX)



In a tall test tube containing 60 ml. of concentrated sulfuric acid was placed 10.0 g. of 1-(2,3,3-trifluoro-2-chlorocyclobutyl)-2,3,3-trifluorocyclobutene (VIII). The mixture was heated with stirring over a steam bath for 2 hours until a single phase was observed. The solution was poured over ice and then extracted with methylene chloride. The extract was dried over magnesium sulfate and filtered. The solvent was stripped off over a steam bath, leaving a slightly brownish fluid with a very piercing odor. It was purified further by vacuum distillation. It boiled 44-46°/.2 mm., n_D^{25}=1.4441. The infrared spectrum contained significant peaks at 1775, 1660, 1420 cm^{-1} and was completely in accord with the proposed structure.

Anal. Calcd. for $C_8H_4ClF_4O$: C, 42.3; H, 1.76; F,33.4.
Found: C, 42.48; H, 2.31; F, 33.59.

1-Vinyl-2-fluorocyclobut-1-ene-3-one(XXI)



Sulfuric acid (50 ml.) was place in a 200 ml. beaker and cooled to 5° in an ice bath. To this was added with cooling and stirring 20 g. (.15 mole) of 1-vinyl-2,3,3,-trifluorocyclobutene(VI). The reaction was very exothermic and large amounts of hydrogen fluoride were evolved (wear gloves!). After the addition 10 ml. of ice was cautiously added with stirring. Five minutes later the mixture was then poured over 200 ml. of ice. A dark brown oil slowly settled to the bottom. This was removed by using a separatory funnel and washed with cold water to remove excess acid. The ketone was best purified by steam distillation. The distillate was a colorless liquid with a piercing odor. It quicly darkened on standing and became progressively more viscous during the day. The freshly steam-distilled product has the following properties: refractive indix at 26°=1.4814, infrared peaks at 1770, 1650, 1200, and 740 cm^{-1}. The residue from the steam distillation was a tan-white solid with infrared spectral peaks at 1775, 1655, 1300, 1170 cm^{-1} and is suspected to be a polymer of XXI. Attempts to further purify XXI yielded only polymeric material. Inhibited samples polymerized even under refrigeration.

Reaction of 2,2'-difluoro-3,3'-diketobicyclobutenyl with piperidine.

A. About 0.1 g. of the above diketone was dissolved in 10 ml. of ether and several drops of piperidine added with stirring. The solution was filtered and the filtrate allowed to evaporate to dryness yielding long red needles of 2-N-piperidino-2'-fluoro-3,3'-diketobicyclobutenyl, m.p. 125°. The infrared spectrum contained characteristic peaks at 1745, 1605, and 1580 cm^{-1}. A similar product could be obtained using diethylamine instead of piperidine.

B. About 0.2 g. of the above diketone was added slowly with vigorous stirring to 5 ml. of piperidine. The reaction was very exothermic. Five minutes later the deep red-orange solid which slowly deposited was filtered off and recrystallized from hot Skellysolve C. Red-orange needles of 2,2'-bis(N-piperidino)-3,3'-diketobicyclobutenyl were obtained melting at 109-110°. The infrared spectrum contained characteristic peaks at 1720 and 1560 cm^{-1}.

2'-N-Morpholino-2,3',3'-trifluoro-3-ketobicyclobutenyl (XXII).

To a solution of 5 ml. morpholine in 10 ml. monoglyme, 1.0 g. of 1-(2,3,3-trifluoro-2-chlorocyclobutyl)-2-fluoro-3-ketocyclobutene (XX) was added dropwise with stirring. The reaction was very exothermic and a white precipitate formed. The reaction mixture was poured into 25 ml. ice water. A bright yellow solid which separated was filtered off and recrystallized from hot Skellysolve C. Bright yellow needles of (A) were thus obtained melting 111°. The infrared spectrum contained peaks 1775, 1630, and 1605 cm^{-1}.

Anal. Calcd. for $C_{12}H_{12}F_3NO_2$: C, 55.6; H, 4.64; F, 22.0; N, 5.40.
Found: C, 55.66; H, 4.76; F, 22.19; N, 5.51.

Similarly, 2'-N-piperidino-2,3',3'-trifluoro-3-ketobicyclobutenyl was obtained by using piperidine instead of morpholine in the above procedure. Yellow-orange needles from Skellysolve C, m.p. 133°, were thus obtained. The infrared spectrum was similar to that of the above morpholine derivative.

2-(3,3,4,4-Tetrafluoro-1-cyclobutenyl-)-2-propanol (XXIII)

A one half-liter stainless steel bomb containing 42 g. (0.50 mole) of 20methyl-3-butyn-2-ol and 1 ml. of "Terpene B" inhibitor was cooled in dry ice/acetone and charged with 65 g. (0.65 mole) of tetrafluoroethylene. It was then heated for 24 hours at 140°. At the end of the heating period, it was cooled and the excess gaseous material bled off. On opening the bomb, 75 g. of liquid was obtained. This was extracted with three-15 ml. portions of water to remove the unreacted methylbutynol. On distillation at 100 mm. pressure, the material decomposed considerably, but 20 g. of product(XXIII) boiling at 101°/100 mm. were obtained (19.9% yield). Infrared spectrum: Bands at 1610, 1650, 2960, and 3350 cm^{-1}. NMR spectrum showed a single peak for hydroxyl-H, a single peak for 2(-CH_3), and a series of peaks corresdponding to a vinylic hydrogen split by a cross-ring -CH_2- and resplit by an adjacent -CH_2-.

Anal. Calcd. for $C_7H_8F_4O$: C, 45.6; H, 4.35; F, 41.3.
Found: C, 45.85; H, 4.38; F, 40.95.

2-(3,3,4-Trifluoro-4-chloro-1-cyclobutenyl-)-2-propanol (XXIV)

A 2-liter steel bomb containing 600 g. (7.15 mole) of 3-methyl-1-butyn-3-ol and 5 ml. of "Terpene B" inhibitor was chilled in a dry-ice bath and then evacuated. Trifluorochloroethylene, 610 g. (5.25 mole), was bled in and the bomb was heated at 160° for 25 hours. On cooling, bleeding off gases, and opening, 1110 g. of brown liquid was obtained. This was steam distilled to yield 676.3 g. (after drying over magnesium sulfate) of steam volatile material. Vapor phase chromatography showed this to be 70% pure adduct XXIV. The yield was thus 45%. The product had the following properties: B.P. 97-8°/38 mm., d_{25}^{25}=1.468; n_D^{26}=1.4198; infrared spectrum; bands at 1610, 2960, and 3350 cm^{-1}; NMR spectrum showed single peaks for hydroxyl H and methyl H, and a series of peaks corresponding to a vinylic hydrogen split once by a cross-ring-CFCl- and split again by an adjacent-CF_2-.

Anal. Calcd. for $C_7H_8ClF_3O$: C, 42.0; H, 4100; Cl, 17.1; F, 28.5.
Found: C, 41.83; H, 3.77; Cl, 18.99; F, 28.93.

1-Isopropenyl-3,3,4-trifluoro-4-chloro-1-cyclobutene (XXV)

About 50 g. (0.25 mole) of the above 2-(3,3,4-trifluoro-4-chloro-1-cyclobutenyl-)-2-propanol (XXIV) added dropwise with stirring into 130 ml. of concentrated sulfuric acid previously cooled to 5° in an ice bath. The temperature was maintained at 5-15° throughout the addition. Afterwards the temperature was allowed to rise to 20° for 2 1/2 hours, at which time it was poured into 500 g. of ice with stirring. A black tar resulted which was extracted several times with dichloromethane (a process which proved very messy and tedious). The extracts were dried over anhydrous magnesium sulfate and then stripped to a volume of about 75 ml. The product was distilled at 38 mm. pressure. XXVI, 12 g. (27% yield), was obtained boiling at 61-65°/38 mm., n_D^{25}=1.4304. Infrared spectrum: bands at 1588 and 1635 cm^{-1}. Sharts and Roberts[5] reported this compound earlier and listed properties as follows: I.R.: bands at 1588 and 1635 cm^{-1}, b.p. 60-5°/32-37 mm., n_D^{25}=1.4288-1.4295.

Table I summarizes various cycloalkylation reactions of unsaturated compounds attempted with chlorotrifluoroethylene. No definite liquid products of value in this project were uncovered or isolated.

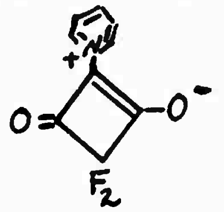
TABLE I

Miscellaneous Cycloalkylation Reactions of Trifluorochloroethylene:

OLEFIN:	Wt. g.	WT: g. CF_2:CFCl	TEMP. °C.	TIME	PRODUCTS
Methylvinylketone	71.0 g.	115 g.	180°	10 1/2 hr.	carbon
	70.0 g.	140 g.	160°	30 hr.	carbon
	127 g.	150 g.	150°	6 hr.	carbon
	87 g.	150 g.	135°	2 hr.	starting materials 65 g. 1:1 cycloadduct
isopropylvinyl ether	86 g.	120 g.	150°	14 hr.	158 g. liquid (1/3 cycloadduct)
mesityl oxide	98.0 g.	130 g.	150°	8 hr.	starting material CF_2=CFCl dimer
1,3-cyclooctadiene	108 g.	135 g.	150°	5.5 hr.	starting material
304. furan	68 g.	240 g.	180°	6 hr.	furan (mainly) 1:1 adduct (trace) 2:1 (furan:CF_2:CFCl) adduct, 20 g.
Thiophene	58 g.	170 g.	130-40°	5 1/2 hr.	thiophene CF_2:CFCl and dimer
2,3-dichloro-1,3-butadiene	60 g.	130 g.	160°	10 hr.	solid polymer
	55 g.	175 g.	135°	8 hr.	solid polymer 10 ml. thick liq.

All of the above bomb reactions were run under qutogenous pressure in a 500 ml. stainless steel Paar bomb in the presence of Terpene B inhibitor.

2,4-Dioxo-3,3-difluoro-1-cyclobutyl pyridinium betaine (XXVII).

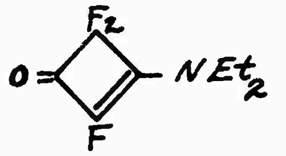


A solution of 15 ml. pyridine in 50 ml. of moist dioxane was placed in a tall test tube cooled in a cold water bath and about 5 g. of perfluorocyclobutene was bubbled through by means of a sintered glass tube. The solution became dark orange in color. After letting the solution set for four days a large amount of crystalline material had collected on the walls of the tube. These crystals were scraped off and filtered. The material darkened above 200° without melting and was identified as 2,4-dioxo-3,3-difluoro-1-cyclobutyl pyridinium betaine by virtue of its close similarity to the corresponding trimethylammonium betaine prepared by Pruett et al.[6] The infrared spectrum had significant peaks at 1790, 1640 (v.broad), 1478, 1255, 833 and 786 cm^{-1}, m.p. 232-3.

Anal. Calcd. for $C_9H_5F_2NO_2$: C, 54.7; H, 2.54; N, 7.11; F, 19.3.
Found: C, 53.3; H, 2.48; N, 6.92; F, 19.6.
Mol. Wt. Calcd.: 197; Mol. Wt. Found (acetone): 197.

This material was found to be soluble without further hydrolysis in concentrated sulfuric acid, the solutions giving colorless needles of XXVII on dilution with water. The betaine dissolved in acetonitrile containing a little potassium hydroxide and water to give a dark green solution. In dimethylsulfoxide containing potassium tert-butoxide a dark crimson color was observed. A dark red-orange solution was obtained on dissolving it in aqueous potassium hydroxide. The nature of these complexes was not investigated any further.

1-Diethylamino-3-keto-2,4,4-trifluorocyclobutene (XXIX).



A. Preparation of 1-diethylaminopentafluorocyclobutene (XXVIII): This compound was prepared by the general method of Pruett et al.[7] Perfluorocyclobutene, 63.9 g. (.394 mole), was bubbled into a solution of diethylamine, 73 g. (1.0 mole), in 200 ml. monoglyme at 20.25° and the reaction mixture quenched in cold water. The crude product separated and was distilled to yield 70.2 g. of pure product XXVIII boiling 66-72°/24 mm. The yield was 88%, the density at 20° was 1.2330, $n_D^{25}=1.3919$ (lit. value=1.3914). The original workers reported a 59% yield using ether as solvent at 0-25°.

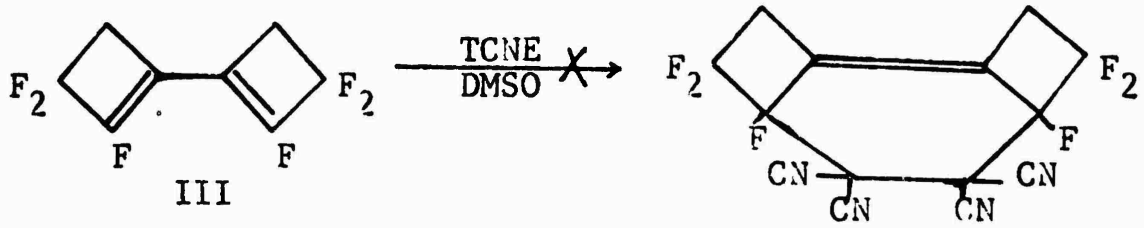
B. Hydrolysis to Cyclobutenone XXIX: The above aminoolefin XXVIII, 41 g. (0.20 mole), was added slowly with stirring and cooling to 200 ml. of concentrated sulfuric acid in a 500 ml. 3-neck flask equipped with an addition funnel, mechanical stirrer, thermometer, and reflux condenser. The temperature was allowed to rise, but not beyond 30°. After the addition of XXVIII, 75 ml. of water was added very slowly and cautiously. The temperature was allowed to rise slowly to 40° (using external ice-bath cooling.) A certain amount of foaming occurred, but this was minimized by cooling and slowing down the water addition rate. After the addition, the mixture was stirred for five minutes, then poured over a large volume of ice chips with stirring. A white solid separated. This was filtered with suction (caution: This material melts at ca. 15°, so it must be kept at ice-water temperature for the entire filtration and washing) and washed with a large volume of ice water (5°). The solid was then quickly transferred to a beaker, allowed to melt, and then separated from the aqueous phase in a separatory funnel. The organic layer was dried over anhydrous magnesium sulfate. Colorless liquid XXIX 24.2 g. (66% yield), d^{20}=1.2266, n_D^{25}=1.4767, was obtained. A sample was distilled giving a single fraction, b.p. 105°/.5mm., n_D^{25}=1.4767, with no pot residue remaining, indicating that the product was already very pure. The infrared spectrum exhibited characteristic peaks at 1840 (sharp, strong) and 1650 cm^{-1} (broad, strong). The F^{19} n.m.r. spectrum showed one strong doublet ($-CF_2-$) at 113.0 ϕ and one weaker triplet ($=CF-$) at 134.6 ϕ. The first order splitting constant was 26.4 c.p.s. and supports assigning the fluorine atoms to positions cross-ring from each other.

Anal. Calcd. for $C_8H_{10}F_3NO$: C, 49.7; H, 5.2; F, 29.2.
Found: C, 49.5; H, 5.3; F, 29.8.

By similar procedure, 1-N-morpholine-3-keto-2,4,4-trifluorocyclobutene was prepared from morpholine and perfluorocyclobutene. Colorless crystals from chloroform were obtained melting 85.7-86.4°. The infrared spectrum contained the expected peaks at 1650 and 1820 cm^{-1}.

I. Reactions of Hexafluorobicyclobutenyl (III)

A Diels-Alder reaction was attempted between Compound III and tetracyanoethylene using dimethylsulfoxide as solvent. After 40 hr. at room temperature, the mixture was worked up and found to be starting material.

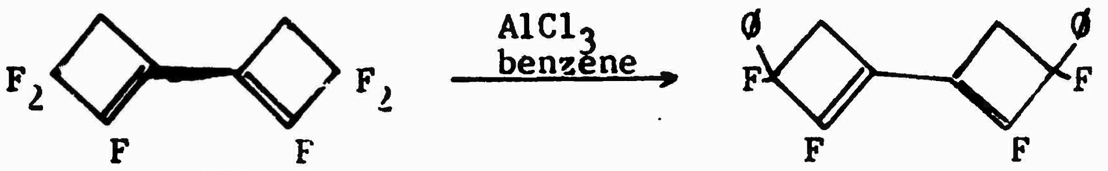


III

Although compound I was dissolved with comparative ease in fuming sulfuric acid to give a colored solution, concentrated sulfuric acid failed to react or even dissolve compound III. The reaction was exothermic and on quenching the solution in ice water, only water-soluble material was formed. The aqueous solution did not give a coloration with ferric chloride (enol test). Apparently severe cleavage, rather than hydrolysis occurred.

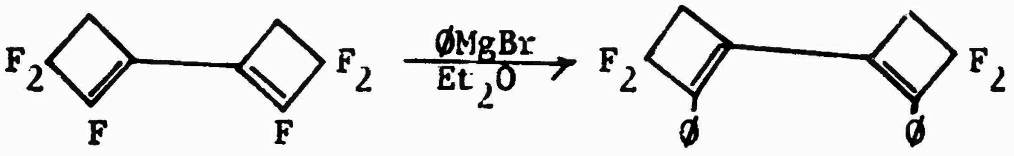
Furthermore, compound III, when added to triethylamine, reacted very readily and exothermically to give a black tarry substance that was not further characterized. Pyridine also reacted, but considerably slower (several hours) yielding also black tars.

This compound was treated with anhydrous aluminum chloride in petroleum ether and found to give a colored complex. It was also treated with $AlCl_3$ in benzene to give a violet Friedel-Crafts type reaction (HCl was evolved). A dark purple complex was obtained which on hydrolysis yielded a yellowish fluorescent solid. The infrared spectrum showed strong aromatic absorption. The product has not been isolated as a pure crystalline solid yet. It is suspected that the phenylation occurred two or more times at the allylic fluorine position as shown below. Perphenylation may have occurred and rearrangement is not at all unlikely.



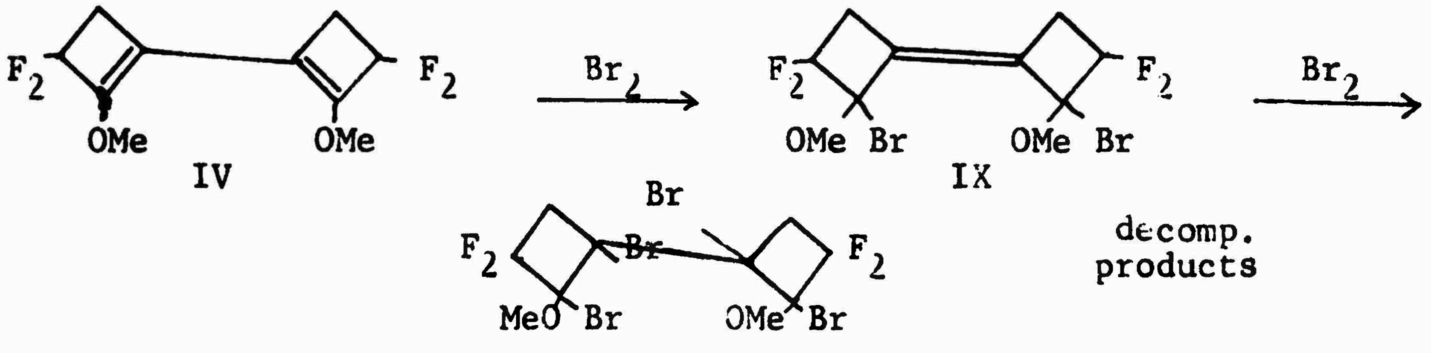
III

As ether solution of III was treated with phenyl magnesium bromide, followed by hydrolysis of the Mg complex. A yellowish solid having a strongly characteristic odor was obtained. Infrared spectra showed than an aromatic product was obtained. It is suspected that the vinylic fluorines were replaced by phenyls:



II. Reactions of 2,2'-dimethoxy-3,3,3',3'-tetrafluoro-bicyclobut-1-enyl IV.

This compound was found to readily add one mole of bromine in acetic acid but adds a second mole rather slowly. The product obtained was a yellow wax which decomposed rapidly on standing to a dark brown liquid. All purification attempts met with failure.



XII

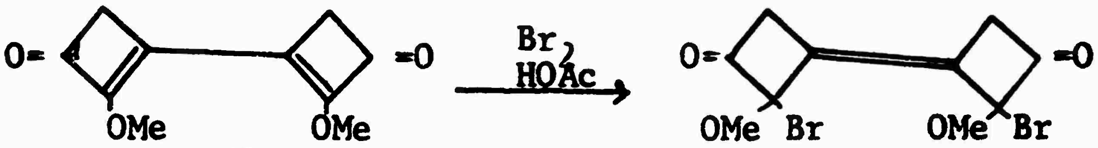
It was found to be incapable of undergoing Diels-Alder adducts with either tetracyanoethylene or maleic anhydride.

In benzene it reacts very vigorously with aluminum chloride to yield a colored complex which on hydrolysis yields a phenylated derivative. The nature of the product is uncertain, but it is probably very similar to that obtained with the hexafluorobicyclobutenyl (III).

Compound IV reacts quite readily with triethylamine to yield complex tar. The reaction is somewhat slower than that of the hexafluoro derivative (III) and the nature of the product is very uncertain.

III. Reactions of 2,2'-dimethoxy-3,3'-diketo-bicyclobut-1-enyl (V)

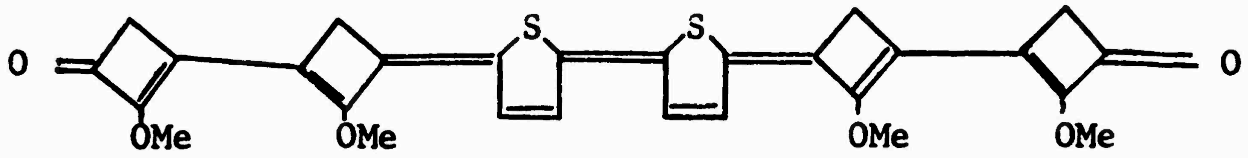
This diketone (V) quite readily added one mole of bromine to yield a colorless dibromide of relatively low stability.



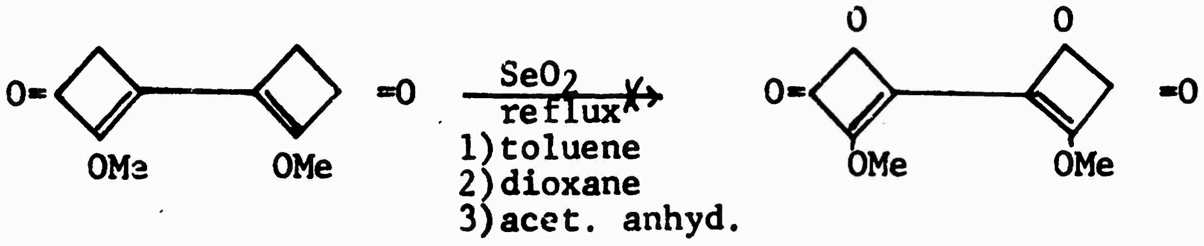
V

The dibromide, when treated with triethylamine and ether, gave an immediate yellow precipitate. The yellow precipitate was very unstable in air, readily absorbing water (the precipitate was partially Et_3N-HBr). The aqueous solutions are dark yellow in color. Ultraviolet spectral studies were made on the various compounds in different solvents and at different pH's. There were definite pH effects on the UV absorption maximum wave length. Much work will be required to isolate and characterize the products.

The diketone V reacts very readily with thiophene and sulfuric acid to give a dark purple solid. By analogy to the known reaction of diketones with thiophene, the product is probably of the type shown below. The product will probably not be characterized further due to its complexity.

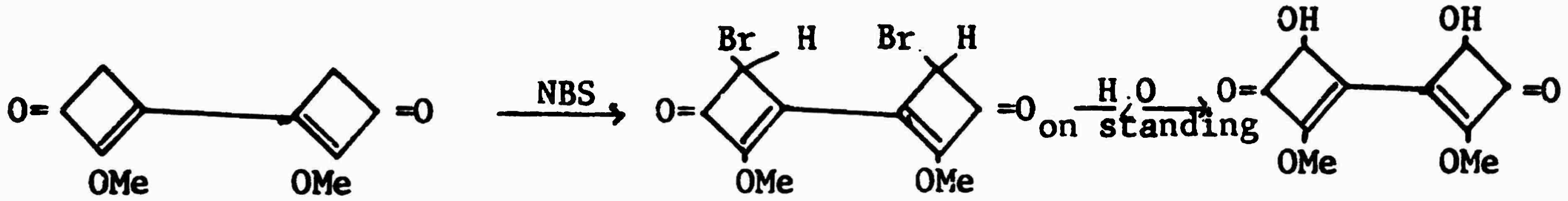


Selenium oxide oxidation of diketone V has been attempted using three different solvents--toluene, dioxane, and acetic anhydride. Freshly sublimed SeO_2 was used and in all three cases, starting material was recovered along with selenium powder.



Compound V reacts readily with malononitrile in the presence of morpholine or pyridine to give transient green and blue colors leading to a dark brown solution (in THF). On dilution of the latter solution with water, a bright red-orange solution results which is probably of radical anion character. On acidification of the products, a greenish-brown solid was obtained. The constitution of the products is very much in question.

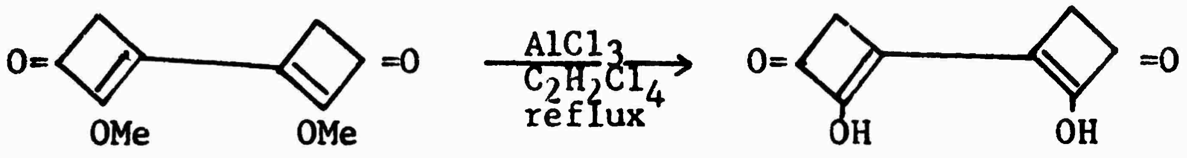
Compound V appears to undergo N-bromo-succinimide bromination quite readily. Using a 5-fold excess of NBS, azo-bis-iso-butyronitrile as initiator, carbon tetrachloride as solvent, and refluxing for four hours, a yellow tar was obtained that readily hydrolyzed in air to a brown dye very soluble in water. Attempts to isolate the dye as a pure solid have not been successful. The fresh yellow tar did not show -OH absorption (IR spectra), but on standing overnight, it formed a brown tar which showed very strong -OH absorption. This reaction will be studied further and the products characterized. Evidently:



V

The diketone was treated with anhydrous aluminum chloride in Skelly B solvent, to give an orange solid complex. The complex was filtered off and allowed to slowly hydrolyze on standing. The original diketone was regenerated and no new product obtained.

However, when the latter reaction was run in refluxing tetrachloroethane, a reddish complex was obtained which on hydrolysis yielded an intensely yellow substance, extremely soluble in water and thus readily extracted from the organic solvent. The yellow solution gives a positive enol test with ferric chloride. Work is in progress towards isolating the solid product, which is possibly the diketone-diol.



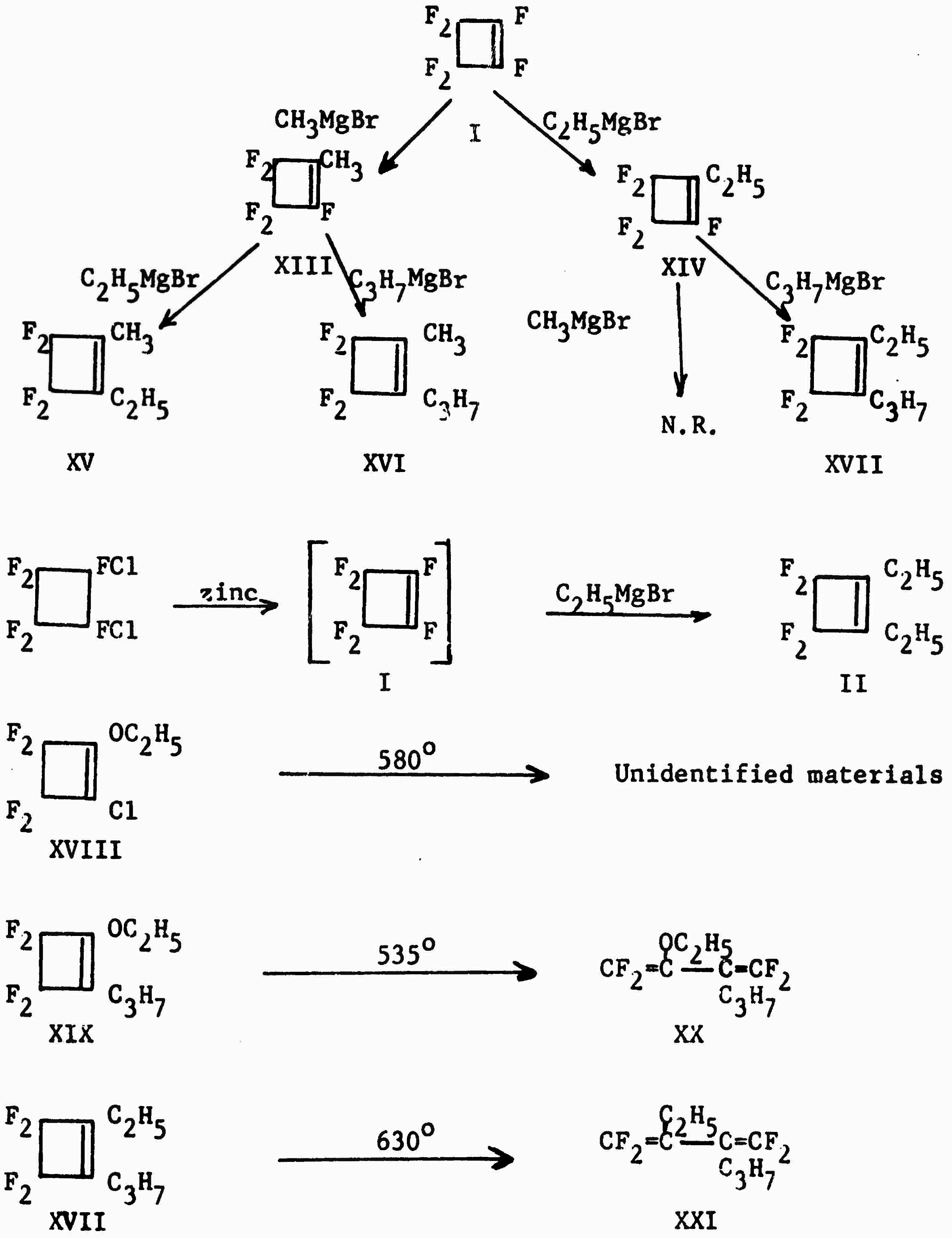
V

XV

The following section (B_1) deals with our studies on the preparation of alkyl substituted tetrafluorocyclobutenes and our attempts to prepare highly reactive dienes by pyrolysis of the cyclobutenes. Figure 2 shows the various pathways which were studied.

(B_1) Grignard Reactions and Pyrolysis Studies

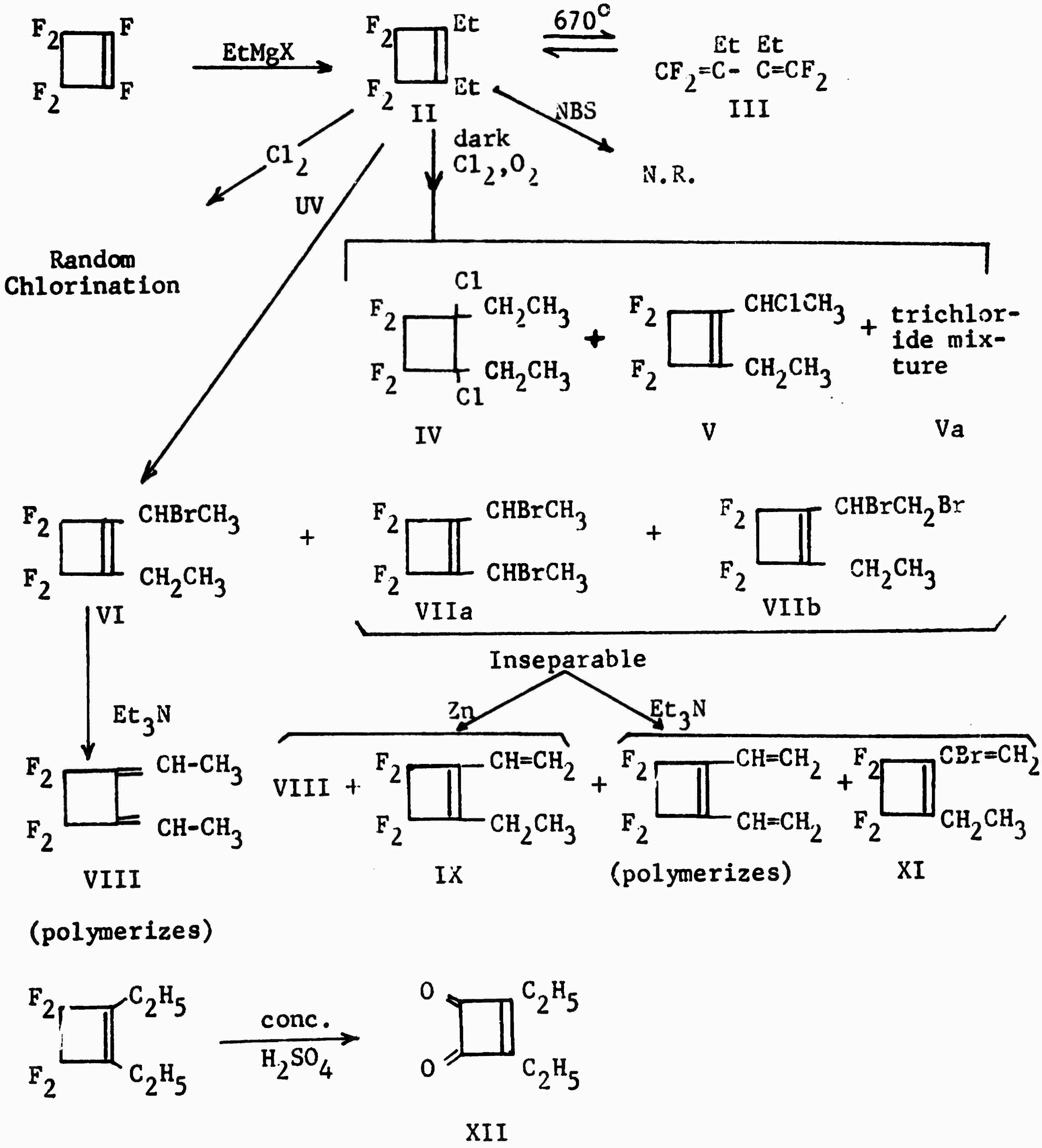
Figure 2



The following Figure 3 summarizes the various pathways which were utilized in our continuing studies for the production of reactive monomer intermediates.

Figure 3

(B_{11}) Cyclobutene Monomer Intermediates and their Reactions.



(B) Cyclobutene Monomer Intermediates

EXPERIMENTAL

Boiling points were taken by the Siwoloboff method.[8] Density determinations were made using a calibrated Hamilton 10-microliter syringe. Infrared spectra were taken by a Perkin-Elmer Infracord, and n.m.r. specta were taken using a Varian A-60 analytical spectrometer with pure liquid samples with tetramethylsilane as a reference compound. Microanalyses were performed by Galbraith Laboratories. The product ratios were determined on an F and M Model 300 Programmed Temperature Gas Chromatograph with a Texas Instruments Inc. Servoriter model recorder with a disc integrator. The column used contained a fluorosilicone 1265 (QFI) substrate unless otherwise designated. The preparative scale column also was of this type.

Perfluorocyclobutene (*I*) was obtained from 1,2-dichloro-3,3,4,4-tetrafluorocyclobutane by dechlorination with zinc.[9]

1-Ethyl-2,3,3,4,4-pentafluorocyclobutene (*XIV*) was obtained from the reaction of ethylmagnesium bromide with perfluorocyclobutene.[10]

1-Methyl-2,3,3,4,4-pentafluorocyclobutene (*XIII*) was obtained from the reaction of methylmagnesium bromide with perfluorocyclobutene as described in the literature.[10]

1-2-Diethyl-3,3,4,4-tetrafluorocyclobutene (*II*) was obtained by a variation of the method previously described.[5] In this procedure, the apparatus consisted of a 2-liter three-neck flask fitted with an addition funnel, a stirrer, and a water cooled condenser. To the condenser was connected a bubbler, which in turn was connected to a gas inlet tube fitted to a second 2-liter three-neck flask. In addition to the gas inlet tube the second flask was fitted with a stirrer and a dry-ice cooled condenser backed with a dry-ice cooled trap connected to a drying tube. Into the first flask was placed 125 g. (1.9 moles) of zinc slurried in 300 ml. of dibutoxytetraglycol, and into the second flask was placed 850 ml. (2.55 moles) of 3 molar tetrahydrofuran solution of ethylmagnesium bromide. The zinc slurry was heated to ca. 80°, then as the slurry was stirred rapidly 295 g. (1.27 moles) of 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane was added slowly so that a steady flow of perfluorocyclobutene was passed into the rapidly stirred Grignard solution. Occasionally, the Grignard solution was cooled with a cold water bath in order to remove heat formed in the exothermic reaction. After completion of the reaction, the reaction mixture in the second flask was refluxed slowly overnight.

The reaction product was worked up by destroying the excess Grignard reagent with dilute hydrochloric acid, and extracting the organic material with ether from the resulting magnesium salts. The extract was neutralized with sodium bicarbonate and dried over anhydrous calcium sulfate. After removal of ether by distillation at atmospheric pressure, 120 g. (50% of theory) of diethylcyclobutene VIII was distilled at 80-82° at 100 mm. pressure. The infrared spectrum was identical with that of an authentic sample. Strong absorptions were observed at 885, 1100, 1210, and 1345 cm^{-1}.

Preparation of 1-Ethyl-2-propyl-3,3,4,4-tetrafluorocyclobutene (XVII.)

About 54 g. (0.13 mole) of ethylperfluorocyclobutene (XIV) was placed into a 500 ml. three-neck Morton flask fitted with a stirrer, a dropping funnel, and a condenser. It was heated to ca. 60°, and 200 ml. (0.60 mole) of a 3 molar ether solution of n-proplymagnesium bromide was added slowly as the reaction mixture was stirred rapidly. After the addition was completed, the reaction mixture was refluxed for 24 hrs. with rapid stirring. The excess Grignard reagent, was then destroyed with dilute hydrochloric acid, and the product was extracted with ether from the solid magnesium salts. The extract was neutralized with sodium bicarbonate and dried over anhydrous magnesium sulfate. Analysis of the extract by g.l.c. indicated a conversion of 35% to the dialkylcyclobutene XVII and a total organic yield of 87%. The product was isolated by fractionation on a 12 in. column packed with glass helices.

The properties of XVII are as follows: b.p. 150°/625 mm., n_D^{25} 1.3845, d_4^{20} 1.090. Molar refraction: calcd., 42.0; obsd., 42.1.

Anal. Calcd. for $C_9H_{12}F_4$: C, 55.1; H, 6.16; F, 38.7. Found: C, 54.8; H, 6.41; F, 38.5.

Preparation of 1-Methyl-2-ethyl-3,3,4,4-tetrafluorocyclobutene (XV).

About 75 ml. (0.23 mole) of a 3 molar tetrahydrofuran solution of ethylmagnesium bromide was placed in a 200 ml. three-neck flask fitted with a stirrer, an addition funnel, and a reflux condenser. This reaction vessel was placed in a cold water bath to remove heat formed in the reaction. As the solution was stirred rapidly, 17.7 g. (0.11 mole) of the methylcyclobutene XIII was added slowly so that only a slight reflux resulted. Any XIII collected in the dry-ice cooled trap following the reflux condenser was recycled. The reaction mixture was then allowed to stir rapidly at reflux temperature for 19 hrs. The reaction product was worked up in a manner similar to that described in the previous procedure. Crude distillation of the extract was accomplished at ca. 50 mm. Analysis of this distillate by g.l.c. indicated a 75% conversion to dialkylcyclobutene (XV) and an over all yield of 80%. Fractional distillation of this material on a 12 in.-column packed with glass helices gave a material which was contaminated with a small amount of side reaction product. Pure material was obtained by separation on the "Autoprep" g.l.c. apparatus.

The properties of XV are as follows: b.p. 121°/625 mm., n_D^{25} 1.3611, d_4^{25} 1.141. Molar refraction: calcd., 32.7; obsd., 32.6.

Anal. Calcd. for $C_7H_8F_4$: C, 50.0; H, 4.76; F, 45.2. Found: C, 49.9; H, 5.04; F, 45.3.

Preparation of 1-Methyl-2-propyl-3,3,4,4-tetrafluorocyclobutene (XVI).

About 11 g. (0.07 mole) of methylcyclobutene XIII was placed in a 100 ml. three-neck flask fitted with a stirrer, a reflux condenser, and a dropping funnel. Under constant stirring, 50 ml. (0.15 mole) of a 3 molar tetrahydrofuran solution of n-propylmagnesium bromide was added slowly to XIII so that a gentle reflux resulted. After the addition of Grignard reagent was completed, the reaction mixture was stirred at reflux temperature for 20 hrs. Then the reaction was worked up in a manner similar to that described in the previous procedures. Crude distillation of the dark brown extract yielded ca. 2 g. (15 % of theory) of 95% pure dialkylcyclobutene XVI. The pure material was obtained by separation on the "Autoprep" g.l.c. apparatus.

The properties of XVI are as follows: b.p. 138°/625 mm., n_D^{28} 1.3700, d_4^{28} 1.108. Molar refraction: calcd., 37.3; obsd. 37.2.

Anal. Calcd. for $C_8H_{10}F_4$: C, 52.8; H, 5.49; F, 41.8. Found: C, 52.7; H, 5.30; F, 41.6.

General Pyrolysis Procedure

The apparatus used in these pyrolysis studies consisted of a vertical vycor tube 1 inch in diameter and 18 inches in length fitted with 24/40 female quartz joint. This tube was packed with small pyrex beads and was heated over a 12 inch length by an electric oven. A small equalizing dropping funnel was fitted to the top of the tube, which in turn was fitted with a special nylon needle valve to allow a higher vacuum in the system. The bottom of the tube was connected to two small dry-ice cooled traps, a liquid-nitrogen cooled trap, and finally to a manifold connected to a vacuum pump and a manometer. The temperature was measured by a thermocouple halfway up the outside of the tube.

The pyrolysis procedure was similar to that described in the literature.[11] It consisted of heating the tube in such a manner that the desired temperature was maintained, placing the starting material in the dropping funnel, and evacuating the system to the desired pressure. The material was then dropped slowly into the tube, and the effluent gases were condensed in the traps.

Pyrolysis of 1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene (XVIII).

At 525° and a pressure of 5 mm. pyrolysis of 8 g. (0.039 mole) of XVIII was attempted, but no product was detected by g.l.c. analysis. However, at 580° and 15 mm. 5% of the reaction mixture was product with the attainment of a 90% yield. In time a crystalline solid formed, and the percentage of product decreased from 5 to 1%. The solid melted at 115°, but it could not be recrystallized without decomposition. It appeared to sublime before melting, but sublimation as a method of purification failed. Elemental analysis of a sample of the material which was dried overnight at room temperature and 0.5 mm. pressure gave the following analysis: C, 31.1; H, 1.12; Cl, 22.3; F, 25.1; O, 20.4, resulting in the following empirical formula: $C_4H_2ClF_2O_2$.

Pyrolysis of 1-Ethoxy-2-propyl-3,3,4,4-tetrafluorocyclobutene (XIX).

At 535° and a pressure of 16 mm., 7.7 g. (0.036 mole) of XIX was pyrolyzed. Analysis by g.l.c. indicated a yield of 96 % was obtained and 7% of the reaction mixture was product. In the reaction mixture, the product became viscous and decomposed very readily, even when under refrigeration. A small amount of 2-ethoxy-3-propyl-1,1,4,4,-tetrafluoro-1,3,-butadiene (XX) was purified on the "Autoprep" g.l.c. apparatus and sent immediately for an elemental analysis.

Anal. Calcd. for $C_9H_{12}F_4O$: C, 51.0; H, 5.64; O, 7.55; F, 35.8. Found: C, 51.5; H, 4.60; F, 35.8; O, 8.06.

The infrared spectrum indicated strong absorptions at 1100, 1380, 1670 and 1800 cm^{-1}.

Pyrolysis of 1-Ethyl-2-propyl-3,3,4,4-tetrafluorocyclobutene (XVII).

At 590° and a pressure of 8 mm. pyrolysis of 8.0 g. (0.041 mole) of XVII was attempted, but no product was detected by g.l.c. analysis. The pressure was kept constant, and the temperature was raised in increments of ca. 15° with the result that increased conversion was obtained. However, no additional conversion was obtained if the reaction mixture was recycled at the same temperature. At 700° g.l.c. analysis indicated 9% of the reaction mixture was product and a 97% yield was obtained. Two small side products were also noted. The three new materials were separated on the "Autoprep" g.l.c. apparatus. The major product, 2-ethyl-3-propyl-1,1,4,4-tetrafluoro-1,3-butadiene (XXI), decomposed quite readily, so a sample was sent immediately for elemental analysis.

Anal. Calcd. for $C_9H_{12}F_4$: C, 55.1; H, 6.12; F, 38.8. Found: C, 54.6; H, 5.25; F, 39.7.

The infrared spectrum showed strong absorptions at 1100, 1210, and 1335 cm^{-1} as well as weak absorptions at 1670 and 1750 cm^{-1}.

On side-reaction product produced an infrared spectrum which indicated strong absorptions at 1045, 1090, 1195, 1210, and 1320 cm^{-1}. An absorption between 1500 and 2000 cm^{-1} was absent, but a small absorption was noted at 2950 cm^{-1}.

The other side-reaction product produced an infrared spectrum which indicated strong absorptions at 1255 and 1725 cm^{-1} as well as a moderate absorption at 2960 cm^{-1}.

Pyrolysis of 1,2-Diethyl-3,3,4,4-tetrafluorocyclobutene (II).

At 670° and a pressure of 8 mm. 113 g. (0.62 mole) of II was pyrolyzed. A small modification in the apparatus facilitated production of the pyrolyzate. Instead of two dry-ice cooled traps, the trap closest to the tube outlet was ice-cooled. This ice-cooled trap collected most of the cyclobutene II and allowed the lower boiling 2,3-diethyl-1,1,4,4-tetrafluoro-1,3-butadiene (III) to pass on to the dry-ice cooled trap. The material in the dry-ice cooled trap contained 20% butadiene III, whereas III composed only 2% of the material in the ice-cooled trap. The material in the ice-cooled trap was then recycled, and the enriched material in the dry-ice cooled trap was collected after each pass and separated on the "Autoprep" g.l.c.

apparatus. Analysis of the reaction mixture by g.l.c. indicated a 98% yield and a 3% conversion per pass. A small side-reaction product was also noted.

The properties of butadiene III are as follows: b.p. 98.5°/625 mm., n_D^{25} 1.3702, d_4^{25} 1.080. Molar refraction: calcd., 38.1; obsd., 38.1.

Anal. Calcd. for $C_8H_{10}F_4$: C, 52.7; H, 5.49; F, 41.7. Found: C, 53.4; H, 5.58; F, 41.1.

The infrared spectrum showed strong absorption at 878, 1255, and 1730 cm^{-1}. A moderate absorption was also found at 2970 cm^{-1}.

The side reaction product gave an infrared spectrum identical with the spectrum of the side reaction product containing no olefin absorption obtained in the pyrolysis of ethylpropylcyclobutene XVII.

Anal. Found: C, 51.2; H, 4.52; F, 44.3 (by difference). The empirical formula is C_2H_2F. The most probable molecular formula is $C_8H_8F_4$. No structure is proposed.

Pyrolysis of 2,3-Diethyl-1,1,4,4-tetrafluoro-1,3-butadiene (III).

At 670° and a pressure of 8 mm. 2.1 g. (0.012 mole) of III was pyrolyzed in an apparatus similar to that used in the previous experiment. Analysis by g.l.c. indicated that an 80% yield was obtained and that 97% of the reaction mixture was the diethylperfluorocyclobutene II. The identity of the major product was verified by an infrared spectrum which was identical with the spectrum of an authentic sample.

Pyrolysis of Perfluorocyclobutene (I) in Sulfur Dioxide Atmosphere.

After the pyrolysis tube was heated to 700°, the complete pyrolysis system was purged with sulfur dioxide; and 100 g. (0.62 mole) of perfluorocyclobutene was passed slowly through the pyrolysis tube along with sulfur dioxide. This was accomplished by merging the delivery tubes of cyclobutene I and sulfur dioxide. In order to indicate the relative rates of flow between the two gases, bubblers were placed between the sources and the point of merger. Both gases were passed into the pyrolysis tube slowly and at approximately the same rate, and the effluent gases were condensed in a dry-ice cooled trap. Upon completion of the run, the trapped material was allowed to distill through water into another dry-ice cooled trap. The scrubbing removed sulfur dioxide and allowed ca. 70 g. (70% recovery) of nearly pure cyclobutene I to be collected in the second trap. About 20 g. of nonvolatile materials remained in the first trap. Distillation of this material on a 5 inch vigreaux column gave a distillate which contained about ten components as indicated by g.l.c. analysis. No pure material was isolated.

Bromination of 1,2-Diethyl-3,3,4,4-tetrafluorocyclobutene II with N-Bromosuccinimide.

About 43 g. (0.28 mole) of N-bromosuccinimide was slurried with 50 ml. of carbon tetrachloride in a 100 ml. three-neck flask fitted with a stirrer, a reflux condenser, and a dropping funnel. As the carbon tetrachloride was refluxed, 25 g. (0.137 mole) of diethylperfluorocyclobutene II was added. After rapid stirring at reflux temperature for 24 hrs., no succinimide appeared at the surface of the carbon tetrachloride. A small amount of azobis-(isopropyl cyanide) was then added as a radical initiator. Again no succinimide appeared after refluxing with rapid stirring for another 24 hours. Diethylperfluorocyclobutene was recovered unchanged.

Random Chlorination of 1,2-Diethyl-3,3,4,4-tetrafluorocyclobutene II.

A fritted glass bubbler was placed into a cylindrical glass vessel and was covered with 25 g. (0.14 mole) of II. Connected to the exit of this vessel was an empty trap to prevent water from sucking back from the following trap which was filled with water to such a depth that a pressure of ca. 6 in. of water could be maintained in the reaction vessel. This water valve also trapped any HCl formed. The reaction vessel was irradiated with a Hanovia Ultraviolet lamp while chlorine gas was bubbled into the liquid at such a rate that only an occasional bubble issued from the water valve.

After 48 hrs. g.l.c. analysis of a small aliquot indicated that no starting material remained and that at least seven products were present. The reaction mixture was then washed with aqueous sodium bisulfite to remove excess chlorine present. The aqueous phase was then washed with carbon tetrachloride, and the wash was placed with the other organic material. This material was washed with aqueous sodium bicarbonate to remove any hydrochloric acid. Anhydrous magnesium sulfate and calcium chloride were used to dry the organic material.

After filtering the drying agent, the carbon tetrachloride was removed by distillation; and the remaining components were separated on the "Autoprep" g.l.c. apparatus. In most cases only enough material was obtained for an infrared spectrum.

Chlorination of 1,2-Diethyl-3,3,4,4-tetrafluorocyclobutene (II) in the Dark at 0°.

Into a small tube fitted with a fritted glass bubbler was placed 24.4 g. (0.134 mole) of II. Atop this tube was placed a small water-cooled condenser backed by a dry-ice cooled trap. The reaction vessel was placed in a Dewar flask filled with ice in a saturated brine solution, and it was covered with a black cloth. Chlorine gas was bubbled slowly through the liquid for 21 hrs. (Chlorine trapped in the dry-ice cooled trap was recycled periodically.) At the end of this time g.l.c. analysis indicated only 10% of the starting material had reacted. After 36 hrs. of total reaction time the reaction was 75% complete.

The clear, slightly greenish reaction mixture was washed with aqueous sodium bisulfite and then with aqueous sodium bicarbonate.

The organic material was dried over Drierite and separated roughly on a 3 in. nichrome spiral column. A complete separation was obtained on the "Autoprep" g.l.c. apparatus.

Analysis of the reaction mixture by g.l.c. indicated a 20% conversion to 1-(1-chloroethyl)-2-ethyl-3,3,4,4-tetrafluorocyclobutene V, a 35% conversion to 1,2-dichloro-1,2-diethyl-3,3,4,4-tetrafluorocyclobutane IV, 20% conversion to heavier materials, and 25% recovery of II.

When a similar reaction was allowed to proceed for 48 hrs., g.l.c. analysis indicated the reaction was 96% complete with a conversion of 11% to allylic chloride V, 34% to dichloride IV, 32% to a trichloride, and 18% to other products. Four % of the starting material was present.

The properties of V are as follows: b.p. 157°/628 mm., n_D^{27} 1.4000, d_4^{27} 1.24. Molar refraction: calcd., 42.2; obsd. 42.3.

Anal. Calcd. for $C_8H_9ClF_4$: C, 44.3; H, 4.15; Cl, 16.4; F, 35.1. Found: C, 45.0; H, 4.01; Cl, 16.0; F, 34.8.

The n.m.r. spectrum showed a triplet at 8.81τ (J = 7.5 c.p.s.) a quartet at 7.61τ (J = 7.5 c.p.s.), a doublet at 8.28τ (J = 7.0 c.p.s.), and a quartet at 5.22τ (J = 7.0 c.p.s.).

The properties of V are as follows: b.p. 165°/628 mm., n_D^{27}1.4119, d_4^{27} 1.31. Molar refraction: calcd., 47.6; obsd., 47.7.

Anal. Calcd. for $C_8H_{10}Cl_2F_4$: C, 37.9; H, 3.95; Cl, 28.0; F, 30.0. Found: C, 38.5; H, 3.83; Cl, 27.2; F, 29.9.

The n.m.r. spectrum showed a triplet at 8.87τ, and a quartet at 7.86τ (J = 7.0 c.p.s.)

The properties of Va are as follows: b.p. 201°/622 mm., n_D^{28} 1.4369, d_4^{28}1.447. Molar refraction: calcd., 52.4; obsd., 52.1.

Anal. Calcd. for $C_8H_9Cl_3F_4$: C, 33.4; H, 3.13; Cl, 37.1; F, 26.4. Found: C, 33.6; H, 3.26; Cl, 37.1; F, 26.6.

The n.m.r. spectrum defied interpretation due to the large number of peaks all through the scan. This may be due to the presence of two isomers, which are indicated by a shoulder in the g.l.c. trace. The infrared spectrum indicated strong absorptions at 828, 842, 1180 (broad), 1240, and 1380 cm^{-1}. There was no absorption between 1500 and 2000 cm^{-1}. This spectrum corresponded exactly to a spectrum of one of the products of random chlorination.

Bromination of 1,2-Diethyl-3,3,4,4-tetrafluorocyclobutene (II) with Molecular Bromine.

About 25 g. (0.14 mole) of II dissolved in 50 ml. of methylene chloride was placed into a 100 ml. three-neck flask fitted with a stirrer and a reflux condenser connected to an ice-cooled trap. About 27 g. (0.17 mole; 25% excess) of bromine was added, and the reaction mixture was stirred while being warmed slightly by an incandescent bulb. An aliquot taken after 50 hrs. and analyzed by g.l.c. on a Silicone Dow 710 column (hereafter SD 710) indicated 20% completion of the reaction. After 5-1/2, 8, and 14 days of reaction time, the reaction mixture was checked for completeness of reaction and found to be 50,62, and 77% complete, respectively. After 14 days the reaction mixture was washed with aqueous sodium bisulfite until the orange color was removed and with sodium bicarbonate to remove the hydrobromic acid. The aqueous phase was washed with methylene chloride to extract any organic material, and the extract was placed with the original organic phase. Analysis of this by g.l.c. (SD 710 column) indicated a quantitative recovery, a 63% conversion to 1-(1-bromoethyl)-2-ethyl-3,3,4,4-tetrafluorocyclobutene (VI), and a 14% conversion to dibromide (VIIa + VIIb).

Fractionation under reduced pressure yielded several fractions of pure monobromide VI (b.p. 40°/1 mm.) and a fraction boiling at 55-60°/0.5 mm. containing impure dibromide. The dibromide was purified on the "Autoprep" g.l.c. apparatus.

Another run was made using slightly different conditions. In this case a 100% excess of bromine was used, and the reaction mixture was heated to ca. 35° by an incandescent bulb. At the end of 14 days, g.l.c. analysis (SD 710 column) indicated a quantitative recovery, a 41% conversion to monobromide VI, and a 58% conversion to dibromide VIIa + VIIb.

Monobromide VI reacted with both silver nitrate in ethanol and sodium iodide in acetone in 5 minutes. The dibromide VIIa + VIIb reacted with silver nitrate in ethanol rapidly but with sodium iodide in acetone slowly.

The properties of monobromide VI are as follows: b.p. 175°/625 mm., n_D^{25} 1.4241, d_4^{25} 1.469. Molar refraction: calcd., 45.1; obsd., 45.3.

Anal. Calcd. for $C_8H_9BrF_4$: C, 36.8; H, 3.45; Br, 30.65; F, 29.1. Obsd.: C, 35.4; H, 3.48; Br, 31.3; F, 29.9.

The n.m.r. spectrum showed a triplet at 8.82τ (J = 7.0 c.p.s.), a quartet at 7.63τ (J = 7.0 c.p.s.), a doublet at 8.13τ (J = 7.0 c.p.s.), and a quartet at 5.26τ (J = 7.0 c.p.s.). These integrated for 3,2,3, and 1 protons, respectively.

Analysis of dibromide VIIab showed C, 28.1%; H, 2.21%; Br, 47.1%; F, 22.6%. The empirical formula was calculated to be $C_4H_4F_2Br$.

Dehydrobromination of 1-(1-Bromoethyl)-2-ethyl-3,3,4,4-tetrafluorocyclobutene (VI).

A solution of 5.5 g. (0.021 mole) of VI dissolved in 10 ml. of ether was place in a 25 ml. Morton flask fitted with a stirrer, a dropping funnel, and a reflux condenser backed by a dry-ice cooled trap. While this solution was stirred rapidly, 5 g. (0.05 mole) of triethylamine was added slowly. When no noticeable heat was evolved and when solid triethylamine hydrobromide formed only slowly, the remainder of the triethylamine was added rapidly. After stirring for 24 hrs. at room temperature and after an additional 11 hrs., at reflux temperature, g.l.c. analysis indicate 50% and 65% completion of reaction, respectively. Analysis by g.l.c. also indicated a 45% conversion to 1,2-diethylidene-3,3,4,4-tetrafluorocyclobutane (VIII) and a 70% yield was obtained.

The reaction mixture was washed thoroughly with 5% hydrochloric acid to remove excess triethylamine. This solution was then extracted to recover any organic material which might be present. The total organic portion was neutralized with sodium bicarbonate and dried over anhydrous magnesium sulfate. Ether was removed by distillation, and the remaining starting material VI and diethylidenecyclobutane VII separated by the "Autoprep" g.l.c. apparatus.

The properties of VII are as follows: b.p. 147°/630 mm., n_D^{25} 1.4192, d_4^{28} 1.17. Molar refraction: calcd., 36.9; obsd., 38.8.

<u>Anal</u>. Calcd. for $C_8H_8F_4$: D, 53.3; H, 4.44; F, 42.2. Found: C, 53.1; H, 4.21; F, 42.1.

The n.m.r. spectrum of VIII showed an ill-defined multiplet centered at 8.07 τ and a triplet or quintet at 3.78 τ (J = 7.5 c.p.s.). Its infrared spectrum indicated strong absorptions at 890, 900, 1100, 1110, 1245, 1300, 1350, and 1670 cm^{-1}.

<u>Dehydrobromination of Dibromide VIIa and VIIb (From the Bromination of Diethylcyclobutene II)</u>.

About 22.2 g. (0.22 mole) of triethylamine dissolved in 50 ml. of ether was placed in a 100 ml. three-neck flask fitted with a dropping funnel, a stirrer, and a reflux condenser backed with a dry-ice cooled trap. Dibromide VIIa and VIIb was then added dropwise as the reaction mixture was stirred rapidly. Since the reaction was quite exothermic, an ice bath was employed to cool the reaction mixture. After addition was completed, the reaction mixture was stirred for one hour. At this point no major product could be detected by g.l.c. (SD 710 column) even though a considerable amount of triethylamine hydrobromide salt was evident in the reaction flask. Consequently, the reaction mixture was stirred overnight at room temperature, during which time it turned black.

The reaction mixture was then washed thoroughly with 5% hydrochloric acid. The wash was extracted with ether, and the entire organic material was neutralized with sodium carbonate and dried over anhydrous magnesium sulfate. Crude distillation at reduced pressure yielded a material which g.l.c. analysis (SD 710 column) indicated contained material resulting from a 25% conversion to 1,2-divinyl-3,3,4,4-tetrafluorocyclobutene (X), a 13% conversion to 1-ethyl-2-(1-bromovinyl)-3,3,4,4-tetrafluorocyclobutene (XI), and a total yield of 45%. A trace product was also noted. Separation was achieved on the "Autoprep" g.l.c. apparatus.

The properties of divinylcyclobutene X are as follows: b.p. ca. 130°/628 mm. (polymerizes), n_D^{26} 1.4417, d_4^{26} 1.194. Molar refraction: calcd., 36.4; obsd., 39.4.

Anal. Calcd. for $C_8H_5F_4$: C, 53.9; H, 3.4; F, 42.6; Found: 53.4; H, 3.6; F, 43.1.

The n.m.r. spectrum showed a complex multiplet centered at ca. 4 τ.

The properties of bromovinylcyclobutene XI are as follows: b.p. 164°/628 mm. (slight decomp.), n_D^{25} 1.4422, d_4^{26} 1.495. Molar refraction: Calcd. 44.7; obsd., 45.8.

Anal. Calcd. for $C_8H_7BrF_4$: C, 37.0; H, 2.70; Br, 30.9; F, 29.3. Found: C, 38.9; H, 3.1; Br, 29.7; F, 28.1.

The n.m.r. spectrum showed a triplet at 8.78 τ (J = 7.5 c.p.s.), a quartet at 7.31 τ (J = 7.5 c.p.s.), and a pair of doublets at 3.95 and 3.67 τ (J = 2.5 c.p.s.). Each doublet in the pair of doublets was unsymmetrical with the inside peak highest, indicating an AB case.

The trace product analyzed for C, 53.5%; H, 3.5%; F, 43.0%. The empirical formula is $C_4H_3F_2$, and the most likely molecular formula is $C_8H_6F_4$.

Dehydrobromination of Dibromide VIIa and VIIb (From the Bromination of Diethylcyclobutene (II) with Potassium Hydroxide.

A solution of 33 g. (0.096 mole) of dibromide VIIa and VIIb in 25 ml. of 95% ethanol was placed into a 250 ml. three-neck flask, fitted with a reflux condenser, a stirrer, and an additional funnel. A solution of 6.5 g. (0.09 mole) of potassium hydroxide in 50 ml. of 95% ethanol was then added dropwise as the solution was stirred rapidly. Due to the heat liberated it became necessary to cool the reaction vessel in a cold water bath. After two hrs. of reaction time the solid material which was formed was filtered and washed with ethanol. The organic portion of the reaction mixture was washed with water to remove ethanol and soluble inorganic salts. This wash was extracted with methylene chloride, which was then placed with the original organic material. After this solution was dried over anhydrous magnesium sulfate, it was distilled in a 12 in. column until all the methylene chloride had been removed. The remaining material was then crudely distilled at 50°/1 mm. Analysis by g.l.c. indicated only one broad peak in the area of starting material was present. Resolution by g.l.c. was unsuccessful even though several different columns at different conditions were used. However, 10.05 g. (0.084 mole: 88% of theory) potassium bromide was recovered. The infrared spectrum was drastically different from that of the starting material. The most striking difference was the presence of a strong absorption at 1650 cm^{-1} in the product. A very weak absorption of 1670 cm^{-1} was the only peak noted in the olefin region in the spectrum of the starting material. N.m.r. of this material gave an irresolvable array of peaks, most of which were very broad.

Debromination of Dibromide VIIa and VIIb.

About 8 g. (0.13 gramatom) of zinc was slurried with 20 ml. of absolute ethanol in a 150 ml. three-neck flask fitted with a stirrer, a dropping funnel, and a reflux condenser. The slurry was heated until ethanol refluxed, and the mixture of VIIa and VIIb was added slowly.

After ca. 2 hrs. reaction time g.l.c. analysis indicated no starting material remained in the reaction mixture and two products VIII and IX were present in the water-white material in the ratio of 1.[illegible] to 1.0. The organic materials were distilled from the reaction vessel at ca. 1 mm. and were isolated by manual collection of the effluent gases from an analytical g.l.c. apparatus. The major product produced an infrared spectrum identical with a spectrum of diethylidene VIII The infrared spectrum of the minor product IX indicated strong absorptions at 890, 900, 1060, 1120, 1235, 1275, 1350, 1440, and 1660 cm^{-1}. When separation of these two materials was attempted on the "Autoprep" g.l.c. apparatus, the minor product IX isomerized to VIII; however, a Ucon Lubricant column allowed separation.

Anal. Found: C, 51.7; H, 4.23; F, 41.6 (97.5 total) The empirical formula is C_2H_2F, and the most probably molecular formula is $C_8H_8F_4$. Positive identification has not been accomplished.

Dechlorination of Trichloride (Va) (From Chlorination of Diethylcyclobutene II).

About 10.5 g. (0.16 gram-atom) of zinc was slurried with 20 ml. dibutoxytetraglycol in a 100 ml. three-neck flask fitted with a stirrer, a reflux condenser, and a dropping funnel. This slurry was warmed to ca. 50°, and trichloride Va was added dropwise. After addition was completed, the reaction mixture was heated to 70° and stirred for 15 hrs. At the end of this time the accessories were removed from the flask, and a vacuum of 1 mm. pressure was applied with the temperature still at 70°. The 16.1 g. of products and starting material were collected in a dry-ice cooled trap. Analysis by g.l.c. indicated a 42% conversion to three products and a yield of 82% was obtained. Separation of the components was accomplished on the "Autoprep" g.l.c. apparatus. Only the lowest boiling material (conversion of 5.4%) was characterized. Its infrared spectrum was identical with the spectrum of allylic chloride XIV. Another of the materials polymerized and decomposed in the receiver.

Preparation of 1,2-Diethylcyclobutene-3,4-dione (XII).

About 50 g. (0.48 mole) of 95% sulfuric acid was placed into a 50 ml. three-neck flask fitted with a stirrer, a reflux condenser, and a dropping funnel. This then was heated to ca. 70° on a steam bath, and 19.2 g. (0.105 mole) of diethylcyclobutene was added rapidly. As this mixture was stirred rapidly, the two phases gradually became miscible; and a gas was evolved. Water that this gas was bubbled through became very acidic. After 1 hr. the black reaction mixture was poured over ice, and the resulting emulsion was washed with ether to remove the organic material. This ether wash was then neutralized with sodium bicarbonate, dried over anhydrous magnesium sulfate, and distilled at reduced pressure using a one-plate apparatus. At 100°/2 mm. 7.3 g. (53% of theory) of a light yellow oil was obtained. This material gives a 2,4-dinitrophenylhydrazone which was recrystallized from an ethanol-ethylacetate mixture (mp. 130-133°). It very slowly decolorized bromine in carbon tetrachloride.

The properties of cyclobutenedione XII are as follows: b.p. 100°/ 2 mm., n_D^{25} 1.4842, d_4^{25} 1.023. Molar refraction: calcd., 37.0; obsd., 38.3.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.6; H, 7.24; O, 23.2. Found: C, 69.3; H, 7.21; O, 23.5.

The infrared spectrum showed absorptions at 1600, 1770, and ca. 1800 (shoulder) cm^{-1}. The n.m.r. spectrum showed a triplet centered at 8.70 τ and a quartet centered at 7.18 τ (J = 7.5 c.p.s.). The ultraviolet spectrum indicated a λmax 216 mu (ϵ 16,400).

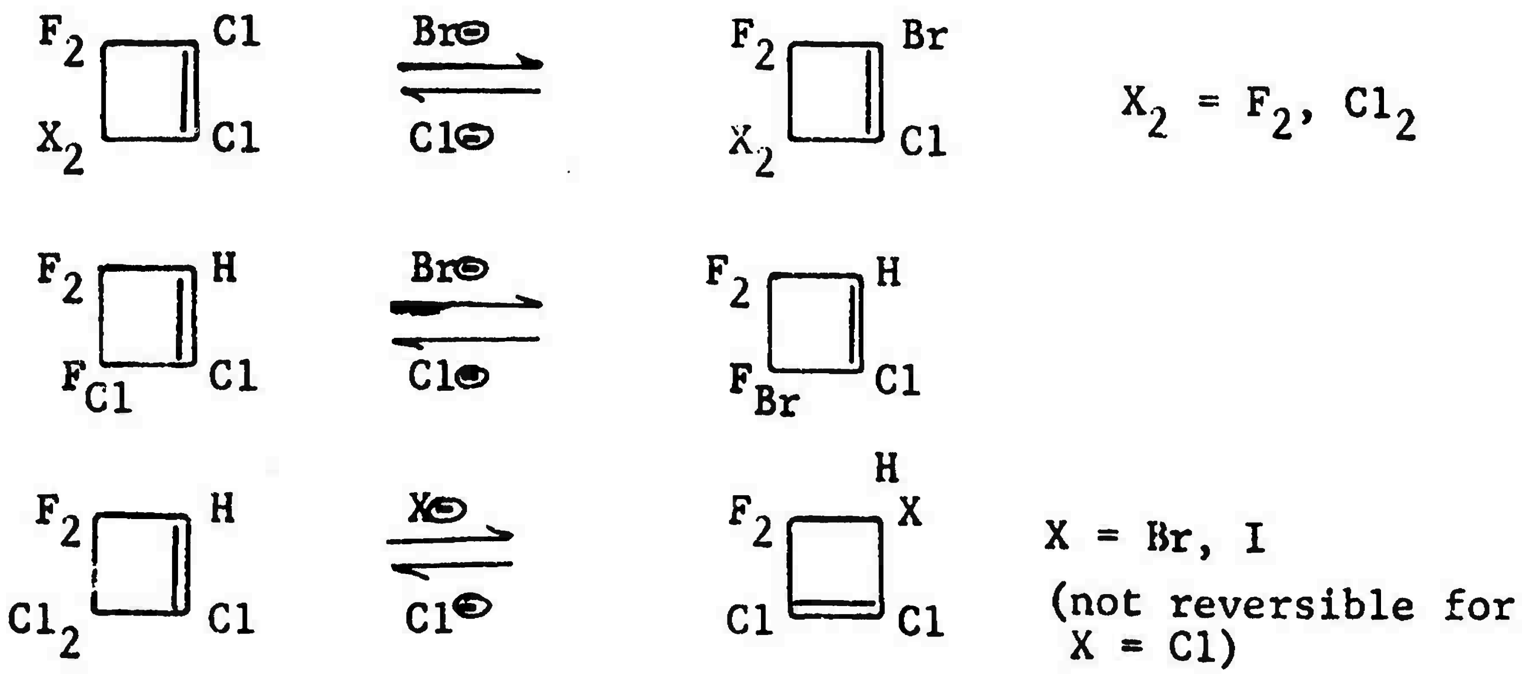
NUCLEOPHILIC DISPLACEMENT BY HALIDE ION ON HALOCYCLOBUTENES

Reversible vs. Irreversible Carbanion Formation. - The reactions of alkoxide ions and amines with halocyclobutenes led to substitution products, with both vinylic and allylic halogen atoms being displaced. The products of such nucleophilic attacks have been rationalized in terms of the ralative stabilities of the two possible carbanionic intermediates. Park, Adams, Dick, and Sullivan[12] have deduced from the alkoxide-cyclobutene reactions an order of stabilizing ability of substituents and to the incipient carbanion. While the hypothesis of carbanion intermediacy is yet to be proven, it provides a working rule for prediction of the reaction products. The present study is concerned with the scope and probably mechanism of the reactions of halide ions with halocyclobutenes.

Twenty-seven reactions of this type were studied, chiefly with the alkali metal halides in acetone. Similar results were found with alkali metal halides in DMF or DMSO and for tetraethylammonium halides in chloroform. The results are summarized below, giving a few examples to justify each generalization.

1) Halide attack involves reversible equilibria.

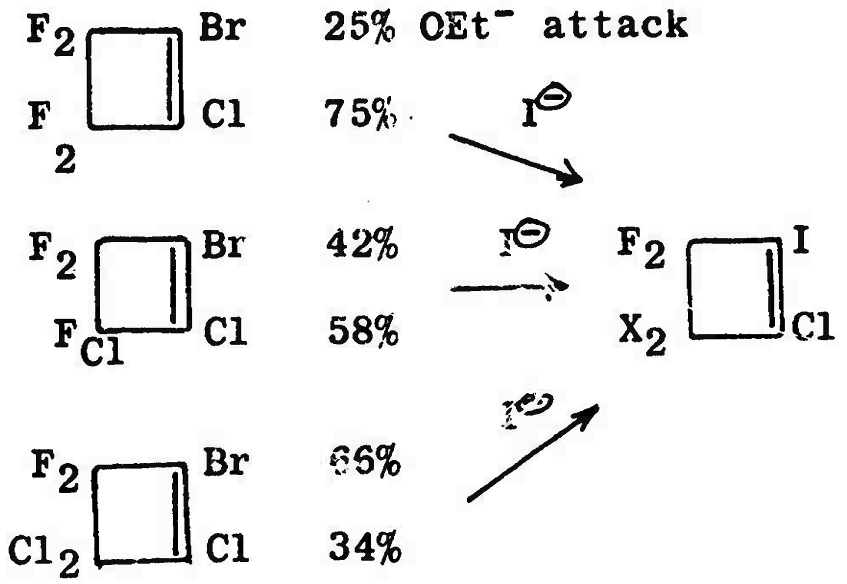
Overall reversibility was demonstrated in several cases. The procedure usually required to force a reaction to near-completion is typical of that expected for an equilibration: addition of one equivalent of halide to a solution of the cyclobutene resulted in time in a steady-composition mixture of product and reactant. Renewal of the halide shifted the composition further in favor of product, a new stable mixture forming. In sharp contrast, alkoxide reactions

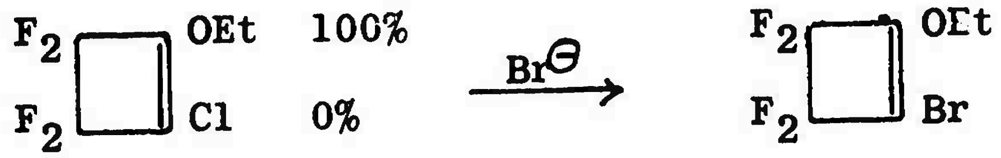


are irreversible and proceed rapidly at low temperatures to completion.

2) The best leaving group is lost.

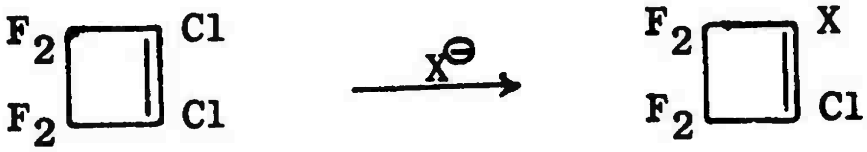
Product analysis, the basis of the alkoxide carbanion theory, clearly shows that halide attack and alkoxide attack differ greatly. The kinetic argument, involving and stabilization of the carbanion, is thus inapplicable here, as would be expected from the reversible nature of halide reactions.



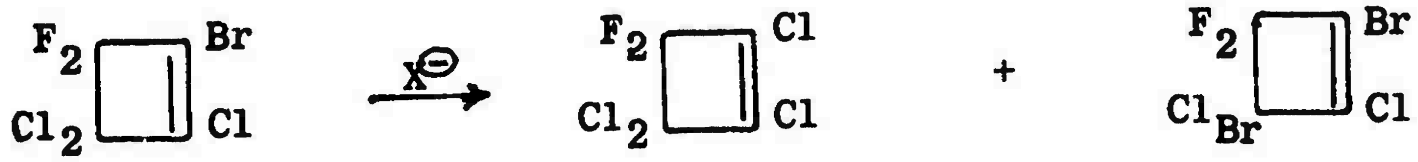


3) The order of reactivity of the metal halides in acetone is Cl > Br > I. Fluoride gave inconsistent results.

Only crude relative reactivities were noted, but it is felt the differences are so great between the metal helides that more precise work is unnecessary at this stage. Two of the sources of these data are shown below.

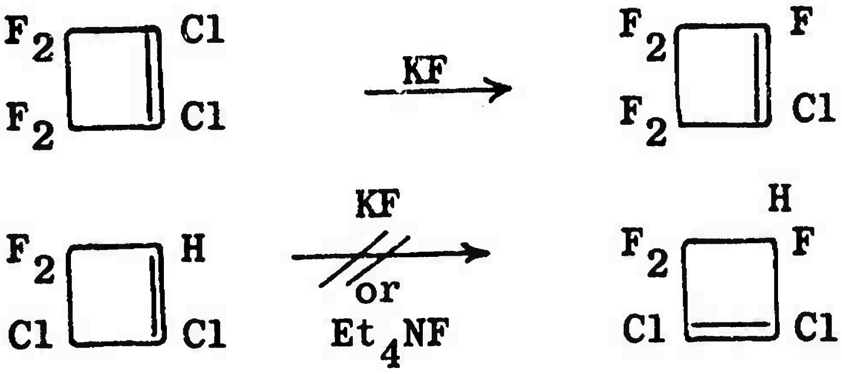


X = Br, 8 hrs., 50%
I, 3 days, 25%



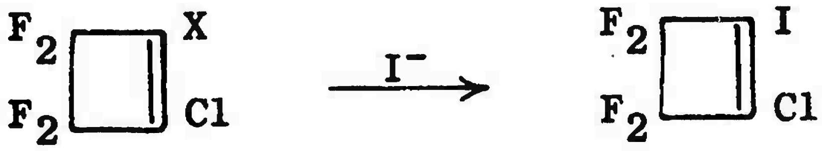
X = Cl, 20 hrs., 55° 58% 7 at equilibrium
Br, 20 hrs., 55° 25% 25 at equilibrium

In the latter series, the dibromide was noted only after 50% of the starting material had been converted to tetrachlorodifluorocyclobutene in the reaction with chloride ion, but in the reaction with bromide, both products formed at equal rates. Thus, chloride ion was much more effective than bromide, despite the concentration differences. Potassium fluoride in DMF readily replaced a vinylic chlorine atom by fluorine but converted 2,3,3-trichloro-4,4-difluorocyclobutene to tars, with no product of allylic displacement found. Cyanide ion gave only water-soluble maroon products with this cyclobutene.

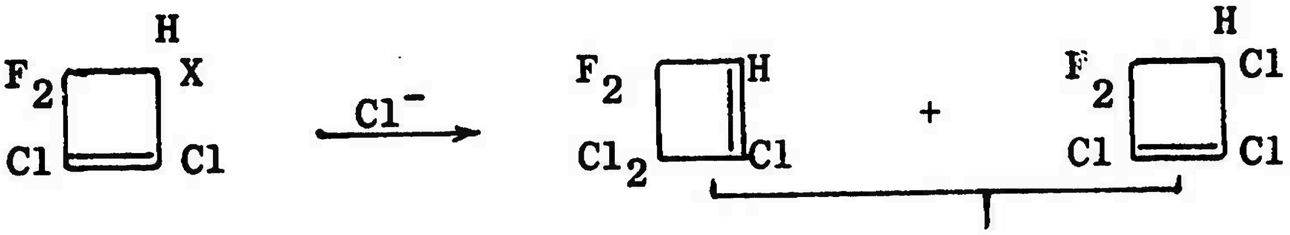


4) The reactivity of cyclobutenylhalides increase in the order $\mathrm{F} \lll \mathrm{Cl} < \mathrm{Br} < \mathrm{I}$.

Fluoride, allylic or vinylic, was never displaced. Examples substantiating the order $RCl < RBr < RI$ are given below.

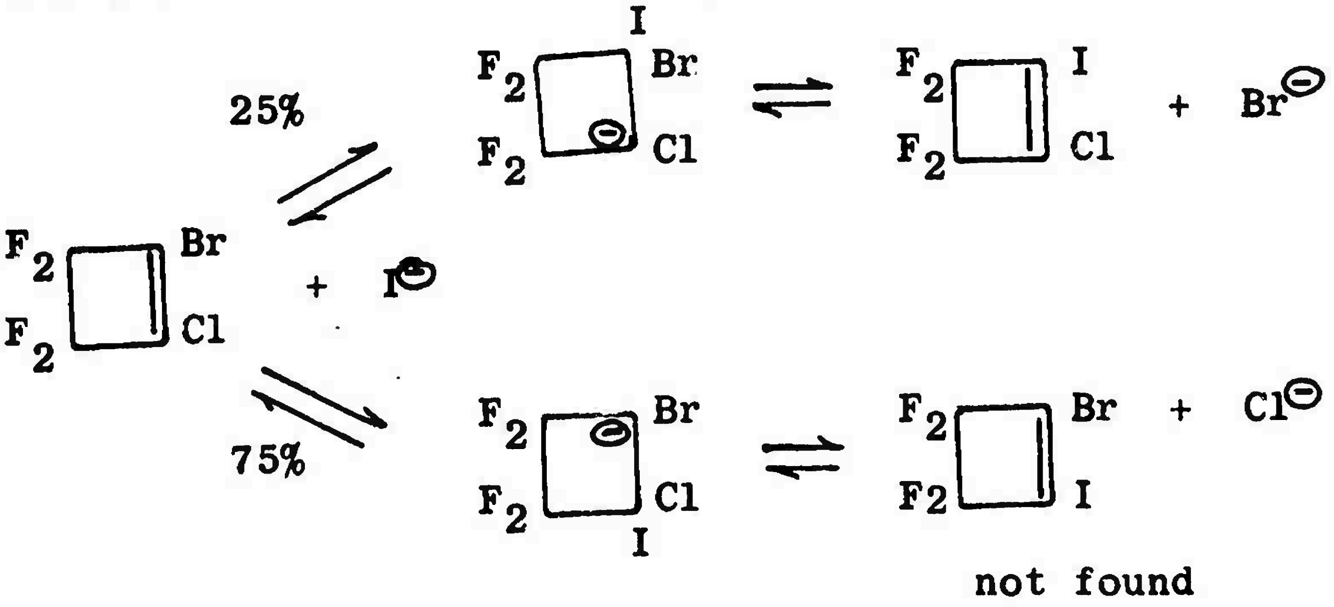


X = Cl, 25°, 55 days, 65%
55°, 8 days, 54%
Br, 25°, 6 days, 42%



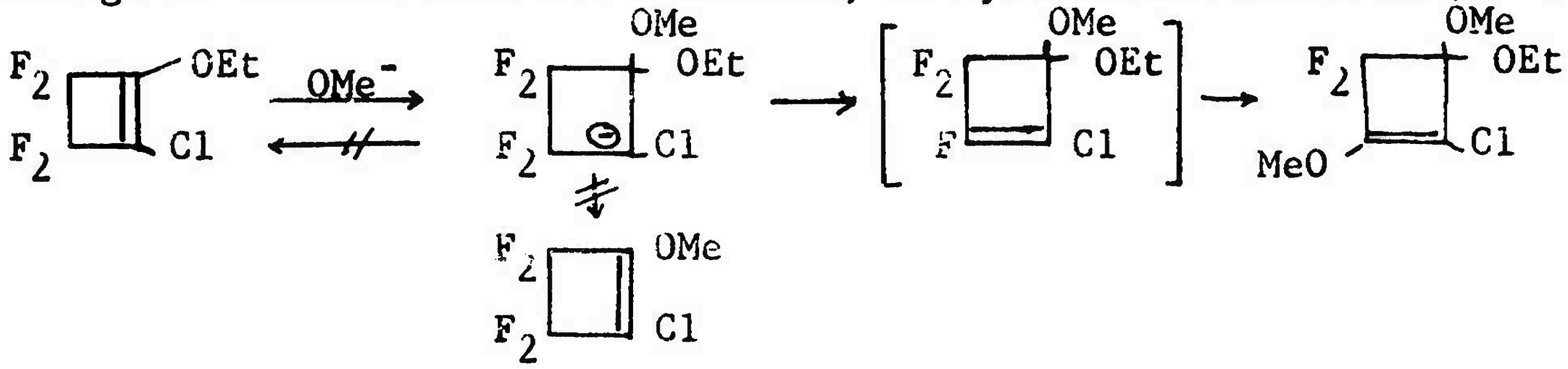
X = Br, 50°, 10 days, 10%
I, 25°, 10 days, 10%

These data are entirely consistent with the reversible formation of carbanions by halide attack, a reasonable hypothesis in view of the similar leaving abilities of the nucleophile and the resident halogen atom. This concept is schematized below in the reaction of 1-bromo-2-chlorotetrafluorocyclobutene with iodide ion.

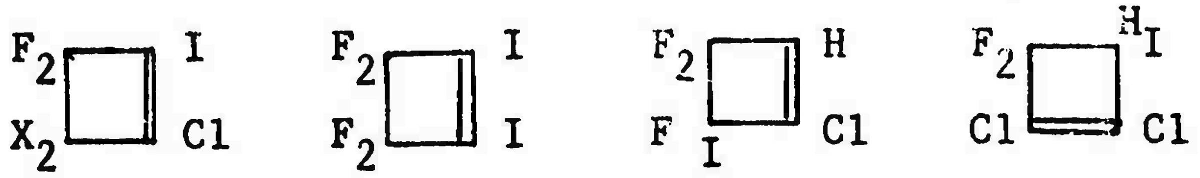


The product forms via the less stable carbanion. Either the greater ability of bromide to leave this carbanion draws the reaction through this path, or more attractively, the lesser stability of a cyclobutenyl bromide to attack by chloride favors the exclusive replacement of bromide by iodide. The order of reactivity of the attacking halide is thus due either to a lesser tendency for chloride attack to reverse (relative to iodide) or the greater stability of the resultant cyclobutenyl chloride. The alternative of competing SN2-SN2' concerted displacements is also consistent with the results, but is less useful as a working rule. Two attempts to trap the intermediate carbanions with halogens gave inconclusive results.

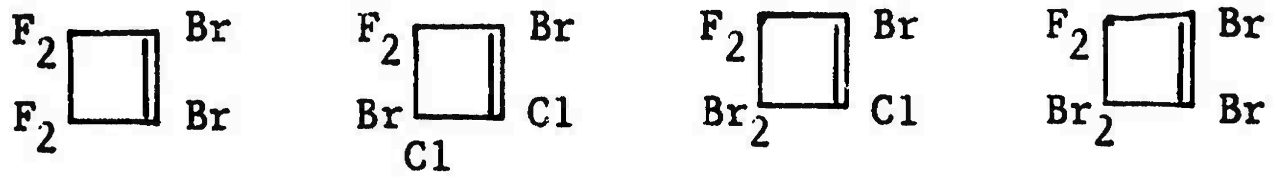
Consideration of the reaction of 1-ethoxy-2-chlorotetrafluorocyclobutene with methoxide ion shows that alkoxide attack must involve irreversible formation of carbanions, as no trimethoxycyclobutene is formed. Although no kinetic data are available, in cyclobutene reactions, the analogous reactions of activated aryl halides support this classification of alkoxides (and amines) as irreversible carbanion-forming reagents and halides as reversible.



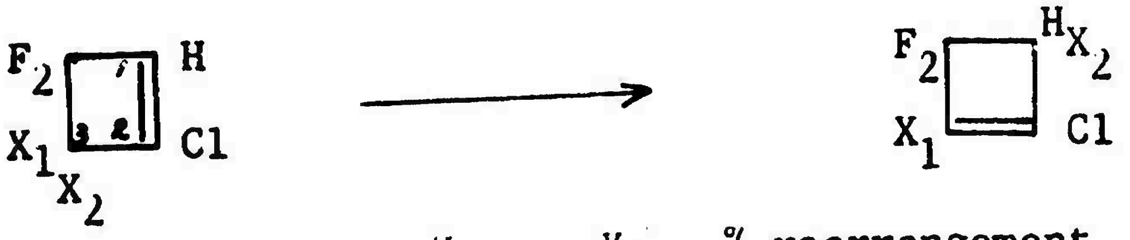
The reaction affords a path to iodo- and bromo-fluorocyclobutenes from readily available chlorofluorocyclobutenes. Examples include the following:



(X_2 = F_2, FCl, Cl_2)



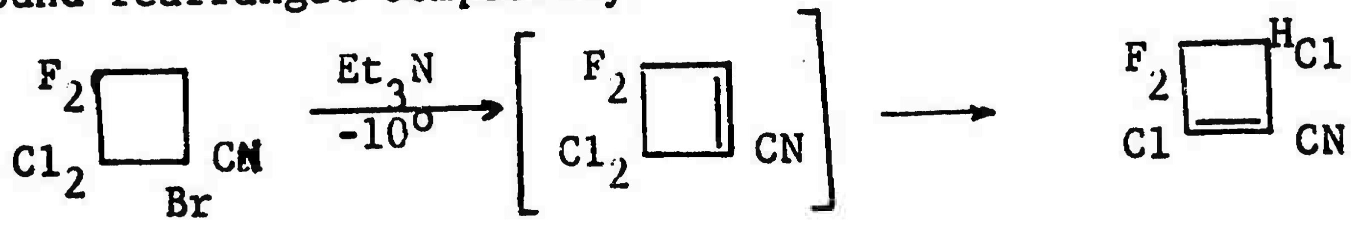
Two specific classes of halide attack of halocyclobutenes have been found. The first is the nucleophile-catalyzed rearrangement of halocyclobutenes. Five 2-chloro-3,3-dihalo-4,4-difluorocyclobutenes were studied in this connection. Examples a, b and d were treated with halide ion in refluxing acetone and with triethylamine and DMSO, both at 90°. Roberts has proposed that triethylamine in similar reactions provides a halide ion by an initial Menschutkin reaction. Compound c was treated only with iodide ion and compound e rearranged rapidly at 25° in the absence of any catalyst. It is attractive to



	X_1	X_2	% rearrangement
a	F	Cl	0
b	F	Br	0
c	F	I	10
d	Cl	Cl	98-100
e	Cl	Br	100

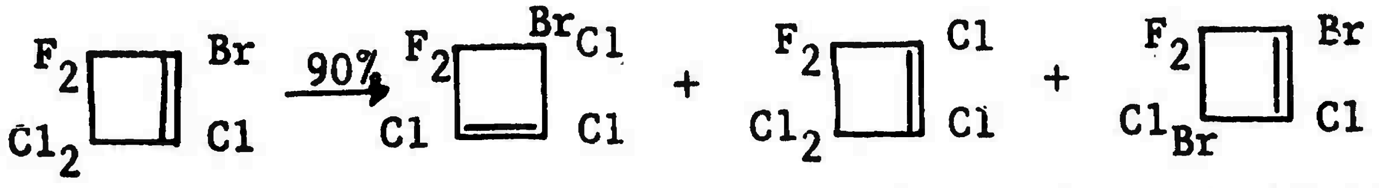
ascribe the observed trend in rearrangement to increasing steric push a→e but the nature of the double bond formed is also important. The instability of the rearranged isomers of a and b is confirmed by the reactions of a with bromide to give b and of b with chloride to give a. Since irreversible attack of similar 1-hydro-3,4,4-triflurocyclobutenes gives SN2'-type products, it is reasonable to assume that halide ion initially forms such products but these are unstable to further rearrangment. Rearranged c isomerized partially back to c with heat.

In order to determine the influence of the ε-2 substituent, 2-cyano-3,3-dichloro-4,4-difluorocyclobutene was synthesized. During low-temperature dehydrobromination of the parent α-bromonitrile, this compound rearranged completely.

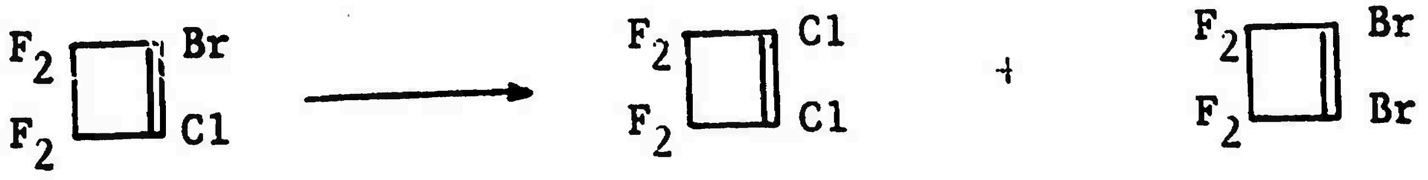


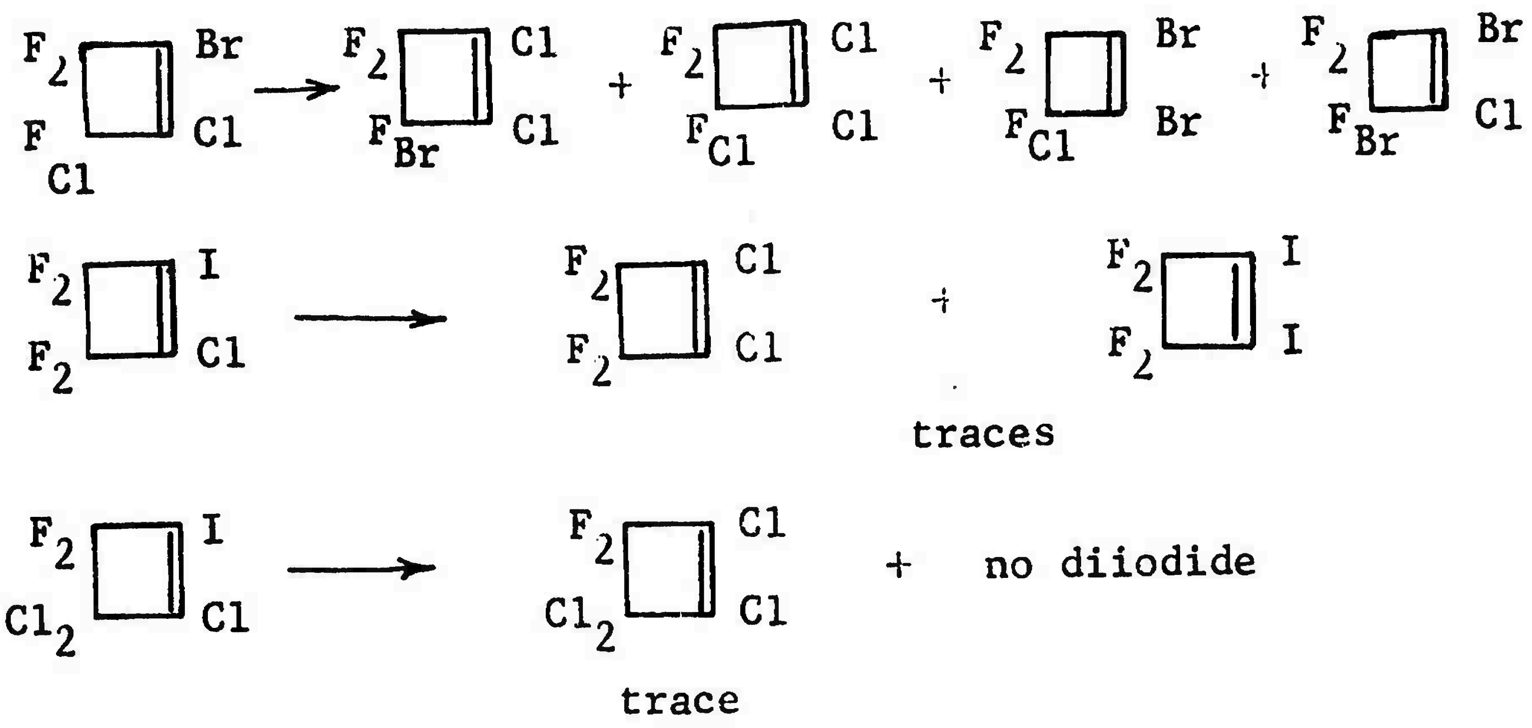
This rate enhancement supports the intermediacy of carbanions, as α-cyano is known to be a strong carbanion-stabilizing group.

Variation at c-1 led to a new type of reaction-intermolecular transfer of halide ion. Thus, 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene in the presence of triethylamine, DMF or DMSO gave partial rearrangement and also 1,2,3,3-tetrachloro-4,4-difluorocyclobutene and 1,3-dibromo-2,3-dichloro-4,4-difluorocyclobutene, in equal amounts.



A similar reaction was found for two other 1-bromo-2-chlorocyclobutenes. Two 1-iodo-2-chlorocyclobutenes gave only trace amounts of transfer products under the same conditions.





Experimental - Rearrangement

The identity of all structures claimed was proven by g.l.c. data and IR spectra. Structure 2,3-dichloro-3,4,4-trifluorocyclobutene (I).

a. Neat Distillation at 85°/630 mm. gave no rearranged product.

b. Et_3N 0.5 ml. I was heated with five drops Et_3N in a sealed tube at 80-82° for 88 hrs. Considerable tarring and two minor (< 2%) components resulted.

c. NaCl/DMSO 0.5 ml. I was heated with five drops of NaCl in DMSO (saturated) at 85° for 17 days. A tan color developed but no new products by g.l.c. analysis.

3-Bromo-2-chloro-3,4,4-trifluorocyclobutene (III).

a. Distillation The crude distillate from the synthesis exhibited weak 1710 cm^{-1} absorption in the IR and 3 minor g.l.c. peaks.

b. Et_3N 0.5 ml. III was heated with 3 drops Et_3N in a sealed tube at 89° for 76 hours to give less than 2% conversion (by g.l.c.) to 4 components.

c. LiBr During the reaction of I with LiBr, no trace of rearranged isomer IV was seen by g.l.c.

2-Chloro-3-iodo-3,4,4-trifluorocyclobutene (V).

KI The preparation of V from reaction of KI with I gave a mixture of 9 parts V to one part 1-chloro-2,3,3-trifluoro-4-iodocyclobutene (VI). The latter was converted 20% to V (g.l.c.) in ten minutes at 124°.

2,3,3-Trichloro-4,4-difluorocyclobutene (VII).

a. Distillation During distillation at 630 mm. nucleophilic impurities cause rearrangment. Rapid distillation at ca. 40°/2 mm. gave only trace amounts of rearranged product, 1,2,3-trichloro-4,4-difluorocyclobutene (VIII).

b. Neat 1.0 g. pure VII was heated at 88-90° for 84 hours in a sealed tube. G.l.c. analysis showed less than 1% VIII. A trace of HX odor was noted but the material did not discolor.

A mixture 98% VII - 2% VIII which contained much HX (by odor and fuming with Et_3N vapor) was heated 93 hours at 90°. G.l.c. of the clear yellow liquid showed 42% VIII. Pure VIII is unstable even at -10°, slowly decomposing to HF, HCl, and tars.

c. Et$_3$N A mixture of 19.3 g. (0.10 m.) 86% VII - 14% VIII, 28 ml. (0.2 m.) Et$_3$N and 4.0 g. (0.03 mole) Et$_3$NHCl was stirred in a 100-ml. flask. At 30°, no change occurred in 24 hours. At 52°, a slow increase in VIII was found at 84°, the mixture went in 13 hours from 44% VIII to 95%. In 25 hours, this mixture went on to 100% VIII with extensive tar and ionic solid formation. A separate experiment with 9.7 g. (0.05 mole) of a mixture 85% VII - 15% VIII and 3.0 ml. Et$_3$N gave in 24 hours at 25° 1.9 g. crude white solid, soluble in H_2O, CH_2Cl_2, MeOH, insol. Et$_2$O, OH, acetone; m.p. 251-258, identical with authentic Et$_3$NHCl in the IR (lit. m.p. 254-55°) after recrystallization from butyrolacetone or dioxane. Two sealed tubes were heated at 90° for 93 hours.

1. 524.7 mg. VII, 19.1 mg. Et$_3$N (14.5 moles VII to one Et$_3$N). A black solid and clear liquid containing 6% VII and 93% VIII resulted.

2. 501.2 mg. VII, 52.4 mg. Et$_3$N (5.2/1) gave mainly black solid, the trace of clear liquid containing 2% VII and 96% VIII. In each case a minor component was also present. The starting material contained 2% VIII and under the same conditions rearranged 40% to VIII, as discussed above.

d. KCl 58.2 g. (0.30 mole) of a mixture 54% VII - 46% VIII was heated to reflux over 3.7 g. (0.05 mole) KCl. The amount of VIII rose to 72% after 40 hours. After cooling, 10 ml. EtOH was added and the mixture heated at 50-70° for 40 hours to give 74% VIII and at 80° for 56 hours, 74% VIII. Ten ml. DMF was added and the mixture heated at 100° for 154 hours to give a dark mixture 98% in VIII. Short-path distillation resulted in 21.3 g. (37%) VIII and much tarry residue.

e. LiCl A mixture of 19.3 g. (0.10 mole) 25% VII - 75% VIII, 4.2 g. (0.10 mole) LiCl, and 100 ml. acetone was heated to reflux for 4 days at which time only 2% of the cyclobutene was VII. In 4 days longer at reflux, the composition remained invariant. Drowning H_2O, CH_2Cl_2 extraction of the H_2O layer, and short-path distillation of the dried organic layer gave 15.4 g. of a mixture 93% in VIII and $<$1% VII, with three other minor components. Separation of FS(110°) gave pure VIII by authentic IR spectrum.

f. Other catalysts

Tubes containing 1 ml. of VII and the indicated amount of catalyst were sealed and heated. Results are shown below.

Catalyst	Temp.	Time	% VIII	Appearance
5 drops saturated NaCl/DMF	50-54°	17 hrs.	3.5	sl. yellow
" " (solid NaCl added)	75	17	16.0	sl. yellow
10 drops DMSO	75	17	25.0	yellow
(resealed)	85	18	70.0	brown
10 drops DMSO, solid NaCl	75	17	30.2	sl. yellow
(resealed)	85	18	77.5	sl. yellow

0.30 ml. of a solution of 117 mg. Et$_4$NCl in 1.0 ml. $CHCl_3$ and 277 mg. (143 mmole) VII were mixed in a closed tube. After 6 days at room temperature, 11% of VII had isomerized to VIII.

3-Bromo-2,3-dichloro-4,4-difluorocyclobutene (IX).

Pure IX, obtained by g.l.c. separation, was allowed to stand at 25° in a closed vial. Initially, the mixture was 94% IX - 6% X, after 36 hours, 50-50, and at 52 hours, 1% IX-95% X and 4% of a new peak at longer retention in the g.l.c. The liquid remained clear and colorless. Pure X was separated on FS (85°), b.p. 31°4 mm. n_D^{25} 1.4780; d^{25} 1.842; MR calc. 36.18, found 36.40; possessed IR absorption at 1625 cm^{-1} and exhibited a quartet in the n.m.r. at 4.83 $J_1 = 2.6$, $J_2 = 0.7$ cps. Calc. for $C_4HBrCl_2F_2$: C, 20.21; H, 0.42; Br, 33.59; Cl, 29.81; F, 15.97. Found (Galbraith): C, 20.40; H, 0.44; Br, 33.47; Cl, 29.70; F, 16.12.

2-Cyano-3,3-dichloro-4,4-difluorocyclobutene (XII).

A solution of 21.4 g. (0.081 mole) of 1-bromo-1-cyano-2,2-dichloro-3,3-difluorocyclobutane (XI) in 75 ml. CH_2Cl_2 was cooled to -10° and a solution of 14 ml. (10.1 g., 0.10 mole) Et_3N in 30 ml. CH_2Cl_2 was added slowly with vigorous stirring. The first few drops turned the mixture yellow. After stirring for eight hours (warming slowly to 25°), the mixture was dark brown, with bits of tar floating about. Cold dilute HCl was added, the organic layer dried and subjected to short-path distillation to give 7.0 g. (0.038 mole, 45%), of a single product. Purification on FS (90°) caused no change by IR comparison, before and after. The pure lachrymatory liquid was assigned structure XIII rather than XII on the bases of 3000 cm^{-1} and 1625 cm^{-1} absorption in the IR (allylic CH and Cl-C=C-CN) and of a quartet at 4.70 , $J_1 = 3.3$, $J_2 = 0.6$ cps. b.p. 34°/4.5 mm., n_D^{25} 1.4548, d^{25} 1.457, MR calc 32.78, found 34.31.

Anal. Calc. for XIII: C, 32.64; H, 0.55; Cl, 38.54; F, 20.65; N, 7.61. Found (Elek): C, 32.68; H, 0.95; Cl, 39.35, 39.64; F, 22.28; N, 6.05, 6.26.

A second run gave the same product, in 50% overall yield from 2,2-dichloro-3,3-difluorocyclobutylnitrile, without isolation of XI.

1-Ethoxy-2,3,3-trichloro-4,4-difluorocyclobutene (XIV).

A mixture of 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene (contaminated by traces of 1-ethoxy-2-chloro-4,4-difluorocyclobuten-3-one); 106.9 g. (0.42 mole as pure triether) and 480 g. (2.4 mole) PCl_5 was heated at 90° overnight and decomposed in 4-1. ice-water. After CH_2Cl_2 extraction and drying, the mixture was fractionated to give a calculated yield of 32.3 g. (0.18 mole) the cyclobutenone and 5.8 g. (0.02 mole) XV (47% total yield) two other minor compoenents were seen in the g.l.c. The IR spectra corresponded exactly to Cohen's cyclobutenone and gem-dichloride XIV. The 1635 cm^{-1} IR peak (Cl-C=C-Cl) and ethoxy methylene quartet at 6.06τ favor assignment of structure XV to the latter compound. The presence of two non-equivalent fluorine atoms by ^{19}F n.m.r. conclusively establishes XV as the correct structure.

Transfer Reaction

Transfer-1-Bromo-2,3,3-trichloro-4,4-difluorocyclobutene (XVI).

The following sealed tube reactions were run:

XVI	Catalyst	Temp.°	Time	% XVIII	XIX	XX
1 ml.	1 drop Et_3N	82	57 hr.	22.8	18.6	---
0.25 ml.	6 drops Et_3N	80	35	36.7	19.3	4.2
0.25 ml.	5 drops NaCl/DMSO	80	35	27.0	17.7	trace
1.0 ml.	1/2 ml. Et_3N	80	35	completely solid		
7.59 g.	3 drops Et_3N	90	45	2.9	2.6	0

The last reaction provide sufficient material for IR identification of XVIII and XIX. Recovered XVI was seen to be partially isomerized to XVII by the broading of 1610 cm^{-1} peak (Cl-C=CBr) to 1625 cm^{-1} (Cl-C=C-Cl). In a more careful study, 3.3764 g. (12.4 mmole) XVI and 0.1831 g. (1.8 mmole) Et_3N were heated 26 hours at 88° to give 30% XVIII, 52% XVI and XVII, 17% XIX and <1% XX, all identified by IR. Short-path distillation gave 2.7920 g. volatile products and 0.2390 g. residue (Structural assignments will be justified in the description of the reaction of XVIII with bromide.

Transfer-1-Bromo-2-chloro-tetrafluorocyclobutene (XXI).

4.2658 g. (17.8 mmole) of pure XXI and 0.1406 g. (1.2 mmole) Et_3N were sealed in a tube and heated at 92° for 46 hours. The black liquid contained a considerable amount of black solid. G.l.c. of the liquid showed 46.7% XXI, 23.2% XXII, and 26.4% XXIII. Distillation yielded 2.7290 g. (64%) of a mixture 63.5% XXI, 15.1% XXII and 20.1% XXIII. Three very minor peaks of short retention were also noted. G.l.c. retention time is thus far the only proof of structure.

Transfer-1-Bromo-2,3-dichloro-3,4,4-trifluorocyclobutene (XXIV).

A sample of XXIV containing 1.8% 1,2-dibromo-3,chloro-3,4,4-trifluorocyclobutene (XXVII) was heated 32 hours at 90° with Et_3N catalyst.

1. 4.4489 g. (17.4 mmole) XXIV, 0.0735 g. (0.7 mmole) Et_3N, a 23.2 to 1 mole ratio, gave 4.8% 1,2,3-trichloro-3,4,4-trifluorocyclobutene (XXVI), by comparison with authentic IR spectrum; 90.3% XXIV, n_D^{26} 1.4418, reported[4] 1.4418; and a mixture of XXVII and 1,3-dibromo-2-chloro-3,4,4-trifluorocyclobutene (XXVIII). Short-path distillation gave 3.620 g. volatile liquid and 0.2655 g. tars.

2. 4.1327 g. (16.2 mmole) XXIV, 0.1417 g. (1.4 mmole) Et_3N, 11.7 to 1 mole ratio, gave 10.6% XXVI, n_D^{26} 1.4170, reported 78.7% XXIV with small but definite IR peaks consistent with XXV, n_D^{26} 1.4420; and 9.6% of a mixture containing more XXVIII than XXVII. Short-path distillation resulted in 2.854 g. volatile products and 0.4053 g. tars.

Pure XXIV was now used, heating for 84 hours at 90°C.

3. 2.755 g. (10.8 mmole) XXIV, 0.0525 g. (0.5 mmole) Et_3N, a 20.8 to 1 mole ratio, gave 14.0% XXVI, 75.6% XXIV and XXV; and 10.4% mixture of XXVII and XXVIII, the major component. This was distilled via a short path and combined with Run 4.

4. 2.8599 (11.2 mmole) XXIV, 0.1383 g. (1.4 mmole) Et_3N, an 8.2 to 1 mole ratio, gave 25.4% of XXVI; 55.6% XXIV and XXV; 18.2% XXVII and XXVIII; and 0.8% of a probable tribromide. Separation on FS (125°) gave a mixture of XXIV and XXV, n^{25} 1.4420, d^{25} 1.824, MR calc. 36.3; found: 37.1; and a mixture of XXVII and XXVIII, b.p. 124.0°/621 mm. n^{25} 1.4699, d^{25} 2.176, MR calc, 39.1, found 38.2. Although pure XXV and XXVIII are as yet unknown, their homogeneity with the known isomers supports their isomeric nature.

Transfer Reaction - 1-Iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene (XXIX). - A tube containing 0.917 g. (3.2 mmole) XXIX and 0.051 g. (0.5 mmole) Et_3N (a 6.4 to 1 ratio) was heated at 90° for 44 hours. The resulting brown liquid contained 97.0% XXIX, 1.5% XXII, 1.3% XXX, (all assignments by g.l.c. retention times, FS (125°)) and 0.2% of an unknown component. The IR spectrum contained strong 1580 (I-C=C-Cl) and weak 1625 cm^{-1} (Cl-C=C-Cl) absorption. After an additional five days at 92°, the reaction had only gone 3-4% to five products. The black material solidified at 25°C.

Transfer Reaction - 1-Iodo-2,3,3-trichloro-4,4-difluorocyclobutene (XXI). - A tube containing 0.5304 g. (.171 mmole) XXI and 0.0254 g. (0.25 mmole) Et_3N (an 8.9 to one ratio) was heated at 92° for 64 hours. The black liquid contained traces of XVIII by g.l.c. and one other minor component in addition to XXI. No high retention peak corresponding to a diiodide was noted.

Experimental - Halide Attack

Reaction of 2,3-dichloro-3,4,4-trifluorocyclobutene (I) with bromide. A mixture of 9.9927 g. (56.5 mmole) I, 4.9246 g. (56.8 mmole) LiBr (Anhyd.) and 75 ml. acetone was heated to reflux. After 11 hrs., 95% of I remained, after 6 days, 75%. At 10 days, 42% of I had been converted to a single product. Addition of H_2O forced out 11.5 g. of a yellow liquid containing traces of acetone. Separation of FS (75°) gave pure I, and slightly impure (acetone) 2-chloro-3-bromo-3,4,4-trifluorocyclobutene (III), both by authentic IR and homogeneity with authentic I and III on FS (75) and UCON (75) in the g.l.c.

Reaction of 2-chloro-3-bromo-3,4,4-trifluorocyclobutene (III) with chloride. - A mixture of 5.3251 g. (24.0 mmole), 2.1307 g. (50.3 mmole) LiCl and 25 ml. acetone was heated to reflux. After 4 hours, only 25% of III remained and after 16 hrs., 85% of III had been converted to a single product. The reaction was quenched with H_2O, the H_2O extracted with CH_2Cl_2, and the cyclobutene-CH_2Cl_2 extracts combined, dried, and subjected to short-path distillation. Separation on FS (80°) afforded pure I, by authentic IR and homogeneity with authentic I on FS (75°) and UCON (75°).

Reaction of 2,3-dichloro-3,4,4-trifluorocyclobutene (I) with iodide. - A mixture of 15.6 g. (0.088 mole) I, 16.6 g. (0.10 mole) KI, and 100 ml. acetone was refluxed 28 days to give a solution 54% I, 4% 1-chloro-2,3,3-trifluoro-4-iodocyclobutene (VI) and 42% 2-chloro-3-iodo-3,4,4-trifluorocyclobutene (V). During this time, the ratio of VI to V remained between 1:9 and 1:15. Filtration and addition of 16.6 g. KI forced the mixture to 47-5-48 in 13 days longer at reflux. The organic material was forced out with cold H_2O; the H_2O layer extracted with CH_2Cl_2, and the combined purple organic layers decolorized with aqueous $NaHSO_3$. Short-path distillation of the dried solution gave in two fractions a calculated yield of 0.8 g. V and 7.2 g. VI, 53% conversion and 69% yield.

The minor component (VI); n_D^{26} 1.4868, d^{26} 2.100, MR calc. 36.45, found 36.5, b.p. 123.5°/629 mm., was quite unstable to formation of iodine at 0° and gave a poor analysis. During 10 minutes at 125°, 19% was converted to V by g.l.c. retention time. The IR spectrum contained strong 1710 cm^{-1} (F-C=C-Cl) and 2980 cm^{-1} (allylic C-H) and the nmr (of a mixture with V) showed two triplets, 5.09 J_1=13.5, J_2=2.0 cps., in agreement with the assigned structure. Calc. for $CHClF_3I$: C, 17.90; H, 0.38; Cl, 13.21; F, 21.23; I, 47.28; Found (Elek): C, 18.23, H, 0.50; Cl, 20.88; I, 37.75. The major product (V), n_D^{26} 1.4793; d^{26} 2.137; MR calc 36.45; found 35.4; b.p. 124.0/629 mm., was relatively stable at 25°. The presence of vinylic hydrogen was proven by the 3100 cm^{-1} (C=C-H) and 1575 cm^{-1} (HC=CCl) abosrptions in the Ir and a septet in the nmr at 3.49τ, J=4.1, 2.4, 1.7 cps. Analysis, calc. as for VI; found (Elek): C, 18.14; H, 0.56; I, 44.71. No rearrangment to VI was noted at 25°.

Reaction of 2,3,3-trichloro-4,4-difluorocyclobutene (VII) with bromide.

a. in DMSO - A mixture of 9.7 g. (0.05 mole) V, 6.0 g. (0.05 mole) KBr, and 25 ml. DMSO was stirred at room temperature for 12 hrs., turning pale yellow, and then at 40° for 3 hrs. Addition of 0.5 l. H_2O forced out 6.1 g. of organic material, containing a trace of DMSO and 38.0% 1,2-dichloro-3-bromo-4,4-difluorocyclobutene (VIII). Separation on FS (110°) gave a mixture of VII and VIII and pure X, by identity with authentic IR spectra and homogeneity with an authentic mixture on FS (125°). n_D^{26} 1.4760, found for authentic, n_D^{26} 1.4752.

b. in DMF - A mixture of 9.4 g. (0.05) VII, 6.0 g. (0.05 mole) KBr, and 25 ml. DMF was heated at 50-60° for 22 hrs. Addition of H_2O separated 4.3 g. of material containing traces of DMF, 69.3% X, 9.4% VIII, and 21.3% recovered VII. Separation on FS (110°) gave a mixture of VII and VIII and X, both samples contaminated by DMF. Identification was based on identity with authentic IR spectra.

Reaction of VII with Iodide. -

a. KI in DMF. - A mixture of 19.3 g. (0.10 mole) VII, 17.0 g. (0.105 mole) KI, and 25 ml. DMF was stirred 8 hrs. at 46°, going maroon in color. Quenching with water followed by extraction with CH_2Cl_2 and stripping of the CH_2Cl_2 yielded 20.0 g. of a liquid containing much DMF, 80% 1,2-dichloro-3-iodo-4,4-difluorocyclobutene (XXXII), no VIII and 20% recovered VII. Separation (FS, 110°) gave samples of VII and XXXII, both contaminated with DMF. The IR of impure XXXII was essentially identical with that of authentic XXXII, prepared below.

b. NaI in acetone. - A solution of 96.7 g. (0.5 mole) of a mixture 62.8% VII - 37.2% VIII was heated to reflux over 87 g. (0.525 mole) NaI in 0.5-l. acetone. The progress of reaction was followed by g.l.c.

Time	VII	VIII	XXXII
17 hrs.	58.3%	33.3%	8.4%
41 "	31.7	33.6	34.7
65 "	23.2	36.4	40.4
22.4 g. (0.135 m.) KI added			
28 hrs.	13.4	36.6	50.0
22.0 g. (0.133 m.) KI added			
11 hrs.	9.2	35.8	55.5
35 "	1.1	36.4	62.5

(The g.l.c. areas were corrected for the interference of acetone.) The organic layer was forced out with 3-l. H_2O and subjected to short-path distillation. Several fractions resulted, calculated to contain 59.7 g. (0.21 mole) XXXII (67% on VII); 1.8 g. VII, and 7.8 g. VIII. Separation on FS (80°) gave XXXII pure by g.l.c. but very pink, with IR absorption at 1622 cm^{-1} (Cl-C=C-Cl) and a quartet in the n.m.r. at 4.00 τ, J=2.4, 1.8 cps. n_D^{25} 1.4170 d^{25} 2.107; MR calc 41.22, found 41.5; Calc. for $C_4HCl_2F_2I$: C, 16.86; H, 0.35; Cl, 24.89; F, 13.40; I, 44.55; Found (Elek): C, 17.14; H, 0.32; Cl, 25.34; F, 13.39; I, 45.22. Decomposition at 25° was rapid, giving a compound of longer retention time and an nmr quartet, 4.91 τ, J=2.5, 0.5 cps.

Chlorination of 1,2-dichloro-3-iodo-4,4-difluorocyclobutene (XXXII). A pink solution of 20.4 g. of a mixture 97.8% in XXXII, 0.2% VII, and 2.0% VIII in 50 ml. CH_2Cl_2 was treated with chlorine gas at 0°. The solution immediately became dark red-brown. After two hours, a yellow solid (which lost Cl_2 (by odor) upon standing and was assumed to be ICl_3) was filtered and the excess halogen destroyed with $NaHSO_3$ (aq.). The dried organic layer was fractionated and 12.2 g. (0.063 mole, 68% on 0.072 mole XXXII) pure VII was recovered. The IR was identical with that of authentic VII.

Attempted coupling of 1,2-dichloro-3-iodo-4,4-difluorocyclobutene (XXXII). - A slurry of 3.2948 g. (0.050 mole) zinc dust in 100 ml. dioxane was heated to reflux with a trace of zinc chloride. A solution of 14.5168 g. (0.0510 mole) XXXII in 25 ml. dioxane was added. An initial brown color later disappeared to leave a white powder and clear solution. An additional 3.3 g. of zinc dust was added to replace the large amount of zinc clinging to the flask wall. Immediately the reaction mixture turned green and then brown. Addition of 1-l. of water and filtration of the suspension gave 4.5 g. brown solid, insoluble in H_2O, dilute HCl, ethanol, ether, CCl_4; soluble in NaOH dilute, con. HCl. Ignition left a substantial residue, presumed zinc. The IR contained peaks at 1725, 1625, 1580, and 1285 cm^{-1}.

Attempted Reaction of VII with Fluoride. -

a. KF in Acetone. - A solution of 19.3 g. (0.10 mole) VII in 30 ml. acetone was mixed with 17.4 g. (0.3 mole) KF (Anhydrous). The reaction was followed by g.l.c.

initial	12.3% VII,	remainder	acetone
15 hrs., 25°	8.6%	"	"
27 hrs., 40°	7.5%	"	"

Addition of water, extraction with Et_2O, and fractionation gave 11.1 g. recovery of VII, by IR and homogeneity on FS (125°) and Dow silicone (125°) in the g.l.c. Addition of aqueous $AgNO_3$ to the aqueous extract gave a heavy white precipitate.

b. KF in Acetone, $AgNO_3$. - A slurry of 9.7 g. (0.05 mole) VII, 3.0 g. (0.05 mole) KF, and 8.5 g. (0.05 mole) $AgNO_3$ in 50 ml. acetone was heated at 45-50° for 24 hrs. Black colloidal silver was filtered from a yellow solution containing only acetone and VII, by g.l.c.

c. KF in DMF. - A mixture of 9.7 g. (0.05 mole) VII and 8.7 g. (0.15 mole) KF in 30 ml. DMF was heated 8 hrs. at 50-60°, 8 hrs. at 75-80°, and finally 26 hrs. at 95-100° to give a viscous black tar, partially water soluble. Crude Al_2O_3 chromatography followed by g.l.c. showed only VII to be present in the volatile position.

A mixture of 19.4 g. (0.10 mole) VII, 5.8 g. (0.10 mole) KF, and 20 ml. DMF was sealed in a 100-ml. tube under N_2. After 4 days at 25° the mixture had become black-brown. Dilution with 1.5-l. H_2O forced out 13.0 g. of black organic material, containing ca. 99% VII plus DMF trace. The aqueous layer gave a strong white precipitate with $AgNO_3$.

d. Et_4NF in chloroform. - Tetraethylammonium fluoride was prepared from silver carbonate, hydrofluoric acid, and tetraethylammonium bromide. A few drops of VII were sealed with a spatula tip of Et_4NF in $CHCl_3$ and heated at 40° for 39 hrs., to give 2% conversion to VIII by authentic g.l.c. retention time. The tube was resealed with fresh Et_4NF and heated to 90° for 4 days. The mixture now contained 23% VIII. In each case ca. 1% of a short retention product resulted. A third run, with 0.5 g. Et_4NF, 3 ml. $CHCl_3$, and 0.5 ml. VII at 88° for 5 days, gave 5% of short retention product, very volatile, and 95% VIII, separated on FS (125°) and confirmed by authentic IR.

Reaction of 2,3,3-trichloro-4,4-difluorocyclobutene (VII) with cyanide. - Immediately upon mixing 19.3 g. (0.10 mole) VII and 13.0 g. (0.2 mole) potassium cyanide in 450 ml. acetonitrile, a maroon color developed. After two weeks, g.l.c. of the dark mixture showed only VII. Treatment with hot dilute nitric acid followed by silver nitrate gave a white precipitate. After one month, the mixture was poured into water but no organic layer separated.

Reaction of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (XXII) with bromide. - A solution of 5.1127 g. (26.2 mmole) XXII in 25 ml. acetone was refluxed over 2.1564 g. (24.8 mmole) LiBr for 20 hrs. to give ca. 50-50 XXII-XXI. After 36 hrs. longer, the mixture contained 53% XXII, 47% XXI and a trace of XXIII. The reaction was quenched with 300 ml. H_2O, the H_2O extracted once with CH_2Cl_2 and the dried CH_2Cl_2 layer distilled through a short path to remove the CH_2Cl_2 and traces of XXI and XXII. The residue now contained 10-60-30 mixture of XXII-XXI-XXIII and some inorganic salt. Separation on FS (60°) failed, but the g.l.c. retention times correspond exactly to those of the products of the transfer reaction.

Reaction of XXII with iodide. -

1. NaI, 25° A mixture of 19.5 g. (0.10 mole) XXII and 14.9 g. 0.10 mole) NaI (anhydrous) turned yellow immediately upon mixing. Addition of 100 ml. acetone enhanced the yellow color. After being stirred at room temperature for 55 days, the mixture contained 65% of a new compound, 1-iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene (XXIX). 20.0 g. KI was added and the mixture stirred 5 days longer. Addition of 1-l. H_2O forced out 27.6 g. of a pink liquid; 34% acetone and 66% cyclobutenes, of which 44% was XXII and 56% XXIX. Separation on UCON (75°) gave pure XXIX by comparison with authentic material in the IR, n_D^{25} 1.4413, d^{28} 2.06; reported[15] n_D^{25} 1.4420, d^{25} 2.066.

2. KI, 55° A mixture of 19.5 g. (0.10 mole) XXII, 16.6 g. (0.10 mole) KI, and 100 ml. acetone in 8 days at reflux was converted to a 46-54 mixture of XXII and XXIX. An additional 16.6 g. KI was added and the composition was changed in 8 more days at reflux to 8% XXII - 86% XXIX - 6% 1,2 diiodo-3,3,4,4-tetrafluorocyclobutene (XXX). The cooled solution was filtered and 16.6 g. KI added. After 13 days at reflux, the orange solution contained 3% XXII - 78% XXIX and 19% XXX. Filtration and renewal of the KI followed by 3 days at reflux and quenching with 1-l. H_2O gave a mixture 85% XXIX and 15% XXX after removal of the CH_2Cl_2 used in extraction. Separation on FS, 90°, gave pure XXIX and XXX.

The new compound XXX, n_D^{26} 1.5110, d^{27} 2.509, MR calc 44.48, found 43.8, b.p. 151.5°/623 mm., proved stable to formation of iodine at 150° for 10 min. and at 25° for one week. The IR contained weak 1550 cm^{-1} absorption, as expected for I-C=C-I. Analysis, Calc. $C_4F_4I_2$: 67.17% I; Found (Elek): 70.00%.

3. Ki, 90° A mixture of 40 g. (0.205 mole) XXII, 83.0 g. (0.5 mole) KI, and 150 ml. acetone was heated at 90-95° for 5 days in a 300 ml. Carius tube, with development of 85 psi. Some tar in the valve discolored the acetone immediately. After quenching in water and extraction with CH_2Cl_2, the dark liquid contained 20% XXII, 54% XXIX and 26% XXX. The CH_2Cl_2 was removed on a 12" column and the residue distilled via a short path to give 39.1 g. of crude products, separated on FS (90°).

Reaction of XVIII with bromide. -

a. Et_4NBr in $CHCl_3$. - To 8.0 g. of a solution containing 55% CH_2Cl_2, 10% acetone, and 35% XVIII was added 1.0 g. Et_4NBr and 3.4 ml. $CHCl_3$. In 8 days at 25°, ca. 0.2% was converted to a peak corresponding to XVI in the g.l.c. An aliquot heated at 40° for 6 days gave 0.7% reaction. A second aliquot heated at 90° for 3 days gave only a trace of XVI.

LiBr in acetone. - A slurry of 15.0 g. (0.066 mole) XVIII and 11.5 g. (0.132 mole) LiBr in 150 ml. acetone was refluxed for 4 days to give a mixture containing 36% XVIII, 43% SVI and SVII, 20% XIX, and 1% XX. The cooled mixture was filtered and 11.5 g. more LiBr added. After 4 days at reflux, the composition was 8% XVIII - 40% XVI and XVII - 43% XIX - 9% XX. Another 11.5 g. LiBr forced the mixture to

3-15-52-30 in 32 hrs. at reflux. Repetition gave in 16 hrs. a mixture 2-19-43-34 and 2% XXIV. Poured into water, the mixture gave 17.2 g. of a solution containing 53% acetone and 3% XVIII - 18% XVI + XVII - 40% XIX - 34% XX - 5% XXXIV. Separation was effected on FS (110°).

Insufficient XIII was recovered for IR.

The IR of the mixture of 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene (XVI) and 3-bromo-1,2,3-trichloro-4,4-difluorocyclobutene (XVII) contained a broad peak 1625 to 1610 cm^{-1} peaks characteristic of XVI but also a similar number of peaks not belonging to XVI. b.p. 149.0°/629 mm.; Calc. for $C_4BrCl_3F_2$: C, 17.64; Br, 29.34; Cl, 39.06; F, 13.95; Found (Elek): C, 17.92; Br, 28.42; Cl, 40.75.

1,3-Dibromo-2,3-dichloro-4,4-difluorocyclobutene (XXIX) was a colorless liquid, n_D^{26} 1.5138; d^{26} 2.128; MR calc. 43.95, found 44.5; b.p. 154.0°/629 mm. Calc for $C_4Br_2Cl_2F_2$: C, 15.16; Br, 50.45; Cl, 22.38; F, 12.00; H, 0.00; Found (Elek): C, 15.35; Br, 50.41; Cl, 22.56; H, 0.11. The IR spectrum contained a strong peak at 1610 cm^{-1}, characteristic of Cl-C=C-Br.

1,3,3-Tribromo-2-chloro-4,4-difluorocyclobutene (XX), also a colorless liquid, had n_D^{26} 1.5410; d^{26} 2.412, MR calc 46.85; found: 46.9; b.p. 187.0°/629 mm., Calc. for $C_4Br_3ClF_2$: C, 13.30; Br, 66.37;' Cl, 9.81; F, 10.52; H, 0.00; Found (Elek): C, 13.46; Br, 65.52; Cl, 10.05, H, 0.10. The IR also contained strong 1610 cm^{-1} absorption.

1,2,3,3-Tetrabromo-4,4-difluorocyclobutene (XXXIV) was isolated in trace amount, melting ca. 20°. The IR contained a weak 1595 cm^{-1} peak, characteristic of Br-C=C-Br; Calc. for $C_4Br_4F_2$: C, 11.84; Br, 78.79; F, 9.37; H, 0.00; Found (Elek): C, 12.10; Br, 76.26; H, 0.10.

Attempted reaction of 1,2,3-trichloro-4,4-difluorocyclobutene (VIII) with halide ion. -

a. KI in acetone. - The previously mentioned treatment of a mixture of VII and VIII with a slurry of KI in refluxing acetone resulted in a slight *increase* in the amount of VIII, due to chloride attack of VII. Thus VIII is inert to iodide.

b. Et_4NBr in $CHCl_3$. - A tube containing 10 drops VIII, 0.2 g. Et_4NBr, and 5.0 ml. $CHCl_3$ was heated 10 days at 89°. The resulting tan solution contained no new product by g.l.c.

Reaction of 1,2-dichloro-3-bromo-4,4-difluorocyclobutene (X) with chloride. - A 10 ml. tube was closed with 0.5020 g. (2.11 mmole) IX and 0.3533 g. (2.13 mmole) Et_4NCl in 5.0 ml. $CHCl_3$. The reaction was followed by g.l.c. The g.l.c. of an authentic mixture of VII, VIII, X, and $CHCl_3$ was superimposable on that of the reaction mixture on FS (125°). The final solution was light tan in color.

TABLE II

Reaction Conditions and Distribution of Products
Reaction of X with Et_4NCl

Temp.	Time	% VII	% VIII
25°	20 hrs.	2.5	5.0
50	10 days	4.0	6.0
90	11 days	3.2	63.2

Reaction of 1,2-dichloro-3-iodo-4,4-difluorocyclobutene (XXXII) with chloride. - A mixture of 0.3810 g. (1.42 mmole) XXXII and 0.3 ml. of a mixture of 0.117 g. Et_4NCl in 1.0 ml. $CHCl_3$ was closed in a 5 ml. tube. The reaction was followed by g.l.c. After 26 hrs. at 25°, 3.1% VII and 4.6% VIII had formed; in 6 days longer, 5.9% - VII - 4.6% VIII, plus an unidentified component, 3.6%. The new peak had retention time between that of VII and XXXII. Comparison with authentic g.l.c. of VII, VIII, and XXXII led to the structural assignments. Considerable iodine had formed, by the dark maroon color.

Reaction of 1-bromo-2-chloro-3,3,4,4-tetrafluorocyclobutene (XXI) with iodide. - A solution of 3.5 g. (0.015 mole) XXI in 100 ml. acetone turned yellow immediately upon addition of 2.4 g. (0.015 mole) KI at room temperature. After stirring 6 days at 25°, the mixture was washed with water and the organic layer dried. G.l.c. showed 42% of the cyclobutene portion to be 1-iodo-2-chlorotetrafluorocyclobutene (XXIX) and 58% unreacted XXI. The material was homogeneous with authentic XXIX on FS (125°) and, after separation on FS (75°) was identical in the IR, n_D^{25} 1.4412, reported[15] 1.4420.

Reaction of 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene (XVI) with bromide. - A solution of 4.9340 g. (18.1 mmole) XVI in 25 ml. acetone was heated to reflux over 1.5973 g. (18.4 mole) LiBr. The reaction was followed by g.l.c.

Time	% XVIII	XIX	XX
1 hr.	6.3	19.1	---
2	9.7	25.3	---
3	21.5	28.2	---
5	22.4	26.3	---
8	26.4	27.2	---
17	26.1	25.3	2.8
36	24.4	25.9	2.9

The reaction was quenched in water at 39 hrs. and the organic layer separated and combined with a single methylene chloride extract of the aqueous portion. After drying, short-path distillation (ca. 60°/2 mm.) gave 4.7619 g. of a mixture 14% methylene chloride, 11% acetone, and 75% organic. The organic portion contained 44% XVI and XVII, 24% XVIII, 28% XIX and 4% XX. This material was combined with the product of LiCl and XVI for separation by g.l.c.

A second run on 13.1 g. (0.048 mole) XVI and 8.7 g. (0.10 mole) LiBr in 150 ml. acetone; gave after 51 hrs. refluxing 11.8 g. of a mixture 25% acetone, 12% methylene chloride and 63% organic, of which 42% was XVI-XVII, 21% XVIII, 30.2% XIX, and XX, XV.

Reaction of 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene (XVI) with chloride. - A solution of 4.9262 g. (18.0 mmole) XVI in 25 ml. acetone was refluxed over 0.7683 g. (18.1 mmole) LiCl (less than 2% by weight H_2O).

Time	XVIII	XIX	Time	XVIII	XIX
1 hr.	13.0	trace	7 hr.	54.8	6.6
2	34.3	trace	9	58.0	7.0
3	38.1	2.7	12	55.7	7.7
4	44.8	7.8	21	56.1	6.7
5	49.6	6.4	50	50.7	10.4 (evaporation of some acetone)
6	49.4	7.9			

The mixture was drowned in water, extracted with methylene chloride, and subjected to short-path distillation to give 3.4025 g. of a distillate 16% in methylene chloride, 15% in acetone, and 69% organic. The organic product was 44% XVI and XVII, 40% XVIII, 14% XIX, and 2.0 XX, which appeared only upon distillation. Separation of this material combined with the product of LiBr and XVI was effected on FS (85°) to give sufficient material for IR.

XVIII identical in the IR with authentic material, n_D^{25} 1.4595, reported[13] 1.4600. The peak corresponding to XVI proved to have consideralbe XVII (by strong 1625 cm^{-1} absorption in the IR), n_D^{26} 1.4867, d^{26} 1.883, MR calc. 41.05, obs. 41.3.

Reaction of 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene (XVI) with NaI. - A mixture of 13.6 g. (0.05 mole) XVI, 7.5 g. (0.05 mole) NaI (anhydrous) and 150 ml. acetone was stirred at room temperature for 4 days to give 41% conversion to a new compound. At this point, 7.5 g. NaI was added and the mixture stirred an additional 10 days to give 88% conversion. Addition of 200 ml. water forced out 12.5 g. of a red liquid, 47% acetone and 53% cyclobutene, of which 84% was 1-iodo-2,3,3-trichloro-4,4-difluorocyclobutene (XXXI) and 16% recovered XVI. Methylene chloride extract of the aqueous layer contained only traces of XVI. Short-path distillation gave considerable decomposition to a brown solid but sufficient material remained for g.l.c. separation (FS, 80°).

The IR spectrum contained 1595 cm^{-1} (I-C=C-Cl) and 1275 cm^{-1} absorption ($-CF_2$). Physical data: n_D^{25} 1.5284; d^{28} 2.10; MR calc. 46.08, 46.6; Calc. for $C_4Cl_3F_2I$: C, 15.04; Cl, 33.31; F, 11.90; I, 39.74; H, 0.00; Found (Elek): C, 15.24; Cl, 32.67; F, 11.88; I, 40.12; H, 0.08.

Reaction of 1-bromo-2,3-dichloro-3,4,4-trifluorocyclobutene (XXIV) with chloride. - A mixture of 20.4 g. (0.08 mole) XXIV, 3.4 g. (0.08 mole) lithium chloride and 150 ml. acetone was refluxed for 5 days. After drowning in water; extraction with methylene chloride, and removal of the solvent by short-path distillation, the product (16.4 g.) contained 62% 1,2,3-trichloro-3,4,4-trifluorocyclobutene (XXVI), 25% of an equimolar mixture of 1,2-dichloro-3-bromo-3,4,4-trifluorocyclobutene (XXV) and XXIV, and 12% of a mixture of 1,2-dibromo-3-chloro-3,4,4-trifluorocyclobutene (XXVII), the major component, and 1,3-dibromo-2-chloro-3,4,4-trifluorocyclobutene (XXVIII). Separation on FS

(125°) gave the three pure fractions. The IR of the fraction corresponding to XXIV showed a broad peak from 1625 to 1610 cm^{-1} and new equal intensity peaks in addition to those expected for XXIV, all consistent with the presence of XXV. The identities of XXVI and the mixture of XXVII and XXVIII were confirmed by IR.

Reaction of 1-bromo-2,3-dichloro-3,4,4-trifluorocyclobutene with bromide. - A mixture of 10.2 g. (0.04 mole) XXIV, 3.5 g. (0.04 mole) lithium bromide and 75 ml. acetone was heated 5 days at reflux to give ca. 20% XXVI, 60% XXIV, and 20% Dibromide fraction. Addition of 3.5 g. LiBr and heating for three days longer followed by quenching in water, gave 14.5 g. of a mixture containing 17% acetone and 83% products of which 22% was XXVI, 47% an equimolar mixture of XXIV and XXV, and 31% a mixture of XXVII (major) and XXVIII. Separation on FS (125°) and IR analysis gave these results.

Reaction of 1-bromo-2,3-dichloro-3,4,4-trifluorocyclobutene (XXIV) with iodide. - A mixture of 17.1 g. (0.067 mole) XXIV, 11.2 g. (0.067 mole) potassium iodide, and 150 ml. acetone was refluxed for 7 days to give a yellow solution containing only acetone and 1-iodo-2,3-dichloro-3,4,4-trifluorocyclobutene (XXXVII). Addition of water forced out 30.1 g. of organic product. Extraction of the water with methylene chloride and short-path distillation of the combined organic layers gave 14.5 g. of crude XXXVII, 0.048 m., 71% yield. Removal of the 1% impurity on FS (125°) gave pure XXXVII, a colorless liquid, n_D^{25} 1.4870; d^{25} 2.098; MR calc. 41.31 found 41.40; b.p. 129.5°/632 mm. with no decomposition. Calcd. for $C_4Cl_2F_3I$: C, 15.86; Cl, 23.41; F, 18.82; I, 41.90; Found (Elek): C, 15.79; Cl, 24.94; I, 38.83; H, 0.00. The IR sepctrum contained strong absorption at 1580 cm^{-1}.

Reaction of 1-ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene (XXXVIII) with bromide.

a. Et_4NBr A sealed tube containing ca. 0.1 g. Et_4NBr, 0.25 ml. XXXVIII, and 4 ml. chloroform was heated 6 days at 50-55° and 2 days at 90°, with no reaction in either case (by g.l.c.). A similar run at 90° for 9 days gave considerable charring and several small decomposition peaks in the g.l.c.

b. LiBr A tube containing ca. 0.5 ml. XXXVIII, 0.1 g. LiBr, and 2 ml. acetone was heated at 90° for 36 hours. The mixture contained 61%XXXVIII, 25% of a new compound, and several minor peaks in the g.l.c.

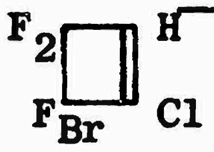
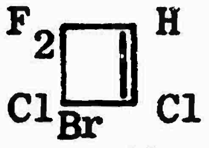
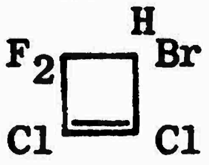
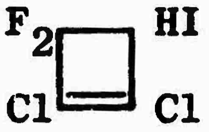
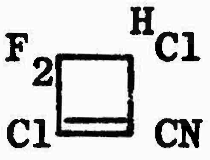
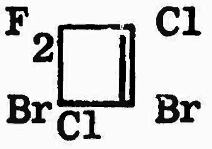
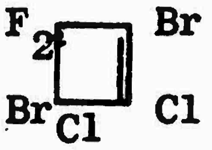
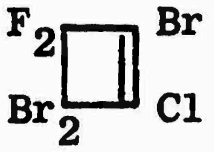
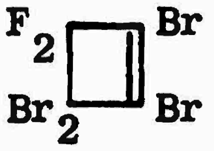
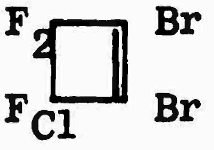
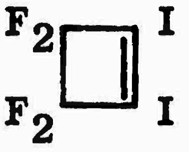
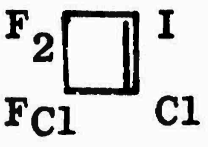
A mixture of 10.034 g. (49.2 mmole) XXXVIII, 4.3891 g. (50.5 mmole) LiBr, and 100 ml. acetone was refluxed on day to give 6% of material corresponding to ethanol in retention time, 38% XXXVIII, and 56% of a new peak, at longer time and broader than that ofXXXVIII. The very black mixture was refluxed two days longer to give a 8033059 mixture. Direct distillation caused complete destruction of the major product and only XXXVIII was isolated.

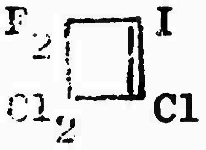
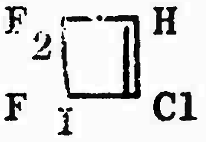
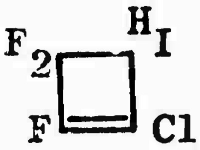
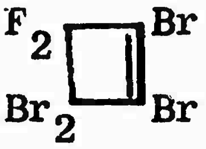
A mixture of 10.0 g. XXXVIII, 4.4 g. LiBr, and 150 ml. acetone turned black and gave a mixture 6% - 25% XXXVIII - 69% new. Addition of water forced out 15.6 g. of crude black liquid. Separation on FS (125o) gave a mixture of XXXVIII and the new compound. The IR contained all peaks expected of XXXIX.

Attempted reaction of 1-chloro-2,3,3-trifluorocyclobutene (XL) with LiCl. - A 90 ml. Carius tube was sealed with 5.115 g. (0.036 mole) XL, 3.8290 g. (0.09 mole) LiCl, and 35 ml. acetone. After 41 hrs. at 60-65, the reaction was quenched with H_2O, The organic layer contained only acetone and XL, and no XLI, by g.l.c.

TABLE III

Summary of New Compounds and their Properties
Nucleophilic Displacement by Halide Ions on Halocyclobutenes

	b.p.	n_D	d	IR of C=C(cm^{-1})
	$102.0^{o}/628^{mm.}$	1.4272^{25^0}	1.825^{25^0}	7575
	$31^{o}/4^{mm.}$	------unstable-------		1580
	$31^{o}/4^{mm.}$	1.4780^{25^0}	1.842^{25^0}	1625
	--------	1.5170^{25^0}	2.107^{25^0}	1620
	$34^{o}/4.5^{mm.}$	1.4548^{25^0}	1.457^{25^0}	1625
	---------	1.5075^{25^0}	2.133^{25^0}	1610
	$154^{o}/629^{mm.}$	1.5138^{26^0}	2.128^{26^0}	1610
	$187^{o}/629^{mm.}$	1.5410^{26^0}	2.412^{26^0}	1610
	m.p. ca. 20^{o}	--------	-----1595	
	$129.5^{o}/629^{mm.}$	1.4661^{26^0}	2.126^{26^0}	1595
	$151.5^{o}/632^{mm.}$	1.5110^{26^0}	2.509^{27^0}	1550
	129.5^{o}	1.4870^{25^0}	2.098^{25^0}	1595

	-----	1.5284^{25°	2.100^{28^0}	1595
	$124.0^\circ/629^{mm.}$	1.4793^{26^0}	2.137^{26^0}	1575
	$123.5^\circ/629^{mm.}$ (d.)	1.4868^{26^0}	2.100^{26^0}	1710
	m.p. ca. 20°	---------	---------	1595 weak

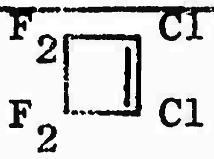
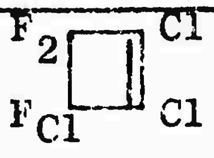
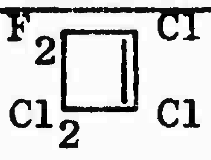
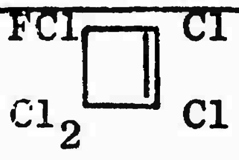
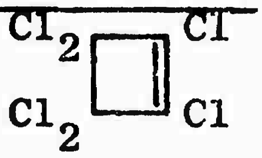
Reaction of aluminum chloride with fluorohalocyclobutenes. -

Aluminum chloride is known to react with saturated and unsaturated acyclic fluorocarbons to give rearrangment or substitution of fluorine atoms by chlorine. This study is concerned with some reactions between fluorochlorocyclobutenes and anhydrous aluminum chloride. All reactions proceeded exothermically, done in the absence of solvent by adding aluminum chloride slowly to the liquid cyclobutene. The extent and in one case, the direction of the reaction were determined by the quality of metal halide used.

Addition of aluminum chloride to 1,2-dichlorotetrafluorocyclobutene (I) resulted in the stepwise replacemtn of fluorine atoms. Those cyclobutenes containing the gem-chlorofluoro group (i.e., II and IV) are more reactive than those with the gem-difluoro group (i.e., I and III). Hexachlorocyclobutene (V) is the first crystalline halocyclobutene known. In these reactions, between 1.2 and 1.3 moles of chloride were required per mole of fluoride replaced.

TABLE IV

Stepwise Replacement of Fluorine Atoms in the Reaction of 1,2-Dichlorotetrafluorocyclobutene with $AlCl_3$

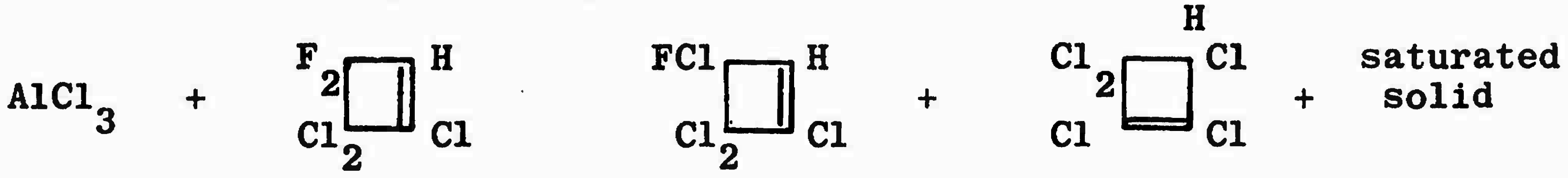
$AlCl_3$ +	 I	 II	 III	 IV	 V
1/3 mole (old)	65	5	28	2	0
1 mole (old)	13	7	75	3	2
1 mole (new)	3	3	68	6	20
(1/2 mole more)	0	0	8	2	90

The reactions of 1,2-dichloro-3,3-difluorocyclobutene (VI) and 1-chloro-2,3,3-trifluorocyclobutene (IX) with aluminum chloride resulted predominantly in the replacement of both allylic fluorine atoms. Both reactions gave considerable amounts of tarring.

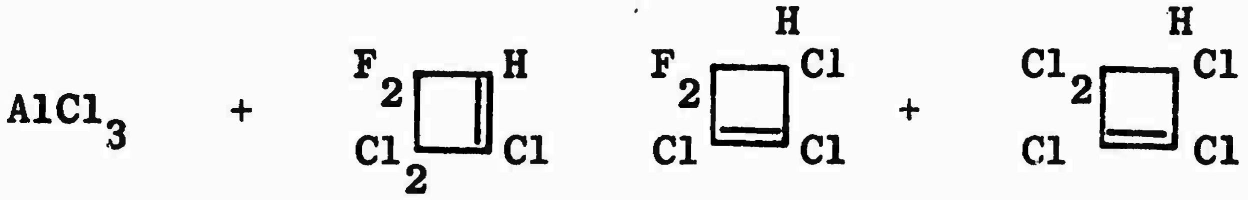
	VI	VII	VIII
1 mole	16	4	80

	IX	X	XI
1/3 mole	71	trace	29
1 mole	40	4	56

The reaction of 2,3,3-trichloro-4,4-difluorocyclobutene (XII) with an old specimen of aluminum chloride gave predominantly the product of <u>mono</u>-substitution, XIII. Although in two experiments this material was found, with any other sample of aluminum chloride the reaction was irreproducible. Instead, XII was partially rearranged to 1,2,3-trichloro-4,4-difluorocyclobutene (XV), and the rest of the product corresponded to complete defluorination of this material.



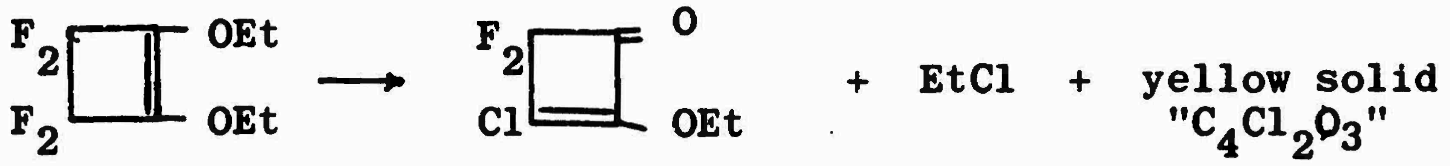
	XII	XIII	XIV	saturated solid
1 mole		36	4	8



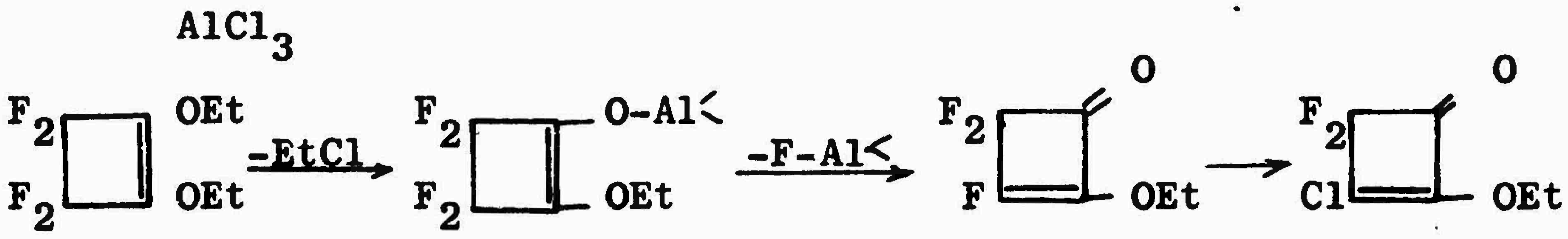
	XII	XV	XIV
1/3 mole	0	64%	36%
1 mole	0	0	99

Cyclobutene XII is known to undergo allylic rearrangment in the presence of chloride ion, a nucleophilic displacement reaction, but heat is required to force the rearrangment to proceed at an apprecialbe rate. The rapid, low-temperature rearrangment noted here suggests that electrophilic attack by aluminum-III is involved, not nucleophilic attack by chloride ion.

Allylic fluorine and vinylic ethoxide were froced to compete for the aluminum chloride in the reaction of 1,2-diethoxytetrafluorocyclobutene (XVI) with aluminum chloride. Immediate evolution of ethyl chloride was observed. The major product proved to be 1-chloro-2-ethoxy-3,4-difluorocyclobutene-3-one (XVII).



Small amounts of an unstable yellow crystal were isolated for which a poor analysis best first $C_4Cl_2O_3$. A reasonable pathway to XVII is the initial conversion of XVI to the vinylog of an acid fluoride, which in turn reacts rapidly with aluminum chloride, according to the following reaction:



XVII

From these reactions, the order of reactivity toward aluminum chloride is:

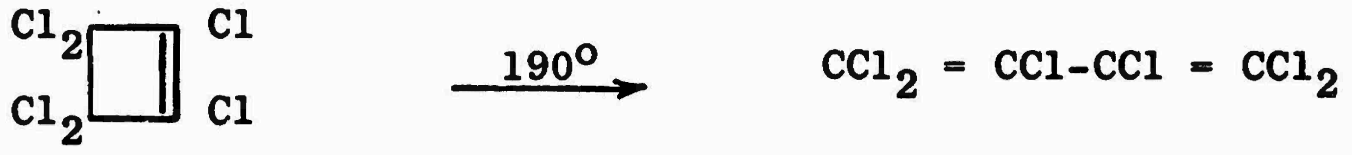
allylic $\underline{CFCl}$ > allylic $\underline{CF_2}$ > vinylic $\underline{CF}$ >

and $\underline{F}$-C=C-$\overset{O}{C}$- > vinylic $C\underline{OEt}$ > allylic $\underline{CF_2}$

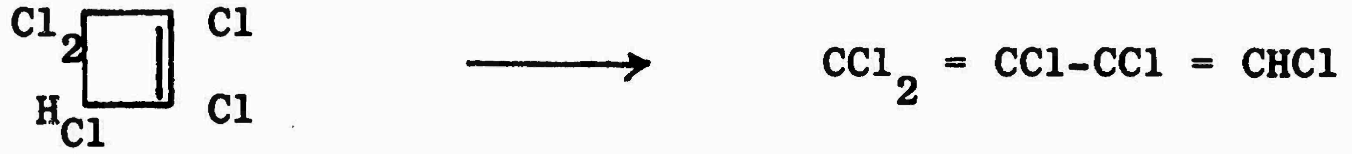
Synthetically the procedure is of great value. The two general syntheses of halocyclobutenes, olefin cyclodimerizations and diene cyclizations, both require the presence of fluorine atoms. Thus, a route to mono- and nonfluorinated chlorocyclobutenes is available. Also, the previous synthesis of III is tedious and slow when compared with the present method.

The new class of compounds, chlorocyclobutenes, proveds an interesting contrast to fluorocyclobutenes. While most fluorinated cyclobutenes are stable to thermal ring opening, both hexachlorocyclobutene (V) and 3-hydropentachlorocyclobutene (XIV) underwnet cleavage to the corresponding dienes at relatively low temperatures.

V



XIV

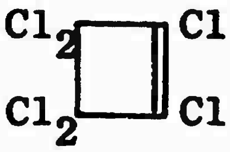
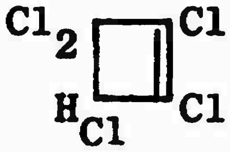
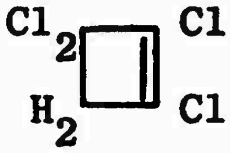
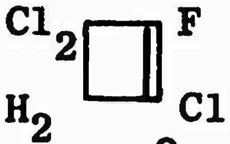
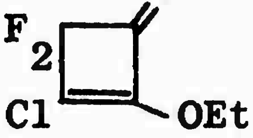


Under the same conditions 3,3-dihydrotetrachlorocyclobutene (VIII) was stable. It is attractive to attribute the instability of V and XIV to allylic cis vicinaldichloride interaction. Hexachlorocyclobutene failed to react with ethanolic potassium hydroxide at 0° and reacted slowly at 25°. The fluorinated analog I reacts rapidly at 0°, while hexachlorobutadiene reacts at 20°.

The instability of the highly chlorinated products has limited solvent study to low-boiling materials. Carbon disulfide in a preliminary experiment proved quite adequate. At present, the effect of bromine atoms and the cyano group on the reaction path is being studied. Aluminum bromide reactions will be reported later.

TABLE V

Properties of New Compounds Obtained from the Reaction of 1,2-Dichlorotetrafluorocyclobutene and $AlCl_3$

	b.p.	n_D	d
	(m. 51.5-52.5° b.p. rearranged with heat)	---	---
	$115^\circ/65^{mm.}$	1.5282^{25°	1.599^{25°
	$136^\circ/620^{mm.}$	1.5106^{28°	1.520^{28°
	$116.5^\circ/629^{mm.}$	1.4688^{25°	1.462^{26°
	$160^\circ/624^{mm.}$	1.4395^{27°	1.402^{27°

Other compounds were isolated in amounts insufficient for other than spectral identification. Work is in progress.

Experimental - Aluminum Chloride Reactions

Reaction of 2,3,3-trichloro-4,4-difluorocyclobutene (VII) with aluminum chloride. -

a. 1:1 $AlCl_3$. - A mixture of 9.7 g. (0.05 mole) VII and 6.7 g. (0.05 mole) old, but fairly pure aluminum chloride underwnet a mildly exothermic reaction at 25°. The initial red color changed to purple and then black. After 5 hrs., the liquid was filtered, washed with water, the solid filtrate decomposed with water and water extracted with methylene chloride. G.l.c. of the solution showed 52% VII, 4% LXI, 8% of a saturated solic, and 35% of LX. Separation on FS (150°) gave pure samples.

The structures of VII and LXI were confirmed by authentic IR spectra. The waxy solid exhibited no C-H and no olefinic absorption, and no CF_2 (1280 cm^{-1}), having only a strong 1220 cm^{-1} peak in the IR.

LX showed strong 1580 cm^{-1} IR absorption (H-C=C-Cl), no 1280 ($-CF_2-$) and strong 1220 cm^{-1}. The n.m.r. spectrum contained a singlet at 3.77τ. Three analyses were obtained: (Galbraith): C, 21.15; H, 0.59; Cl, 75.69; F, 1.33.

(Elek): C, 23.70; H, 0.45; Cl, 66.57; Difference, 9.30.
(Elek): C, 23.32; H, 0.47; Cl, 65.63; F, 10.27; Calcd. for C_4HCl_4F: C, 22.89; H, 0.48; Cl, 67.57; F, 9.05. The two Elek analyses and the IR support structure LX. No physical data were obtained and the preparation proved irreproducible.

b. 1:1 $AlCl_3$. - Addition of 15.4 g. (0.1 mole) VII to a suspension of 13.3 g. (0.1 mole) fairly pure aluminum chloride in 50 m. petroleum ether gave a vigorous reaction after a few minutes. Work up with water and rying gave a solution containing 33% VII (by authentic IR) and 55% LX - 12% LXI. (Both assignations by on g.l.c. retention time). Redistillation at $60^{o}/1^{mm.}$ and purification (FS, 125^{o}) gave ostensibly pure LX. The IR showed strong 1580 cm^{-1} and medium 1550 cm^{-1} peaks. The n.m.r. spectrum contained two singlets in a 60-40 ratio, at 2.89τ and 3.60τ, respectively. The IR spectrum contained all peaks attributed to LX and a similar number of others. The similarity of the n.m.r. relation (3.6τ to 2.9τ) to that of LXI to 1-hydropentachlorobutadiene (4.6τ to 3.3τ) supports assignation of structure LXIIa to the new component.

c. A preliminary experiment with 0.5 ml. VII and 3-4 spatula tips of aluminum chloride (from the same lot as above) gave 92% of the waxy solid found in Part a.

d. 1:1 old $AlCl_3$. - A mixture of 19.3 g. (0.1 mole) VII and 13.3 g. (0.1 mole) greyish aluminum chloride reacted slowly to give a purple slush in 5 hrs., at which time water was added to give mild heat evolution. After methylene chloride extraction, the mixture contained 6% VII, 91% of 1,2,3,3,4-pentachlorocyclobutene (LXI) and 2% and 1% of two intermediate peaks on g.l.c. Short-path distillation gave ca. 16 g. of cyclobutenes and 0.5 g. tarry residue. Fractionation of 15.2 g. of 99% pure LXI gave a series of fractions (14.1 g. total) boiling $114\text{-}120^{o}/65^{mm.}$ which proved to be mixtures of LXI and 1-hydropentachlorobutadiene, in ca. a 40-60 total ratio after 2 hrs. heating. LXI, purity greater than 99%, exhibited 1630 cm^{-1} IR absorption (Cl-C=C-C) and a singlet in the n.m.r. at 4.59τ (allylic C-H); n_D^{25} 1.5282; d^{25} 1.599; MR calcd. 42.82. Found 43.4; Calcd. C_4HCl_5: C, 21.23; H, 0.45; Cl, 78.33; Found (Elek): C, 21.47; H, 0.51; Cl, 78.28.

1-Hydropentachlorobutadiene, purified on FS (125^{o}), IR absorption at 1630 (weak) and 1565 cm^{-1} (strong), exhibited a singlet in the n.m.r. at 3.39τ (vinylic C-H); n_D^{20} 1.5515 (reported[70] n_D^{20} 1.5516, d^{20} 1.6121); n_D^{25} 1.5471; n_D^{26} 1.5478, d^{26} 1.608; MR calcd. 42.8. Found 44.3; b.p. $195.0/629^{mm.}$, reported[16] $193\text{-}200^{o}/720^{mm.}$, $78.5^{o}/12^{mm.}$ The butadiene had a turpentine-like odor. The other isomer, 2-hydropentachlorobutadiene, with n_D^{20} 1.5627 and d^{20} 1.6159, is excluded as a possible structure.

e. 1:1/3 old $AlCl_3$. - A mixture of 9.7 g. (0.05 mole) VII and 2.2 g. (0.017 mole) greyish aluminum chloride was stirred 5 hrs. at 25° and quenched in water. G.l.c. of the methylene chloride extract showed 64% 1,2,3-trichloro-4,4-difluorocyclobutene (VIII), 30%

LXI, and 9% and 1% of two intermediate peaks. G.l.c. separation (FS, 125°) gave pure VIII, by authentic IR; n_D^{25} 1.4469, d^{25} 1.535 (reported[5] 1.4468, 1.5366) and a mixture of LXI and 1-hydropentachlorobutadiene by IR spectrum, n_D^{25} 1.5455, d^{25} 1.59, probably from rearrangement on the column (15 min. cycle). No VII was recovered.

Reaction of 1,2-dichlorotetrafluorocyclobutene (XXII) with aluminum chloride.

a. 1:1/3 old $AlCl_3$. - A mixture of 9.7 g. (0.05 mole) XXII and 2.2 g. (0.017 mole) greyish aluminum chloride gave a mildly exothermic reaction at 25°. A colorless liquid (5.5 g.) was filtered off the black solid residue after 5 days, containing 65% XXII, 5% 1,2,3-trichloro-3,4,4-trifluorocyclobutene (XXVI) (by g.l.c. retention time), 28% 1,2,3,3-tetrachloro-4,4-difluorocyclobutene (XVIII) and 2% 1,2,3,3,4-pentachloro-4-fluorocyclobutene (LXIV). Separation on FS (125°) gave pure XXII, by authentic IR and n_D^{26} 1.3678; (reported) n_D^{25} 1.3681 and pure XVIII, by authentic IR and n_D^{25} 1.4588, reported 1.4600. Structure LXIV is based solely on the IR absorption at 1635 cm^{-1} (Cl-C=C-Cl), the lack of 1280 cm^{-1} (CF_2) and the presence of 1225 and 1180 cm^{-1} absorption, found also in the spectrum of LX, which also has the CFCl group.

b. 1:1/3 old $AlCl_3$. - A mixture of 9.7 g. (0.05 mole) XXII and 6.7 g. (0.05 mole) greyish aluminum chloride turned from pink to purple in 3 hrs. Hydrolysis gave 9.0 g. of a mixture of 13% XXII, 7% XXVI, 75% XVIII, 3% LXIV, and 2% perchlorocyclobutene (LXV), addition of 6.7 g. aluminum chloride gave 2.2 g. (0.001 mole, 17%) of LXV (structure proof given below).

c. 1:1 new $AlCl_3$. - A mixture of 19.5 g. (0.1 mole) XXII and 13.3 g. fresh aluminum chloride gave a vigorously exothermic reaction after 2 minutes, necessitating cooling. After 30 min., the reaction was over. One day later, g.l.c. showed the purple suspension to contain 3% XXII, 3% XXVI, 67% XVIII, 6% LXIV, and 20% LXV. Addition of 6.7 g. more aluminum chloride over 2 hrs. gave much heat and turned this mixture completely solid. Addition of water forced out a tan solid. Methylene chloride extraction gave a solution 8% in XVIII, 2% in LXIV, and 90% in LXV. The solvent was stripped and the resulting solid (25 g.) recrystallized in part from n-hexane (clear rhomboids) and partly from ethanol (white feathery plates) to give a total of 15.5 g. (0.006 mole, 60%) LXV, m.p. 51.5-52.5°, IR absorption at 1635 cm^{-1} (Cl-C=C-Cl). The b.p. rose steadily from ca. 110° to 198°/626$^{mm.}$ in 10 minutes. (Perchlorobutadiene boils at 197.5°/626$^{mm.}$). A sample heated at 190° for 10 min. proved to be an approximately equimolar mixture of LXV and perchlorobutadiene, by the IR spectrum.

LXV reacted rapidly at 25° with pyridien to give a water-soluble dark solid.

d. Controlled reaction. - A reflux condenser 10" x 1/2" (diameter) was charged with 15.0 g. fresh aluminum chloride and 20.0 g. XXII was heated to reflux below it. After 5 days, the pot mixture, now dark, boiled at 63.5°, an increase of 2.0°. The mixture had been converted only ca. 2% to XXVI and XXII in a 1:2 mixture, by g.l.c. The aluminum chloride was purple in color.

Reaction of 1-chloro-2,3,3-trifluorocyclobutene (XL) with aluminum chloride. - *A mixture of 7.1 g. (0.05 mole) XL and 2.2 g. (0.017 mole)* greyish aluminum chloride gave a vigorous reaction at 25°. After 4 days, the brown liquid was filtered off a black solid to give 3.5 g. of a mixture of 71% XL and 29% 1,3,3-trichloro-2-fluorocyclobutene (LXVI). Washing with water gave a yellow solution, separated on FS (125°). The identity of recovered XL was established by authentic IR. LXVI exhibited IR absorption at 1710 cm^{-1} (F-C=C-Cl) and a doublet in the n.m.r. at 6.83 , J=12.0 c.p.s., n_D^{25} 1.4688; d^{26} 1.462; MR calcd. 33.18, found 33.1; b.p. 116.5°/629 mm. Calcd. for C_4HCl_3F: C, 27.39; H, 1.15; Cl, 60.63; F, 10.83; found (Elek); C, 27.01; H, 1.16; Cl, 60.93.

A second trial using 14.2 g. (0.1 mole) XL and 13.3 g. (0.1 mole) fresh aluminum chloride gave 12.0 g. crude product after decomposition with water, of which 40% was XL, 4% 1,3-dichloro-2,3-difluorocyclobutene (LXXII) and 56% LXVI. The identity of LXXII was deduced from the g.l.c. retention time only.

Reaction of 1,2-dichloro-3,3-difluorocyclobutene (XLI) with aluminum chloride. - *To 15.9 g. (0.1 mole) XLI was slowly added 13.3 g. (0.1 mole)* fresh aluminum chloride. A very vigorous reaction ensued. The resulting black slurry was hydrolysed after 8 hrs., giving much heat and black liquid. After methylene chloride extraction and short-path distillation, 8.0 g. of a mixture containing 16% XLI, 4% presumed 1,2,3-trichloro-3-fluorocyclobutene (LXXIII), and 80% 1,2,3,30tetrachlorocyclobutene (LXVII). Separation on FS (125°) gave pure XLI (calcd. yield 1.2 g. 0.008 mole, 8%), a mixture of XLI and LXXII, the latter having 1630 cm^{-1} absorption also, and pure LXII (6.7 g., 0.036 mole, 36%), a colorless liquid, n_D^{28} 1.5106; d^{28} 1.520; MR calcd. 3795, found 37.7; b.p. 136°/620 mm. The IR spectrum of LXII contained absorption at 1640 cm^{-1} (Cl-C=C-Cl). A singlet at 6.51 was observed in the n.m.r. Calcd. for $C_4H_2Cl_4$: C, 25.04, H, 1.05; Cl, 73.91; found (Elek): C, 24.94; H, 1.09; Cl, 73.32. After 15 min. heating at 150-180°, no ring opening had occurred, by authentic IR and g.l.c. retention time.

Reaction of 1,2-diethoxytetrafluorocyclobutene (LXVIII) with aluminum chloride. -

a. Old $AlCl_3$. - A total of 4.8 g. (0.036 mole) greyish aluminum chloride was added slowly to 10.7 g. (0.05 mole) LXVIII. Violent evolution of ethyl chloride (by authentic g.l.c. retention time) and formation of a red-brown mixture resulted. The solid mixture was hydrolysed with cold water and extracted with methylene chloride. Analytical g.l.c. showed only one volatile compoenent other than solvent, but two products were found in preparative-scale g.l.c. (FS, 90°). The major product proved to be 1-chloro-2-ethoxy-4,4-difluorocyclobutene-3-one (LXIX), with IR absorption at 1700 and 1650 cm^{-1} (C=C-C=C) and a triplet at 9.57 τ and quartet at 5.58 τ, coupled with J=7.2 c.p.s.; characteristic[7] of $C=C-OCH_2CH_3$. n_D^{25} 1.4404; n_D^{27} 1.4395; d^{27} 1.402; MR calcd. 34.44, found 34.2 b.p. 160°/624 mm. Calcd. for $C_6H_5ClF_2O_2$: C, 39.45; H, 2.73; Cl, 19.45; F, 20.80; O, 17.52; found (Galbraith):

C, 39.30; H, 0.89; Cl, 19.33: F, 21.68. Both the n.m.r. and IR spectra are quite similar to those of 1-chloro-2-ethoxy-3,3-difluorocyclobuten-4-one, the n.m.r. showing the quartet at 5.24τ in this case.

The minor product was a fragrant yellow solid, m.p. 51.5-52.5°, soluble in ether, methylene chloride, and methanol (with decomposition in the latter to a brown oil), with a strong 1800 and 1760 cm^{-1} absorption in the IR. Decomposition to a brown oil was rapid. A poor analysis was obtained (Galbraith): C, 26.66; H, 0.11; Cl, 43.96; F, 3.11; which best fits $C_4Cl_2O_3$ (C, 28.8; Cl, 42.4; O, 28.8).

A second run with 10.7 g. (0.05 mole) LXVIII and 4.4 g. (0.034 mole) fresh aluminum chloride gave traces of LXIX and 8.9 g. of the yellow solid, sublimed at 40°/2^{mm}. A third run, with 21.4 g. (0.10 mole) diether and 26.6 g. (0.20 mole) fresh aluminum chloride gave no LXVIII and little, if any, product other than ethylchloride.

Cyclopentene Chemistry

Although considerable work has been reported on highly fluorinated cyclobutene systems, little is known of the corresponding cyclopentene compounds.

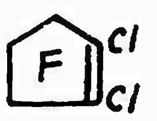
This section is concerned with recent studies of highly fluorinated cyclopentenes carried out in the Laboratory of the University of Colorado.

Part I deals with studies concerning nucleophilic displacement reactions. Part II outlines work done with Grignard reagents while Part III describes preliminary work on the synthesis of vinyl heptahalo cyclopentenes.

I. Attempted Nucleophilic displacements and related reactions.

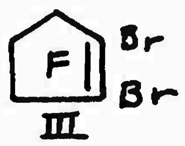
It had been found previously[17] that 1,2-dichlorohexafluorocyclopentene-1, (I) when treated with anhydrous lithium bromide in acetone, gave 1-bromo-2-chlorohexafluorocyclopentene-1 in a manner analogous to that reported for the corresponding cyclobutene series.[18]

However, preliminary findings indicated no detectable reaction between anhydrous sodium iodide and 1,2-dichlorohexafluorocyclopentene-1 in acetone.[1]



I

II



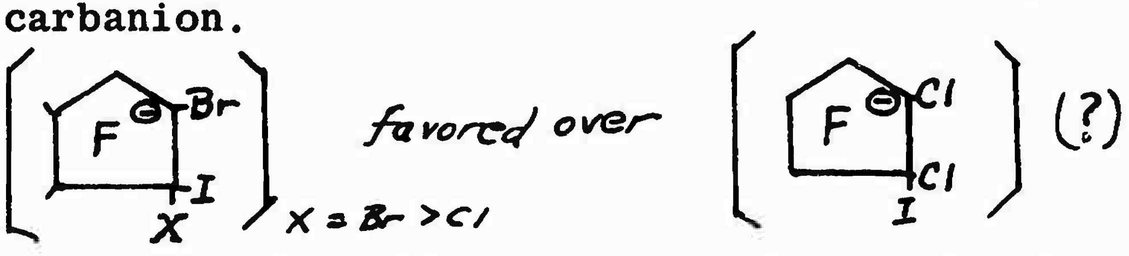
III

It has been found that prolonged heating (30 days) at vigorous reflux of anhydrous sodium iodide in acetone with 1-bromo-2-chlorohexafluorocyclopentene-1 (II) and 1,2-dibromohexafluorocyclopentene-1 (III) gave small amounts of higher boiling materials.

It is proposed that the two new compounds isolated are the previously unreported 1-chloro-2-iodo-hexafluorocyclopentene-1 (IV) and 1-bromo-2-iodo-hexafluorocyclopentene-1 (V).

It is somewhat presumptuous at the present time to attempt to assay accurately the ease of halide displacement by I$^-$ ion in this systme; particularly since the reaction involving compound I (1,2-dichlorohexafluorocyclopentene-1) was not carried out under identical reaction conditions.

However, it appears that the order of reactivity of the 1,2-dihalohexafluorocyclopentene-1's is Br, Br > Br, Cl > Cl, Cl. It is suggested that this order of reactivity may be explained on the basis of liability of halide ion displaced and α-stabilization of the ensuing carbanion.



Unfortunately, this reaction has not been studied with 1,2-dibromotetrafluorocyclobutene-1 and a comparison with the analogous cyclobutene system is thus impossible at the present time.

Properties of New Compounds

IV Not characterized at present

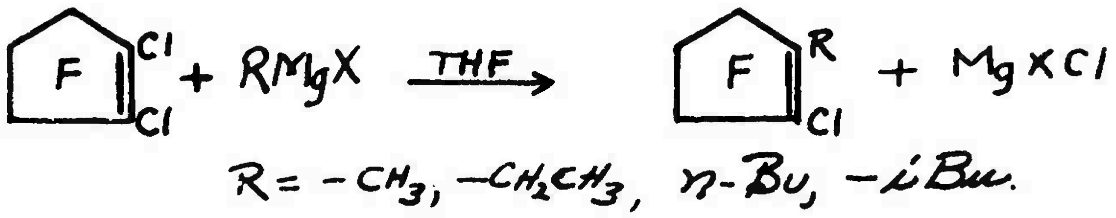
	I.R.	b.p.	refractive index	
V	p 12	142°(626 mm)	1.4488 (28°)	(clear, colorless liquid)

II. Attempted Grignard reactions of 1,2-dihalo-hexafluorocyclopentene-1.

The reaction(s) of compounds I, II and III with various Grignard reagents have been examined as part of a continuing study of highly fluorinated ring systems with Grignard reagents.

In most examples the isolated reaction products correspond to those previously encountered with ethylmagnesium bromide. e.g. Coupling of the 1,2-dichloro compd. (I) with the R moiety of the Grignard reagent and apparent destruction of the bromo chloro (II), and dibromo (III) compounds. Table VI summarizes the results of attempted coupling or exchange of the cyclopentenes I, II and III with methylmagnesium bromide/THF, and phenylmagnesium bromide/THF.

The observed coupling of 1,2-dichlorohexafluorocyclopentene-1 (I) with alkyl Grignard reagents appears to be a general reaction.

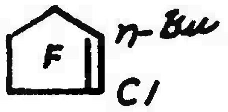


However, attempts to introduce a second R-group into the cyclopentene ring have not proved successful and apparently conditions more vigorous than those employed are necessary to effect this reaction.

Preliminary studies of the reactions of compounds I, II and III with phenylmagnesium bromide produced rather unexpected (and questionable) results. No 1-phenyl-2-chlorohexafluorocyclopentene-1 was isolated from the reaction of phenylmagnesium bromide with 1,2-dichlorohexafluorocyclopentene-1 (II). Even more surprising was the isolation in substantial amounts of a higher boiling fraction from the reaction of phenyl magnesium bromide with (III) which (IR spectra, refractive index) was tentatively identified as biphenyl. This result was obtained using separate sources of phenylmagnesium bromide and differing reaction temperatures. No higher boiling fraction was observed using the same Grignard with either compound I or II.

TABLE VI

Characterization of new compounds
Reaction of Grignard Reagents with 

		refractive index	(28°) b.p.
VI		1.3561	97.5° (621.0)
VII		1.3811	151° (632.0)
VIII		1.3820	142° (630.7)

Compounds VI, VII and VIII are colorless liquids at room temperature.

* appendum

The NMR of previously reported 1-ethyl-2-chlorohexafluorocyclopentene-1 has now been obtained.

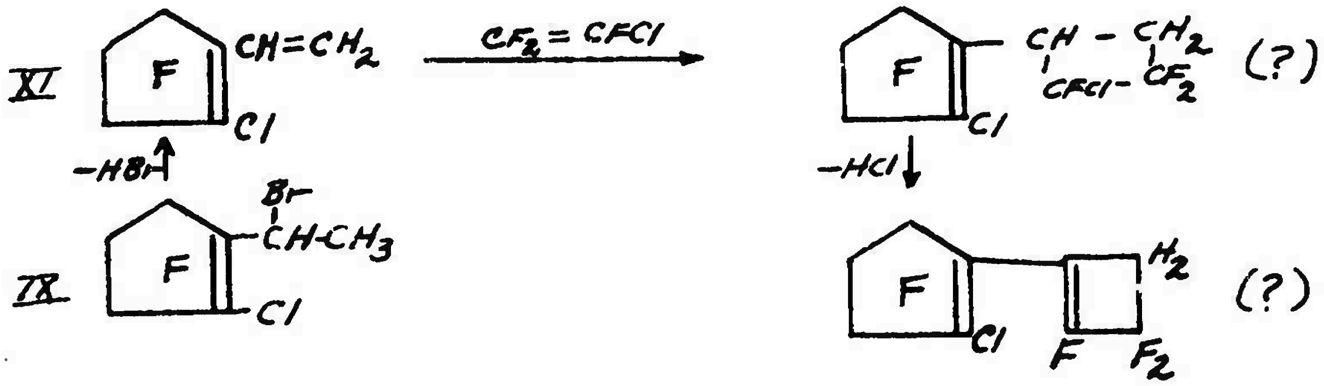
	J	Assignment
quartet 7.52	7.5 cps	$-CH_2-$
triplet 8,80	7.5 cps	$-CH_3$

(TMS internal standard, neat, Varian A60)

This spectra is consistent with the assigned structure of

III. Vinyl heptahalocyclopentene systems

With a preparative route available for the synthesis in quantity of 1-chloro-2-ethylhexafluorocyclopentene-1 (X), the synthesis of 1-chloro-2-vinylhexafluorocyclopentene-1 and related compounds appeared feasible. In addition to their possible intrinsic values as monomers they might be expected to dimerize with a variety of fluoro olefins to yield a series of highly fluorinated systems containing a 4 and 5 membered ring.



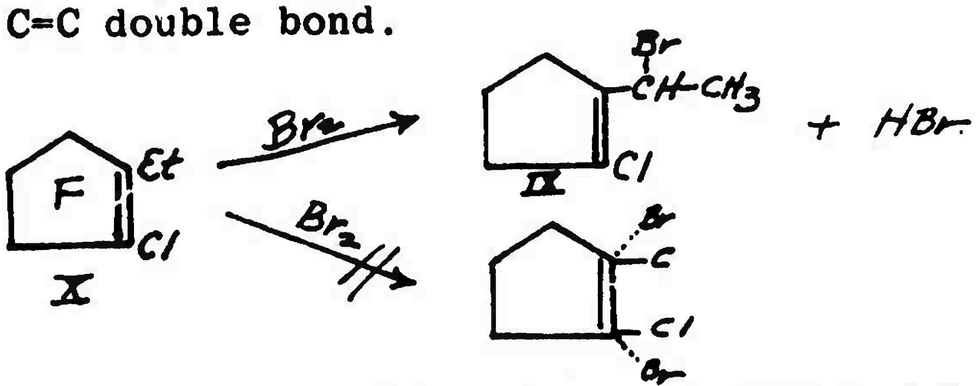
It was decided to initially attempt the synthesis of compound XI via allylic bromination of X.

Two alternate routes were selected:
1) direct bromination in methylene chloride and
2) bromination with NBS (free radical initiator) in carbon tetrachloride.

As will be noted later, apparently both methods offer convenient synthetic routes to compound IX.

1) Direct bromination

It was hoped that an allylic bromination analogous to that reported in the corresponding cyclobutene compound[19] could occur; that is, an X attack by a Br at an allylic carbon in preference to addition across the C=C double bond.

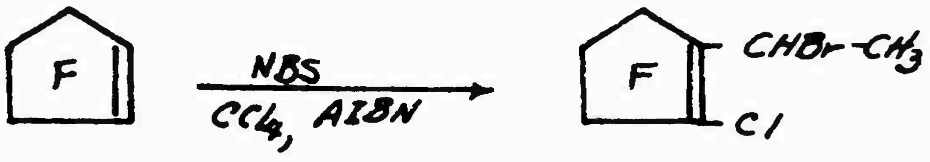


The only higher boiling fraction detected by G.L.C. analysis appeared identical in all respects (IR, physical properties, G.L.C. retention time) to that obtained by NBS bromination (see below).

2) Bromination with N-bromosuccinamide

If the direct bromination reaction is postulated to proceed through the formation of an allylic free radical then bromination with NBS under free radical conditions should yield a similar product. Surprisingly, in the case of the analogous cyclobutene, this is not reported to be the case.[3]

With the cyclopentene system, however, allylic bromination w/NBS reaction appears to go readily and in a high yield.



b.p. 158°/626mm
n 1.4182

Using a free radical initiator (AIBN) over 90% conversion was obtained in less than 24 hours rxn. time. Thus, this is an example of the possible error invoked when attempting to equate the chemistry of analogous 4- and 5- membered ring systems.

EXPERIMENTAL

Reaction with sodium iodide in acetone

In a typical reaction, 10 g of the cyclopentene, 25 ml of acetone and 15 g of anhydrous potassium iodide were placed in a 100 ml 1-neck round bottom flask fitted with a reflux condenser. The reaction mixture was heated to a vigorous reflux with a glas-col heating mantle and this temperature maintained for the desired period of time.

The Grignard was added slowly via the dropping funnel to a rapidly stirred solution of the cyclopentene in THF

Notes: Cooling (where indicated) 0^{o}-ice-water bath; pre-purified nitrogen sweeps.
The phenyl-, n-butyl, and i-butylmagnesium bromide reagents were prepared in the usual manner; the halide was slowly added to a rapidly stirred mixture of magnesium turnings in dried tetrahydrofuran. The methylmagnesium bromide (in diethyl ether) was obtained from Arapahoe Chemical Co.

Bromination of 1-ethyl-2-chlorohexafluorocyclopentene-1

a) Br_2 CH_2Cl_2

In a 250 ml 1-neck round bottom flask fitted with reflux condenser was placed 12.0 g. (0.05 moles) of I, 30 ml of methylene chloride and 15.1 g (0.09 moles) of bromine. A 100 watt light bulb was placed beneath the flask, the heat being sufficient to keep the reaction mixture at a gentle reflux.

b) NBS in CCl_4

In a 100 ml 1-neck round bottom flask fitted with reflux condenser, was placed 12.0 g. (0.05 moles) of I, 10.5 g (0.07 moles) of NBS, 0.2 g of AIBN, and 25 ml of carbon tetrachloride. The mixture was heated to a gentle reflux with a glas-col heating mantle.

TABLE VII

Reactions of Grignard Reagents with 1,2-Dihalohexafluorocyclopentene-1

Run	Compound	Grignard	RXN Temp.	Solvent	Observations
1	I	CH_3MgBr	0°	THF/Et_2O *b	extensive tarring; formation of blk. ppt. *c
2	III	CH_3MgBr	0°	THF/Et_2O *b	extensive formation of tarry residue, destruction of *c*a starting material
3	I	n-BuMgBr	28°	THF	extreme darkening of soln., dk. ppt.
4	I	n-BuMgBr	0°	THF	same as above
5	II	n-BuMgBr	28°	THF	extensive discoloration; final syn. mixture has *a a blk. solid present.
6	III	n-BuMgBr	28°	THF	extensive discoloration; final syn. mixture a dk. *a oily tar
7	I	i-BuMgBr	28°	THF	darkening of solution, tar formation
8	I	ØMgBr	28°	THF	extensive formation of tar & discoloration of syn. products
9	II	ØMgBr	28°	THF	same [illegible] *a
10	III	ØMgBr	28°	THF	[illegible] as above
11	III	ØMgBr	0°	THF	same as above

*a) analysis by G.L.C. indicated no higher boiling fractions in the crude reaction products

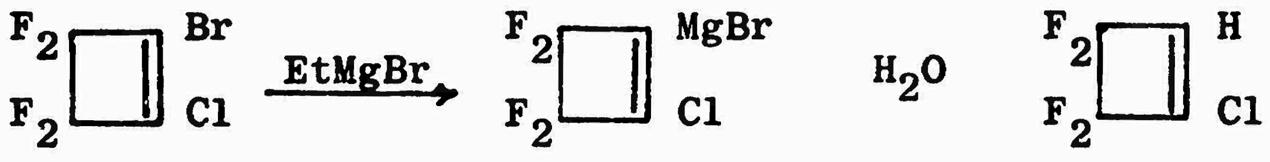
*b) a commercially prepared solution of MeMgBr in diethyl ether was added to the cyclopentene in THF (see exp. sec.)

*c) marked exothermic reaction

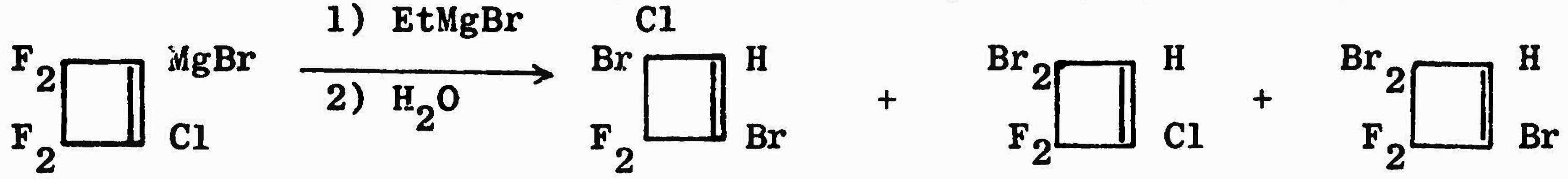
Cyclic Grignard Reagents

Discussion

In the previous reports, the preparation and some reactions of the cyclobutenylmagnesium bromide (II) was discussed. It was noted that, on standing, the cyclic Grignard reagent decomposed. Several rearranged products have now been isolated and identified from the reaction of II with excess ethyl magnesium bromide. These compounds (III, IV, V) have been identified by proton and F^{19} n.m.r., by infrared and elemental analysis and mass spectrographic analysis.



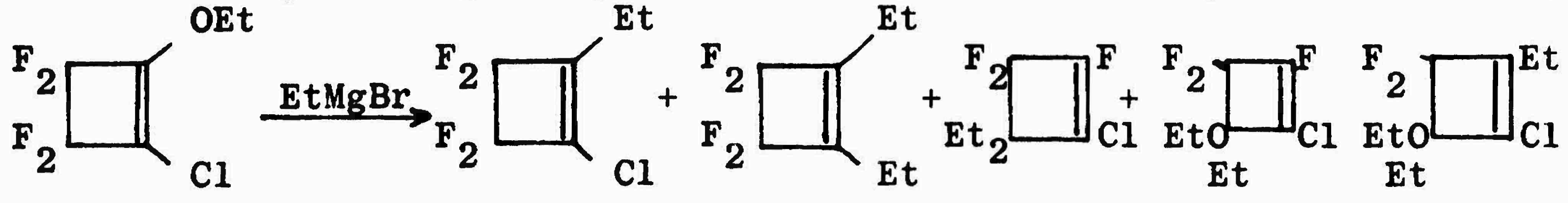
I　　II



II　　III　　IV　　V

All three occur in very low yields. Compounds III and IV are isomers and were separated by preparative scale VPC using a tricresylphosphate column at 100°.

It was previously reported that 1-ethoxy-2-bromo-3,3,4,4-tetrafluorocyclobutene reacts with ethyl magnesium bromide to give hydrocarbons. The high reactivity of this olefin was surprising and it was thought that the vinylic ethoxy group might be contributing to this reactivity. For this reason, 1-ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene (VI) was treated with ethyl magnesium bromide in the hope that some products would be isolated which would indicate reaction involving the ether linkage and replacemtn of fluorine by ethyl groups. When this reaction was carried out, five products were isolate, although many others were present in very small amounts.

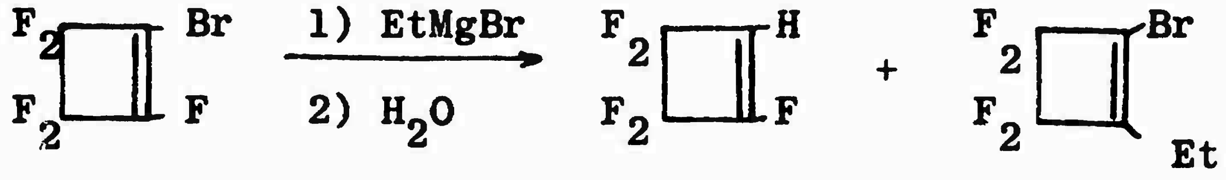


VI　　VII　　VIII　　IX　　X　　XI

Compounds VIII and IX arise by reaction of ethyl magnesium bromide on VII. This was shown by carrying out this reaction on VII prepared in an independent manner. Compounds VII and VIII are known and were identified by infrared analysis. Compounds IX, X and XI were identified by elemental and infrared analysis and from their n.m.r. spectra. Molecular weights were determined by the mass spectrograph.

Compound VIII was present in 16.6% conversion, VII in 15.3%, IX; 4.2%, X; 5%, XI; 1.8%.

1-bromo-2,3,3,4,4-pentafluorocyclobutene (XII) was prepared. Synthesis was achieved by codimerization of CF_2=CBr_2 and CF_2=CFCl in a 1/2 l. stainless steel bomb to give the cyclobutane in 18% yield. This was treated with zinc to give the olefin (XII).



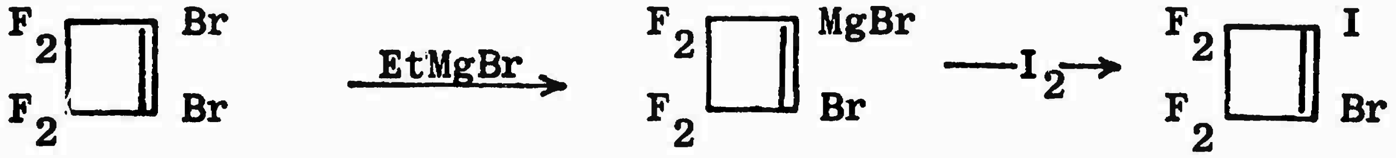
XII XIII XIV

Treatment of XII with ethyl magnesium bromide gave principally the cyclic Grignard reagent, which, upon reaction with water produced XIII. The thyl substituted cyclobutene (XIV), was produced in a competing reaction in small yield.

Other reactions carried out include reaction of i-iodo-2-bromo-3,3,4,4-tetrafluorocyclobutene (XV) with ethyl magnesium bromide in ether and in tetrahydrofuran. In each case, the product isolated was 1-bromo-3,3,4,4-tetrafluorocyclobutene (XVI).

XV XVI

Compound XV was prepared as follows: Treatment of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene with ethyl magnesium bromide gives the cyclic Grignard which reacts with iodine to give XV.



EXPERIMENTAL

Reaction of 1-ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene (VI) with ethyl magnesium bromide. A solution of 123.8 g. (0.60 mole) of VI in 300 ml. anhydrous tetrahydrofuran in a 1-l. three-neck flask was stirred and warmed to 50°C. To this was added dropwise 400 ml. (1.2 mole) of ethyl magnesium bromide in ether. The ether was distilled off during addition. After stirring for 4 hrs., a heavy precipitate formed and the reaction had to be discontinued. Water was added to dissolve the solid and the product was taken up in ether and dried over magnesium sulfate. Distillation yielded 12 g. (15.3% conversion) of VII; b.p. 98-99°/620 mm. This was identified by comparison of the infrared spectrum with an authentic sample. Also recovered by distillation was a mixture of compounds VIII, IX, X and starting material VI.

Separation of VIII was effected in 16.6% conversion using a fluorosilicone preparative scale v.p.c. column (12.6 g., b.p. 134-136°/620 mm.). Also separated in this manner was 40 g. of starting material (VI) and a mixture of IX and X. This mixture was resolved by use of a tricresylphosphate preparative scale v.p.c. column and gave 3.4 g. of IX (4.2% conversion), b.p. 133°/619 mm.; d_{25}^{25} 1.1591; n_D^{25} 1.4018, and 4.2 g. of X (5% conversion), b.p. 136-137°/619 mm.; d_{25}^{25} 1.1852; n_D^{25} 1.3979.

Anal. Calcd. for $C_8H_{10}F_3Cl$ (IX): C, 48.37; H, 5.07; F, 28.70; Cl, 17.85. Found: C, 48.33; H, 5.17; F, 28.82, Cl, 17.86.

Anal. Calcd for $C_8H_{10}F_3ClO$ (X): C, 44.76; H, 4.70; F, 26.56; Cl, 16.62. Found: C, 44.82; H, 4.80; F, 26.77, Cl, 16.71.

Also isolated was 1.5 g. (1.8% conversion) of XI, b.p. 175°/619 mm. (with some decomposition); d_{25}^{25} 1.0814; n_D^{25} 1.4239. The compound turns yellow after several weeks at room temperature.

Anal. Calcd for $C_{10}H_{15}F_2ClO$: C, 53.45; H, 6.73; F, 16.92; Cl, 15.78. Found: C, 54.47; H, 7.09; Cl, 15.85; F, 17.18.

1-2-Dibromo-2-chloro-2,3,3,4,4-pentafluorocyclobutane. -

A 1/2 l. stainless steel Paar bomb was charged with 156 g. of chlorotrifluoroethylene (1.34 mole) and 149 g. (0.67 mole) of 1,1-difluoro-2,2-dibromoethylene. The bomb was shaken and heated to 175° over a period of 24 hr. and then maintained at this temperature for 24 hr. Distillation gave as the major product a fraction of semi-solid material which was crystallized from methanol and water to give 41 g. (18%) of a colorless solid, b.p. 126-126.5°/623 mm. The material has a high vapor pressure and a camphor-like odor.

Anal. Calcd. for $C_4F_5ClBr_2$: C, 14.20; F, 28.08; Cl, 10.47; Br, 47.24. Found: C, 14.15; F, 28.29, Cl, 10.43; Br, 47.45.

1-Bromo-2,3,3,4,4-pentafluorocyclobutene (XII). - A solution of 8.8 g. (0.026 mole) of 1,2-dibromo-2-chloro-2,3,3,4,4-pentafluorocyclobutane in ethanol was added to a warm slurry of zinc in ethanol. A vigorous reaction ensued to yield 5 g. (85% conversion) of XII, b.p. 48°/ 626 mm; d_{25}^{25} 1.799; n_D^{25} 1.3494.

Anal. Calcd. for C_4F_5Br: C, 21.54; F, 42.61; Br, 35.84. Found: C, 21.68; F, 42.63; Br, 35.48.

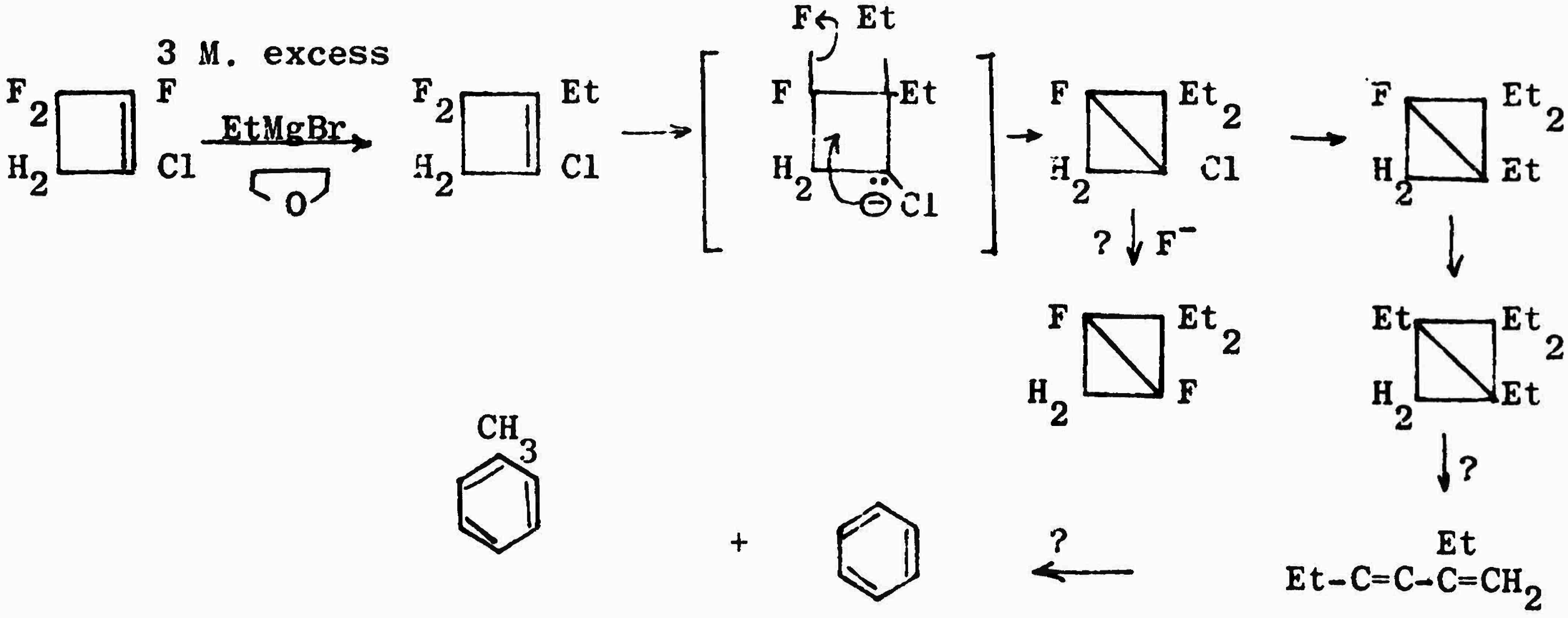
Reaction of XII with ethyl magnesium bromide. - To a solution of 4.9 g. of XII in 10 ml. of anhydrous ether and cooled to 0°, was added rapidly 15 ml. (0.045 mole) of 3-M ethyl magnesium bromide. After stirring 1 hrs., water was added and the ether solution was dried and the products separated by preparative scale v.p.c. to yield 0.92 g. of 2,3,3,4,4-pentafluorocyclobutene (30% recovery), and 0.55 g. (23% recovery) of ethyl bromide. These compounds were identified by their infrared spectra. Also isolated was 0.06 g. of i-ethyl-2-bromo-3,3,4,4-tetrafluorocyclobutene (XIV) (0.9%). The infrared spectrum of this compound was nearly identical to that for VII. The low yields are attributed to poor recovery from the chromatograph. No other products were observed.

Anal. Calcd. for $C_6H_5F_4Br$: C, 30.92; H, 2.16; F, 32.62; Br, 34.30. Found: C, 30.95; H, 2.10; F, 32.81; Br, 34.15.

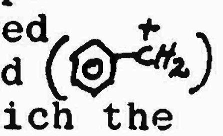
C) Ethyl Grignard Reaction with 1-chloro-2,3,3-trichlorocyclobutene. - Novel Production of Bicyclobutanes and Aromatics.

Successful Grignard reactions have been carried out by Fontanelli, Sullivan and Anderson on 3,3,4,4-tetrafluorocyclobutenes in ether at 0° C. with vinylic halogens being replaced by ethyl groups. However, when 1-chloro-2,3,3-trifluorocyclobutene was reacted with ethyl magnesium bromide in ether up to 30°C., no reaction took place.

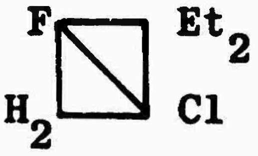
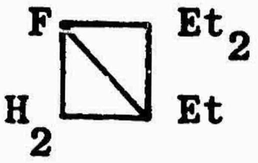
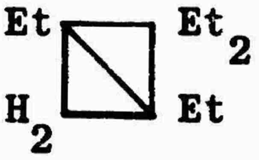
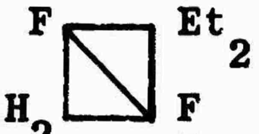
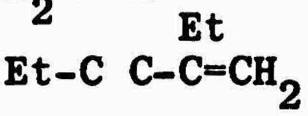
The reaction was repeated with ethyl grignard in tetrahydrofuran at 35-45°C. to yield, 20% recovery of starting material, 28% and high boiling unidentifiable hydrocarbons, and 43% of a mixture of twelve products, eight of which have been definitely identified. The reaction scheme with all of the compounds identified to date looks like this:

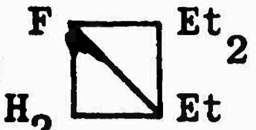


Curiously enough, the most unusual product (the vinyl acetylene) was present in the largest amount. Four other materials have yet to be identified. Their physical properties and spectral information are recorded in the experimental section. The tetraethyl hydrocarbon is not positively identified at this time.

Mass spectrometry helped a great deal in identification, and the cracking patterns were extremely interesting and lent strong evidence to the amazing formation of benzene and toluene. The cracking pattern for all of the bicyclobutanes and the vinyl acetylene showed large mass no. peaks at M 77 and M 81 corresponding to $C_6H_5^+$ and  $C_7H_7^+$ (CH_2) ions. This information showed the ease with which the compounds rearranged to the aromatic compounds under mass spectral ionizing conditions anyway. Whether this fact can be applied toward solution conditions at 40-50° is a moot question.

To supplement the experimental section, below is a chart showing the magnitude of the aromatic mass peaks encountered with the reaction products.

Compound	$C_6H_5^+$ (77) % of max. peak	C_7H_7 (91) % of max. peak
	24	33
	80	69
	33	28
	87	33
 $Et-C\ C-\overset{Et}{C}=CH_2$	100	60

The fact that  and  $Et-C\ C-\overset{Et}{C}=CH_2$ show the greatest percent of max. peak for the aromatic species make one tend to believe they are the precursors of the benzene and toluene.

Experimental

Reaction of 2-chloro-1,4,4-trifluorocyclobutene with Ethyl Magnesium Bromide.

Twenty ml. of 3 molar ethyl magnesium bromide in ether (0.06 mole) were added to 8.5 g. (0.06 mole) of 2-chloro-1,4,4-trifluorocyclobutene in a 50 ml. 3-neck flask fitted with stirrer and reflux-condenser. The reaction mixture was heated to ether reflux (30°C.) for 15 hrs. with no noticeable reaction. After work up, only starting material was detected by g.l.c. analysis. 4.7 g. (56% of theory) of the 2-chloro-1,4,4-trifluorocyclobutene was recovered.

Reaction was repeated with Grignard reagent with tetrahydrofuran which was first dried over KOH pellets and distilled from $LiAlH_4$ before being used as solvent for the reaction of magnesium with ethyl bromide.

Eight hundred ml. of 1.78 molar ethyl magnesium bromide in tetrahydrofuran (1.42 moles) in an addition funnel were added slowly dropwise for 10 hours to 51.0 g. (0.357 mole) of 2-chloro-1,4,4-trifluorocyclobutene kept at 35°. in a one-liter 3-neck flask fitted with stirrer and refluxcondenser which was connected further to dry ice trap, $CaCl_2$ drying tube and mineral oil bubbler. The reaction mixture was stirred at 40°-50° for 14 hrs. and at room temperature for 10 hrs. The trap containing starting material was periodically emptied back into reaction mixture. A claisen head and condenser tube leading to 500 ml. flask immersed in dry ice was put in place of the reflux condenser. While continuing to stir, the lower boiling compounds were distilled off under aspirator vacuum until only solid was left. The reflux condenser was then placed back and 200 ml. of H_2O and 100 ml. of ether added. This mixture was stirred until the solid was broken up.

After letting the ether and water layers separate, the ether layer was removed by a suction separatory apparatus. Ether was again added, stirred, and vacuumed off in 100 ml. portions in this manner six more times in order to extract out higher boiling products. These ether extracts were washed twice with water, dried over anhyd. $MgSO_4$ and fractionally distilled. Most of the ether was distilled off leaving the higher boiling products. The lower boiling compounds that were distilled from the reaction mixture under aspirator pressure were fractionally distilled to yield 10.2 g. of starting material (20.0% of theory) and 300 ml. of THF. The residue of this distillation was combined with the residue of the ether distillation and poop distilled to give 27 grams of a mixture of products and 17.33 grams of high boiling hydrocarbons left as a residue with a boiling point greater than 130°C/0.5 mm. Analysis by g.l.c. discerned at least six ompounds. The infrared spectrum showed only carbon-hydrogen peaks.

Fractional distillation under reduced pressure gave fifteen fractions. Subsequent g.l.c. analysis showed none of the (at least twelve) discernible products to be pure. The products were obtained pure upon separation via a preparative scale gas-liquid chromatograph and are as follows in order of g.l.c. retention time. Overall yields are based on g.l.c. integration of all fractions.

The first product was 0.4 g. (0.1% of theory) of benzene. The infrared spectrum and the g.l.c. retention time were identical to that of an authentic sample.

The second product was 3.9 g. (7.2% of theory) of 1-chloro-2-ethyl-3,3-difluorocyclobutene; b.p. 99.5°C/625 mm., $n_D^{25^\circ}$ 1.4044, $d_4^{25^\circ}$ 1.142. Molar refraction: Calcd., 32.79; obsd. 32.71.

Anal. Calcd. for $C_6H_7ClF_2$: C, 47.23; H, 4.62; Cl, 23.24; F, 24.91. Found: C, 47.13; H, 4.50; Cl, 25.10; F, 23.25.

Analysis by gas-liquid chromatography showed this material to be 100% pure. The infrared spectrum contained a medium sharp absorption at 1650 cm-1, characteristic of a 1-chloro-2-ethylcyclobutene. The n.m.r. spectrum contained a triplet (J_{HF}=3cps) with complex splitting at 6.95 due to the ring protons, a quartet with complex splitting at 7.84 and a triplet at 8.87 ; the latter two due to a vinylic ethyl group on a cyclobutene ring.

The third product is believed to be 4 g. (0.2% of theory) of 1,3-difluoro-2,2-diethyl (1.1.0) bicyclobutane; b.p. 112°C (620 mm.), n_D^{25} 1.3994, d_4^{25} 0.94. Molar refraction: calcd. 36.84; obsd. 37.64.

Anal. Calcd. for $C_8H_{12}F_2$: C, 65.73; H, 8.27; F, 26.00. Found: C, 65.54; H, 8.50; F, 25.84.

Analysis by gas-liquid chromatography showed this material to be 99% pure. The infrared spectrum contained strong carbon-hydrogen absorption from 2850 cm^{-1} to 3000 cm^{-1}, a strong absorption at 1770 cm^{-1}, and strong wide, jagged absorptions from 1100-1400 cm^{-1}, the C-F region. The n.m.r. spectrum contained an equal intensity quartet centered at 7.98 (J^1_{HF}=13.5 cps, J^2_{HF}=5.35 cps) due to the ring protons, and two triplets centered at 8.44τ and 9.08τ due to the hindered gem diethyl group. Integration of the spectrum showed a ratio of 2 to 4 to 6 protons, respectively. Mass spectra analysis showed the molecular ion peak to be 146 which was also the 100% peak. The cracking pattern is not inconsistent with the assigned structure.

The next product was less than 0.1 g. of unidentified material. The infrared spectrum showed medium C-H absorption at 2850-3000 cm^{-1}, a medium sharp absorption at 1760 cm^{-1}, a strong sharp absorption at 1700 cm^{-1} and strong C-F absorption at 1320 cm^{-1}.

The fifth product was 0.2 g. (0.1% of theory) of toluene; b.p. 106^{o}C/625 mm. The infrared spectrum, n.m.r. spectrum and g.l.c. retention time were identical to that of an authentic sample.

The sixth and major product was 5.0 g. (12.8% of theory) of 2-ehtyl-1-hexen-3-yne: b.p. 120^{o}C/625 mm., n_D^{25} 1.4492, d_4^{25} 0.769 . Molar refraction: Calcd. 36.84; obsd. 37.74. (Difference due to exhaltation factor in conjugated systems.)

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 86.44; H, 10.81

Analysis by g.l.c. showed this material to be 99% pure. The infrared spectrum contained strong C-H absorption at 2850-3000 cm^{-1}. A small sharp absorption occurred at 3100 cm^{-1} characteristic of a terminal methylene group. A small sharp absorption occurred at 2210 cm^{-1} characteristic of a rigid system. The olefin absorption occurred at 1610 cm^{-1}, characteristic of a conjugated double bond. The n.m.r. spectrum contained a complex integrating for two protons at 4.88τ and 4.90τ showing much long-range coupling, due to the terminal methylene protons. It also contained two complex quartets centered at 7.72τ and 7.88τ showing long-range coupling and integrating for four protons; and two complex triplets centered at 8.88τ and 8.95τ showing long-range coupling and integrating for six protons. The quartets and triplets were due to two nonequivalent ethyl groups. The long-range coupling was due to the rigid vinyl acetylene system. The ultraviolet spectrum showed an absorption at λmax. 223, ε =13,500 with a minor peak almost as a shoulder at λmax. 233 ε=10,500. This spectrum was not inconsistent with the assigned structure. Mass spectral analysis showed the molecular ion peak to be 108. (72% of max. peak which was 77.)

The seventh product was 4.6 g. (8.1% of theory) of 1-fluoro-2,2,3-triethyl (1.1.0) bicyclobutane; b.p. 141^{o}C/625 mm. sl. decomp., n_D^{25} 1.4224, d_4^{25} 0.857. Molar refraction: calcd. 45.98; obsd. 46.36.

Anal. calcd. for $C_{10}H_{17}F$: C, 76.88; H, 10.97; F, 12.15. Found: C, 77.86; H, 11.17; F, 10.92.

Analysis by g.l.c. showed this material to be 89% pure. The infrared spectrum contained two equally strong C-H peaks at 2920 cm^{-1} and 2970 cm^{-1}, a sharp strong peak at 1720 cm^{-1}, and absorption peaks in the C-F region. The n.m.r. spectrum contained two complex quartets centered at approximately 8.33τ and 8.45τ and two triplets centered at approximately 9.0τ and 9.1τ consistent with the type of ethyl groups encountered on the molecule. The ring protons were presumably present as a doublet buried in the methylene quartets. It was suspected to be a doublet centered at about 8.37τ with $J_{HF} \approx 13.8$ cps. Integration of the spectrum bore this assumption out as the methylene region showed eight protons to nine in the methyl region. Mass spectral analysis showed the molecular ion peak to be 156 (16% of max. peak which was 127.)

The eighth product was 1.0 g. (0.2% of theory) of 1-fluoro-3-chloro-2,2-diethyl (1.1.0) bicyclobutane; b.p. 139°C/622 mm. sl. decomp., n_D^{25} 1.4347, d_4^{25} ---. Molar refraction: calcd. 41.61; obsd. ---.

Anal. calcd. for $C_8H_{12}ClF$: C, 59.08; H, 7.44; Cl, 21.80; F, 11.68. Found: C, 73.63; H, 8.81; F, 11.20.

Analysis by g.l.c. showed this material to be 88% pure. The infrared spectrum contained C-H absorption at 2850-3000 cm^{-1} and a strong sharp peak at 1705 cm^{-1}. The n.m.r. spectrum contained a doublet at 7.98τ with $J_{HF}=13.7$ cps due to the ring protons being split by the adjacent fluorine on the strained cyclopropane ring; and two triplets centered at 8.35τ and 9.07τ due to the hindered gem-diethyl protons. Integration of the n.m.r. spectrum is consistent with the proposed structure. Mass spectral analysis showed the molecular ion peak to be 162 (21% of max. peak which was 32) and showed the definite presence of chlorine in the molecule.

Synthesis of New Fluorine-Containing Monomers

As a continuation of earlier investigations of special fluorine-containing monomers from which to obtain elastomers with special properties, trifluoronitroethylene was prepared from 1,2-dichlorotrifluoronitrosoethane.

$$CF_2{=}CFCl \xrightarrow{NOCl} CF_2Cl\text{-}CFClNO \xrightarrow{(O)} CF_2Cl\text{-}CFClNO_2$$

$$CF_2Cl\text{-}CFClNO_2 \xrightarrow{Zn} CF_2{=}CFNO_2$$

1,2-Dichlorotrifluoronitrosoethane was prepared by the addition of nitrosyl chloride to chlorotrifluoroethylene by a method previously reported. By allowing the nitroso compound to remain in the refrigerator for several days, the nitro compound was formed and isolated by simple distillation. Dechlorination of the nitro compound yielded an unsaturated compound, supposedly $CF_2{=}CFNO_2$ which hasn*t been entirely characterized as yet. Chlorotrifluoroethylene was also found as a reaction product.

Preparation of 1,2-dichlorotrifluoronitrosoethane

The method used for the synthesis of 1,2-dichlorotrifluoronitrosoethane was one previously reported using a solution of chlorobenzene with ferric chloride and a trace of acetic anhydride. By using a solution of 150 g. chlorobenzene, 15 g. of ferric chloride and 5 g. of acetic anhydride as the reaction mixture, 210 g. (1.15 mole) of the nitroso compound was prepared from chlorotrifluoroethylene and nitrosylchloride. b.p. 31°/627 mm.; n_D^{20}, 1.3461.

Prepartion of 1,2-dichlorotrifluoronitroethane

Several oxidation schemes were tried in order to prepare good yields of 1,2-dichlorotrifluoronitroethane. Using acid dichromate, very low yields of the nitro compound were prepared. From 100 g. of 1,2-dichlorotrifluoronitrosoethane using the method of Stefani, only 5 g. of 1,2-dichlorotrifluoronitroethane was formed.

The remaining nitroso compound in the refrigerator was noted to be changing in color and upon redistillation yielded 61 g. of pure (by G.L.C.) 1,2-dichlorotrifluoronitroethane. b.p. 70°/625 mm.; n_D^{20}, 1.3699.

Prepartion of trifluoronitroethylene

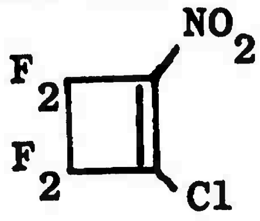
Into a 500 ml. three-neck flask was placed 25 ml. of activated zinc in dibutoxytetraglycol prepared previously by J. H. Adams. To this suspension was added 33 g. (0.5 mole) of zinc powder and 200 g. of dibutoxytetraglycol. From a dropping funnel, 50 g. (0.25 mole) of 1,2-dichlorotrifluoronitroethane was added dropwise to the rapidly stirred mixture and the reaction rate was controlled by the rate of addition. The product was collected in a cold trap. Analysis of the product by G.L.C. showed two peaks, one peak 77%, the other 23%.

Distillation of the product using a special system for low temperature distillation resulted in the separation of two components. One of these components, approximately 5 g., was identified by IR and a comparison of the G.L.C. retention time as chlorotrifluoroethylene and was the minor component. The main fraction was collected between -12° and -10°. The molecular weight was determined by Regnault vapor density method and found to be 129 compared with 127 for the known. Approximately 10 g. of this material was obtained. Attempts to characterize it further are in progress.

A preliminary explanation for the presence of chlorotrifluoroethylene in the product might be that the zinc removed the nitro group instead of the chlorine atom in the dehalogenation step. However, since the yield of product was approximately 40%, other explanations are probably just as feasible.

$$CF_2Cl\text{-}CFClNO_2 \xrightarrow{Zn} CF_2{=}CFCl \quad + \quad Zn^{++} \quad + \quad Cl^- \quad + \quad \bar{N}O_2$$

Plans for future work include attempts to prepare the following compounds:



, $CF_2{=}CClNO_2$

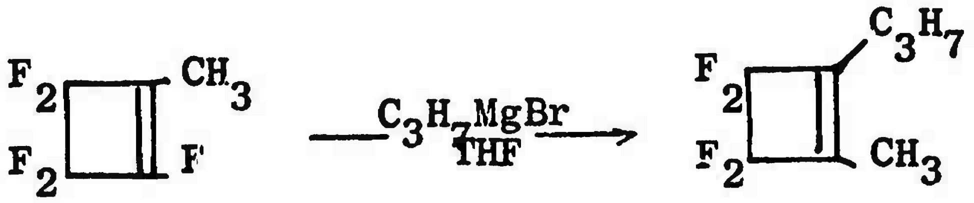
General Reactions

Reactions of Grignard Reagents on Cyclobutenes and Pyrolysis of the Reaction Products

The object of this investigation is to prepare new cyclic compounds which then can be pyrolyzed to dienes.

This type of reaction on cyclobutenes has been carried out previously by Fontanelli[10], but he dealt mainly with the mono-and symmetrical dialkyl derivatives. Pyrolysis of certain types of cyclobutenes has also been done previously.[11]

Several new compounds have been prepared during this period. They consist of two new cyclobutene derivatives and a new butadiene derivative. Several interesting mechanistic implications were also observed.



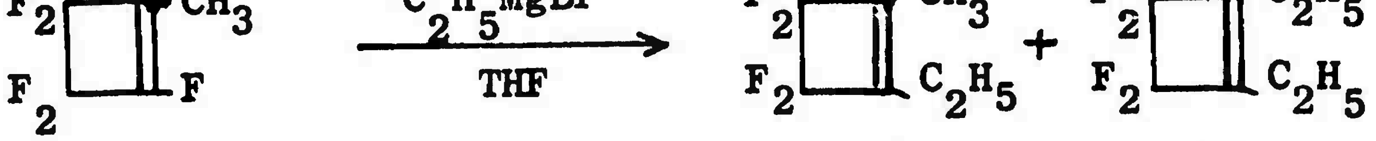
I II

A small scale run was made in which ca. 12 g. of I was refluxed for 20 hr. with excess PrMgBr in tetrahydrofuran. After extraction, crude distillation of the extract, and separation of the product on the autoprep, a small amount of material was obtained.

II analyzed as follows:

	%C	%H	%F
Calcd.	52.75	5.49	41.76
Obsd.	52.66	5.30	41.59

A micro boiling point determination indicated a boiling point of 138°/625 mm. Refractive index and density will be determined when a large quantity of the compound is prepared for further pyrolysis reactions.



I III IV

Ca. 18 gr. of I were refluxed for 19 hr. with excess EtMgBr in tetrahydrofuran. After extraction, crude distillation of the extract, and separation on the autoprep, two products were obtained. The major product was III.

Since the starting material was somewhat impure, the reaction will be repeated. However, there did not seem to be sufficient impurity to account for the relatively high conversion to IV. VPC of the extract indicated a total conversion of 90%, 74% to III and 16% to IV. The identity of IV was confirmed by comparison of the infrared spectrum with one of a known sample.

The properties of III are as follows:

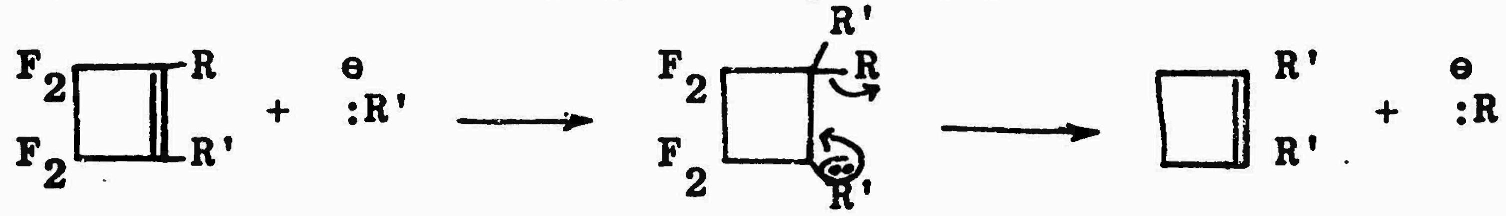
		molar refraction
boiling point	121°/625 mm.	calcd. 32.7
refractive index	$n_D^{25.1}$ 1.3611	obsd. 32.6
density	$d^{25.1}$ 1.141	
freezing point	below -80°	

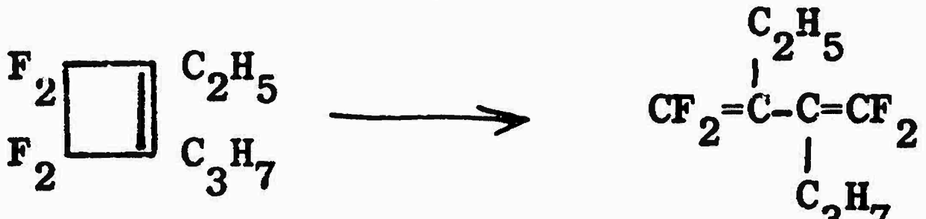
elemental analysis

	%C	%H	%F
Calcd.	50.0	4.76	45.2
Obsd.	50.78	5.17	43.7

If I can be converted to IV, this may indicate that the double bond is attacked by a carbanion; and the more stable carbanion is "kicked off" when the electron pair flips back.

e.g.





V → VI

Ca. 11 g. of V was passed through a pyrolysis tube at reduced pressure. The follwing date in Table VIII indicate the conversion at various temperatures.

Table VIII

Conversion of 1-Ethyl-2-Propyl-Perfluorocyclobutene to 2-Ethyl-3-Propyl-1,3-Butadiene

Temperature (°C)	Total Conversion (%)
610	2.5
630	3.6
655	4.6
655	5.5
670	6.5
670	6.8
675	6.3
690	7.5
700	8.9

The yield was 98%.

The product was separated on the "Autoprep" G.L.C. apparatus. Since a very small amount was obtained, only an infrared spectrum and an elemental analysis was obtained. Other properties will be obtained when a large scale run is made, assuming the material is stable and will not polymerize too readily.

VI analyzed as follows:	%C	%H	%F
calc.	55.1	6.1	38.8
obsd.	54.61	5.25	39.69

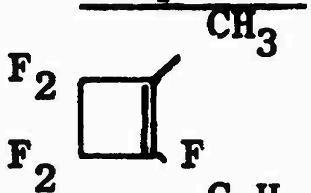
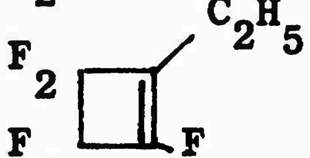
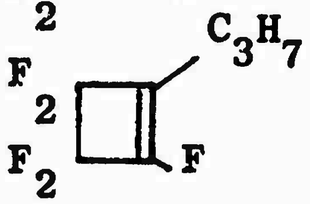
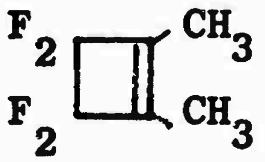
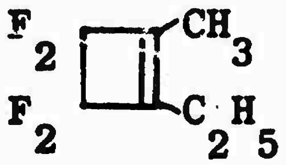
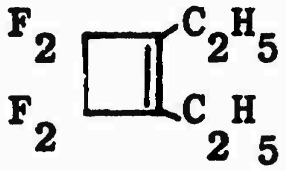
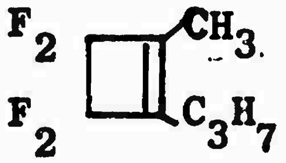
The infrared spectrum indicated two unequivalent double bonds by two weak peaks, one at 1660 cm^{-1} and the other at 1740 cm^{-1}.

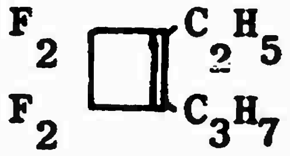
The data in Table VIII seems to indicate that the reaction probably is in equilibrium since recycling at a given temperature gave no appreciable differences in the conversions.

Since all of the mono- and di- alkyl derivatives of perfluorocyclobutene substituted at the vinyl positions by CH_3, C_2H_5, and C_3H_7 have been prepared, it may be of value to have a table of their boiling points. Table IX shows these data.

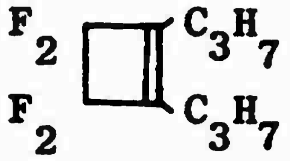
Table IX

Various Cyclic Compounds and Their Boiling Points

Compound	Boiling Point
	44-5°
	67°
	87°
	102°
	121°
	135°
	138°



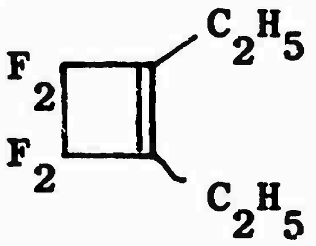
150°



165-70°
(estimated from vac. b.p.)

Plans for the future are as follows:

Preparation of



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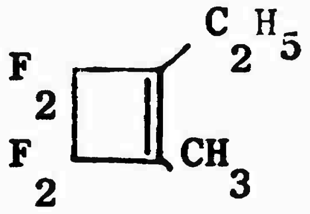

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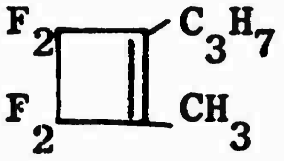
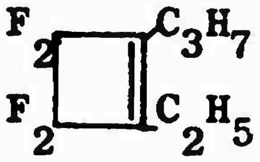


and



in large quantities. Also, study the possibility of replacing the alkyl groups by perhaloalkyl groups.

The reaction of various alkyl di-substituted cyclobutenes will be checked for alkyl displacement by Grignard reagent in tetrahydrofuran.

Several alkyl di-substituted cyclobutenes will be hydrolyzed to the diketones.

EXPERIMENTAL

1-Methyl-2-propyl-3,3,4,4-tetrafluorocyclobutene (II)

Into a 90 ml. three-neck flask fitted with a stirrer, dropping funnel, and reflux condenser, 11.8 g. (0.075 mole) of I was introduced. 50 ml. of 3M (0.15 mole) PrMgBr in tetrahydrofuran was then added dropwise in order to keep the reaction from getting out of control. A white solid formed as the reaction proceded. After the addition was completed, the reaction mixture was refluxed for 20 hr.

The reaction mixture was then cooled in an ice bath, and cold water was dropped slowly into the reaction to decompose the excess Grignard reagent. Care was taken to add the water slowly enough to prevent a violent reaction. The product was extracted from the solid magnesium salt with ether until most of the yellow color was gone. Bicarbonate was added to the combined extracts to neutralize any HF which may have formed from decomposition. Then the extract was dried over anhydrous magnesium sulfate. The product was crudely distilled and then isolated on an autoprep.

1-Methyl-2-ethyl-3,3,4-tetrafluorocyclobutene (III)

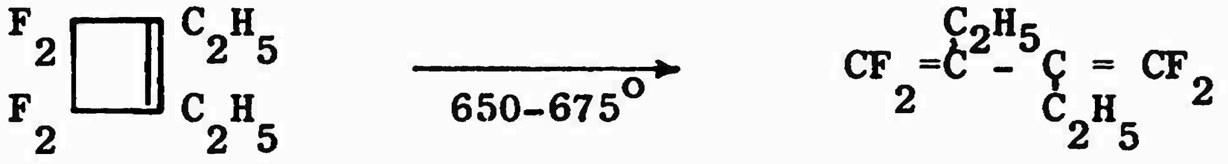
The reaction was carried out similarly to that above. 11.7 g. (0.112 mole) of I was reacted with 75 ml. of 3M EtMgBr (0.225 mole) in tetrahydrofuran, and the mixture was refluxed for 19 hr. The workup was also similar to that above.

2-Ethyl-3-propyl-1,1,4,4-tetrafluoro-1,4-butadiene (VI)

The pyrolysis apparatus consisted of a vertical glass tube 1" in diameter and 18" in length packed with small glass beads and heated over 12" by an electric oven. The top of the tube was closed by a small equalizing dropping funnel, and the bottom was connected to two small dry ice traps and a liquid air trap, which then was connected to a vacuum pump and manometer via a manifold.

The tube was heated to 610°, as measured by a thermocouple wired half way up the outside of the pyrolysis tube. VI was placed in the dropping funnel, and the pressure was reduced to 8 mm. VI was then dropped quite slowly into the tube. The organic recovery was 98%. Separation by autoprep gave only enough material for an infrared spectrum and an elemental analysis.

Pyrolyses Studies. -



VI VIII

113 g. of 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (VI) was passed through a pyrolysis tube heated from 650° to 675°. The higher boiling VII was collected in an ice-cooled trap, and a mixture of VI and 2,3-diethyl-1,1,4,4-tetrafluoro-1,3-butadiene (VIII) was collected in a dry-ice trap. This mixture of somewhat concentrated VIII was separated on the Autoprep G.L.C. apparatus. A conversion of 3% and yield of 98% was obtained.

The properties of VIII are as follows: b.p. 98.5°/655 mm., refractive index $n_D^{25.2}$ 1.3702, density $d^{25.2}$ 1.080, freezing point, below -80°. Molar refraction: Calcd. 38.09; Obsd. 38.05.

elemental analysis

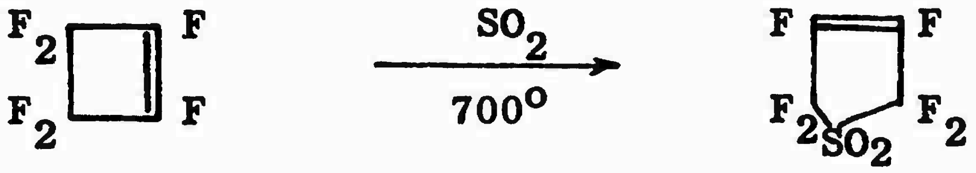
	%C	%H	%F
Calcd.	52.7	5.5	41.7
Obsd.	53.40	5.58	41.09

A minor product was also separated on the Autoprep G.L.C. apparatus in a large enough quantity to obtain an infrared spectrum and an elemental analysis. The infrared spectrum was identical to the spectrum of a minor product obtained from the pyrolysis of 1-ethyl-2-propyl-3,3,4,4-tetrafluorocyclobutene (IX). The results of the analysis have not yet been obtained.

For reasons which were described in an earlier report it appeared that the pyrolysis of cyclobutenes involved an equilibrium. In order to check this VIII was passed through the pyrolysis tube at 670°, and G.L.C. analysis indicated that 3.2% VIII was present in the reaction mixture. This was within experimental error of the 2.9% VIII found when VI was pyrolyzed at 670°. The reaction product of the pyrolysis of VIII was shown to be VI by comparison of the infrared spectrum with that of an authentic sample.

A minor product was also found, which G.L.C. analysis indicated was the same material as was produced in the reverse reaction.

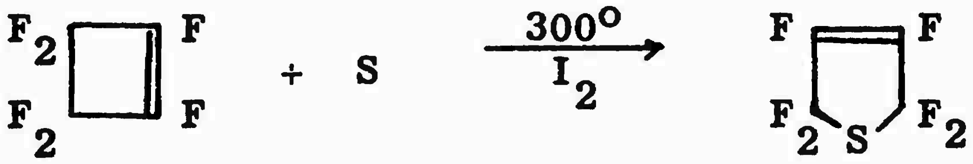
The fact that the above pyrolysis appears to be an equilibrium agrees with the conclusion of other work done on perfluorocyclobutene.[20]



I X

An attempt was made to trap the proposed free radical intermediate in the pyrolysis of I by carrying out the reaction in a SO_2 atmosphere. The reaction mixture was recycled once, and ca. 20% conversion to crude nonvolatile material and ca. 85% yield was obtained. The products have not yet been isolated in a pure form.

Fluorinated Thiolene Derivatives

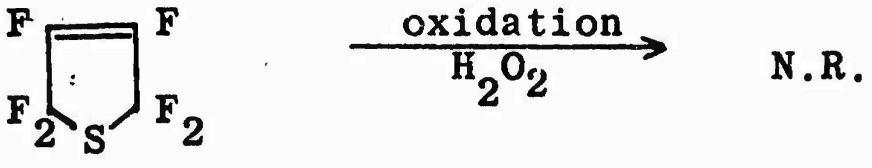


I XI

This reaction was carried out in the usual manner by Krespan.[21] However, the conversion was only ca. 15%.

The product analyzed as follows:

	%C	%F	%S
Calcd.	24.7	58.7	16.5
Obsd.	24.91	58.76	16.32



XI

4.4 g. of hexafluoro-3-thiolene (XI) was allowed to mix with a two-fold excess of 30% hydrogen peroxide at room temperature for one hour. There was no heat liberated, and there was no disappearance of the organic layer. The reaction mixture was then heated to 40° (b.p. of XI) and stirred for 8 hrs. There was still no evidence of reaction.

Peracetic acid was then added in an attempt to oxidize in this manner. The mixture was again heated for 15 hrs. Two phases still existed, bu a very small amount of white material formed.

XI was then recovered and placed in a flask with enough acetone to dissolve most of it. Hydrogen peroxide was then added and the reaction was warmed overnight. When the reaction mixture was dried, a very small amount of white waxy material was present. It melted over a flame but not at 290°. It was expected that the sulfone would be a semi-solid.[22]

5.25 g. of XI were placed dropwise into a flask containing two-fold excess alcoholic KOH. Even though the reaction flask was cooled in ice, it warmed up; and the solution turned yellow. The solution was stirred for 2 hrs. at 0° then warmed to room temperature and stirred for 2-1/2 hrs.

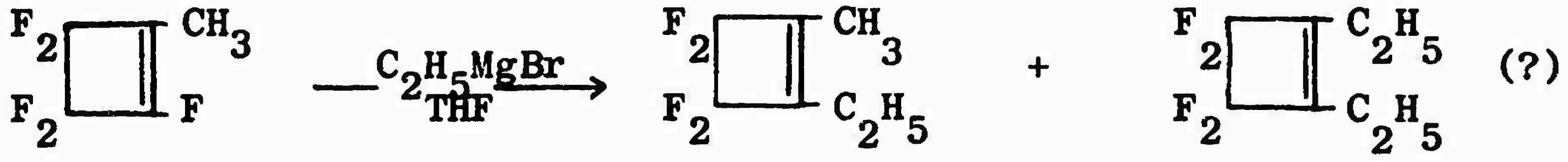
The reaction mixture was extracted with ether to remove any organic material, and the extract was then washed with water to remove the alcohol. This is the procedure normally used for the work up of ethoxy substitution on cyclobutene systems. Unexpectedly, the yellow color concentrated in the water washings. As a result, the washings were continuously extracted with ether. An oil appeared to collect in the ether extract; however, no product could be isolated.

The minor product obtained from the pyrolysis of 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (see above) analyzed to give an empirical formula of C_2H_2F. No structure has been proposed.

The pyrolysis of perfluorocyclobutene in an atmosphere of SO_2 gave a multitude of products such that an adequate separation of the components of the reaction mixture would be nearly impossible.

Miscellaneous

Alkyl Exchange by Grignard Reagents



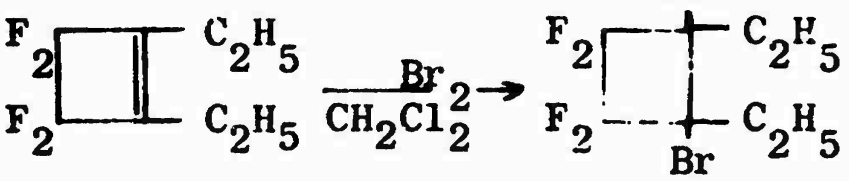
IVa V VI

1-Methyl-2,3,3,4,4-pentafluorocyclobutene (IVa) was prepared by the reaction of methyl lithium with perfluorocyclobutene. After at least two fractionations the enriched fractions were purified on the Autoprep G.L.C. apparatus. Absolutely pure material was needed because impure material gave a small amount of 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (VI) along with 1-methyl-2-ethyl-3,3,4,4-tetrafluorocyclobutene (V), and this result needed to be checked starting with pure material.

The reaction with pure (IVa) was carried out exactly the same as the previous reaction with the impure (IVa). The extract of the reaction mixture was shown to contain only one product, which was shown not to be VI by comparing the retention time of this product with a known sample of VI. Rough fractionation gave a fairly pure sample of the product, which gave an infrared spectrum identical with that of an authentic sample of V.

On the basis of this experiment the idea of alkyl exchange by Grignard reagents is discounted.

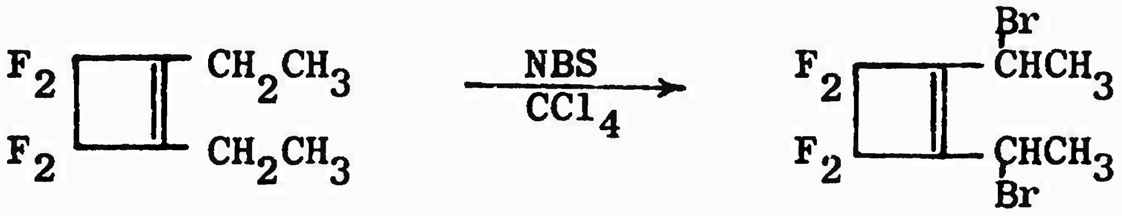
Synthesis of Conjugated Olefins



VI VII

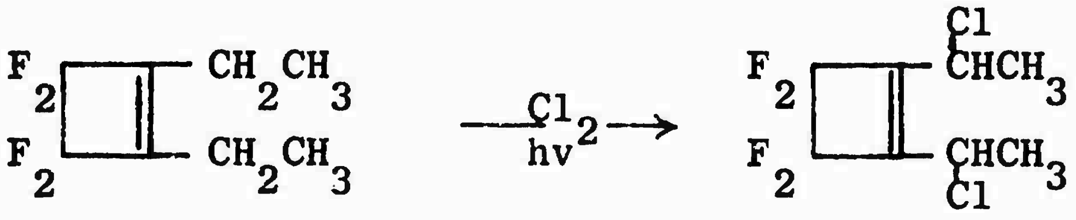
VI was placed in a flask with a 25% excess of Br_2 and stirred slowly in the presence of slight warming by an incandescent lamp. After 50 hrs. an aliquot was taken. $NaHSO_3$ solution was added to the aliquot to destroy the Br_2, and the mixture was extracted with CH_2Cl_2. After drying the extract it was analyzed by G.L.C. and found to contain a new material in a proportion to starting material which indicated the reaction had gone 20% to completion. After 5-1/2 days a similar procedure was followed, and 50% completion was indicated.

A more detailed write up will be made when the reaction is completed, the product is analyzed, and the properties are determined.



VI VIIIa

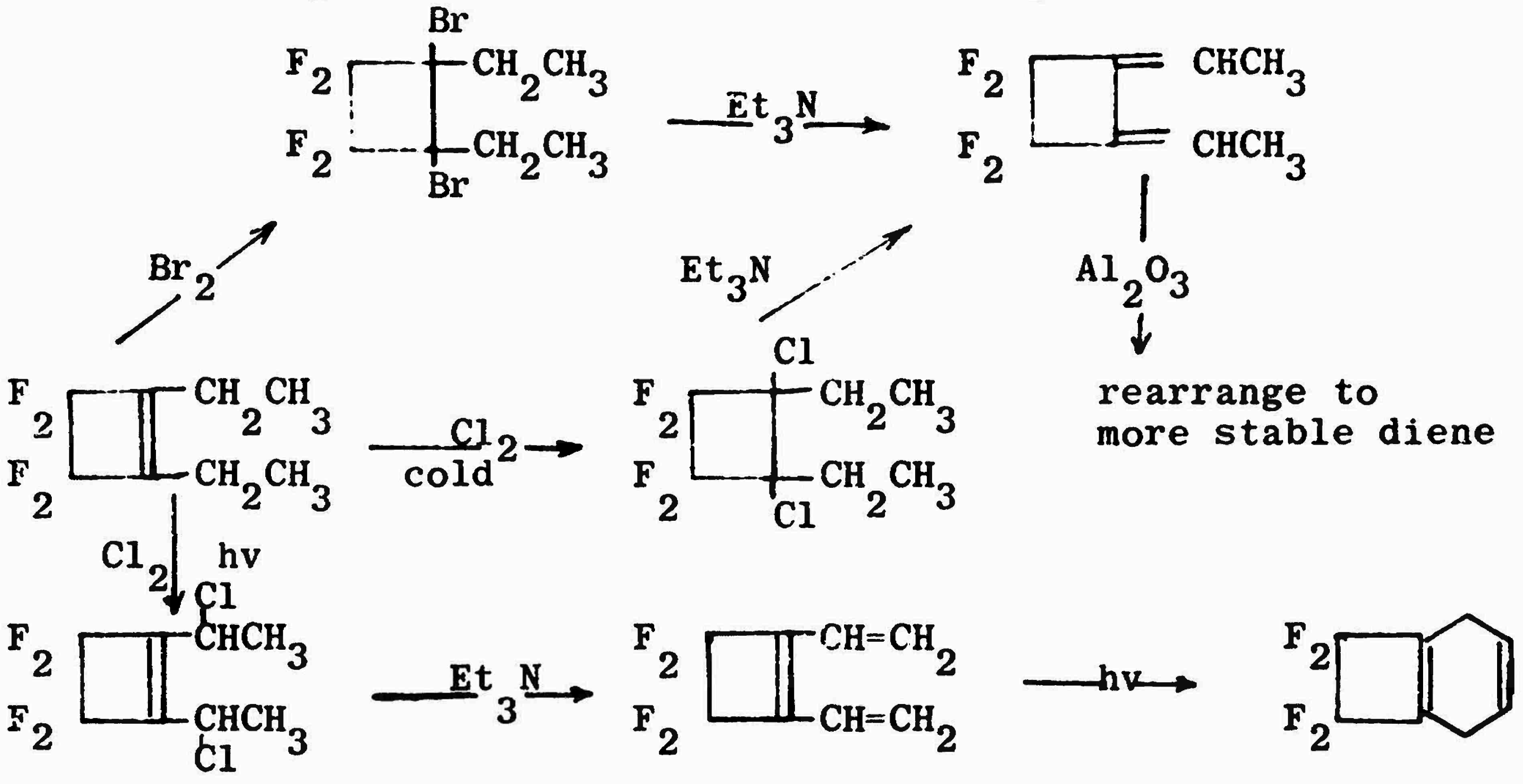
The N-bromosuccinimid was slurried with CCl_4, and VI was added. After stirring at the reflux temperature of CCl_4 for 24 hrs. no succinimid was evident at the top of the liquid layer, and G.L.C. analysis did not indicate any other material beside CCl_4 and VI. As a result, the NBS was filtered off, and the resulting solution was used in the following reaction.



VI IX

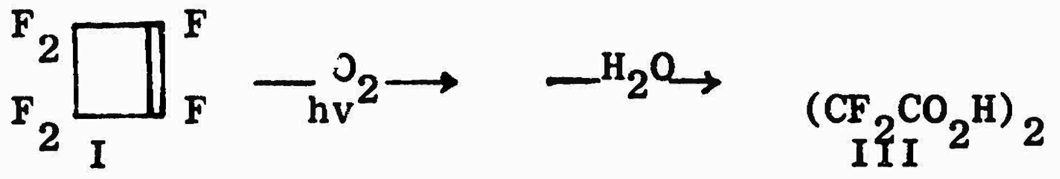
VI was placed in a vessel equipped with a gas bubbler and irradiated with an Hanovia ultraviolet lamp while Cl_2 was bubbled in slowly. After one day there appeared to be a reaction. A more complete discussion of the reaction will be written after the product has been isolated and characterized.

The following reaction scheme will be attempted:



<u>Epoxidation Studies</u>. - The object of this investigation is to prepare <u>fluorinated epoxides</u>, to determine the nature of halocyclobutene pyrolyses, and to explore the basic chemistry of fluorinated thiolene derivatives.

<u>Attempted Epoxidation of Haloolefins</u>



9.0 g. (0.05 mole) of perfluorocyclobutene (I) was placed in the reaction vessel along with 150 ml. methylene chloride and allowed to react for 8-1/2 hrs. with oxygen that was slowly bubbled into the solution in the presence of ultraviolet light. Ca. 3 g. of a white solid was recovered from the sides of the vessel and from the solution. This amounted to a 30% conversion. Analysis on the G.L.C. apparatus indicated that only 25% of the starting material was present in the final solution. A 55% yield was then calculated. The remaining 45% was probably lost through evaporation since the boiling point of I is 5° and since the solution was only slightly discolored.

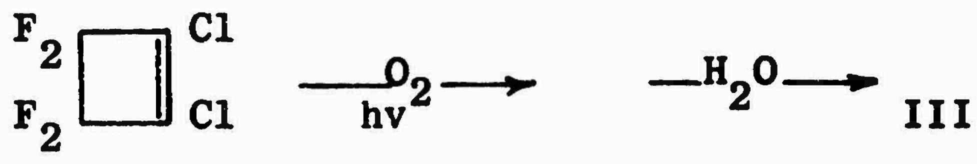
The product was very soluble in ether and in water but only slightly soluble in carbon tetrachloride or benzene. It could be recrystallized from benzene. The pure crystals lost solvent of crystallization at ca. 80° and melted at $116-118^\circ$. They could also be obtained by subliming at ca. 80° and 0.5 mm. pressure.

Identical material was obtained from the reaction vessel and from a water solution which had been evaporated to dryness. This indicated that the crude product did not react with water. However, a water solution was quite acidic. The compound gave a positive Beilstein test, but sodium fusion and subsequent analysis for chlorine indicated that there was no chlorine present, which may have been picked up from the reaction solvent.

Elemental analysis from Galbraith gave C, 23.72%; H, 1.92%;

F, 36.30%; O, 38.06%. The empirical formula calculated to $C_4H_4F_4O_5$, which is impossible. However, 3-M analyzed the compound to be C, 24.7%; H, 2.00%; F, 39.3%; O, 34.0%. The empirical formula calculated to be $C_4H_4F_4O_4$. This was consistent with 1,1,2,2-tetrahydroxy-3,3,4,4-tetrafluorocyclobutane (II). However, reaction of a small amount of material with P_2O_5 failed to give the blue diketone (B.P. 873, 222; C.A., 56, 1363 (1962).); and the infrared spectrum corresponded exactly to a spectrum of perfluorosuccinic acid (III) (Simons, "Fluorine Chemistry", Vol. II, p.488). This differed from the emprical formula by two hydrogen atoms and did not represent a very large error in the value for the hydrogen analysis. A neutralization equivalent of 98.6 was found; theory for III is 95.0. This error could have resulted from incomplete removal of solvent from the crystals.

Obtaining III from the reaction is not altogether unexpected since irradiation of oxygen with ultraviolet light produces ozone. Apparently, either the solvent or the starting material contained a small amount of water which reacted with the ozonide.



IV

10.5 g. (0.054 mole) of 1,2-dichloro-3,3,4,4-tetrafluorocyclcbutene (IV) was allowed to react for 8-1/2 hrs. in a manner similar to the reaction of I. At the end of this time 80% of the starting material was still present according to G.L.C. analysis. Upon evaporation of solvent a small amount of heavy oil was obtained on which an unsuccessful attempt was made to isolate the pure material on an alumina column. A rerun of this indicated that this material could have been a mixture of product and starting material.

A second rerun was made utilizing 17 g. of IV and allowing ca. 36 hrs. reaction time. A yield of ca. 90% and a conversion of ca. 15% was obtained. The solid gave a melting point and infrared spectrum identical to III.

$$\underset{\text{Ia}}{CF_3CCl = CClCF_3} \xrightarrow[h\nu]{O_2} \xrightarrow{H_2O} \underset{\text{II}}{CF_3CO_2H}$$

Oxygen was bubbled into 2,3-dichloroperfluoro-2-butene (Ia) in the presence of ultraviolet light for 16 hrs. at 0°. At the end of this time G.L.C. analysis showed that no starting material was present in the reaction mixture. However, there was one peak which represented a heavy material. Later separation on the Autoprep G.L.C. apparatus and subsequent infrared analysis showed this material to be $CHCl_2CHCl_2$. The origin of this material undoubtedly was reaction of the solvent (CH_2Cl_2).

The reaction mixture was wahed with water, which was then neutralized with bicarbonate. The water extract was then washed with ether to remove any organic materials other than salts. This wash was placed with the original organic material, which had previously been extracted with water. This material was dried and analyzed by G.L.C. Again only the $CHCl_2CHCl_2$ peak existed in addition to those peaks of the solvents.

The water extract of the reaction mixture was evaporated to dryness and then extracted with absolute ethanol. A material giving an infrared spectrum corresponding to a known spectrum of CF_3CO_2Na was isolated in an amount which indicated a 6.5% conversion.

Due to inefficient cooling of the reaction much of the light material was eventually lost, making a meaningful calculation of the yield impossible.

$$CF_3CF = CF_2 \xrightarrow{O_2} \xrightarrow{H_2O} CF_3CO_2H + HCO_2H$$

IIIa II

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13. 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 and pyrolysis materials obtained therefrom (c) unsaturated fluorine-containing halogenated (Br, Cl, I) cyclobutenes and (d) various α,ω-diolefins. Most of the above compounds were new to the arts.

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High-temperature research					8	
Low-temperature research			8			
Synthesis (Chemistry)	8					
Fluorochemicals	1		1		1	
Elastomers	2,4		2,4		2,4	
Flexibility	4		4			
Stability	4				4	

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