Distribution of this
document is unlimited

AD _____

AD 6[illegible]

TECHNICAL REPORT
68-5-CM

THE SYNTHESIS OF SPECIAL FLUORINE-CONTAINING MONOMERS

by

J. D. Park and J. R. Lacher

University of Colorado
Boulder, Colorado

Contract No. DA19-129-AMC-869(N)

Project Reference:
1C024401A329

July 1967

RECEIVED
AUG 7 1967
CFSTI

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

46

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official indorsement or approval of the use of such items.

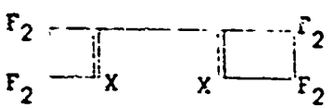
Destroy this report when no longer needed. Do not return it to the originator.

ABSTRACT:

Research on the synthesis of fluorine containing olefins and diolefins is reported. Dimerization reactions aimed at producing "dibox" compounds are of particular interest.

Reactions of note were those between 1,1,2,2-tetrafluorobutadiene 1,3 and difluorodihaloethylene followed by dihydrohalogenation with alkali as follows:

$$CF_2{=}CHCH{=}CF_2 + 2CF_2{=}CX_2 \xrightarrow{-2HX}$$



Methods of dehydrohalogenations applied to these reactions makes available a number of dienes in good yield. Codimerization of these dienes is being continued.

1. INTRODUCTION

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

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

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

This research is authorized under U. S. Army Contract DA-19-129-AMC-869(N) and is the third semi-annual report for the period December 1, 1966 to June 1, 1967 under this project with Dr. Malcolm Henry as project officer. Previously, similar researches authorized under Contract No. DA-129-1926(01 6028-62) under Dr. Malcolm Henry as project officer were summarized in three semi-annual reports and a final report and covered the period October 1, 1963 to October 1, 1965.

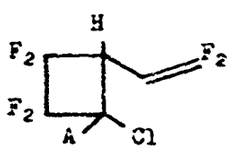
These reports should be used in conjunction with the present series to bring the historical portion up to date.

II Summary of Current Progress

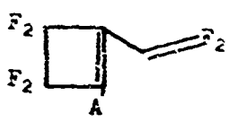
Intermediate for Polymer Studies

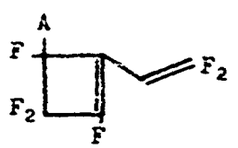
I The synthesis of a series of new olefins and diolefins are still in progress. These are possible candidates for polymer evaluation as well as basic intermediates for the synthesis of other monomers containing a hetero-atom or atoms. Some of the above types of compounds will be used to prepare highly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

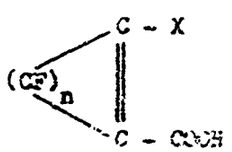
II Among the number of many interesting monomers which were newly synthesized may be mentioned the following:



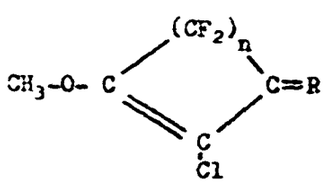
A = F, Cl





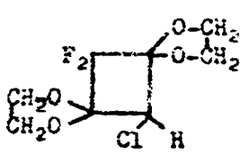


X = I, Br, Cl, F.



n = 2, 3

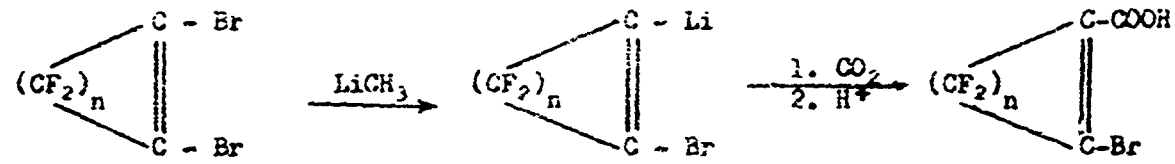
R = CH_2, $CHCH_3$, $C(CH_3)_2$



III In our attempts to synthesize various fluorinated cyclobutenes as starting materials for many of our synthesis, a heretofore boronfluoride catalyzed rearrangement was uncovered.

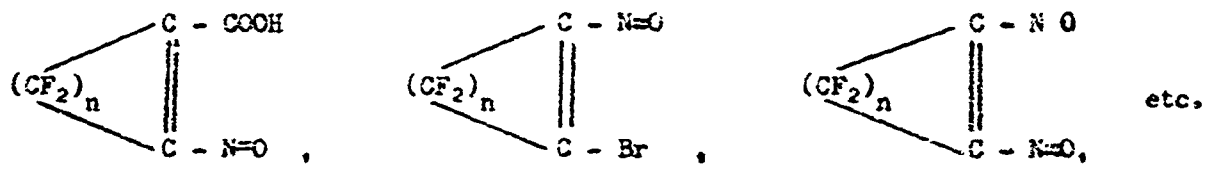
This rearrangement made possible the synthesis of compounds heretofore either unavailable or very difficult to prepare.

IV A new route was discovered for the synthesis of fluorinated cyclic acids through the following sequence of reactions:



n= 2 or 3

V Attempts will also be made to obtain the corresponding dibasic acids. The mono- and dibasic acids will then be subjected to various reactions in order to obtain the corresponding nitroso and dinitroso-compounds, for example:



etc.

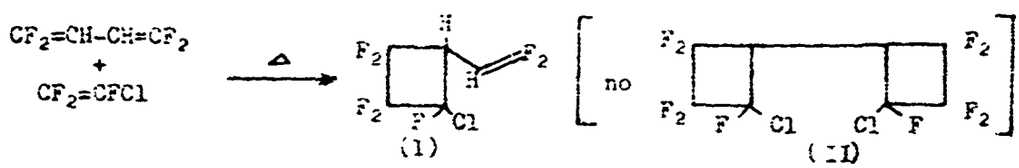
TITLE: Further Studies on the Synthesis and Reactions of Perhalobicyclobuteneyl Compounds.

Part A: Synthetic Pathways

OBJECT: To develop a useful synthetic pathway to perhalobicyclobuteneyl compounds.

HISTORICAL: Historical aspects of this problem were discussed at length in the preceding research report (Semi-Annual Report No. 2) and will not be included here.

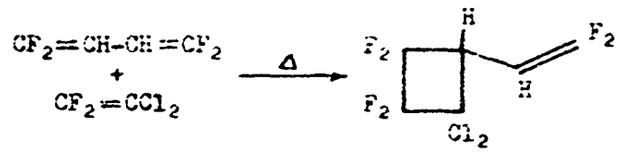
RESULTS AND DISCUSSION: As reported previously, 1-chloro-1,-2,2-trifluoroethylene adds to 1,1,4,4-tetrafluorobutadiene in good yield to form 1-(β,β-difluoro)-vinyl-2,3,3,4,4-Pentafluoro-2-chlorocyclobutane (I). No diadduct (II) was isolated in this thermal dimerization at 160°C.



In the hope that some diadduct could be isolated, the reaction was repeated at 260°C. Again I was found to be the only major product derived from the butadiene. A multi-component high boiling fraction was obtained along with some sludge, but this does not represent a suitable synthesis of II even if it is later found to be present. It is interesting to note the wide temperature range over which this codimerization can be effected with no significant changes in products or yields.

In a parallel experiment 1,1-dichloro-2,2-difluoroethylene was codimerized at 200°C. with 1,1,4,4-tetrafluorobutadiene to afford the new fluorocarbon, 1-(β,β-difluoro)-vinyl-2,2-dichloro-3,3,4,4-difluorocyclobutane (III), in moderate yield.

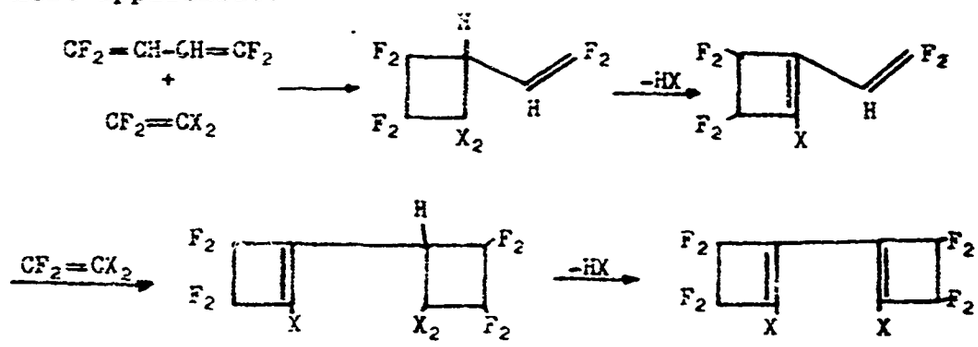
Several high boiling components have been isolated from this reaction in low yield (~ 5%). These are currently being characterized.



+ high boilers

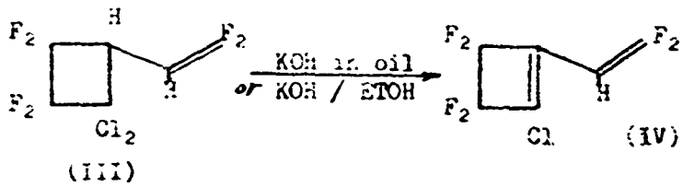
(III)

Since the preceding reactions are not suitable for the preparation of diadducts, alternate routes to dibox compounds had to be sought. The following sequence of reactions seems most applicable.

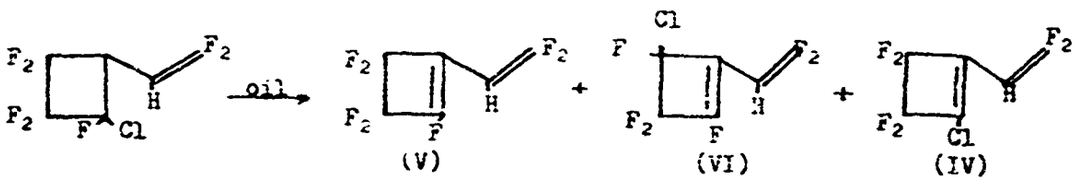


The second step in the above sequence is the dehydrohalogenation of the monoadducts, I and III. The reaction of III with KOH in light mineral oil at 20°C. proceeds slowly but in good yield to 1-(β,β-difluoro)-vinyl-2-chloro-3,3,4,4-tetrafluorocyclobutene (IV). Similarly, III reacts with KOH in 95% ethanol to afford IV in a much faster reaction, but IV further reacts with exce · ethoxide to form a mixture of ethers.

These have not yet been characterized. Polymerization occurred to a minor extent in both reactions (no inhibitor was employed).



The reaction of I with KOH in light mineral oil at room temperature led to an unexpected mixture of products as shown below. Greater than 50 % of the observed products result from loss of HF rather than HCl.



These dehydrohalogenations make available a number of dienes in good yield. Codimerizations of these dienes are now being investigated.

EXPERIMENTAL: Synthesis of 1-(β,β-difluoro-vinyl-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (I).

A 500 ml stainless steel autoclave was charged with 60.1 gm of 1,1,4,4-tetrafluorobutadiene, 225 gm of chlorotrifluoroethylene, and 3 ml of d-limonene. The mixture was heated to 260° in 3 hours and maintained at that temperature for another 18 hours. On cooling the bomb was vented and the light orange

product mixture collected. Fractional distillation gave 67.5 gm of a clear colorless liquid b.p. 75-78° at 650 mm. This liquid is identical to I prepared previously.

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

A 500 ml stainless steel autoclave was charged with 41.9 gm of 1,1,4,4-tetrafluorobutadiene, 205 gm of 1,1-dichloro-2,2-difluoroethylene, and 4 ml of d-limonene. The mixture was heated at 205° for 24 hours before cooling in ice. The crude product was a black liquid. Fractional distillation gave 38.2 gm of III, a clear colorless liquid b.p. 105°-107° at 630 mm, $n_D^{27} = 1.3754$, d at 27° = 1.59. IR: peaks at 3100, 2990 and 1750 cm^{-1}.

Molar refraction: calcd., 36.87; obsd., 37.5.

Anal. calcd. for $C_6H_2Cl_2F_6$: C, 27.8; H, 0.8; Cl, 27.4; F, 44.0. Found: C, 27.71; H, 0.76; Cl, 27.47; F, 44.02.

Dehydrohalogenation of III.

A. Reaction with KOH in mineral oil.

A three-necked 50 ml round bottom flask was fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. Light mineral oil (10 ml) and 2.8 gm KOH (0.05 moles) were mixed in the flask. To this mixture 8.15 gm of III (0.031 moles) was added without cooling during one hour. The reaction was very exothermic and occurred with refluxing and discoloration. Stirring without heat was continued for sixteen hours at which time the product was removed from the oil by vacuum distillation.

Chromatographic analysis of the product revealed 60% conversion to the new compound, IV with n_D^{27} = 1.5897, d at 27° 1.64, and characteristic infrared absorptions at 3100, 2990, 1655, 935, 855, 820 and 775 cm^{-1}.

Molar refraction: calcd., 3152; obsd., 32.0.

Anal. calcd. for $C_6H_1Cl_1F_6$: C, 32.4; H, 0.5; Cl, 15.9; F, 51.2. Found: C, 30.16. H, 0.51; Cl, 16.39; F, 52.66.

B. Reaction with KOH in 95% ethanol.

A three-necked 50 ml round bottom flask was fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. A mixture of 2.8 gm of KOH (0.05 moles) in 10 ml of 95% ethanol was added to the flask and cooled to 5°. Addition of 5.15 gm of III (0.031 moles) was carried out in an hour with stirring in an ice bath. Stirring was continued for an additional six hours during which the ice bath was removed after one and a half hours. After quenching with water the crude organic layer was subjected to chromatographis analysis which revealed a 45% conversion to IV and a 35% conversion to a mixture of ethers. Characterization of these ethers is now in progress.

Dehydrohalogenation of I.

A three-necked 50 ml round bottom flask was fitted with a mechanical stirrer, a reflux condenser, and an additional funnel. A mixture of 10 ml light mineral oil and 2.8 gm of KOH (0.05 moles) was prepared in the flask. To this was added

8.10 gm (0.033 moles) of I over a period of one and a half hours, the reaction mixture being kept below 120°. Some difficulty in controlling exothermicity was experienced. Stirring and heating (~ 75°) was continued for eight hours after which the product mixture was vacuum distilled. Chromatographic analysis and separation revealed the presence of reactant, I, and three diene products, V, VI, and IV in the ratio of 5:2:3 respectively.

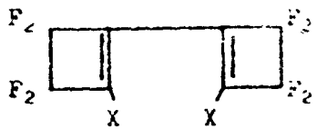
V has been shown to be the expected product formed by loss of HCl. It is a clear colorless liquid which discolors and polymerizes readily. $n_D^{27} = 1.3453$, d at 27° = 1.62. IR: characteristic absorptions at 3150, 1750 and 1700 cm^{-1}.

Molar refraction: calcd., 26.56; obsd., 27.0. Analysis is pending.

VI has been shown to result from the loss of HF from I. It is a relatively unstable clear colorless liquid. Identity is at this time based on the infrared spectrum showing a strong conjugated diene absorption at 1700 and 1750 cm^{-1} indicative of $-CF = C-CH = CF_2$ and by its retention time on an SE-30 column suggesting it to be an isomer of compound IV. Analysis and physical data are pending.

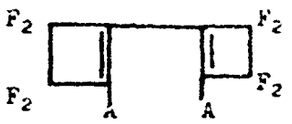
The third diene isolated from the reaction also results from HF elimination and is identical to IV as characterized previously.

Efforts are now being directed towards the preparation of larger quantities of 2,2'-dihalo-3,3,3',3',4,4,4',4'-octafluorobicyclobutene



X = I, Br, Cl or F

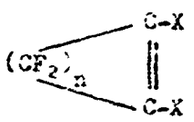
as possible intermediates for the preparation of difunctional intermediates of the following type.



A = -COOH, -CN, -OR, -MO, $-NO_2$, -COONO

<u>Preparation of 1,2-Dihaloperfluorocycloalkenes.</u>

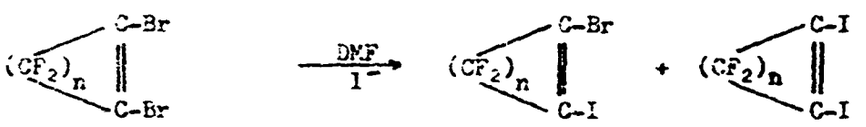
In the previous report (Semi-annual Report No. 2) the preparation of 1,2-dihaloperfluorocycloalkenes of the general type was reported.



n = 2 or 3

X = I, Br, Cl, F.

This paper reports an improvement in the procedure for bringing about the halide ion attack for the replacement of the lower molecular weight halogens by the higher molecular weight halogens in the vinylic position



through the use of dimethylformamide as a solvent in the place of acetone or diglyme as previously used.

1-Carboxy-2-Haloperfluorocycloalkenes

Introduction:

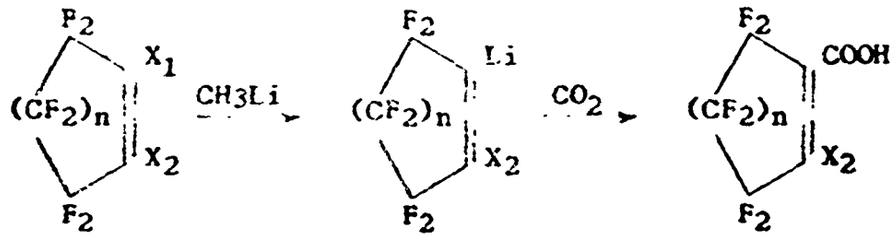
Although nucleophilic attack on perhalocycloalkenes has been actively investigated in detail in this laboratory and others, specific studies aimed at the introduction of functionalities other than halogen at the vinylic position in these haloölefins have received but meager attention. As a consequence, many salient areas remain relatively unexplored.

The present undertaking was initiated in light of these considerations.

Discussion and Results:

Metal-halogen interchange, a reaction known since 1938[1] and well documented, provided entry into the desired carboxy-polyhalocycloalkenes. Thus, when 1-iodo-2-chlorohexafluorocyclopentene-1 (Ia), 1-iodoheptafluorocyclopentene-1 (IIa), 1,2-dibromohexafluorocyclopentene-1 (IIIa), and 1-iodo-2-chlorotetrafluorocyclobutene-1 (IVa) were treated with methyl-

lithium and followed by carbonation with excess Dry Ice, varying yields of the corresponding acids were obtained.



Comp'd	n	X_1	X_2
Ia	1	I	Cl
IIa	1	I	F
IIIa	1	Br	Br
IVa	0	I	Cl

Not surprisingly, the lithium halogen interchanges were confined exclusively to the vinylic iodo- and bromo- substituents. Indeed, the literature is bereft of any references to fluoro- or chloro- substituents entering into halogen metal interchange reactions.

The requisite polyhalocycloalkenes were prepared via a modification of the methods of McMurtry[2] and Moore[3] involving, in the case of the iodoölefins, the use of dimethylformamide (DMF) as a reaction medium in place of acetone and diglyme. In general, shorter reaction times and greater yields of the desired iodoölefins were realized. It is uncertain, how-

ever, whether the use of DMF served to favorably alter the equilibrium between reactants and products or merely functioned to kinetically accelerate the reaction due to higher attainable reaction temperatures. The results of further studies in this area will be forthcoming shortly. The 1,2-dibromohexafluorocyclopentene-1 was prepared after the manner described by McMurtry[2] - the only difference being a higher reaction temperature.

Experimental:

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

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

1-Iodoheptafluorocyclopentene-1: A mixture of 45.7 gm. (0.20 mole) of 1-chloroheptafluorocyclopentene-1, 66.4 gm.

(0.40 mole) of potassium iodide, and 75 ml. of DMF was refluxed for 3 days. At the end of this time, the reaction mixture was worked up in the manner described above to yield 19.7 gm. of unreacted starting olefin and 12.5 gm. (19.5% of theory) of 1-iodoheptafluorocyclopentene-1, b.p. 114°/623 mm.

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

1-Iodo-2-chlorotetrafluorocyclobutene-1: A mixture of 39.0 gm. (0.20 mole) of 1,2-dichlorotetrafluorocyclobutene-1, 66.4 gm. (0.40 mole) of potassium iodide, and 50 ml. of DMF was refluxed together for 5 hours. At the end of this time, the reaction mixture was worked up in the manner described above to yield 20.3 gm. (35.6% of theory) of 1-iodo-2-chlorotetrafluorocyclobutene-1, b.p. 48°/70 mm. (lit.[4] 48°/70 mm.). and 14.8 gm. (19.6% of theory) of 1,2-diiodotetrafluorocyclobutene, b.p. 148°/623 mm. (lit.[3] 151.5/632 mm.).

The infrared spectrum of 1-iodo-2-chlorotetrafluorocyclobutene-1 contained a sharp absorption at 1580 cm^{-1} corresponding to the (c=c) stretching frequency.

1,2-Dibromohexafluorocyclopentene-1: The reaction was accomplished by passing a mixture of the olefin and hydrogen bromide through a 100 cm. x 2.5 cm. pyrex glass tube packed with a 25/75:$BaSO_4$/activated carbon catalyst heated to ca. 280°. The catalyst was prepared after the manner originally described by Sharrah[5]. In a typical run, 250 gm. (1.02 mole)

of 1,2-dichlorohexafluorocyclopentene-1 was swept through the reaction tube together with roughly a two-fold excess of hydrogen bromide. The resulting products were washed well with water and dried over anhydrous magnesium sulfate. Fractional distillation afforded 136 gm. of unreacted starting olefin, 64 gm. (22% of theory) of 1-bromo-2-chlorohexafluorocyclopentene-1, b.p. 101°/629 mm. (lit.[2] 101°/629 mm.), and 53 gm. (16% of theory) of the desired 1,2-dibromohexafluorocyclopentene-1, b.p. 119°/629 mm. (lit.[2] 119°/629 mm.).

The infrared spectrum of 1,2-dibromohexafluorocyclopentene-1 contained a sharp absorption at 1605 cm^{-1} corresponding to the (c=c) stretching frequency.

1-Carboxy-2-chlorohexafluorocyclopentene-1: In a nitrogen swept, elongated, 3-neck reaction vessel cooled in a Dry Ice acetone bath and containing 39.7 gm. (0.118 mole) of 1-iodo-2-chlorohexafluorocyclopentene-1 in 60 ml. of anhydrous diethyl ether was added 46 ml. of a 2.58 M ethereal solution of methyllithium. The resulting dark blue reaction mixture was stirred for 60 minutes at -78° then carbonated with excess Dry Ice. The carbonation mixture was allowed to attain room temperature whereupon it was hydrolyzed with water and treated with a dilute solution of sodium hydroxide. The basic aqueous phase was drawn off, washed with ether, warmed to expel any dissolved organic solvent, then acidified with 6N hydrochloric acid. The resulting oil was taken up in ether and dried over anhydrous magnesium sulfate. Removal

of the ether at reduced pressure and subsequent vacuum sublimation of the residual solid afforded 18.5 gm. (61.5% of theory) of the pure acid, m.p. 62.5-64.0°.

Anal. Calcd. for $C_6HF_6ClO_2$: C, 28.31; H, 0.39; F, 44.75, Cl, 13.93. Found: C, 28.09; H, 0.18; F, 44.60; Cl, 13.71.

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

1-Carboxy-2-bromohexafluorocyclopentene-1: In a nitrogen swept, elongated, 3-neck reaction vessel cooled in a Dry Ice acetone bath and containing 16.7 gm. (0.050 mole) of 1,2-dibromohexafluorocyclopentene-1 in 60 ml. of anhydrous diethyl ether was added 40.8 ml. of a 2.45 M ethereal solution of methyllithium. The resulting reaction mixture was stirred for 30 minutes at -78° then carbonated with excess Dry Ice. The carbonation mixture was allowed to attain room temperature and worked up in the manner described above - affording 5.20 gm. of the pure acid, m.p. 71-72°.

Anal. Calcd. for $C_6HF_6BrO_2$: C, 24.10; H, 0.34; F, 38.13; Br, 26.73. Found: C, 23.93; H, 0.40; F, 38.16; Br, 26.52.

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

1-Carboxy-2-chlorotetrafluorocyclobutene-1: In the manner described above, 10.0 gm. (0.035 mole) of 1-iodo-2-chlorotetrafluorocyclobutene-1 was treated with 20 ml. (0.035 mole) of a 2.45 M ethereal solution of methyllithium. Work up in the usual fashion afforded 2.89 gm. (40.6% of theory) of the pure acid, m.p. 85.5-88°.

The infrared spectrum contained absorptions at 3000 cm^{-1} (broad), 1735 cm^{-1} (sharp), and 1640 cm^{-1} (sharp) corresponding to (-OH), (C=O), and (C=C) stretching frequencies respectively.

1-Carboxyheptafluorocyclopentene-1: In the manner described above, 12.5 gm. (0.039 mole) of 1-iodoheptafluorocyclopentene-1 was treated with 16 ml. (0.039 mole) of a 2.45 M ethereal solution of methyllithium. Work up in the customary fashion afforded 2.70 gm. (28.4% of theory) of the pure acid, m.p. 56.5-58°

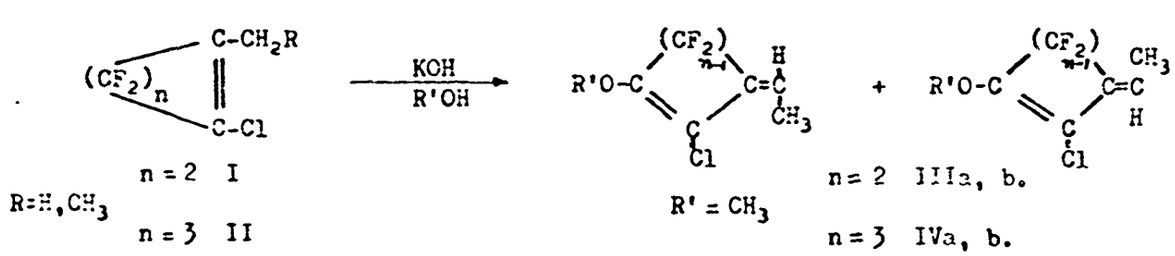
References

1. H. Gilman and R. Jacoby, J. Org. Chem., 3, 108(1938).
2. R. J. McMurtry, Ph.D. Thesis, University of Colorado, 1967.
3. G. G. I. Moore, Ph.D. Thesis, University of Colorado, 1965.
4. R. Sullivan, Ph.D. Thesis, University of Colorado, 1964.
5. J. D. Park, M. L. Sharrah, and J. R. Lacher, J. Am. Chem. Soc., 71, 2337(1949).

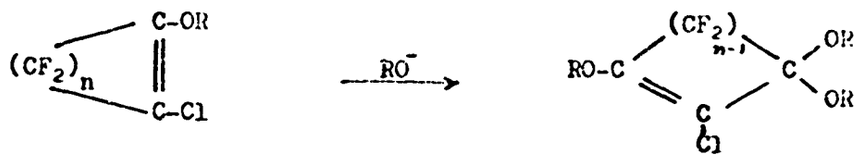
A Novel 1,4-Elimination Reaction of 1-Chloro-2-Alkyl Perfluorocycloalkenes with Alkoxide Ion.

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

In the course of our studies of nucleophilic attack by alkoxide ion on alicyclic polyfluoroolefins, a novel 1,4-elimination reaction was encountered when 1-chloro-2-alkyl-tetrafluorocyclobutene-1 (I) and 1-chloro-2-alkylhexafluoro-cyclopentene-1 (II) respectively, were treated with alcoholic potassium hydroxide. A mixture of geometrical isomers of the corresponding 1-alkoxy-2-chloro-3-alkylideneperfluorocyclo-alkene-1 and 1-alkoxy-2-chloro-3-methyleneperfluorocycloalkene-1 was obtained in high yield. Thus, abstraction of an α-hydrogen from the alkyl group by alkoxide ion is apparently preferred

A. 

to the "normal" nucleophilic displacement of vinylic or allylic halogen.

B. 

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

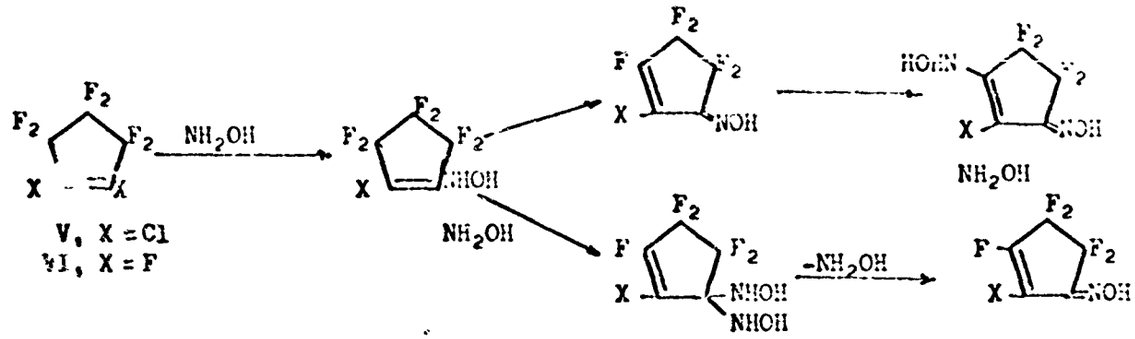
Although no other example of an analogous 1,4-elimination of hydrogen fluoride involving proton abstraction from a carbon atom has been reported to the best of our knowledge, a similar mechanism may be involved in the reaction of alicyclic polyfluoroolefins with an excess of amines[3], hydroxylamine[4],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

McBee[4] reported that both 1,2-dichlorohexafluorocyclopentene-1 (V) and octafluorocyclopentene-1 (VI) gave 1,3-iminoamines upon treatment with hydroxylamine. Two competitive reaction paths are available to initially formed 1-halo-2-hydroxylaminohexafluorocyclopentene-1 in this reaction: elimination of hydrogen fluoride or additional attack by hydroxylamine.

---

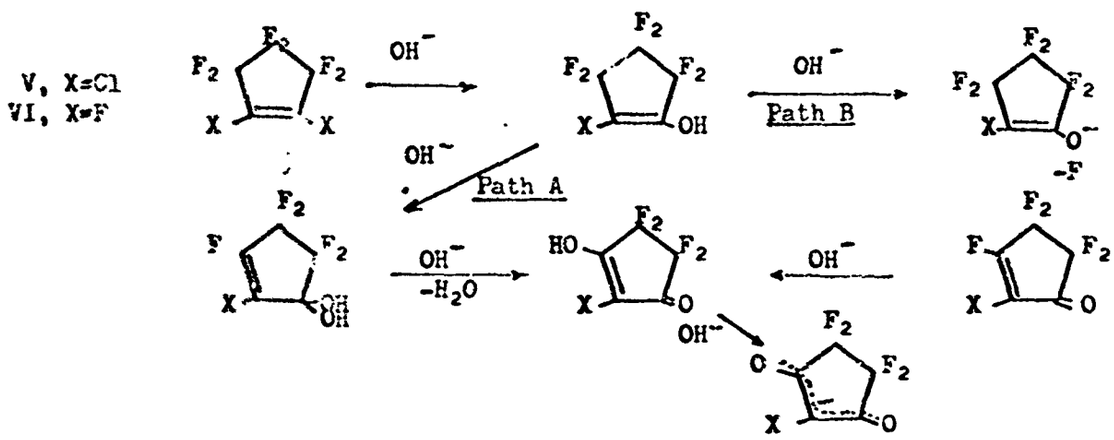
*The inductive effect of the γ-carbon fluorines in this example may be relatively unimportant. However, the acidity of a proton with adjacent β-difluorogroups is well documented.[13]

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



evidence against the latter possibility since all previous studies in these systems indicated that the remaining vinylic fluorine would be displaced preferentially[2].

A similar conclusion has recently been suggested by Stockel and coworkers[5] concerning the hydrolysis of polyhaloolefins with potassium hydroxide in polar aprotic solvents. Two plausible reaction paths were advanced and are illustrated below:

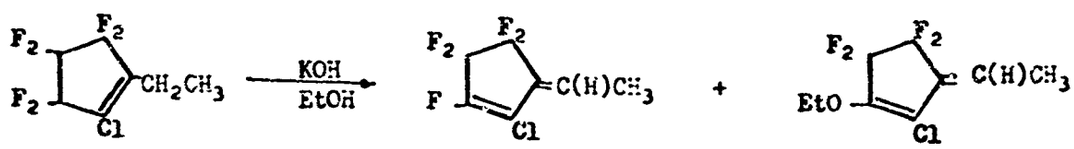


Path B is capable of explaining why the reaction of VI with hydroxide ion differs from that with alkoxide ion[2] since the formation of enolate ion is not possible in the latter case.

The overall similarity of these reactions is apparent, if the hetero-atom in the previously mentioned examples is equated with the α-carbon of the ethyl group in I and II.

Failure of recovered I to exhibit deuterium incorporation in the allylic position when D-O-methanol was employed, suggests that either the loss of hydrogen fluoride occurs in a concerted manner or that proton abstraction is the rate determining step if a discrete allylic carbanion is involved in this reaction.

The isolation of trace amounts of 2-chloro-3-ethylidenepentafluorocyclopentene-1 (VIIa,b)[6] in the reaction of II with a deficiency of potassium hydroxide indicates that these re-



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

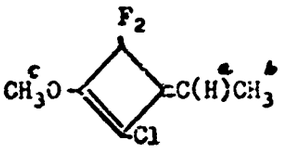
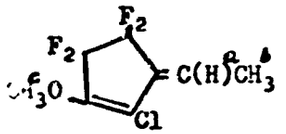
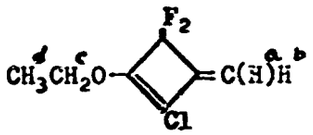
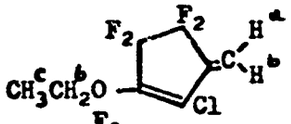
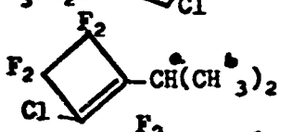
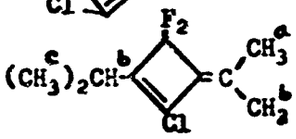
Treatment of the corresponding methyl compounds, 1-chloro-2-methyltetrafluorocyclobutene-1 (VIII) and 1-chloro-2-methylhexafluorocyclopentene-1 (IX) with ethanolic potassium hydroxide yielded 1-ethoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X) and 1-ethoxy-2-chloro-3-methylenetetrafluorocyclopentene-1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

These compounds, particularly X, were found to polymerize far more readily than the analogous ethylidenecyclo-olefins, presumably because of the removal of the bulky methyl group from the α-carbon of the side chain.

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

TABLE I

Spectral data of New Compounds

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

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

Although potassium fluoride has been demonstrated to effect isomerization in similar systems[7], the origin of the isomer ratio a/b is believed to reflect kinetic control rather than an equilibration of initially formed products since IIIa was found to undergo no detectable isomerization when refluxed in methanol containing the inorganic salts present in the reaction mixture.

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

The data seems to be most consistent with a relatively free rotation of the ethyl side chain with minor differences in

ground state energy between the possible rotamers. Assuming that an allylic carbanionic intermediate formed in a non-concerted elimination would be geometrically stable[8], incorporation of geometrical identity would occur with proton abstraction by the attacking base irregardless of whether the reaction proceeded via a concerted or stepwise loss of hydrogen fluoride.

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

That a delicate balance exists between this course of reaction and nucleophilic displacement of halide ion is evidenced by the observation that only products resulting from the latter pathways were detected in the reaction of 1-chloro-2-ethyltetrafluorocyclobutene-1 with excess ethylmagnesium bromide[9]. Preference for one route over the other is probably dependent on both the acidity of the hydrogen in question and the bulk of the attacking Grignard species.

Experimental

Preparation of the Cyclopentenes

Two general synthetic methods were employed in the preparation of the new halogenated alicyclic olefins.

The first involved a catalytic replacement of vinylic halogen by bromine in the preparation of 1-bromo-2-chlorohexafluorocyclopentene and 1,2-dibromohexafluorocyclopentene from the commercially available 1,2-dichlorohexafluorocyclopentene and anhydrous hydrogen bromide.

Displacement of vinylic halide by lithium halide in polar aprotic solvents was utilized to obtain the other desired olefins.

All boiling points were taken by the Siwoloboff method[10]. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were taken on a Perkin-Elmer Infracord while nmr spectra were obtained using a Varian A-60 analytical spectrometer.

1-Bromo-2-chlorohexafluorocyclopentene-1 and 1,2-dibromohexafluorocyclopentene-1. - A mixture of 1,2-dichlorohexafluorocyclopentene and hydrogen bromide was passed through a 100 cm 2.5 cm pyrex glass tube packed with a 25/75 $BaSO_4$/carbon catalyst heated to ca. 225°. The catalyst was prepared in the manner of Sharrah.[11] In a typical run, 500 g (2.04 mole) 1,2-dichlorohexafluorocyclopentene was swept through the tube with ca. 3.7 molar excess of anhydrous hydrogen bromide. The crude

reaction products were washed with aqueous sodium bicarbonate and ice water. The aqueous extracts were extracted with ether and the combined organic layers dried over anhydrous magnesium sulfate. Fractional distillation yielded 275 g of unreacted olefin, 128 g (22% of theory) of 1-bromo-2-chlorohexafluorocyclopentene, bp 101°(629 mm), and 106g (16% of theory) of 1.2-dibromohexafluorocyclopentene, bp 119°(629 mm).

Anal. Calcd. for C_5BrClF_6: C, 20.82; Cl, 12.30; Br, 27.71; F, 39.52. Found: C, 20.60; Br, 27.44; Cl, 12.36; F, 39.21.

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

1-Chloro-2-alkyltetrafluorofluorocyclobutene-1 (where alkyl is CH_3 or C_2H_5) were prepared according to the method of Park and Fontanelli[12] from the reaction of 1,2-dichlorotetrafluorocyclobutene and the Grignard reagent.

1-Chloro-2-ethylhexafluorocyclopentene-1 (II). - In a 500 ml three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, 50g (0.204 mole) of 1,2-dichlorohexafluorocyclopentene in 250 ml of tetrahydrofuran was introduced and cooled to 0°. With rapid stirring, 80 ml of a 3M solution of ethylmagnesium bromide in tetrahydrofuran was added dropwise over a 1.0 hr period. The contents of the flask were allowed to reach room temperature and then gently heated to ca. 50° for an additional 2.0 hr. After cooling, unreacted Grignard reagent was destroyed by the cautious addition of 25 ml of dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with ether. The extracts and

product layer were dried over anhydrous magnesium sulfate. Distillation yielded 40.6 g (83% of theory) of II, bp 112.5°/ 629 mm., n_D^{28} 1.3644.

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

The n.m.r. spectrum contained a quartet centered at τ 7.52 and a triplet at τ 8.80 with $J_{H_1H_2}$ = 7.5 c.p.s.[9]

1-Methoxy-2-chloro-3-ethylidene difluorocyclobutene-1 (IIIa,b). - In a 250 ml., three-neck flask, equipped with stirrer, condenser, and addition funnel was placed 10.0 g (0.053 mole) of 1-chloro-2-ethyltetrafluorocyclobutene-1 (I) in 15 ml of absolute methanol. The flask was cooled in an ice-water bath, and 6.2 g (0.11 mole) of potassium hydroxide dissolved in 15 ml. of absolute methanol was added dropwise with rapid stirring for 1 hr.

The reaction mixture was then stirred for an additional 2 hr. then poured through a filter into a separating funnel half filled with ice water. The flask and filter were washed with methylene chloride which was added to the funnel. The organic layer was drawn off and the aqueous layer extracted twice with methylene chloride. The methylene chloride and product mixture was dried over anhydrous magnesium sulfate and fractionally distilled under vacuum to yield 7.4 g (78 % of theory) of crude IIIa,b. Analysis by g.l.c. showed this material to consist of two components in a 40:60 ratio. Preparative scale g.l.c. yielded pure IIIa and IIIb.

IIIa: Anal. Calcd. for $C_7H_7ClF_2O$ = C, 46.55; H, 3.91; Cl, 19.64; F, 21.04. Found: C, 46.53; H, 4.01; Cl, 15.94; F, 16.87.

Spectral data in Table I

IIIb: Anal. Calcd. for $C_7H_7ClF_2O$: C, 46.55; H, 3.91; Cl, 19.64; F, 21.04. Found: C, 44.24; H, 3.79; Cl, 16.75; F, 21.90.

Spectral data in Table I

1-Methoxy-2-chloro-3-ethylidenetetrafluorocyclopentene-1 (IVa,b). -The reaction of 1-chloro-2-ethylhexafluorocyclopentene-1 (10 g, 0.042 mole) with methanolic potassium hydroxide (4.8 g, 0.086 mole in 10 ml methanol) was carried out according to the previously described procedure for alkoxide attack of alkyhaloolefins to yield 8.0 g (83% of theory) of a 74:26 mixture of IVa and IVb.

Separation of the geometrical isomers IVa and IVb was effected by preparative scale g.l.c. on a 18' x 1/4" Carbowax 20 M column at 140°.

IVa: Anal. Calcd. for $C_8H_7ClF_4O$: C, 41.66; H, 3.06; Cl, 15.38; F, 32.95. Found: C, 41.60; H, 3.07; Cl, 15.52; F, 33.13.

Spectral data in Table I

IVb: Anal. Calcd. for $C_8H_7ClF_4O$ = C, 41.66; H, 3.06; Cl, 15.38; F, 32.95. Found: C, 41.70; H, 3.01; Cl, 15.50; F, 32.98.

Spectral data in Table I

1-Chloro-2-methylhexafluorocyclopentene-1 (II). -In a 500 ml three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, 50g (0.261 mole) of 1,2-dichlorohexafluorocyclopentene in 250 ml of tetrahydrofuran was introduced and cooled to 0°. With rapid stirring, 53 ml of a 3M solution of ethylmagnesium bromide in tetrahydrofuran was added dropwise over a 1.0 hr period. The contents of the flask were allowed to reach room temperature and then gently heated to ca. 50° for an additional 2.0 hr. After cooling, unreacted Grignard reagent was destroyed by the cautious addition of 25 ml of dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with ether. The extracts and product layer were dried over anhydrous magnesium sulfate. Distillation yielded 40.6 g (83% of theory) of II, bp 112.5°/ 629 mm., n_D^{28} 1.3644.

Anal. Calcd. for $C_7H_5ClF_6$: C, 35.23; H, 2.12; Cl, 14.87; F, 47.78. Found: C, C, 35.50; H, 2.15; Cl, 15.02; F, 47.73.

The n.m.r. spectrum contained a quartet centered at τ 7.52 and a triplet at τ 5.50 with $J_{H^1H^2}$ = 7.5 c.p.s.

1-Ethoxy-2-chloro-3-methylenedifluorocyclobutene-1 (X). - 1-chloro-2-methyltetrafluorocyclobutene-1 (VIII) (10.0 g, 0.057 mole) was treated according to the previously described procedure for an alkoxide reaction with 6.0 g (0.107 mole) of potassium hydroxide in 15 ml absolute ethanol to effect an ca. 40% conversion to 1-ethoxy-2-chloro-3-methylenedifluorocyclo-

butene-1 (X), which was shown by g.l.c. to consist of 98% or better of the reaction products. The minor component, of longer g.l.c. retention time, was tentatively identified as 1-methyl-2-chloro-3,3-diethoxydifluorocyclobutene-1 (XIIa).

X. Anal. Calcd. for $C_7H_7ClF_2O$: C, 46.55; H, 3.91; Cl, 19.64; F, 21.04. Found: (polymeric material) C, 42.76; H, 3.88; Cl, 21.08; F, 19.67.

Spectral data in Table I

XIIa. Anal. Calcd. for $C_9H_{13}ClF_2O_2$: C, 47.68; H, 5.77 Cl, 15.65. Found: C, 47.69; H, 5.86; Cl, 15.92.

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

1-Ethoxy-2-chloro-3-methylenetetrafluorocyclopentene-1 (XI). - 1-Chloro-2-methylhexafluorocyclopentene-1 (5.0 g, 0.022 mole) was treated according to the previously described procedure for an alkoxide reaction with 3.0 g (0.054 mole) of potassium hydroxide in 10 ml of absolute ethanol. Workup yielded 3.4 g (64% of theory) of crude XI. Preparative scale g.l.c. on a 10' x 1/4" Ucon LB 550X column yielded pure XI, n_D^{28} 1.4391; d_4^{28} 1.39; bp. 163°/621 mm (decompn).

Anal. Calcd. for $C_8H_7ClF_4O$: C, 41.66; H, 3.06; Cl, 15.38; F, 32.95. Found: C, 41.50; H, 3.05; Cl, 15.18; F, 32.92.

Spectral data in Table I

1-Chloro-2-isopropyltetrafluorocyclobutene-1 (XIII). - 1,2-Dichlorotetrafluorocyclobutene (25 g, 0.126 mole) was treated with an ca. 2M solution of isopropyl magnesium bromide in tetrahydrofuran (70 ml, ca. 0.14 mole) according to the previously described procedure. Workup of the reaction products in the previously described manner yielded 11.7 g (45% of theory) of XII, bp 122°(630 mm), n_D^{28} 1.3746.

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

Reaction of 1-Chloro-2-isopropyltetrafluorocyclobutene-1 (XIII) with isopropylmagnesium bromide. - The reaction of XIII with isopropyl magnesium bromide was carried out according to the previously described procedure utilizing 5.0 g (0.02 mole) of XIII and 60 ml of an ca. 2M solution of isopropylmagnesium bromide in tetrahydrofuran to yield 3.2 g of unreacted XIII and 1.6 g (34% of theory) of 1-isopropyl-2-chloro-3-isopropylidenedifluorocyclobutene-1, (XIV) - bp 180°(629 mm) (decomposition); d_4^{26} 1.90; n_D^{28} 1.4591.

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

Bibliography

1. This paper represents part of a Ph.D. thesis submitted to the Graduate School, University of Colorado, 1967.
2. R. D. Chambers and R. H. Mobbs in Advances in Fluorine Chemistry, IV, Butterworths, 1965, p.50.
3. R. L. Pruett, J. T. Barr, et al., J. Am. Chem. Soc., 72, 3646 (1950).
4. E. T. McBee, J. J. Turner, C. J. Morton and A. P. Stefani, J. Org. Chem., 30, 3698 (1965).
5. R. F. Stockel, M. T. Beachem and F. H. Megson, ibid. 30 1629 (1965).
6. J. D. Park and R. J. McMurtry, Tetra. Letters, in press.
7. D. H. Burton and D. J. Herkes, ibid., 4509 (1965)
8. D. J. Cram and D. H. Hunter, J. Am. Chem. Soc., 86, 5478 (1964).
9. J. D. Park, R. Sullivan and R. J. McMurtry, Tetra. Letters, 173 (1967).
10. A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York City, New York, 1948, p.86.
11. J. D. Park, M. L. Sharrah and J. R. Lacher, J. Am. Chem. Soc., 71
12. J. D. Park and R. Fontanelli, J. Org. Chem., 28, 258 (1963).

The Synthesis of Fluorinated Bicyclic Compounds.

1) The Reaction of CF_2=CFCl with Various Dienes and Olefins. This type of reaction was explored to obtain new bicyclic intermediates as a source for reactive monomers. These reactions yielded several addition products when 1,3-cyclohexadiene and 1,4-cyclohexadiene were separately reacted with CF_2=CFCl. The identification of the products are still in progress and will be reported on after full identification has been made. These products are definitely bicyclic in nature.

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

Object of the Study

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

EXPERIMENTAL

I. Reaction of ethylene glycol with perfluorocyclobutene.

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

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

The reaction product was neutralized with 15% HCl and excess water was added to dissolve the KF and extract unreacted glycol. The dense organic layer was separated. This organic material was kept under refrigeration. (After storage for about 2 weeks under refrigeration evolution of HF can be detected). Fractional distillation of 25 ml. of the liquid was attempted at 10 mm. pressure. Decomposition with evolution of HF took place as expected. Partial separation of components was effected by elution chromatography using alumina and eluting with diethyl ether. The fractions obtained were vacuum distilled to drive off the eluent. A clear liquid was obtained. VPC analysis using a 20 foot carbowax at 165 C showed the presence of at least 5 components. Two components were separated by VPC.

Results to date:

Sample I.

IR (NEAT):	carbonyl absorption at 1760 cm^{-1} no hydroxy absorption methylene absorption at 3000 cm^{-1}
NMR:	sharp singlet at 5.85 τ

Sample II.

IR (NEAT): carbonyl absorption at 1760 cm^{-1}
no hydroxy absorption

NMR: sharp singlet at 5.46 τ

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

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

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

Properties of the solid:

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

2. melting point - 131 degrees C.

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

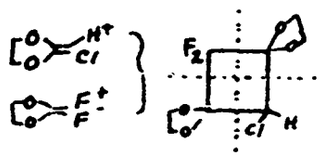
4. Elemental Analysis,%

	Experimental Results	Calculated (based on structure III)
C	39.61	39.60
H	3.73	3.74
Cl	14.40	14.61
F	15.79	15.66
O	26.47	26.38

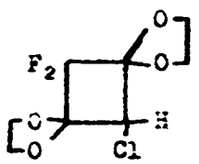
5. Mass Spectra: no molecular ion

m/e
207 -Cl

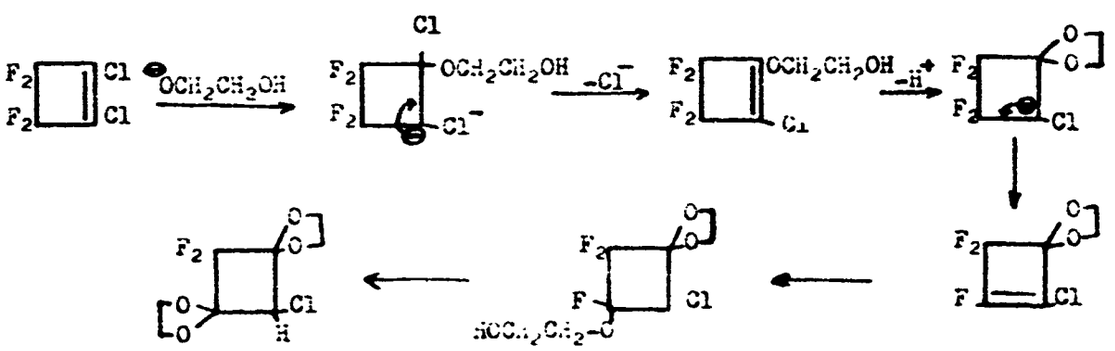
120
122



Structure of Compound:



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

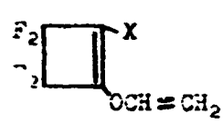


FUTURE EXPERIMENTS

I. Complete separation and identification of products of the perfluorocyclobutene system will be attempted. The thermal instability of the reaction products here make this difficult. Evidence to date indicates that any alcohol product obtained may, by intramolecular nucleophilic attack and halide displacement, yield ketals and/or dioxanes.

II. The fact that no product IV or analogous alcohols has been observed in the above experiments does not mean they cannot be isolated. By variations of the base strengths and dilution of media it should be possible to isolate the alcohols. Also, increase in chain length of the diol used will decrease likelihood of ketal formation.

III. Ethylene chlorohydrin will be treated with I and perfluorocyclobutene in base in an attempt to obtain compounds of structure IV.



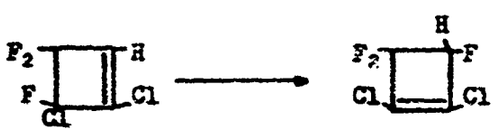
IV

BORON TRIFLUORIDE CATALYZED REARRANGEMENTS OF FLUORINATED HALOCYCLOBUTENES

Joseph D. Park and Edwin A. Kjeldgaard

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

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

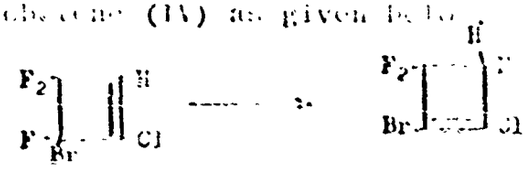


I II

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

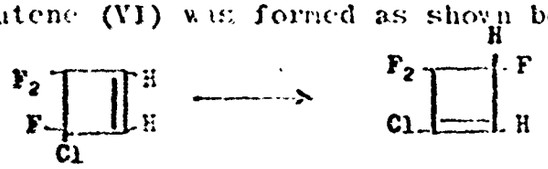
Under similar conditions two other compounds were found to isomerize. Isomerization of 3-bromo-2-chloro-3,4,4-trifluorocyclobutene (III) proceeded

[illegible] under condition [illegible] to get [illegible] trifluorocyclobutene (IV) as given below.



III IV

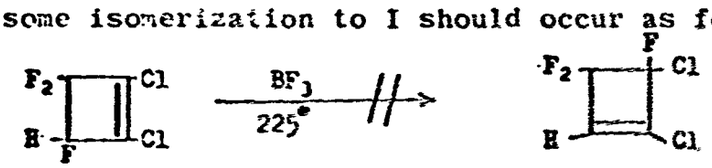
Considerable decomposition occurred in the isomerization of 3-chloro-3,4,4-trifluorocyclobutene (V), but a small amount of 2-chloro-3,3,4-trifluorocyclobutene (VI) was formed as shown below:



V VI

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

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



II I

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

The structures of new compounds described in this communication were determined by elemental analysis and infrared and nuclear magnetic [illegible]

(NMR) spectroscopy. Proton NMR was particularly useful in this study since the coupling constants, J_{HF}, for the gem-hydrofluoro group were in the range of 60-64 Hz. All other coupling constants were under 20 Hz.

Table I

Properties of the Various Compounds

Compounds	B.P. °C/mm.Hg.	n_D^{25}
I[2]	91-92°/763	1.3942
II	84-85°/630	1.4053
III	108° /628	1.4272
IV	103° /629	1.4331
V[3]	76.5°/630	1.3270
VI	77° /628	1.3681

References

1) A. L. Henne and R. C. Arnold, J. Am. Chem. Soc., 70, 758-60 (1948).

2) M. S. Raasch, R. E. Miegel and John E. Castle, ibid., 81, 3678 (1959).

3) G. Groppelli, Unpublished work, University of Colorado (1961).

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

University of Colorado
Boulder, Colorado

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

THE SYNTHESIS OF SPECIAL FLUORINE-CONTAINING MONOMERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Semi-annual Report #3 - 1 December 1966 - 1 June 1967

5. AUTHOR(S) (Last name, first name, initial)

Park, J. D., and Lacher, J. R.

6. REPORT DATE

Sept. 1967

7a. TOTAL NO. OF PAGES

41

7b. NO. OF REFS

3

8a. CONTRACT OR GRANT NO.

DA-19-129-AMC-869(N)

b. PROJECT NO.

1C024401A329

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

68-5-CM

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited.
Release to CFSTI and DDC is authorized.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

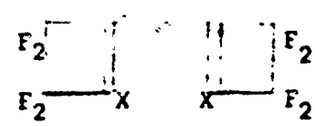
U. S. Army Natick Laboratories
Natick, Massachusetts 01760

13. ABSTRACT

Research on the synthesis of fluorine containing olefins and diolefins is reported. Dimerization reactions aimed at producing "dibox" compounds are of particular interest.

Reactions of note were those between 1,1,2,2-tetrafluorobutadiene 1,3 and difluorodihaloethylene followed by dihydrohalogenation with alkali as follows:

$$CF_2{=}CHCH{=}CF_2 + 2CF_2{=}CX_2 \xrightarrow{-2HX}$$



Methods of dehydrohalogenations applied to these reactions makes available a number of dienes in good yield. Codimerization of these dienes is being continued.

DD FORM 1473

Unclassified
Security Classification

Security Classification

KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Synthesis (Chemistry)	8					
Fluorochemicals	2,4					
Monomers	2					
Fluorine	2					
Polymerization	4					
Elastomers	4					

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (*TS*), (*S*), (*C*), or (*U*).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Security Classification