Rubber Research

The Synthesis of Special Fluorine-Containing Monomers

67-48-CM

Semi-Annual Report No. 2

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For the Period June [illegible] 1966 to December 1, 1966

December 15, 1966

by

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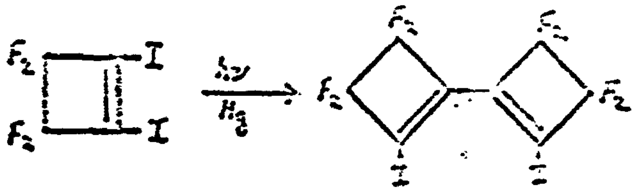
ABSTRACT

Further work on the syntheses of fluorine containing olefins and diolefins is reported. Studies directed toward syntheses of derivatives of perfluorobicyclobutyl and perfluorobicyclobutenyl have been initiated. Of particular interest is the preparation of 2,2'-diiodo-per-fluorobicyclobutenyl by photolysis of 1,2-diiodotetrafluorocyclobutene.



Starting from 1,2-dichlorohexafluorocyclopentene, other dihalo- and mixed dihalohexafluorocyclopentenes have been prepared, and from these have been prepared the monoethoxy derivatives, such as 1-iodo-2-ethoxyhexafluorocyclopentene.

I. 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 second semi-annual report for the period June 1, 1966 to December 1, 1966 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.

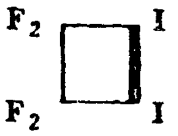
II. SUMMARY OF CURRENT PROGRESS

Intermediate for Polymer Studies

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.

The synthesis of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene has been developed and improved. Along similar lines, 1,2-diiodoperfluorocyclopentene has also been prepared. These two compounds will serve as valuable intermediates in the syntheses of dibasic acids, nitroso acids, dinitroso derivatives and possibly as sources for fluorinated keto-acids.

The following compounds have been synthesized and their properties obtained:



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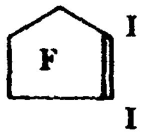

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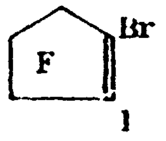

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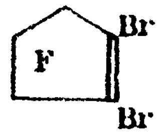
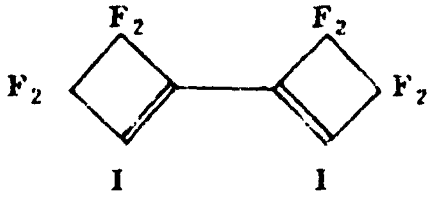
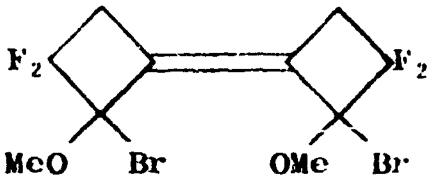


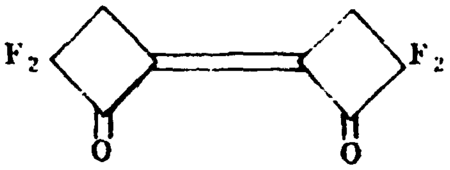


The following samples were prepared and sent to Dr. Douglas Relyea:

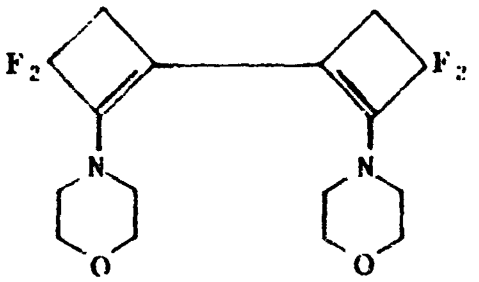
FC-312 18.2 g.



FC-313 2.0 g.

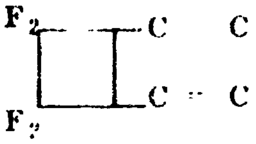


FC-314 22.0 g.



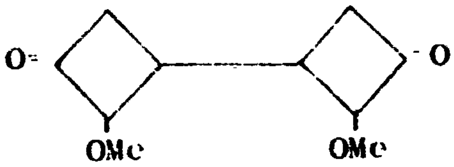
FC-315 2.0 g.

Polymer of



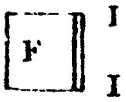
FC-316 5.0 g.

Disodium salt of



FC-317 7.0 g.

FC-318 7.0 g.



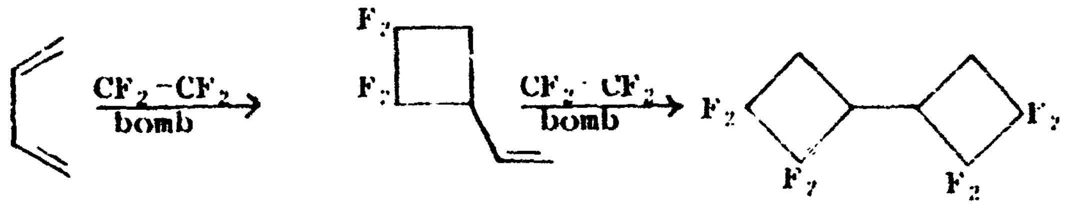
TITLE: Investigations on the Synthesis and Reactions of Perhalobicyclobuteneyl compounds.

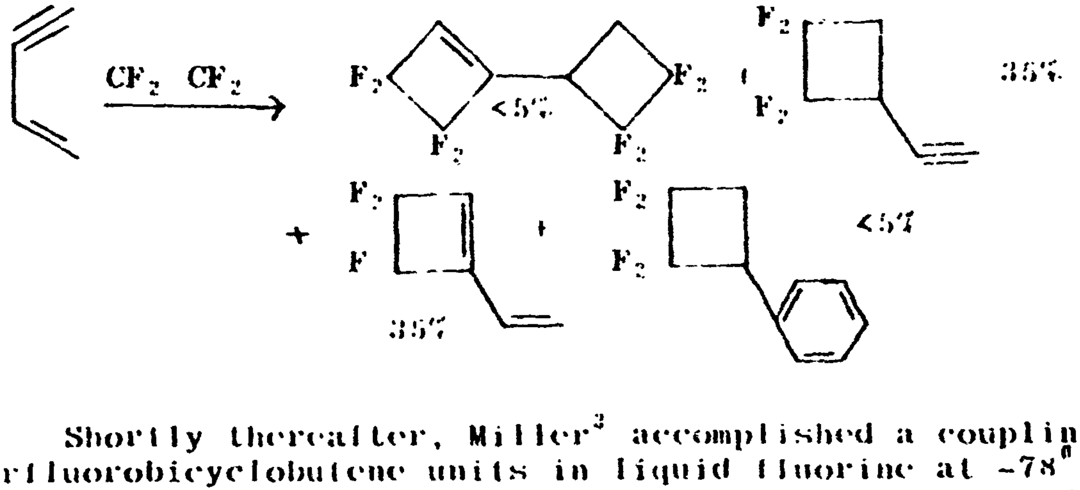
Part A: Synthesis Pathways

OBJECT: To develop a useful synthetic pathway to perhalobicyclobuteneyl compounds which should be important intermediates in the syntheses of diketodicarboxylic acids.

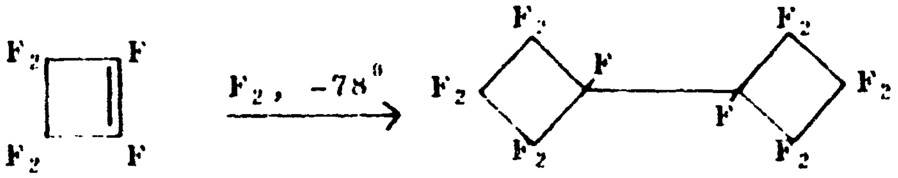
HISTORICAL: There are relatively few syntheses of bicyclobutyl or bicyclobuteneyl compounds (hereinafter referred to as dibox compounds) reported in the literature. An adequate review of earlier work in this area has been compiled by Frank.[1]

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

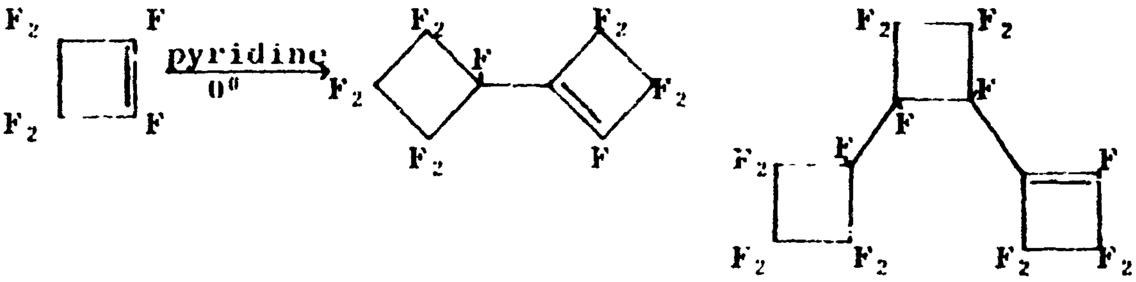




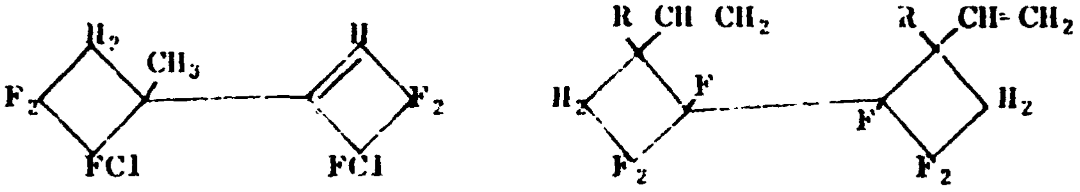
Shortly thereafter, Miller[3] accomplished a coupling of two perfluorobicyclobutene units in liquid fluorine at -78° to yield perfluorobicyclobutyl. The product was an inert liquid at 86-87°.



Pruett et al.[4] prepared a mixture of the dimer and trimer of perfluorocyclobutene by the treatment of the monomer with pyridine at 0°.

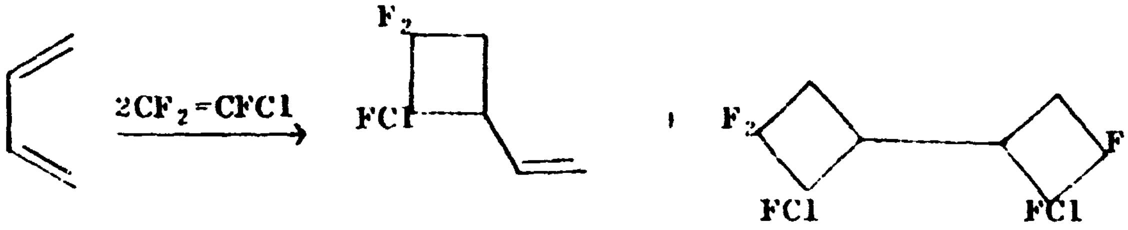


Sharts and Roberts[5] again applied thermal alkylation reactions in treating isopropenyl acetylene with chlorotrifluoroethylene to give the two expected 1:1 adducts and less than 5% of a dibox derivative. Similarly, Ryananova[6] et al. reported 10-15% yields of 2:1 adducts from the thermal addition of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

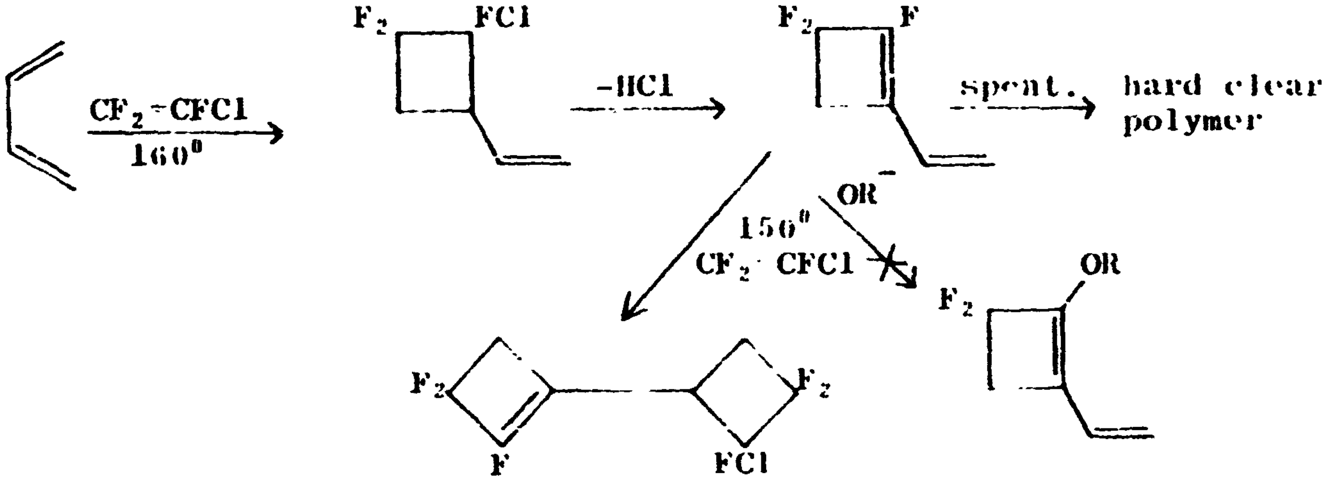


R = -H, $-CH_3$

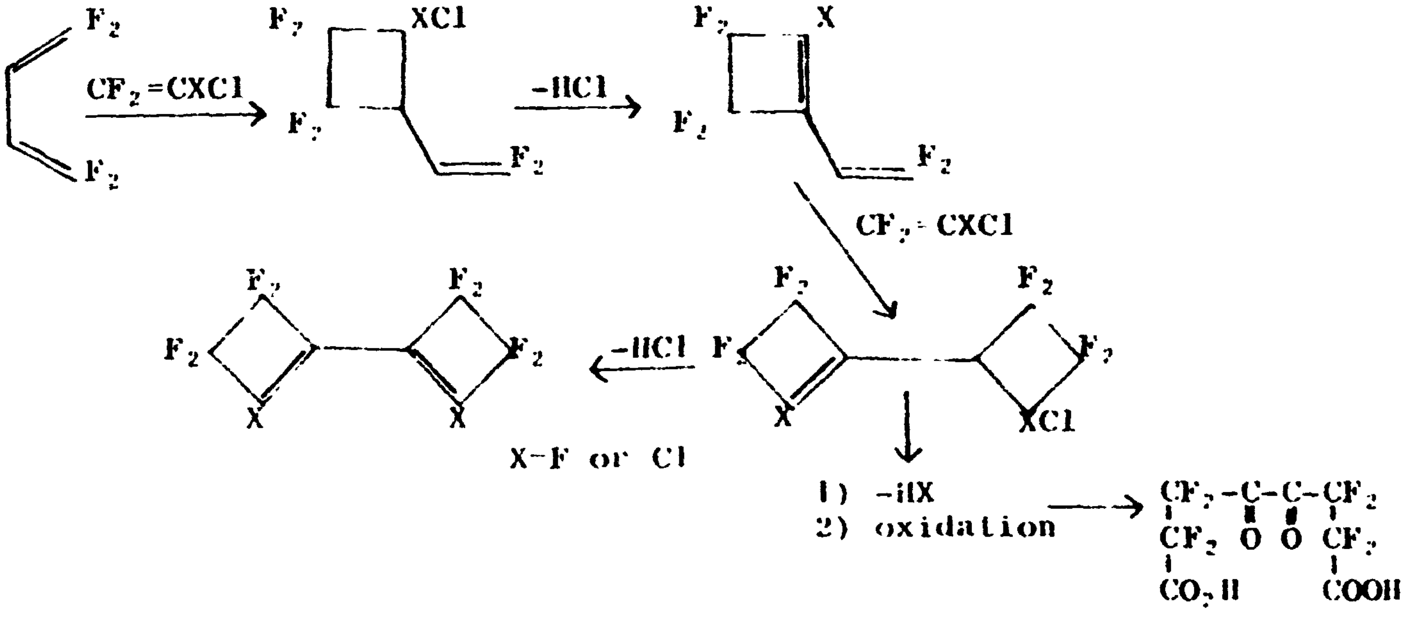
Frank of this laboratory extended the knowledge of thermal cycloalkylation reactions of haloethylenes in preparing cyclobutanes (several reviews have recently been published[2,7]) to the synthesis of dibox derivatives. In reacting 1,3-butadiene with trifluorochloroethylene in an autoclave he isolated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



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

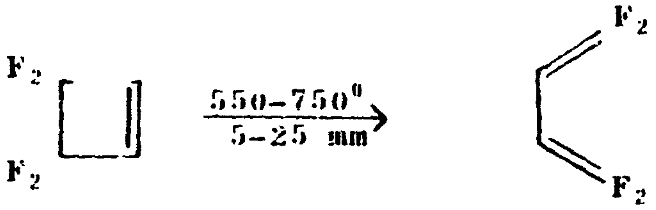


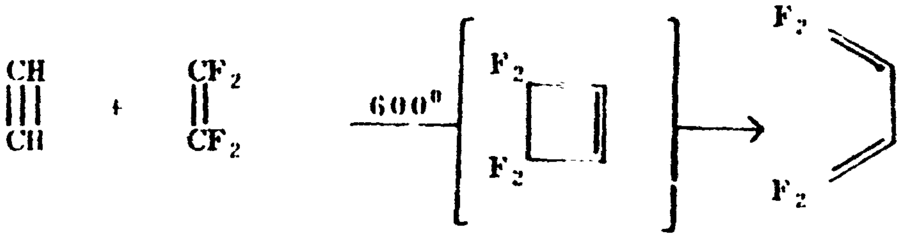
RESULTS AND DISCUSSION: It is apparent that a logical pathway to perhalobicyclobuteneyl compounds would involve thermal addition of haloethylenes to 1,1,4,4-tetrafluorobutadiene followed by dehydrohalogenation.



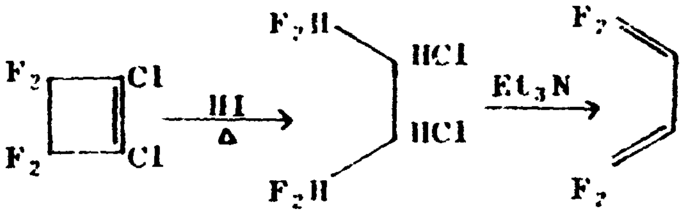
The initial step in developing such a synthesis involves preparation of the butadiene. Two syntheses of 1,1,4,4-tetrafluorobutadiene have been reported to give reasonable yields from available starting materials.

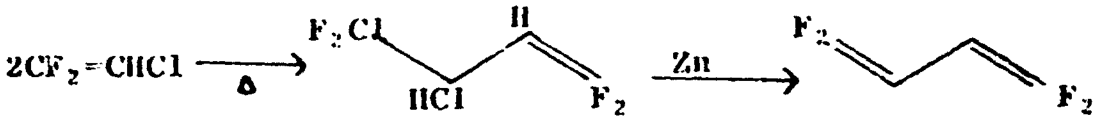
Anderson, Putnam, and Sharkey[8] report the thermal scission of 3,3,4,4-tetrafluorocyclobutene at 550-750° and 5-25 mm to give the desired butadiene quantitatively. In the same paper they report preparation of the butadiene by copyrolizing equimolar amounts of acetylene and tetrafluoroethylene at 600°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



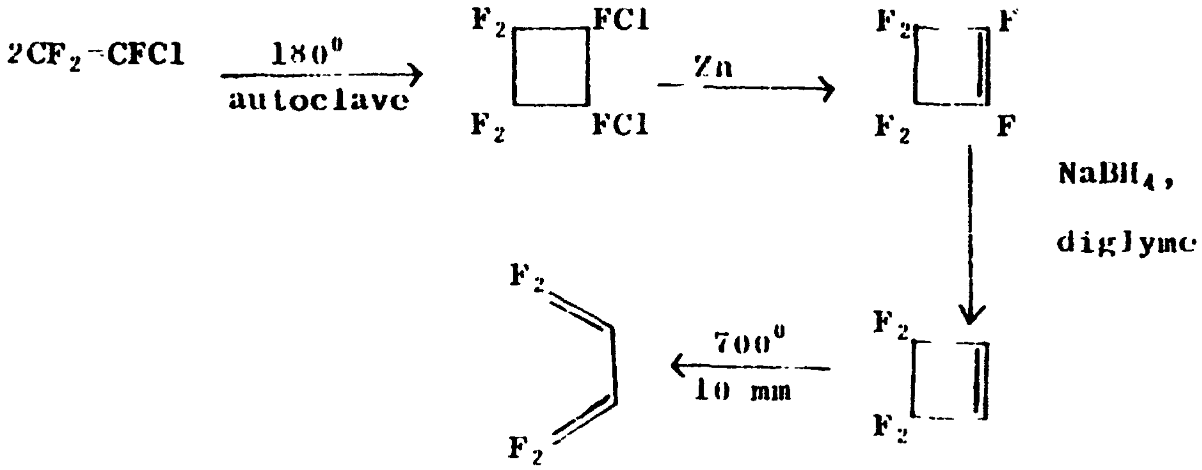


Two further syntheses of the diene logically develop from the work of Haszeldine and Osborne.[9] They are outlined below:

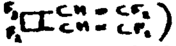




To date the following route has been successfully used to prepare the desired diene:



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

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

Failure of any diadduct to result from this reaction is surprising in view of Frank's work cited earlier. I is surely more activated to cycloalkylation than the analogous vinyl compound due to the CF_3 moiety. It remains possible, though, that the temperature of the reaction was not sufficient to initiate the second addition.

The next step in the synthesis is dehydrohalogenation of I to regenerate the diene system and thus activate the molecule to cycloalkylation. These reactions are currently in progress.

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 46.2 gm. of 1,1,4,4-tetrafluorobutadiene, 215 gm. of chlorotrifluoroethylene, and 5 ml. of d-limonene. The mixture was allowed to slowly warm to room temperature and then to 90° after twelve hours. The temperature was increased to 135° at twenty-four hours and 160° at thirty-six hours. This was maintained for twelve hours. The autoclave was vented at room temperature but only traces of gas were evolved. The pale yellow liquid product was fractionally distilled to give 53.7 gm. of a clear colorless liquid, b.p. 75-78° at 629 mm. IR: peaks at 3120, 2990, 1750 plus numerous peaks in the region 750 to 1400 cm^{-1}.

Anal. Calcd. for $C_6H_2ClF_7$: C, 29.7; H, 0.83; Cl, 14.6; F, 54.9.

Found : C, 27.51; H, 1.12; Cl, 13.53; F, 57.77.

Plans for Future: It is planned to work further with the unsaturated "dibox" derivatives in the hopes of synthesizing dinitroso compounds from the diketo dibasic acids.

REFERENCES:

1. W. C. Frank, Ph.D. Thesis, University of Colorado (1965).
2. D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, J. Am. Chem. Soc., 71, 490 (1949).
3. W. I. Miller, U. S. Patent 2,716,141 (1951) to Du Pont (C. A. 50: P7852a).
4. R. L. Pruett, C. I. Bahner, and H. A. Smith, J. Am. Chem. Soc., 74, 1638 (1952).
5. C. M. Sharts and J. D. Roberts, Ibid., 83, 871 (1961).
6. R. M. Ryananova, I. M. Dolgopol'skii, and A. L. Klebanskii, Zhurnal Obshchei Khimii, 6, 356 (1961) (C. A. 55: 27008 f).
7. J. D. Roberts and C. M. Sharts in "Organic Reactions," Vol. 12, John Wiley and Sons, Inc., New York, N. Y., 1962, p.1.
8. J. L. Anderson, R. E. Putnam, and W. H. Sharkey, J. Am. Chem. Soc., 83, 382 (1961).
9. R. N. Haszeldine and J. E. Osborne, J. Chem. Soc., 3880 (1955).
10. D. J. Burton, private communication.
11. R. E. Putnam, J. L. Anderson, and W. H. Sharkey, J. Am. Chem. Soc., 83, 386 (1961).

TITLE: Further Studies on the Preparation and Reactions of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene (I). (See Semi-Annual Report No. 1 for previous work)

Part A. Synthesis of I.

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

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

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

Distillation of the organic residue gave rise to compounds I, II, and III. I Still contained a conteminant of unknown origin in small amounts. On cooling to -20^{0}C a fractional crystallization was effected. Upon repeating this twice a VPC pure sample of I could be obtained. The impure fraction from the fractional crystallization contained nearly thirty percent of the total I and was thus reserved for further investigation.

Part B: UV Catalized Reactions of I

OBJECT: To study the photochemical reactions of I with particular interest addressed to obtaining coupling products.

HISTORICAL: It is well known that the normal carbon-iodine bond is cleaved by UV irradiation to yield the respective carbon and iodine radicals. In normal alkyl iodides wavelengths on the order of 3130A^{0} or shorter are required to effect this clevage. The products of such reactions can be predicted by examination of the probable fates of the radicals formed.

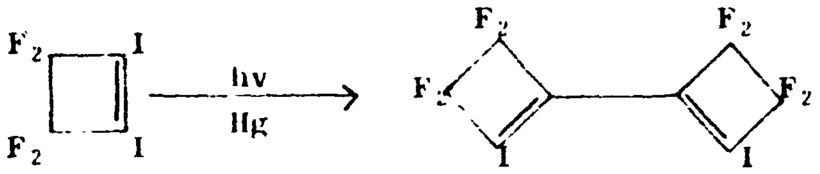
Haszeldine[1] has studied the UV absorption spectra of a number of halogen-containing alphatic iodo compounds and has correlated the broad absorption maximum in the 2500-3500A^{0} region to structure. In particular, the presence of halogens in the β-position and the tertiary nature of the carbon to which iodine is attached will be expected to cause a distinct bathochromic shift and an increase in the extinction coefficient of the absorption. Conversely, the vinyl nature of the carbon-iodine bond will result in a dramatic shift to shorter wavelength. This is illustrated in studies by Park, Seffl, and Lacher[2] on $CF_2 = CFI$ vapor. They observed λ_{max} to occur at 2580A^{0}. This is nearly identical to ethyl iodide vapor having λ_{max} at 2580A^{0} with an extinction coefficient of 310.

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

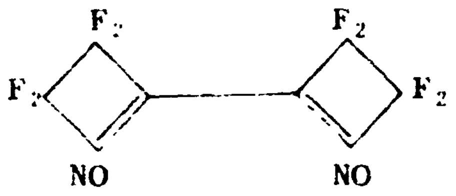
An ultraviolet spectrum of I was obtained in an effort to seek optimum conditions for photochemical reaction. The compound exhibits a broad absorption band with λ_{max} at 2400A^{0} and $\epsilon = 2050$. The upper limit of the band occurs at 2970A^{0} where zero absorbence is found.

The observed spectra is in good general agreement with that predicted for I. The somewhat large extinction coefficient explains the observed high light sensitivity. The sensitivity in Pyrex glassware, however, is not explained since Pyrex affords near zero transmittance below 3650A⁰. It is hoped that this matter will soon be resolved.

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



Compound IV will be used to obtain the corresponding dinitroso-derivative.



IV, however, does not agree either as to chemical or physical properties with the solid obtained earlier by irradiation in a pyrex vessel. This reaction over mercury now being repeated in an effort to isolate more IV and to characterize the other products. The rate of the reaction with the different ultraviolet sources will also be studied in a crude effort to correlate reactivity to wavelength.

EXPERIMENTAL:

Sunlight Irradiation of I.

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

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

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

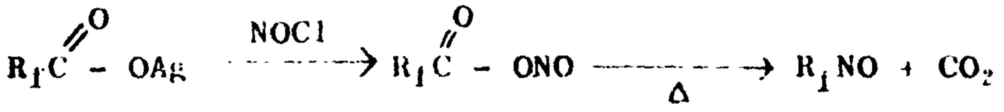
Part C: Nitroso Derivatives of I

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

HISTORICAL: Perfluoroalkylnitroso compounds have been synthesized in several laboratories in recent years. They have been shown to form dimers and polymers with perhalo olefins[3,4,5]. The polymers thus formed can be oils, waxes, or elastimers depending on the reactants used and the conditions of polymerization. The synthesis of V would make available an important and versatile new starting material for the development of such polymers.

Previous syntheses of perfluoroalkylnitroso compounds can be roughly divided into two categories. The first category makes use of perfluorocarboxylic acid derivatives. Haszeldine[6] was the first to react the silver salt of trifluoroacetic acid with nitrosyl chloride to obtain trifluoronitrosomethane in low yield. Rosser[7] extended this reaction to get good yields of perfluoronitrosoalkanes and isolated the intermediate perfluoroacyl nitrites. His work also shed some light on the nature of the Hunsdiecker reaction occurring during decarboxylation of the intermediate.

This decarboxylation can occur with explosive violence if R_f contains less than three carbon atoms.



$$R_fC(=O)-OAg \xrightarrow{NOCl} R_fC(=O)-ONO \xrightarrow[\Delta]{} R_fNO + CO_2$$

The second general method of preparation of these nitroso derivatives employs the corresponding perfluoroalkyliodo compounds. Iodine in these compounds is replaced by NO in a photochemically induced free radical reaction in the presence of mercury to remove nitrogen dioxide and iodine[3,4]. This method has been proven useful with compounds containing vinylic iodine[3] and thus seems most adaptable to the proposed synthesis.

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

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

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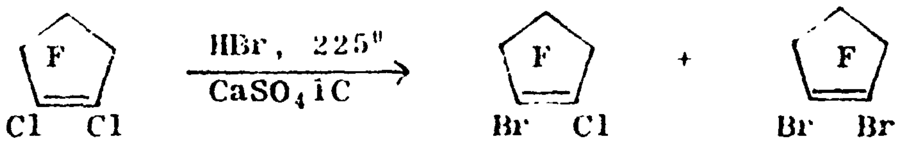
PREPARATION OF THE CYCLOPENTENES

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

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

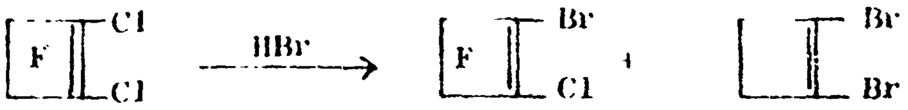


III I II

Sharrah[1] reported the addition of hydrogen bromide to chlorotrifluoroethylene ("Freon-1113") yielded 1-chloro-2-bromo-1,2,2-trifluoroethane. Subsequent work in this laboratory has shown that the formation of several more highly brominated products is greatly enhanced by an increase in reaction temperature. The isolation of the more highly brominated products was rationalized by Park and McClure[2] in terms of the formation of vinylic free radicals derived from the initially formed addition product.

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

When this reaction was extended to 1,2-dichlorotetrafluorobutene (IV)

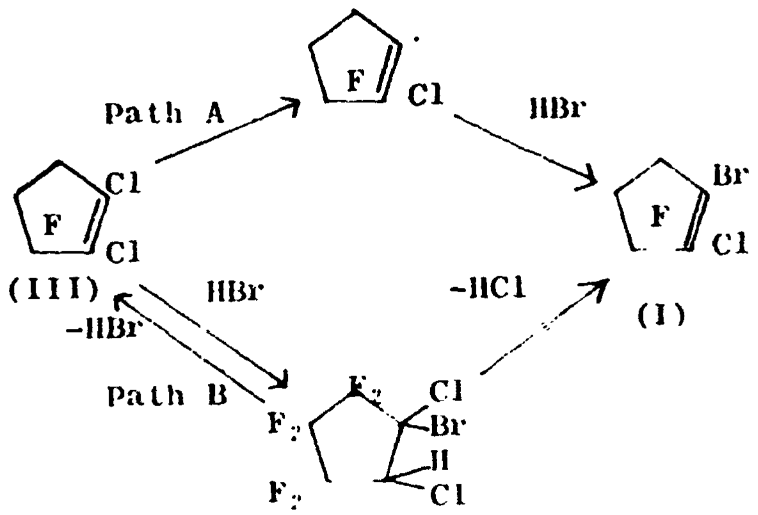


IV

only unreacted starting material and compounds identified as 1-bromo-2-chlorotetrafluorocyclobutene-1 and 1,2-dibromotetrafluorocyclobutene-1 were isolated under the reaction conditions employed.

Similar vinylic substitution was observed with the analogous 1,2-dichlorohexafluorocyclopentene-1 (III). However, the yield was much higher, due presumably to the inherent greater stability of the cyclopentenyl ring to the reaction conditions.

Two mechanistic interpretations are apparent for this reaction.



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

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

Baranauckas and Carr[3] have recently reported the isolation of 1,2-dichlorohexafluorocyclopentene from the reaction of 1-chloroheptafluorocyclopentene-1 and hydrogen chloride, a reaction which may be similar in nature.

Halide Ion Attack

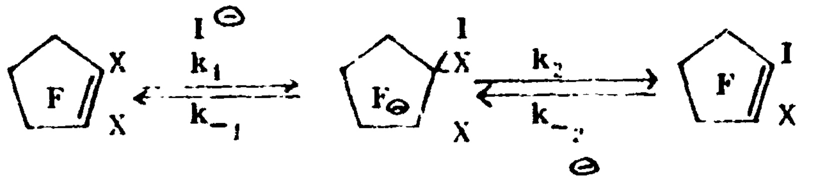
The concept of reversible carbanion formation in halocyclobutenes by halide ion attack was developed by Moore[4] in this laboratory. No attempt will be made to cover the fine points inherent to this hypothesis other than to explain the source of some of the synthetic difficulties encountered.

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

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

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

Moore[4] reported the isolation of 1-chloro-2-iodotetrafluorocyclobutene-1 and 1,2-diiodotetrafluorocyclobutene-1 from the reaction of potassium iodide and 1,2-dichlorotetrafluorocyclobutene-1. Unfortunately, the cyclopentenes are not as receptive toward attack by the iodide ion. This was circumvented by employing a starting material with a vinylic halogen more similar in "leaving group ability" to the iodide ion. That is, if $k_{-1} >> k_2$ for X=Cl, little conversion to the monoiodo-compound would be expected and even less to the diiodo-compound. If the magnitude of k_{-1} and k_2 are more nearly equal when X=Br, then increased conversion to the iodo-compounds should be affected. Use of 1,2-dibromohexafluorocyclopentene-1 (II)



afforded the bromo-, iodo- and diiodo-products in appreciable yields. When large-scale preparative runs were initiated, minor

[a] These findings have recently been verified by Dr. G.G.I. Moore[4], who working independently, has arrived at very similar results.

amounts of unidentified higher boiling compounds were also detected. The identity and source of these compounds is not known at present.

Although the bromochloro- and dibromohexafluorocyclopentenes could also be synthesized through this method using lithium bromide in diglyme, the hydrogen bromide addition-elimination reaction was preferred because of its high yield, freedom from side reactions, and ease or workup.

EXPERIMENTAL

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

Preparation of 1-bromo-2-chlorohexafluorocyclopentene-1 (I) and 1,2-dibromohexafluorocyclopentene-1 (II). The reaction was carried out by passing a mixture of the olefin and hydrogen bromide through a 100-cm x 2.5-cm pyrex glass tube packed with a 25/75 $BaSO_4$' activated carbon catalyst heated to ca. 225°C. The catalyst was prepared in the manner described by Sharrah.[1] In a typical run, 500 gm (2.04 mole) of 1,2-dichlorohexafluorocyclopentene-1 (X) was swept through the tube with about 3.7 molar excess of hydrogen bromide. The crude reaction products were washed with an aqueous sodium bicarbonate solution and twice with 50-ml portions of ice water. The aqueous layers were extracted with two 25-ml portions of diethyl ether and the combined organic layer and ether extracts dried over anhydrous magnesium sulfate. Fractional distillation yielded 275 gm of unreacted X; 128 gm (22% of theory) of 1-bromo-2-chlorohexafluorocyclopentene-1 (I); b.p., 101°C/629 mm; d_4^{28} 1.92; n_D^{25} 1.3890.

Anal. Calculated for C_5ClBrF_6: C, 20.82; Cl, 12.30; Br, 27.71; F, 39.52. Found: C, 20.69; Cl, 12.36; Br, 27.44; F, 39.21.
and 106 gm (16% of theory) of 1,2-dibromohexafluorocyclopentene-1(V); b.p., 119°/629 mm; d_4^{28} 2.17; n_D^{25} 1.4114.

Anal. Calculated for $C_5Br_2F_6$: C, 17.98; Br, 47.87; F, 34.15. Found: C, 17.95; Br, 47.63; F, 34.02.

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

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

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

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

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

Preparation of 1-bromo-2-iodohexafluorocyclopentene-1 (VI) and 1,2-diiodohexafluorocyclopentene-1 (VII). A mixture of 9.8 gm of 1,2-dibromohexafluorocyclopentene-1 (II), 18.2 gm of anhydrous potassium iodide, and 50 ml of diglyme were refluxed for 3 days. Addition of water forced out 11.3 gm of organic product. Extraction of the aqueous layer with methylene chloride and distillation of the combined organic layers gave 3.1 gm unreacted II, 4.6 gm of 1-bromo-2-iodohexafluorocyclopentene-1 (VI) and 3.8 gm of crude 1,2-diiodohexafluorocyclopentene-1(VIII).

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

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

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

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

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

The infrared spectrum of VIII contained a sharp absorption at 1560 cm^{-1} corresponding to the (C = C) stretching frequency.

Reaction of 1,2-dichlorohexafluorocyclopentene-1 (III) with Ethanolic Potassium Hydroxide. In a 25-ml, 3-neck, round-bottom flask, fitted with condenser, pressure equalizing addition funnel, and magnetic stir-bar, was placed 10.0 gm (0.0366 mole) of 1,2-dichlorohexafluorocyclopentene-1 (X) in 10 ml of absolute ethanol. After cooling of 0°C, 2.24 gm (0.040 mole) of potassium hydroxide in 10 ml of absolute ethanol were added dropwise with rapid stirring. After addition of the KOH/EtOH solution, the reaction mixture was stirred for an additional 2 hours at room temperature, and then poured into a separatory funnel half-filled with ice water. The reaction flask and filter were washed with methylene chloride which was added to the funnel. The organic layer was drawn off first and washed with water, followed by a wash with saturated sodium chloride solution. The washings and aqueous layer were then extracted with methylene chloride. The organic layer and methylene chloride extracts were combined and dried over anhydrous magnesium sulfate. Fractional distillation yielded 8.1 gm of 1-chloro-2-ethoxyhexafluorocyclopentene-1 (IX). Found: b.p. 137°C/628 mm; n_D^{28} 1.3754. Reported: b.p. 143-144°C/ 750 mm; n_D^{20} 1.3774.

Reaction of 1,2-dibromohexafluorocyclopentene-1 (II) with Ethanolic Potassium Hydroxide. In a 25-ml, 3-neck, round-bottom flask, fitted with condenser, addition funnel, and magnetic stir-bar, was placed 5.0 gm (0.0144 mole) of 1,2-dibromohexafluorocyclopentene-1 (XI) in 5 ml of absolute ethanol. After cooling to 0°C, 0.84 gm (0.015 mole) of potassium hydroxide in 3.0 ml of absolute ethanol were added dropwise with constant stirring. The reaction mixture was stirred for an additional 2 hours at room temperature. Distillation yielded 3.8 gm of crude bromo-ether. Pure 1-bromo-2-ethoxyhexafluorocyclopentene-1 (X) was isolated via G.L.C. (10' FS 1265 at 140°C); b.p. 150°C/629 mm; d_4^{28} 1.72; n_D^{28} 1.3958.

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

The infrared spectrum of X contained a sharp absorption at 1655 cm^{-1} corresponding to the (C C) stretching frequency.

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

Reaction of 1,2-diiodohexafluorocyclopentene-1 (VIII) with Ethanolic Potassium Hydroxide. In a 25-ml, 3- neck, round-bottom flask, fitted with dropping funnel, condenser and magnetic stir-bar, was placed 1.5 gm (0.0034 mole) of 1,2-diiodohexafluorocyclopentene-1 (VIII) in 2 ml of ethanol. After cooling to 0°C, 0.20 gm (0.0036 moles) of potassium hydroxide in 2 ml of absolute ethanol was added dropwise with constant stirring. After addition of the KOH/EtOH solution, the reaction mixture was stirred for an additional

2 hours at room temperature. Workup in the previously described manner for an alkoxide reaction (see compound IX) yielded 1.1 gm of crude 1-iodo-2-ethoxyhexafluorocyclopentene-1 (XI). Pure XI was isolated via preparative scale G.L.C. (18' x 1/4" Ucon 550X at 150°C); b.p. 172.5°C/628 mm; d_4^{28} 1.78; n_D^{28} = 1.4371.

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

The infrared spectrum of V contained a (C C) absorption at 1635 cm^{-1}.

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

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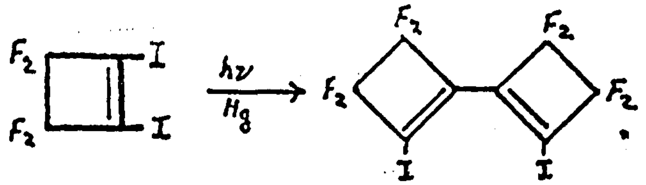
Further work on the syntheses of fluorine containing olefins and diolefins is reported. Studies directed toward syntheses of derivatives of perfluorobicyclobutyl and perfluorobicyclobutenyl ~~have been~~ were initiated. Of particular interest is the preparation of 2,2'-diiodo-per-fluorobicyclobutenyl by photolysis of 1,2-diiodotetrafluorocyclobutene.



Starting from 1,2-dichlorohexafluorocyclopentene, other dihalo- and mixed dihalohexafluorocyclopentenes were ~~have been~~ prepared, and from these ~~have been~~ were prepared the monoethoxy derivatives, such as 1-iodo-2-ethoxyhexafluorocyclopentene.

14. KEY WORDS	LINK A		LINK B		LINK C	
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