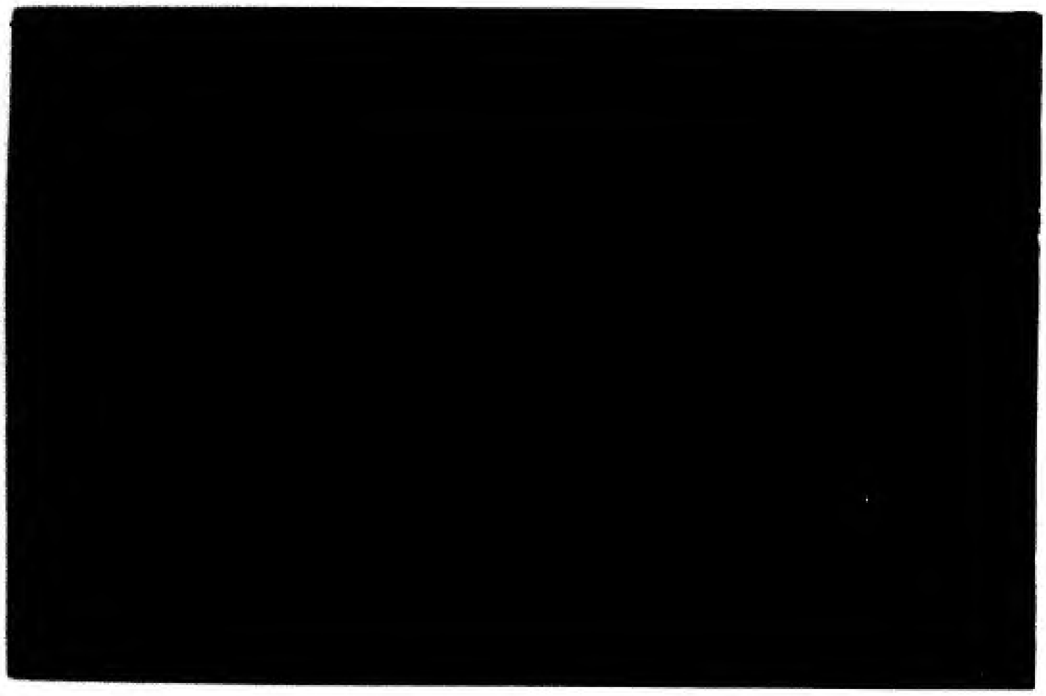


(5) Florida Univ., Gainesville.

(6) RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS.

(15) Contract DA19-129-AMC-79(N)
~~Between~~
~~U. S. Army Natick Laboratories~~
~~and~~
~~The University of Florida~~

~~Semiannual Report [illegible] October 1, 1964 - March 31, 1965~~

(10) ~~By~~ Paul Tarrant,
Doug Perry,
Jai Tandon,
Alan Wright and
Susumu Misaki.

(9) Semiannual rept. no. 4, 1 Oct 64 - 31 Mar 65,

I. INTRODUCTION

The purpose of this project is to conduct the necessary research for the preparation of unsaturated organic compounds containing fluorine and, when synthetic methods have been developed, to prepare various fluoroölefins which may give elastomers which are oil and fuel resistant and which retain their elasticity at low temperatures.

It is estimated that 65% of the work has been completed to date and that 65% of the estimated costs have been incurred to date.

This research is authorized under Contract Number DA 19-129-AMC-79(N) and is a further continuation of the work initiated under DA-44-109-QM-522 and continued under DA-44-109-QM-1469 and DA-19-129-QM-500.

This is the 4th report under the contract but the 51st since the project was initiated in 1951.

II. SUMMARY OF CURRENT PROGRESS

~~A study has been made of~~ methods ~~for producing~~ perfluoroallyl bromide and iodide. The latter olefin reacted with alcohols to produce ethers such as $CF_3CH_2OCF_2CF{=}CF_2$. The reaction of haloethylenes and haloalkanes in the presence of Lewis acids were ~~has been~~ studied and variations from the literature were ~~have been~~ noted.

Attempts were made to prepare $(CF_2{=}CFCH_2CH_2CH_2)_2O$ from the allyl ethers ~~have been carried out~~ but cyclic ethers were formed.

An investigation was initiated of the radical addition of $CF_3CF_2CCl_3$, $CF_2ClCF_2CCl_3$, CFClBrCFClBr and $CCl_3CF_2CFClBr$ with various olefins ~~has been initiated~~.

~~Studies of the~~ preparation of perfluoroalkane epoxides ~~have also~~ been ~~initiated~~. were investigated.

III. DISCUSSION

Perfluoroallyl Systems

Work was continued on investigation of the preparation and reactions of both perfluoroallyl bromide and iodide. The bromide was prepared[1] by the dehydrohalogenation of the adduct of CF_2Br_2 and $CHF{=}CF_2$. The techniques were improved to give yields up to 71% of the allyl bromide and up to 82% of the allyl iodide. The yield of the bromide is limited by the fact that the initial addition gives both $CF_2BrCHFCF_2Br$ and CF_2BrCF_2CHFBr which are present in 82–87% and 18–13%, respectively, as shown by the NMR spectra.

Perfluoroallyl bromide (PFAB) was heated at 100° for 2 hours, 100° for 4.5 hours, and 140° for 19 hours, then 176° for 4 hours in an attempt to prepare 1,2—(bromodifluoromethyl)-hexafluorocyclobutane. In none of these cases was any higher boiling material formed.

All attempts to prepare the perfluoroallyl Grignard and lithium reagents failed. In the Grignard preparation the magnesium turnings quickly became coated and did not react even after prolonged heating. When perfluoroallyl iodide (PFAI) was treated with magnesium in anhydrous ether in the presence of Me_3SiCl under a nitrogen atmosphere, only $Me_3SiOSiMe_3$ was obtained after hydrolysis.

When PFAB was allowed to react with phenylmagnesium bromide, unreacted PFAB, benzene, and only traces of higher boiling components were noted. With methyllithium, however, a product which appeared to be $CH_3CF_2CF{=}CF_2$ was obtained in small yield. Reactions similar to these have been reported by Tarrant and Warner[2]. With PFAI and phenyllithium an immediate exothermic reaction occurred to form a high boiling material which was identified as iodobenzene. Unreacted PFAI, benzene, and bromobenzene were also detected. The production of iodobenzene would seem to indicate the formation of $CF_2{=}CFCF_2Li$ by halogen-metal exchange. No reaction occurred with PFAI and pentafluorophenyllithium, as on hydrolysis only unreacted PFAI and pentafluorobenzene were obtained.

Treatment of PFAB with zinc dust in refluxing dioxane gave no evidence of reaction. Further heating at 105-8° for 3.5 hours in a sealed tube also gave no indication of reaction. When refluxing acetic anhydride was used as solvent, 55% of the PFAB were recovered and a lower boiling material was formed but not in a large enough amount to identify.

Perfluoroallyl iodide was prepared easily[3] by the S_N2' reaction of sodium iodide and PFAB in anhydrous acetone.

The additions of alcohols to fluoroölefins under base catalysis are well known[4-6]. When PFAI was treated with ethanolic potassium hydroxide two products were obtained which have been tentatively assigned the structures $C_2H_5OCF{=}CFCF_2OC_2H_5$ and $C_2H_5OCF_2CHFCF_2OC_2H_5$. With CF_3CH_2OH and KOH a 35.7% yield of $CF_3CH_2OCF_2CF{=}CF_2$ was obtained. This reaction had previously been carried out with perfluoroallyl chloride[7,8].

The ease of preparation of PFAI from PFAB using sodium iodide in anhydrous acetone is due to the large (10^4) difference in the solubilities of sodium iodide and sodium bromide. This led to the reaction of perfluoropropene with both sodium iodide and lithium bromide in anhydrous acetone, as possible simple, one step, cheap routes to this perfluoroallyl system. The solubility data[9] are given below (in moles/liter at 18°):

$$\mathrm{CF_3CF{=}CF_2 + \underset{1.3}{NaI} \longrightarrow CF_2{=}CFCF_2I + \underset{5 \times 10^{-7}}{NaF}}$$

$$\mathrm{CF_3CF{=}CF_2 + \underset{1.0}{LiBr} \longrightarrow CF_2{=}CFCF_2Br + \underset{1 \times 10^{-7}}{LiF}}$$

However in both cases the olefin was recovered unchanged. This lack of reaction was probably due to the fact that two liquid phases were present, the olefin being insoluble in acetone. In cases where this type of reaction has occurred, a homogeneous system was present.

In order to prepare large quantities of the perfluoroallyl compounds, a more economical route than the one used here was needed. Recently the following reaction was reported[10]:

$$\mathrm{CFCl_3 + CFCl{=}CFCl \xrightarrow{AlCl_3} CFCl_2CFClCFCl_2}$$

This reaction could then lead to the desired system via the following sequence of steps:

$$\mathrm{CFCl_2CFClCFCl_2 \xrightarrow{SbF_3Cl_2} CF_2ClCFClCF_2Cl \xrightarrow{Zn} CF_2{=}CFCF_2Cl}$$

$$\mathrm{CF_2{=}CFCF_2Cl \xrightarrow[acetone]{X^-} CF_2{=}CFCF_2X}$$

$$\mathrm{X = Br,\ I}$$

The addition of $\mathrm{CFCl_3}$ to $\mathrm{CFCl{=}CFCl}$ under $\mathrm{AlCl_3}$ catalysis has been accomplished with 86% conversion and 52% yield of $\mathrm{C_3Cl_5F_3}$ and about 3% $\mathrm{C_3Cl_6F_2}$. The fluorination of the former was attempted with $\mathrm{SbF_3}$ and 10% $\mathrm{SbCl_5}$ but no reaction occurred. However, with $\mathrm{SbF_3Cl_2}$ a quantitative conversion was obtained to give a 4:1 mixture of $\mathrm{C_3Cl_4F_4}$ and $\mathrm{C_3Cl_3F_5}$. When the nuclear magnetic resonance spectra for these materials were investigated, it was discovered that these were not pure compounds but actually mixtures of isomers. For example, the adduct $\mathrm{C_3Cl_5F_3}$ was shown to contain 58% $\mathrm{CF_2ClCFClCCl_3}$, 15% $\mathrm{CF_3CCl_2CCl_3}$, only 16% $CFCl_2CFClCFCl_2$ and 11% $CFCl_2CF_2CCl_3$. This result does not prove which mode of addition occurs ($CFCl_3$ adding as $-F$ and $-CCl_3$ or as $-Cl$ and $-CFCl_2$) since the possibility of rearrangements has not been eliminated. Further work on this aspect will be done. However, it appears that the former mode of cleavage predominates. The $C_3Cl_3F_5$ fraction was found to be 71% $CF_2ClCFClCF_2Cl$ and 25% $CF_3CCl_2CF_2Cl$, hence this route is feasible for the preparation of the perfluoroallyl system although it is not as simple as the literature would lead one to believe. The dehalogenation of $C_3Cl_5F_3$ with zinc in dioxane gave a 29% yield of the olefin, $C_3Cl_3F_3$, which consisted of 80% $CF_2ClCF{=}CCl_2$ and 20% $CF_3CCl{=}CCl_2$. With ethanol as the solvent a 46% yield of olefin was obtained containing 82% and 18% of the above isomers, respectively.

Some Lewis Acid Catalysed Additions of Haloalkanes to Haloölefins

Since the above type of addition of a fluorochloromethane to a fluorochloroölefin under the influence of aluminum chloride led to some interesting results, it was decided to investigate this reaction further using a variety of alkanes, olefins and catalysts.

The reaction of $CFCl_3$ with $CF_2{=}CFCl$ has been reported to give $CFCl_2CF_2CFCl_2$[11] and $C_3Cl_4F_4$[12]. We have found that this reaction gives a 72% yield of $C_3Cl_4F_4$ with a small amount of $C_3Cl_5F_3$. NMR spectroscopy has shown that the former contains 51% $CF_3CFClCCl_3$ and 37% $CF_2ClCF_2CCl_3$. Treatment of this mixture with zinc dust in ethanol gave only the reduction product, $C_3HCl_3F_4$, which was 79% $CF_2ClCF_2CHCl_2$. With dioxane as the solvent a small amount of olefin $C_3Cl_2F_4$ was produced but the $C_3Cl_4F_4$ was chiefly unreacted. When acid-washed zinc in dioxane was used both products, $CF_3CF{=}CCl_2$ and $CF_2Cl{-}CF_2CHCl_2$, were formed. Treatment of the $C_3Cl_5F_3$ fraction with ethanolic zinc dust gave a mixture of 48% $CF_2ClCF{=}CCl_2$ and 52% $CF_3CCl{=}CCl_2$.

The addition of $CFCl_3$ to $CF_2{=}CCl_2$ yielded $C_3Cl_5F_3$ in 53% yield, with small amounts of $C_3Cl_6F_2$. However, when perfluoropropene, tetrachloroethylene, perfluoro-2-butene and perfluorocyclobutene were used, no adducts were formed. In the last case the only products isolated were cyclo-$C_4Cl_4F_2$ and cyclo-C_4Cl_6. When perfluorocyclobutene alone was treated with aluminum chloride, the chief product was cyclo-$C_4Cl_2F_4$ with some monochloro derivative formed also.

When CF_2Cl_2 was treated with $CFCl{=}CFCl$, no desired adduct was formed. The only materials present were CCl_4, $CCl_2{=}CCl_2$ and $C_3Cl_5F_3$. As with all the reactions involving $CFCl_3$, carbon tetrachloride is always a by-product. Consequently the formation of the higher boiling materials, in addition to the expected adducts, can occur either by addition of CCl_4 to the olefin or by replacement of a fluorine of the adduct by a chlorine from the aluminum chloride.

The reaction of CF_2Cl_2 and $CF_2{=}CFCl$ took place very slowly to give none of the expected adduct, but instead gave chiefly $C_3Cl_4F_4$. Treatment of this material with zinc dust in dioxane gave chiefly unreacted starting material plus some olefin, $C_3Cl_2F_4$, and reduction product, $C_3HCl_3F_4$.

A study was made of the effect of other Lewis acids as catalysts for this type of addition reaction. The system $CFCl_3$ + $CFCl{=}CFCl$ was used with concentrated H_2SO_4, fuming H_2SO_4, $SnCl_4$, $AlBr_3$, $SbCl_5$ and $SiCl_4$ under a variety of conditions. Only in the case of aluminum bromide did any reaction at all occur and then it produced only a 3% yield of adduct after 3 days at room temperature and 5 hours at 70°. It was concluded that only aluminum chloride was effective as a catalyst in this reaction.

This study was also extended to the investigation of the addition of polyhalogenated ethanes to fluoroölefins. For example, $CF_2BrCFClBr$ and $CF_2ClCFCl_2$ were both reacted in the presence of CFCl=CFCl and aluminum chloride. In neither case was any addition observed; instead, the ethanes either rearranged or reacted with the aluminum chloride. With $CF_2BrCFClBr$, the chief product was CFClBrCFClBr along with C_2Cl_6. When $CF_2BrCFClBr$ was treated with $AlCl_3$ only, a product having the same formula as the starting material was obtained but its physical properties were different. This result is supported by the work of Madai and Mueller[13] and this compound has tentatively been assigned the structure CF_3CBr_2Cl. However, no data could be found for the other possibility, $CF_2ClCFBr_2$.

The reaction of CFCl=CFCl with $AlCl_3$ to form $CCl_2=CCl_2$ was also attempted using both 15/1 and 5/1 mole ratios of olefin to $AlCl_3$ but in neither case was any reaction detected.

The Synthesis of Some Unsaturated Fluoroethers

Addition of $CF_2BrCFClBr$ and CF_2Br_2 to Diallyl Ether.

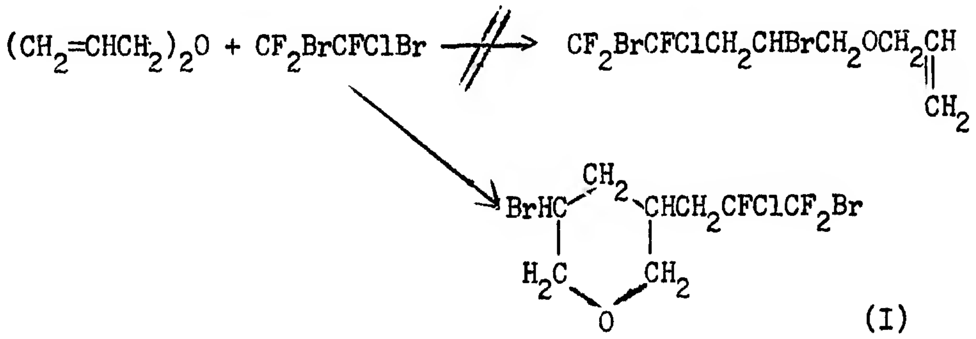
The addition of haloalkanes to some vinyl and allyl ethers has been investigated and some unsaturated fluoroethers have been obtained by dehalogenation of the straight chain adducts[14]. In contrast, Friedlander reported[15,16] that the treatment of the haloalkane with diallyl ether under free radical conditions gave a six-membered cyclic product i.e. a substituted tetrahydropyran. Bromotrichloromethane was used as a haloalkane but the use of a fluorine compound has not been reported.

Attempts were made to prepare linear fluoroethers as follows:

$$(CH_2{=}CHCH_2)_2O + 2CF_2BrCFClBr \longrightarrow (CF_2BrCFClCH_2CHBrCH_2)_2O.$$

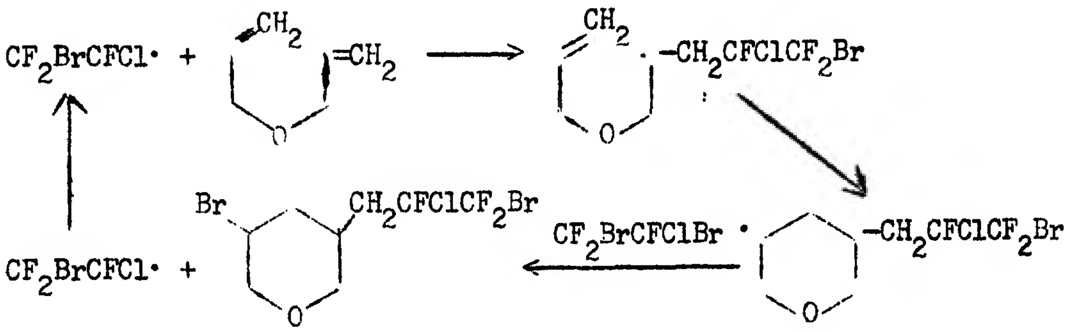
$$(CH_2{=}CHCH_2)_2O + 2CF_2Br_2 \longrightarrow (CF_2BrCH_2CHBrCH_2)_2O.$$

Though the reactions were carried out using a large excess of the haloalkanes to prevent cyclization, the adducts were saturated one to one addition products. It is proposed the reactions follow a mechanism similar to that proposed by Friedlander[15]:

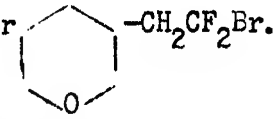


(I)

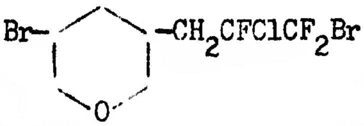
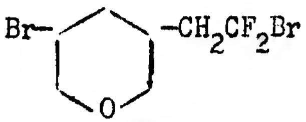
$$CF_2BrCFClBr + R\cdot \longrightarrow CF_2BrCFCl\cdot + RBr$$



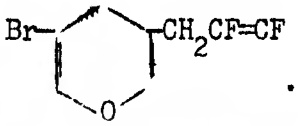
(I)

A similar mechanism is postulated for the formation of 

The adducts from both reactions were highly viscous slightly yellow liquids.

Dehalogenation of  (I) and  (II).

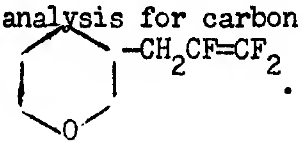
Dehalogenations were carried out by the usual method. The dehalogenated product from I had a strong infra-red absorption at 5.56µ which is characteristic of the $CF_2{=}CF-$ group. Elemental analysis and MR_D were consistent with the proposed structure,



.

Dehalogenation of II failed because of polymerisation during the distillation.

Attempts to react I with $LiAlH_4$ in ether at 0°, room temperature and 35°, showed a slow reaction in the last case only. A rapid reaction occurred using tetrahydrofuran as solvent[17] and two main products were separated by VPC. One product was identical to the dehalogenation product of (I). The other had a strong infra-red absorption at 5.56µ and MR_D and the elemental analysis for carbon and hydrogen were consistent with the structure



.

Addition of Chlorine to Diallyl Ether.

Since the attempts at a direct synthesis of the linear ethers failed, another route was attempted:

$$\begin{tikzcd}
\mathrm{(CH_2{=}CHCH_2)_2O + Cl_2} \arrow[r] & \mathrm{CH_2ClCHClCH_2OCH_2CH{=}CH_2} \quad \text{(III)} \arrow[d, "\mathrm{CF_2BrCFClBr}"] \\
\mathrm{CF_2{=}CFCH_2CHBrCH_2OCH_2CH{=}CH_2} \arrow[d, "\mathrm{CF_2BrCFClBr}"] & \mathrm{CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl} \arrow[l, "\mathrm{Zn}"'] \\
\mathrm{CF_2{=}CFCH_2CHBrCH_2OCH_2CHbrCH_2CFClCF_2Br} \arrow[r, "\mathrm{Zn}"] & \text{(IV)} \quad \mathrm{(CF_2{=}CFCH_2CHBrCH_2)_2O} \arrow[d, "\mathrm{LiAlH_4}"] \\
 & \mathrm{(CF_2{=}CFCH_2CH_2CH_2)_2O}
\end{tikzcd}$$

The chlorination of diallyl ether was carried out as reported[18]. Best results were obtained when the reaction was carried out at temeratures between 3° and 7°.

Addition of $CF_2BrCFClBr$ to III.

A large excess of the haloalkane was used but the reaction did not go smoothly and almost half of the starting ether was recovered. The adduct, $CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (IV), was a viscous liquid.

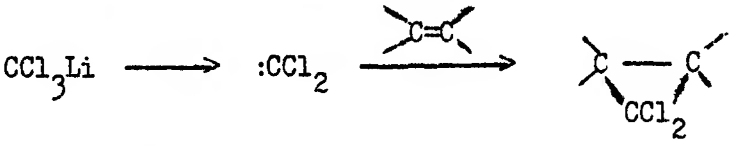
Dehalogenation of IV.

Dehalogenation was effected by zinc in ethanol. Two main products were separated by VPC. One component was identified as $CH_2ClCHClCH_2OH$ from its physical properties. The other gave an elemental analysis, infrared spectrum and MR_D consistent with $CF_2{=}CFCH_2CHBrCH_2OCH_2CHClCH_2Cl$.

Some Reactions of Haloalkyllithium Compounds with Fluoroölefins.

Reaction of Dichloromethyllithium and Trichloromethyllithium with Fluoroölefins.

The preparation of polychloromethyllithium compounds and their reaction with various compounds has been investigated previously[19–21]. The lithium compounds reacted with olefins even at low temperatures to give the corresponding cyclopropanes:



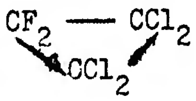
In contrast Dixon reported that alkyl lithium replaced fluorine atoms in fluoroölefins[22]:

$$C_4H_9Li + CF_2 = CFCl \longrightarrow C_4H_9CF = CFCl.$$

It was therefore of interest to investigate the mode of reaction of $CHCl_2Li$ and CCl_3Li with fluoroölefins at low temperatures:

i.e. $CCl_3Li + CF_2 = CCl_2 \longrightarrow CCl_3CF = CCl_2 + LiF$

or



$+ LiCl$

Trichloromethyllithium was prepared by the reported method[19,20]; and reacted with CF_2=CCl_2 at -78° and -110° to -115°. The product of the reaction at -110° showed no infrared absorption in the C=C region. Infrared absorption at 9.54μ and 11.91μ and elemental analysis were consistent with the cyclopropane structure. Further work is continuing.

The reaction of $CHCl_2Li$ with CF_2=CFCl at -78° produced a compound which absorbed at 5.63μ in the infrared region, characteristic of the CFCl=CF- grouping.

Preparation of Dichlorofluoromethyllithium and Its Reaction with Some Olefins and Mercuric Chloride.

Preparation of $CFCl_2Li$ was attempted by reacting $CFCl_2H$ and C_4H_9Li in various solvents, e.g., tetrahydrofuran, ether, petroleum ether, n-pentane and their mixtures at -115° to -120°. The product was reacted in situ with fluoroölefins, cyclohexene and mercuric chloride at the same temperature. The product in each case showed $\geq$C – H infrared absorption and physical properties consistent with n-octane. The precipitate filtered from the reaction gave a positive fluoride ion test.

Chlorotrifluoroethylene, dichlorodifluoroethylene, hexafluorocyclobutene and cyclohexene were used as the olefins, but no substituted compounds were obtained. No reaction was detected with mercuric chloride.

Radical Induced Additions to Olefins.

Silane Studies.

Several addition reactions of triethyl trifluorovinyl silane have been reported. Bromine and hydrogen bromide have been added to the double bond, as have methanes of the form CX_3Br (X=Cl, Br), under the influence of benzoyl peroxide, to produce $(C_2H_5)_3SiCFBrCF_2CX_3$.[23]

No adduct was detected from the attempt to react $CF_2BrCFClBr$ and $(CH_2)_3SiCF=CF_2$ in the presence of benzoyl peroxide.

Addition Reactions of Haloalkanes and Olefins.

Although the reactions between haloalkanes and olefins have been widely investigated[24,25], there has been little mention of the additions of $CCl_3CF_2CF_3$, $CCl_3CF_2CF_2Cl$, $CFCl_2CFCl_2$, $CFCl_2CF_2Cl$, $CFClBrCFClBr$ and $CCl_3CF_2CFClBr$ to olefins.

It was found that $CCl_3CF_2CF_3$ and $CCl_3CF_2CF_2Cl$ do not react with allyl chloride, but they react with olefins in the presence of benzoyl peroxide to give mainly one to one addition products:

$$CF_2ClCF_2CCl_3 + CH_2{=}C(CH_3)_2 \xrightarrow{Bz_2O_2} CF_2ClCF_2CCl_2CH_2C(CH_3)_2Cl. \qquad \text{(IX)}$$

The product, IX, dehydrohalogenated very easily on distillation to give either $CF_2ClCF_2CCl_2CH{=}C(CH_3)_2$ or $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$, X. Alcoholic potassium hydroxide dehydrohalogenation of the product (IX) gave X and products of further dehydrohalogenation which were identified as $CF_2ClCF_2CCl{=}CHC(CH_3){=}CH_2$, $CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$ and $CF_2ClCF_2C{\equiv}C{-}C(CH_3){=}CH_2$ by infrared spectroscopy and elemental analysis.

$CFCl_2CFCl_2$ and $CFCl_2CF_2Cl$ failed to react with ethylene in the presence of benzoyl peroxide.

The attempt to make the triene $CH_2{=}CHCF{=}CFCH{=}CH_2$ by addition of $CFClBrCFClBr$ to ethylene to form $CH_2BrCH_2CFClCFClCH_2CH_2Br$ followed by dehalogenation and dehydrohalogenation, failed, as only the one to one adduct was formed (in 17% yield). A considerable amount of $CFCl{=}CFCl$ (20%) was obtained by debromination of $CFClBrCFClBr$. Tarrant et al[26] have reported elimination by radical decay in the addition of CCl_3Br to $CF_2BrCFClCH{=}CH_2$ to produce an olefin:

$CF_2BrCFCl\dot{C}HCCl_3 \longrightarrow CF_2BrCF{=}CHCH_2CCl_3 + Cl.$

The radical, CFClBrCFCl, seems to be more unstable and decays to the olefin before it can attack the double bond of ethylene.

The addition of $CCl_3CF_2CFClBr$ to ethylene gave $CCl_3CF_2CFClCH_2Br$, which was identified by its NMR spectrum. The aqueous phase of dehydrohalogenation of the product gave a positive test for bromide.

The attempt to make 1-trichloromethyl-2-bromohexafluorocyclobutane by the addition of CCl_3Br to hexafluorocyclobutene in the presence of benzoyl peroxide failed.

Attempted Preparation of Some Fluoro-epoxides.

It was proposed to prepare some fluorocarbon epoxides and examine their reactions. The preparation of some fluoroepoxides has been reported[27] but, to date, very little work has been published on their reactions.

Using the method previously described[27], of bubbling the olefin through alkaline hydrogen peroxide in aqueous methanol for the preparation of octafluoro-2,3-epoxybutane from octafluoro-2-butene, only trace amounts of epoxide were detected in the product and the olefin was only recovered in poor yields. Reactions at low temperatures with octafluoro-2-butene gave the same result. It was considered at this point that the fluoroepoxides when formed would be liable to nucleophilic attack by methoxide and hydroxide ions in the solution. Therefore the solvent was changed from aqueous methanol to aqueous acetone. This produced samples of the epoxides free from olefin, but in poor yield. To minimize the effect of the nucleophilic hydroxide ion, a reaction was attempted using neutral hydrogen peroxide in aqueous acetone. The olefin was recovered in 83% yield, but there was no trace of epoxidation. Therefore the presence of the base is essential to the formation of ${}^{\ominus}O{-}O{-}H$, the proposed attacking species. A change of base from potassium hydroxide to potassium carbonate produced a mixture of olefin and epoxide. At present it seems that the epoxide is an intermediate in the reaction of fluoro-olefins with alkaline hydrogen peroxide and that the epoxide formation and destruction is temperature sensitive. Unless yields of the epoxide can be increased considerably this reaction is to be abandoned.

An attempt to epoxidise hexafluorocyclobutene with oxygen in presence of ultra-violet light produced tetrafluorosuccinic acid[28]. Attempts to prepare the epoxide using alkaline hydrogen peroxide in aqueous acetone failed. The olefin reacted vigorously even at -50°. The recovered volatile product was hexafluorocyclobutene (22%). The residue was worked up and the white solid recovered is still under investigation.

Attempts have been made to epoxidise 1,1,2-trifluoro-1,3-butadiene to show the relative ease of epoxidation of the $CF_2{=}CF{-}$ and $CH_2{=}CH{-}$ systems. The diene was obtained by dehalogenation of 3,4,4-trifluoro-3-chloro-4-bromobutane[29]. The diene suffers the disadvantage of dimerisation even at room temperature. No definite conclusions have been reached, but this work is continuing.

IV. EXPERIMENTAL

Perfluoroallyl Systems.

Reaction of Perfluoroallyl Bromide with Methyllithium.

Methyllithium (10 ml., 0.91 M in ether) was cooled in a dry ice-acetone bath, ether (10 ml.) added, and then PFAB (2.27 g., 0.0107 mole) was added dropwise over 7 minutes with stirring. A dark solution was formed immediately. After stirring at -78° for 45 minutes $CF_2{=}CCl_2$ (1.3 g., 0.01 mole) was added and stirred for 15 minutes, then at room temperature for 1 hour. Some low boiling material distilled from the condenser into a cooled trap. VPC showed $CF_2{=}CCl_2$, PFAB, ether and an unknown, but no product with a b.p. greater than ether. The unknown product was isolated by VPC (D.N.P. column, 24°) and was assumed to be $CH_3CF_2CF{=}CF_2$, b.p. 24-6°. There was insufficient sample for positive identification.

Reaction of Perfluoroallyliodide with Phenyllithium.

Phenyllithium (0.02 mole in ether), prepared from bromobenzene and lithium dispersion in the normal manner, was cooled in an ice bath and PFAI (4.81 g., 0.0186 mole) was added dropwise to give a vigorous reaction. After the addition of ether (10 ml.) and stirring to room temperature over 1.5 hours, the mixture was hydrolyzed with dilute acid, the ethereal solution was washed with water, and the organic material dried over Drierite. Distillation gave a residue (3.9 g.) which VPC showed to contain ether, PFAI, benzene, bromobenzene and one higher boiling component. Separation on a Silicon Elastomer (S.E.) prep. column at 120° gave 0.5 g. pure material, b.p. 180-1° (micro), $n_D^{19.8}$ 1.5735, whose infrared agreed with that of iodobenzene.

Preparation of PFAI.

PFAB (34.2 g., 0.162 mole) was added dropwise over 14 minutes to a solution of sodium iodide (30 g., 0.20 mole) in anhydrous acetone (60 ml.) at 35-42°. After 20 minutes at 46° the mixture was washed with $NaHSO_3$ solution, and water, and the organic layer dried over Drierite to give pure PFAI (34.2 g., 82% yield).

Reaction of PFAI with C_2H_5OH and KOH.

A saturated solution (10 ml.) of potassium hydroxide pellets in absolute ethanol was diluted with ethanol (10 ml.). PFAI (2.96 g., 0.0115 mole) was added dropwise over 8 minutes. A white solid formed immediately. After stirring for 1 hour, the mixture was poured into water, extracted with ether and the ethereal solution was washed with dilute nitric acid, water and dried over Drierite. Distillation gave a sample, b.p. 46–63° and residue (1.5 g.). VPC separation of the residue (S.E., 55°) gave two compounds: The first (0.4 g.) had b.p. 63–4° (micro), $n_D^{20.0}$ 1.3624, with a strong infrared band at 5.80μ. Analysis for $C_7H_{10}O_2F_4$, $C_2H_5OCF{=}CFCF_2OC_2H_5$: Calcd.: C, 41.59; H, 4.97; O, 15.84; F, 37.60. Found: C, 40.81; H, 6.95; O, 15.54 (by difference); F, 36.70. The second (0.7 g.) had b.p. 140–1° (micro). $n_D^{24.0}$ 1.3526, d_4^{24} 1.228 g./cc.. This had a very pungent odor, pH[illegible]1, fumed in air and had strong infrared bands at 5.49μ and 5.90μ. Analysis for $C_7H_{11}O_2F_5$, $C_2H_5OCF_2CHFCF_2OC_2H_5$: Calcd.: C, 37.84; H, 5.00; O, 14.40; F, 42.76. Found (average): C, 37.86; H, 4.90; O, 15.55 (by difference); F, 41.70.

No other possibilities fit the analyses as well as the above.

Reaction of PFAI with CF_3CH_2OH and KOH.

CF_3CH_2OH (19.0 g., 0.19 mole) and KOH pellets (1.66 g., 0.0297 mole) were cooled in ice bath and PFAI (7.2 g., 0.0279 mole) was added over 9 minutes. A white precipitate formed immediately. After warming to room temperature and refluxing for 30 minutes the mixture was distilled through 6" Vigreaux column to give two fractions (b.p. 54–72°) which were combined, washed with water and dried over Drierite to give almost pure product (2.3 g., 36%). VPC purification (S.E., 40°) gave 1.70 g. pure material which was too volatile to obtain a b.p. or n_D. The infrared had a strong band at 5.57μ indicative of a $-CF=CF_2$ group. Analysis for $C_5H_2OF_8$, $CF_3CH_2OCF_2CF=CF_2$: Calcd.: C, 26.10; H, 0.88; F, 66.07; O, 6.95. Found: C, 25.10; H, 0.48; F, 65.15; O, 9.27 (by difference).

Addition of $CFCl_3$ to CFCl=CFCl Catalyzed by $AlCl_3$.

When $CFCl_3$ (174 g., 1.26 mole), CFCl=CFCl (140 g., 1.05 mole) and aluminum chloride (22 g., 0.16 mole) were stirred at room temperature for 6.5 hours, fresh $AlCl_3$ (10 g.) added and the mixture stirred for another 1.5 hours, 262.5 g. material was obtained, which by VPC contained 25% unreacted starting materials, 23% CCl_4, 49% $C_3Cl_5F_3$ and 3% $C_3Cl_6F_2$. Distillation gave pure $C_3Cl_5F_3$ (126.5 g.), b.p. 68-9°/41mm.. Based on 0.90 mole olefin reacted the conversion was 86% and the yield was 52%.

Fluorination of $C_3Cl_5F_3$.

Treatment of $C_3Cl_5F_3$ (52 g., 0.22 mole) with SbF_3 (13 g., 0.073 mole) and $SbCl_5$ (3.0 g., 0.01 mole) at 78-87° for 3 hours and 87-92° for 19 hours gave no lower boiling material.

Into an autoclave containing SbF_3 (216 g., 1.20 mole) and cooled in acetone-dry ice was poured liquid chlorine (46 g., 0.65 mole). After 3 hours at room temperature $C_3Cl_5F_3$ (122 g., 0.45 mole) was added and heated to 150° and rocked overnight. After washing with dilute HCl and water the organic liquid was dried over Drierite to give 70.2 g. material. VPC indicated this was 73% $C_3Cl_4F_4$ and 27% $C_3Cl_3F_5$, hence a 45% yield of the former and an 18% yield of the latter. Distillation and vapor chromatographic purification gave pure $C_3Cl_3F_5$ (9.3 g.), b.p. 72-3°, $n_D^{26.0}$ 1.3498 and pure $C_3Cl_4F_4$ (38.6 g.), b.p. 111-12°, $n_D^{20.5}$ 1.3960.

Another run using SbF_3 (220 g., 1.23 mole), Cl_2 (48 g., 0.68 mole) and $C_3Cl_5F_3$ (116 g., 0.43 mole) at 150° for 17 hours gave 75 g. product containing 20% $C_3Cl_3F_5$ and 80% $C_3Cl_4F_4$ in yields of 15% and 55% respectively.

Dehalogenation of $C_3Cl_5F_3$ with Zinc in Dioxane.

$C_3Cl_5F_3$ (61.1 g., 0.226 mole) was added during 45 minutes to a hot mixture of zinc dust (19.5 g., 0.30 mole), zinc chloride (1 g.) and dioxane (100 ml.) and refluxed for 1.5 hours. Zinc (5 g.) was added and the mixture was refluxed for another 1.5 hours. After filtration the mixture was washed with dilute HCl, and water, and dried (Drierite) to give an organic product (33.7 g.) which was shown to contain 29% $C_3Cl_3F_3$, 6% others, and 65% unreacted $C_3Cl_5F_3$ by VPC. Distillation and chromatographic purification (S.E., 105°) gave pure material, b.p. 85-6° (micro), $n_D^{20.0}$ 1.4060, d_4^{23} 1.589 g./cc. with infrared bands at 6.06µ (s) and 6.30µ (m). Analysis for $C_3Cl_3F_3$: Calcd.: C, 18.07; Cl, 53.34; F, 28.59. Found: C, 17.86, H, 0.10; Cl, 53.09; F, 28.95 (by difference). Also present was a small amount of lower boiling material with an infrared band at 5.83µ.

Dehalogenation of $C_3Cl_5F_3$ with Zinc in Ethanol.

$C_3Cl_5F_3$ (48.6 g., 0.18 mole) was added in 40 minutes to a refluxing suspension of zinc dust (16 g., 0.25 mole) in absolute ethanol (100 ml.) and refluxed 20 minutes. Work up gave 25.2 g. material which by VPC was shown to contain 65% (16.5 g.) $C_3Cl_3F_5$ (46% yield). Distillation and chromatographic purification gave the following: Fraction A, ethanol; Fraction B, b.p. 70-1° (micro), $n_D^{26.8}$ 1.3857, infrared bands at 5.58μ (w) and 5.82μ (s), analysis for $C_3HCl_2F_3$: Calcd.: C, 21.84; H, 0.61; Cl, 42.99; F, 34.56. Found: C, 22.61; H, 0.80; Cl, 41.17; F, 35.42 (by difference); Fraction C, b.p. 85-6° (micro), $n_D^{21.0}$ 1.4050, infrared band at 6.05μ (s) and 6.30μ (m), identical with previously prepared $C_3Cl_3F_3$; Fraction D, $n_D^{26.8}$ 1.4211, infrared bands at 6.06μ (w) and 6.33μ, unidentified; and Fraction E, b.p. 153-4° (micro), $n_D^{26.8}$ 1.4365, unreacted $C_3Cl_5F_3$.

Addition of $CFCl_3$ to CF_2=CFCl Catalyzed by $AlCl_3$.

In an autoclave at -78° was placed $AlCl_3$ (20 g., 0.15 mole), CF_2=CFCl (100 g., 0.86 mole), and $CFCl_3$ (194 g., 1.41 mole). After rocking at room temperature for 5.5 hours the autoclave was vented (no gas) and the liquid washed and dried to give a product (273 g.) containing $C_3Cl_4F_4$ (158 g., 58%) or 72% yield. Distillation gave low boiling material (8 g.), CCl_4 (ca 65 g.), $C_3Cl_4F_4$ (ca 153 g.), and a residue ($C_3Cl_5F_3$, 31 g.). Pure $C_3Cl_4F_4$ (140 g.) had b.p. 107-110°, $n_D^{20.9}$ 1.3980. Analysis for $C_3Cl_4F_4$: Calcd.: Cl, 55.86. Found: Cl, 54.08. The yield of pure $C_3Cl_4F_4$ was 64%.

A similar reaction was run by passing CF_2=CFCl (175 g., 1.51 mole) through an ice-cooled mixture of $AlCl_3$ (30 g., 0.22 mole) and $CFCl_3$ (316 g., 2.30 mole). Work up gave a product (391 g.) which on distillation gave: cut 1, mixture (28 g.), b.p. 20-76°; cut 2, CCl_4 (50 g.), b.p. 77-9°; cut 3, CCl_4 + $C_3Cl_4F_4$ (5:1) (24 g.), b.p. 79-102°; cut 4, CCl_4 + $C_3Cl_4F_4$ (1:5) (14 g.), b.p. 103-110°; cut 5, $C_3Cl_4F_4$ (163 g.), b.p. 111-2°, $n_D^{20.8}$ 1.3991; cut 6, chiefly $C_3Cl_5F_3$ (21 g.), b.p. 119-151°; cut 7, $C_3Cl_5F_3$ (9 g.), b.p. 152-6°; residue (48 g.). The yield of

$C_3Cl_4F_4$ was 42%. A purified sample of cut 6 had b.p. 152–3° (micro), $n_D^{19.8}$ 1.4414. Analysis for $C_3Cl_5F_3$: Calcd.: C, 13.33; Cl, 65.58; F, 21.09. Found: C, 12.87; H, 0.13; Cl, 65.25; F, 21.62.

Reaction of $C_3Cl_4F_4$ with Zinc in Ethanol.

$C_3Cl_4F_4$ (64.5 g., 0.254 mole) was added dropwise to a hot mixture of zinc dust (20 g., 0.31 mole), zinc chloride (1 g.), and absolute ethanol (150 ml.) over 1.5 hours, refluxed for 1.5 hours, filtered, washed and dried to give material which VPC showed to contain ethanol, product, and a small amount of unreacted $C_3Cl_4F_4$. Preparative VPC separation gave a pure product (ca. 6 g.), b.p. 91–2° (micro), $n_D^{20.9}$ 1.3775. Analysis for $C_3HCl_3F_4$: Calcd.: C, 16.42; H, 0.47; Cl, 48.47; F, 34.64. Found: C, 16.31; H, 0.61; Cl, 48.21; F, 34.56. The yield was ca 11%. A large portion was probably lost during the purification steps.

Reaction of $C_3Cl_4F_4$ with Zinc in Dioxane.

$C_3Cl_4F_4$ (72.2 g., 0.284 mole) was added over 1 hour to a hot mixture of zinc dust (21.9 g., 0.337 mole), zinc chloride (1 g.) and dioxane (150 ml.). After heating for 2.5 hours and standing at ambient for 2 days, the mixture was washed and dried to give a liquid (56.9 g.) containing a low boiling component, dioxane and chiefly unreacted $C_3Cl_4F_4$. Distillation and chromatographic separation gave small amount (ca 3 g.) material, b.p. 47–9°, infrared bands at 6.04µ and 5.97µ (shoulder). Analysis for $C_3Cl_2F_4$: Calcd.: C, 19.70; Cl, 38.75; F, 41.55. Found: C, 19.87; H, 0.13; Cl, 38.51; F, 41.49 (by difference). The calculated yield was 9%.

Reaction of $C_3Cl_4F_4$ with "Activated" Zinc in Dioxane.

"Activated" zinc was prepared by washing zinc dust (200 g.) with 2N HCl (500 ml.) for 4 minutes, filtered, washed several times with distilled water, and vacuum dried for 5 hours (100°, 25-80 mm.).

$C_3Cl_4F_4$ (21.9 g., 0.86 mole) in dioxane (10 ml.) was added over 1 hour to a heated mixture of "activated" zinc (10 g., 0.15 mole) in dioxane (100 ml.) with zinc chloride added. After refluxing for 2.5 hours, the mixture was filtered, washed and dried to give a liquid (8.3 g.) containing $C_3Cl_2F_4$, $C_3HCl_3F_4$, $C_3Cl_4F_4$ and traces of other components. VPC separation gave $C_3Cl_2F_4$ (1.4 g.), b.p. 45-6° (micro), $n_D^{20.0}$ 1.3518, infrared band at 6.03μ with shoulders at 5.85μ and 5.77μ and $C_3HCl_3F_4$ (1.9 g.), b.p. 85-6° (micro), $n_D^{20.0}$ 1.3920. The calculated yield of olefin was 17%.

Reaction of $C_3Cl_5F_3$ with Zinc in Ethanol.

$C_3Cl_5F_3$ (22.9 g., 0.085 mole) in ethanol (25 ml.) was added in 1 hour to a heated mixture of zinc dust (7.0 g., 0.107 mole) and absolute ethanol (100 ml.) then refluxed for 3 hours and left at ambient overnight. Work up gave a liquid (11.0 g.) containing $C_3Cl_3F_3$ (64%, yield 41%). Chromatographic purification (S.E., 100°) gave pure $C_3Cl_3F_3$, b.p. 88-9° (micro), $n_D^{21.0}$ 1.4020, d_4^{23} 1.596 g./cc., infrared bands at 6.07μ (w) and 6.28μ (s); identified by comparison with an authentic sample.

Some Lewis Acid Catalyzed Additions of Haloalkanes to Haloölefins

Addition of $CFCl_3$ to $CF_2{=}CCl_2$ Catalyzed by $AlCl_3$.

A Fisher-Porter tube was charged with $CFCl_3$ (63 g., 0.46 mole),

CF_2=CCl_2 (30 g., 0.225 mole) and $AlCl_3$ (12 g., 0.09 mole) and rocked at room temperature for 24 hours. Work up gave a liquid (79 g.) containing unreacted material (15%), CCl_4 (39%), $C_3Cl_5F_3$ (41%, 32 g., 53% overall yield), and $C_3Cl_6F_2$ (5%). Distillation gave pure $C_3Cl_5F_3$, b.p. 60°/28 mm.-60°/26 mm.. This material contained both liquid and crystals. The solid was separated by fractional crystallization to give a waxy white solid, m.p. 81-84.5°. Both materials are currently being investigated by NMR.

Reaction of $CFCl_3$ and Perfluorocyclobutene Catalyzed by $AlCl_3$.

The olefin (46 g., 0.28 mole) was bubbled slowly through a mixture of $CFCl_3$ (123 g., 0.90 mole) and $AlCl_3$ (10.7 g., 0.08 mole) at 0°. This was repeated four times in 4 hours. Normal work up gave a material (37 g.) which was solid at room temperature. In addition to $CFCl_3$ and CCl_4 was isolated a compound (11%, 1.9 g.), b.p. 135-6° (micro), $n_D^{20.8}$ 1.4606, d_4^{23} 1.579 g./cc., with a strong infrared band at 6.13µ. Analysis for cyclo-$C_4Cl_4F_2$: Calcd.: C, 21.08; Cl, 62.23; F, 16.69. Found: C, 22.03; H, 0.21; Cl, 59.96; F, 18.35. Also found as the chief product (65%) was a compound (18 g.), b.p. 208-12°, m.p. 32-3°, infrared bands at 6.12µ (s) and 6.41µ (m). Analysis for cyclo-C_4Cl_6: C, 18.42; Cl, 81.58. Found: C, 19.13; H, 0.49; Cl, 79.19; F, 0.96. This latter was a doublet by VPC and could not be resolved.

Reaction of Perfluorocyclobutene with $AlCl_3$.

Perfluorocyclobutene (46 g., 0.28 mole) and $AlCl_3$ (11 g., 0.082 mole) were sealed in a Fisher-Porter tube at -78°. After rocking for 3 hours at 0°, the mixture was left at room temperature for 1.5 days. Normal work up gave a liquid (21.5 g.) containing three components.

These were identified after purification as cyclo-$C_4Cl_2F_4$ (60%), b.p. 66–7° (micro), $n_D^{20.0}$ 1.3724, d_4^{23} 1.537 g./cc., with a strong infrared band at 6.17μ; the other two components, combined, had infrared bands at 5.56μ (vs), 5.81μ (vs) and 6.12μ (w) and were cyclo-C_4F_6 (18%) and cyclo-C_4ClF_5 (22%).

A second run using perfluorocyclobutene (27 g., 0.167 mole) and $AlCl_3$ (11 g., 0.082 mole) and rocked at room temperature for 4.5 hours gave an exothermic reaction. Aluminum chloride (2 g.) was added and the mixture was rocked for a further 4 hours. Work up gave material (17.7 g.) consisting of unreacted cyclo-C_4F_6 (2%), cyclo-C_4ClF_5 (12%) and cyclo-$C_4Cl_2F_4$ (86%).

Addition of CF_2Cl_2 to CFCl=CFCl Catalyzed by $AlCl_3$.

A Fisher-Porter tube was charged with CF_2Cl_2 (43 g., 0.35 mole), CFCl=CFCl (41 g., 0.31 mole) and $AlCl_3$ (4.4 g., 0.033 mole) and rocked for 1 hour at room temperature when $AlCl_3$ (5 g.) was added and left overnight. Venting gave unreacted material (46 g.) and a material (21.2 g.) which VPC showed did not contain any $C_3Cl_4F_4$. After two more runs and chromatographic purification the three components of the product were identified as: CCl_4; CCl_2=CCl_2, b.p. 118–9° (micro), $n_D^{21.0}$ 1.5015, infrared bands only at 10.95μ (vs), 12.45μ (m), 12.83μ (vs) and 13.2μ (w), identified by comparison with a pure sample; and $C_3Cl_5F_3$, b.p. 152–3° (micro), $n_D^{21.0}$ 1.4411.

Addition of CF_2Cl_2 to CF_2=CFCl Catalyzed by $AlCl_3$.

Into a cooled autoclave (−78°) was placed $AlCl_3$ (20 g., 0.15 mole), CF_2=CFCl (94 g., 0.80 mole) and CF_2Cl_2 (132 g., 1.09 mole). After 6 hours at room temperature, venting gave low boiling material (189 g.) but no adduct.

A second run, using the above product (165 g.) and $AlCl_3$ (20 g.), kept at 60° for 6 hours and then at room temperature overnight, gave low boiling material (111 g.) and product (20.4 g.).

A third run using $AlCl_3$ (30 g., 0.225 mole), CF_2Cl_2 (87 g., 0.72 mole) and CF_2=CFCl (85 g., 0.73 mole) was heated at 60° for 44.5 hours to give low boiling material (4 g.) and a liquid (79 g,) (after combination with above product) which on distillation gave a chief product, $C_3Cl_4F_4$ (35 g.), b.p. 113-5°. Analysis: Calcd.: Cl, 55.86. Found: Cl, 53.61.

Reaction of $C_3Cl_4F_4$ with Zinc in Dioxane.

$C_3Cl_4F_4$ (20.9 g., 0.082 mole) was added in 10 minutes to a heated mixture of zinc dust (8.5 g., 0.13 mole), zinc chloride (1 g.) and dioxane (100 ml.) and then heated for 4 hours. Work up gave a four component mixture which was separated (S.E., 170°) into: Cut 1, a very volatile product with a strong infrared band at 6.01μ. Analysis for olefin $C_3Cl_2F_4$: Calcd.: C, 19.70; Cl, 38.75; F, 41.55. Found: C, 19.48; H, 0.15; Cl, 36.22; F, 44.15 (by difference). Cut 2, b.p. 89-90° (micro), $n_D^{21.0}$ 1.3811, weak infrared band at 6.06μ. Analysis for $C_3HCl_3F_4$: Calcd.: C, 16.42; H, 0.47; Cl, 48.47; F, 34.64. Found: C, 17.04; H, 0.30; Cl, 49.76; F, 32.90 (by difference). Cut 3, b.p. 111-2° (micro), $n_D^{21.0}$ 1.3971, $C_3Cl_4F_4$. Cut 4, b.p. 119-20° (micro), $n_D^{21.0}$ 1.4996. Analysis for C_2Cl_4: Calcd.: C, 14.48: Cl, 85.52. Found: C, 14.95; H, 0.03; Cl, 83.96. This was present in the original sample of $C_3Cl_4F_4$.

Reaction of $CF_2BrCFClBr$ and CFCl=CFCl Catalyzed by $AlCl_3$.

$CF_2BrCFClBr$ (292 g., 1.06 mole) was added to $AlCl_3$ (29 g., 0.22 mole) followed by CFCl=CFCl (134 g., 1.01 mole). VPC showed only one product being formed. The mixture was filtered and fresh $AlCl_3$ (28 g.) was added, refluxed for 2 hours and left at room temperature overnight. CFCl=CFCl (93 g.) was distilled out, followed by $CF_2BrCFClBr$ (146 g.); and an almost pure material (41 g.), b.p. 61°/52 mm. (140°/760 mm.), m.p. 40-1°, identified as CFClBrCFClBr. Elemental analysis for $C_2Br_2Cl_2F_2$: Calcd.: C, 8.19; Br, 54.63; Cl, 24.21; F, 12.97. Found: C, 8.35; Br, 54.36; Cl, 23.95; F, 13.34 (by difference); and a residue (33 g.), chiefly C_2Cl_6.

Reaction of $CF_2BrCFClBr$ with $AlCl_3$.

$CF_2BrCFClBr$ (104 g., 0.38 mole) and $AlCl_3$ (10 g., 0.075 mole) were stirred in an ice bath (0-15°) for 5.5 hours but no reaction occurred. After 4 days at ca 5°, no change had taken place but on stirring at 25-30° for 1 hour with careful temperature control the mixture turned solid. Extraction with ether followed by distillation gave a residue (100 g.) from which further distillation gave a product (58 g.), b.p. 92.5°, m.p. 41-2°. Analysis for $C_2Br_2ClF_3$: Calcd.: C, 8.69; Br, 57.85; Cl, 12.83; F, 20.63. Found: C, 7.53; H, 0.03; Br, 58.27; Cl, 11.73; F, 21.46. This has been tentatively identified as CF_3CBr_2Cl. Also present was some CFClBrCFClBr.

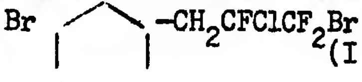
Reaction of CFCl=CFCl with $AlCl_3$.

A Fisher-Porter tube containing CFCl=CFCl (42 g., 0.316 mole) and $AlCl_3$ (3 g., 0.022 mole) was heated to 62-8° for 22 hours. VPC indicated no reaction had occurred.

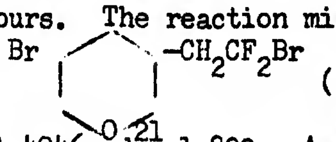
A second run using CFCl=CFCl (43 g., 0.32 mole) and $AlCl_3$ (9 g., 0.067 mole) at room temperature for 24 hours, at 54° for 12 hours with more $AlCl_3$ (3 g.,) and then overnight at room temperature also gave no reaction.

Preparation of Unsaturated Ethers

Addition of $CF_2BrCFClBr$ to Diallyl Ether.

A stirred solution of $CF_2BrCFClBr$ (498 g., 1.8 mole), diallyl ether (32.7 g., 0.3 mole) and benzoyl peroxide (5 g.) was refluxed for 3 hours. Unreacted starting materials were distilled off and the residue was washed with sodium bicarbonate solution and water, and dried. Fractional distillation gave  (I), (69.7 g., 62.1%. An analytical sample which was separated by VPC had the following properties: b.p. 88°/0.15 mm., n_D^{20} 1.4940, d^{20} 1.878. Analysis calcd. for $C_8H_{10}Br_2ClF_3O$: MR_D 58.98; C, 25.92; H, 2.70; F, 15.23. Found: MR_D 58.24; C, 25.67; H, 2.70; F, 15.23%.

Addition of CF_2Br_2 to Diallyl Ether.

A solution of CF_2Br_2 (763 g., 3.63 mole), diallyl ether (89 g., 0.91 mole) and benzoyl peroxide (12 g.) was heated in an autoclave (300 ml.) at 100° ± 5° for 5 hours. The reaction mixture was worked up as described above to yield  (II) (82.6 g., 29.2%); b.p. 70°/0.2 mm., n_D^{21} 1.4946; d^{21} 1.823. Analysis calcd. for $C_7H_{10}Br_2F_2O$: MR_D 49.60; C, 27.30; H, 3.27. Found: MR_D 49.34; C, 27.26; H, 3.27

Dehalogenation of I.

A stirred suspension of powdered zinc (13.1 g.), zinc chloride

(0.5 g.) and ethanol (100 ml.) was refluxed while (I) (37.4 g., 0.1 mole) was added dropwise. The refluxing mixture was stirred for a further 3 hours. The solution was washed, dried, and fractionally distilled to give 3-(1;1;2'-trifluoroallyl)-5-bromo-tetrahydropyran (III) (7.3 g., 28.2%). An analytical sample which was separated by VPC had the following properties: b.p. 62°/0.2 mm.; n_D^{21} 1.4594; d^{21} 1.546. Analysis calcd. for $C_8H_{10}BrF_3O$: MR_D 46.11; C, 37.09; H, 3.89; Br, 30.84; F, 22.00. Found: MR_D 45.84; C, 36.93; H, 3.89; Br, 30.88; F, 22.12

Reaction of I with $LiAlH_4$.

Lithium aluminum hydride (9.4 g., 0.24 mole) was placed in a cooled 1 lt. flask and tetrahydrofuran (100 ml.) was added with stirring. The suspension was heated to reflux and the ether (I) (91.0 g., 0.24 mole) was added dropwise at a rate sufficient to maintain reflux without external heating.

The mixture was refluxed for another hour, cooled and water added carefully. The mixture was stirred into cold dilute sulphuric acid, the organic layer was separated, washed with water and dried. Fractional distillation gave 3-(1;1;2'-trifluoroallyl)-tetrahydropyran (IV) (13.0 g., 30.1%) and 3-(1;1;2'-trifluoroallyl)-5-bromo-tetrahydrofuran (III), which was consistent with the previously prepared sample.

An analytical sample of (IV) which was separated by VPC, had the following properties: b.p. 76°/32 mm., n_D^{20} 1.4107; d^{20} 1.137. Analysis calcd. for $C_8H_{11}F_3O$: MR_D 38.43; C, 53.33; H, 6.15; F, 31.63. Found: MR_D 39.53; C, 54.33; H, 6.61; F, 28.82.

Addition of Chlorine to Diallyl Ether.

Chlorine was bubbled through a solution of diallyl ether (98 g., 1.0 mole) and conc. hydrochloric acid (600 g.) at 3°– 7°. The organic layer was separated, washed with water and dried. Fractional distillation gave $CH_2ClCHClCH_2OCH_2CH{=}CH_2$ (V) (44.7 g., 27.4%) and $(CH_2ClCHClCH_2)_2O$ (VI) (78.0 g., 32.5%), which had properties consistent with an authentic sample.

An analytical sample of (V) had the following properties: b.p. 52°/2.6 mm.; n_D^{21} 1.4645, d^{21} 1.152. MR_D calcd.: 40.68; found: 40.89.

Addition of $CF_2BrCFClBr$ to (V).

A solution of $CF_2BrCFClBr$ (110 g., 0.4 mole), the ether V (16.9 g., 0.1 mole) and benzoyl peroxide (3 g.) was refluxed for 3 hours. Unreacted starting materials were distilled off and the residue was washed with sodium bicarbonate solution, and water and finally dried. Fractional distillation of the residue gave $CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (VII) (12.9 g., 29.0%). An analytical sample separated by VPC had the following properties: b.p. 105°/0.2 mm., n_D^{20} 1.4911, d^{20} 1.808. Analysis calcd. for $C_8H_{10}Br_2Cl_3F_3O$: MR_D 70.91; C, 21.58; H, 2.26; F, 12.78. Found: MR_D 71.40; C, 22.84; H, 2.63; F, 13.33.

Dehalogenation of $CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (VII).

The ether (VII) (55.0 g., 0.12 mole) was added dropwise to a stirred refluxing suspension of powdered zinc (31.2 g., 0.48 mole) and zinc chloride (1.0 g.) in absolute ethanol (100 ml.). The mixture was refluxed for a further hour. The suspension was poured into water, extracted with ether and dried. Fractional distillation gave CH_2ClCH $ClCH_2OH$ (8.5 g.) and $CF_2{=}CFCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (VIII) (9.3 g.); b.p. 76°/0.3 mm; n_D^{20} 1.4661; d^{20} 1.584. Analysis calcd. for $C_8H_{10}BrCl_2F_3O$: MR_D 57.92; C, 29.16; H, 3.05; F, 17.26. Found: MR_D 57.74; C, 29.91; H, 3.04; F, 18.51.

Some Reactions of Haloalkyllithium Compounds with Fluoroölefins

Reaction of Dichloromethyllithium with Chlorotrifluoroethylene.

A solution of n-butyl lithium in n-hexane (10 g., 0.023 mole) was added over a period of 1 hour to a solution of methylene chloride (17.0 g., 0.20 mole) and tetrahydrofuran (50 ml.) at -78°. Chlorotrifluoroethylene was then bubbled through the mixture. After being allowed to attain room temperature, the reaction mixture was treated with dilute hydrochloric acid and dried. Unreacted olefin and solvent were distilled off and the residue was separated by VPC to yield a product which gave infrared absorption at 5.66μ. Further identification was not made due to lack of material.

Reaction of Trichloromethyllithium with $CF_2=CCl_2$.

A solution of chloroform (7.2 g., 0.06 mole) and tetrahydrofuran/ether/petroleum ethers (4:1:1, 60 ml.) was treated with n-butyl lithium in n-hexane (10.2 g., 0.024 mole) at -110° to -115° and then with excess 1,1-dichlorodifluoroethylene. After being allowed to attain room temperature, the reaction mixture was worked up as before. Fractional distillation gave 1,1-difluorotetrachloropropane (3.9 g., 75.3%). An analytical sample which was separated by VPC had the following properties:

b.p. 136-137°, n_D^{20} 1.4437, d^{20} 1.612.

Analysis calcd. for $C_3Cl_4F_2$: MR_D 33.31, C, 16.70; F, 17.61. Found: MR_D 34.02; C, 17.13; F, 18.84%.

Preparation of Trichlorofluoromethyllithium and Its Reaction with Hexafluorocyclobutene.

A solution of dichlorofluoromethane (9.5 g., 0.092 mole) and tetrohydrofuran/ether/ pet. ether (4:1:1, 60 ml.) was treated with n-butyllithium in hexane (16.8 g., 0.04 mole) at -110° to -115° over the period of 2 hours and then with hexafluorocyclobutene (6.2 g., 0.05 mole).

After being allowed to attain room temperature the reaction mixture was filtered and the filtrate was worked up as before. The white solid residue (0.9 g., 86.6%) was identified as lithium fluoride by a fluoride ion test.

Fractional distillation of the filtrate gave n-octane (1.40 g.); b.p. 125.5° (lit. 125.8°), n_D^{21} 1.4189; d^{21} 0.7372 (lit. d^{18} 0.7042). MR_D, Calcd.: 39.15. Found: 38.91.

n-Buthyllithium was treated with various reactants in various solvents, as indicated in the table below but the product was always n-octane, with very small amounts of unidentified material.

TABLE I

SOLVENT	REACTANT
Tetrahydrofuran/ether/petroleum ether (2:1:1)	CF_2=CFCl.
Ether; petroleum ether (1:1)	CF_2=CFCl.
Ether	CF_2=CFCl.
n-Pentane	
Tetrahydrofuran/n-pentane (1:1)	CF_2=CCl_2.
Tetrahydrofuran/n-pentane (1:2)	cyclohexene
Tetrahydrofuran/n-pentane (1:1)	$HgCl_2$

Radical Induced Additions to Olefins

Preparation and Reaction of $(CH_3)_3SiCF{=}CF_2$.

Bromomethane was bubbled through ether (250 ml.) containing freshly sliced lithium (14 g., 2 mole) at −10 to + 10°, until the lithium dissolved. The mixture was cooled to −78° and $CF_2{=}CFBr$ (1 mole) was bubbled through the mixture. After standing at −78° for 2 hours, $(CH_3)_3SiCl$ (1 mole) was added and the mixture allowed to attain room temperature, at which it stood for 30 minutes. The mixture was cooled to 0° and hydrolysed by 5% aqueous hydrochloric acid. The ethereal solution was dried and fractionated to yield $(CH_3)_3SiCF{=}CF_2$ (38 g.).

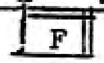
$CF_2BrCFClBr$ (83 g., 0.3 mole), $(CH_3)_3$ $SiCF{=}CF_2$ (15 g., 0.1 mole) and benzoyl peroxide (0.3 g.) were heated in a Pyrex sealed tube at 100° for 2 hours. Gas chromatographic examination of the product showed no products of higher b.p. than starting materials.

Addition of $CCl_3CF_2CF_3$ and $CCl_3CF_3CF_2Cl$ to Olefins.

A stainless steel autoclave containing $CCl_3CF_2CF_3$ (248 g., 1.04 mole), isobutylene (20 g., 0.35 mole) and benzoyl peroxide (5 g.) was agitated at 100° for 12 hours. The product was dried and fractionated to yield unreacted $CF_3CF_2CCl_3$ (182 g.). The residue was vacuum distilled to yield $CF_3CF_2CCl_2CH_2C(CH_3)_2Cl$ (41 g.) with the properties shown in Table II, and some dehydrochlorination product.

The reaction was repeated with various olefins and alkanes and the results were summarised in Table II.

TABLE II

Haloalkane	Olefin	Structure	Conv.%	b.p.°/mm.	n_D^{21}	d^{24}	MR_D Calcd.	MR_D Found	Cl Analysis Calcd. %	Cl Analysis Found %
$CF_3CF_2CCl_3$	$CH_2=CH_2$	$CF_3CF_2CCl_2CH_2CH_2Cl$	15	33/10	1.3942	1.5225	39.95	41.35	40.11	37.54
	$CH_2=CHCH_3$	$CF_3CF_2CCl_2CH_2CHClCH_3$	16	70/32	1.3970	1.4871	44.58	44.22	38.10	37.91
	$CH_2=C(CH_3)_2$	$CF_3CF_2CCl_2CH_2C(CH_3)_2Cl$	40	50/6	1.4065	1.4397	49.21	49.61	36.28	36.12
	$CH_2=CHCH_2Cl$	No Reaction								
$CF_2ClCF_2CCl_3$	$CH_2=CHCH_3$	$CF_2ClCF_2CCl_2CH_2CHClCH_3$	20	47/2	1.4276	1.4902	51.39	50.96	47.93	49.14
	$CH_2=C(CH_3)_2$	$CF_2ClCF_2CCl_2CH_2C(CH_3)_2Cl$	15	47/0.5	1.4344	1.4301	56.02	56.50	45.81	44.88
	$CH_2=CHCH_2Cl$	No Reaction								
CFClBrCFClBr	$CH_2=CH_2$	1. $CFCl=CFCl$	20	Known Compound					Br Analysis:	
		2. CH_2BrCH_2Br	—	Known Compound						
		3. $CFClBrCFClCH_2CH_2Br$	17	53/2					50.16	49.98
$CCl_3CF_2CFClBr$	$CH_2=CH_2$	$CCl_3CF_2CFClCH_2CH_2Br$*	40	60/0.5	Identified by NMR spectroscopy.					
CCl_3Br	 F	No Reaction								
$CFCl_2CFCl_2$	$CH_2=CH_2$	No Reaction								
$CFCl_2CF_2Cl$	$CH_2=CH_2$	No Reaction								

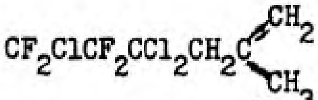
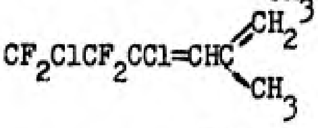
---

* Also identified by detection of $Br^{\ominus}$ from dehydrohalogenation.

Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2C(CH_3)_2Cl$.

$CF_2ClCF_2CCl_2CH_2C(CH_3)_2Cl$ (15 g., 0.05 mole) was refluxed with ethanolic (25 ml.) potassium hydroxide (11 g., 0.2 mole) for 2 hours. The reaction mixture was poured into water (200 ml) and the organic product separated and dried. The product (8 g.) showed four major components by VPC, three of which were isolated in a pure state and identified (see properties in Table III). The fourth product contained trace impurities, but the infrared spectrum showed absorption at 5.02μ which is associated with the allene structure.

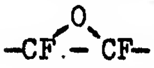
TABLE III

Molecular Formula	Possible Structure	Analysis Calcd. Cl	Analysis Found Cl	Infrared Absorption(μ)
$C_7H_7Cl_3F_4$	$CF_2ClCF_2CCl_2CH{=}C(CH_3)_2$  $CF_2ClCF_2CCl_2CH_2C(=CH_2)CH_3$	38.95	38.55	6.1
$C_7H_6Cl_2F_4$	 $CF_2ClCF_2CCl{=}CHC(=CH_2)CH_3$	30.05	29.96	6.12, 6.26
$C_7H_5ClF_4$	 $CF_2ClCF_2C{\equiv}CC(=CH_2)CH_3$	17.69	17.62	4.44, 6.18
*$C_7H_5ClF_4$	$CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$	—	—	5.04

*Trace impurities present.

Attempted Preparation of Fluoroepoxides

Attempted Epoxidation of Octafluoro-2-butene.

Potassium hydroxide (8.4 g.) was dissolved in water (10 ml.) and acetone (75 ml.) was added. The mixture was cooled to -40° and 30% hydrogen peroxide (60 ml.) was added. The mixture was stirred at -40° while octafluoro-2-butene (4.7 g.) was condensed into the flask and the total mixture was stirred vigorously at -30° for 3 hours. After warming up to room temperature, the low boiling products (1.0 g.) distilled into a trap cooled in acetone/dry ice. VPC purification removed a trace component to give a main product of suspected 2,3-epoxyoctafluorobutane with infrared absorption at 6.67μ characteristic of the  $-CF\overset{O}{-}CF-$ grouping.

Attempted Epoxidation of Hexafluorocyclobutene.

Perfluorocyclobutene (10.8 g.) was condensed into a solution of potassium hydroxide (8.4 g.) in water (10 ml.), acetone (75 ml.) and hydrogen peroxide (60 ml.) at -60°. On stirring at -50° a vigorous reaction took place which was completed by stirring for 3.5 hours while the mixture warmed up to room temperature. The low boiling material (2.2 g.) which was distilled into a trap cooled in acetone/dry ice, was shown by VPC and infrared spectroscopy to be mainly hexafluorocyclobutene.

The residue was distilled under reduced pressure to remove acetone and extracted with ether. The ethereal solution was shaken with ferrous ammonium sulphate solution and dried (Drierite). Evaporation to dryness yielded a white solid (3.0 g.) which is still under investigation.

Attempted Epoxidation of 1,1,2-Trifluoro-1,3-butadiene.

1,1,2-Trifluoro-1,3-butadiene (4.4 g.) was condensed into a flask containing stirred potassium hydroxide (8.4 g.), acetone (75 ml.), water (10 ml.), hydrogen peroxide (60 ml.) and hydroquinone (0.4 g.) at −30°. The mixture was stirred at −30° for 3.5 hours then quickly warmed to +25° to distill out volatile products (2.4 g.). The infrared spectrum of the volatile product was very similar to starting material.

V. FUTURE WORK

Additional study will be made of the reactions leading to the production of $CF_2=CFCF_2I$, which is a precursor to $CF_2=CFCF_2NO$.

Work will be continued toward the preparation of nitroso acids. Specifically attempts will be made to prepare $CF_2ClCF(NO)C_6H_4CO_2H$ by the addition of NOCl to trifluorovinylbenzoic acid.

Research will be carried out to determine if new and interesting monomers can be made from dibromides such as CF_2BrCF_2Br, $CF_3CFBrCF_2Br$ and $CF_3CFBrCFBrCF_3$.

Research will also be carried out to find means of alkylating fluoro-aromatic compounds. For instance, it is expected that $CF_2BrCFClBr$ and C_6F_5H can be made to react to give $CF_2BrCFClC_6F_5$, which could be dehalogenated to perfluorostyrene.

VI. BIBLIOGRAPHY

1. Semiannual Report 3, April 1964 - September, 1964, p. 17.
2. P. Tarrant and D. Warner, J.A.C.S., 76, 1624 (1954).
3. A. H. Fainberg, W. T. Miller Jr., ibid., 79, 4170 (1957).
4. W. T. Miller Jr., E. W. Fager, P. H. Griswold, ibid. 70, 431 (1948).
5. J. D. Park, D. K. Vail, K. R. Lea, J. R. Lacher, ibid. 70, 1550 (1948).
6. P. Tarrant, H. C. Brown, ibid. 73, 1781 (1951).
7. E. S. Lo, U.S. Pat. 2,856,435 (Oct. 14, 1958).
8. E. S. Lo, U.S. Pat. 2,975,163 (March 14, 1961).
9. A. Lannung, Z. physik. Chem., A 161, 255; A162, 262 (1932).
10. A. Posta, O. Paleta, Czech. Pat. 106,812 (March 15, 1963).
11. D. D. Coffman, R. Cramer, G. W. Rigby, J.A.C.S. 71, 979 (1949).
12. A. Posta, O. Paleta, Czech. Pat. 105,966 (Dec. 15, 1962).
13. H. Madai, R. Mueller, J. Prakt. Chem., 19, 83 (1962).
14. P. Tarrant, E. C. Stump, Jr. J. Org. Chem., 26, 4646 (1961); ibid., 29, 1198 (1964).
15. W. S. Friedlander, Abstract of Papers, 133rd Meeting A.C.S., April 1958, 18N.
16. W. S. Friedlander et al., Ger. Pat. 109,849, (Sept. 29, 1958).
17. J. E. Johnson et al., J.A.C.S., 70, 3664 (1948).
18. H. Williams, T. W. Evans, U.S. Pat. 2,464,758, (March 15, 1949).
19. G. Köbrich et al., Angew. Chem., 3, 513 (1964).
20. W. T. Miller, Jr. et al., J.A.C.S., 86, 2089 (1964).
21. D. F. Hoeg et al, Abstract of Papers, 149th Meeting A.C.S., April 1965, 52P.
22. S. Dixon, J. Org. Chem., 21, 400 (1956).
23. D. Seyferth, T. Wada, G. E. Macial, Inorg. Chem., 1, 232 (1962).
24. C. Walling, "Free Radicals in Solution", J. Wiley and Sons, Inc. New York, N. Y.,
25. A. Lovelace et al., Reinhold Publishing Corp. New York, N.Y., 1958.

26. P. Tarrant, H. Muramatsu, J. Org. Chem. 29, 1796 (1964).

27. E. I. du Pont de Nemours, Brit. Pat., 904,877 (Sept. 5, 1962).

28. J. D. Park, J. R. Lacher. Univ. of Colorado, Contract Report U. S. Army, April - October 1964.

29. P. Tarrant, M. Lilyquist, J.A.C.S., 77, 3640 (1955).

AD ______________________ Accession No. ______

Department of Chemistry, University of Florida, Gainesville, Fla. RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS – Paul Tarrant, Doug Perry, Jai Tandon, Alan Wright, Susumu Misaki. March 31, 1965, 38pp. (Semiannual Report 4) Unclassified Report. A study has been made for producing perfluoroallyl bromide and iodide. The latter olefin reacted with alcohols to produce ethers such as CF_3-$CH_2OCF_2CF{=}CF_2$. Attempts to prepare $(CF_2{=}CFCH_2CH_2CH_2)_2O$ from the allyl ethers have been carried out but cyclic ethers were formed. An investigation of the radical addition of $CF_3CF_2CCl_3$, CF_2ClCF_2-CCl_3, CFClBrCFClBr and $CCl_3CF_2CFClBr$ with various olefins has been initiated. Studies of the preparation of perfluoroalkane epoxides have been initiated.

UNCLASSIFIED
1. Organic Fluorine Chemistry
2. Elastomers

I. Tarrant, Paul
II. UNSATURATED FLUOROCARBONS
III. University of Florida

AD ______________________ Accession No. ______

Department of Chemistry, University of Florida, Gainesville, Fla. RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS – Paul Tarrant, Doug Perry, Jai Tandon, Alan Wright, Susumu Misaki. March 31, 1965, 38pp. (Semiannual Report 4) Unclassified Report. A study has been made for producing perfluoroallyl bromide and iodide. The latter olefin reacted with alcohols to produce ethers such as CF_3-$CH_2OCF_2CF{=}CF_2$. Attempts to prepare $(CF_2{=}CFCH_2CH_2CH_2)_2O$ from the allyl ethers have been carried out but cyclic ethers were formed. An investigation of the radical addition of $CF_3CF_2CCl_3$, CF_2ClCF_2-CCl_3, CFClBrCFClBr and $CCl_3CF_2CFClBr$ with various olefins has been initiated. Studies of the preparation of perfluoroalkane epoxides have also been initiated.

UNCLASSIFIED
1. Organic Fluorine Chemistry
2. Elastomers

I. Tarrant, Paul
II. UNSATURATED FLUOROCARBONS
III. University of Florida

AD ______________________ Accession No. ______

Department of Chemistry, University of Florida, Gainesville, Fla. RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS – Paul Tarrant, Doug Perry, Jai Tandon, Alan Wright, Susumu Misaki. March 31, 1965, 38pp. (Semiannual Report 4) Unclassified Report. A study has been made for producing perfluoroallyl bromide and iodide. The latter olefin reacted with alcohols to produce ethers such as CF_3-$CH_2OCF_2CF{=}CF_2$. Attempts to prepare $(CF_2{=}CFCH_2CH_2CH_2)_2O$ from the allyl ethers have been carried out but cyclic ethers were formed. An investigation of the radical addition of $CF_3CF_2CCl_3$, CF_2ClCF_2-CCl_3, CFClBrCFClBr and $CCl_3CF_2CFClBr$ with various olefins has been initiated. Studies of the preparation of perfluoroalkane epoxides have also been initiated.

UNCLASSIFIED
1. Organic Fluorine Chemistry
2. Elastomers

I. Tarrant, Paul
II. UNSATURATED FLUOROCARBONS
III. University of Florida

AD ______________________ Accession No. ______

Department of Chemistry, University of Florida, Gainesville, Fla. RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS – Paul Tarrant, Doug Perry, Jai Tandon, Alan Wright, Susumu Misaki. March 31, 1965, 38pp. (Semiannual Report 4) Unclassified Report. A study has been made for producing perfluoroallyl bromide and iodide. The latter olefin reacted with alcohols to produce ethers such as CF_3-$CH_2OCF_2CF{=}CF_2$. Attempts to prepare $(CF_2{=}CFCH_2CH_2CH_2)_2O$ from the allyl ethers have been carried out but cyclic ethers were formed. An investigation of the radical addition of $CF_3CF_2CCl_3$, CF_2ClCF_2-CCl_3, CFClBrCFClBr and $CCl_3CF_2CFClBr$ with various olefins has been initiated. Studies of the preparation of perfluoroalkane epoxides have also been initiated.

UNCLASSIFIED
1. Organic Fluorine Chemistry
2. Elastomers

I. Tarrant, Paul
II. UNSATURATED FLUOROCARBONS
III. University of Florida