Distribution of this
document is unlimited

AD

AD 662712

TECHNICAL REPORT
67-79-CM

RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS

Final Report

by

P. Tarrant, O. J. Stewart, F. G. Drakesmith,
D. Sayers, J. Heyes, W. Oliver, A. C. Wright,
D. Perry, J. Tandon, A. Wright and S. Misaki.

University of Florida

Contract No. DA19-129-AMC-79(N)

Project Reference:
1C024401A329

Series: C & OM-33

March 1967

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

FOREWORD

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

This research is authorized under Contract Number DA19-129-AMC-79(N) and is a further continuation of the work initiated under DA44-109-QM-522 and continued under DA44-109-AM-1469 and DA19-129-QM-500.

This is the 8th report prepared under the contract and the 55th since the project was initiated in 1951.

S. J. KENNEDY
Director
Clothing & Organic Materials Division

APPROVED:

DALE H. SIELING, PhD.
Scientific Director

W. M. MANTZ
Brigadier General, USA
Commanding

CONTENTS

ABSTRACT

Synthesis of a variety of fluorine-containing compounds was studied. A convenient synthesis of perfluoroallyl halides was developed. Lewis acid catalyzed addition of haloalkanes to olefins resulted in new fluoroölefins. A series of fluorine monomers were prepared for polymerization studies. A number of partially fluorinated norbornadienes were prepared by the reaction of cyclopentadiene with haloölefins and subsequent dehalogenation. Several new fluorinated nitroso monomers were prepared. A series of compounds of the general structure $(CH_3)_3SiCF=CFR$ were synthesized utilizing organolithium reagents. Alcoholysis of these compounds provides a convenient route to 1,2-difluoroölefins. Several other unsaturated fluoro-organometallic compounds were prepared and their reactions studied. It was found that they could be reacted with carbonyl compounds to produce alcohols which on dehydration gave fluorinated dienes.

RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS

I. SUMMARY

1. A convenient synthesis of perfluoroallyl halides was developed and a number of reactions of these compounds studied. A number of useful fluoroölefins were obtained from their reaction with (1) alkoxides and (2) allyl magnesium bromide.

2. Lewis acid catalyzed addition of haloalkanes to haloölefins were studied. A number of halogenated alkanes were obtained and many of these were converted to fluoroölefins by dehalogenation and/or dehydrohalogenation.

3. An investigation addition of haloalkanes to olefins in the presence of peroxide was carried out, and the olefins were prepared from many of the products by dehalogenation and/or dehydrohalogenation.

4. A number of monomers were prepared for contract associates.

5. Attempts were made, by various means, to prepare radicals from $CF_2BrCFClBr$ and $CF_2BrCFClI$ and react them <u>in situ</u> with aromatic compounds to give substituted aromatics. Success was limited and work on this reaction was terminated.

6. A number of partially fluorinated norbornadienes were prepared by the reaction of cyclopentadiene with haloölefins followed (where necessary) by dehalogenation of the product.

7. Addition of nitrosyl chloride to a number of unsaturated fluorine compounds afforded nitroso compounds which were generally of limited stability.

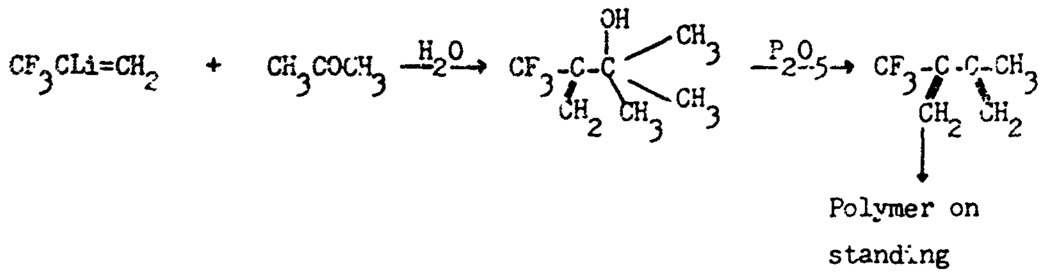
8. A number of reactions of fluoroketanes were described.

9. A series of compounds of general structure $(CH_3)_3SiCF=CFR$ were synthesized by reaction of trimethyltrifluorovinylsilane with organolithium reagents (RLi). Alcoholysis of these products provided a convenient route to 1,2-difluoroölefins. Numerous other silanes containing the trifluorovinyl group were also prepared.

10. Reactions of unsaturated Grignard and organolithium reagents

were studied. (1) Reaction of Allylmagnesium bromide with fluoroölefins afforded fluorine-containing dienes. Similar reactions of fluorinated unsaturated organometallic reagents with fluoroölefins failed. (2) Several other unsaturated fluoro-organometallic compounds were prepared and their reactions studied. Of particular interest was their reaction with carbonyl compounds to produce alcohols which, on dehydration, afforded fluorinated dienes.

e.g.



II. DISCUSSION

A. Preparation and Some Reactions of Perfluoroallyl Halides

Perfluoroallyl chloride was obtained, only in low yield, by pyrolysis of chlorotrifluoroethylene (1).

This route was abandoned in favor of one involving benzoyl peroxide promoted addition of dibromodifluoromethane to trifluoroethylene (2) and subsequent dehydrohalogenation of the product with aqueous potassium hydroxide. The yield of the bromide was limited by the fact that the initial addition gave both $CF_2BrCHFCF_2Br$ (85%) and CF_2BrCF_2CHFBr (15%) as shown by NMR

$$\begin{array}{ccccl} CF_2Br_2 & + & CHF{=}CF_2 & \longrightarrow & CF_2BrCHFCF_2Br \xrightarrow{KOH} CF_2{=}CFCF_2Br \\ & & & & \quad + \\ & & & & CF_2BrCF_2CHFBr \end{array}$$

To prepare large quantities of the perfluoroallyl compounds, a more economical route than either of those described above was required. Recently, the following reaction was reported (3):

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

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

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

$$CF_2{=}CFCF_2Cl \xrightarrow[acetone]{X^-} CF_2{=}CF\text{-}CF_2X \quad \text{where } X = Br, \text{ or } I$$

Various sets of conditions for the above reactions were attempted. Treatment of fluorotrichloromethane with dichlorodifluoroethylene in the presence of aluminum trichloride, at best, afforded 70% of a mixture of isomers with formula $C_3Cl_5F_3$. A small amount of $C_3Cl_6F_2$ was also isolated. The optimum conditions for the fluorination of $C_3Cl_5F_3$ were found to involve heating at 190 - 200° in an autoclave for 12 hours with antimony trifluoride and chlorine. Under these conditions, all the starting material was converted into chiefly $C_3Cl_3F_5$ with some $C_3Cl_4F_4$. Dehalogenation of the $C_3Cl_3F_5$ fraction, which was shown to contain a mixture of $CF_2ClCFClCF_2Cl$ (71%) and $CF_3CCl_2CF_2Cl$ (25%) gave perfluoroallyl chloride in 80% yield. Perfluoroallyl iodide was prepared easily (4) by the SN_2^1 reaction of sodium iodide and perfluoroallylbromide in anhydrous acetone.

Perfluoroallylbromide was heated at 100° for two 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.

Reaction of perfluoroallyl bromide with zinc dust in refluxing dioxane gave no evidence of reaction. Further heating at 105 - 108° 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 perfluoroallyl bromide was recovered along with a small amount of unidentified material of lower boiling point.

Attempted formation of perfluoroallyl Grignard and lithium reagents met with no success.

The addition of alcohols to fluoroölefins under base catalysis is well known (5-7). When perfluoroallyl iodide 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 $C_2H_5OCF_2CHFCF_2OC_2H_5$. Perfluoroallyl halides were also treated with trifluoroethanol/KOH, allyl alcohol/KOH, methanol/sodium methoxide and dioxane/sodium methoxide. For these cases, the following scheme and table account for all the major products:

$$(1)\quad RO^- + CF_2{=}CFCF_2X \longrightarrow ROCF_2\text{-}\bar{C}FCF_2X$$

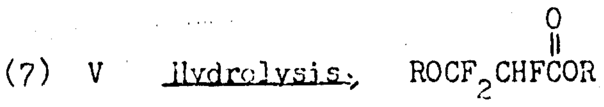
$$(2)\quad ROCF_2\text{-}\bar{C}FCF_2X \longrightarrow \underset{I}{ROCF{=}CFCF_2X} + F^-$$

$$(3)\quad ROCF_2\bar{C}FCF_2X \longrightarrow \underset{II}{ROCF_2CF{=}CF_2} + X^-$$

$$(4)\quad ROCF_2\bar{C}FCF_2X \longrightarrow \underset{III}{ROCF_2CF{=}CFX} + F^-$$

$$(5)\quad ROCF_2\bar{C}FCF_2X + ROH \not\longrightarrow \underset{IV}{ROCF_2CHFCF_2X} + RO^-$$

$$(6)\quad II + RO^- \longrightarrow ROCF_2\bar{C}FCF_2OR \xrightarrow{ROH} \underset{V}{ROCF_2CHFCF_2OR} + RO^-$$



$$(7)\quad V \xrightarrow{\text{Hydrolysis}} ROCF_2CHF\overset{O}{\overset{\|}{C}}OR$$

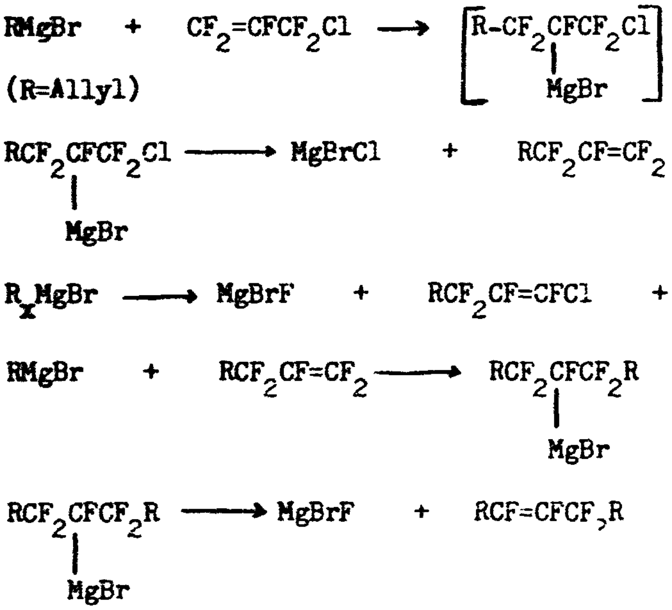
Table I

X	R	I + III (%)	II (%)	IV (%)	V (%)	VI (%)
I	CF_3CH_2	----	35.7	----	----	----
Cl	allyl	14	19	0	36	20
Cl	MeOH/CH_3	15	16	0	46	0
Cl	dioxane/CH_3	trace	Major	0	0	0

The reaction of potassium trifluoroethoxide in trifluoroethanol had previously been carried out with perfluoroallyl chloride (8,9).

As can be seen from the above table, reaction of perfluoroallyl chloride with potassium allyloxide in allyl alcohol afforded only 19% of the unsaturated ether (II). It was felt that reaction of sodium allyloxide in the absence of a hydrogen donor would give the desired ether in much better yield. However, reaction in dioxane and acetone gave no product at all. Apparently the sodium allyloxide was too insoluble in these solvents. Attempts to find a solvent for this salt which did not contain labile hydrogens were unsuccessful. These included methyl ethyl ketone, N,N-dimethylformamide, dimethylsulfoxide. and t-butyl alcohol.

The reaction of $CF_2=CFCF_2Cl$ with allylmagnesium bromide was successfully carried out to give two new materials: $C_6H_5ClF_4$, (probably a mixture of $CH_2=CHCH_2CF_2CF=CFCl$ and $CH_2=CHCH_2CF=CFCF_2Cl$,) and $C_9H_{10}F_4$, ($CH_2=CHCH_2CF=CFCF_2CH_2CH=CH_2$.) No $CH_2=CHCH_2CF_2CF=CF_2$ was detected. The following scheme is proposed to account for these products:



$$\underset{(R=Allyl)}{RMgBr} + CF_2=CFCF_2Cl \longrightarrow \left[R-CF_2\underset{\underset{MgBr}{|}}{C}FCF_2Cl\right] \qquad (1)$$

$$RCF_2\underset{\underset{MgBr}{|}}{C}FCF_2Cl \longrightarrow MgBrCl + RCF_2CF=CF_2 \qquad (2)$$

$$R_xMgBr \longrightarrow MgBrF + RCF_2CF=CFCl + RCF=CFCF_2Cl \qquad (3)$$

$$RMgBr + RCF_2CF=CF_2 \longrightarrow RCF_2\underset{\underset{MgBr}{|}}{C}FCF_2R \qquad (4)$$

$$RCF_2\underset{\underset{MgBr}{|}}{C}FCF_2R \longrightarrow MgBrF + RCF=CFCF_2R \qquad (5)$$

B. Lewis Acid Catalyzed Addition of Haloalkanes to Haloölefins

Aluminum trichloride catalyzed addition of fluorotrichloromethane to 1,2-dichloro-1,2-difluoroethylene was described in the previous sections as the first step in the preparation of perfluoroallyl halides. It had been previously reported (3) that the above reaction gave $CFCl_2CFClCFCl_2$ and no other product was mentioned. In our laboratories, a 72% yield of isomers with formula $C_3Cl_5F_3$ was obtained as well as a small amount of

$C_3Cl_5F_3$. Although it was not reported in the previous section, (A), NMR study of the mixture $C_3Cl_5F_3$ showed that it contained $CF_2ClCFClCCl_3$ (81%), $CF_3CCl_2CCl_3$ (1%) and $CFCl_2CFClCFCl_2$ (18%). In view of this interesting discovery, it was decided to study further the Lewis acid catalyzed addition of haloalkanes to olefins.

A number of other Lewis acids were substituted for $AlCl_3$ in the reaction of $CFCl_3$ with CFCl=CFCl. These included concentrated sulphuric acid, fuming H_2SO_4, $SnCl_4$, $AlBr_3$, $SbCl_5$, $SiCl_4$, BF_3, BF_3 etherate, and $HgCl_2$, under a variety of conditions. Only in the case of aluminum bromide did any reaction occur and then it produced only a 5% yield of adduct after 3 days at room temperature and 5 hours at 70°. Aluminum trichloride was used as catalyst in all other reactions.

To elucidate the mechanism of the $AlCl_3$ catalyzed addition of $CFCl_3$ to CFCl=CFCl, a study of the isomerization of the main adduct $C_3Cl_5F_3$ ($CF_2ClCFClCCl_3$ (81%), $CFCl_2CFClCFCl_2$ (18%) and $CF_3CCl_2CCl_3$ (1%)) in the presence of $AlCl_3$, was carried out. The main product was $C_3Cl_6F_2$, due to replacement reaction, although enough rearranged $C_3Cl_5F_3$ was recovered for NMR analysis. The latter material consisted of $CF_2ClCFClCCl_3$ (95%) and $CF_3CCl_2CCl_3$ (5%). Hence, the $CFCl_2CFClCFCl_2$ was completely rearranged to $CF_2ClCFClCCl_3$. This type of $AlCl_3$ catalyzed rearrangement also occurred with the $C_3Cl_6F_2$ fraction formed in the addition reaction. The initially formed $C_3Cl_6F_2$ consisted of $CF_2ClCCl_2CCl_3$ (46%) and $CFCl_2CFClCCl_3$ (54%). The $C_3Cl_6F_2$ fraction isolated as the major product from the attempted isomerization of $C_3Cl_5F_3$ consisted of only $CF_2ClCCl_2CCl_3$.

The following scheme is proposed to account for these results:

$$CFCl_3 + AlCl_3 \rightleftharpoons CCl_3^+ + AlCl_3F^- \qquad (1)$$

$$CCl_3^+ + CFCl{=}CFCl \rightleftharpoons CCl_3CFClCFCl^+ \qquad (2)$$

$$CCl_3CFClCFCl^+ + AlCl_3F^- \rightleftharpoons CCl_3CFClCF_2Cl + AlCl_3 \qquad (3)$$

$$CFCl_3 + AlCl_3 \rightleftharpoons CFCl_2^+ + AlCl_4^- \qquad (4)$$

$$CFCl_2^+ + CFCl{=}CFCl \rightleftharpoons CFCl_2CFClCFCl^+ \qquad (5)$$

$$CFCl_2CFClCFCl^+ \quad + \quad AlCl_4^- \rightleftharpoons CFCl_2CFClCFCl_2 \quad + \quad AlCl_3 \qquad (6)$$

$$CFCl_2CFClCFCl_2 \xrightarrow{AlCl_3} CF_2ClCFClCCl_3 \qquad (7)$$

From the fact that (7) is an irreversible rearrangement, it is concluded that (4) (followed by (5) and (6)) must be operative to some extent since there was produced initially (18%) $CFCl_2CFClCFCl_2$ which can only arise in this manner. An attempt to detect the $CFCl_2^{+2}$ cation using ^{19}F NMR by scanning a mixture of $AlCl_3$ and $CFCl_3$ at both high and low yields was unsuccessful. However, this is not proof of the absence of this ion.

Reactions of $CFCl_3$ and $CHFCl_2$ with various other fluoroölefins were carried out and the results are shown in Tables I, II and III.

The addition of $CFCl_3$ to $CF_2{=}CCl_2$ yielded $C_3Cl_5F_3$ in 53% yield, with small amounts of $C_3Cl_6F_2$.

The reaction of $CFCl_3$ with $CF_2{=}CFCl$ has been reported to give $CFCl_2CF_2CFCl_2$ (10) and $C_3Cl_4F_4$ (11). 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 $CF_3CFClCCl_3$ (51%) and $CF_2ClCF_2CCl_3$ (37%). Treatment of this mixture with zinc dust in ethanol gave only the reduction product, $C_3HCl_3F_4$, which contained $CF_2ClCF_2CHCl_2$ (79%). With dioxane as a 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.

The addition of $CFCl_3$ to $CF_2{=}CFBr$ was shown to give $CF_3CFBrCCl_3$ (56%) and $CF_2BrCF_2CCl_3$ (44%) in 5 hours. In an effort to determine the effect of the reaction time on possible isomerization of these isomers, another run was made (70 hours) and the product consisted of these isomers in 57% and 43%, respectively. It was concluded that in this case essentially no further change in the isomer distribution occurred in the presence of $AlCl_3$. Hence, it appears that each reaction must be considered separately as the mechanism apparently differs with the olefin used.

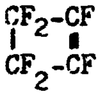
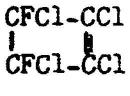
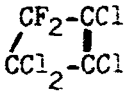
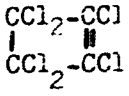
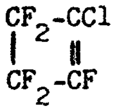
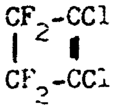
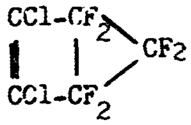
TABLE II

ADDITIONS OF ALKANES TO OLEFINS IN THE PRESENCE OF $AlCl_3$

Alkane	Olefin	Yield (%)	Product	Isomer Distribution (by NMR)
$CFCl_3$	$CF_2{=}CF_2$	55	$C_3Cl_3F_5$	$CF_3CF_2CCl_3$ (79%), $CF_2ClCF_2CFCl_2$ (21%)
"	$CF_2{=}CFCl$	64	$C_3Cl_4F_4$	$CF_3CFClCCl_3$ (51), $CF_2ClCF_2CCl_3$ (37), $CFCl_2CF_2CFCl_2$ (8)
"	$CF_2{=}CCl_2$	52	$C_3Cl_5F_3$	$CF_3CCl_2CCl_3$ (49), $CFCl_2CF_2CCl_3$ (45), $CF_2ClCCl_2CFCl_2$ (6)
"	$CF_2{=}CFBr$	76	$C_3BrCl_3F_4$	$CF_3CFBrCCl_3$ (56), $CF_2BrCF_2CCl_3$ (44)
"	$CFCl{=}CCl_2$	9	$C_3Cl_6F_2$	————
"	$CF_2{=}CHF$	--	$C_3HCl_3F_4$	$CF_3CHFCCl_3$ (100)
"	$CCl_2{=}CCl_2$	N.R.	----	————
"	$CCl_2{=}CHCl$	N.R.	----	————
$CHFCl_2$	$CF_2{=}CFCl$	34	$C_3HCl_3F_4$	$CF_2ClCF_2CHCl_2$ (81)
"	$CF_2{=}CCl_2$	18	$C_3HCl_4F_3$	$CFCl_2CF_2CHCl_2$ (96), $CF_3CCl_2CHCl_2$ (4)
"	$CFCl{=}CFCl$	61	$C_3HCl_4F_3$	$CF_2ClCFClCHCl_2$ (70), CF_2ClCCl_2CHFCl (25), $CF_3CCl_2CHCl_2$ (5)
"	$CCl_2{=}CCl_2$	36	C_3HCl_6F	$CFCl_2CCl_2CHCl_2$ (100)
"	$CF_2{=}CFBr$	79	$C_3HBrCl_2F_4$	$CF_2BrCF_2CHCl_2$ (66), $CF_3CFBrCHCl_2$ (34)
"	$CFCl{=}CCl_2$	44	$C_3HCl_5F_2$	$CFCl_2CFClCHCl_2$ (65), $CF_2ClCCl_2CHCl_2$ (35)
CF_2Cl_2	$CF_2{=}CFCl$	17	$C_3Cl_4F_4$	$CF_2ClCF_2CCl_3$ (44), $CF_3CFClCCl_3$ (38), $CFCl_2CF_2CFCl_2$ (11)

TABLE III

REACTION OF ALKANE AND OLEFIN IN THE PRESENCE OF $AlCl_3$

Alkane	Olefin	Products
$CFCl_3$		 or  and 
None	"	 and 
$CFCl_3$	$CF_3CF{=}CFCF_3$	$CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCFCl_2$
$CFCl_3$	$CF_3CF{=}CF_2$	$CF_3CF{=}CFCl$ and $CF_3CF{=}CCl_2$
None		Cyclo-$C_5Cl_xF_{8-x}$, x = 3,4,5,6
$CFCl_3$	"	" x = 4,6,8

STRUCTURES OF CYCLO-$C_5Cl_xF_{8-x}$

x = 3 $CF_2CCl{=}CClCF_2CFCl$ and $CF_2CCl{=}CClCFClCF_2$ *ca.* 50:50

x = 4 $CF_2CCl{=}CClCF_2CCl_2$ and $CF_2CCl{=}CClCCl_2CF_2$ 22:78

x = 6 $CCl_2CCl{=}CClCCl_2CF_2$

x = 8 $CCl_2CCl{=}CClCCl_2CCl_2$

An attempt was made to study the effect of fluoride ion on this type of reaction by conducting the addition of $CFCl_3$ to CFCl=CFCl with $AlCl_3$ in the presence of potassium fluoride. However, the potassium fluoride appeared to interact with the aluminum chloride to form a viscous gray polymeric mass, slowly soluble in water. Only 2% $C_3Cl_5F_3$ was formed. Since it was difficult to obtain pure anhydrous potassium fluoride, sodium fluoride (0.190 mole) was used in a series of three runs (see Table IV), each having 0.313 mole $CFCl_3$, 0.203 mole CFCl=CFCl and 0.067 mole $AlCl_3$. It was concluded that the presence of fluoride ion has no marked effect on the preferential production of one isomer, as only a 3 - 4% difference was noted. It can also be seen that as the reaction time is lengthened the yield of replacement product, $C_3Cl_6F_2$, increases.

Attempts to extend this type of reaction to alkanes other than $CFCl_3$ and $CHFCl_2$ have been unsuccessful. Instead, rearrangement or replacement reactions of the starting alkane occurred, e.g., with CCl_4 and CFCl=CFCl the product mixture contained $CCl_2=CCl_2$ (46%), $C_3Cl_5F_3$ (8%) and C_3Cl_7F (46%). When $CBrCl_3$ was treated with $AlCl_3$, it disproportionated to give CBr_2Cl_2 and CCl_4. This was the only reaction when $CBrCl_3$ was treated with CFCl=CFCl and $AlCl_3$. Benzotrichloride and CFCl=CFCl gave no reaction at all.

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 adduct, 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 $CHCl_3F_4$.

This study was also extended to the investigation of the addition

TABLE IV

THE EFFECT OF F^-(NaF) ON THE REACTION OF $CFCl_3$ WITH CFCl=CFCl IN THE PRESENCE OF $AlCl_3$

		Yield (%)		$C_3Cl_5F_3$ Isomers (%) by NMR			
NaF	Time(hr.)	$C_3Cl_5F_3$	$C_3Cl_6F_2$	$CF_2ClCFClCCl_3$	$CF_3CCl_2CCl_3$	$CFCl_2CFClCFCl_2$	$CFCl_2CF_2CCl_3$
No	6.50	75	5.8	70	2	24	None
Yes	6.25	66	5.5	74	2	21	None
Yes	35	65	9.3	76	3	18	None

of polyhalogenated ethanes to fluoroolefins. For example, $CF_2BrCFClBr$ and $CF_2ClCFCl_2$ were both treated with 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 Nadai and Mueller (12) and this compound has tentatively been assigned the structure CF_3CBr_2Cl. However, no data could be found for the other possibility, $CF_2ClCFBr_2$.

A repeat of the attempted addition of $CF_2ClCFCl_2$ to CFCl=CFCl was run to check the possibility of alkane rearrangement. Previous workers(13) have shown that $CF_2ClCFCl_2$ readily rearranges to CF_3CCl_3 or undergoes replacement reactions, but these were all done at reflux temperature (47°). Under carefully controlled temperature conditions (24 - 7°), was found that neither addition nor rearrangement (as determined by NMR) occurred. A very small amount of CF_2ClCCl_3 was obtained.

Attempted reaction of $CFCl_3$ with olefins, other than halogenated ethylenes, in the presence of $AlCl_3$ also met with little success. With perfluoropropene, perfluorobutene-2, and perfluorocyclobutene, no adducts were formed (see Tables II and III). A high boiling product from the latter reaction was shown to be a mixture of hexachlorobutadiene-1,3 and hexachlorocyclobutene. The indication was that the cyclobutene rearranged to the butadiene on distillation (14). When perfluorocyclobutene alone was treated with $AlCl_3$, the main product was 1,2-dichloroperfluorocyclobutene with a little of the monochloro-compound. Thus, aluminum chloride catalyzed addition reaction seems to occur only with halo-ethylenes.

C. Free-Radical Initiated Addition of Haloalkanes to Unsaturated Compounds

A number of workers (15) have reported the addition of various haloalkanes to unsaturated compounds in the presence of peroxides, or visible or ultraviolet light. Tarrant and co-workers synthesized a number of haloalkanes in this manner (2,16,17) and converted these addition products into various unsaturated compounds by treating them with base, with zinc, or both. It was decided to further explore the addition of various haloalkanes to olefins under free-radical conditions with a view to preparing unsaturated compounds from their addition products through simple reactions like dehalogenation and dehydrohalogenation.

Reactions of this type are believed to follow the mechanism proposed by Kharasch as shown below (18), using bromotrichloromethane as perhaloalkane and a peroxide as the initiator.

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow{\Delta} R\cdot + RCOO\colon + CO_2$$

$$R. + CCl_3Br \longrightarrow RBr + .CCl_3$$

$$Cl_3C. + RCH{=}CH_2 \longrightarrow CCl_3CH_2\dot{C}HR$$

$$CCl_3CH_2\dot{C}HR + CCl_3Br \longrightarrow CCl_3CH_2CHRBr + \dot{C}Cl_3$$

Higher molecular weight products may be formed as follows:

$$\begin{array}{lllll} CCl_3CH_2\dot{C}HR + CH_2{=}CHR & \longrightarrow & CCl_3CH_2CHRCH_2\dot{C}HR & + & nCH_2{=}CHR \\ & & \downarrow & & \\ & & CCl_3(CH_2CHR)_nCH_2\dot{C}HR & & \\ & & \downarrow CCl_3Br & & \\ & & CCl_3(CH_2CHR)_nCH_2CHRBr & + & \dot{C}Cl_3 \end{array}$$

1. Reaction of Haloalkanes with Ethylene in the Presence of Benzoyl Peroxide (See Table V)

a. CFClBrCFClBr

It was hoped that CFClBrCFClBr would add to ethylene to give the 2:1 adduct, $CH_2BrCH_2CFClCFClCH_2CH_2Br$, which could easily be converted to the 1,3,5-triene, $CH_2{=}CHCF{=}CF\text{-}CH{=}CH_2$, by successive dehalogenation and dehydrohalogenation. However, the addition occurred mostly in one direction to give a 30% yield of the 1:1 adduct, $CFClBrCFClCH_2CH_2Br$ with only a little 2:1 adduct. The 1:1 adduct was converted into

TABLE V

BENZOYL PEROXIDE INITIATED ADDITION OF HALOALKANES TO ETHYLENE

Unsaturated Compound (mole)	Haloalkane (mole)	Time (hr.)	Products (a) Yield (%) and Properties
Ethylene (0.72)	CFClBrCFClBr (1.0)	16	CFCl=CFCl, 20, b.p. 22°, n_D^{21} 1.3763 (lit. (26) 22°, n_D^{20} 1.3798) CH_2BrCH_2Br, 20, b.p. 131.2°, n_D^{21} 1.5377 (lit. (27) 131.6°, n_D^{25} 1.5379) $CFClBrCFClCH_2CH_2Br$, 30, b.p. 53°/2 mm., n_D^{21} 1.4486, (*Anal.* Calcd. for $C_4Br_2Cl_2F_2H_4$: Br, 50.16. Found: Br, 49.98%)
Ethylene (0.52)	$CF_3CFBrCFBrCF_3$ (0.96)	8	$CF_3CF{=}CFCF_3$, 20, b.p. 2° (lit. (26) 0°/740 mm.) CH_2BrCH_2Br, 20, see above
Ethylene (0.25)	$CF_3CFBrCClBrCF_3$ (0.64)	4	$CF_3CF{=}CClCF_3$ and CH_2BrCH_2Br (both in quantitative yields)
Ethylene (0.58)	CF_2ICF_2I (1.0)	12	Only starting materials recovered

TABLE V (continued)

BENZOYL PEROXIDE INITIATED ADDITION OF HALOALKANES TO ETHYLENE

Ethylene (0.25)	$CF_2BrCFBrCF_3$ (0.76)	16	$CF_2BrCF(CF_3)CH_2CH_2Br$, 51, b.p. 145°, n_D^{21} 1.4017, (<u>Anal</u>. Calcd. for $C_5Br_2F_6H_4Br$: Br, 47.34, Found: Br, 47.34%)
Ethylene (0.57)	$C_6H_5CCl_3$ (1.54)	16	No reaction
Ethylene (0.20)	1,2-Dibromoperfluoro-cyclobutane (0.26)	12	No reaction
Ethylene (0.32)	$CF_2BrCHFBr$ (1.13)	12	No reaction
Ethylene (0.54)	$CFCl_2CFCl_2$ (2.06)	16	No reaction
Ethylene (0.63)	CF_2BrCF_2Br (1.54)	12	$CF_2BrCF_2CH_2CH_2Br$, 32, b.p. 72°/80 mm., n_D^{21} 1.4167, (<u>Anal</u>. Calcd. for $C_4Br_2F_4H_4$: Br, 55.56. Found: Br, 55.81%)

TABLE V (continued)

BENZOYL PEROXIDE INITIATED ADDITION OF HALOALKANES TO ETHYLENE

			$CF_2BrCF_2(CH_2)_3CH_2Br$, 20, b.p. 76°/10 mm., n_D^{21} 1.4337, (<u>Anal</u>. Calcd. for $C_6Br_2F_4H_8$: Br, 50.63. Found: Br, 50.41%)
Ethylene (0.46)	$CCl_3CF_2CF_2Br$ (1.10)	8	$CCl_3CF_2CF_2CH_2CH_2Cl$, 7, b.p. 187°, n_D^{21} 1.4297, (<u>Anal</u>. Calcd. for $C_5Cl_4F_4H_4$: C, 21.24; H, 1.42 F, 25.92. Found: C, 21.35; H, 1.46; F, 27.18%) $CCl_3CF_2CF_2CH_2CH_2Br$, 40, b.p. 209°, n_D^{21} 1.4486, (<u>Anal</u>. Calcd. for $C_5BrCl_3F_4H_4$: Br, 24.48. Found: Br, 24.87%) $CF_2BrCF_2CCl_2CH_2CH_2Br$, 9, b.p. 216°, n_D^{21} 1.4664 (<u>Anal</u>. Calcd. for $C_5Br_2Cl_2F_4H_4$: Br, 43.12. Found: Br, 43.24%) A fourth product was probably $CF_2BrCF_2CCl_2CH_2CH_2Cl$ (1.5) Found: Br, 42.40%

(a) ^1H and ^{19}F NMR spectra was consistent with the structures shown

$CFCl{=}CFCH_2CH_2Br$ and $CFClBrCFClCH{=}CH_2$ by dehalogenation and dehydrohalogenation, respectively. Dehydrohalogenation of $CFCl{=}CFCH_2CH_2Br$ afforded the diene, $CH_2{=}CH\text{-}CF{=}CFCl$, which polymerized at room temperature but could be stored at liquid nitrogen temperature with little or no polymerization. In the initial reaction of $CFClBrCFClBr$ with ethylene, a major product (20%) was $CFCl{=}CFCl$ <u>via</u> debromination of the starting halide.

b. <u>$CF_3CFBrCFBrCF_3$</u>

Debromination of starting halide was also observed when addition of $CF_3CFBrCFBrCF_3$ to ethylene was attempted. This dibromide gave no reaction with ethylene in the presence of a 0.01 molar proportion of benzoyl peroxide. When the proportion of the latter was increased to greater than 0.04 molar, perfluorobutene-2 and CH_2BrCH_2Br were isolated in 29% and 21% yields, respectively.

c. <u>$CF_3CFBrCClBrCF_3$</u>

Bromination of $CF_3CF{=}CClCF_3$ afforded $CF_3CFBrCClBrCF_3$ which gave no 1:1 adduct in the attempted addition to ethylene under the usual conditions. A considerable amount of debromination occurred similar to that observed in the above two cases ($CFClBrCFClBr$ and $CF_3CFBrCFBrCF_3$). It appears that the radicals $CFClBr\dot{C}FCl$, $CF_3CFBr\dot{C}FCF_3$ and $CF_3CFBr\dot{C}ClCF_3$ are sterically hindered and that they decay very quickly into olefin and bromine atom. Although $CFCl{=}CFCl$ can be easily brominated without uv light, $CF_3CF{=}CFCF_3$ and $CF_3CF{=}CClCF_3$ brominate only in the presence of uv light and bromination of $CF_3CCl{=}CClCF_3$ is still more difficult. Tarrant <u>et.al</u>. (19) have reported elimination by radical decay in the addition of CCl_3Br to $CF_2BrCFClCH{=}CH_2$ to produce an olefin:

$$CF_2BrCFCl\dot{C}HCH_2CCl_3 \longrightarrow CF_2BrCF{=}CHCH_2CCl_3 \quad + \quad Cl\cdot$$

Addition of CF_2BrCF_2Br to ethylene gave a 1:1 adduct ($CF_2BrCF_2CH_2CH_2Br$) in 30% yield and smaller amounts of higher boiling products. These included the 2:1 adduct $CF_2BrCF_2(CH_2)_3CH_2Br$. Attempted dehydrohalogenation of this 2:1 adduct using potassium hydroxide in ethanol gave a poor yield of the expected olefin, $CF_2BrCF_2(CH_2)_2CH{=}CH_2$, and a good yield of ether, $CF_2BrCF_2(CH_2)_3CH_2OCH_2CH_3$, produced by nucleophilic substitution of terminal bromine. The 1:1 adduct was dehydrohalogenated to yield $CF_2BrCF_2CH=CH_2$.

Ethylene was bubbled through CF_2ICF_2I and benzoyl peroxide at 100°, but no higher boiling product was detected. An attempted reaction of the same mixture at 100° in an autoclave gave less than 1% of higher boiling material. An autoclave reaction at 220° gave a polymeric solid which gave no liquid product on attempted dehydrohalogenation. This is in contrast to the report that ethylene and CF_2ICF_2I in the presence of benzoylperoxide at 220° gave $CF_2ICF_2CH_2CH_2I$ in 80% yield (20).

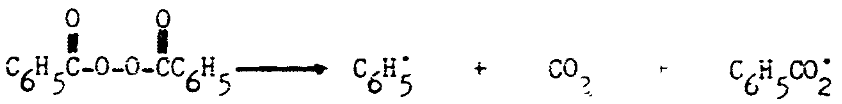
Reaction of $CF_3CFBrCF_2Br$ with ethylene gave a 51% yield of 1:1 adduct which was identified as $CH_2BrCH_2CF(CF_3)CF_2Br$.

Benzotrichloride, 1,2-dibromohexafluorocyclobutane, $CF_2BrCHFBr$ $CFCl_2CFCl_2$ and $CFCl_2CF_2Cl$ failed to react with ethylene under the experimental conditions employed.

The addition of $CCl_3CF_2CF_2Br$ to ethylene was carried out to compare the reactivities of the end groups - CCl_3 and - CF_2Br towards radical abstraction of chlorine and bromine. It was found that the addition of $CCl_3CF_2CF_2Br$ to ethylene gave four main products, $CCl_3CF_2CF_2CH_2CH_2Cl$, $CF_2BrCF_2CCl_2CH_2CH_2Cl$ (not positively identified - see below), $CCl_3CF_2CF_2CH_2CH_2Br$, and $CF_2BrCF_2CCl_2CH_2CH_2Br$ in 7, 1.5, 40 and 9% yields, respectively.

The second product, which could not be isolated, had a v.p.c. retention time between those of $CCl_3CF_2CF_2CH_2CH_2Cl$ and $CCl_3CF_2CF_2CH_2CH_2Br$ which suggested that this product could be $CF_2BrCF_2CCl_2CH_2CH_2Cl$.

The following mechanism could explain the formation of these products:



$$C_6H_5\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5^{\cdot} + CO_2 + C_6H_5CO_2^{\cdot} \qquad (1)$$

R = C_6H_5

$$R^{\cdot} + CCl_3CF_2CF_2Br \begin{array}{l} \nearrow RCl + CF_2BrCF_2\dot{C}Cl_2 \\ \searrow RBr + CCl_3CF_2\dot{C}F_2 \end{array} \qquad (2)$$

$$CF_2BrCF_2\dot{C}Cl_2 + CH_2{=}CH_2 \xrightarrow{k_2} CF_2BrCF_2CCl_2CH_2\dot{C}H_2 \qquad (3)$$

$$CCl_3CF_2\dot{C}F_2 + CH_2{=}CH_2 \xrightarrow{k_2'} CCl_3CF_2CF_2CH_2\dot{C}H_2 \qquad (4)$$

$$CCl_3CF_2CF_2CH_2\dot{C}H_2 + CCl_3CF_2CF_2Br \begin{array}{l} \overset{k_3}{\nearrow} \underset{VII}{CCl_3CF_2CH_2CH_2Cl} + CF_2BrCF_2\dot{C}Cl_2 \\ \underset{k_4}{\searrow} \underset{VIII}{CCl_3CF_2CF_2CH_2CH_2Br} + CCl_3CF_2\dot{C}F_2 \end{array} \qquad (5)$$

$$CF_2BrCF_2CCl_2CH_2\dot{C}H_2 + CCl_3CF_2CF_2Br \begin{array}{l} \overset{k_3}{\nearrow} \underset{IX}{CF_2BrCF_2CCl_2CH_2CH_2Cl} + CF_2BrCF_2\dot{C}Cl_2 \\ \underset{k_4}{\searrow} \underset{X}{CF_2BrCF_2CCl_2CH_2CH_2Br} + CCl_3CF_2\dot{C}F_2 \end{array} \qquad (6)$$

It is reasonable to make the following approximations:

(a) $k_1 = k_3 = k_4 = k$ and $k_1' = k_3' = k_4' = k'$

(b) $k_2 = k_2'$

If the above approximations are made, then the rate of formation of products VII and VIII will be proportional to the concentration of radical, $CCl_3CF_2CF_2CH_2\dot{C}H_2$. Similarly, the rate of formation of products IX and X will be proportional to the concentration of radical, $CF_2BrCF_2CCl_2CH_2\dot{C}H_2$. The relative reactivities of $-CCl_3$ and $-CF_2Br$ end groups towards radical abstraction of chlorine and bromine will be the ratio of amount of product VII formed to the amount of product VIII formed, or the amount of product IX formed to the amount of product X formed. From these studies it appears that $-CF_2Br$ end group is at least six times more reactive than $-CCl_3$ end group for radical abstraction of bromine and chlorine. Tarrant and Gillman obtained only $CF_2BrCFClCH_2CHBrCH_3$ in the addition of $CF_2BrCFClBr$ to propylene in the presence of benzoyl peroxide and none of the other isomer, $CFClBrCF_2CH_2CHBrCH_3$ was obtained. The qualitative reactivities of $-CCl_3$, $-CF_2Br$, and -CFClBr towards radical abstraction of chlorine and bromine were found to be in the order -CFClBr $\gg$ $-CF_2Br$ > $-CCl_3$ in compounds $CCl_3CF_2CFClBr$ and $CCl_3CF_2CF_2Br$.

2. Free-Radical Initiated Addition to Allyl Compounds (See Table VI)

a. Allyl Chloride

The addition of $CF_3CFBrCF_2Br$ and CF_2ICF_2I to allyl chloride in the presence of benzoyl peroxide gave no higher boiling products. Similar results were also obtained when $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ were allowed to react with the same halide. In contrast, allyl chloride produced $CCl_3CH_2CHBrCH_2Cl$ and $CF_2BrCFClCH_2CHBrCH_2Cl$ on reaction, under free-radical conditions with CCl_3Br and $CF_2BrCFClBr$, respectively.

b. Allyl ethyl ether

Attempted addition of $CF_3CFBrCFClBr$ and CF_2BrCF_2Br to allyl ethyl ether in the presence of peroxide was unsuccessful. This is in contrast to the reported (21) reaction of CCl_3Br and $CF_2BrCFClBr$ with the unsaturated ether under free-radical conditions to produce $CCl_3CH_2CHBrCH_2OCH_2CH_3$ and $CF_2BrCFClCH_2CHBrCH_2OC_2H_5$, respectively.

c. 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 adducts (20,22). Friedlander reported (23,24) that treatment of the haloalkane with diallyl ether under free-radical conditions gave a six-membered cyclic product, i.e., a substituted tetrahydrofuran. 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:

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

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

Though the reactions were carried out using large excess of the haloalkanes to diallyl ether to prevent cyclization instead of using equi-molar amounts

TABLE VI

BENZOYL PEROXIDE INITIATED ADDITION OF HALOALKANES TO OTHER UNSATURATED COMPOUNDS

Unsaturated Compound (mole)	Haloalkane (mole)	Time (hr.)	Product $^{(a)}$, Yield, % and Properties
Allyl Chloride (0.20)	$CF_3CF_2CCl_3$ (0.30)	5	No product
Allyl Chloride (0.20)	$CF_2ClCF_2CCl_3$ (0.30)	5	No product
Allyl Chloride (0.50)	$CF_2BrCFBrCF_3$ (0.82)	12	No product
Allyl Chloride (0.10)	CF_2ICF_2I (0.20) ^{b}	8	No product
Allyl Etnyl ether (0.12)	$CF_2BrCFBrCF_3$ (0.20)	16	No product
Allyl Ethyl ether (0.10)	CF_2BrCF_2Br (0.20) ^{b}	16	No product
$CH_2{=}CHCFClCF_2Br$ (0.112)	$CF_2BrCFClBr$ (0.504)	3	$CF_2BrCFClCH_2CH{=}CFCF_2Br$, 10, b.p. 200-3° $n_D^{23.5}$ 1.4323 (<u>Anal</u>. Calcd. for $C_6H_3Br_2ClF_6$:

TABLE VI (continued)

			C, 18.74; H, 0.78; Br, 41.59; F, 29.66; Cl, 9.23. Found: C, 18.81; H, 1.39; Br, 41.84; F, 29.00; Cl, 8.96 (by difference)).
$CF_2=CF_2$ (0.38)	$CH_2=CHCH_2I$ (0.60)	8	CH_3CHICH_3, (28), b.p. 89°, n_D^{21} 1.3996, (lit. (27) 89.5, n_D^{20} 1.4996) (Anal. Calcd. for C_3H_7I: C, 21.09; H, 4.12. Found: C, 21.43; H, 4.29; I, 73.11%) $CH_2=CHCH_2CF_2CF_2CH_2CH=CH_2$, (6), b.p. 118°, n_D^{21} 1.3721 (Anal. Calcd. for $C_8F_4H_{10}$: C, 52.75; H, 5.49; F, 41.76. Found: C, 52.33; H, 5.31; F, 42.36% (by difference)) $CH_2=CHCH_2CF_2CF_2I$, (34), b.p. 114°, n_D^{21} 1.4188 (Anal. Calcd. for $C_5F_4H_5I$: C, 22.39; H, 1.87; I, 47.78. Found: C, 22.93; H, 1.99; I, 47.65%) CF_2ICF_2I, 17.5, b.p. 108.5°, n_D^{21} 1.4892

TABLE VI (continued)

BENZOYL PEROXIDE INITIATED ADDITION OF HALOALKANES TO OTHER UNSATURATED COMPOUNDS

			(lit.(26) 112 - 3°, n_D^{25} 1.4895)
Isobutylene (0.50)	$CF_2ClCF_2CCl_3$	4	$CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$, 25, b.p. 172.5°, n_D^{21} 1.4421 (<u>Anal</u>. Calcd. for $C_7Cl_3F_4H_7$: Cl, 38.95. Found: Cl, 38.62%) $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$, 13, b.p. 47°/0.5 mm., n_D^{21} 1.4344 (<u>Anal</u>. Calcd. for $C_7Cl_4F_4H_8$: Cl, 45.81. Found: Cl, 44.88%)
Acrylonitrile (0.25)	$CF_2BrCFClBr$ (0.50)^b	2	Polymer
Hexafluorocyclobutene (0.50)	CCl_3Br (1.50)	16	No product
1,3 butadiene (0.16)	1,2-Dibromoperfluorocyclobutane (0.21)	12	No product
$CF_2=CFCl$ (0.30)	$CF_3CF_2CCl_3$	12	No product

TABLE VI (continued)

BENZOYL PEROXIDE INITIATED ADDITION OF HALOALKANES TO OTHER UNSATURATED COMPOUNDS

$CF_2=CFCl$ (0.02)	CF_2BrCF_2Br (0.68)	12	No product
$CF_2=CF_2$ (0.13)	$CH_2=CHI$ (0.16)	4	No product
$(CH_3)_3SiCF=CF_2$ (0.10)	$CF_2BrCFClBr$ (0.30)[b]	2	No product
1,3-butadiene (1.0)	CF_3I	8	Polymer (carried out at 200°)

(a) ^1H and ^{19}F NMR spectra of the adducts formed were consistent with the proposed structures

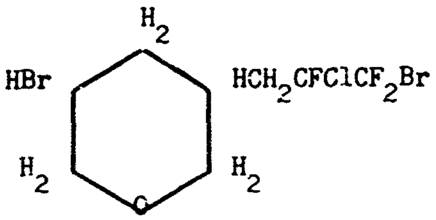
[b] A Fischer Porter tube was used instead of an autoclave in these experiments

[c] This reaction was carried out in s small flask at reflux temperature. Using acetyl peroxide as initiator and refluxing for 2 hours gave the desired product (16.5%)

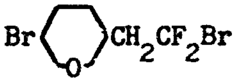
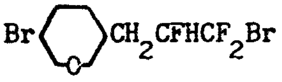
as reported (24) the adducts were saturated one-to-one addition products. Infrared and NMR spectroscopy showed no unsaturation. It is proposed that the reactions follow a mechanism similar to that proposed by Friedlander (23).

$$(CH_2{=}CHCH_2)_2O \quad + \quad CF_2BrCFClBr \;\nrightarrow\; CF_2BrCFClCH_2CHBrCH_2OCH_2CH{=}CH_2$$

XI



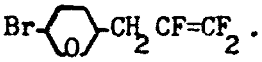
Similar mechanisms are postulated for the formation of

 and 

XII XIII

The adducts were highly viscous, slightly yellow liquids. $CF_3CFBrCF_2Br$ and CFClBrCFClBr gave only small amounts of tar after two days reaction.

The order of reactivity of haloalkane to diallyl ether was as follows: $CF_2BrCFClBr > CF_2Br_2 > CF_2BrCHFBr \gg CF_3CFBrCF_2Br$, CFClBrCFClBr. Dehalogenations were carried out by the usual method. The dehalogenated product from XI had a strong infrared 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 XII failed because of polymerization during the distillation.

Attempts to react XI with $LiAlH_4$ in ether at 0°, room temperature, and 35°, showed a slow reaction in the latter case only. A rapid reaction occurred using tetrahydrofuran as solvent and two main products were separated by v.p.c. One product was identical to the dehalogenation product of XI. The other showed strong infrared absorption at 5.50μ and MR_D

and the elemental analysis was consistent with the structure $-CH_2CF=CF_2$. Since the attempts at a direct synthesis of the linear ethers failed, another route was attempted:

$$\begin{tikzcd}
(CH_2=CHCH_2)_2O \quad + \quad Cl_2 \arrow[r] & CH_2ClCHClCH_2OCH_2CH=CH_2 \arrow[d, "CF_2BrCFClBr"] \\
CF_2=CFCH_2CHBrCH_2OCH_2CH=CH_2 \arrow[d, "CF_2BrCFClBr"] & CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl \arrow[l, "Zn"'] \\
CF_2=CFCH_2CHBrCH_2OCH_2CHBrCH_2CFClCF_2Br \arrow[r, "Zn"'] & (CF_2=CFCH_2CHBrCH_2)_2O \arrow[d, "LiAlH_4"] \\
 & (CF_2=CFCH_2CH_2CH_2)_2O
\end{tikzcd}$$

The chlorine addition to diallyl ether was carried out as reported. Best results were obtained when the reaction was carried out at temperatures between 3° and 7°.

Addition of $CF_2BrCFClBr$ to $CH_2ClCHClCH_2OCH_2CH=CH_2$ was carried out using a larger ratio of $CF_2BrCFClBr$ to ether. The adduct was dehalogenated with zinc and ethanol. Two main liquid products were separated by v.p.c. One component was identified as $CH_2ClCHClCH_2OH$, and the other gave an elemental analysis, infrared spectrum and MR_D consistent with $CF_2=CFCH_2CHBrCH_2OCH_2CHClCH_2Cl$.

3. Benzoyl Peroxide Initiated Addition of Haloalkanes to Other Olefins

The reaction of $CF_2BrCFClBr$ with $CH_2=CHCFClCF_2Br$ was studied under free-radical conditions; both benzoyl and acetyl peroxide gave the same major product, $CF_2BrCFClCH_2CH=CFCF_2Br$ in agreement with the recent work of Muramatsu and Tarrant (19). This compound was treated with zinc dust to give a complex mixture. Treatment of this unresolved mixture with an excess of aqueous potassium hydroxide gave a dark brown solid as the only product. It was hoped to effect 1,4-elimination of HBr to give the triene,

$$CF_2=CFCH_2CH=CFCF_2Br \xrightarrow{KOH} CF_2=CFCH=CH-CF=CF_2.$$

Treatment of acrylonitrile with $CF_2BrCFClBr$ in the presence of benzoyl peroxide in various ratios gave only a white polymer. and v.p.c. did not show any simple adducts.

Reaction of CCl_3Br and CBr_4 with triethyl-trifluorovinyl silane, under the influence of benzoyl peroxide, has been reported to give $(C_2H_5)_3SiCFBrCF_2CCl_3(Br_3)$. No adduct was detected from the attempt to react $CF_2BrCFClBr$ and $(CH_3)_3SiCF=CF_2$ under similar conditions.

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

Additions to 1,3-butadiene of 1,2-dibromohexafluorocyclobutane and iodotrifluoromethane were attempted under free-radical conditions. In the former reaction no high-boiling products were formed, and in the latter reaction a polymeric solid, iodine, and a low boiling gas only were detected.

Reaction of both $CF_3CF_2CCl_3$ and CF_2BrCF_2Br with $CF_2=CFCl$ in the presence of benzoyl peroxide produced white polymers only.

Reaction of $CF_2ClCF_2CCl_3$ with isobutylene, in the presence of peroxide, gave $CF_2ClCF_2CCl_2CH_2C(CH_3)_2Cl$. This product dehydrohalogenated very easily on distillation to give either $CF_2ClCF_2CCl_2CH=C(CH_3)_2$ or $CF_2ClCF_2CCl_2CH_2C(CH_3)=CH_2$. Treatment with alcoholic potassium hydroxide, the addition product gave a number of compounds including $CF_2ClCF_2CCl_2CH_2-C(CH_3)=CH_2$, $CF_2ClCF_2CCl=CHC(CH_3)=CH_2$, $CF_2ClCF_2CCl=C=C(CH_3)_2$ and $CF_2ClCF_2C\equiv C-C(CH_3)=CH_2$.

Vinyl iodide and tetrafluoroethylene were exposed to sunlight for some time but most of the tetrafluoroethylene was recovered. The only other product isolated was a very high-boiling viscous mixture. No 1:1 adduct was formed.

Allyl iodide was allowed to react with tetrafluoroethylene in the presence of benzoyl peroxide to yield four products which have been identified as CH_3CHICH_3, $CH_2=CHCH_2CF_2CF_2I$, CF_2ICF_2I and suspected $CH_2=CHCH_2CF_2CF_2CH_2CH=CH_2$. The yield of 1:1 adduct was increased from 20% to 40% when reaction time was halved.

D. Monomer Synthesis for Contract Associates

1. The following silanes have been prepared and sent to F. M. C.

for evaluation: trimethyl-(trifluorovinyl) silane, $CF_2{=}CFSi(CH_3)_3$; (3,4,4-trifluoro-3-butenyl)-trimethylsilane; $CF_2{=}CFCH_2CH_2Si(CH_3)_3$; 1,3-di(3,4,4-trifluoro-3-butenyl)-1,1,3,3-tetramethyldisiloxane; $(CF_2{=}CFCH_2CH_2Si(CH_3)_2)_2O$.

2. Preparation of Octafluoroacetophenone

Octafluoroacetophenone has been prepared by the action of pentafluorophenylmagnesium bromide on lithium trifluoroacetate as described in the literature (31). Attempts to prepare this ketone by alternative routes have been made without success. The first attempt involved the action of pentafluorophenylmagnesium bromide on trifluoroacetic anhydride. The second was an attempt to apply the Friedel-Craft reaction to fluoroaromatics by reacting pentafluorobenzene with trifluoroacetyl chloride using tetrachloroethane as solvent in the presence of aluminum chloride.

3. Preparation of Octafluorostyrene

Octafluorostyrene has been prepared by a method outlined by Antonucci and Wall (32). This method involves the following stages:

$$CF_2ClCOOH \xrightarrow{LiH} CF_2ClCOOLi \xrightarrow{LiAlH_4} CF_2ClCHO \xrightarrow{C_6F_5MgBr}$$

$$CF_2ClCHOHC_6F_5 \xrightarrow{SF_4} C_6F_5CHFCF_2Cl \xrightarrow{\text{Molten KOH}} C_6F_5CF{=}CF_2$$

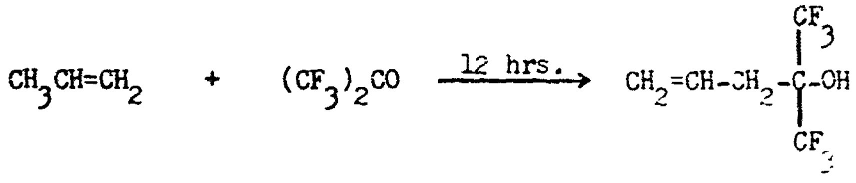
Without doubt the most difficult stage is the preparation of chlorodifluoroacetaldehyde as this material is very prone to polymerize. The remaining three stages can be accomplished very easily and in high yield. This reaction with the Grignard goes in 70 - 80% yield and the reaction with SF_4 which may be carried out on the crude alcohol is quantitative at 80°. The reaction of the ethylbenzene so formed with molten KOH depends critically on the temperature and contact time. It was found that at 170° and with a fast addition rate to the molten KOH, followed by immediate removal in a nitrogen stream, a 64% conversion was obtained. The octafluorostyrene was easily separated from starting material and minor products by preparative v.p.c., although fractional distillation would probably be more effective on a scale larger than 20 g.

4. The Preparation of 1,1,2-Trifluorohexene

The reactions of several organic lithium compounds with fluoroölefins have been reported in the literature (34). Applying the same general technique, butyl lithium was allowed to react with tetrafluoro-ethylene at low temperature to give the desired product, 1,1,2-trifluorohexene-1, b.p. 70 - 71° (lit. (34) b.p. 70°), in 64% yield. A small amount (<5%) of high-boiling product was also observed. This was probably 5,6-difluorodecene-5.

5. Preparation of Allylbis(trifluoromethyl)carbinol

Allylbis(trifluoromethyl)carbinol was prepared by a modification of the method reported by Gambaryan (116). Hexafluoroacetone was heated with excess propene in an autoclave to 150° for 12 hours. The carbinol, b.p. 95 - 96° (lit. (116) b.p. 95 - 8°) was produced in quantitative yield (based on hexafluoroacetone).



$$CH_3CH{=}CH_2 \quad + \quad (CF_3)_2CO \xrightarrow{12\ hrs.} CH_2{=}CH{-}CH_2{-}\overset{CF_3}{\underset{CF_3}{C}}{-}OH$$

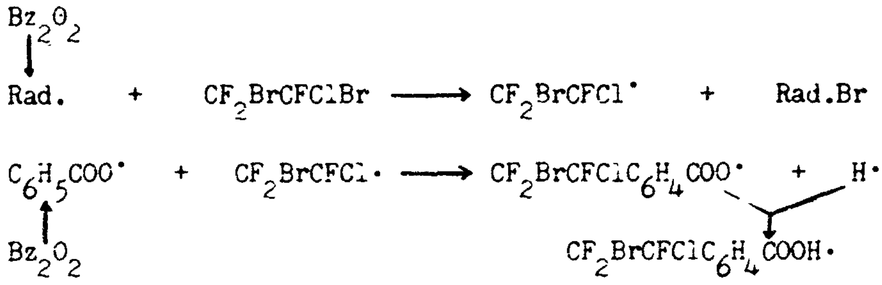
100%

E. Aromatic Substitutions

1. Attempted Formation of a Radical from $CF_2BrCFClBr$ and Its Reaction in situ with Aromatic Compounds

a. Ultraviolet Irradiation Initiation of $CF_2BrCFClBr$

Previously $CF_2BrCFClBr$ had been reacted with benzoyl peroxide to give one of the adducts p-$CF_2BrCFClC_6H_4COOH$ (35). It would seem that the relevant reactions in its formation are:



$$\overset{\mathrm{Bz_2O_2}}{\overset{\downarrow}{\mathrm{Rad.}}} + \mathrm{CF_2BrCFClBr} \longrightarrow \mathrm{CF_2BrCFCl^{\bullet}} + \mathrm{Rad.Br}$$

$$\underset{\mathrm{Bz_2O_2}}{\underset{\uparrow}{\mathrm{C_6H_5COO^{\bullet}}}} + \mathrm{CF_2BrCFCl\cdot} \longrightarrow \mathrm{CF_2BrCFClC_6H_4COO^{\bullet}} + \mathrm{H\cdot} \longrightarrow \mathrm{CF_2BrCFClC_6H_4COOH\cdot}$$

In the present investigation it was proposed to react the haloalkane radical formed, in situ with a hydrogen-containing aromatic compound, from which, hydrogen may be abstracted and a substituted alkyl benzene formed. Initially, ultraviolet light was used as the radical initiator to decrease the possible number of products. Thus a mixture of $CF_2BrCFClBr$ and benzene was irradiated. The reaction product showed no high-boiling product by v.p.c., but on distillation to remove starting materials followed by v.p.c. separation, bromobenzene and suspected $C_6H_5CFClCF_2Br$ (infrared and ^1H and ^{19}F NMR spectra were consistent) were isolated in 0.25% yield.

In an attempt to isolate the known compound p-$CF_2BrCFClC_6H_4COOH$, benzoic acid in benzene solution and $CF_2BrCFClBr$ were irradiated with ultraviolet light. There was no apparent reaction and benzoic acid was recovered in 90% yield.

Reaction of bromobenzene with a haloalkane radical should give a useful intermediate compound for the formation of a monomer, also bromobenzene is 75% more reactive than benzene with phenyl radicals from benzoyl peroxide. Therefore, bromobenzene and $CF_2BrCFClBr$, at an elevated temperature, were irradiated with ultraviolet light. Again there was little reaction but there was a greater percentage conversion to high-boiling products than the benzene reaction. The high-boiling products on the v.p.c. showed (mainly) two long retained overlapping peaks which have not been separated to date. There was a possibility of abstraction of a bromine atom in preference to a hydrogen atom from bromobenzene but no product of similar v.p.c. retention time to suspected $C_6H_5.CFClCF_2Br$ was present.

In the previous reactions there was a large evolution of hydrogen halide, therefore, in case the acidic gas caused any inhibiting action, basic pyridine was irradiated with $CF_2BrCFClBr$. The product of this reaction showed no indication of a substituted pyridine and only starting materials and a black residue were obtained.

It was predicted that irradiation of pentafluorobenzene would give a haloethylpentafluorobenzene which on dehalogenation would produce perfluorostyrene, a difficult compound to prepare by other routes. It has previously been shown that even a fluorine atom can be abstracted from hexafluorobenzene by benzoyl peroxide (36), but ultraviolet irradiation of pentafluorobenzene with $CF_2BrCFClBr$ gave only starting materials in good yield and a small residual tar.

In conjunction with the ultraviolet irradiation reactions, benzoic acid in benzene and pentafluorobenzene have been mixed with $CF_2BrCFClBr$ and have been exposed to sunlight. The latter experiment gave no apparent reaction on v.p.c. examination. The former experiment is continuing.

The ultraviolet irradiation reactions have been abandoned as the reaction, even where some product is isolated, is very inefficient. This must be due to lack of reactivity of the radicals produced from $CF_2BrCFClBr$ or inefficiency of ultraviolet light in producing those radicals.

b. Pyrolysis Experiments with $CF_2BrCFClBr$

$CF_2BrCFClBr$ has been pyrolyzed in a platinum tube at 500° and 600° and the products isolated (37). The proposed initiation mechanism involves production of a bromine atom and a haloalkane radical. The same experiment was repeated using a steel pyrolysis tube and it was found that maximum yield and conversion was obtained at 400°. At lower temperatures there was much unchanged starting material and at higher temperatures there was decomposition to carbon. Pyrolysis using a steel pyrolysis tube gave a more complex mixture than that using a platinum tube.

A mixture of benzene and $CF_2BrCFClBr$ was pyrolyzed at various temperatures. The optimum temperature of pyrolysis appeared to be 400 -

500° when minor products of longer v.p.c. retention time were observed, but there was no product of retention time similar to suspected $C_6H_5CFClCF_2Br$ obtained from the ultraviolet irradiation energized reaction. There appeared to be very little interraction of $CF_2BrCFClBr$ and benzene, as benzene was the only major product in experiments at all temperatures.

Pyrolysis of bromobenzene and $CF_2BrCFClBr$ seemed to give more high-boiling products at a furnace temperature of 500° than at lower temperatures, although there was a decrease in the weight of recovered material. Three high-boiling components, two of which corresponded by v.p.c. to the products isolated from the ultra violet initiated reaction, were still very minor products and bromobenzene appeared to be largely unchanged. Similarly, both pentafluorobenzene and bromopentafluorobenzene on pyrolysis with $CF_2BrCFClBr$ gave only traces of high-boiling products.

A preliminary experiment on pyrolysis of $CF_2BrCFClBr$ with olefins using a mixture of olefins showed a major product of longer v.p.c. retention time than starting materials, but as this was off the main course of investigation, it was not pursued.

A mixture of $CF_2BrCFClBr$ and bromine was pyrolyzed in an effort to obtain more $CF_2BrCFBr_2$ in the pyrolysis product than that obtained from pyrolysis of $CF_2BrCFClBr$ alone. This would give a convenient route to the preparation of the monomer, vinyl bromide. A pyrolysis of the mixture at 400° gave 26% yield of the suspected tribromotrifluoroethane compared to 8% on pyrolysis of $CF_2BrCFClBr$ alone. Also, in an attempt to prepare vinyl bromide, a mixture of bromine and $CF_2=CFCl$ was pyrolyzed, but the bromine reacted with the olefin before pyrolysis occurred.

There was no detectable reaction between benzene and $CF_2BrCFClBr$ when heated alone, therefore, an experiment was carried out in the presence of a 1/10 molar proportion of benzoyl peroxide as an initiator. Two high-boiling products were detected by v.p.c., corresponding to bromobenzene and suspected $C_6H_5CFClCF_2Br$ (as isolated from a previous experiment). They formed 9% and 5% of the volatile products, respectively. Non-volatile products, which may include derivatives of benzoic acid, were not examined.

2. Attempted Formation of a Radical from $CF_2ClCFClI$ and Its Reaction in situ with Aromatic Nuclei

Recently, it has been shown that trifluoromethyliodide wil react with monohalobenzenes to yield trifluoromethylmonohalobenzenes (38). This work has been adapted in an attempt to produce potential difunctional monomers. Benzene was reacted with $CF_2ClCFClI$ under conditions used in reference, but there was considerable decomposition to carbonaceous material and only 5% of the substituted benzene was formed. Under milder conditions the amount of decomposition decreased and the yield of suspected $C_6H_5CFClCF$ Cl increased to 24%. $CF_2ClCFClH$ (6% yield) was also identified (39). . The structure of $C_6H_5CFClCF_2$ was based on consistent infrared, ^1H and ^{19}F NMR, and ultraviolet spectra.

It seems that even milder conditions for the reaction above may increase the yield of $C_6H_5CFClCF_2Cl$, but there is an optimum as an experiment in which benzene and $CF_2ClCFClI$ were refluxed for 140 hours gave very little reaction.

As benzoyl peroxide seems to assist the reaction of benzene and $CF_2ClCFClBr$, it was used in a comparison experiment in an attempt to increase the yield of $C_6H_5CFClCF_2Cl$ from benzene and $CF_2ClCFClI$. A blank experiment in which only benzene and $CF_2ClCFClI$ were heated was run under identical conditions. The former experiment showed an 18% conversion to higher boiling products compared to the conversion in the latter which was only 2%. The higher boiling product from the former experiment was a single peak on a silicon gum packed gas chromatography column at 180°, but on the same packing at 100° it separated into two peaks in the ratio of 18:82. The minor component was identified as iodobenzene and the major component was identified as $C_6H_5CFClCF_2Cl$ by gas chromatographic retention time. Therefore, the overall conversion to $C_6H_5CFClCF_2Cl$ was 14.8% in the benzoyl peroxide initiated reaction, but in the blank experiment the conversion to $C_6H_5CFClCF_2Cl$ was only 2%.

A different approach was used next in an attempt to increase the yield of $C_6H_5CFClCF_2Cl$ from benzene and $CF_2ClCFClI$. Rather than use a free-radical source as an initiator, the reaction was carried out in the presence of a metal which would easily take up the liberated iodine atoms (viz. mercury and copper dust). A blank experiment was again run under identical conditions for comparison. The blank experiment showed a 2.3% conversion to $C_6H_5CFClCF_2Cl$, whereas the experiment in the presence of mercury showed a 9.3% conversion to a higher boiling product corresponding to $C_6H_5CFClCF_2Cl$. The experiment, in the presence of electrolytic copper dust, could not be compared directly as the organic liquid formed a slurry with the dust.

Reaction of pentafluorobenzene with $CF_2ClCFClI$, which would give a facile preparation of perfluorostyrene, could not be effected by heating alone. In a preliminary reaction of pentafluorobenzene and $CF_2ClCFClI$, in the presence of benzoyl peroxide, there was a 6% conversion to a higher boiling product. Therefore, three comparison reactions were set up under identical conditions. The first tube (1) contained pentafluorobenzene, $CF_2ClCFClI$ in equimolar proportions and 0.425 molar proportion of benzoyl peroxide. The second tube (2) contained pentafluorobenzene and $CF_2ClCFClI$ in equimolar proportions and a 0.2 molar proportion of benzoyl peroxide. The third tube (3) contained pentafluorobenzene and $CF_2BrCFClBr$ in equimolar proportions and 0.2 molar proportion of benzoyl peroxide. The percentages of high-boiling products from gas chromatographic peak areas were (1) 27%, (2) 8%, (3) 23%. The high-boiling product was isolated from (1) by gas chromatography and was shown to be iodobenzene by infrared spectroscopy. The major high-boiling product from (3) had the same gas chromatographic retention time as bromobenzene. The minor product of slightly longer retention time than bromobenzene was in insufficient quantity for identification. Only volatile products were investigated.

Although dechlorination of $C_6H_5CFClCF_2Cl$ will only yield the known α,β,β-trifluorostyrene, which has been polymerized, the same radical reaction may be effected using substituted benzene derivatives and $CF_2ClCFClI$ to yield monomers through which cross-linking is possible. Thus bromobenzene was heated with $CF_2ClCFClI$. The product of long retention time is suspected to be $BrC_6H_4CFClCF_2Cl$ (14% yield). It was of interest to note that in addition to suspected $BrC_6H_5CFClCF_2Cl$, a product whose v.p.c. retention time corresponded to $C_6H_5CFClCF_2Cl$ was present in the ratio $BrC_6H_4CFClCF_2Cl:C_6H_5CFClCF_2Cl::8:1$. This ratio was reversed by effecting the reaction in the presence of copper dust.

Refluxing bromobenzene with $CF_2ClCFClI$ at a liquid temperature of ca. 115° gave a 13% conversion (by v.p.c. peak area) to suspected $BrC_6H_4CFClCF_2Cl$ after 90 hours. This indicates that the ideal temperature for liberation of radicals from $CF_2ClCFClI$ is $>115^\circ$ and $<165^\circ$.

In experiments between phenol and $CF_2ClCFClI$ and nitrobenzene and CF_2ClCF_2ClI, a poor conversion to the haloethyl substituted products was indicated.

An experiment to compare the reactivity of benzene and iodobenzene (i.e., ease of removal of hydrogen and iodine atoms from an aromatic nucleus) with $CF_2ClCFClI$ was attempted, but conditions were too mild to detect any reaction in either case.

As this whole series of experiments, using $CF_2BrCFClBr$ and $CF_2ClCFClI$ as sources of radicals to react with aromatic nuclei and form ethyl benzenes, gave poor yields, this route to styrenes has been abandoned.

3. Other Attempted Aromatic Substitutions

The reaction of pentafluorobenzoic acid with ammonia was investigated; however, none of the expected 4-amino-tetrafluorobenzoic acid was observed.

Attempts to react 1,4-dibromotetrafluorobenzene with silver isocyanate were unsuccessful. Several solvents were used.

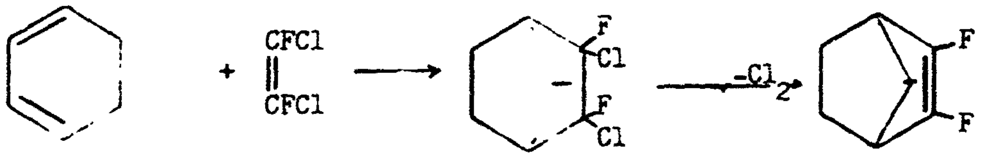
It is well-known that hexafluorobenzene is susceptible to attack by anionic species. Attempts to react hexafluorobenzene with potassium bromide and sodium iodide in solvents, such as acetone, dimethylsulphoxide and dimethylformamide have failed to produce any of the desired bromo- or iodopentafluorobenzenes. It was learned that a similar attempted reaction between sodium iodide in acetone with chloropentafluorobenzene was also unsuccessful (40). The preparation of certain fluoroperhalocarbanions has been reported by Miller (41,42).

The feasibility of a reaction between the heptafluoro-iso-propyl carbanion and hexafluorobenzene has been investigated; however, in all cases the hexafluorobenzene was recovered without attack. The experiments were performed with hexafluorobenzene, hexafluoropropene and potassium fluoride in formamide and dimethylformamide at room temperature and at 70° in a sealed tube. In each case, analytical gas chromatography indicated that a low-boiling product apart from hexafluoropropene was formed, presumably 2H-heptafluoropropane (41), but no aromatic compound other than hexafluorobenzene was present.

F. Attempted Preparation of Partially Fluorinated Norbornadienes

The hydrocarbon norborna-2,5-diene was prepared by Diels-Alder addition of sym-dichloroethylene to cyclopentadiene, followed by dechlorination (43).

It was proposed to prepare a partially fluorinated norbornadiene by a Diels-Alder addition to cyclopentadiene and sym-dichlorodifluoroethylene, followed by dechlorination of the Diels-Alder adduct to yield 2,3-difluoro-norborna-2,5-diene thus:



The initial reaction of cyclopentadiene and sym-dichlorodifluoroethylene gave a product which could be separated into an ether-insoluble solid and an ether-soluble gum, neither of which have been purified. The formation of ether-insoluble solid indicated that the reaction had proceeded beyond the simple Diels-Alder adduct, so the experiment was repeated under milder conditions. As the product, if any, could not be isolated from this reaction, dechlorination of the impure product was attempted using magnesium and iodine in ether, followed by zinc in ethanol, but no diene product was detected.

To test the procedure, the previously known Diels-Alder addition of cyclopentadiene and perfluoropropene (44) was attempted and the adduct isolated in 19% yield. Similarly, perfluorobutene-2 was allowed to react with cyclopentadiene and the adduct was formed in 88% yield. The adduct gave a consistent infrared, ^{19}F NMR spectra and elemental analysis; decolorized a bromine solution and was oxidized by potassium permanganate. The proton NMR spectrum showed a Diels-Alder (1,4-) adduct rather than a 1,2- adduct (45).

Dehalogenation of the Diels-Alder adduct, 5,6-difluoro-5,6-bis (trifluoromethyl)-norborn-2-ene was attempted using zinc in isopropanol, but only starting material was detected. Dehydrohalogenation was attempted by dropping the adduct on to molten potassium hydroxide. It was thought that if the bridge-head carbonium ion could be formed that it might rearrange, but only starting material was recovered in 84% yield.

As the Diels-Alder adduct from perfluorobutene-2 could not be dehalogenated, a Diels-Alder addition between cyclopentadiene and 2,3-dichlorohexafluorobutene-2 was attempted. The reaction mixture showed starting materials, dicyclopentadiene (trace) and adduct by gas chromatography. The product was isolated (33% conversion) as a white waxy solid which easily was oxidized by potassium permanganate and decolorized a bromine solution. A consistent infrared spectrum and elemental analysis were obtained for an adduct, which from the proton NMR spectrum was shown to be a Diels-Alder adduct, 5,6-dichloro-5,6-bis(trifluoromethyl)-norborn-2-ene (45). The pure product gave an unsymmetrical gas chromatographic peak.

Dechlorination of the adduct was attempted by two methods. The hydrocarbon norbornadiene was prepared by addition of cyclopentadiene to sym-dichloroethylene, followed by dechlorination by magnesium iodide in ether (43).

Dechlorination of 5,6-dichloro-5,6-bis(trifluoromethyl)-norborn-2-ene was attempted under identical conditions, but only trace quantities of product were detected by gas chromatography and a quantitative yield of starting material was recovered. The second dechlorination route attempted was using activated zinc in isopropanol. The dechlorination product was formed in at least 86% yield and was identified by infrared spectroscopy as 2,3-bis(trifluoromethyl)norbornadiene This product was also obtained from addition of cyclopentadiene to hexafluorobutyne-2.

Hexafluorobutyne was prepared by a known route (46). The addition between cyclopentadiene and hexafluorobutyne was facile and the adduct was formed in 84% yield, the remainder being low-boiling starting material and a trace of dicyclopentadiene. The pure adduct was oxidized by potassium permanganate and decolorized bromine. The adduct had a consistent infrared spectrum, particularly the medium intensity absorption at 5.92μ attributable to $CF_3-C=C-CF_3$. The elemental analysis was consistent for the adduct. The proton NMR spectrum was consistent for a Diels-Alder adduct, 2,3-bis(trifluoromethyl)norbornadiene.

The addition of cyclopentadiene to sym-dichlorodifluoroethylene was attempted at 150° on a small scale. A shoulder was noticed on the dicyclopentadiene peak. The reaction was therefore repeated at 170°, at which temperature dicyclopentadiene cleaves to give the monomer. This reaction increased the area of the shoulder so that it came larger than the dicyclopentadiene peak. An autoclave reaction of 0.5 molar scale gave an 11.5% conversion to the adduct, the major product being a highly viscous high-boiling liquid, which crystallized on standing. Identification of the latter product has not been attempted, although from the similarity of its infrared spectrum to the Diels-Alder adduct and from previous literature, it is suspected to be the product of further addition of cyclopentadiene.

The product formed in 11.5% yield, which was a low-melting solid, which was oxidized by potassium permanganate solution and decolorized bromine. It gave a consistent infrared spectrum and elemental analysis for an adduct. The proton NMR spectrum was consistent for the 1,4-adduct, 5,6-dichloro-5,6-difluoro-norborn-2-ene (45). The ^{19}F NMR spectrum was inconclusive.

As dechlorination of 5,6-dichloro-5,6-bis(trifluoromethyl)norborn-2-ene was easily effected by activated zinc in isopropyl alcohol, the same system was used in an attempt to dechlorinate 5,6-dichloro-5,6-difluoronorborn-2-ene. The starting material was recovered in 95.5% yield.

The addition of cyclopentadiene to trifluoroethylene was attempted, as dehydrofluorination of the adduct should give the same product as the dechlorination attempted on 5,6-dichloro-5,6-difluoronorborn-2-ene. Initial attempts at the addition on a small scale gave recovered olefin in 76 - 92% yield. It was noted in these experiments that there was always a minor product of suitable gas chromatographic retention time for an adduct. Also, an increase in the reaction temperature gave a decrease in the percentage of unchanged olefin recovered. In this whole series of experiments it was found that the autoclave reaction where the whole vessel was heated gave superior yields to the small scale experiments in Fischer-Porter tubes where only part of the vessel was heated. Also, additions that had to be effected at higher temperatures gave poor yields of simple adduct accompanied by higher boiling products.

An autoclave addition of cyclopentadiene and trifluoroethylene was carried out at 165° and 53% of the unchanged olefin was recovered. The adduct, which was a waxy solid, was formed in 33% yield based on unrecovered olefin, the major product being a high-boiling liquid which was not identified. The purified simple adduct was oxidized by potassium permanganate and decolorized bromine. It gave consistent infrared spectrum and elemental analysis for an adduct. The ^{19}F NMR spectrum indicated a mixture of two isomers of 5,5,6-trifluoronorborn-2-ene, but the proton NMR spectrum was inconclusive.

Dehydrofluorination of the adduct was attempted using aqueous and alcoholic aqueous potassium hydroxide but no product was detected, the yield of starting material being quantitative in both cases.

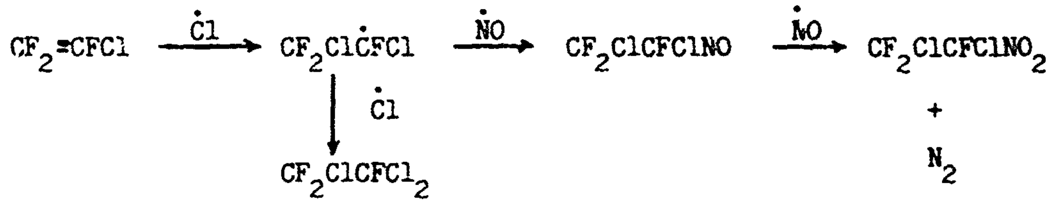
Small scale addition of cyclopentadiene to chlorotrifluoroethylene gave a 44% recovery of starting olefin, but an autoclave reaction gave a negligible amount of low-boiling product. A large amount of brown viscous liquid of low volatility was formed. The adduct, which was a liquid, was formed in 26% yield. It easily was oxidized by potassium permanganate and decolorized bromine solution. The adduct gave a consistent infrared spectrum and elemental analysis. The proton and ^{19}F NMR spectra indicated at least four components which seemed to be isomers of both the 1,4- and 1,2- adducts .

The last addition attempted used isopropenylacetylene as a diene. It was allowed to react with octafluorobutene-2 as this olefin gave a facile reaction with cyclopentadiene. Under the conditions used, no adduct was detected and a very good recovery of starting material was obtained.

G. Fluoronitroso Compounds

The preparation of fluoronitroso compounds by the addition of nitrosyl chloride to fluoroölefins has been reported (47-49) but only fluoroalkenes were used. No attempt has been made to prepare nitroso compounds from unsaturated fluoro-esters and ethers. The addition of nitrosyl chloride to fluoroolefins was usually effected by ultraviolet irradiation or sunlight and a blue nitroso compound together with some nitro- and chloro-derivatives of olefin were obtained as follows:

$$NOCl \xrightarrow{uv} \dot{N}O + \dot{C}l$$



$$CF_2{=}CFCl \xrightarrow{\dot{C}l} CF_2Cl\dot{C}FCl \xrightarrow{\dot{N}O} CF_2ClCFClNO \xrightarrow{\dot{N}O} CF_2ClCFClNO_2 + N_2$$

$$CF_2Cl\dot{C}FCl \xrightarrow{\dot{C}l} CF_2ClCFCl_2$$

Park (47,48) has reported that powdered ferric chloride will catalyze the reaction and that a free-radical mechanism is followed similar to that in ultraviolet light. In our laboratory it has been found that nitrosyl chloride and fluoroölefins react in a suspension of aluminum chloride and dimethylformamide (49). The following mechanism was suggested:

$$AlCl_3 \quad + \quad NOCl \qquad NO^+AlCl_4^-$$

$$CF_2{=}CFCl \quad + \quad AlCl_4^- \longrightarrow \left[AlCl_3\cdots Cl\cdots CF_2\cdots CFCl\right]^-$$

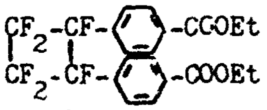
$$\longrightarrow AlCl_3 \quad + \quad CF_2ClCFCl^-$$

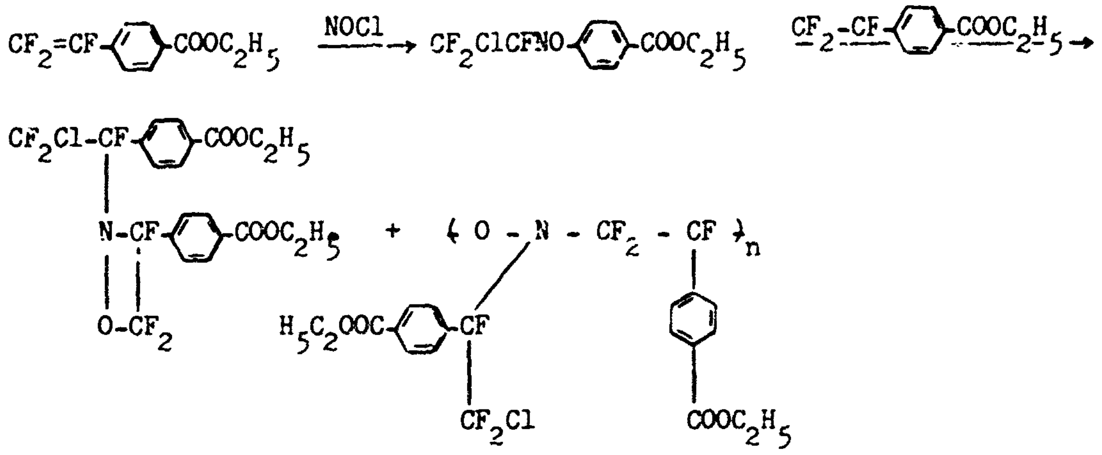
$$CF_2ClCFCl^- \quad + \quad NO^+ \longrightarrow CF_2ClCFClNO$$

In the current work this method has been used to prepare nitroso compounds from fluoro-esters and -ethers.

1. <u>Preparation of p-trifluorovinyl Ethyl Benzoate and Reaction with Nitrosyl Chloride</u>

The preparation of trifluorovinyl benzoic acid has been investigated(35). . Trifluorovinyl ethyl benzoate was prepared via this method (35) and the p-substituted structure was confirmed by NMR.

During vacuum distillation over 150°, the ester formed a viscous oil which showed infrared absorption at 884 cm^{-1} consistent with a cyclic structure. NMR data confirmed the structure  for this compound. The reaction of trifluorovinyl ethyl benzoate with nitrosyl chloride was carried out at 0° using the method reported (49). The reaction product was a light green viscous oil which decomposed at room temperature after <u>ca</u>. 7 hours. An attempt was made to separate the product by alumina chromatography. The light green compound collected was not the expected nitroso compound but a mixture of two compounds, as on standing at 0°, a white solid crystallized out. Olefins and nitroso compounds reacted to form oxazetidines and polymers (50) and elemental analysis of the light green mixture and elemental, infrared and NMR analysis of the solid was consistent with an analogous reaction:



The solid is probably the oxazetidine.

2. Reaction of Unsaturated Fluoroesters with Nitrosyl Chloride

$CF_2=CFCF_2COOC_2H_5$, $CF_2=CFCF_2COOCH_3$ and $CF_2=CFCOOC_2H_5$ were used as the esters. In each case, the blue nitroso compounds were separated from the chloro derivatives by v.p.c. The nitroso products decomposed below their boiling points.

3. Reaction of Unsaturated Fluoroethers with Nitrosyl Chloride

$C_6H_5OCF=CCl_2$ and $CH_2=CHCH_2OCF_2CFClH$ were used as the ethers. The phenolic ether produced a nitroso compound as identified by the blue color and infrared spectrum but $CH_2=CHCH_2OCF_2CFClH$ did not give a blue nitroso product.

4. Preparation of Fluoronitroso Compounds from Olefins

The reaction of $CF_2=CFCH_2CH=CH_2$ and nitrosyl chloride was effected to yield $CF_2ClCF(NO)\cdot CH_2CH=CH_2$.

The diene was prepared by the known route (17) of addition of $CF_2BrCFClBr$ to allyl chloride, followed by dehalogenation. By the usual procedure (49), the addition of nitrosyl chloride to the diene was predominantly at the $CF_2=CF$- grouping. The yield of nitroso compound was poor and nearly 30% of the starting diene was recovered when equimolar proportions of nitrosyl chloride and diene were used, but if an excess of nitrosyl chloride was used, several unidentified high-boiling products were formed. The infrared spectrum of the high-boiling products showed absorption at 5.55μ and 5.78μ, compared to N-O and -HC=CH- absorption of the nitroso adduct at 6.31μ and 6.1μ (weak), respectively. The nitroso adduct was decomposed by air and heat from a blue liquid through green and yellow to give finally a dark brown viscous liquid. The compound was sufficiently stable to allow gas chromatographic separation at 50 - 60°.

The reaction of $CF_2=CFCH=CH_2$ with nitrosyl chloride has been studied in this laboratory before and a small amount of blue liquid was obtained, but no further work was done. In the present work the addition was attempted using aluminum chloride and D. M. F. as solvent as before. Orange or light green colored reaction mixtures were obtained depending on the conditions used, but in both cases the low-boiling nitroso compound was a minor product, the major product (>95%) being a colorless high-boiling compound. This main product showed absorption in the infrared spectrum of 5.78μ and 6.05μ but the structure is still under investigation.

The reaction of $CF_2=CFCH=CHCF_3$ with nitrosyl chloride also gave a high-boiling colorless product rather than a low-boiling blue nitroso compound. The main product had absorption peaks in the infrared spectrum at 5.80μ and 6.05μ, respectively.

No nitroso compound was formed when $BrCF_2CF_2CH=CH_2$ was treated with nitric oxide in the presence of mercury and sunlight. A reaction under similar conditions using $CF_2ICF_2CH_2CH=CH_2$ gave a blue color indicative of a nitroso compound, which was discharged when the product was brought to ambient in the presence of oxygen.

H. Fluoroketone Studies

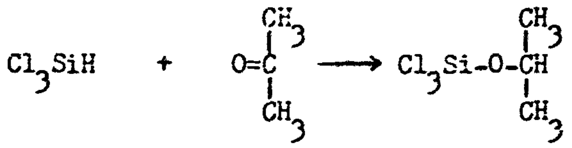
It is well-established that fluorinated ketones react readily with nucleophilic reagents. Useful surveys of the literature are contained in two publications (56,57).

The reaction of hexafluoro- and sym-dichlorotetrafluoro- acetones with Grignard reagents appear to give two types of products, the expected tertiary carbinol and in some cases a reduction product, 1,1,1,3,3,3-hexafluoroisopropanol with the former ketone. In the present work, the above-mentioned ketones have been reacted with methyllithium and trifluorovinylmagnesium bromide, and hexafluoroacetone has been reacted with 2,2-difluorovinylmagnesium bromide. The latter two reactions are described later.

The reaction of methyllithium with sym-dichlorotetrafluoroacetone and hexafluoroacetone gave, respectively, the ether azeotropes of 1,1-bis (chlorodifluoromethyl)ethanol, and 1,1-bis(trifluoromethyl)ethanol. The carbinols were purified by preparative gas chromatography. The former was characterized by spectroscopic (NMR and i.r.) and elemental analyses, the latter had identical physical characteristics to the carbinol described by Knunyants and co-worker (51) who prepared it by the reaction of methylmagnesium bromide with hexafluoroacetone.

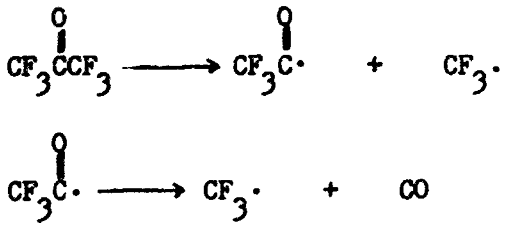
Attempts have been made to react metallic salts of the carbinols with chlorotrifluoroethylene to form olefinic derivatives. The lithium salts of 1,2-bis(trifluoromethyl)- and 1,1-bis(chlorodifluoromethyl)-ethanols (formed in their preparation) did not react with chlorotrifluoroethylene. The sodium salt of perfluoro-1,1-dimethylprop-2-en-1-ol was prepared by reaction of the alcohol with sodium in ether or an excess of alcohol. However, there was no reaction between the alcohol salt and chlorotrifluoroethylene in diethylether, tetrahydrofuran or in the alcohol itself. Reactions that were performed in tetrahydrofuran gave a product due to a combination of tetrahydrofuran and chlorotrifluoroethylene; the product has not been fully characterized.

Calas and Duffant (58) reported that trichlorosilane added to aliphatic ketones under u.v. irradiation in the following manner:



$$Cl_3SiH \quad + \quad O{=}\overset{CH_3}{\underset{CH_3}{C}} \longrightarrow Cl_3Si{-}O{-}\overset{CH_3}{\underset{CH_3}{CH}}$$

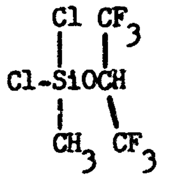
It has been reported that u.v. irradiation induces fluoroketones to disproportionate by the following mechanism: (59)



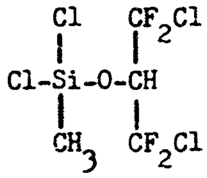
$$CF_3\overset{O}{\overset{\|}{C}}CF_3 \longrightarrow CF_3\overset{O}{\overset{\|}{C}}\cdot + CF_3\cdot$$

$$CF_3\overset{O}{\overset{\|}{C}}\cdot \longrightarrow CF_3\cdot + CO$$

In reaction of methyl dichlorosilane with hexafluoro- and sym-dichlorotetrafluoroacetones under u.v. irradiation, it was found that the predominant reaction was addition of the silane to the ketones to give respectively



and



A study of the stability of the Si-O bond in these compounds towards hydrolysis is to be made.

I. Preparation and Reactions of Some Silanes Containing the Trifluorovinyl Group

1. Reaction of Organolithium Compounds with Trimethyl Trifluorovinylsilane

Seyferth and Wada (60) have reported the reaction of organolithium reagents and sodium alkoxides with triethyltrifluorovinylsilane to prepare compounds of the type $(C_2H_5)_3SiCF{=}CFR$ and $(C_2H_5)_3SiCF{=}CFOR$.

A similar reaction using trimethyltrifluorovinylsilane and organolithium reagents was investigated and, in general, a good yield of the product $(CH_3)_3SiCF{=}CFR$ was formed. (R = methyl, n-butyl, allyl, vinyl, phenyl, 3-trifluoromethylphenyl, 2-thiophenyl and 1-napthyl.) Alcoholysis of these products provides a convenient route to the 1,2-difluoroölefins. The compounds from these reactions, and their physical properties are listed in Table VI.

$$(CH_3)_3SiCF{=}CF_2 \xrightarrow[Et_2O]{RLi} (CH_3)_3SiCF{=}CFR \xrightarrow[Ethanol]{KOH} RCF{=}CFH$$

Reactions with ferrocenyl lithium and 2-styryl lithium were unsuccessful; however, it is questionable whether the lithium reagents were actually formed.

2. Other Syntheses of Silanes Containing the Trifluorovinyl Group

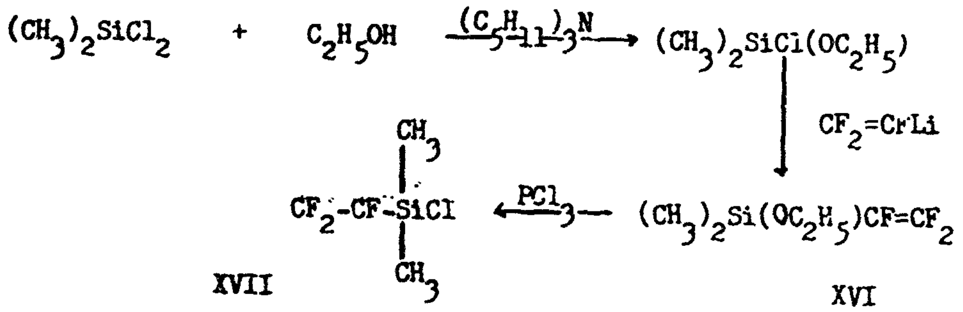
As part of this continuing program on the preparation and reactions of fluoroölefins, it seemed desirable to synthesize and study the reactions of silanes containing the trifluorovinyl group separated from the silicon atom by varying numbers of methylene units.

[illegible] first trifluorovinylsilane was prepared by Knunyants (61), who obtained $(CF_2=CF)_4Si$ as the reaction product of trifluorovinylmagnesium iodide and silicon tetrachloride. Seyferth (62,63) prepared $CF_2=CFSi(C_2H_5)_3$ by the Grignard method and $CF_2=CFSi(CH_3)_3$ by the reaction of trimethylchlorosilane with trifluorovinyllithium, which was prepared by treating trifluorovinyltin compounds with phenyllithium.

In our laboratory, trifluorovinyltrimethylsilane XIV was prepared in 65% yield by a two-step reaction in which bromotrifluoroethylene reacted with methyllithium to give trifluorovinyllithium, which was allowed to react with trimethylchlorosilane.

An attempt was made to prepare trifluorovinyldimethylchlorosilane from the reaction of trifluorovinyllithium and dimethyldichlorosilane in a 1:1 molar ratio, but only bis(trifluorovinyl)dimethylsilane XV was obtained. This experiment confirms the results of Knunyants in indicating the increased reactivity of the silicon-chlorine bond in silanes containing both this group and a trifluorovinyl group attached to silicon.

Alkoxysilanes undergo approximately the same reactions as chlorosilanes, although they are somewhat less reactive; therefore, a synthetic procedure was devised which led to the formation of trifluorovinyldimethylchlorosilane by the scheme shown in eq 1. The compounds were identified by elemental analysis . MR_D, and infrared spectra.

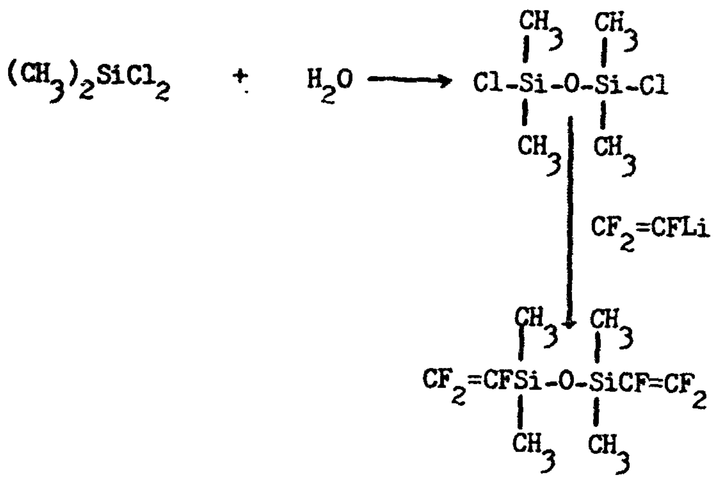


(1)

XVII

XVI

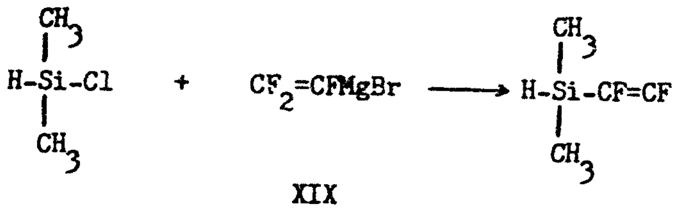
The sym-tetramethylbis(trifluorovinyl)disiloxane was prepared by the route shown in eq 2.



(2)

XVIII

Another compound of the series was prepared by allowing dimethylchlorosilane to react with trifluorovinylmagnesium bromide to give trifluorovinyldimethylsilane eq 3.



(3)

XIX

Elemental analysis and infrared data were consistent with this structure. When trifluorovinyllithium was used instead of the Grignard reagent, a brown tar was obtained.

Pentafluorophenylmagnesium bromide was prepared and allowed to react with $CF_2=CFSi(CH_3)_2Cl$ to give the trifluorovinylpentafluorophenyldimethylsilane XX. It was of some interest to determine whether one or both fluorine-containing groups would be cleaved by reaction with base. Consequently, a sample of the product was treated with alcoholic potassium hydroxide and a gas, presumably $CHF=CF_2$, was obtained. Examination of the liquid products showed that pentafluorobenzene had also been formed, thus indicating the cleavage of both groups.

A different approach was used to prepare $(CH_3)_3SiCH_2CF=CF_2$ XXI. Earlier Tarrant and Warner (64) had shown that Grignard reagents reacted with fluoroölefins to give alkylated or arylated fluoroölefins while Dixon (34) reported that lithium reagents behaved in the same manner. With tetrafluoroethylene, lithium reagents often give disubstituted products such as RCF=CFR.

$$RMgX + CF_2=CX_2 \longrightarrow RCF=CX_2 + MgFX$$

$$RLi + CF_2=CX_2 \longrightarrow RCF=CX_2 + LiF$$

A Grignard reagent was prepared from trimethylchloromethylsilane and was treated with tetrafluoroethylene under a variety of conditions, but no 2,3,3-trifluoroallyltrimethylsilane was obtained. However, the desired compound was made by treating the corresponding lithium reagent with tetrafluoroethylene

$$(CH_3)_3SiCH_2Li + CF_2=CF_2 \longrightarrow (CH_3)_3SiCH_2CF=CF_2$$

in a sealed tube at 0°. Elemental analysis and infrared data support the structure shown.

The preparation of the next member of the series, $(CH_3)_3SiCH_2CH_2CF=CF_2$ XXII, was adapted from a synthetic route used by Tarrant and Tomasino(65).

It is shown in eq 4.

$$CF_2BrCFClBr \quad + \quad CH_2{=}CHSi(CH_3)_3 \longrightarrow$$

$$CF_2BrCFClCH_2CHBrSi(CH_3)_3 \xrightarrow{C_2H_5OH\text{-}HCl\text{-}Zn} CF_2{=}CFCH_2CH_2Si(CH_3)_3 \qquad (4)$$

XXII

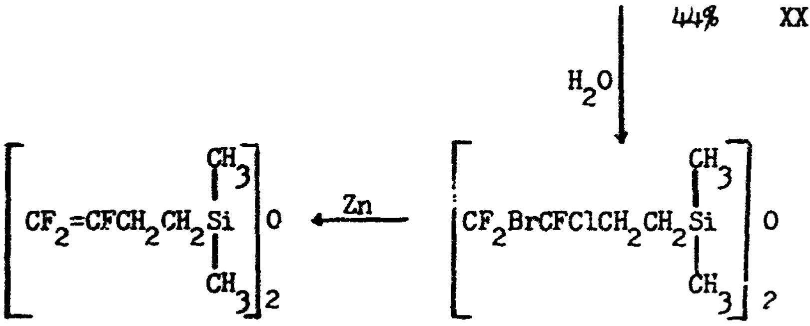
By carrying out a combined dehalogenation with zinc and reduction using zinc and hydrochloric acid, a 65% yield of the desired olefin was realized.

The reaction of dimethylchlorosilane and $CH_2{=}CHCFClCF_2Br$ gave the corresponding adduct which was used to make the disiloxane as shown in eq 5.

$$(CH_3)_2SiHCl \quad + \quad CH_2{=}CHCFClCF_2Br \longrightarrow$$

$$(CH_3)_2Si(Cl)CH_2CH_2CFClCF_2Br \qquad (5)$$

44% XXIII

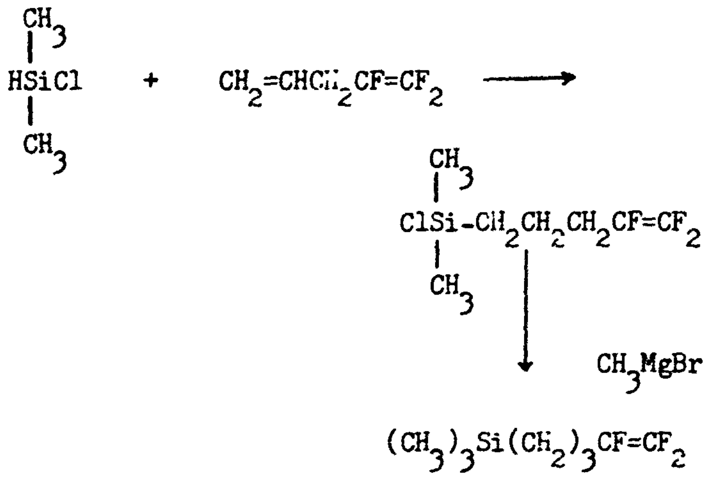


$$\left[CF_2{=}CFCH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}\right]_2 O \xleftarrow{Zn} \left[CF_2BrCFClCH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}\right]_2 O \xleftarrow{H_2O} XXIII$$

XXV XXIV

This compound had been prepared previously (63) but the yields by the method described here are much greater. An attempt to prepare $CF_2{=}CFCH_2CH_2Si(CH_3)_2Cl$ directly by the addition of dimethylchlorosilane to 1,1,2-trifluorobutadiene in a sealed tube at 70° was unsuccessful, as an explosion occurred. The chloroplatinic acid-initiated addition of methyldichlorosilane to $CH_2{=}CHCFClCF_2Br$ was carried out successfully to give the adduct $CF_2BrCFClCH_2CH_2Si(CH_3)Cl_2$ XXVI in 71% yield.

The last member of the trimethyltrifluorovinylalkylsilanes prepared was $CF_2{=}CFCH_2CH_2CH_2Si(CH_3)_3$ XVII. It was made by the sequence shown in eq 6.



$$\underset{CH_3}{\overset{CH_3}{HSiCl}} + CH_2{=}CHCH_2CF{=}CF_2 \longrightarrow \underset{CH_3}{\overset{CH_3}{ClSi}}{-}CH_2CH_2CH_2CF{=}CF_2 \xrightarrow{CH_3MgBr} (CH_3)_3Si(CH_2)_3CF{=}CF_2 \qquad (6)$$

XXVII

Thus, dimethylchlorosilane shows the same preference for reaction with a hydrocarbon vinyl group rather than a trifluorovinyl group that is displayed by CCl_3Br which gives $CCl_3(CH_2)_3CF{=}CF_2$ as reported by Muramatsu and Tarrant (19).

The chlorosilane XXVIII so formed was hydrolyzed to the corresponding disiloxane XXIX.

Seyferth (60) has studied the reaction of nucleophilic reagents with trifluorovinyltriethylsilane and found, in general, that the normal reactions of fluoroölefins containing the $CF_2{=}$ group occurred. An exception was the reaction with sodium ethoxide in ethanol, which led to the cleavage of the carbon-silicon bond predominantly.

Surprisingly, $CF_2{=}CFCH_2CH_2Si(CH_3)_3$ XVII was found to be resistant to attack by certain nucleophilic reagents. No reaction occurred on refluxing with a mixture of sodium ethoxide in ethanol over a period of 20 hours or when the mixture was heated to 150° in a sealed tube for 12 hours.

However, phenyllithium reacted with the olefin to give the substituted compound in good yield, eq 7.

$$C_6H_5Li \quad + \quad CF_2{=}CFCH_2CH_2Si(CH_3)_3 \longrightarrow$$

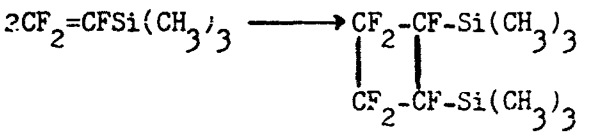
$$\text{XXX} \qquad C_6H_5CF{=}CFCH_2CH_2Si(CH_3)_3 \qquad (7)$$

The product was identified by elemental analysis and infrared spectroscopy.

It should be noted that other compounds containing the $CF_2{=}CFCH_2CH_2$- group have been found to be resistant to attack by reagents which attack simpler fluoroölefins containing the $CF_2{=}$ group. For example, allylmagnesium bromide has been found to react with $CF_2{=}CF_2$, $CF_2{=}CFBr$, $CF_2{=}CFCl$, etc., but no reaction occurred with $CF_2{=}CFCH_2CH_2Br$ (66). These results suggest that 1,1,2-trifluoroölefins containing an electron-releasing group, such as the alkyl group, are not as susceptible to attack by nucleophiles as are such olefins containing electronegative groups.

Fluoroethylenes containing the $CF_2{=}$ group, upon heating, dimerize to cyclobutane derivatives. A study was made of this reaction with a number of vinylsilanes prepared.

Trifluorovinyltrimethylsilane was heated for 2 days at 200° in a sealed tube to give a small amount of a product tentatively identifed as the dimer by elemental analysis and infrared data. An attempt was made to obtain either a Diels-Alder adduct or a cyclobutane derivative with butadiene, but polymeric products were obtained.



$$2CF_2{=}CFSi(CH_3)_3 \longrightarrow \begin{array}{l} CF_2-CF-Si(CH_3)_3 \\ |\qquad\ \ | \\ CF_2-CF-Si(CH_3)_3 \end{array}$$

XXXI

Heating $CF_2{=}CFCH_2CH_2Si(CH_3)_3$ for 2 days at 200° gave a 33% yield of the cyclic dimer XXXII which was identified by elemental analysis and infrared and NMR spectra. Furthermore, the unsaturated silane reacted with butadiene to give a vinylcyclobutane derivative (eq 8). The thermal dimerization of a pentenyl derivative occurred in 42% yield (eq 9).

TABLE VII

PHYSICAL PROPERTIES AND ANALYSES OF COMPOUNDS PREPARED

Compound	Structure	Yield %	B.p. °C	n^{20}_D	d^{20}_{20}	Calculated % C	Calculated % H	Calculated % F	Found % C	Found % H	Found % F
XIV	$CF_2=CFSi(CH_3)_3$	65	67[b]	1.3580	0.983						
XV	$(CF_2=CF)_2Si(CH_3)_2$	56	98	1.3633	1.272	32.73	2.74	51.77	32.43	2.97	51.48
XVI	$CF_2=CFSi(CH_3)_2(OC_2H_5)$	50	104	1.3642	1.028	39.12	6.02	30.94	38.90	6.26	31.05
XVII	$CF_2=CFSi(CH_3)_2Cl$	55	87	1.3764	1.154	27.51	3.46	32.64	27.74	3.68	32.81
XVIII	$[CF_2=CFSi(CH_3)_2]_2O$	50	54 (20)	1.3691	1.136	32.60	4.11	38.72	32.54	4.23	38.46
XIX	$CF_2=CFSi(CH_3)_2H$	25	50	1.3513	0.976	34.26	5.03	40.65	34.55	5.28	40.29
XX	$CF_2=CFSi(CH_3)_2C_6F_5$	57	89 (20)	1.4214	0.976	38.22	1.97	49.64	38.45	2.18	49.40
XXI	$CF_2=CFCH_2Si(CH_3)_3$	42	89	1.3745	0.949	42.84	6.59	33.89	43.16	6.61	33.49
XXII	$CF_2=CFCH_2CH_2Si(CH_3)_3$	75	112-114[c]	1.3808	0.962						
XXIII	$CF_2BrCFClCH_2Si(CH_3)_2$	44	205	1.4400	1.513	22.65	3.16	17.91	22.69	3.57	18.97
XXIV	$[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$	82	125 (1)	1.4345	1.4712	24.78	3.47	19.62	24.93	3.52	19.74
XXV	$[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$	42	95 (6)[d]	1.3932	1.085						
XXVI	$CF_2BrCFClCH_2CH_2Si(CH_3)Cl_2$	71	220	1.4451	1.6076	17.74	2.08	16.84	17.92	2.23	17.07
XXVIII	$CF_2=CFCH_2CH_2CH_2Si(CH_3)_2Cl$	35	163	1.4046	1.116	38.79	5.58	26.30	38.85	5.55	26.16
XXVII	$CF_2=CFCH_2CH_2CH_2Si(CH_3)_3$	85	136	1.3885	0.959	48.94	7.73	29.04	48.71	17.52	28.77

TABLE VII (continued)

PHYSICAL PROPERTIES AND ANALYSES OF COMPOUNDS PREPARED

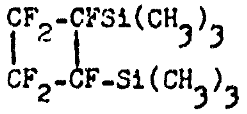
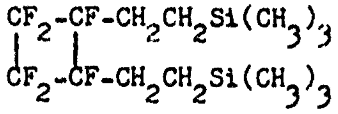
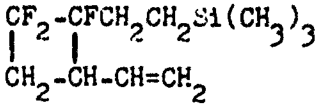
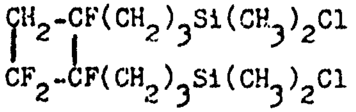
XXIX	$[CF_2=CFCH_2CH_2CH_2Si(CH_3)_2]_2O$	88	117 (10)	1.4016	1.078	44.42	6.40	30.12	44.60	6.43	30.31
XXX	$C_6H_5CF=CFCH_2CH_2Si(CH_3)_3$	69	90 (2)	1.4990	1.007	64.93	7.56	15.82	65.01	7.67	15.82
XXXI		4	96 (24)			38.94	4.88	36.96	39.19	6.07	37.22
XXXII		33	70 (0.8)	1.4059	1.069	46.12	7.19	31.26	46.31	7.19	31.52
XXXIII						55.85	8.11		56.87	8.11	
XXXIV		42	145 (5) m.p. 53-56			38.79	5.58	26.30	39.65	5.58	27.07
XXXV	$CF_2ClCFNO(CH_2)_2Si(CH_3)$					33.89	5.29		33.76	5.43	

TABLE VII (continued)

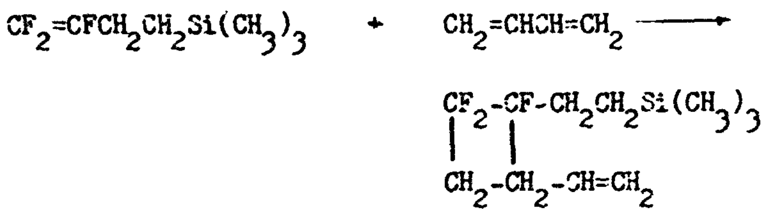
Compound	Calculated MR_D[a]	Found MR_D
XIV		
XV	38.3	38.5
XVI	39.9	40.3

TABLE VII (continued)

PHYSICAL PROPERTIES AND ANALYSES OF COMPOUNDS PREPARED

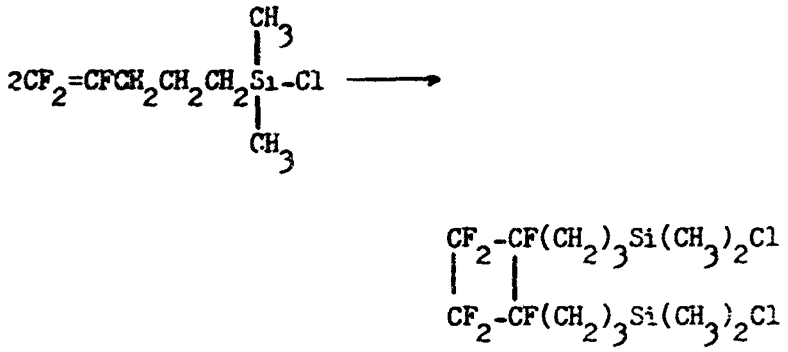
XVII	34.2	34.7
XVIII	57.4	58.3
XIX	30.2	30.9
XX		
XXI	39.2	40.4
XXII		
XXIII	56.4	56.0
XXIV	101.9	102.7
XXV		
XXVI	56.1	56.0
XXVIII	48.0	47.6
XXVII	48.4	48.3
XXIX	85.2	85.6
XXX		
XXXI		
XXXII	84.3	83.9
XXXIII		
XXXIV		
XXXV		

[a] Bond refractions according to E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946). [b] lit. (63) b.p. 65° n_D^{20} 1.3569, 5.83μ. [c] lit. (65) b.p. 114°, n_D^{23} 1.3790. [d] lit. (65) 95° (6 mm), n_D^{20} 1.3975.



(8)

XXIII



(9)

XXXIV

It was also found that nitrosyl chloride reacted with $CF_2=CFCH_2CH_2Si(CH_3)_3$ to give a nitroso compound with a characteristic deep blue color. It was separated by passage of a pentane solution through an alumina column, and the material from the passage of the narrow blue band through the column was collected after evaoporation of the pentane. The product

$$CF_2=CFCH_2CH_2Si(CH_3)_3 \quad + \quad NOCl \longrightarrow$$

$$CF_2ClCF(NO)CH_2CH_2Si(CH_3)_3$$

XXXV

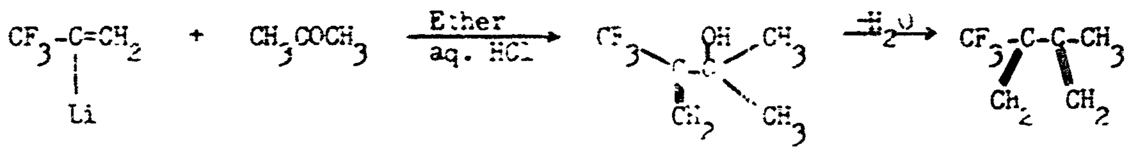
was tentatively identified by elemental analysis and NMR spectra. Nitrosyl chloride is known to add chlorine perferentially to the CF_2 end of a double bond with the NO going to the other carbon atom.

The infrared spectra of compounds containing the trifluorovinyl group attached directly to silicon show an absorption peak associated with the double bond at 5.83μ. The same group attached to carbon, hydrogen, bromine, or chlorine absorbs between 5.5 and 5.6μ. Triphenyltrifluorovinyltin, prepared in this laboratory, absorbs at 5.88μ, while tris-(trifluorovinyl)boron absorbs at 5.95μ. All of the metal compounds mentioned have empty p or d orbitals which are perhaps responsible for the large shift from the usual absorption frequency. Stone, et al.,(67) use this shift as evidence of carbon-boron π bonding.

The infrared absorption for the double bond in $CF_2=CFCH_2Si(CH_3)_3$ was also found to be 5.57μ, which would again indicate that the d orbitals on the silicon do not significantly affect the trifluorovinyl group in this case. The double bond absorption for $CF_2=CFCH_2CH_2Si(CH_3)_2Cl$ occurred at 5.52μ, indicating a normal trifluorovinyl group.

J. Reactions of Unsaturated Grignard and Lithium Reagents

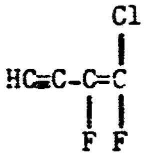
The main object of this work was the use of unsaturated organometallic compounds to prepare a series of enynes or dienes which might afford useful polymers. Two general methods were used in the attempted synthesis of these monomers: 1. Unsaturated organometallic reagents were reacted with fluoroölefins to give the desired product. The most likely mechanism involves addition of the organometallic reagent to the olefin, followed by metal halide elimination e.g. $CH_2=CHCH_2MgBr + CF_2=CFX \rightarrow CH_2=CHCH_2CF_2CFXMgBr \rightarrow CH_2=CHCH_2CF=CFX + MgBrF$. 2. The organometallic compound was reacted in the normal way with aldehydes and ketones and the product dehydrated to give enynes or dienes e.g.



1. Reaction of Unsaturated Organometallic Compounds with Haloölefins

It has been shown that Grignard reagents reacted with fluoroölefins to give alkylated or arylated fluoroölefins. Dixon reported(34) that lithium reagents behaved in a similar manner. e.g. $C_4H_9Li + CF_2=CF_2 \rightarrow C_4H_9CF=CF_2 + LiF$. England and his associates(68) reported briefly that the sodium salt of 1-hexyne and phenyl acetylene reacted with tetrafluoroethylene to give, respectively, 30% and 9% of the corresponding difluoroethylene derivative $2RC\equiv CNa + CF_2{=}CF_2 \rightarrow R{-}C\equiv CF{=}CFC\equiv CR + 2NaF$. The reaction of propynyllithium with various fluoroölefins to give good yields of the corresponding enynes has been carried out in these laboratories (69).

Attempts to extend this reaction using other acetylenic Grignard and lithium reagents have proved unsuccessul. Reaction of ethyoxyethynyl lithium with chlorotrifluoroethylene in tetrahydrofuran at room temperature gave only black polymeric material. When carried out at -15° to -20°, the same reaction afforded a small amount of 3-ethoxy-1-chloro-1,2-difluoropropene but none of the expected enyne. The mechanism of formation of this compound is not known. Dilithium acetylide was prepared and reacted with chlorotrifluoroethylene giving a very small yield of 4-chloro-3,4-difluorobut-3-en-1-yne



$HC\equiv C{-}\overset{}{\underset{F}{C}}{=}\overset{Cl}{\underset{F}{C}}$

and considerable polymeric material.

The corresponding di-Grignard, with fluoroölefins, gave only a black polymeric tar. Reaction of 3-bromopropynyllithium and 3,3,3-trifluoropropynyllithium with chlorotrifluoroethylene gave only polymeric material. A similar result was obtained from the reaction of the latter lithium reagent with dichlorodifluoroethylene ($CF_2{=}CCl_2$) in ether. No reaction was obtained when fluoroölefins were added to ethynylmagnesium bromide.

Attempts have also been made to prepare fluorinated dienes by reaction of vinylic fluorinated and non-fluorinated Grignard and lithium reagents with fluoroölefins.

It had been reported (70) that trifluorovinyllithium does not react with 1,1-dichlorodifluoroethylene. Attempts to prepare dienes by reaction of trifluorovinyllithium with chlorotrifluoroethylene, bromotrifluoroethylene and 1,1,2-trifluorobutadiene gave no reaction. Similarly, no diene was obtained on reaction of trifluoroisopropenyllithium with dichlorodifluoroethylene.

It was thought that perfluoroaromatic organometallic reagents with fluoroölefins would give products in which the olefinic double bond was stablized by conjugation with the aromatic ring. A previous attempt to react pentafluorophenylmagnesium bromide with trifluoroiodobenzene gave only pentafluoroiodobenzene (71). It has been found that the above Grignard reagent has no reaction with chlorotrifluoroethylene or octafluoro-2-butene in diethyl ether, and that on hydrolysis, pentafluorobenzene is obtained. If the reaction with chlorotrifluoroethylene is carried out in tetrahydrofuran, reaction occurs to leave a gummy material which is probably a perfluoropolyphenylene of the type described by Fear, Thrower, and White(72).

Attempts to react pentafluorophenyllithium with chlorotrifluoroethylene and tetrafluoroethylene have been unsuccessful, pentafluorobenzene again being recovered in each case. It has, however, been discovered that both pentafluorophenylmagnesium bromide and pentafluorophenyllithium react with hexafluorocyclobutene to give a single product, 1,2-bis(pentafluorophenyl)-tetrafluorocyclo-1-butene. With pentafluorophenylmagnesium bromide, tetrahydrofuran is the preferred solvent, but with pentafluorophenyllithium, diethyl ether is adequate.

It seems from the above results that the presence of fluorine on the aromatic nucleus renders the carbanions unreactive by removing electron density from the nucleus. Only in the case of perfluorocyclobutene, which was the most reactive olefin tried, was a positive result obtained. On the other hand, phenyllithium and phenylmagnesium bromide have been shown to be capable of reaction in the normal way with fluoroölefins (64).

The next approach to the problem of synthesis of fluorinated dienes was to react nonfluorinated unsaturated organometallic reagents with fluoroölefins. 1,1-Dichlorodifluoroethylene was reacted with both vinyl magnesium chloride and vinyllithium under varying conditions. However, the Grignard did not react and the vinyllithium gave only a tar. It is suggested that the latter reagent gave the diene $CH_2=CHCF=CCl_2$ which polymerized immediately.

In a further effort to prepare a fluorodiolefin, the reaction between allylmagnesium bromide and olefins containing the trifluorovinyl group was investigated. In general, a reasonable yield of the allyl-substituted fluoroölefin was formed.

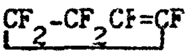
$$CH_2{=}CHCH_2MgBr \quad + \quad CF_2{=}CFX \longrightarrow$$

$$CH_2{=}CHCH_2CF{=}CFX$$

The products of these reactions are shown in Table VIII. The reactions were carried out using equimolar amounts of the fluoroölefin and the Grignard reagent in diethyl ether solution. The yield of the diolefin was not altered when an excess of the Grignard was used.

TABLE VIII

ALLYLMAGNESIUM BROMIDE AND FLUOROÖLEFINS

	Olefin		Product	Yield %
1.	$CF_2{=}CF_2$	XXXVI	$CH_2{=}CHCH_2CF{=}CFBr$	30
		XXXVII	$CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	10
2.	$CF_2{=}CF_2$ [a]	XXXVIII	$CH_2{=}CHCH_2CF{=}CFCl$	7
		XXXVII	$CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	15
	$CF_2{=}CFCl$	XXXVIII	$CH_2{=}CHCH_2CF{=}CFCl$	50
	$CF_2{=}CFBr$	XXXVI	$CH_2{=}CHCH_2CF{=}CFBr$	30
	$CF_2{=}CCl_2$	XXXIX	$CH_2{=}CHCH_2CF{=}CCl_2$	40
	$CF_2{=}CFCF_2$	XL	$CH_2{=}CHCH_2CF{=}CFCF_3$	38
	 $CF_2{-}CF_2CF{=}CF$		b	
	$CF_2{=}CFCH{=}CH_2$	XLI	$CH_2{=}CHCH_2CF{=}CFCH{=}CH_2$ [c]	30

[a] Reacted with allylmagnesium chloride. [b] Tar formed immediately at -78°.
[c] Polymerizes on standing.

The reaction with tetrafluoroethylene gave none of the expected monoallyl derivate, although a low yield of the disubstituted compound XXXVII was formed: the main product was 1-bromo-1,2-difluoro-1,4-pentadiene XXXVI.

$$CH_2=CHCH_2MgBr \quad + \quad CF_2=CF_2 \longrightarrow$$

$$\underset{\text{XXXVI}}{CH_2=CHCH_2CF=CFBr} \quad + \quad \underset{\text{XXXVII}}{\left[CH_2=CHCH_2CF_2\right]=}$$

It is unlikely that the bromide ion as such attacks tetrafluoroethylene as the reaction of anhydrous magnesium bromide with neither tetrafluoroethylene nor 1,1,2-trifluoro-1,4-pentadiene, in diethyl ether, led to a bromine-containing product. It is more likely that the Grignard reagent itself brominated the fluoroolefin. No reaction took place between 1,1,2-trifluoro-1,4-pentadiene and allylmagnesium bromide. These results suggest that the allylmagnesium bromide reacts first with tetrafluoroethylene to form bromotrifluoroethylene, which then reacts with another molecule of Grignard reagent to give 1-bromo-1,2-difluoropentadiene XXXVI.

The reaction of allylmagnesium chloride with tetrafluoroethylene gave more of the expected diallylfluoroethylene XXXVII than did the bromide; a small amount of allylchlorodifluoroethylene XXXVIII was observed.

The reaction of allylmagnesium bromide with 1,1,2-trifluorobutadiene gave 3,4-difluoro-1,3,6-heptatriene, which slowly polymerized on isolation. It was identified as the tetrabromide. The bromine saturated only the terminal double bonds, as indicated by infrared analysis.

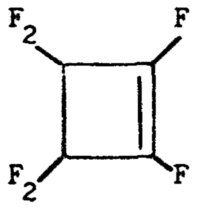
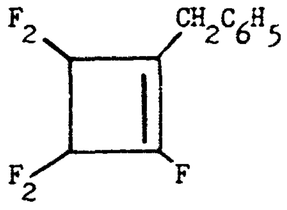
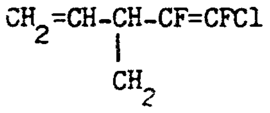
Allylmagnesium bromide was allowed to react with perfluorocyclobutene to form a tar even at -78°. Since half of the hexafluorocyclobutene was recovered, it seems probable that the initial product of the reaction was 1,2-diallyltetrafluorocyclobutene, which polymerized spontaneously. Perfluorocyclobutene has been found by workers in this laboratory to be by far the most reactive of the fluoroolefins toward attack by Grignard reagents.

No reaction occurred between allylmagnesium bromide and trifluoroethylene, 1,1,2-trifluoro-4-bromo-1-butene, or 1,1,2-trifluoro-1,4-pentadiene. The inactivity of the former two olefins with organometallic compounds has been observed before; (69) it appears that an electron-withdrawing group should be attached to the trifluorovinyl group for the reaction to occur.

Further reactions of fluoroölefins with Grignard reagents containing the allylic system are shown in Table IX.

TABLE IX

FURTHER REACTIONS OF ALLYLIC GRIGNARD REAGENTS AND FLUOROÖLEFINS

Grignard	Olefin	Product (%)
$C_6H_5CH_2MgBr$	$CF_2=CFCl$	No reaction
$C_6H_5CH_2MgBr$		 40% XLII
$CH_3CH=CHCH_2MgBr$	$CF_2=CFCl$	 $CH_2=CH-\underset{\displaystyle CH_2}{\underset{\vert}{CH}}-CF=CFCl$ 15% XLIII

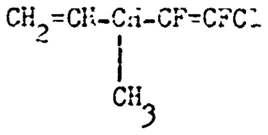
No reaction occurred between chlorotrifluoroethylene and benzylmagnesium bromide. This result is somewhat unexpected when compared with the good yield of the diolefin obtained from the reaction of chlorotrifluoroethylene and allylmagnesium bromide. However, the more reactive perfluorocyclobutene gave a reasonable yield of 1-benzylpentafluorocyclobutene XLII when allowed to react with benzylmagnesium bromide.

The reaction of chlorotrifluoroethylene and crotonylmagnesium bromide would be expected to give 1-chloro-1,2-difluoro-1,4-hexadiene

XLIV; however, the nuclear magnetic resonance spectrum of the product showed only the presence of 1-chloro-1,2-difluoro-3-methyl-1,4-pentadiene XLIII.

$CH_3CH{=}CHCH_2CF{=}CFCl$

XLIV

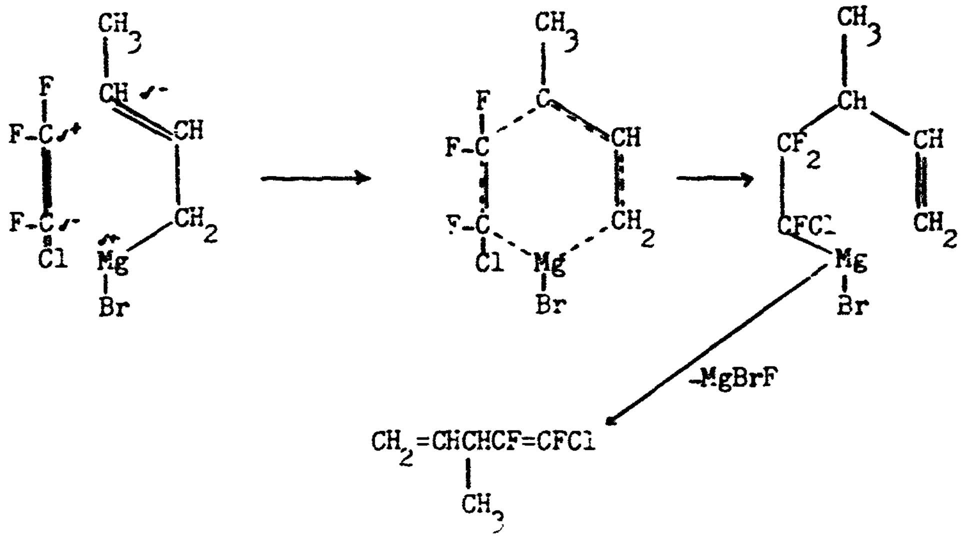


$CH_2{=}CH{-}CH(CH_3){-}CF{=}CFCl$

XLIII

There has been some discussion in the literature concerning the structure of crotonylmagnesium bromide as to whether it exists in the crotonyl form or the α-methylallyl form (73). Recent work using nuclear magnetic resonance and infrared spectroscopy, however, indicates that it exists exclusively as the crotonyl form (74-76).

It would appear that the normal mechanism associated with this reaction, i.e., the attack of the electronegative -carbon atom of the Grignard reagent in the crotonyl form with the electropositive carbon atom of the fluoroölefin, is not taking place. It is more likely that the reaction is occurring by a mechanism similar to that suggested by Young and Roberts (77) for the addition of allylic Grignard reagents to carbonyl compounds.



The allylic system is able to transfer the negative charge induced on the α-carbon atom by the electropositive magnesium atom to the α-carbon atom, which can then combine with the polarized fluoroölefin to give the transient six-membered ring. The newly formed addition product will then lose magnesium halide to give the fluoro diolefin.

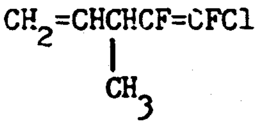
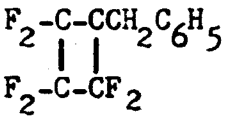
Three reasons can be offered to support this mechanism for the reaction of allylic Grignard reagents with fluoroölefins. First, the reaction of crotonylmagnesium bromide gives only the methylpentadiene, as explained above. Second, the yield of the products using allylmagnesium bromide is much better than those from other aliphatic Grignard reagents such as vinylmagnesium chloride and methyl- or ethylmagnesium bromide; the latter reactants would be unable to form this six-membered ring system. Third, no reaction occurred with benzylmagnesium bromide and chlorotrifluoroethylene; this suggests that the reaction does not occur at the α-carbon atom, for it would otherwise be difficult to explain how the two structurally similar compounds, benzylmagnesium bromide and allylmagnesium bromide, behave so differently. A logical explanation for the lack of reaction at the allylic carbon atom in benzylmagnesium bromide is that the aromatic resonance energy would have to be overcome in forming this reaction site.

The physical properties and results of analyses of the new fluoroolefins are shown in Table X.

In order to gain information that would be useful in future syntheses involving fluoroölefins, the relative reactivity of some fluoroölefins in the reaction with allylmagnesium bromide was determined. Equimolar amounts of the Grignard reagent and two fluoroölefins were reacted in a sealed tube at room temperature; after the reaction was completed, any unreacted olefins were condensed and analysed by v.p.c. In all cases the olefins were present in excess, and the ratio of unreacted olefins was the same as that of the products from the reaction. The yields of the fluorodiolefins from several repeated reactions were found to be consistent within experimental error. As the reaction takes place within the

TABLE X

NEW FLUOROÖLEFINS

Compound	No.	B.p. °C	$n^{22}D$	d^{22}	% carbon		% hydrogen		% fluorine	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_2=CHCH_2CF=CFBr$	XXXVI	98	1.4315	1.463	32.79	32.94	2.73	2.90	20.76	20.61
$CH_2=CHCH_2CF=CFCl$	XXXVIII	78.5	1.3986	1.141	43.32	43.60	3.61	3.88	27.44	27.22
$CH_2=CHCH_2CF=CFCF_3$	XL	63	1.3346	1.197	41.86	42.04	2.91	3.08	55.23	55.29
$CH_2=CHCH_2CF=CFCH=CH_2$[b]	XLI	....	1.4349	0.960	Polymer contains 23.13% F					
$(CH_2=CHCH_2CF)_2=$	XXXVII	114.5	1.4146	0.965	66.67	66.56	6.94	7.18	26.39	26.14
$CH_2=CHCH_2CF=CCl_2$	XXXIX	119	1.4472	1.205	38.72	38.50	3.23	3.41	12.26	12.50
 $CH_2=CHCH(CH_3)CF=CFCl$	XLIII	94	1.4067	1.065	47.22	47.53	4.59	4.78	24.92	25.25
 $F_2C-C(CH_2C_6H_5)=C(CF_2)-CF_2$	XLII	180	1.4434	1.300	56.41	56.20	2.99	3.10	40.60	40.28

[a] Analyses were by Galbraith Laboratories, Knoxville, Tenn. [b] Polymerizes on standing.

liquid phase, the fluoroölefins are gases at room temperature, the solubility of each fluoroölefin will control the yield of the fluorodiolefin product. Thus the solubility of the pairs of fluoroölefins were investigated by taking equimolar amounts of the two fluoroölefins and sealing them in a tube containing ether. After equilibrating for two hours at room temperature, the liquid was analyzed by v.p.c. The results are shown in Table XI, and the ratio of the reactivity of the fluoroölefins shown in Table XII corrected.

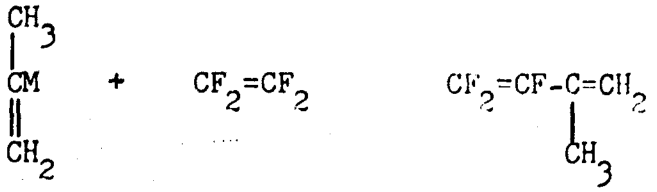
The reactivity of these fluoroölefins is shown below:

$$\underline{\mathrm{CF_2CF_2CF{=}CF}} \gg \mathrm{CF_2{=}CCl_2} \gg \mathrm{CF_2{=}CFBr} > \mathrm{CF_2{=}CFCF_3} > \mathrm{CF_2{=}CFCl} \gg \mathrm{CF_2{=}CF_2}$$

The hexafluorocyclobutene is more reactive than the 1,1-dichlorodifluoroethylene as it reacts with two moles of allylmagnesium bromide. Even at -78° the disubstituted cyclobutene forms a polymeric tar. These reactions have been shown by v.p.c. analysis to be virtually completed at room temperature within five minutes.

2. Synthesis of Isopropenyl Metal Compounds and Their Reactions

Attempts were made to prepare isopropenyllithium or magnesium halide with the specific aim of reacting these with tetrafluoroethylene in order to synthesize 1,1,2-trifluoroisoprene, which may give rise to interesting polymers.



$$\mathrm{CH_2{=}C(CH_3)M} \quad + \quad \mathrm{CF_2{=}CF_2} \qquad \mathrm{CF_2{=}CF{-}C(CH_3){=}CH_2}$$

(M = Li, MgX)

By analogy with the satisfactory exchange reaction between butyllithium and trifluoroisopropenyl bromide to produce the desired trifluoroisopropenyllithium, it was hoped that the reaction between an alkyl lithium and isopropenyl bromide would yield isopropenyllithium.

This proved not to be the case. When isopropenyl bromide was

TABLE XI

SOLUBILITY RATIO OF FLUOROÖLEFINS IN ETHER AT ROOM TEMPERATURE

Olefins	b.p. °C	Mole %	Relative Solubility
1. $CF_2=CFCl$	-27	42.2	1.0
$CF_2=CCl_2$	19	57.8	1.37
2. $CF_2=CFCl$	-27	46.8	1.0
$CF_2=CFBr$	-6.5	53.2	1.14
3. $CF_2=CFCl$	-27	50.8	1.0
$CF_2=CFCF_3$	-29	49.2	0.97
4. $CF_2=CFCl$	-27	62.8	1.0
$CF_2=CF_2$	-76	37.2	0.59
5. $CF_2=CFBr$	-6.5	43.1	....
$CF_2=CCl_2$	19	56.9	....
6. $CF_2=CFCl$	-27	45.6	1.0
$\underbrace{CF_2CF_2}CF=CF$	5	54.4	1.19

TABLE XII

RELATIVE REACTIVITY OF ALLYLMAGNESIUM BROMIDE WITH FLUOROOLEFINS[a]

Olefins	Products	Yields %	Relative Reactivity	Corrected[b] Relative Reactivity
1. $CF_2=CFCl$	$CH_2=CHCH_2CF=CFCl$	1.5	1.0	1.0
$CF_2=CCl_2$	$CH_2=CHCH_2CF=CCl_2$	16.8	11.2	8.2
2. $CF_2=CFCl$	$CH_2=CHCH_2CF=CFCl$	7.9	1.0	...
$CF_2=CCl_2$[c]	$CH_2=CHCH_2CF=CCl_2$	16.2	2.05	...
3. $CF_2=CFCl$	$CH_2=CHCH_2CF=CFCl$	4.8	1.0	1.0
$CF_2=CFBr$[d]	$CH_2=CHCH_2CF=CFBr$	9.7	2.02	1.94
4. $CF_2=CFCl$	$CH_2=CHCH_2CF=CFCl$	3.5	1.0	1.0
$CF_2=CFCF_3$	$CH_2=CHCH_2CF=CFCF_3$	4.3	1.23	1.27
5. $CF_2=CFCl$	$CH_2=CHCH_2CF=CFCl$	8.7	1.0	1.0
$CF_2=CF_2$	$CH_2=CHCH_2CF=CFBr$	0.4	0.05	0.08
6. $CF_2=CFBr$	$CH_2=CHCH_2CF=CFBr$	1.6	1.0	1.0
$CF_2=CCl_2$	$CH_2=CHCH_2CF=CCl_2$	23.4	13.0	11.5
7. $CF_2=CFCl$	Tar	....		
$CF_2CF_2CF=CF$				

[a] All reactions were at room temperature for 16 - 20 hours.

[b] See text.

[c] At 450 lb/in^2 pressure

[d] Similar reactions under high pressure did not alter the yields.

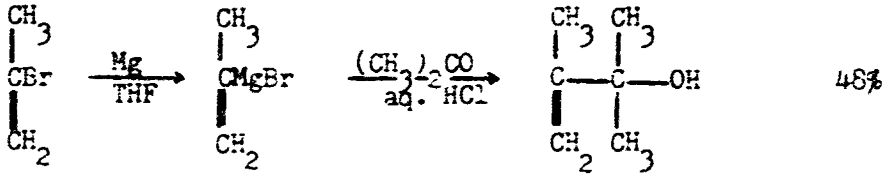
treated with butyllithium in ether solution at -78° and was allowed to warm to room temperature, no butyl bromide was formed, indicating that the exchange metallation reaction did not occur. In a subsequent reaction, the mixture of butyllithium and isopropenyl bromide was allowed to warm from -78° to 0° and then carbon dioxide bubbled into the system. On working up, again no butyl bromide was found, the main products being valeric acid, butynoic acid and probably dibutyl ketone. Butynoic acid is possibly formed by initial exchange with a vinylic proton, followed by elimination of

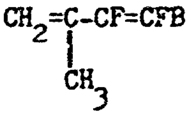
$$CH_3CBr{=}CH_2 \xrightarrow{BuLi} CH_3CBr{=}CHLi \xrightarrow{-LiBr} CH_3C{\equiv}CH \xrightarrow[CO_2,\ H^+]{BuLi} CH_3C{\equiv}CCOOH$$

lithium bromide to give propyne. The acidic proton of the latter would exchange with lithium and react normally with carbon dioxide to give the acid [83,84].

Since this approach was not successful, it was decided to attempt to prepare the Grignard reagent from isopropenyl bromide.

Both diethyl ether and tetrahydrofuran were used as solvents. Tetrahydrofuran proved to be more suitable as Grignard formation proceeded more quickly, the magnesium being consumed quantitatively. In order to confirm that the desired reagent was formed, acetone was added to the reaction mixture. After work up, dimethylisopropenyl carbinol, b.p. 120° (lit. b.p. 121 - 2°), was obtained in 48% yield.



Thus, isopropenyl magnesium bromide could be prepared in good yield and its reaction with tetrafluoroethylene was studied. The Grignard reagent was prepared by the action of isopropenyl bromide on magnesium in tetrahydrofuran. Excess tetrafluoroethylene was bubbled into the system which was fitted with a reflux condenser maintained at -100°. After work up, v.p.c. showed the presence of two products in poor yield. Attempts to separate these by distillation on prep. scale v.p.c. resulted in decomposition. So it was not possible to obtain pure samples of the products. However, I. R. and NMR spectroscopic evidence of the mixture suggested that only one of these compounds contained fluorine. Only two fluorine atoms were present in the molecule, suggesting that disubstitution had occurred, causing fluorine at either end of the tetrafluoroethylene to be replaced. The mixture of two compounds decomposed quickly on standing at room temperature. The fluorine containing product was probably  $CH_2=C(CH_3)-CF=CFBr$, formed by an analogous reaction to that of allylmagnesium bromide with tetrafluoroethylene as reported by Tarrant and Heyes (16).

3. Synthesis and Reactions of Other Fluorinated Unsaturated Grignard and Lithium Reagents

The main objective of this work was the preparation of unsaturated alcohols by reaction of the organometallic with carbonyl compounds. Dehydration of these alcohols afforded an alternative route to the desired dienes or enynes. However, several other reactions of the organometallic reagents have been described (See Table XIII).

a. Trifluorovinylmagnesium Halides

The reaction of trifluorovinylmagnesium bromide with various fluorinated and non-fluorinated ketones has been studied in these laboratories by Richardson (78). It was found that with ketones containing no fluorine the expected carbinol was not formed and that an acidic product, formed by rearrangement of the carbinol, was isolated. In the case of 1,1,1-trifluoroacetone, both the carbinol and the acid derivative were formed. In the present study, no evidence was found for rearrangement of the carbinols formed by the reaction of trifluorovinylmagnesium bromide with sym-dichlorotetrafluoro- and hexafluoroacetones, but the carbinol was obtained in good yield as an azeotropic mixture which was purified in small quantities by preparative gas chromatography. (GLPC)

b. Attempted Preparation of 4-Bromomagnesium and 4-Lithio-1,1,2-trifluorobutene

An attempt to prepare the Grignard and lithium reagent from 4-bromo-1,1,2-trifluorobutene-1 ($CF_2=CFCH_2CH_2Br$) was unsuccessful, no butyl bromide being produced by exchange with butyllithium in the latter case, while reaction with magnesium in ether gave only the coupled product, 1,1,2,7,8,8-hexafluoroocta-1,7-diene ($(CF_2=CFCH_2CH_2)_2$. When the Grignard was prepared in diethyl-ether with trimethylchlorosilane *in situ*, the coupled product was formed and no evidence for the presence of trimethyl-(3,4,4-trifluoro-4-butenyl)silane, was found. Using tetrahydrofuran as solvent, gas chromatographic evidence indicated that approximately 5% of the product was trimethyl-(3,4,4-trifluoro-4-butenyl)silane, the major product being 1,1,2,7,8,8-hexafluoroocta-1,7-diene. Another unidentified minor product was observed in each of the experiments.

c. Perfluoroallyl Organometallic Compounds

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(64). 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 $CF_2=CF-CF_2Li$ by halogen-metal exchange. No reaction occurred between PFAI and pentafluorophenyllithium, as on hydrolysis only unreacted PFAI and pentafluorobenzene were obtained.

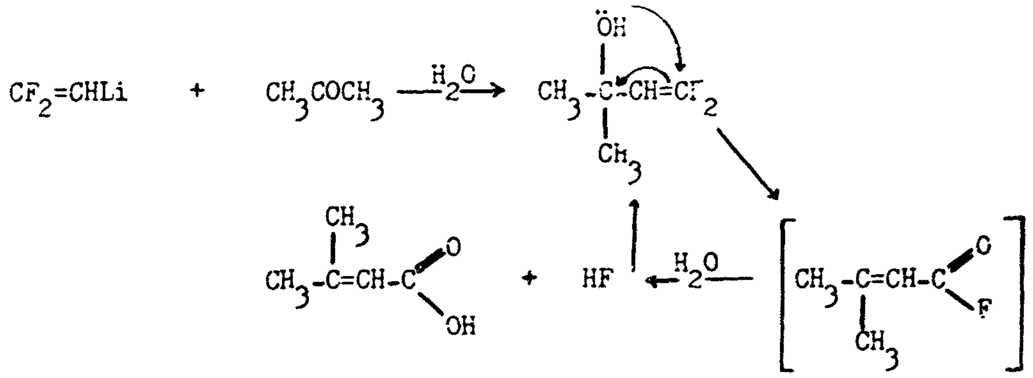
d. 2,2-Difluorovinyl Organometallic Compounds

1-Bromo-2,2-difluoroethylene was readily formed *via* a two-step synthesis involving bromination of vinylidene fluoride in the presence of light and reaction of the resulting dibromide with potassium hydroxide. 2,2-Difluorovinyl bromide reacted vigorously with magnesium in tetrahydrofuran and the Grignard thus formed was shown to be unstable at 0° but stable enough at -20° to react with trimethylchlorosilane *in situ* to give trimethyl-(2,2-difluorovinyl)silane, $CF_2=CHSi(CH_3)_3$, in 17% yield. Addition of the chlorosilane after preparation of the Grignard reagent gave only a 5% yield. An attempt to form $CF_2=CH-C(CF_3)_2OH$ from 2,2-difluorovinyl magnesium bromide and hexafluoroacetone gave only partial success in that several by-products were formed and the carbinol, which was formed in about 5 - 10% yield, could not be purified by GLPC or distillation.

Attempts to prepare 2,2-difluorovinyllithium from 2,2-diflurovinyl bromide *via* an exchange reaction with butyllithium met with only limited success. ($CF_2=CHBr + C_4H_9Li \longrightarrow CF_2=CHLi + C_4H_9Br$) Butyl bromide was produced in 34% (Maximum) yield, indicating this degree of conversion to the desired lithium reagent (see above equation).

Reaction of 2,2-difluorovinyllithium with benzaldehyde gave a number of products which could not be separated by distillation or by GLPC. One of these had a GLC retention time similar to that of α-n butyl benzyl alcohol, which could have been formed by reaction of butyllithium with benzaldehyde.

In reaction of 2,2-difluorovinyllithium with acetone, the lithium reagent was formed in 16% yield (16% C_4H_9Br produced). This may have been due to the fact that a solution of butyllithium in ether, and not hexane, was used for the exchange reaction. This change was made since the desired product was expected to have a GLC retention time similar to that of the hexane. It was later shown that the ether solution of butyllithium used contained some lithium ethoxide. During the work-up procedure, it was evident from solution color changes that some product decomposition was taking place. The product obtained (7 - 10%) was β,β-dimethylacrylic acid and this probably arose from rearrangement of the expected alcohol as shown below.

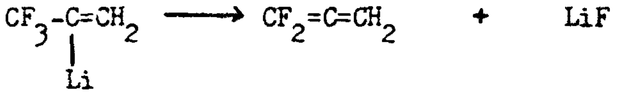


(7 - 10%)

Initial attack on the difluoromethylene group by the lone pair electrons of the oxygen atom is postulated. The resulting acid fluoride undergoes facile hydrolysis to give the acid with the accompanying evolution of hydrogen fluoride (some glass etching was observed). The difluoromethylene group is known to be very susceptible to nucleophilic attack and there are several reports of rearrangement of similar alcohols or their lithium salts in the literature (79,80). Apart from less volatile products, two with greater volatility than ether were observed. One of these had the same retention time as the starting halide and the second was more volatile. The latter might well be monofluoroacetylene, arising by elimination of lithium fluoride from the expected lithium reagent.

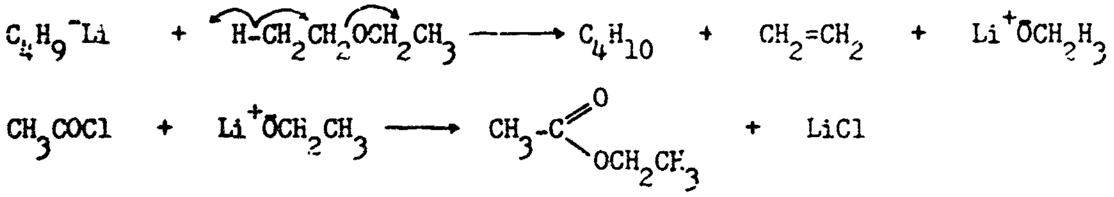
$$CH_2{=}CFLi \longrightarrow CH{\equiv}CF \quad + \quad LiF$$

Difluoroallene has been isolated from similar reactions of trifluoroisopropenyllithium



$$CF_3-\underset{\displaystyle Li}{\underset{|}{C}}{=}CH_2 \longrightarrow CF_2{=}C{=}CH_2 \quad + \quad LiF$$

Reaction of 2,2-difluorovinyllithium, again formed *via* an exchange involving an ether solution of butyllithium, with acetyl chloride afforded only ethyl acetate (9%) and butyl bromide (13%). The ester must have arisen by the following scheme:

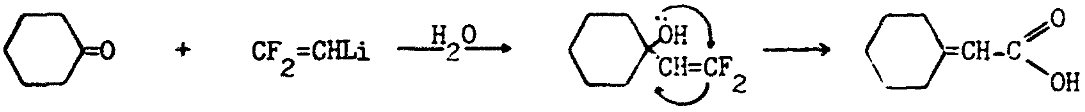


$$C_4H_9^{-}Li + H\text{-}CH_2CH_2OCH_2CH_3 \longrightarrow C_4H_{10} + CH_2{=}CH_2 + Li^{+}\bar{O}CH_2H_3$$

$$CH_3COCl + Li^{+}\bar{O}CH_2CH_3 \longrightarrow CH_3\text{-}C(=O)OCH_2CH_3 + LiCl$$

As a consequence of this discovery, the use of butyllithium in ether alone for these exchange reactions was abandoned.

Reaction of 2,2-difluorovinyllithium with cyclohexanone gave a product which decomposed during the work-up procedure. Butyl bromide was obtained in 34% yield, indicating 34% formation of the lithium reagent. The only other product obtained was cyclohexylidine acetic acid (25%) which can only have arisen from the desired alcohol <u>via</u> a rearrangement similar to that described earlier.



It had been hoped that this rearrangement would not have occurred since it required the formation of an exocyclic double bond.

2,2,-Difluorovinylmagnesium bromide reacted with trimethylchlorosilane to give trimethyl-(2,2-difluorovinyl)silane in low yield (17%). It was surprising then to find that the corresponding lithium reagent did not give any of the desired product in reaction with triethylchlorosilane. GLC again indicated that the product which formed decomposed during the work-up. The desired product $(CH_3CH_2)_3SiCH{=}CF_2$ might be anticipated to be of limited stability in view of the reported instability of silicon compounds containing a β-chlorinated group (81). On the other hand, trialkyl(trifluorovinyl)silanes have been prepared without difficulty (62,63).

The conclusion must be that 2,2-difluorovinyl Grignard and lithium reagents are unsuitable for reaction with aldehydes etc., to give alcoholic products, which, on dehydration, would give fluorinated dienes.

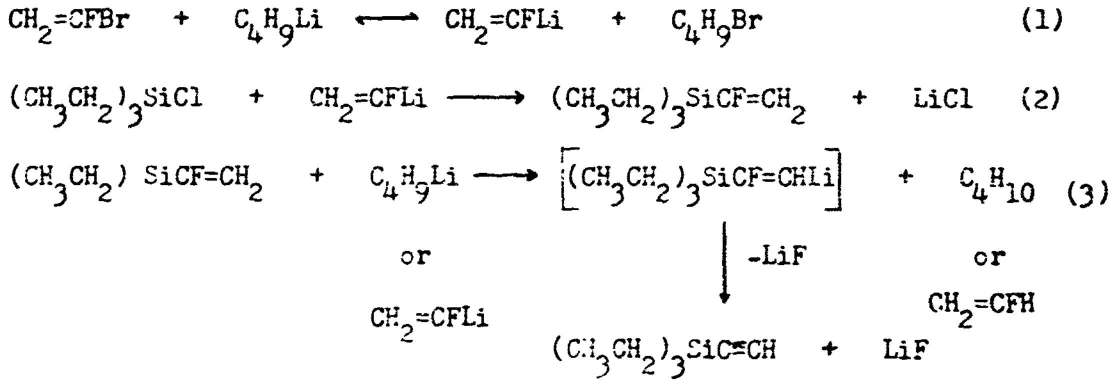
e. 1-Fluorovinyl Organometallic Compounds

1-Fluorovinyl bromide does not have a terminal difluoromethylene group in the molecule and therefore it was hoped that the Grignard or lithium reagent from this halide would give stable products.

1,2-Dibromo-1-fluoroethane was prepared (68%) by bromination of vinyl fluoride in the presence of light. Attempts to eliminate hydrogen bromide from this molecule using potassium hydroxide pellets and heating, either alone or in mineral oil, gave 1-bromo-1-fluoroethylene (20 - 45%) along with an undetermined amount of monofluoroacetylene. The latter initiated considerable minor explosions, flashes, and carbon formation on distillation, rendering the preparation of the halide dangerous. Monofluoroacetylene is known to decompose at its boiling point (82). Treatment of 1,2-dibromo-1-fluoroethane with potassium hydroxide in ethanol gave no 1-bromo-1-fluoroethylene.

The reaction of 1-fluorovinyl bromide with butyllithium followed by addition of ethyl methyl ketone gave butyl bromide, again in low yield (24%), and five other products which were inseparable by GLPC or distillation.

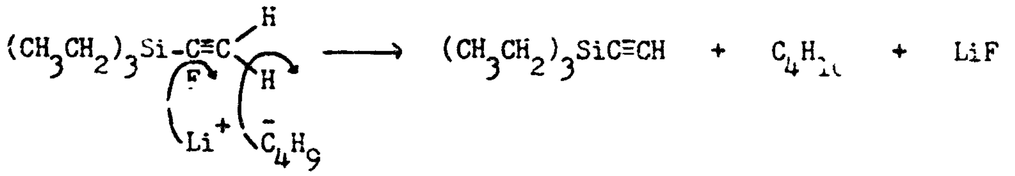
Reaction of 1-fluorovinyllithium, prepared in the usual way, with triethylchlorosilane afforded butyl bromide (36%) and triethylethynylsilane ($Et_3SiC{\equiv}CH$) (30%). The latter compound was possibly formed by the following route:



$$\mathrm{CH_2{=}CFBr} \;+\; \mathrm{C_4H_9Li} \;\longleftrightarrow\; \mathrm{CH_2{=}CFLi} \;+\; \mathrm{C_4H_9Br} \qquad (1)$$

$$\mathrm{(CH_3CH_2)_3SiCl} \;+\; \mathrm{CH_2{=}CFLi} \;\longrightarrow\; \mathrm{(CH_3CH_2)_3SiCF{=}CH_2} \;+\; \mathrm{LiCl} \qquad (2)$$

$$\begin{array}{ccccccc} \mathrm{(CH_3CH_2)\ SiCF{=}CH_2} & + & \mathrm{C_4H_9Li} & \longrightarrow & \left[\mathrm{(CH_3CH_2)_3SiCF{=}CHLi}\right] & + & \mathrm{C_4H_{10}} \quad (3) \\ & & \text{or} & & \Big\downarrow \mathrm{-LiF} & & \text{or} \\ & & \mathrm{CH_2{=}CFLi} & & & & \mathrm{CH_2{=}CFH} \\ & & & & \mathrm{(CH_3CH_2)_3SiC{\equiv}CH} \;+\; \mathrm{LiF} & & \end{array}$$



$$(CH_3CH_2)_3Si\text{-}C{\equiv}C(H)F + Li^{+}\,\bar{C}_4H_9 \longrightarrow (CH_3CH_2)_3SiC{\equiv}CH + C_4H_{10} + LiF \quad (4)$$

This scheme involves formation of the expected product triethyl(1-fluorovinyl)silane by steps 1 and 2 and its further reaction with another molecule of organometallic reagent to give triethylethynyl silane. The latter process might be described as one in which the olefinic proton is exchanged and the product $(CH_3CH_2)_3SiCF{=}CHLi$ then easily eliminates lithium fluoride to give triethylethynyl silane (step 3). Alternatively, the concerted mechanism depicted in step 4 may be a more accurate description of the route to the acetylenic product.

Another possible method of product formation involves production of the desired lithium reagent ($CH_2{=}CFLi$) followed by 1,1-elimination of lithium fluoride, a 1,2-hydride shift, exchange of a proton in the acetylene produced, and reaction of this new lithium reagent with triethylchlorosilane. Similar reaction sequences have been previously postulated.

$$CH_2{=}CFBr + C_4H_9Li \longrightarrow CH_2{=}CFLi + C_4H_9Br$$

$$CH_2{=}CFLi \longrightarrow CH_2{=}C{:} + LiF$$

$$CH_2{=}C{:} \longrightarrow HC{\equiv}CH \xrightarrow{C_4H_9Li} HC{=}CLi + C_4H_{10}$$

$$(CH_3CH_2)_3SiCl + HC{\equiv}CLi \longrightarrow (CH_3CH_2)_3Si\text{-}C{=}CH + LiCl$$

Examples of this type of reaction are given later in this report.

It might be possible to prepare 1-fluorovinyllithium by reaction of the corresponding bromide with lithium metal. This would mean that there was no excess butyllithium in the system, thus decreasing the possibility of formation of the acetylene. It has, however, been found that the reaction of perfluorovinyl bromide with lithium gave only tar and no perfluorovinyllithium (63). It was thought that reaction of triethylchlorosilane with 1-fluorovinylmagnesium bromide, which is less basic in character than the corresponding lithium reagent, would give the desired product. It was found to be impossible to prepare the above Grignard reagent either in ether or tetrahydrofuran.

In view of these difficulties it was decided to abandon the use of this organometallic reagent in the attempted synthesis of dienes.

f. Trifluoro-isopropenyllithium

The preparation of lithium derivaties and Grignard reagents of several fluoro-organic compounds has been accomplished by the direct reaction of lithium or magnesium with fluoro-organic halides*, and also by means of the exchange reaction between a Grignard reagent or alkyllithium with a fluoro-organic halide* or a fluoro-organic compound containing "acidic" hydrogen atoms.

Thus, in order to prepare trifluoroisopropenyl derivatives, it seemed reasonable to use 1,1,1-trifluoro-2-bromo-propene-2 ($CF_3CBr{=}CH_2$), trifluoro-isopropenyl bromide, as starting material.

g. Preparation of Trifluoro-isopropenyl Bromide

Trifluoro-isopropenyl bromide was readily prepared by a two-step synthesis:

(1) The quantitative bromination of trifluoropropene to give trifluorodibromopropane, followed by,

(2) Dehydrobromination of this saturated compound to the desired olefin in almost quantitative yield.

$$CF_3CH{=}CH_2 \xrightarrow[\text{light}]{Br_2} \underset{\text{quant.}}{CF_3CHBrCH_2Br} \xrightarrow[\text{no solvent}]{KOH} \underset{\text{quant.}}{CF_3CBr{=}CH_2}$$

The second step was accomplished by the addition of trifluorodibromopropane to potassium hydroxide pellets in the absence of solvent and allowing the product to distill from the system as it was formed. This procedure proved more suitable than that reported by other workers using ethanol as a solvent (85).

---

* halide = I, Br

h. Metallation of Trifluoro-isopropenyl Bromide

The initial attempts to prepare trifluoro-isopropenyllithium by the exchange reaction between butyllithium and trifluoro-isopropenyl bromide were unsuccessful. Typical of these early experiments was that in which trifluoro-isopropenyl bromide in diethyl ether was treated with butyllithium in mixed solvent (hexane/diethyl ether) at -78°. The reaction mixture was allowed to stand for 50 minutes while maintaining the temperature -78° and then, after warming to -60°, dry carbon dioxide was bubbled into the solution. The introduction of carbon dioxide was continued as the reaction temperature was allowed to attain that of the room. The reaction mixture contained a solid suspension which was shown to be lithium fluoride together with polymeric organic material. No carboxylic acid was isolated. Apparently, if the desired lithium derivative had been formed, it decomposed before carbonation could take place.

Similarly, when trifluoro-isopropenyl bromide in ether was added to butyllithium in a mixed solvent (hexane/ether) at -78° and allowed to stand for 30 minutes at that temperature before an ethereal solution of benzaldehyde was added, none of the desired trifluoro-isopropenyl adduct of benzaldehyde was formed. V.p.c. analysis showed unreacted benzaldehyde and butylbromide were present, together with a small amount ($\sim 5\%$) of higher boiling material, in the reaction product. Infrared spectroscopy suggested that this higher boiling compound was not a carbinol but probably a fluoroölefin containing a butyl group, e.g., $CF_2=CBr-CH_2-C_4H_9$.

An insoluble solid, separated from the reaction mixture by filtration was shown to be lithium fluoride, produced in 60 - 65% yield.

From the results of these and several other exploratory experiments, it seemed that trifluoro-isopropenyllithium was formed in an exchange reaction with butyllithium in diethyl ether solution, since butyl bromide was produced, but under the conditions used (temperatures -78°) the lithium compound was so unstable that it decomposed before reaction with the desired carbonyl reagent could occur. Also, it appeared advisable to add butyllithium to trifluoro-isopropenyl bromide rather than vice-versa in order to reduce the possibility of side reactions.

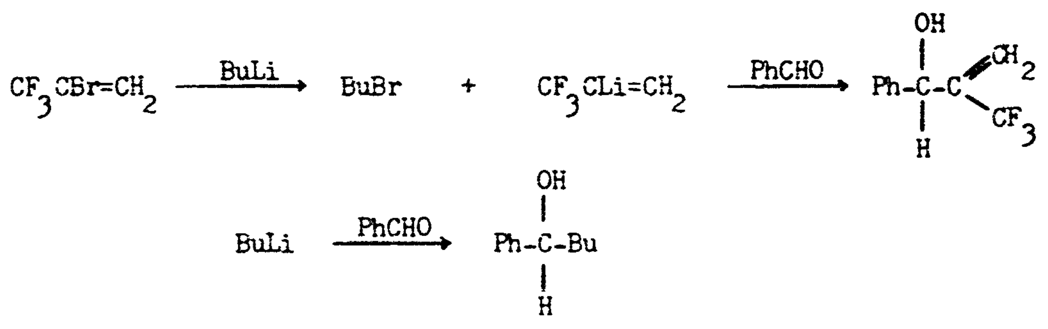
With these considerations in mind, a further attempt to prepare the trifluoro-isopropenyl adduct of benzaldehyde was made. A solution of butyllithium in mixed solvent (hexane/ether), precooled to -78°, and an ethereal solution of benzaldehyde were added alternatively in aliquots to a stirred ethereal solution of trifluoro-isopropenyl bromide at -95° (ethanol/liq. N_2 bath). After the final addition of reactants, the temperature was maintained at -95° - 90° for a further 2 hours and then allowed to rise slowly to that of the room. Aqueous acid was added and the organic layer analyzed by v.p.c. Butyl bromide together with two higher boiling products were present, but no unreacted benzaldehyde was observed. Fractionation of the dried ethereal layer yielded, at atmospheric pressure, butyl bromide (33% yield), and, at reduced pressure, the two products, which were shown to be:

(1) α-(trifluoro-isopropenyl)benzyl alcohol, b.p. 122°/21 mm.Hg (32% yield), and

(2) α-butyl benzyl alcohol, b.p. 95°/1 mm. Hg (13% yield)

Analytical samples of these compounds were obtained by prep. scale v.p.c.

Thus, by applying a lower reaction temperature and the aliquot addition technique, it was possible to prepare trifluoro-isopropenyllithium and trap it by reaction with a carbonyl compound. Since α-butyl benzyl alcohol is also produced in the reaction, it would seem that competition between the fluoro-organic lithium derivative and butyllithium for reaction with the carbonyl compound occurs.



$$CF_3CBr{=}CH_2 \xrightarrow{BuLi} BuBr + CF_3CLi{=}CH_2 \xrightarrow{PhCHO} Ph\text{-}\overset{OH}{\underset{H}{C}}\text{-}C(=CH_2)CF_3$$

$$BuLi \xrightarrow{PhCHO} Ph\text{-}\overset{OH}{\underset{H}{C}}\text{-}Bu$$

Preparation of Substituted Butadienes

If the type of reaction described above could be accomplished with carbonyl compounds in general, then it seemed likely that reaction with compounds to produce carbinol possessing hydrogen on a α-carbon atom would be capable of dehydration and so afford a general route to substituted butadienes.

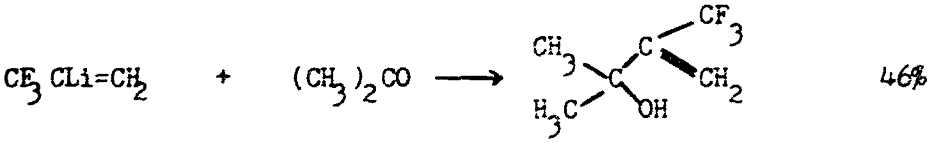
Thus, using the same technique, trifluoro-isopropenyllithium was prepared and reacted with acetone at -90°. After the final addition of reactants, the mixture was maintained between -90° and -80° for 1-1/2 hours and then allowed to warm slowly to room temperature. Addition of aqueous hydrochloric acid was followed by separation and drying of the ethereal layer. V.p.c. analysis showed that butyl bromide was present together with an approximately equivalent amount of product. A very small quantity (~2% yield) of a high-boiling product was also observed.

Fractionation yielded:

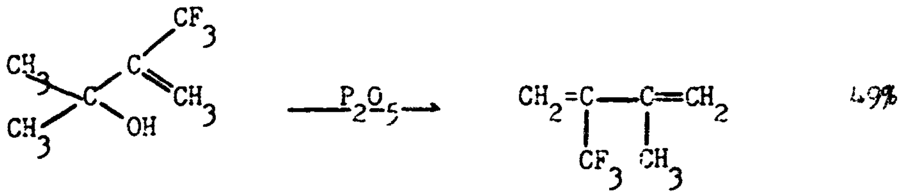
a. butyl bromide (43%) yield and,

b. the major product, b.p. 116° - 117° which was shown to be dimethyl-(trifluoro-isopropenyl)-carbinol (46%) yield

The small amount of high-boiling product was probably dimethyl butyl carbinol.

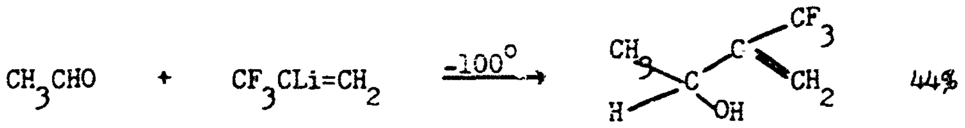


Dimethyl (trifluoro-isopropenyl) carbinol was successfully dehydrated by heating with phosphorus pentoxide to give 2-trifluoromethyl-3-methyl butadiene, b.p. 64° - 65°, in 49% yield.

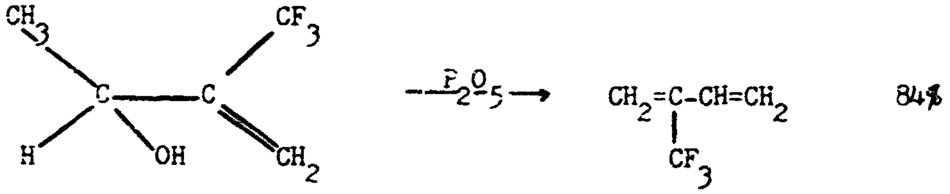


When this butadiene was sealed in a tube for several days, polymerization took place to produce a clear elastomeric material.

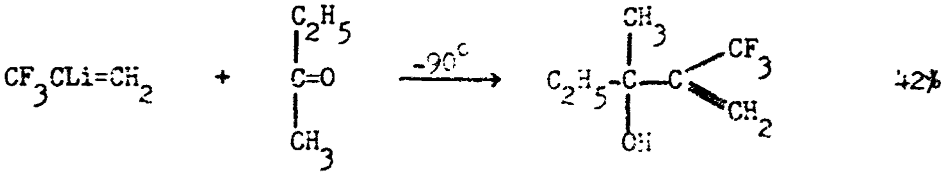
Acetaldehyde was also reacted with trifluoro-isopropenyllithium at -100° using the technique described above to produce the desired secondary alcohol, 2-trifluoromethyl-but-1-en-3-ol, b.p. 110° - 111° in 44% yield.



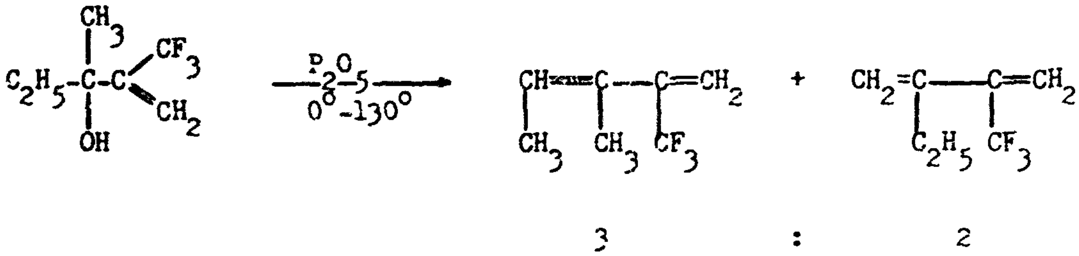
Dehydration of this alcohol also was accomplished by heating with phosphorus pentoxide, to give what is probably the known compound 2-trifluoromethyl-butadiene, b.p. 34 - 35° (lit. (84) 35 - 35.5°) in 84% yield. Infrared, ^{1}H and ^{19}F NMR spectra are consistent with this structure.



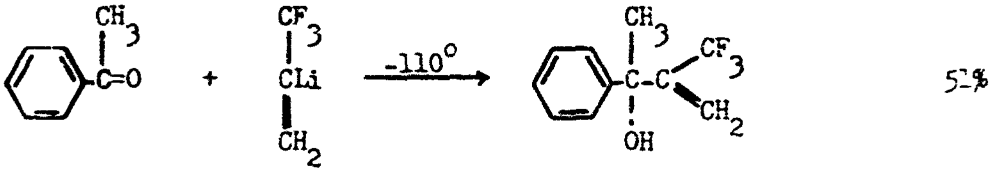
Ethylmethyl ketone reacted with trifluoro-isopropenyllithium at -90°, using the aliquot technique, to produce the desired carbinol, ethyl methyl (trifluoro-isopropenyl) carbinol b.p. 130° - 131°, in 42% yield.



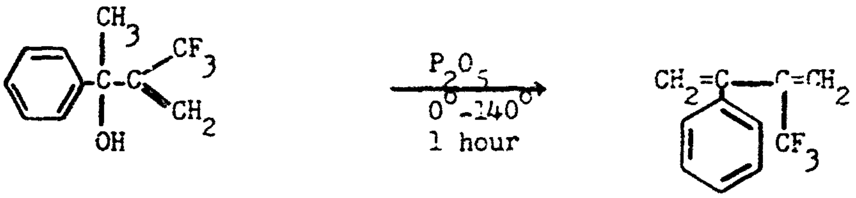
Dehydration of this alcohol, by heating with phosphorus pentoxide, gave a mixture of two compounds, boiling range 70° - 90° which was shown by analysis, I. R., ^{19}F and ^{1}H NMR spectroscopy to contain a 3:2 isomeric mixture of substituted pentadienes in 78% yield.

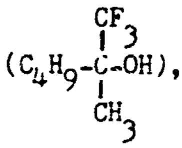
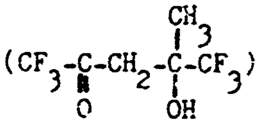


Acetophenone was allowed to react with trifluoro-isopropenyllithium which had been prepared by addition of butyllithium in mixed solvent (pentane/ether) to trifluoro-isopropenyl bromide in ether at -110° ± 3° in a single batch. At this temperature, apparently the exchange reaction occurred and the trifluoro-isopropenyllithium formed was sufficiently stable to exist until the ketone was added after 10 minutes, since the desired carbinol was produced, after work-up, in 51% yield.

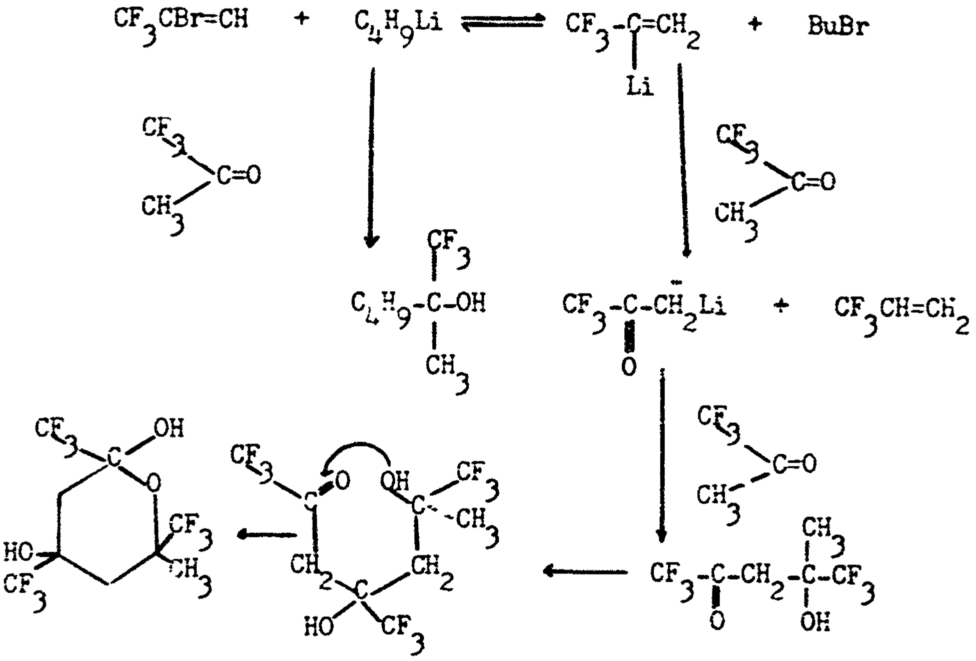


Phenylmethyl(trifluoro-isopropenyl) carbinol was dehydrated by heating with phosphorus pentoxide to 140° for 1 hour under reduced pressure. The product was then vacuum distilled from the system to give 2-phenyl-3-trifluoromethylbutadiene.



The reaction between trifluoro-isopropenyllithium and trifluoroacetone has been studied. In none of the several experiments performed was the desired trifluoro-isopropenyl methyl trifluoromethyl carbinol formed, but, depending on the reaction conditions, mixtures of butylmethyltrifluoromethyl carbinol  $(C_4H_9\text{-}C(CF_3)(CH_3)\text{-}OH)$, and 1,1,1,5,5,5-hexafluoro-2-methyl-pentan-4-on-2-ol  $(CF_3\text{-}C(=O)\text{-}CH_2\text{-}C(CH_3)(OH)\text{-}CF_3)$, together with some relatively involatile white solid material, which was probably a pyran derivative formed by the cyclisation reaction of trifluoroacetone $^{(70)}$.

Even in experiments in which good yields of butyl bromide were obtained, indicating the formation of trifluoro-isopropenyllithium, no desired carbinol was produced. Thus, it would appear that the trifluoro-isopropenyl "carbanion" preferentially abstracts a proton from trifluoroacetone before attack on the carbonyl function can occur.



Decomposition of Trifluoro-isopropenyllithium

Since the preceding evidence appeared to suggest that trifluoro-isopropenyl magnesium bromide decomposed to give an allene, it was decided to investigate the controlled decomposition of trifluoro-isopropenyllithium, prepared in the manner previously described. Trifluoro-isopropenyl bromide in ether was treated with butyllithium in mixed solvent (hexane/ether) at -90°. The temperature was maintained at -90° for a further 30 minutes and then allowed to warm to room temperature. The over-gases were condensed in an acetone/dry ice trap. The solution became colored (yellow/brown) at approximately -30° and the formation of a precipitate increased as the temperature rose. This solid was filtered and shown to be lithium fluoride (1.4 gm., 95%) together with some polymeric organic material.

The organic solution from the reaction was examined by v.p.c. and shown to contain only ether, hexane and butyl bromide.

Fractionation gave butyl bromide (5.8 gm., 74% yield). The over-gases from the acetone/dry ice trap were distilled to give a compound b.p. -20° → -21° with an i.r. spectrum identical to that of difluoroallene (85).

Yield of difluoro-allene, 3.1 gm., 72%. (lit. (85) b.p. -20°)

$$CF_3CLi{=}CH_2 \longrightarrow CF_2{=}C{=}CH_2 \quad + \quad LiF$$

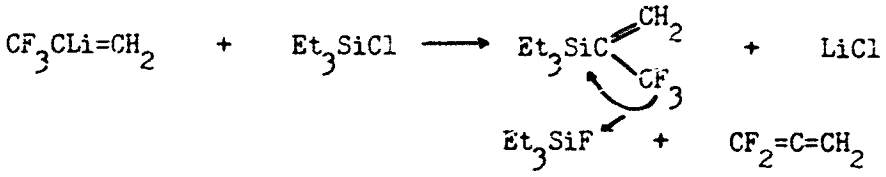
A sample of difluoroallene was sealed in a tube and allowed to stand at room temperature for several days to give a viscous polymeric semi-solid material.

Reaction of Trifluoro-isopropenyllithium with Triethylchlorosilane

In pursuing the further possibilities of reactions involving trifluoro-isopropenyllithium, the reaction with triethylchlorosilane was studied. Trifluoro-isopropenyllithium was prepared by the batch method, i.e., all the butyllithium was added over 5 minutes to trifluoro-isopropenyl bromide at -110° and after a further 20 minutes treated with triethylchlorosilane at -100°. The temperature was allowed to rise slowly to that of the room. A white precipitate formed, was filtered and shown to contain no organic material. The dried solid was weighed, stirred in boiling water, filtered and the solid redried and reweighed. This solid was lithium fluoride. The aqueous filtrate gave a positive test for chloride when treated with silver nitrate solution. From this separation it was estimated that the solid consisted of lithium fluoride and lithium chloride produced in 61% yield and 29% yield, respectively.

The organic solution from the reaction mixture was examined by analytical v.p.c. Unreacted triethylchlorosilane with an approximately equal quantity of butyl bromide was present, also a product of slightly longer retention time than butyl bromide. A pure sample of this product was obtained by prep. scale v.p.c. and shown to be triethylfluorosilane, b.p. 109° (lit. (86) b.p. 110°). The i.r. spectrum of this compound was identical to an authentic sample of triethylfluorosilane. Estimated yield of triethylfluorosilane, 17% (by v.p.c.).

The mechanism of this reaction and the route by which the fluorosilane was formed is not clear, but possibly initial formation of triethyl(trifluoro-isopropenyl)silane, followed by fluorine migration to the silicon atom (87) with the elimination of difluoroallene took place.



$$CF_3CLi{=}CH_2 + Et_3SiCl \longrightarrow Et_3SiC(=CH_2)CF_3 + LiCl$$

$$Et_3SiF + CF_2{=}C{=}CH_2$$

Lithium fluoride did not react with triethylchlorosilane under the conditions described above.

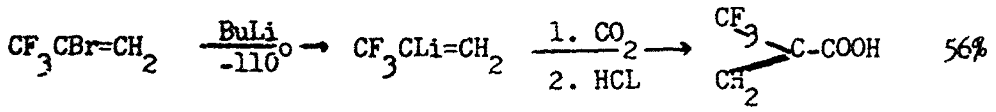
Carbonation of Trifluoro-isopropenyllithium

Several attempts to carbonate trifluoro-isopropenyllithium have been made. When butyllithium is added to trifluoro-isopropenyl bromide at temperatures -78°, the fluoro-organic metal compound decomposes before carbonation can occur.

Thus, while the aliquot technique is suitable for reactions in which the second reactant (*e.g.* ketone) can be added quickly, before complete decomposition of the trifluoro-isopropenyllithium takes place, reactions such as carbonation, in which the second reactant is bubbled into the mixture, require a different technique. To prevent excessive decomposition of trifluoro-isopropenyllithium, it was decided to lower the reaction temperature further. At lower temperatures exchange metallation reaction proceeds more slowly so that the experimental technique employed must be modified. A typical example of this batch technique is described below.

Butyllithium in mixed solvent (pentane/ether), precooled to -73°, was added to trifluoro-isopropenyl bromide in ether at -110° ± 3° over 5 minutes. During a further 10 minutes, the temperature was allowed to rise to -100° and dry carbon dioxide bubbled into the reaction. The introduction of carbon dioxide was continued until the reaction temperature attained -78°. The passage of carbon dioxide was then stopped and the reaction allowed to warm to room temperature. Hydrochloric acid was added and the ether solution separated, and dried. Distillation gave butyl bromide (68%) yield and a white crystalline residue of crude acid (56% yield). This was sublimed and a pure sample obtained by prep.scale v.p.c. The acid was shown to be 2-trifluoromethyl acrylic acid, m.p. 50° - 51° (lit.(91) 50 - 52°).

The infrared, ^1H and ^{19}F NMR spectra were consistent with this structure.



$$CF_3CBr{=}CH_2 \xrightarrow[-110^{\circ}]{BuLi} CF_3CLi{=}CH_2 \xrightarrow[2.\ HCL]{1.\ CO_2} \begin{array}{l}CF_3\\ CH_2\end{array}\!\!>C\text{-}COOH \quad 56\%$$

Attempted Replacement of Fluoride Ion by Trifluoro-isopropenyllithium

Many organo-lithium compounds have been used in nucleophilic substitution reactions to replace fluorine by the organic group of the reagent. Thus, it was decided to explore the possibility of using trifluoro-isopropenyllithium to perform such a reaction.

Trifluoro-isopropenyllithium was prepared at -100° by the aliquot method and treated immediately with hexafluorobenzene. The temperature was maintained at -100° for two hours and then allowed to warm slowly to room temperature overnight. After work-up, butyl bromide was shown to be present together with unreacted hexafluorobenzene, but no useful substitution products were detected.

Similarly, when trifluoro-isopropenyllithium was treated with 1,1-difluorodichloroethylene at -100° and allowed to warm to room temperature, no useful substitution products were observed. Butyl bromide was produced in 57% yield, and the unreacted fluorochloroolefin recovered.

In both reactions trifluoro-isopropenyllithium was formed, as confirmed by the production of butyl bromide, but obviously the reagent decomposed before nucleophilic replacement of fluorine in the benzene or ethylene by trifluoro-isopropenyl carbanions could occur. These experiments again demonstrate the overriding feature of this work, that it is absolutely necessary for trifluoro-isopropenyllithium to attack the other reagent at temperatures below approximately -78°, otherwise no useful products are produced.

Attempted Preparation of Lithium Derivaties from Trifluoropropene

There have been a number of reports (83,92,93,94) of exchange of hydrogen atoms in unsaturated compounds with lithium, from an alkyl lithium reagent, to give a new lithium derivative of the unsaturated compound. It was decided to study the reaction of butyllithium with trifluoropropene with a view to preparing new fluoro-organic lithium compounds.

e.g. $$CF_3CH=CH_2 \quad + \quad BuLi \longrightarrow CF_3CLi=CH_2 \quad + \quad BuH$$

It was found, however, that reactions of the type described above did not take place.

Several experiments were performed under varying conditions in which trifluoropropene was treated with butyllithium in ether at low temperature. Typical of these was one in which trifluoropropene in diethyl ether at -95° was treated with butyllithium in pentane/ether solution.

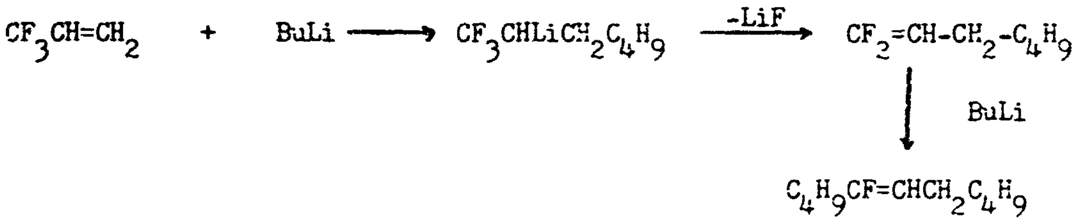
After maintaining the temperature at $-95^{\circ} \pm 2^{\circ}$ for one hour, acetone was added and the mixture allowed to warm slowly to room temperature. The only product isolated after work-up was butyl dimethyl carbinol in 69%

yield. Obviously no exchange reaction took place, leaving unchanged butyllithium free to react normally with acetone.

It was known from previous work that trifluoro-isopropenyllithium was unstable and tended to eliminate lithium fluoride with the production of 1,1-difluoroallene. To further test whether any exchange metallation occurred with the 2-hydrogen atom, a reaction was carried out in which trifluoropropene in diethyl ether at -100° was treated with butyllithium and the mixture allowed to warm to room temperature. The mixture developed a yellow coloration and became gelatinous (probably with precipitated lithium fluoride). A slow current of nitrogen was bubbled through the mixture and the over-gases collected in an acetone/CO_2 trap.

The trap did not contain difluoroallene, indicating that no exchange metallation occurred. The ethereal solution contained a mixture of three products, which were separated by prep. scale v.p.c. and shown to be 1,1-difluoroheptene-1 (5%), and an inseparable mixture of cis and trans 5-fluoroundecene-5. (25%)

These products were obviously formed by the addition of butyllithium across the double bond in trifluoropropene followed by elimination of lithium fluoride to give the heptene (88). Nucleophilic replacement of fluorine by a butyl carbanion on the terminal difluoromethylene group would produce the undecenes.



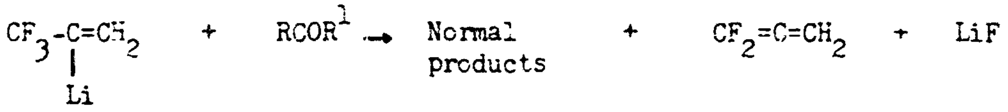
$$
\begin{tikzcd}
CF_3CH=CH_2 + BuLi \arrow[r] & CF_3CHLiCH_2C_4H_9 \arrow[r, "-LiF"] & CF_2=CH-CH_2-C_4H_9 \arrow[d, "BuLi"] \\
 & & C_4H_9CF=CHCH_2C_4H_9
\end{tikzcd}
$$

G. Trifluoropropynyllithium

At this stage, in view of the results to date, it would be useful to summarize some of the desirable structural features of any new unsaturated fluoro-organometallic reagent chosen. Three main features must be considered.

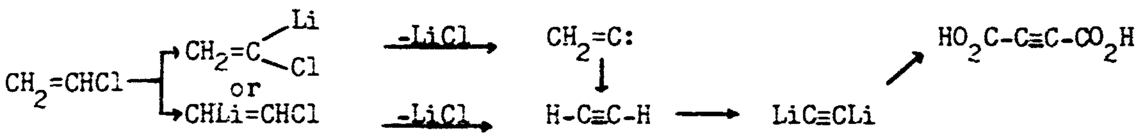
(1) There must not be a terminal difluoromethylene group in the molecule since this could give rise to products of attack on this group by nucleophiles in the system, or to rearrangement of the normal reaction products (e.g., alcohols $\rightarrow$ α,β-unsaturated acids.)

(2) It would also be undesirable to have halogen on the carbon adjacent to that carrying the lithium atom since there is then an easy route for decomposition of the organometallic reagent via elimination of lithium halide. It has been found that trifluoro-isopropenyllithium, with substrates of limited reactivity, decomposes in this way to produce difluoroallene.

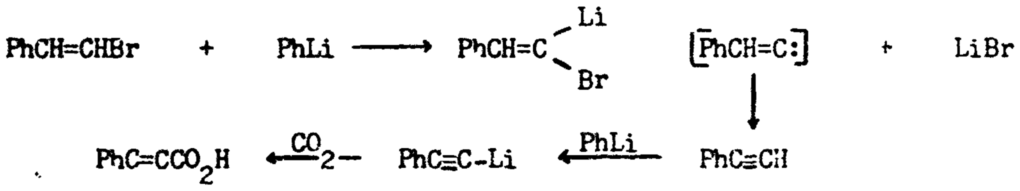


$$CF_3\text{-}\underset{\displaystyle |\atop \displaystyle Li}{C}=CH_2 \quad + \quad RCOR^1 \longrightarrow \text{Normal products} \quad + \quad CF_2=C=CH_2 \quad + \quad LiF$$

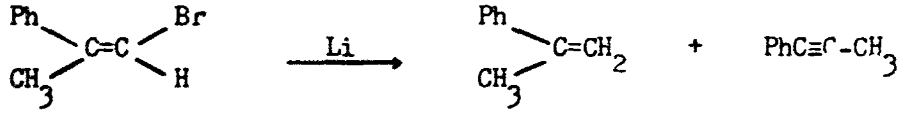
(3) There are a number of reports in the literature of exchange of an olefinic proton with an organometallic reagent to give a new unsaturated organometallic compound. Kobrich and Flory (89) treated $CH_2=CHCl$, trans-$CHCl=CHCl$ and $Cl_2C=CHCl$ with butyllithium at -110° and then added carbon dioxide after stirring for one hour. The products were, respectively, $CH_2=CClCOOH$, trans $ClCH=CClCOOH$, and $Cl_2C=CClCOOH$ in almost quantitative yield and these can only have arisen via initial proton exchange. The reaction of vinyl chloride with butyllithium at higher temperatures followed again by carbonation afforded acetylene dicarboxylic acid by the following route:



Similarly, reaction of vinyl bromide with butyllithium in ether at 0° and subsequent carbonation gave acetylene dicarboxylic acid (34%) (90). These acetylene formation reactions involved proton rather than halogen exchange, elimination of lithium halide, further exchange with the more acidic acetylenic protons, and carbonation of the dilithio compound. Similar treatment of β-bromostyrene gave $PhC\equiv C\text{-}COOH$ (42.5%). This reaction has been further studied by Cristol and Bly (91) and they proposed an α-elimination mechanism on the basis of studies with cis and trans-isomers.



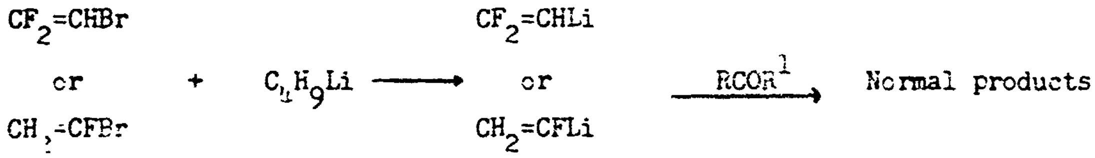
The following interesting reaction is described by Curtin and Crump (100):



XLV XLVI XLVII

Compound XLVI must have been formed by abstraction of a proton from XLV by the lithium reagent resulting from halogen exchange in XLV. The most likely route to XLVII involves proton exchange in XLV, elimination of lithium bromide, and 1,2- migration of the methyl group. Several other examples of preferred proton exchange in the presence of halogen are given by Normant (92) in a paper on the reaction of organometallics with haloölefins and acetylenes.

As described earlier, 2,2-difluorovinyl- and 1-fluorovinyllithium reagents were not formed in high yield when an exchange reaction of the corresponding bromides was attempted with butyllithium. It is not inconceivable that proton exchange was also taking place, thus giving rise to some of the numerous reaction possibilities described below.



$$\begin{matrix} CF_2{=}CHBr \\ \text{or} \\ CH_2{=}CFBr \end{matrix} + C_4H_9Li \longrightarrow \begin{matrix} CF_2{=}CHLi \\ \text{or} \\ CH_2{=}CFLi \end{matrix} \xrightarrow{RCOR^1} \text{Normal products}$$

$$\begin{array}{ccccccc} CF_2{=}CHBr & & & & CF_2{=}CLiBr & & \\ \text{or} & + & C_4H_9Li & \longrightarrow & \text{or} & \xrightarrow{RCOR^1} & \text{Normal products} \\ CH_2{=}CFBr & & & & CHLi{=}CFBr & & \end{array}$$

Alternatively, any of the above lithium reagents could eliminate lithium halides and the acetylenic products could, by further exchange, give new lithium reagents which would also react normally with ketones <u>etc</u>.,

$$CF_2{=}CHLi \xrightarrow{-LiF} CF{\equiv}CH \longrightarrow CF{\equiv}CLi$$

$$CH_2{=}CFLi \xrightarrow{-LiF} CH_2{=}C: \longrightarrow CH{\equiv}CH \longrightarrow LiC{\equiv}CH \text{ or } LiC{\equiv}CLi$$

$$CF_2{=}CLiBr \xrightarrow{-LiBr} CF_2{=}C: \longrightarrow ?$$

$$CF_2{=}CLiBr \xrightarrow{-LiF} CF{\equiv}CBr \longrightarrow CF{\equiv}CLi$$

$$CHLi{=}CFBr \xrightarrow{-LiF} CH{\equiv}CBr \longrightarrow LiC{\equiv}CBr \text{ or } CH{\equiv}CLi \text{ or } LiC{\equiv}CLi$$

$$CHLi{=}CFBr \xrightarrow{-LiBr} CH{\equiv}CF \longrightarrow LiC{\equiv}CF$$

In reaction of 2,2-difluorovinyl bromide and 1-fluorovinyl bromide with butyllithium followed by addition of aldehydes and ketones, numerous products were indicated by GLC but none of those isolated contained an acetylenic group. However, one of the possible routes to triethyl ethynyl silane involves the latter type of scheme.

To summarize, any new lithium reagent chosen should not contain (1) a terminal difluoromethylene group (2) lithium and halogen atoms on adjacent carbon atoms or (3) "acidic" protons.

These conditions are satisfied in 3,3,3-trifluoropropynyllithium and so we would expect the latter reagent to give good yields of alcoholic products on reaction with aldehydes and ketones. This reagent was prepared from 3,3,3-trifluoropropyne *via* exchange of the proton with butyllithium. The above propyne was prepared by dechlorination of 1,1,2-trichloro-3,3,3-trifluoropropene-1 using zinc dust in dimethylformamide (93).

A literature search has revealed that a number of trifluoropropynyl metal compounds have already been prepared, e.g., $CF_3C{\equiv}CAg$, $CF_3C{\equiv}CCu$ and $(CF_3C{\equiv}C)_2Hg$ (94). Trifluoropropynylmagnesium bromide has been made and reacted with acetone to give the desired alcohol in high yield (75%) (95). Trifluoropropynyl zinc (or $CF_3C{\equiv}CZnCl$) is also known (96). Recently the the latter compound has been treated with cupric chloride and a number of oxidation products including the diyne $CF_3C{\equiv}C\text{-}C{\equiv}C\text{-}CF_3$ were isolated (97). There is a recent report (98) of the preparation of trifluoropropynyllithium by reaction of trifluoropropyne with lithium amide. The lithium reagent and the corresponding Grignard were used to introduce trifluoropropynyl groups into steroids by reaction with steroidal ketones.

In this laboratory trifluoropropynyllithium was prepared by reaction of trifluoropropyne with butyllithium. Good yields of alcohols have been obtained by reacting trifluoropropynyllithium with various aldehydes and ketones (Table XIII).

Reaction with triethylchlorosilane gave triethyl(trifluoropropynyl) silane in high yield (81%). The corresponding trifluoropropynyl magnesium iodide has been reacted previously (99) with various organometallic halides and the substitution products obtained in good yield.

Reactions with benzonitrile and dichlorodifluoroethylene gave insoluble, non-melting solids but no monomeric organic products.

TABLE XIII

REACTION OF FLUORINATED UNSATURATED ORGANOMETALLIC COMPOUNDS WITH CARBONYL COMPOUNDS AND TRIETHYLCHLOROSILANE

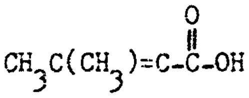
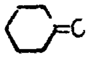
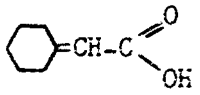
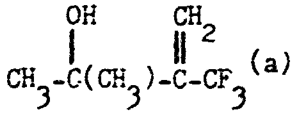
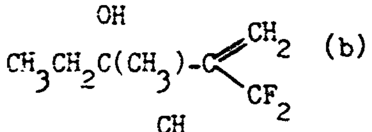
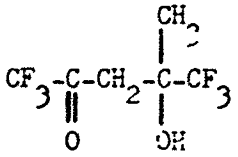
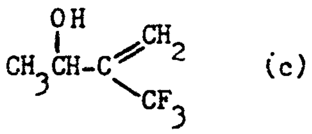
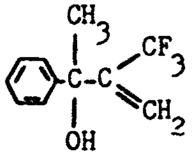
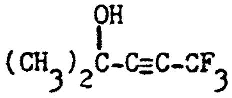
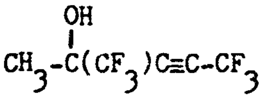
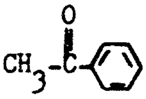
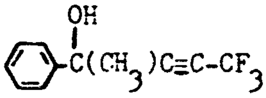
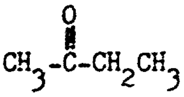
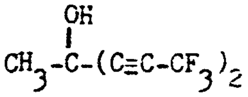
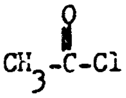
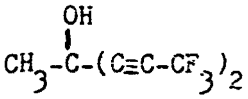
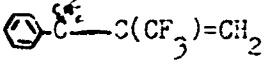
Organometallic Reagent	Reactant	Product	Yield
$CF_2=CFMgBr$	$CF_2ClCOCF_2Cl$	$CF_2=CF-C(CF_2CCl)_2OH$	55
$CF_2=CFMgBr$	CF_3COCF_3	$CF_2=CF-C(CF_3)_2OH$	65
$CF_2=CHLi$	CH_3COCH_3	 $CH_3C(CH_3)=C-\overset{\overset{O}{\|}}{C}-OH$	9
$CF_2=CHLi$			25
$CF_2=CHMgBr$	CF_3COCF_3	$CF_2=CH-C(CF_3)_2OH$	5-10
$CF_2=CHMgBr$	Me_3SiCl	$Me_3SiCH=CF_2$	17
$CF_2=CHLi$	Et_3SiCl	no stable product	..
$CH_2=CFLi$	$CH_3COCH_2CH_3$	5 inseparable products	..
$CH_2=CFLi$	Et_3SiCl	$Et_3SiC\equiv CH$	30
$CF_3CLi=CH_2$	CH_3COCH_3	 $CH_3-\overset{\overset{OH}{\vert}}{C}(CH_3)-\overset{\overset{CH_2}{\|}}{C}-CF_3$ (a)	46
$CF_3CLi=CH_2$	$CH_3COCH_2CH_3$		42
$CF_3CLi=CH_2$	CF_3COCH_3	 $CF_3-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{CH_2}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CF_3$	variable
$CF_3CLi=CH_2$	CH_3CHO		44

TABLE XIII (continued)

REACTION OF FLUORINATED UNSATURATED ORGANOMETALLIC COMPOUNDS WITH CARBONYL COMPOUNDS AND TRIETHYLCHLOROSILANE

$CF_3CLi=CH_2$	Acetophenone		(d)	51
$CF_3CLi=CH_2$	Et_3SiCl	Et_3SiF		17
$CF_3CLi=CH_2$	CO_2	$CH_2=C(CF_3)COOH$		56
$CF_3C{\equiv}CLi$	Et_3SiCl	$Et_3SiC{\equiv}CCF_3$		81
$CF_3C{\equiv}CLi$	CH_3COCH_3	 $(CH_3)_2\overset{OH}{C}-C{\equiv}C-CF_3$		70
$CF_3C{\equiv}CLi$	CH_3COCF_3	 $CH_3-\overset{OH}{C}(CF_3)C{\equiv}C-CF_3$		55
$CF_3C{\equiv}CLi$	CF_3COCF_3	$(CF_3)_2C(OH)C{\equiv}CCF_3$		
$CF_3C{\equiv}CLi$	CH_3CH_2CHO	$CH_3CH_2CH(OH)C{\equiv}C-CF_3$		54
$CF_3C{\equiv}CLi$				69
$CF_3C{\equiv}CLi$	 $CH_3-\overset{O}{C}-CH_2CH_3$ (e)	 $CH_3-\overset{OH}{C}-(C{\equiv}C-CF_3)_2$		25
$CF_3C{\equiv}CLi$	 $CH_3-\overset{O}{C}-Cl$ (e)	 $CH_3-\overset{OH}{C}-(C{\equiv}C-CF_3)_2$		56

Some of the above alcohols (a → d) were dehydrated giving the following products, (%) (a) $CH_2=C(CH_3)-C(CF_3)=CH_2$ (49), (b) Mixture of two isomers (c) $CH_2=CH-C(CF_3)=CH_2$ (84) (d)  (82) (e) 2:1 mole ratio of lithium reagent to reactant employed.

III EXPERIMENTAL

A. Preparation and Some Reactions of Perfluoroallylhalides

Fluorination of $C_3Cl_5F_3$ Prepared by $AlCl_3$ Catalyzed Addition of $CFCl_3$ to CFCl=CFCl

SBF_3 (142 g., 0.79 mole) and chlorine (33 g., 0.46 mole) were combined in an autoclave at -78° and left at room temperature for 3 hours. $C_3Cl_5F_3$ (153 g., 0.56 mole) was added and heated at 150° for 3 hours with rocking. During the next 2.5 hours the temperature rose to 185 - 190° due to a thermo-couple malfunction. After further heating at 190 - 200° for 2.5 hours, the mixture was left overnight at ambient. V.p.c. indicated only a small amount of fluorination had occurred so the mixture was reheated at 190 - 200° for 7 hours. Work-up gave a material (113 g.) which on distillation yielded $C_3Cl_3F_5$ (99 g., 74% yield).

Preparation of Perfluoroallylchloride (PFAC)

$C_3Cl_3F_5$ (94 g., 0.39 mole) in ethanol (50 ml.) was added dropwise over a period of 1.25 hours to a suspension of zinc (32 g., 0.49 mole) in gently refluxing ethanol (100 ml.). The mixture was refluxed for 1.5 hours and the product was collected in a dry ice/acetone cooled trap to give a material (64 g.) which on distillation gave PFAC (53 g., 85% yield).

Preparation of Perfluoroallyl Bromide (PFAB)

Potassium hydroxide pellets (112 g., 2.0 mole) were placed in water (100 cc) in a 500 cc flask equipped with a magnetic stirrer, dropping funnel, and 6-inch glass helice packed column with a variable take-off head. $CF_2BrCHFCF_2Br$ (50.1 g., 0.172 mole) was placed in the dropping funnel and added slowly over a period of 50 minutes to warmed solution. Pentafluoroallyl bromide (20.3 g.) was distilled out as it formed. V.p.c. indicated the product was pure, b.p. 27 - 8°. Yield 56%. The infrared spectrum showed the CF_2=CF- absorption at 5.58μ and agreed with the spectra of previously prepared material. The organic layer remaining after the reaction was separated, was washed and dried to give 6.7 g. material believed to be CF_2BrCF_2CHFBr.

Preparation of Perfluoroallyliodide (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 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.). V.p.c. 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. (<u>Analysis</u> Calcd. for $C_7H_{10}O_2F_4$, $C_2H_5OCF{=}CFCF_2OC_2H_5$: 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-1, fumed in air and had strong infrared bands at 5.49µ and 5.90µ. (<u>Analysis</u> Calcd. for $C_7H_{11}O_2F_5$, $C_2H_5OCF_2CHFCF_2OC_2H_5$: 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-inch 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%). V.p.c. 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. (<u>Analysis</u> Calcd. for $C_5H_2OF_8$: 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).)

<u>Reaction of $CF_2=CFCF_2Cl$ with CH_3ONa in CH_3OH</u>

Sodium methoxide (7 g., 0.13 mole) was added to methanol (100 ml.) at 0° to give a white suspension to which was added PFAC (16 g., 0.096 mole) <u>via</u> a gas inlet tube over 42 minutes. The mixture was stirred up to room temperature over 2.5 hours, then poured into water. The organic layer was separated, washed with ice-HCl and cold saturated NaCl solution to give a product (7.4 g.) containing four components: 23% A, 16% B, 15% C, and 46% D. These were purified on S. E. prep. v.p.c. column and identified as follows:

A: PFAC by infrared comparison

B: b.p. 43 - 4° (micro), $n_D^{20.5}$ 1.3040, with strong infrared band at 5.56μ and a weak shoulder at 5.67μ, hence (101) $CH_3OCF_2CF=CF_2$.

C: b.p. 78 - 9° (micro), $n_D^{20.5}$ 1.3305, with broad infrared band at 5.83μ (<u>Analysis</u> Calcd. for $C_4H_3ClF_4O$, $CH_3OCF_2CF=CFCl$ and/or $CH_3OCF=CFCF_2Cl$: F, 42.57. Found: F, 42.13%)

D: b.p. 120 - 1° (micro), $n_D^{20.5}$ 1.3273, d_4^{25} 1.348 g./cc. (<u>Analysis</u> Calcd. for $C_5H_7F_5O_2$, $CH_3OCF_2CHFCF_2OCH_3$: C, 30.94; H, 3.64. Found: C, 30.75; H, 3.19%)

<u>Reaction of $CF_2=CFCF_2Cl$ with CH_3ONa in Dioxane</u>

A suspension of sodium methoxide (6 g., 0.111 mole) in dioxane (72 g.) was cooled to 0° and PFAC (15 g., 0.090 mole) was bubbled in over 33 minutes. The mixture was stirred up to room temperature over 2 hours, then for 2 hours at ambient. Washing gave a product (4.9 g.), containing chiefly two low-boiling compounds. These were identified as PFAC and a compound suspected to be $CH_3OCF_2CF=CF_2$ (b.p. <u>ca</u>. 55 - 6°, n_D^{21} <u>ca</u>. 1.30, and strong infrared band at 5.65μ by comparison with previous experiments.

<u>Addition of $CH_2=CHCH_2OH$ to $CF_2=CFCF_2Cl$ in the Presence of KOH</u>

Potassium hydroxide pellets (3.4 g., 0.61 mole) were dissolved in allyl alcohol (21.0 g., 0.36 mole) in a Fischer-Porter tube, the solution was cooled to -78°, and PFAC (12.5 g., 0.075 mole) was added rapidly. A white precipitate was formed immediately and an exothermic reaction occurred, even at -78°. The tube was sealed and kept at room temperature for 2 hours with occasional shaking and was then heated at 68 - 70° for 1.5 hours. After cooling, the tube was vented (ca. 0.5 g., PFAC obtained).

The mixture was poured into ice-dil. HNO_3. The organic layer was separated and washed twice with water to give a product (5.7 g.) which by v.p.c. contained 3% PFAC, 19% D, 14% A-1, 36% A-2, 8% unknown, and 20% A-3.

The experiment was repeated using a flask equippped with a magnetic stirrer, gas inlet tube, and a dry ice reflux condenser connected to a dry ice/acetone trap. A solution of KOH pellets (3.4 g., 0.061 mole) in allyl alcohol (19.9 g., 0.34 mole) was cooled in an ice bath then PFAC (11.0 g., 0.066 mole) was bubbled in slowly during 0.5 hour at 0°. A white precipitate formed immediately. After stirring at room temperature for 1 hour, the mixture was refluxed gently for 0.5 hour then left over the weekend at ambient. The mixture poured into an excess of water. Samples of the aqueous layer gave positive tests for fluoride and chloride ions. The organic layer was washed to give a product (5.2 g.) containing 3% PFAC, 12% D, 14% A-1, 53% A-2, 3% unknown, and 15% A-3. These components were separated and purified on a S. E. preparative v.p.c. column to give the pure fractions which were identified as follows:

D: b.p. 78 - 9° (micro), $n_D^{21.0}$ 1.3353, with a strong infrared band at 5.57μ. (Analysis Calcd. for $C_6H_5F_5O$, $CH_2=CHCH_2OCF_2CF=CF_2$: F, 50.50. Found: F, 46.77%).

A-1: b.p. 117 - 8° (micro), $n_D^{20.5}$ 1.3616, d_4^{24} 1.309 g./cc., with weak infrared bands at 5.62μ, 5.84μ, and 6.08μ. (Analysis Calcd. for $C_6H_5ClF_4O$, $CH_2=CHCH_2OCF_2CF=CFCl$ and/or $CH_2=CHCH_2OCF=CFCF_2Cl$: Cl, 17.33. Found: Cl, 15.92%)

A-2: b.p. 166 - 7° decomp. (micro), $n_D^{20.5}$ 1.3775, d_4^{24} 1.219 g./cc., with weak infrared band at 6.08μ. (Analysis Calcd. for

$C_9H_{11}F_5O_2$, $CH_2=CHCH_2OCF_2CHFCF_2OCH_2CH=CH_2$: F, 38.59. Found: F, 36.32; Cl, 1.08%)

A-3 b.p. 185° decomp. (micro), $n_D^{20.8}$ 1.4242, with strong infrared band at 5.66µ and a weak band at 6.09µ. (Analysis Calcd. for $C_9H_{11}F_3O_3$, $CH_2=CHCH_2OCF_2CHF\overset{\overset{O}{\|}}{C}OCH_2CH=CH_2$: F, 25.43. Found: F, 22.90; Cl, 3.46%).

Attempted Reaction of Sodium Allyloxide with $CF_2=CFCF_2Cl$ in Dioxane

A suspension of sodium allyloxide (8.0 g., 0.10 mole) in dry dioxane (50 ml.) was cooled in an ice bath and $CF_2=CFCF_2Cl$ (16.8 g., 0.10 mole) was added over 0.5 hour. The mixture was stirred up to room temperature over 1.5 hours but gas chromatography showed no reaction had occurred.

Attempted Reaction of Sodium Allyloxide with $CF_2=CFCF_2Cl$ in Acetone

A suspension of sodium allyloxide (8.0 g., 0.10 mole) in dry acetone (130 ml.) was cooled to 0° then $CF_2=CFCF_2Cl$ (14.2 g., 0.085 mole) was added in 40 minutes. The mixture was stirred to room temperature for 4 hours but none of the expected product was formed.

Reaction of Allylmagnesium Bromide with $CF_2=CFCF_2Cl$

Magnesium (8.5 g., 0.352 mole) and dry ether (120 ml.) were combined in a dry flask under nitrogen. The magnesium was activated by adding a few drops of CH_2BrCH_2Br and stirring at room temperature for 18 minutes. The flask was then cooled in an ice bath and allyl bromide (18.0 g., 0.149 mole) in dry ether (20 ml.) was added dropwise during 20 minutes. The resulting mixture was stirred for 6 minutes then filtered into a dry dropping funnel. The solid residue was also washed with ether and the ether was combined with the Grignard solution.

Dry ether (20 ml.) and $CF_2=CFCF_2Cl$ (13.0 g., 0.078 mole) were combined at 0°. The Grignard solution was added dropwise to give an immediate white precipitate. After 0.25 hour (ca. one-fourth the Grignard had been added) a gray sludge had formed which made stirring difficult. The remaining Grignard was added during 0.5 hour. After stirring to room temperature for 7 minutes, water was added and the mixture was left overnight. The ether layer was washed with dilute sulfuric acid, then dried over

Drierite. The aqueous layer gave positive tests for chloride and fluoride ions. Distillation gave a residue (12.5 g.) containing some ether, a small amount of allyl bromide and compounds XLVIII and XLIX. Further distillation gave ether (4.2 g.), allyl bromide (0.4 g.), XLVIII (1.7 g.), and a residue (5.0g.) This latter contained XLVIII (34%, 1.7 g.), XLIX (40%, 2.0 g.), and three higher boiling components (26%, 1.3 g.). Preparative gas chromatographic separation (silicon elastomer, 110°) gave pure XLVIII b.p. 96 - 8° (micro), $n_D^{20.5}$ 1.3787, with a strong infrared band at 5.94μ and a weaker band at 6.08μ and pure XLIX, b.p. 139 - 40° (micro), $n_D^{20.5}$ 1.3970, with medium infrared bands at 5.78μ and 6.08μ. (*Analysis* for XLVIII, Calcd. for $C_6H_5ClF_4$: Cl, 18.81; F, 40.32. Found: Cl, 16.93; F, 37.14% identified as CH_2=$CHCH_2CF_2CF$=CFCl). (*Analysis* for XLIX, Calcd. for $C_9H_{10}F_4$: C, 55.64; H, 5.20; F, 39.16. Found: C, 55.77; H, 5.20; F, 39.45% identified as CH_2=$CHCH_2CF$=$CFCF_2CH_2CH$=CH_2).

B. Lewis Acid Catalyzed Addition of Haloalkanes to Haloolefins

Preparation and Purification of CFCl=CFCl

$CFCl_2CFCl_2$ (566 g., 2.77 mole) was added dropwise to zinc dust (200 g., 3.07 mole) in absolute ethanol (300 ml.) at reflux over 4.5 hours. After refluxing for 1.5 hours, a total of 337 g. crude olefin was collected. Distillation gave material (307 g. 84%), b.p. 22.5 - 23.5°, having infrared bands at 5.73μ (CF_2=O) and 5.86μ (*cis* -CF=CF-).

Removal of the CF_2=CCl_2 was accomplished by adding the crude olefin mixture (192 g.) from dropping funnel over 0.75 hour to a solution of sodium (0.5 g.) in absolute ethanol (200ml.) at 18 - 24°. After stirring for 2.5 hours, distillation gave pure CFCl=CFCl (172 g., 90% recovery), b.p. 22 - 3° with no infrared band at 5.73μ.

Addition of $CFCl_3$ to CFCl=CFCl using $AlCl_3$

$CFCl_3$ (281 g., 2.04 mole) and pure CFCl=CFCl (200 g., 1.50 mole) were combined in a flask at 0°, $AlCl_3$ (15 g.) was added and the ice bath was removed. After 18 minutes, $AlCl_3$ (15 g.) was added as the first batch had adhered to the side of the flask. After 22 minutes, another 15 g. $AlCl_3$ were added, then the mixture was stirred for 3 hours. $AlCl_3$ (10 g.) was added and the mixture stirred at room temperature for 2.5 hours. The total $AlCl_3$ used was 55 g. (0.42 mole) and the total time was 6.25 hours. Normal work-up gave material (467 g.) which on distillation gave CCl_4 (78 g.), $C_3Cl_4F_4$ (3.3 g.), $CCl_2=CCl_2$ (14.2 g.), $C_3Cl_5F_3$ (294 g., 72%), $C_3Cl_6F_2$ (43 g., 10%), and higher boiling material (3 g.).

Reaction of CFCl=CFCl with $AlCl_3$

A Fischer-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. V. p.c. indicated no reaction had occurred.

Cleavage of $C_3Cl_5F_3$ by $AlCl_3$

$C_3Cl_5F_3$ (41.4 g., 0.153 mole) and $AlCl_3$ (5 g., 0.037 mole) were placed in a Fischer-Porter tube and rocked occasionally for 44 hours at room temperature. The gaseous products were vented directly into a gas infrared cell. This contained at least CF_2Cl_2 and $CF_2=CFCl$. Washing gave a liquid (31 g.) which contained 6% CCl_4, 52% A, 7% $C_3Cl_5F_3$, and 36% $C_3Cl_6F_2$. Compound A had $n_D^{19.5}$ 1.5048 and was identified by infrared as $CCl_2=CCl_2$. The $C_3Cl_6F_2$ had b.p. 65 - 6°/4.5 mm. (b.p. 202 - 3°/760 mm.) and m.p. 44.0 - 45.5°.

Isomerization of $C_3Cl_5F_3$ by $AlCl_3$ in CCl_4

$C_3Cl_5F_3$ (24.0 g., 0.089 mole), CCl_4 (56 g.), and $AlCl_3$ (4 g., 0.03 mole) were combined in a Fischer-Porter tube at room temperature and rocked occasionally for 61 hours. Work-up gave material (66 g.), which after removal of CCl_4 (35 g.,), gave a residue (30 g.) containing CCl_4 (33%, 9.9g.), $CCl_2=CCl_2$ (25%, 7.5 g.), $C_3Cl_5F_3$ (15%, 4.5 g.), and $C_3Cl_6F_2$ (27%, 8.1 g.). Distillation gave the latter two in pure state for NMR analyses.

Attempted Addition of $CFCl_3$ to CFCl=CFCl Catalyzed by BF_3

Boron Trifluoride was bubbled slowly through a mixture of CFCl=CFCl (28 g., 0.21 mole) and $CFCl_3$ (47 g., 0.34 mole) at -64°. The solution was stirred up to room temperature over 0.5 hour, then stirred for 5 hours. V.p.c. showed no adduct formed. Boron trifluoride fumes were still present at the end of the reaction.

Attempted Addition of $CFCl_3$ to CFCl=CFCl Catalyzed by $BF_3.Et_2O$

$CFCl_3$ (35.5 g., 0.258 mole), CFCl=CFCl (26.01 g., 0.195 mole), and BF_3 etherate (11.2 g., 0.079 mole), 0.038 mole BF_3) were combined in a flask at 0°. The mixture was stirred to room temperature over 3 hours, then left for 3 hours longer. No adduct was detected.

Attempted Addition of $CFCl_3$ to CFCl=CFCl Catlyzed by $HgCl_2$

A Fischer-Porter tube was charged at 0° with $CFCl_3$ (32 g., 0.23 mole) CFCl=CFCl (27 g., 0.20 mole), and $HgCl_2$ (6 g., 0.022 mole). After rocking at room temperature for 18 hours, no adduct was formed.

Addition of $CFCl_3$ to CFCl=CFCl, Catalyzed by $AlCl_3$, in Presence of KF

$CFCl_3$ (36 g., 0.26 mole), CFCl=CFCl (20 g., 0.15 mole), $AlCl_3$ (6 g., 0.045 mole) and freshly ground KF (10 g., 0.17 mole) were placed in a Fischer-Porter tube at 0°. An exothermic reaction occurred immediately. After rocking at room temperature for 6.5 hours, $AlCl_3$ (5 g., 0.037 mole) and KF (5 g., 0.085 mole) were added. Within 10 minutes another exothermic reaction occurred. After two days at room temperature, the mixture was worked up to give a liquid (36 g.) which v.p.c. indicated was 94% unreacted material, 4% CCl_4, and only 2% $C_3Cl_5F_3$.

Addition of $CFCl_3$ to CFCl=CFCl Catalyzed by $AlCl_3$, in Presence of NaF

Reference Reaction

$CFCl_3$ (43 g., 0.313 mole), CFCl=CFCl (27 g., 0.203 mole), and $AlCl_3$ (5 g., 0.037 mole) were combined in a Fischer-Porter tube at 0° and rocked for 3 hours at room temperature. $AlCl_3$ (4 g., 0.03 mole) was added and the mixture was rocked for 3.5 hours. Normal work-up and distillation gave pure $C_3Cl_5F_3$ (41 g. 75%) b.p. 149 - 150° and $n_D^{21.0}$ 1.4394. Also obtained was $C_3Cl_6F_2$ (3.4 g., 5.8%)

First Reaction

The same quantities were used as above, only NaF (8 g., 0.190 mole) was added at the beginning. The procedure was identical to the above. Distillation gave pure $C_3Cl_5F_3$ (36 g., 66%), b.p. 144.0 - 146.5° and $n_D^{20.0}$ 1.4398. Also formed was $C_3Cl_6F_2$ (3.2 g., 5.5%)

Second Reaction

The amounts and procedure were the same as in the previous reaction except the mixture was left at room temperature for 35 hours. Distillation gave pure $C_3Cl_5F_3$ (35.6 g., 65%), b.p. 147 - 150° and $n_D^{20.0}$ 1.4396. Also formed was $C_3Cl_6F_2$ (5.4 g., 9.3%)

Addition of $CFCl_3$ to $CF_2=CCl_2$ Catalyzed by $AlCl_3$

A Fischer-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°.

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 a compound was isolated (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: Reqd. for cyclo-$C_4Cl_4F_2$: 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: Reqd. 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 v.p.c. 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 Fischer-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%).

Attempted Addition of $CFCl_3$ to $CF_3CF=CF_2$ Catalyzed by $AlCl_3$

$CFCl_3$ (50 g., 0.36 mole), $CF_3CF=CF_2$ (52 g., 0.35 mole), and $AlCl_3$ (6 g., 0.045 mole) were placed in a Fischer-Porter tube. This was rocked for 1 day then worked-up to give unreacted material (41 g.) and liquid (22.7 g.) containing about equal amounts of two low-boiling compounds and CCl_4. The infrared spectrum of the mixture had strong bands at 5.80μ and 6.01μ, indicative of $CF_3CF=CFCl$ and $CF_3CF=CCl_2$. No higher boiling components were formed.

Attempted Addition of $CFCl_3$ to $CF_3CF=CFCF_3$ Catalyzed by $AlCl_3$

A flask containing $CFCl_3$ (44 g., 0.32 mole) and $AlCl_3$ (2 g., 0.015 mole) was cooled to 0° and C_4F_8 (25 g., 0.125 mole) was bubbled in during 17 minutes. After stirring at 0° for 2 hours, the mixture was warmed to room temperature, then cooled to 0° and the material from the cold trap was recycled. V.p.c. showed that no reaction had occurred except CCl_4 formation. The contents of the flask were transferred to a Fischer-Porter tube and rocked overnight at room temperature. Venting gave unreacted olefin (30 g.) and $CFCl_3$, and a liquid (19.7 g.), chiefly CCl_4.

The above unreacted starting materials were combined in a tube with $AlCl_3$ (2 g., 0.015 mole) and heated at 77° overnight. After venting, only 5.2 g. liquid was obtained, which by v.p.c. contained 6% unreacted material, 12% low-boiling component, 28% CCl_4, and 46% high-boiling component. Chromatographic purification gave material believed to be $CF_3CF=CClCF_3$, b.p. 32°, with weak infrared bands at 6.04μ and 6.23μ, and $CF_3CCl=CClCFCl_2$, b.p. 140-1° (micro), $n_D^{21.0}$ 1.4304, d_4^{24} 1.692 g./cc., with strong infrared band at 6.12μ.

Addition of $CFCl_3$ to CF_2=CFBr Using $AlCl_3$

$CFCl_3$ (308 g., 2.24 mole) and $AlCl_3$ (10 g.) were combined in a flask at -52°, then CF_2=CFBr (44 g., 0.273 mole) was bubbled through the mixture at -40° to -6° during 0.75 hour. The mixture was cooled to -20°, then stirred for 3 hours whilst attaining room temperature. $AlCl_3$ (6 g.) was added and the mixture was stirred for 1.5 hours, then left in a stoppered flask for 60 hours. The total $AlCl_3$ used was 16 g. (0.12 mole). Work-up gave $C_3BrCl_3F_4$ (61 g., 75%), b.p. 125 - 7°

Attempted Addition of $CFCl_3$ to Cyclo-$C_5Cl_2F_6$ Catalyzed by $AlCl_3$

$CFCl_3$ (42 g., 0.30 mole), olefin (40 g., 0.16 mole), and $AlCl_3$ (6 g., 0.045 mole) were combined in a Fischer-Porter tube at 0° then rocked at room temperature for 17 hours. Work-up gave a material (39 g.) containing by v.p.c. 11% low-boiling material, 24% unreacted olefin, 7% CCl_4, 15% C, and 43% E. No desired adduct was present. Distillation gave pure E, b.p. 70°/2.8 mm.-72°/3.0 mm. (220 - 1°/760 mm.), $n_D^{20.5}$ 1.5175, d_4^{23} 1.778 g./cc., with a strong infrared band at 6.20µ, identifed as cyclo-$C_5Cl_6F_2$. A small amount of higher boiling residue was present which solidifed, m.p. 34 - 6°, and had a strong infrared band at 6.19µ. Recrystallization from absolute ethanol-water gave white crystals, m.p. 36.5 - 37.5°, identifed as cyclo-C_5Cl_8.

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

$CFCl_3$ (60 g., 0.44 mole) and $AlCl_3$ (8 g., 0.06 mole) were placed in a Fischer-Porter tube at 0°. CF_2=CF_2 (40 g., 0.40 mole) was vacuum transferred (at liquid nitrogen temp.) to the tube and the mixture was rocked up to room temperature over 5 hours, then left overnight. Normal work-up gave a liquid (77 g.) which contained 5% low-boiling material, 23% CCl_4, 68% $C_3Cl_3F_5$ and 4% higher boiling material. The yield was 55%. Distillation and v.p.c. gave a pure sample of $C_3Cl_3F_5$, b.p. 72 - 3° (micro), $n_D^{20.0}$ 1.3535, and d_4^{24} 1.648 g./cc.

Addition of $CFCl_3$ to CF_2=CFBr Catalyzed by $AlCl_3$

$CFCl_3$ (130 g., 0.94 mole) and $AlCl_3$ (7 g.) were placed in a flask at -30°. CF_2=CFBr (39 g., 0.24 mole) was bubbled in over 0.5 hour with the temperature between - 22° and -9°. After stirring up to room temperature over 2.5 hours, the mixture was cooled in an ice bath; $AlCl_3$ (5 g.) was added; the mixture was stirred for 0.5 hour, then allowed to warm to ambient during 1.25 hours. Normal work-up gave a product (150 g.) which was distilled to give $C_3BrCl_3F_4$ (54.2 g., 76%), b.p. 127 - 8°, $n_D^{20.0}$ 1.4238, and d_4^{25} 1.9693 g./cc.

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

$CFCl_3$ (41.0 g., 0.30 mole), $CFCl{=}CCl_2$ (30.5 g., 0.20 mole), and $AlCl_3$ (5 g., 0.037 mole) were combined in a Fischer-Porter tube at 0°, then rocked at room temperature for 13.5 hours. Normal work-up gave a liquid (60 g.) which was chiefly unreacted material and CCl_4. This was combined again with $AlCl_3$ (6 g.) and rocked at room temperature for 10 hours, then left overnight. On venting, a considerable amount of gas was noted. Work-up gave a material (49 g.) which v.p.c. showed as 49% CCl_4, 40% $CCl_2{=}CCl_2$, and 11% $C_3Cl_6F_2$. Distillation and recrystallization from petroleum ether gave a pure white solid, $C_3Cl_6F_2$ (9% yield), m.p. 47.5 - 49.5°, b.p. 63°/7.8 mm. (189 - 194°/760 mm.)

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

$AlCl_3$ (7 g., 0.052 mole) was added to $CFCl_3$ (151 g., 1.10 mole) at -72° and $CF_2{=}CHF$ (48 g., 0.585 mole) was bubbled in from cylinder at -76° during 0.75 hour. The mixture was warmed up to -23° over 1.5 hours, then the material which had collected in the cold trap was recycled twice. After being left at room temperature overnight, $AlCl_3$ (4 g., 0.030 mole) was added and the unreacted material re-cycled four times during 4 hours at room temperature. A liquid (38 g.) was recovered from the cold trap. Work-up of the reaction mixture gave a liquid (87 g.) which on distillation gave a material (40.3 g.) consisting of CCl_4 and product. The CCl_4 was removed from the desired product by azeotropic distillation with methanol. Washing with water gave 1-2 ml. containing ca. 90% product and ca. 10% CCl_4.

Further purification was not necessary for NMR analysis.

Attempted Addition of $CFCl_3$ to $CCl_2=CCl_2$ Catalyzed by $AlCl_3$

$CFCl_3$ (134 g., 0.07 mole), $CCl_2=CCl_2$ (109 g., 0.66 mole) and $AlCl_3$ (6 g., 0.045 mole) were stirred at 20 - 30° for 1 hour, then $AlCl_3$ (3 g., 0.022 mole) was added and the mixture heated at 80° for 2 hours. After leaving it at room temperature overnight, the mixture was again heated at 91 - 2° for 1.5 hours. $CFCl_3$ (54 g.) added and stirred for 2 hours more. Normal work-up gave a material (189 g.) containing $CCl_2=CCl_2$ (100 g., 92% recovery). No adduct was formed.

Attempted Addition of $CFCl_3$ to $CHCl=CCl_2$ Catalyzed by $AlCl_3$

$CFCl_3$ (42 g.,0.305 mole), $CHCl=CCl_2$ (37.0 g., 0.281 mole), and $AlCl_3$ (5 g., 0.037 mole) were combined in a Fischer-Porter tube at 0°, then rocked at room temperature for 3.5 hours. $AlCl_3$ (4 g., 0.030 mole) was added and rocked for 6 hours. After leaving it overnight at ambient, the mixture was worked-up to give a material (72 g.) which was distilled to give unreacted olefin, CCl_4, unidentified material (5 g.), and high-boiling residue (19 g.). The unknown material had a b.p. 43 - 4°/30 mm. (133 - 4°/760 mm.) $n_D^{21.0}$ 1.4816, d_4^{24} 1.531 g./cc. and a M. W. of 165. (Analysis Calcd. for $C_2H_2Cl_4$, CH_2ClCCl_3: Cl, 84.49. Found: Cl, 84.60.) This was positively identified by comparison of the infrared spectrum with that in the literature (102). The residue could not be vacuum distilled.

Addition of $CHFCl_2$ to $CF_2=CFCl$ Catalyzed by $AlCl_3$

$CHFCl_2$ (58 g., 0.56 mole) was treated with a small amount of $AlCl_3$ at -78°, then added to $CF_2=CFCl$ (60 g., 0.51 mole). $AlCl_3$ (5 g., 0.037 mole) was added and the mixture stirred up to 0° during 1.25 hours. $AlCl_3$ (2 g., 0.015 mole) was added and the material which had collected in the dry ice/acetone trap was re-cycled three times at 0° during 1.25 hours. The mixture was stirred at room temperature for 4 hours and volatile material (14 g.) was recovered from the cold trap. Work-up of the residue gave a material (69 g.) which on distillation gave pure $C_3HCl_3F_4$ (43 g., 38%), b.p. 91.0°, $n_D^{20.2}$ 1.3735, and d_4^{25} 1.616 g./cc.

The experiment was repeated by charging a Fischer-Porter tube at -78°

with CF_2=CFCl (37 g., 0.32 mole), $CHFCl_2$ (41 g., 0.40 mole), and $AlCl_3$ (6 g., 0.045 mole). Within 4 minutes of the tube's removal from the cold bath, a violent explosion occurred. This was attributed to the exothermic reaction of $CHFCl_2$ with $AlCl_3$ to form $CHCl_3$.

Addition of $CHFCl_2$ to $CF_2=CCl_2$ Catalyzed by $AlCl_3$

A small amount of $AlCl_3$ was added to a trap at -78° containing $CHFCl_2$ (44 g., 0.43 mole) and $CF_2=CCl_2$ (32 g., 0.24 mole). After 7 minutes with occasional shaking, the liquid was decanted into a Fischer-Porter tube at -78° and $AlCl_3$ (5 g., 0.037 mole) was added. The tube was placed in an ice bath and warmed to room temperature over 5 hours. After 29 hours at ambient, the mixture was worked up to give a material (40 g.) containing 29% unreacted material, 45% $CHCl_3$, and 26% desired product. Distillation and v.p.c. purification gave $C_3HCl_4F_3$(18%), b.p. 131 - 3°, $n_D^{20.0}$ 1.4180, and d_4^{23} 1.656 g./cc.

Addition of $CHFCl_2$ to CFCl=CFCl Catalyzed by $AlCl_3$

$CHFCl_2$ (32 g., 0.3[illegible] mole) and CFCl=CFCl (26 g., 0.195 mole) were combined at 0°, treated with $AlCl_3$, then transferred to a Fischer-Porter tube at 0°. $AlCl_3$ (6 g., 0.045 mole) was added and the mixture left at room temperature overnight. Work-up gave a liquid (41.8 g.) which was distilled to give $C_3HCl_4F_3$ (17.2 g., 61%), b.p. 125 - 6°, $n_D^{20.0}$ 1.4184, and $d_4^{23.5}$ 1.683 g./cc.

Addition of $CHFCl_2$ to $CCl_2=CCl_2$ Catalyzed by $AlCl_3$

$CCl_2=CCl_2$ (136 g., 0.82 mole) and $AlCl_3$ (6 g., 0.045 mole) were combined in a flask at 0°. $CHFCl_2$ (99 g., 0.96 mole) was treated with $AlCl_3$ at -78°, then bubbled through the olefin at 0° over 34 minutes. The mixture was stirred to room temperature over 3 hours. $AlCl_3$ (3 g., 0.022 mole) was added and after 1 hour $CHFCl_2$ (63 g., 0.61 mole) and $AlCl_3$ (4 g., 0.03 mole) were added at 0°. After stirring at ambient overnight, the mixture was washed with ice/HCl and water to give a liquid (243 g.) containing two products, the desired adduct C_3HCl_6F (40% yield) and the replacement product C_3HCl_7 (34% yield). Distillation gave pure C_3HCl_6F, b.p. 70°/5 mm. (206°/760 mm.), $n_D^{20.0}$ 1.5041, and d_4^{23} 1.769 g./cc. The tan crystals of C_3HCl_7 were air dried and had m.p. 30 - 1°.

Addition of $CHFCl_2$ to $CF_2=CFBr$ Catalyzed by $AlCl_3$

$CHFCl_2$ (65.0 g., 0.63 mole) and $AlCl_3$ (4 g., 0.03 mole) were combined in a flask at -38°, then $CF_2=CFBr$ (67.0 g., 0.416 mole) was bubbled in at -35° to -32° over 20 minutes. During 1 hour, the mixture warmed to +8° but since material condensed into the dry ice/acetone trap, the flask was cooled to -20°, $AlCl_3$ (4 g., 0.03 mole) added, and the cold trap material re-cycled. After 10 minutes, the mixture was placed in an ice bath then, 20 minutes later, the cold trap material was recycled and the mixture was allowed to warm to room temperature over 2.5 hours. Work-up gave a material (117 g.) which was distilled to give pure $C_3HBrCl_2F_4$ (86.5 g., 79%), b.p. 110 - 2°, $n_D^{20.0}$ 1.4009, and d_4^{25} 1.9088 g./cc.

Addition of $CHFCl_2$ to $CFCl=CCl_2$ Catalyzed by $AlCl_3$

$CHFCl_2$ (36 g., 0.35 mole), $CFCl=CCl_2$ (30 g., 0.20 mole), and $AlCl_3$ (5 g., 0.037 mole) were combined in a Fischer-Porter tube at -78°, then rocked at room temperature for 3.5 hours. After standing overnight, the mixture was hydrolyzed to give a material (54 g.) which was vacuum distilled to give $C_3HCl_5F_2$ (22 g., 44%), b.p. 79°/39 mm. (168 - 170°/760 mm.), $n_D^{21.0}$ 1.4601, and d_4^{25} 1.710 g./cc.

Addition of CF_2Cl_2 To $CF_2=CFCl$ Catalyzed by $AlCl_3$

CF_2Cl_2 (87 g., 0.72 mole), $CF_2=CFCl$ (85 g., 0.73 mole), and $AlCl_3$ (30 g., 0.224 mole) were placed in an autoclave and heated at 60° for 44.5 hours with rocking. Normal work-up gave a liquid (79 g.) which was distilled to give $C_3Cl_4F_4$ (32 g., 17%), b.p. 113-5°. (Analysis Calcd. for $C_3Cl_4F_4$: Cl, 55.86. Found: Cl, 53.61%) No expected $C_3Cl_3F_5$ was formed.

No adducts were formed in the following similar reactions:

$CFCl=CFCl$ + $CBrCl_3$, CF_2Br_2, CCl_4, $C_6H_5CCl_3$, CF_2Cl_2, $CF_2BrCFClBr$ and $CF_2ClCFCl_2$, $CF_2=CFCl$ + CCl_4, and CF_2Br_2 + CF_2CCl_2

C. Radical Initiated Addition to Olefins

1. Preparation of Starting Materials

a. $CF_3CFBrCFBrCF_3$

The above haloalkane was made by passing perfluorobutene-2 into bromine.

b. $CF_3CFBrCClBrCF_3$

This was prepared from $CF_3CFClCCl_2CF_3$ by dechlorination followed by product bromination.

c. $CF_3CFBrCF_2Br$

Light was shone on bromine (60 ml., 180 g., 1.1 mole) in a flask fitted with a dry ice/acetone condenser, and hexafluoropropene was bubbled through. When the bromine color was discharged the product was distilled to yield $CF_3CFBrCF_2Br$ (236 g.)

d. 1,2-Dibromohexafluorocyclobutane

Bromotrifluoroethylene (BTFE) (240 g., 1.5 mole) was heated in an autoclave at 200° for 12 hours. On venting the autoclave, unreacted BTFE (40 g.) was recovered. Distillation of the residue gave 1,2-dibromohexafluorocyclobutane (80 g., 40%) b.p. 95 - 6° and a residual high-boiling material.

e. $CCl_3CF_2CF_2Br$

CCl_3Br (396 g., 2 mole), Bz_2O_2 (3 g.), and $CF_2=CF_2$ (78.5 g., 0.78 mole) were heated in an autoclave at 100° for 8 hours. The autoclave was vented and gaseous material (1 g.), which was mainly $CF_2=CF_2$, was condensed out. A liquid mixture (448.5 g.) which contained 29.6% adduct (44.5% yield based on $CF_2=CF_2$ used) was obtained. On distillation almost pure $CCl_3CF_2CF_2Br$ (135 g.) was obtained from the reaction mixture.

2. Addition of Haloalkanes to Olefins

A stainless steel autoclave (300 ml. capacity) was charged with the haloalkane and a catalytic amount of benzoyl peroxide. The olefin was then transferred into the autoclave which was heated at 100° for a number of hours with constant rocking. (The heating period, and the amounts of haloalkane and olefin used, are given in Table V). The autoclave was cooled and vented. Low-boiling material was condensed. Distillation and/or GLPC of the residue afforded pure products. Physical properties and yields of products are given in Table V.

3. Dehalogenation and Dehydrohalogenation of the Adducts Obtained

Dehydrohalogenation of $CFClBrCFClCH_2CH_2Br$ with Potassium Hydroxide

$CFClBrCFClCH_2CH_2Br$ (10.3 g., 0.32 mole) was dropped slowly into a mixture of potassium hydroxide (5.6 g., 0.1 mole) and ethyl alcohol (4.6 g., 0.1 mole) at reflux temperature. The reaction mixture was refluxed for 30 minutes and poured into water and the organic layer separated, washed and dried. Crude material (6.8 g., 75% yield) was obtained. Gas chromatography showed the presence of one main product in this crude material. It was separated by preparative v.p.c. and identified as $CFClBrCFClCH{=}CH_2$, b.p. 144° (micro), n_D^{21} 1.4571, d_4^{21} 1.7209, (I. R. C=C 6.1μ), (Analysis Calcd. for $C_4BrCl_2F_2H_3$: Br, 33.30. Found: Br, 33.29%). The ^1H and ^{19}F NMR spectra were consistent with the above structure.

Dehalogenation of $CFClBrCFClCH_2CH_2Br$ with Zinc

$CFClBrCFClCH_2CH_2Br$ (16.1 g., 0.05 mole) was dropped slowly into a mixture of zinc (6.5 g., 0.1 g. atom), ethanol (4.6 g., 0.1 mole) and zinc chloride (0.1 g., 0.001 mole) at reflux temperature. The reaction mixture was refluxed for 30 minutes and the low-boiling material (12.9 g.) was distilled directly from the reaction mixture. Gas chromatography showed the presence of one new main product in this material. This was separated by preparative v.p.c. and identified as an isomeric mixture of cis (44%) and trans (56%), $CFCl{=}CF{-}CH_2CH_2Br$, b.p. 138° (micro), n_D^{21} 1.4514, d_4^{21} 1.6808 (I. R. C=C 5.76μ). (Analysis Calcd. for C_4BrClF_2H: Br, 38.94; Cl, 17.27. Found: Br, 38.82; Cl, 17.40). The ^1H and ^{19}F NMR spectra were consistent with the above structure.

Dehydrohalogenation of $CFCl{=}CFCH_2CH_2Br$ with Potassium Hydroxide

$CFCl{=}CFCH_2CH_2Br$ (5. g., 0.025 mole) was dropped slowly into a mixture of potassium hydroxide (5.6 g., 0.1 mole) and ethanol (4.6 g., 0.1 mole).

The low-boiling material (2.4 g., 80% yield) distilled directly from the reaction mixture as it was formed. Gas chromatography showed the presence of one new main product in this material. This was separated by prep. v.p.c. and identified as an isomeric mixture of cis (44%) and trans (56%) $CFCl{=}CF{-}CH{=}CH_2$, which polymerizes on standing at room temperature. (*Analysis* Calcd. for $(C_4ClF_2H_2)_n$: Cl, 27.68. Found: Cl, 28.29%) The ^1H and ^{19}F NMR spectra were consistent with the above structure.

Dehydrohalogenation of $CF_2Br(CF_3)CFCH_2CH_2Br$

$CF_2Br(CF_3)CFCH_2CH_2Br$ (20.2 g.), potassium hydroxide (7 g.), and ethanol (5 ml.) were refluxed for 1 hour. The reaction mixture was poured into water and the organic layer was separated and dried. Distillation yielded suspected $CF_2Br(CF_3)CFCH=CH_2$, b.p. 79°, n_D^{22} 1.3469, d^{21} 1.663. (*Analysis* Calcd. for $C_5H_3BrF_6$: MR_D 32.67; Br, 31.17. Found: MR_D 32.99 Br, 31.58%).

Dehydrohalogenation of $CF_2BrCF_2CH_2CH_2Br$

$CF_2BrCF_2CH_2CH_2Br$ (21 g.), potassium hydroxide (8 g.), and ethanol (20 ml.) were heated in a flask fitted with a fractionation column. $CF_2BrCF_2CH=CH_2$ (15.2 g.) fractionated off during the reaction. It showed the following properties: b.p. 54.5°, n_D^{21} 1.3556, d^{21} 1.604. (*Analysis* Calcd. for $C_4H_3BrF_4$: MR_D 27.98; Br, 38.65, Found: MR_D 28.14; Br, 38.44%).

Dehydrohalogenation of $CF_2BrCF_2(CH_2)_3CH_2Br$ with Potassium Hydroxide

$CF_2BrCF_2(CH_2)_3CH_2Br$ (9.6 g., 0.03 mole) was dropped slowly to a mixture of KOH (5.6 g., 0.1 mole), ethanol (9.2 g., 0.2 mole) and water (9 g., 0.5 mole) at reflux temperature. The reaction mixture was kept at reflux temperature for another 30 minutes and it was poured into water. The organic layer was separated, washed and dried. Gas chromatography showed the presence of two main products in this material. Their amounts were estimated by v.p.c. analysis. They were separated by preparative v.p.c. and identified as $CF_2BrCF_2(CH_2)_2CH=CH_2$ (1.0 g., 14% yield), b.p. 119.5° (micro), n_D^{21} 1.3851, (I. R. C=C 6.07μ), (*Analysis* Calcd. for $C_6BrF_4H_7$: Br, 34.02. Found: Br, 33.22%) and $CF_2BrCF_2(CH_2)_3CH_2OCH_2CH_3$ (5.7 g., 67% yield), b.p. 185.7° (micro), n_D^{21} 1.3964, d_4^{21} 1.3670, (*Analysis* Calcd. for $C_8BrF_4H_{13}O$: Br, 28.48. Found: Br, 28.34%).

Treatment of $CF_2BrCFClCH_2CH=CFCF_2Br$ with Zinc

To a solution of olefin (14.9 g., 0.039 mole) in isopropanol (30 ml.) was added zinc dust (7 g., 0.107 mole). The solution was stirred with heating until a vigorous reaction occurred and then cooled in a water bath.

After 15 minutes of a self-sustained reaction, the mixture was heated to reflux for 20 minutes. The organic layer was washed with a large amount of water and dried with magnesium sulfate and calcium chloride. V.p.c. showed poor resolution and the probable presence of isopropanol. Further washing with water did not markedly improve the separation. The material was quite viscous.

This mixture was added to aqueous potassium hydroxide (7.4 g., 0.13 mole; 20 cc water) and then refluxed for 30 minutes. The mixture turned dark brown and washing with water gave no organic liquid, only a dark brown solid.

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 v.p.c., three of which were isolated in a pure state and identified (see properties in Table XIV). The fourth product contained trace impurities, but the infrared spectrum showed absorption at 5.02μ which is associated with the allene structure.

4. Some Free Radical Additions of Haloalkenes 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 material were distilled off and the residue was washed with sodium bicarbonate solution, water and dried.

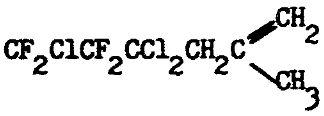
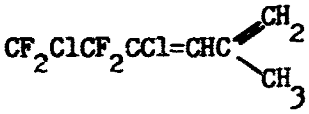
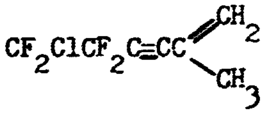
Fractional distillation gave Br  $-CH_2CFClCF_2Br$ (XI), 69.7 g. (62.1%). An analytical sample which was separated by v.p.c. had the following properties: b.p. 88/0.15 mm., n_D^{20} 1.4940, d^{20} 1.878 (Analysis Calcd. for $C_8H_{10}Br_2ClF_3O$: MR_D 58.24; C, 26.02; H, 2.74; F, 15.76%).

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 at 100 ± 5° for 5 hours. The reaction mixture was worked up as described above to

TABLE XIV

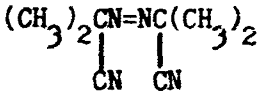
PROPERTIES OF PRODUCTS OBTAINED ON TREATMENT OF $CF_2ClCF_2CCl_2CH_2C(CH_3)_2Cl$ WITH ETHANOLIC POTASSIUM HYDROXIDE

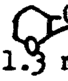
Molecular Formula	Possible Structure	Analysis		Infrared Absorption (μ)	
		Calcd. Cl	Found Cl		
$C_7H_7Cl_3F_4$	$CF_2ClCF_2CCl_2CH{=}C(CH_3)_2$  $CF_2ClCF_2CCl_2CH_2C\genfrac{}{}{0pt}{}{=CH_2}{-CH_3}$	38.95	38.55	6.1	
$C_7H_6Cl_2F_4$	 $CF_2ClCF_2CCl{=}CHC\genfrac{}{}{0pt}{}{=CH_2}{-CH_3}$	30.05	29.96	6.12	6.26
$C_7H_5ClF_4$	 $CF_2ClCF_2C{\equiv}CC\genfrac{}{}{0pt}{}{=CH_2}{-CH_3}$	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.

yield Br CH_2CF_2Br (XII) 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, 3.24%).

Addition of $CF_2BrCHFBr$ to Diallyl Ether

A solution of $CF_2BrCHFBr$ (362 g., 1.5 mole), diallyl ether (40 g., 0.4 mole) and  $(CH_3)_2\underset{CN}{C}N{=}N\underset{CN}{C}(CH_3)_2$ (7 g.) was refluxed for 48 hours. The reaction mixture was worked up as described above to yield:

Br CH_2CFHCF_2Br 12.8 g. (9.4%); b.p. 90/1.3 mm., n_D^{20} 1.4443, b.p. 90/1.3 mm., n_D^{20} 1.443. (Analysis Calcd. for $C_8H_{11}Br_2F_3O$: C, 28.24; H, 3.24. Found: C, 28.27; H, 2.68%).

Dehalogenation of Br--$CH_2CFClCF_2Br$ (XI)

A stirred suspension of powdered zinc (13.1 g., 0.44 mole), zinc chloride (0.5 g.) and ethanol (100 ml.) was refluxed while (XI) (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 Br-$CH_2CF{=}CF$ (7.3 g., 28.2%). An analytical sample was separated by v.p.c. 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 XI with $LiAlH_4$

Lithium aluminum hydride (9.4 g., 0.24 mole) was placed in a cooled flask and tetrahydrofuran (100 ml.) was added with stirring. The suspension was heated to reflux and XI (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 -$CH_2CF{=}CF_2$ (L) 13.0 g. (13.1%) and Br  $CH_2CF{=}CF_2$ 16.1 g. (25.9%) which was consistent with the previously prepared sample.

An analytical sample of (L) which was separated by v.p.c., had the following properties: b.p. 76°/32 mm., n_D^{21} 1.4107; d^{20} 1.137. (<u>Analysis</u> Calcd. for $C_8H_{11}F_3O$: MR_D 38.43; C, 53.33; H, 6.15. Found: MR_D 38.64; C, 53.14; H, 6.27%).

<u>Addition of Chlorine to Diallyl Ether</u>

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 $CH_2ClCHClCH_2OCH_2CH{=}CH_2$ (LI) (44.7 g., 27.4%) and $(CH_2ClCHClCH_2)_2O$ (LII) (78.0 g., 32.5%, which had properties consistent with an authentic sample.

An analytical sample of (LI) 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.

<u>Addition of $CF_2BrCFClBr$ to (LI)</u>

A solution of $CF_2BrCFClBr$ (110 g., 0.4 mole), the ether (LI) (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 $CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (LIII) (12.0 g., 29.0%). An analytical sample separated by v.p.c. had the following properties: b.p. 105°/0.2 mm., n_D^{30} 1.4911, d^{20} 1.808. (<u>Analysis</u> 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%.

<u>Dehalogenation of $CF_2BrCFClCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (LIII)</u>

The ether (LIII) (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 $CH_2ClCHClCH_2OH$ (8.5 g.) and $CF{=}CFCH_2CHBrCH_2OCH_2CHClCH_2Cl$ (LIV) (9.3 g., 23.5%) b.p. 76°/0.3 mm., n_D^{20} 1.4661, d^{20} 1.584. (<u>Analysis</u> 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%).

D. Monomers Synthesis for Contract Associates

1. Preparation of Octafluoroacetophenone

a. Pentafluorophenylmagnesium bromide, prepared from bromopentafluorobenzene (26.8 g.), was reacted with lithium trifluoroacetate (13.1 g.) under the conditions described in the literature (31) to give octafluoroacetophenone (9.2 g.).

b. Pentafluorophenylmagnesium bromide, prepared from bromopentafluorobenzene (2.46 g.), was added to a stirred solution of trifluoroacetic anhydride (2.2 g.) in ether (20 cc.) at -78°. The mixture was allowed to warm to room temperature, and hydrolyzed with ammonium chloride solution. Inspection of the ethereal layer by gas chromatography indicated that no octafluoroacetophenone had been formed.

c. Trifluoroacetyl chloride (1.4 g.) and aluminum chloride (1.5 g.) were added to a stirred solution of pentafluorobenzene (1.2 g.) in tetrachloroethane (15 cc.) at -40°. The mixture was allowed to warm up and was stirred at room temperature for 7 hours under a Dry Ice condenser. Analytical gas chromatography indicated that no octafluoroacetophenone had been formed.

2. Preparation of Octafluorostyrene

Chlorodifluoroacetaldehyde. Lithium hydride (8.0 g.) was added slowly to a well-stirred, cooled (0°) solution of chlorodifluoroacetic acid (130.5 g.) in ether (400 cc.). Simultaneously, a solution of lithium aluminum hydride (9.5 g.) in ether (250 cc.) was prepared by refluxing the hydride in the ether for 4 hours. The solution of lithium aluminum hydride was added dropwise to the stirred, cooled solution of lithium chlorodifluoroacetate. After all the lithium aluminum hydride had been added, the solution was hydrolyzed carefully with water (200 cc.) and then dilute hydrochloric acid. The ether layer was separated, dried over $MgSO_4$ to remove excess water and fractionally distilled through a glass packed column. Ether was removed first at 34.5°, then the temperature rose to about 80°, and then it dropped to about 20°. The most plausible explanation is that the hydrate of the aldehyde was disproportionating under strong heating to give the aldehyde (b.p. 18°) and a higher hydrate. The low-boiling fraction 20 - 30° was collected, some more ether added, and fractionally redistilled to give aldehyde (28 g.) b.p. 18° and a mixture of ether and aldehyde (approx. 4 g. of the latter) b.p. 18 - 33°. An attempt was made to dehydrate the hydrate of the aldehyde by adding it to a stirred solution of phosphorus pentoxide in concentrated sulphuric acid. Considerable polymer was formed and only a little aldehyde distilled off. (By using reduced pressure it may be possible to remove the aldehyde to a cold trap before the polymerization, which appears to accelerate in the presence of acid, takes place to any large extent.)

<u>2-Chloro-2,2-difluoro-1-pentafluorophenylethanol</u> Chlorodifluoroacetaldehyde (30 g.) was bubbled into a stirred solution of pentafluorophenylmagnesium bromide (from pentafluorobromobenzene (60 g.). After all the aldehyde had been added, the solution was hydrolyzed with dilute hydrochloric acid, the ether layer was separated and dried ($MgSO_4$). The excess ether was removed to give dark solid material (54 g.). (A previous small-scale reaction had shown that this was 60 - 70% by weight alcohol, the residue being involatile material; purification if necessary is extremely facile as the alcohol readily sublimes.) An analytical gas chromatogram indicated only one product.

<u>2-Chloro-1,2,2-trifluoroethylpentafluorobenzene</u> The crude alcohol was placed in an autoclave (300 ml.) with excess sulfurtetrafluoride. The autoclave was rocked at 80° for 6 hours and allowed to cool in an ice bath. Excess SF_4 was bled off slowly over a period of 2 - 3 hours. The contents of the pot were thrown into water (200 cc.). (Some solid polymeric material is evident at this stage if the crude alcohol is used; however, in a small-scale reaction with the pure alcohol, the product is a clear liquid.) Enough ether was added to form an organic layer lighter than water; in this way the insoluble polymeric material separated to the bottom, while all the desired product was obtained in the ether layer which was separated, dried ($MgSO_4$) and fractionally distilled to remove

the ether. The residual product was vacuum distilled for P_2O_5 to give 2-chloro-1,2,2-trifluoroethylpentafluorobenzene (38 g.). This product was chromatographically pure.

Octafluorostyrene 2-Chloro-1,2,2-trifluoroethylpentafluorobenzene (17 g.) was added at a fast drop rate to a vigorously stirred solution of fused potassium hydroxide (200 g.) at 170° in a three-necked copper flask. A stream of nitrogen was flowing through to assist immediate removal of the product which was trapped in two traps in series, which were cooled in a CO_2/acetone bath. The product (12.0 g.) was inspected by analytical gas chromatography (Si gum) and shown to consist of one major product, a little starting material and a small quantity of two products having a similar retention time to that of the starting material. The mixture was separated by preparative gas chromatography (Si gum packing) to give:

(i)	Octafluorostyrene	9.4 g.	(64% conversion)
(ii)	residue	2.0 g.	

Similar attempts to dehydrochlorinate the substituted ethyl benzene at higher temperatures gave the following results:

Temp.	Weight of Starting Material (g.)	Weight of Product (g.)	Weight of styrene separated
195°	9	4	2.6
220°	12	3	1.7

The conversion was 33 and 16% respectively.

The structure of the styrene was confirmed by reference to published physical data (103). There was considerable discrepancy in the refractive index (our sample n_D^{19} 1.3995, literature quoted 1.3550). This is without doubt due to a mistake in the literature as all other data were consistent.

i.r. absorption at 1793 cm^{-1} indicated $-CF=CF_2$

u.v. absorption at 235 mμ; w, 6200

shoulder 265 mµ; w, 1120

Mass spectrum peaks at 248 molecule ion C_8F_8
198 C_7F_6
179 C_7F_5

b.p. 121° by Swoboloff method.

Reaction of Butyllithium with Tetrafluoroethylene

Dry diethyl ether (150 ml.) was placed in a three-necked flask, fitted with a gas-lead, reflux condenser and dropping funnel, and cooled to -100° under an atmosphere of dry nitrogen.

Tetrafluoroethylene (12 g., 0.12 mole) was bubbled in at such a rate that all the olefin condensed and dissolved. Butyllithium (0.1 mole) in ether (50 ml.), precooled to -78°, was added dropwise with stirring and the reaction temperature allowed to rise slowly to that of the room, while maintaining the reflux condenser temperature below -80°. The reaction mixture became gelatinous with the precipitation of lithium fluoride. Hydrochloric acid (20%) was added until the mixture became clear, and the ethereal layer separated. The aqueous layer was extracted with ether and the total ether solutions combined and dried ($CaCl_2$).

Analytical v.p.c. showed the presence of a major product together with a small amount ($<$ 8%) of high-boiling material.

Fractional distillation gave 1,1,2-trifluorohexane, b.p. 70 - 71° (lit. (34) b.p. 70°), (8.8 g. 64% yield).

E. Aromatic Substitutions

1. Chloro-1,2-dibromo-1,2,2-trifluoroethane as a Source of Radicals

Ultraviolet Irradiation of Benzene with $CF_2BrCFClBr$

Benzene (56.2 g., 0.72 mole) and $CF_2BrCFClBr$ (200 g., 0.716 mole) were irradiated in quartz apparatus with a mercury vapour lamp for 50 hours at ca. 75°. The product was washed out with benzene and washed with aqueous sodium bisulfite and water to remove bromine. The organic product, which showed no high-boiling material on v.p.c. examination, was fractionated to remove most of the starting materials. The residue (18.3 g.) was further distilled to remove more $CF_2BrCFClBr$ (8.2 g.) and the residue was vacuum distilled to give a volatile material (5.7 g.) and a residual black tar (3.9 g.).

The high-boiling material (5.7 g.) was separated by v.p.c. (Si gum at 115°) to yield (i) $CF_2BrCFClBr$ (0.71 g.), (ii) bromobenzene (0.31 g.), both identified by infrared spectroscopy, (iii) high-boiling products (1.44 g.). Further separation of (iii) yielded: (a) suspected $C_6H_5CFClCF_2Br$ (0.5 g., 0.25% yield). The ^{19}F NMR spectrum, which showed a doublet and triplet, the ^{1}H NMR spectrum and the infrared spectrum were consistent with the proposed structure. The NMR spectra showed <u>ca</u>. 5% impurity present; (b) three components (0.27 g.) corresponding to (a) and two longer retained components.

Similar u.v. irradiations were carried out using benzoic acid, bromobenzene, pyridine and pentafluorobenzene as the aromatic substrates but no desired substituted products were obtained on distillation.

<u>Pyrolysis of $CF_2BrCFClBr$</u>

The furnace consisted of an empty steel tube (1 in. i.d.) of which a length of 12 in. was heated in the furnace. The furnace temperature was recorded by a thermocouple.

The general procedure for all experiments was to flush the apparatus with nitrogen. The material to be pyrolyzed was added dropwise over a slow stream of nitrogen (<u>ca</u>. 1 bubble/sec.). The apparatus was flushed with nitrogen for a further 0.5 hour to remove organic products. The organic products were collected in a trap which was usually cooled in dry ice/acetone.

$CF_2BrCFClBr$ (2.32 g.) was dropped into the pyrolysis tube at 400° over a period of 20 minutes to yield a product (1.44 g., 60% recovery by weight) which by v.p.c. showed seven peaks in the following percentages: (1) 4%; (2) 17%; (3) 3%; (4) 10%; (5) 31%; (6) 27% ($CF_2BrCFClBr$); and (7) 8% (suspected $CF_2BrCFBr_2$.)

From a similar experiment at a furnace temperature of 550° no liquid material was recovered, and at 470° only 7.5% by weight was recovered which contained a trace of longer retained material. At 330° the product

(83% recovery) was ca. 90% $CF_2BrCFClBr$. The pyrolysis products caused considerable etching of the glass trap, thus HF was evolved in addition to the more expected HBr and HCl.

Pyrolysis of Benzene with $CF_2BrCFClBr$

Using the same procedure and apparatus as in the previous experiment, an intimate mixture of benzene (2.06 g.) and $CF_2BrCFClBr$ (2.05 g.) was added dropwise into the pyrolysis tube at 400° to yield a product (2.86 g., 70% recovery) which was mainly benzene, but contained a longer retained product whose v.p.c. retention corresponded to bromobenzene.

Pyrolysis at 500° gave a reduced recovery of 59% with the longest retained product corresponding to bromobenzene and the major component corresponding to benzene. Pyrolysis at 330° produced very little reaction and at 590° the recovery dropped to 42% of which ca. 95% was benzene.

Passage of mixtures of $CF_2BrCFClBr$ and (1) bromobenzene, (2) pentafluorobenzene and (3) a mixture of $CF_3CH{=}CHBr$ and $CF_3CBr{=}CH_2$, under the same conditions as above gave none of the desired products.

Pyrolysis of $CF_2BrCFClBr$ in the Presence of Bromine

Passage of a mixture of $CF_2BrCFClBr$ (2.00 g.) and bromine (1.04 g.) through the pyrolysis tube at 400° over a period of 30 minutes gave a product (1.8 g., 59%) which by v.p.c. showed nine peaks in the following percentages: (1), (2) and (3) 1.5%; (4) 7%; (5) 23%; (6) 35% ($CF_2BrCFClBr$); (7) 25.5% (suspected $CF_2BrCFBr_2$); (8) 3%; and (9) 3%. The peak numbering corresponds to that in the pyrolysis of $CF_2BrCFClBr$ alone. (8) and (9) were not detected in the pyrolysis of $CF_2BrCFClBr$ alone.

A repeat experiment produced only 14% of the suspected $CF_2BrCFBr_2$.

Pyrolysis of $CF_2{=}CFCl$ with Bromine

Bromine (2.23 g.) was dropped into a tube heated at 53°. A stream of nitrogen and $CF_2{=}CFCl$ was passed through the heated tube to carry the mixture with bromine into the furnace at 400°. It was noted that bromine reacted with the olefin before entering the pyrolysis tube, thus the products were similar to those of the pyrolysis of $CF_2BrCFClBr$ and there was no increase in yield of suspected $CF_2BrCFBr_2$.

Similar results were obtained when the bromine was added dropwise at a point adjacent to the furnace.

2. <u>1,2-Dichloro-1,2,2-trifluoroiodoethane as a Source of Radicals</u>

<u>Reaction of Benzene with $CF_2ClCFClI$</u>

(a) $CF_2ClCFClI$ was washed with aqueous sodium bisulfite, and water and dried (Drierite) and distilled.

Dry benzene (1.6 g.) and $CF_2ClCFClI$ (2.8 g.) were sealed in a Fischer-Porter tube and heated at 200° for 72 hours. Some hydrogen halide, which was detected as chloride, was evolved on opening the tube. The tube contained black solid (carbon and iodine) and a liquid which on examination by v.p.c. showed two products, one of shorter retention time and the other of longer retention time than both the starting materials. The product was washed out with ether and the ethereal solution was washed with aqueous sodium bisulfite and water to remove iodine, and dried (Drierite). The ethereal solution was evaporated to near-dryness on a rotary vacuum pump to leave a residue (0.68 g.) of almost pure long retained product, which was purified by v.p.c. (Si gum, 122°) to yield $C_6H_5CFClCF_2Cl$ (0.11 g., 4.8% based on $CF_2ClCFClI$) with a consistent infrared spectrum. The ultraviolet spectrum was measured in ethanolic solution to show $\lambda_{max.}$ 214μ ($\varepsilon_{max.}$ 6860), $\lambda_{max.}$ 256 mμ ($\varepsilon_{max.}$ 559), $\lambda_{max.}$ 262 mμ ($\varepsilon_{max.}$ 686), $\lambda_{max.}$ 268 mμ ($\varepsilon_{max.}$ 580), consistent with a monosubstituted benzene.

(b) Benzene (2.34 g.) and $CF_2ClCFClI$ (4.67 g.) were sealed in a Carius tube at 0° and heated at 165° for 96 hours.

The liquid product which contained carbon particles was washed with aqueous sodium bisulfite to remove iodine and washed with water. The product and benzene washings were dried (Drierite) and separated by v.p.c. (Si gum, 115°) to yield: (1) $CF_2ClCFClH$ (0.16 g., 6.25%) based on $CF_2ClCFClI$, (2) benzene and $CF_2ClCFClI$, (3) $C_6H_5CFClCF_2Cl$ (0.90 g., 23.5%). The proton NMR showed a phenyl group, and ^{19}F NMR showed a triplet and two close doublets of equal intensity. A precise explanation for the splitting of the doublet cannot be made. There was a minor peak of longer retention time which was not isolated.

(c) Benzene (5 g.) and $CF_2ClCFClI$ (5 g.) were refluxed under nitrogen for 140 hours. V.p.c. examination of the product showed only a trace of a product corresponding to $C_6H_5CFClCF_2Cl$.

A similar experiment using bromobenzene with a reaction time of 90 hours at 180 - 190° gave a product which was suspected to be $BrC_6H_4CFClCF_2Cl$ but it was impossible to obtain a pure sample by GLPC or distillation. Repetition of this experiment in the presence of copper dust was equally unsatisfactory.

Reactions of pentafluorobenzene, phenol and nitrobenzene with $CF_2ClCFClI$ under the same conditions as above for times varying between 22 and 96 hours gave mostly recovered starting materials.

Reaction of benzene (0.01 mole), $CF_2BrCFClBr$ (0.01 mole) and benzoyl peroxide (0.001 mole) in a Fischer-Porter tube at 155° for 96 hours afforded bromobenzene (9%) and $C_6H_5CFClCF_2Br$ (5%). A similar reaction in the absence of peroxide gave none of these products.

The Effect of Benzoyl Peroxide on the Reaction of Benzene with $CF_2ClCFClI$

A Fischer-Porter tube was charged with benzene (2.34 g., 0.03 mole), $CF_2ClCFClI$ (4.19 g., 0.015 mole) and benzoyl peroxide (0.38 g., 0.0015 mole). A similar tube was charged only with benzene (2.34 g.) and $CF_2ClCFClI$ (4.19 g.). The tubes were sealed and heated together on an oil bath at 170° for 89 hours.

A gas chromatogram of the products showed that long retained material (pure $C_6H_5CFClCF_2Cl$) formed 2% of the volatile products when benzoyl peroxide was absent (98% unchanged starting materials). In the presence of benzoyl peroxide, long retained material (one peak on Si gum at 180°) formed 18% of the volatile products (82% unchanged starting material). Re-examination of the gas chromatogram on Silicon gum at 100° and 130° showed that the long retained material was 18% iodobenzene and 82% $C_6H_5CFClCF_2Cl$: overall yield of $C_6H_5CFClCF_2Cl$ in benzoyl peroxide initiated reaction was 14.8%.

Comparison of the Reaction of Iodobenzene and Benzene with $CF_2ClCFClI$

Iodobenzene (2.04 g., 0.01 mole) and $CF_2ClCFClI$ (2.79 g., 0.1 mole) were sealed in a Fischer-Porter tube. In an similar tube benzene (0.8 g., 0.01 mole) and $CF_2ClCFClI$ (2.79 g., 0.01 mole) were sealed. The tubes were heated together on an oil bath at 140 - 4° for 88 hours.

There was insufficient reaction to measure gas chromatographic peak areas to obtain a comparison.

Reaction of Benzene and $CF_2ClCFClI$ in the Presence of Mercury or Copper

A Fischer-Porter tube was charged with benzene (0.78 g., 0.01 mole), $CF_2ClCFClI$ (2.79 g., 0.1 mole) and clean dry mercury (7.5 g., 0.0375 mole). A similar tube was charged with benzene (0.78 g., 0.01 mole), $CF_2ClCFClI$ (2.79 g., 0.01 mole) and electrolytic copper dust (1.92 g., 0.0303 mole). Another tube was charged with benzene (0.78 g., 0.01 mole) and $CF_2ClCFClI$ (2.79 g., 0.01 mole) only. The tubes were sealed and heated together, with occasional shaking, on an oil bath at 170° for 88 hours.

The organic liquid of the first (Hg) and last tubes (blank) was examined by gas chromatography. In the second tube (Cu) the organic liquid and copper powder formed a solid mass and, therefore, a direct gas chromatographic examination could not be made with the two other reactions. The reaction in the presence of mercury showed a 9.3% conversion to $C_6H_5CFClCF_2Cl$ (free from C_6H_5I) whereas in the blank experiment the conversion was 2.3%.

The Reaction of Pentafluorobenzene with $CF_2ClCFClI$ in the Presence of Benzoyl Peroxide

Pentafluorobenzene (2.79 g., 0.0166 mole), $CF_2ClCFClI$ (4.19 g., 0.015 mole) and benzoyl peroxide (0.36 g., 0.0015 mole) were sealed in a Fischer-Porter tube and heated on an oil bath at 171 - 8° for 84 hours. A long retained peak formed 6% of the volatile products (by gas chromatography).

Reaction of Pentafluorobenzene with $CF_2ClCFClI$ and $CF_2BrCFClBr$ in the Presence of Benzoyl Peroxide (A Comparison Experiment)

Pentafluorobenzene (1.70 g., 0.01 mole), $CF_2ClCFClI$ (2.79 g., 0.01 mole) and benzoyl peroxide (1.03 g., 0.00425 mole) were sealed in a Fischer-Porter tube (tube 1). Pentafluorobenzene (1.74 g.), $CF_2ClCFClI$ (2.79 g.) and benzoyl peroxide (0.5 g., 0.002 mole) were sealed in a Fischer-Porter tube (tube 2). Pentafluorobenzene (1.71 g.), $CF_2BrCFClBr$ (2.77 g., 0.01 mole) and benzoyl peroxide (0.5 g., 0.002 mole) were sealed in a similar tube (tube 3). The three tubes were heated together on an oil bath at 168 - 172° for 114 hours.

The products were examined by gas chromatography to show the following percentages of long retained products: Tube 1, 26.8%; Tube 2,8.4%; Tube 3 22.8%. The remaining 73.2% and 81.6% in tubes 1 and 2 were starting materials and very minor short retained products. In tube 3, in addition to starting materials, there was also 2.6% of a long retained product.

The product in tube 1 was separated by preparative gas chromatography (Si gum, 110°) to yield the long retained product (0.29 g.) which was shown by infrared spectroscopy to be iodobenzene containing a minor impurity. The major long retained product in tube 3 corresponded by v.p.c. to bromobenzene.

3. Other Aromatic Substitutions

Pentafluorobenzoic Acid and Ammonia

Pentafluorobenzoic acid (44.8 g., 95% yield) was conveniently made by treating pentafluorobenzene with butyllithium and then bubbling carbon dioxide through the solution.

Ethanol (20 ml.), ammonia (10 ml. of sp. gravity 0.9 gm/cc. 0.25 mole) and pentafluorobenzoic acid (5.3 g., 0.025 mole) were placed in a Carius tube which was sealed under a vacuum and shaken at 70° for 16 hours. The resulting liquid was neutralized and ether extracted. The ether layer was dried, and the ether distilled off to give a brown gum (0.5 g.)

1,4-Dibromotetrafluorobenzene and Silver Isocyanate

1. Silver isocyanate (3.0 g., 0.02 mole) and 1,4-dibromotetrafluorobenzene (3.08 g., 0.01 mole) were placed in a Carius tube with ether (25 ml.) and shaken at 75° for 16 hours. The ethereal solution was decanted from the isocyanate and distilled to give 2.65 g. of the recovered dibromobenzene (m.p. 75°).

2. A similar reaction with dimethylformamide at 100° gave no reaction.

3. A similar reaction with no solvent and four times excess isocyanate at 100° gave no reaction.

F. Attempted Preparation of Partially Fluorinated Norbornadienes

Diels-Alder Addition of Cyclopentadiene and CFCl=CFCl

Cyclopentadiene was prepared immediately before use by fractionation of dicyclopentadiene and collection of the fraction, b.p. 40.5°.

Cyclopentadiene (1.98 g., 0.03 mole), sym-dichlorodifluoroethylene (3.63 g., 0.03 mole) and hydroquinone (0.1 g.) were sealed in a Fischer-Porter tube and heated on an oil bath at 207 - 210° for 18 hours.

The product was shaken with ether to leave a light brown sol i (2.85 g.) which was removed by filtration. The ethereal solution was dried (Drierite) and evaporated under reduced pressure to leave a brown gum. The gum did not separate on the alumina column and was not affected by decolorizing charcoal.

Two experiments heating the same quantities as above for 69 hours at 140 - 148° and for 30 hours at 170 - 180° were carried out. As the products could not be isolated pure, the products of these two experiments were combined and dechlorination was attempted.

(a) Iodine (0.4 g.) was added to magnesium (1.8 g.) in ether (50 ml.). The mixture was heated to reflux and the products of the above experiments were added dropwise. The mixture was refluxed for a further 12 hours. The ethereal solution was filtered to remove a black residue and magnesium. The magnesium was washed and dried to yield 1.8 g. (100% recovery). The ethereal solution was fractionated and the residue on v.p.c. examination showed components corresponding to ether and dicyclopentadiene and a shoulder on the dicyclopentadiene peak from an unknown compound.

(b) The ethereal residue from (a) was refluxed with zinc dust (6.5 g.) suspended in ethanol (100 ml.) for 9 hours. The mixture was filtered to remove zinc and fractionated to yield v.p.c. pure ethanol and a residue which by v.p.c. showed no appreciable change from starting material.

Diels-Alder Addition of Cyclopentadiene and Perfluoropropene

A Fischer-Porter tube was charged with freshly distilled cyclopentadiene (2.06 g., 0.031 mole) and hydroquinone (0.1 g.). Perfluoropropene (5.2 g., 0.035 mole) was condensed into the tube under vacuum and the tube was heated at 170° for 117 hours. Unchanged perfluoropropene (1.5 g., 29%) was recovered and the residual liquid examined by gas chromatograpy to show ca. 91% Diels-Alder adduct, the other components being perfluoropropene and dicyclopentadiene (trace). The liquid was separated by gas chromatography (Si gum, 100°) to give 5-trifluoromethyl-5,6-difluoronorborn-2-ene (1.0 g., 19%, based on unrecovered olefin) b.p. 140°; n_D^{20} 1.3774 (lit. b.p. 141°; n_D^{20} 1.3741), which was oxidized by an acetone solution of potassium permanganate and decolorized 3% bromine in carbon tetrachloride. The low recovery of Diels-Alder adduct may be due to poor gas chromatographic recovery but probably is due to the presence of a high percentage of involatile material in the product, such as the products of further Diels-Alder additions.

The proton NMR spectrum of the simple adduct was typical of a 1,4-adduct.

Diels-Alder Addition of Cyclopentadiene and Perfluorobutene-2

A Fischer-Porter tube was charged with freshly distilled cyclopentadiene (2.0 g., 0.0303 mole) and hydroquinone (0.1 g.). Perfluorobutene-2 (6.3 g., 0.0315 mole) was condensed into the tube under vacuum and the mixture was heated on an oil bath at 146 - 156° for 69 hours. The Fischer-Porter tube leaked during the reaction and 1.0 g. of material was lost. Unchanged perfluorobutene-2 (0.05 g.) was recovered on opening the tube. The residual crude product (6.0 g.), which contained perfluorobutene-2 and traces of cyclopentadiene in addition to a main product of the suspected Diels-Alder adduct, was separated by gas chromatography (Si gum, 100°) to yield 5,6-bis(trifluoromethyl)-5,6-difluoro-norborn-2-ene (4.0 g., 50% based on cyclopentadiene), $n_D^{22.5}$ 1.3655. (Analysis Calcd. for $C_9H_6F_8$: C, 40.62; H, 2.27; F, 57.11. Found: C, 40.46; H, 2.26; F (by difference), 57.28%). The norbornene was oxidized by an acetone solution of potassium permanganate and decolorized a 3% bromine solution in carbon tetrachloride. It gave consistent infrared and ^{19}F NMR spectra. The proton NMR spectrum proved the adduct to be a Diels-Alder adduct rather than a 1,2-adduct.

Attempted Dehalogenation of 5,6-Difluoro-5,6-bis(trifluoromethyl) norbornene

The norborn-2-ene (30.0 g.) was added dropwise over a period of 15 minutes to a stirred suspension of zinc (12 g.) and zinc chloride (0.1 g.) in isopropanol (40 ml.). The refluxing was continued for a further 4 hours. No reaction was indicated by gas chromatography. A further 10 g. of zinc was added and the stirred mixture refluxed for 1.75 hours. There was no apparent reaction. The zinc was filtered off and the filtrate fractionated to remove most of the isopropanol. The residue was separated by gas chromatography (Si gum, 100°) to yield the norbornene (21.9 g., 73% recovery), as indicated by infrared spectroscopy.

Attempted Dehydrohalogenation of 5,6-Difluoro-5,6-bis(trifluoromethyl)norbornene

The norborn-2-ene (2.75 g.) was dropped onto molten potassium hydroxide (10 g.) at 220°. After refluxing for 1 minute, the mixture was cooled, water was added and the organic layer separated to yield unchanged starting material (2.3 g., 84% recovery) as shown by gas chromatography and infrared spectroscopy.

Dechlorination of $CF_3CCl_2CCl_2CF_3$

A stirred suspension of zinc dust (150 g.) and zinc chloride (2.5 g.) in reagent grade dioxane (150 ml.) was brought to reflux in a 3-necked flask fitted with a 1-foot fractionation column and head. The outlet of the fractionation head lead to a trap cooled at -78°.

A saturated solution of 2,2,3,3-tetrachlorohexafluorobutane (304 g.) in dioxane was added dropwise to the suspension at such a rate to give a steady reflux at the fractionation head, where the fraction boiling up to 72° was collected. Fractionation was continued after the chlorofluoroalkane had been added and the fraction up to b.p. 95° was collected.

The experiment was repeated with 196 g. of alkane and proportionate amounts of zinc, etc.

The distillates were combined and fractionated to give: $CF_3CCl=CClCF_3$ (368 g., 96% yield) containing small traces of low-boiling component and dioxane.

Only traces of material condensed in the cooled (-78°) trap.

Addition of Cyclopentadiene to 2,3-Dichlorohexafluorobutene-2

Freshly distilled cyclopentadiene (19.8 g., 0.3 mole), 2,3-dichlorohexafluorobutene-2 (78.4 g., 0.336 mole) and hydroquinone (1.0 g.) were rocked in a 300 ml. autoclave at 145° for 16 hours.

The product was steam distilled. The distillate was an immiscible liquid at first, but soon a solid condensed. The condenser was changed to an air condenser which extended under iced water. The total organic distillate in ether (65.19 g.) contained 53% of the adduct by gas chromatographic peak area. Therefore, estimated yield of adduct based on cyclopentadiene was 38.6%.

A sample was purified by gas chromatography (Si gum, 110°) and dried by sublimation at 125° under reduced pressure to yield 5,6-dichloro-5,6-bis(trifluoromethyl)norborn-2-ene. (Analysis Calcd. for $C_9H_6Cl_2F_6$: C, 36.15; H, 2.02. Found: C, 35.91; H, 1.89%). The sublimate was easily oxidized by an acetone solution of potassium permanganate and slowly decolorized 3% bromine in carbon tetrachloride. The infrared spectrum showed very weak C-H absorption and C=C absorption could not be detected above the background noise. There was absorption at 7.7µ - 9.1µ attributable to C-F.

The proton NMR spectrum in $CFCl_3$ solution was consistent with a

1,4 adduct.

Dechlorination of 5,6-Dichloro-5,6-bis(trifluoromethyl)-norborn-2-ene Magnesium Iodide

Iodine was dried by sublimation under reduced pressure. The norbornene (53% solution in ether) was dried over Drierite.

Iodine (0.41 g.), magnesium (1.94 g.) and dry ether (100 ml.) were refluxed for 0.5 hour. 5,-6-Dichloro-5,6-bis(trifluoromethyl)norborn-2-ene (30 g. of a 53% solution in ether = 15.9 g. norbornene) was added to the refluxing mixture over a period of 5 minutes. Refluxing was continued for 8 hours. The magnesium turnings (2.07 g.) were filtered off and washed, but remained dull after repeated washings with ether.

The filtrate was distilled using a 6-inch Vigreux column to remove most of the ether. A gas chromatogram of the residue (27.22 g.) showed a trace of the dechlorination product, but starting material formed 59.7% of the mixture (from gas chromatogram peak area). This is equivalent to 16.2 g.; therefore, recovery of norbornene was quantitative.

(2) Zinc powder was activated prior to use by washing with dilute hydrochloric acid, water, and acetone and drying on a vacuum line.

5,6-Dichloro-5,6-bis(trifluoromethyl)norborn-2-ene (30.0 g. of a 53% solution in ether = 15.9 g. norbornene) was added to a refluxing stirred suspension of activated zinc dust (5.0 g.) in isopropanol (50 ml.) over a period of 15 minutes. There was an apparent increase in reflux rate, but this may have been due to the presence of ether. Refluxing and stirring were continued for a further 2 hours, when more activated zinc (4.0 g.) was added and the reaction continued for another 3 hours.

A gas chromatogram of the filtered product showed a main peak corresponding to 2,3-bis(trifluoromethyl)norbornadiene. The product was fractionated (1' column) to yield a distillate (17.71 g.) containing 12.4% of the product. The residual liquid (52.64 g.) contained an estimated 10.95% of the dechlorination product.

A sample (3.30 g.) of the residual liquid was separated by gas chromatography (Si gum, 90°) to yield the dechlorination product 2,3-bis(trifluoromethyl)norbornadiene (0.51 g.) which had an identical infrared spectrum to an authentic sample (see later). Estimated yield of norbornadiene: 0.51 g. in 3.30 g. Therefore, residual liquid contains ca. 8.15 g. Distillate contains 12.4% (≡2.2 g.). Therefore, estimated yield = 10.35 g. = 86%.

Dechlorination of 2,3-Dichlorohexafluorobutene-2

2,3-Dichlorohexafluorobutene-2 (233 g., 1.0 mole) was dried over Drierite and added dropwise over a period of 3 hours to a stirred refluxing suspension of zinc (85 g.) and zinc chloride (1 g.) in glacial acetic acid (200 ml.). The acetylene was collected through the top of the water condenser in an acetone/dry-ice cooled trap. The reaction was continued for 2 hours when more zinc (20 g.) was added and the reaction continued for a further 2 hours.

The material in the acetone/dry-ice trap was distilled into another trap to yield hexafluorobutyne-2 (17.6 g., 35% yield based on unreacted olefin), which gave an infrared spectrum consistent with an authentic specimen.

The zinc dust was filtered from the liquid in the flask and the filtrate fractionated to yield 2,3-dichlorohexafluorobutene-2 (160.9 g.), which was contaminated with small quantity of low-boiling compound (probably a reduction product).

Addition of Cyclopentadiene to Hexafluorobutyne-2

Hydroquinone (0.2 g.) and freshly distilled cyclopentadiene (5.62 g. 0.085 mole) were weighed into a hard glass tube (ca. 100 ml. capacity). Hexafluorobutyne (17.6 g.) was condensed in, the tube sealed under vacuum and heated at 130° for 15 hours.

On opening the tube, hexafluorobutyne (1.3 g.) distilled out and was identified by its infrared spectrum. A gas chromatogram of the residual liquid (22.71 g.) showed low-boiling components, a main peak with a small shoulder and a trace of dicyclopentadiene.

Separation of 20.7 g. by gas chromatography (Si gum 104°) yielded (1) low boilers + (4) dicyclopentadiene, (3.37 g.) (2) main peak, 2,3-

bis(trifluoromethyl)norbornadiene (14.48 g.). (<u>Analysis</u> Calcd. for $C_9H_6F_6$: C, 47.38; H, 2.65; F, 49.97. Found: C, 47.43; H, 2.75; F (by difference), 49.82%). The pure product was easily oxidized by a potassium permanganate solution in acetone and decolorized a 3% bromine solution in carbon tetrachloride. The infrared spectrum showed moderate intensity absorption at 5.92µ which is consistent with $CF_3C{=}C{-}CF_3$, and C-H and C-F absorptions. The proton NMR was completely consistent with a Diels-Alder adduct, (3) main peak residue + shoulder (0.41 g.), contained 77% of the norbornadiene. Total yield norbornadiene: 14.8 g., 76% (based on cyclopetnadiene).

<u>Addition of Cyclopentadiene to sym-Dichlorodifluoroethylene</u>

A 300 ml. autoclave was charged with hydroquinone (1 g.), freshly distilled cyclopentadiene (33 g., 0.5 mole) and CFCl=CFCl (68 g., 0.51 mole) and heated at 165 - 170° for 65 hours. No low-boiling products distilied out on opening the autoclave.

The black liquid product (96.7 g.) was steam distilled. The organic material (11.3 g.), distilling over after several hours, was a pure high-boiling viscous liquid, which showed C-H, weak C=C and C-F absorptions in the infrared spectrum. This material partially solidifed on standing.

The first part of the steam distillate was distilled under high vacuum to yield (1) a liquid (10.29 g.) containing 61.8% adduct, (2) pure adduct (3.27 g.), (3) a residue (21.62 g.) which contained only a trace of simple adduct. Therefore, estimated yield of simple adduct - 6.35 g. (from fraction 1) + 3.27 g. = 9.62 g. = 9.7% based on cyclopentadiene. Total yield of high-boiling viscous products was 32.96 g.

A sample of the simple adduct was purified by gas chromatography to yield 5,6-dichloro-5,6-difluoronorborn-2-ene. (<u>Analysis</u> Calcd. for $C_7H_6Cl_2F_2$: C, 42.24; H, 3.04. Found: C, 42.54; H, 3.29%).

The infrared spectrum showed relatively strong C-H absorption and absorption attibutable to C-F and C-Cl. The pure product was easily oxidized by an acetone solution of potassium permanganate and decolorized a 3% solution of bromine in carbon tetrachloride. The proton NMR spectrum was completely consistent with a 1,4-(Diels-Alder) adduct. The ^{19}F NMR spectrum was inconclusive.

Attempted Dehalogenation of 5,6-Dichloro-5,6-Difluoro-norborn-2-ene

5,6-Dichloro-5,6-difluoronorborn-2-ene (12.5 g. of a 65% solution in ether ≡ 8.1 g. norbornene) was added dropwise over a period of 10 minutes to a stirred refluxing suspension of activated zinc (5 g.) in isopropanol (30 ml.). The reaction was continued for 1.5 hours when additional activated zinc (5 g.) was added and the reaction continued for a further 3 hours. A chromatogram of the product showed only starting material and isopropanol. The product was filtered and fractionated. The first 1 ml. of distillate was pure isopropanol as was the remaining distillate. Most of the isopropanol was fractionated off to leave a residue (26.10 g.) of 45.6% norbornene in isopropanol. This is equivalent to 11.9 g. norbornene = 95% recovery of starting material.

Addition of Cyclopentadiene to Trifluoroethylene

A 300 ml. autoclave was charged with freshly distilled cyclopentadiene (300 g., 0.5 mole) and hydroquinone (1.0 g.). Trifluoroethylene (44 g., 0.537 mole) was condensed under vacuum into the autoclave which was heated at 165° for 17 hours. On opening the autoclave, trifluoroethylene (23.4 g., 53%) distilled out.

The residual liquid and ether washings were steam distilled to give an initial organic steam distillated (37.1 g.) and a later organic distillate which was a high-boiling viscous liquid (8.25 g.) of at least three components. The initial steam distillate was distilled to give (1) ether + trace of adduct (5.54 g.), (2) adduct (3.58 g.) > 95% pure, (3) 4.68 g. containing 73.6% adduct, (4) 17.84 g. containing 28.6% adduct, (5) 2.38 g. of high-boiling material containing trace of the simple adduct, (6) a small brown tarry residue. Estimated yield of simple adduct: 12.1 g. = 33% based on unrecovered olefin.

A sample of the adduct was separated by preparative gas chromatography (Si gum, 95°) to yield 5,5,6-trifluoronorborn-2-ene. (Analysis Calcd. for $C_7H_7F_3$. C, 56.75; H, 4.77; F, 38.48. Found: C, 56.91; H, 4.68%;

F (by difference), 38.41%). The proton NMR spectrum was inconclusive but the ^{19}F NMR spectrum indicated a mixture of two isomers of the Diels-Alder adduct.

Attempted Dehydrofluorination of 5,5,6-Trifluoronorborn-2-ene

(1) Aqueous Potassium Hydroxide

The norbornene (ca. 8.52 g. in high-boiling material, total wt. 22.54 g.) was refluxed for 4 hours with aqueous potassium hydroxide (13 g. in 40 ml. H_2O). A gas chromatogram of the organic phase (20.98 g.) showed only starting materials.

(2) Aqueous Alcoholic Potassium Hydroxide

The norbornene mixture (19.46 g.) was added over a period of 20 minutes to a refluxing solution of potassium hydroxide (9 g.) in ethanol (20 ml.) - water (5 ml.) solution. The mixture was refluxed for 7 hours. There was a considerable darkening of both phases. After normal work-up, an organic product (18.7 g.) containing 46% of the norbornene was recovered. Therefore, recovery of starting material was quantitative. A gas chromatogram showed no dehydrofluorination product.

Addition of Cyclopentadiene to Chlorotrifluoroethylene

A 300 ml. autoclave was charged with hydroquinone (1.0 g.) and freshly distilled cyclopentadiene (41.96 g., 0.635 mole). Chlorotrifluoroethylene (76.5 g., 0.657 mole) was condensed under vacuum into the autoclave which was heated at 170° for 16 hours. On opening the autoclave, low-boiling material (0.4 g.) distilled out. The residual liquid (112.6 g.) was steam distilled to yield an organic distillate (68.7 g.), which was dried, and a residual brown viscous liquid (32.9 g.).

A sample (10.8 g.) of the steam distillate was separated by gas chromatography (Si gum, 110°) to yield (1) low-boiling components (not collected), (2) the adduct (4.56 g.). Therefore, the yield of adduct is 26% based on cyclopentadiene, n_D^{23} 1.430 ± 0.001. (Analysis Calcd. for $C_7H_6ClF_3$: C, 46.05; H, 3.31. Found: C, 46.26; H, 3.28%) The infrared spectrum showed medium C-H absorption, weak C=C absorption and absorption attributable to C-F and C-Cl. The proton and ^{19}F NMR spectra suggested a mixture of at least four isomers, which were probably the isomers of the 1,4- and 1,2- adducts. On standing, the adduct darkened.

Attempted Addition of Octafluorobutene-2 to Isopropenylacetylene

A 300 ml. autoclave was charged with hydroquinone (0.6 g.). Isopropenylacetylene (10.0 g.) was vacuum distilled into the autoclave followed by octafluorobutene-2- (42.3 g.). The autoclave was sealed under vacuum and heated at 120° for 16 hours.

On opening the autoclave, volatile material (44.8 g.) distilled out to leave a residual liquid which was greater than 95% isopropenylacetylene with a trace of higher boiling material. The isopropenylacetylene was allowed to evaporate to leave a small brown viscous liquid residue. Total recovery of starting material was 90%.

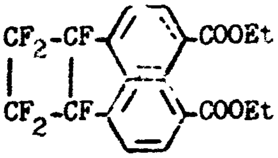
G. Fluoroaromatic Compounds

Preparation of p-Trifluorovinyl Ethyl Benzoate

Benzoyl peroxide (60. g., 0.25 mole) was added in 5 g. aliquots to stirred, refluxing $CF_2BrCFClBr$ (138 g., 0.5 mole) over a period of 3 hours. The reaction mixture was extracted with 12% aqueous sodium bicarbonated (4 X 50 ml.). The aqueous solution was acidified to yield crude $CF_2BrCFClC_6H_4COOH$. The reaction was carried out six times and the total yield of $CF_2BrCFClC_6H_4COOH$ was 272 g. (28.7%).

A solution of ethanol 300 g., conc. H_2SO_4 (10 ml.) and the acid (136 g., 0.425 mole) was refluxed for 5.5 hours. Ethanol was distilled off and water added to the mixture. The organic layer gave $CF_2BrCFClC_6H_4COOC_2H_5$ (113 g., 77.5%).

To a refluxing solution of Zn (42.5 g., 0.65 mole), $ZnCl_2$ (2 g.) and ethanol (200 ml.), the above ester (113 g., 0.327 mole) in ethanol (50 ml.) was added dropwise over the period of 30 minutes. The mixture was refluxed for 1 hour and the solution was poured into cold water, extracted with ether and dried. Fractional distillation gave $CF_2=CFC_6H_4COOC_2H_5$ (34.5 g., 47.5%) and viscous oil (24.2 g.). $CF_2=CFC_6H_4COOC_2H_5$, b.p. 80°/15 mm., n_D^{20} 1.4966, d^{20} 1.274. The infrared spectrum showed $CF_2=CF-$ and $-COOC_2H_5$ absorption at 5.96μ, and 5.81μ: NMR data showed the compound had a CF_2=CF- group <u>para</u> to the ester group. Redistillation of viscous oil gave



(20 g.). b.p. 169 - 170°/0.3 mm., n_D^{20} 1.5404l.

An infrared spectrum showed the absorption peak at 11.32μ and the NMR spectrum was consistent with the structure.

Reaction of $CF_2=CFC_6H_4COOC_2H_5$ with NOCl

Dimethylformamide (100 ml.) was added slowly to cooled aluminum chloride (3.5 g., 0.002 mole). After the suspension became cool, $CF_2=CFC_6H_4COOC_2H_5$ (11.5 g., 0.054 mole) was added and NOCl bubbled into the mixture at 0°. After ca. 2 hours v.p.c. of the reaction mixture showed no starting ester. Water was added slowly, and the product extracted with a small amount of pentane and dried. The pentane solution was eluted on alumina (80 - 200 mesh acid) with pentane. The solvent was distilled off under vacuum to leave a light green oil (7.3 g.) (Analysis Calcd. for $C_{22}H_{18}ClF_6NO_5$: C, 50.23; H, 3.43. Found: C, 49.66; H, 3.80%).

After four weeks at 0°, the oil became a mixture of white solid and viscous liquid. The white solid was separated and recrystallized from pentane. m.p. 104.5°. (Analysis Calcd. for $C_{22}H_{18}ClF_6NO_5$: Cl, 6.76. Found: Cl, 6.80%). Infrared absorption at 7.00μ and 6.31μ was consistent with an oxazetidine and N-O bond, respectively. The ^1H and ^{19}F NMR spectra were consistent with proposed structure.

Preparation of $CF_2=CFCF_2COOEt$ and Its Reaction with NOCl

A mixture of ethanol (55.2 g., 1.2 mole), and $CF_2ClCFClCF_2COONa$ (117 g., 0.4 mole) was cooled to 0° and conc. H_2SO_4 (51.2 g.) was added dropwise with vigorous stirring. The reaction mixture was stirred for 2 hours, left overnight at room temperature and refluxed for a further 2 hours. The solution was filtered and the filtrate neutralized with Na_2CO_3 solution, washed with water and dried. Fractional distillation gave $CF_2ClCFClCF_2COOC_2H_5$ (90 g., 87%): b.p. 66°/20 mm., n_D^{20} 1.3741, (lit. b.p. 64°/20 mm., n_D^{20} 1.3694).

To a refluxing suspension of ethanol (300 ml.), Zn (44.5 g., 0.68 mole) and $ZnCl_2$ (2.0 g.), the ester (88 g.,0.34 mole) was added over a period of 30 minutes and refluxed another 2 hours. The reaction mixture was filtered, and the filtrate poured into water, and the organic layer separated and dried. Fractional distillation gave $CF_2=CFCF_2COOC_2H_5$ (31.8 g., 46%): b.p. 109°, n_D^{20} 1.3403, d^{20} 1.3450. MR_D: Calcd.: 31.36. Found: 31.98.

$CF_2=CFCF_2COOC_2H_5$ (9.0 g., 0.044 mole), $AlCl_3$ (6.0 g., 0.44 mole) and dimethylformamide (100 ml.) were reacted with NOCl as described before. The yield calculated from v.p.c. peak areas was $CF_2ClCFNOCF_2COOC_2H_5$ 6.2 g. (51.7%) and $CF_2ClCFClCF_2COOC_2H_5$ 4.2 g. (37.5%). An analytical sample which was separated by v.p.c. had the following properties: no definite boiling point. Color became faint at *ca*. 140°. (*Analysis* Calcd. for $C_6H_5ClF_5NO_3$: C, 26.75; H, 1.86. Found: C, 26.96; H, 2.37%).

Reaction of $CF_2=CFCF_2COOCH_3$ with NOCl

$CF_2=CFCF_2COOCH_3$ (10.0 g., 0.05 mole) (supplied by the University of Colorado) and $AlCl_3$ (6.7 g., 0.05 mole) in dimethylformamide (100 ml.) were reacted with NOCl as described before. Yield calculated from v.p.c. was $CF_2ClCFNOCF_2COOCH_3$ 5.3 g. (41.6%) and $CF_2ClCFClCF_2COOCH_3$ 2.8 g. (21.5%) An analytical sample which was separated by v.p.c. had the following properties: no definite boiling point. Color became faint at about 125°. (*Analysis* Calcd. for $C_5H_3ClF_3NO_3$: C, 23.51; H, 1.18. Found: C, 24.64; H, 1.98%).

Preparation of $CF_2=CFCOOC_2H_5$ and Its Reaction with NOCl

$CF_2BrCFClCH=CH_2$ (56.2 g., 0.25 mole) was added to a solution of $KMnO_4$ (18 g., 0.75 mole) and water (600 ml.) at 60 - 65° over a period of 2 hours. The mixture was stirred for 6 hours at 60° and cooled to 0°, acidified with dil. H_2SO_4, treated with $NaHSO_3$ solution, and extracted with ether. Distillation gave $CF_2BrCFClCOOH$ (19.0 g., 32.1%): b.p. 71 - 72°/4.5 mm., n_D^{20} 1.4213, (lit. b.p. 78 - 80°/5.0 mm., n_D^{20} 1.4180).

A solution of $CF_2BrCFClCOOH$ (19.6 g., 0.08 mole), ethanol (40 g.)

and conc. H_2SO_4 (2 ml.) was refluxed for 5 hours. $CF_2BrCFClCOOC_2H_5$ (12.5 g., 58%) was obtained; b.p. 82 - 3°/45 mm. (lit. 83 - 4°/60 mm.).

To a refluxing mixture of ether (100 ml.), Zn (12.3 g., 0.19 mole) and ZnCl (1.0 g.), $CF_2BrCFClCOOC_2H_5$ (25.1 g., 0.093 mole) was added dropwise over a period of 50 minutes. The mixture was refluxed for 8 hours, filtered and the filtrate distilled. During the distillation, some of the compound was polymerized and only a small amount of $CF_2=CFCOOC_2H_5$ (2.8 g., 19.5%) was obtained: b.p. 101 - 102°, n_D^{20} 1.3656 (lit. b.p. 100 - 101°, n_D^{25} 1.3618.).

$CF_2=CFCOOC_2H_5$ (2.8 g.,0.018 mole), and $AlCl_3$ (2.4 g., 0.018 mole) in dimethylformamide (80 ml.) was reacted with NOCl as before. Yield calculated from v.p.c. was $CF_2ClCFNOCOOC_2H_5$ 1.0 g. (25.3%) and $CF_2ClCFClCOOC_2H_5$ 0.3 g. (7.4%). An analytical sample was separated by v.p.c. It had no definite boiling point and the color became faint at about 90°. (Analysis Calcd. for $C_5H_5ClF_3NO_3$: C, 27.39; H, 2.30. Found: C, 27.99; H, 2.74%).

Preparation of C_6H_5-O-CF=CCl_2 and Its Reaction with NOCl

Phenol (94 g., 1.0 mole) was dissolved in acetone (250 ml.) and potassium hydroxide (11.2 g., 0.2 mole). $CF_2=CCl_2$ (133 g., 1.0 mole) was added over the period of 3 hours. After addition of the olefin, the mixture was distilled up to 70° to remove acetone, the residue was cooled and excess base added. The mixture was then steam distilled, and the ether separated, washed and dried. Fractional distillation gave a mixture of C_6H_5-O-CF=CCl_2 and C_6H_5-OCF_2CCl_2H (154 g.). The mixture was treated with potassium hydroxide and water for 20 hours and separated by v.p.c. to yield $C_6H_5OCF=CCl_2$; b.p. 60 - 61°/2.1 mm., n_D^{22} 1.5147 (lit. 60 - 61°/2.1 mm., n_D^{20} 1.5162.)

C_6H_5-O-CF=CCl_2 (2.1 g., 0.01 mole) and $AlCl_3$ (0.7 g., 0.005 mole) in dimethylformamide (50 ml.) were reacted with NOCl as before. The reaction mixture which was separated by ether elution on a alumina column gave suspected $C_6H_5OCF(NO)CCl_3$ (1.6 g.). (Analysis Calcd. for $C_8H_5Cl_3FNO_2$: C, 35.27; H, 1.85. Found: C, 36.96; H, 2.27%.)

Reaction of $CH_2=CHCH_2OCF_2CFClH$ with NOCl

$CH_2=CHCH_2OCF_2CFClH$ (17.5 g., 0.1 mole) and $AlCl_3$ (1.4 g., 0.01 mole) in dimethylformamide (100 ml.), were reacted with NOCl as before. After one hour, the color of the reaction mixture became red. The reaction mixture was cooled and treated with water. The organic product, which consisted of two compounds, did not have the characteristic blue coloration of nitroso compounds, so further work was abandoned.

Preparation of $CF_2=CFCH=CHCF_3$ and Its Reaction with NOCl

$CF_2ClCFClI$ (279 g., 1.0 mole), $CF_3CH=CH_2$ (28.8 g., 0.03 mole, and benzoyl peroxide (2 g.) were allowed to react in an autoclave at 100° for 4 hours. Excess $CF_2ClCFClI$ was distilled off and the residue was fractionated to give $CF_2ClCFClCH_2CHICF_3$ (90 g., 77.5 %), b.p. 61°/18 mm. Dehydroiodination was effected by aqueous potassium hydroxide (100 g. in 60 ml.) and $CF_2ClCFClCH=CHCF_3$ (40 g., 57.4%) was obtained. Dechlorination by zinc dust in ethanol gave $CF_2=CFCH=CHCF_3$ (15.8 g., 56%), b.p. 49°

$CF_2=CFCH=CHCF_3$ (13.8 g., 0.08 mole), NOCl (9.8 g., 0.15 mole), $AlCl_3$ (6.7 g., 0.05 mole), and DMF (100 ml.) were allowed to react at 0°. After 2 hours, the mixture was treated with H_2O and a light yellow product (17.3 g.) was obtained. The main product was a colorless liquid rather than a blue nitroso compound. A sample has been submitted for elemental analysis.

Preparation of $CF_2=CFCH_2CH=CH_2$ and Its Reaction with NOCl

$CH_2=CHCH_2Cl$ (114 g., 1.5 mole) and benzoyl peroxide (24 g.,0.092 mole) were added to a refluxing solution of $CF_2BrCFClBr$ (1100 g., 4.0 mole). Reaction was continued for another 7 hours. Excess $CF_2BrCFClBr$ was distilled off and the residue was washed with sodium carbonate solution and H_2O and dried. Distillation gave the adduct $CF_2BrCFClCH_2CHBrCH_2Cl$ (146 g., 28.2%), b.p. 90°/6 mm. (lit. b.p. 90°/6mm.). Dehalogenation of the adduct was carried out as usual by zinc in ethanol. Fractional distilation gave the diene $CF_2=CFCH_2CH=CH_2$ (23 g., 45.8%), b.p. 38° (lit. 38°/870 mm.).

Nitrosyl chloride (3.3. g., 0.05 mole) was added to a stirred mixture of $CF_2=CFCH_2CH=CH_2$ (6.2 g., 0.05 mole), $AlCl_3$ (6.7 g., 0.05 mole) and DMF (100 ml.) at 0°, and the reaction continued for 3 hours. The color of the solution changed from yellow to greenish brown. Water was added slowly to a reaction mixture and a blue organic liquid (2.1 g.) was obtained. Gas chromtographic analysis of the product showed $CF_2=CFCH_2CH=CH_2$ (1.8 g.), $CF_2ClCF(NO)CH_2CH=CH_2$ (0.3 g.) and a trace of high-boiling material. $CF_2ClCF(NO)CH_2CH=CH_2$, which was purified by preparative gas chromatography, had the following properties: no definite boiling point at normal pressures, color changed slowly to green at ca. 100°, to greenish yellow at ca. 110°, to yellowish brown at ca. 115°, to dark brown at ca. 120°. (Analysis Calcd. for $C_5H_5ClF_3NO$: C, 32.02; H, 2.68. Found: C, 32.22; H, 2.76%)

Preparation of $CF_2=CFCH=CH_2$ and Its Reaction with NOCl

$CF_2BrCFClCH=CH_2$ (135 g., 0.5 mole), which was prepared by addition of $CF_2BrCFClBr$ to $CH_2=CH_2$, followed by dehydrobromination, was added to a stirred refluxing suspension of Zn (60 g., 0.7 mole), $ZnCl_2$ (2.0 g.) and in EtOH (200 ml.) over a period of 2 hours and the reaction was continued for another 2 hours. The product which was collected in a cold trap (-78°) was distilled to give $CF_2=CFCH=CH_2$ (48 g., 89%), b.p. 8°.

$CF_2=CFCH=CH_2$ (10.8 g., 0.1 mole) was condensed into a stirred mixture of $AlCl_3$ (13.4 g., 0.1 mole), NOCl (9.8 g., 0.15 mole) and DMF (100 ml.) at 0°. The color of the solution changed from orange to greenish yellow shortly after the addition of the diene and then changed to orange again. After 5 hours, water was added and the organic layer was separated and dried.

The crude light yellow product (13 g.), which consisted of one major component (over 95%), was separated by preparative gas chromatography to yield the major product as a colorless liquid, b.p. 177 - 178° (micro), n_D^{26} 1.3975. The infrared absorption peaks at 5.70 and 6.05 are characteristic of -CF=CH-, and CH_2=CH-, respectively. When the reaction was carried out with $CF_2=CFCH=CH_2$ (7.8 g., 0.07 mole), NOCl (5.9 g., 0.09 mole) and DMF (80 ml.), the color of the reaction mixture was light green, which after treatment with water, yielded a blue liquid (6.9 g.).

Though the main product was the same, a trace of a blue compound, probably a nitroso compound, was obtained.

H. Fluoroketane Studies

Attempted Addition of Carbinols to Chlorotrifluoroethylene (See Table XV)

Pentafluorophenyltrifluorovinyldimethylsilane

Pentafluorophenylmagnesium bromide was prepared in ether from 10.0 g. (0.0405 mole) pentafluorobromobenzene. The solution was filtered and added to 7.10 g. (0.0405 mole) trifluorovinyldimethylchlorosilane. The mixture was refluxed for 4 hours and hydrolyzed. Upon distillation of the dried ether layer, the product was obtained in 57% yield.

(1,1,1,3,3,3-Hexafluoroisopropoxy)methyldichlorosilane and (1,1,3,3-Tetrafluoro-1,3-dichloroisopropoxy)methyldichlorosilane

The appropriate ketone (hexafluoroacetone or 1,3-dichlorotetrafluoroacetone) was added to an equimolar quantity of methyldichlorosilane in a thick walled glass tube and sealed under vacuum. The solution was irradiated in sunlight for two weeks. Distillation of the reaction mixtures gave 65% and 64% of the desired products.

I. Preparation and Reactions of Some Silanes Containing the Trifluorovinyl Group

1. Reaction of Trimethyltrifluorovinyl Silane and Organolithium Reagents

Methyl-, n-butyl- and phenyllithium reagents were prepared by direct reaction with the bromides and lithium metal, 3-trifluoromethylphenyl-, 1-napthyl- and 2-thiophenyllithium reagents by exchange of the bromides with butyllithium, and allyl- and vinyllithium reagents by exchange of phenyllithium with the tetrasubstituted tin compounds(104).

$(CH_3)_3SiCF=CF_2$ (0.1 mole) was added to the lithium reagent (0.1 mole in diethyl ether solution) and stirred for about two hours. The mixture was then hydrolyzed with dilute acid, and the ether layer separated, dried (Drierite) and the product obtained by distillation. These com-

TABLE XV

ATTEMPTED ADDITION OF CARBINOLS TO CHLOROTRIFLUORETHYLENE

Carbinol	Salt	Conditions	Reaction
$CH_3\cdot C\ (CF_2Cl)_2\cdot OH$	Li	a. Reflux in diethyl ether	none
		b. 90° sealed tube in THF	none with carbinol CTFE-THF adduct formed
$CF_2{:}CF\cdot C(CF_3)_2\cdot OH$	Na	a. Reflux in diethyl ether	none
		b. 90° sealed tube in THF	none with carbinol CTFE-THF adduct formed
		c. 90° sealed tube in excess $CF_2{:}CF\cdot C(CF_3)_2\cdot OH$	none

TABLE XVI

YIELDS AND PROPERTIES OF SILANES PREPARED

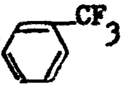
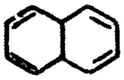
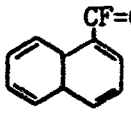
Compound	Yield %	b.p./mm.	n_D^{20}	d^{20}
a $Me_3SiCF=CFCH_3$	20	86°	1.3921	0.917
b $Me_3SiCF=CF$ 	72	72°/2	1.5062	1.030
c $Me_3SiCF=CF$ 	50	103°/6	1.4640	1.181
d $Me_3SiCF=CFC_4H_9$	70	76°/40	1.4112	0.887
e $Me_3SiCF=CF$ 	34	100°/1	1.5588	1.224
f $Me_3SiCF=CFCH_2CH=CH_2$	20	50°/30	1.4180	0.924
g $Me_3SiCF=CFCH=CH_2$		45°/40	1.4400	0.944
h $Me_3SiCF=CF$ 	50	60°/2	1.5201	1.135
i  $CF=CHF$	61	74°/60	1.5056	1.155
j  $CF=CHF$	75	75°/40	1.4467	1.353
k $C_4H_9CF=CHF$	62	73°	1.3680	0.885

TABLE XVI (continued)

YIELDS AND PROPERTIES OF SILANES PREPARED

l	CF=CHF	83	70°/1	1.5975	1.224
m	$Me_3SiCH_2CH_2CF=CF$	69	90°/2	1.4990	1.007

	C%		H%		F%	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
a.	47.97	47.86	8.06	8.07	25.30	25.14
b.	62.22	62.51	6.64	6.53	17.90	17.75
c.	51.42	51.31	4.68	4.57	33.89	33.22
d.	56.21	56.39	9.44	9.48	19.76	19.53
e.	68.69	68.43	6.15	6.35		
f.	54.32	54.33	7.97	7.81	21.58	21.76
g.	51.74	52.14	7.45	7.30	23.41	21.26
h.	49.50	49.62	5.54	5.52	17.38	17.17
i.				- known compound-		
j.	51.94	51.79	2.42	2.50	45.65	45.28
k.	60.00	59.89	8.39	8.21	31.61	31.30
l.	75.77	75.23	4.24	4.10	19.97	19.14
m.	64.93	65.01	7.56	7.67	15.81	15.82

pounds were then treated for about 2 hours in alcoholic potassium hydroxide. Excess water was added and the organic layer extracted with ether. The ethereal solution was washed twice, dried (Drierite) and distilled.

The structures, physical properties and analytical data are given in Table XVI.

2. Other Syntheses of Silanes Containing the Trifluorovinyl Group

Trifluorovinyllithium

Methyllithium was prepared by the reaction of methyl bromide with freshly cut lithium chips in enough ethyl ether to make an approximately 1 M solution. The solution was then cooled to -78° in a Dry Ice-acetone bath and a slight excess of bromotrifluoroethylene (previously condensed in a cold trap) was bubbled into the solution. The solution turned dark blue after about 30 minutes. Stirring was continued for about 2 hours to allow completion of the exchange reaction before the chlorosilane was added.

Trifluorovinyltrimethylsilane (XIV)

Trimethylchlorosilane (28 g., 0.26 mole) was added dropwise to a stirred solution of the trifluorovinyllithium (0.26 mole) in ethyl ether at -78°. The reaction mixture was allowed to come to room temperature slowly. The mixture was then hydrolyzed with water, and the ethereal solution was separated and dried over calcium chloride. Distillation gave XIV (26 g., 65%), the properties and analysis of which are given in Table VII.

Bis(trifluorovinyl)dimethylsilane (XV)

Trifluorovinyllithium (1.0 mole) in ether at -78° was added to dichlorodimethylsilane (65 g., 0.5 mole) at -78°. The mixture was allowed to come to room temperature. The lithium chloride was filtered and the filtrate was distilled. The only product, in addition to recovered dichlorodimethylsilane, was XV (30.5 g., 56%).

Trifluorovinyldimethylethoxysilane (XVI)

Dimethylchloroethoxysilane was prepared by adding dropwise 1 mole of absolute ethanol to 1 mole of dimethyldichlorosilane in triamylamine with stirring. Fractional distillation gave a yield of ca. 50% of the desired product with small amounts of the dichloro and diethoxy compounds as impurities.

Dimethylchloroethoxysilane (30 g., 0.22 mole) was slowly added to a stirred solution of trifluorovinyllithium (0.22 mole) at -78°. The mixture was allowed to come to room temperature slowly. The lithium chloride was filtered, and the remaining solution was distilled to give XVI (20 g., 50%).

Trifluorovinyldimethylchlorosilane (XVII)

Trifluorovinyldimethylethoxysilane (XVI) (15 g., 0.085 mole) was slowly added to PCl_3 (6.1 g., 0.045 mole) at 0° with stirring. Stirring was continued for 5 hours and the solution was distilled, yielding XVII (8.1 g., 55%).

sym-Tetramethylbis(trifluorovinyl)disiloxane (XVIII)

sym-Tetramethyldichlorodisiloxane was prepared by adding water in dioxane slowly to a solution of dichlorodimethylsilane in ether in the manner described by Patnode and Wilcox (105). The product (11.5 g., 0.056 mole) was then added to a stirred solution of trifluorovinyllithium (0.12 mole) at -78°. The mixture was allowed to come to room temperature, water was added, and the organic layer was separated and dried. Distillation yielded XVIII (8.3 g., 50%).

Trifluorovinyldimethylsilane (XIX)

Bromotrifluoroethylene was bubbled into tetrahydrofuran (THF) 120 ml. and magnesium (5 g., 0.2 g-atom). When the reaction had started, the mixture was cooled in an ice-water bath, and dimethylchlorosilane (17 g., 0.2 mole) was added. Bromotrifluoroethylene was added slowly until most of the magnesium had disappeared. A fraction with a boiling range of 40 - 63° was distilled from the mixture. This fraction was washed twice with cold water and dried over calcium chloride. Distillation yielded XIX (7.0 g., 25%).

Pentafluorophenyltrifluorovinyldimethylsilane (XX)

Pentafluorophenylmagnesium bromide was prepared in ether from bromopentafluorobenzene (10 g., 0.04 mole). The mixture was filtered and the solution was added dropwise to trifluorovinyldimethylchlorosilane XVII (7.1 g., 0.04 mole) in ether. The mixture was refluxed 4 hours, then hydrolyzed. The ether layer was dried and distillation yielded XX (7.2 g., 57%).

2,3,3-Trifluoroallyltrimethylsilane (XXI)

Bromomethyltrimethylsilane (8.4 g., 0.05 mole) was allowed to react with an excess of dispersed lithium in ether (50 ml.). Excess lithium was filtered off. The filtrate and tetrafluoroethylene (6 g. 0.06 mole) were kept in a 100 ml. evacuated thick-walled glass tube at 0° for 16 hours and at room temperature for 12 hours. The volatile products were condensed out under reduced pressure and distilled to give XXI (3.6 g., 42%).

(3,4,4-Trifluoro-3-butenyl)trimethylsilane (XXII)

A stirred mixture of isopropyl alcohol (200 ml.) and zinc dust (130 g., 2 g-atoms) was heated to reflux. (1,4-Dibromo-3-chloro-3,4,4-trifluorobutyl)trimethylsilane (188 g., 0.51 mole) was added at a rate to maintain reflux without further heating. The mixture was refluxed for an additional 1 hour, and on cooling hydrochloric acid(100 ml. 38%) was added slowly. Upon completion of the reaction, the mixture was filtered to remove the zinc. Water and ether were added to the two-phase system. The ethereal solution was washed twice more with water and dried over $CaCl_2$. Distillation yielded XXII (68.5 g., 75%). (Lit. (65) b.p. 114°, n_D^{23} 1.3790.

(3,4,4-Trifluoro-3-chloro-4-bromobutyl)dimethylchlorosilane (XXIII)

A solution of dimethylchlorosilane (25 g., 0.37 mole), 3,4,4-trifluoro-3-chloro-4-bromo-1-butene (57 g., 0.26 mole), and a 1 M solution of H_2PtCl_6 in isopropyl alcohol (0.5 ml.) was refluxed for 24 hours. Distillation of the two products gave dimethyldichlorosilane (11 g.) and XXIII (35.8 g., 44%).

1,3-Bis(3,4,4-trifluoro-3-chloro-4-bromobutyl)-1,1,3,3-tetramethyldisiloxane (XXIV)

(3,3,4-Trifluoro-3-chloro-4-bromobutyl)dimethylchlorosilane (36 g., 0.11 mole) and water (25 ml.) were heated with stirring for 16 hours. The organic layer was separated and dried over $CaCl_2$. Distillation yielded XXIV (23 g., 82%).

1,3-Bis(3,4,4-trifluoro-3-butenyl)-1,1,3,3-tetramethyldisiloxane (XXV)

(22 g., 0.045 mole) was slowly added to a refluxing mixture of zinc (10 g.) in isopropyl alcohol. Water was added and the product was extracted with ether. The ethereal solution was washed twice and dried over $CaCl_2$. Distillation yielded XXV (6.8 g., 42%).

(3,4,4-Trifluoro-3-chloro-4-bromobutyl)methyldichlorosilane (XXVI)

A solution of methyldichlorosilane (23 g., 0.020 mole), 3,4,4-trifluoro-3-chloro-4-bromo-1-butene (40 g., 0.18 mole), and 1 M H_2PtCl_6 solution in isopropyl alcohol (0.5 ml.) was refluxed for 24 hours. Distillation gave XXVI (45 g., 71%).

(4,5,5-Trifluoro-4-pentenyl)dimethylchlorosilane (XXVIII)

1,1,2-Trifluoro-1,4-pentadiene (50 g.. 0.41 mole), was prepared by the method of Tarrant and Gilman (17), was sealed in a thick-walled tube with dimethylchlorosilane (40 g., 0.42 mole) and 1 M H_2PtCl_6 solution in isopropyl alcohol (0.5 ml.). The tube was heated at 75° for 16 hours. Distillation of products yielded XXVIII (75 g., 85%).

(4,5,5-Trifluoro-4-pentenyl)trimethylsilane (XXVII)

XXVIII (34.5 g., 0.16 mole) was added slowly to CH_3MgBr ca. 0.2 mole in ether (150 ml.) with cooling. The resulting mixture was hydrolyzed with water, and the ethereal solution was separated and dried over calcium chloride. Distillation yielded XXVII (26 g., 85%).

1,3-Bis(4,5,5-trifluoro-4-pentenyl)-1,1,3,3-tetramethyldisiloxane (XXIX)

XXVIII (16 g., 0.074 mole) was heated overnight with stirring in 20 ml. of water. The organic layer was extracted with ether and dried over calcium chloride. Distillation yielded XXIX (12 g., 88%).

(4-Phenyl-3,4-difluoro-3-butenyl)trimethylsilane (XXX)

XXII (9.1 g., 0.05 mole) was slowly added to a solution containing phenyllithium (0.05 mole) in ether. The mixture was stirred for 2 hours and hydrolyzed, and the organic layer was dried. Distillation gave XXX (8.3 g., 69%).

Dimerization of XIV

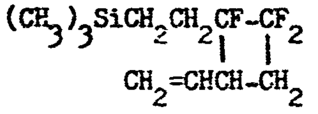
(XIV) (7.0 g., 0.045 mole) was sealed in a glass tube and heated to 200° for 2 days. Considerable decomposition was evident but distillation gave XXXI (0.25 g., 3.8%).

Thermal Dimerization of XXII

(XXII) (25 g., 0.14 mole) and hydroquinone (ca. 0.2 g.) were heated to 210° for 47 hours. Distillation of the reaction mixture yielded the dimer XXXII (8 g. 33%).

Reaction of XXII with 1,3-Butadiene

XXII (8.2 g., 0.045 mole) and 1,3-butadiene (4.8 g., 0.09 mole) were sealed in a thick-walled tube and heated at 200° for 24 hours. Distillation of the liquid residue gave 3.6 g. (33.6%) of a compound tentatively identified as XXXIII.



$$\begin{array}{l}(CH_3)_3SiCH_2CH_2\underset{|}{C}F-\underset{|}{C}F_2\\ \qquad\qquad CH_2=CHCH-CH_2\end{array}$$

XXXIII

Infrared analysis showed a vinyl group to be present. Butadiene is known to react with $CF_2=CFX$ compounds to give products with the CH_2 group adjacent to the CF_2 group.

Thermal Dimerization of (4,5,5-Trifluoro-4-pentenyl)dimethylchlorosilane

XXVIII (25 g., 0.12 mole) was heated in sealed tube at 200° for 48 hours. Distillation yielded XXXIV (10 g. 42%).

Reaction of XXII with NOCl

Nitrosyl chloride was bubbled into a mixture of dimethylformamide (DMF) (160 ml.), $AlCl_3$ (11 g., 0.082 mole), and XXII (11 g., 0.06 mole) until no further reaction was obvious. (The reaction was exothermic.) The solution was extracted with n-pentane, and the pentane layer, containing the blue product, was passed through an alumina (acid) column. The blue material was collected and the pentane was evaporated under vacuum.

A deep blue product, tentatively identified as $(CH_3)_3SiCH_2CH_2C(NO)FCF_2Cl$ XXXV, was obtained.

J. Reactions of Unsaturated Grignard and Lithium Reagents

1. Reactions with Haloölefins

Reaction Between Ethoxyethynyl Lithium and Chlorotrifluoroethylene

a. A methyl lithium solution in diethyl ether (0.975 M; 41.0 cc.) was added to a stirred solution of ethoxyethyne (2.3 g.) in anhydrous ether (50 cc.). A white precipitate of ethoxyethynyl lithium was observed. Chlorotrifluoroethylene (6.0 g.) was bubbled into the stirred suspension of ethoxyethynyl lithium at room temperature. No evidence for any reaction was observed and the suspension was evaporated to dryness (behind safety glass in a hood) and then dissolved in tetrahydrofuran (50 cc.). Chlorotrifluoroethylene (6 g.) was bubbled into the solution at room temperature. The solution darkened and some heat was evolved. The solution was poured into dilute hydrochloric acid (200 cc.; 5%) and this solution was steam distilled. No organic material, other than tetrahydrofuran, was collected, but black polymeric material (7 g.) remained as a residue.

b. A solution of ethoxyethynyl lithium in tetrahydrofuran was prepared on the same scale as above. Chlorotrifluoroethylene (6.0 g.) was bubbled slowly into the solution cooled in a dry ice/acetone bath at -20°. The solution was then allowed to warm up to room temperature over a period of 2 hours, after which it was worked up as described above. It was noted that some of the acetylide appeared not to have reacted as there was effervescence when the solution was added to the dilute hydrochloric acid solution. Analytical gas chromatography indicated some organic product had been distilled over during the steam distillation and this was purified by washing with water to remove tetrahydrofuran. This gave a compound (0.72 g., 10.5%) believed to be 3-ethoxy-1-chloro-1,2-difluoroprop-1-ene (Analysis Found: C, 39.2; H, 4.54. $C_5H_7ClF_2$ requires C, 38.4; H, 4.47.) b.p. 158°; n_D^{19} 1.4080. Polymeric residue (4.5 g.) was found in the steam distillation pot.

Reaction Between Lithium Acetylide and Chlorotrifluoroethylene

A precipitate of lithium acetylide, prepared by passing acetylene into a solution of butyllithium (15 g.), was dissolved in tetrahydrofuran and reacted with chlorotrifluoroethylene (ca. 40 g.) at 0° in the manner described above. A small quantity of monomeric material (ca. 5 g.) was isolated and preliminary spectroscopic evidence indicated that it was probably 4-chloro-3,3-difluorobut-3-en-1-yne ($CH{\equiv}C\text{-}CF{=}CFCl$). The major product was a polymeric gum.

Reaction Between Acetylene Grignards and Fluoroölefins

The mono- and di-Grignard reagents of acetylene were prepared as in the literature [106]. (1) Chlorotrifluoroethylene (excess) was bubbled into a solution of the mono-Grignard in THF (0.29 mole, 250 ml.) at room temperature. The mixture was hydrolyzed with water after standing for 15 hours. The organic layer was shown by gas chromatography to contain only the solvent. (2) 1,1-Dichlorodifluoroethylene (34 g., 0.245 mole) was added at 0° to the mono-Grignard in THF (0.2 mole, 250 ml.). The solution was stirred at room temperature for a further 4 hours. Hydrolysis and distillation gave a small amount of a compound whose infrared spectrum gave no indication of a triple bond. There was insufficient material for further identification. (3) 1,1-Dichlorodifluoroethylene (28 g., 0.21 mole) was added to a solution of the di-Grignard in diethyl ether (0.2 mole, 170 ml.) at 0°. The mixture was stirred at room temperature for a further 15 hours and then hydrolyzed. The ethereal layer was distilled to give a thick black residue.

Reaction Between 3-Bromopropynyl Lithium and Chlorotrifluoroethylene

A precipitate of 3-bromopropynyl lithium was formed by the addition of butyllithium in hexane (3.2 g. in 21.4 g. of solution) to propargyl bromide (5.9 g.) in hexane (100 cc.) at -10°. Most of the hexane was drawn off and the precipitate was dissolved in tetrahydrofuran. The solution was cooled to -40° and chlorotrifluoroethylene (6 g.) was bubbled in and the mixture worked up as described for ethoxyethynyl lithium; however, only polymeric material was obtained. The lithium salt was found to be explosive when dry.

Reaction Between 3,3,3-Trifluoropropynyl Lithium and Chlorotrifluoroethylene

Butyllithium (0.1 mole, 60 cc.) in hexane was added to a solution of 3,3,3-trifluoropropyne in hexane at -78°. A white precipitate was formed. Chlorotrifluoroethylene (ca. 20 g.) was added and the solution was permitted to warm up to room temperature after standing for 30 minutes at -78°. Dilute hydrochloric acid was added and the mixture was then transferred to a large flask for steam distillation. There was considerable polymeric material left as a residue but no monomeric material was isolated. It should be noted that a small amount of material which was on the side of the original reaction flask, after washing with dilute hydrochloric acid, caused a very violent explosion.

Reaction Between 3,3,3-Trifluoropropynyl Lithium and 1,1-Dichloro-2,2-difluoroethylene

The above lithium reagent (0.05 mole) was prepared in ether (200 ml.) and the olefin (0.05 mole) added in ether (30 ml.) at -78°. The solution was allowed to warm to room temperature. The only product was a brown insoluble solid.

Reaction Between Trifluorovinyl Lithium and Fluoroolefins

Bromotrifluoroethylene (34 g. 0.2 mole) was added to a stirred solution of butyllithium (0 18 mole) in hexane (solution weight, 76.0 g.) at -78°. 1,1,2-Trifluorobuta-1:3-diene (ca. 21 g., 0.19 mole) was added and the reaction mixture allowed to warm up to room temperature slowly. The mixture was treated with dilute hydrochloric acid. Inspection of the organic layer by analytical gas chromatography showed that no product, other than butyl bromide produced in the first stage of the reaction, was present.

Two reactions were carried out on the same scale and under similar reaction conditions with chlorotrifluoroethylene and bromotrifluoroethylene in place of the diene in the above experiment. In each case, no product was obtained.

Attempted Reactions Between Pentafluorophenyl Lithium and Fluoroolefins

Pentafluorophenyl lithium was prepared from pentafluorobromobenzene (5. g.) by direct metallation as described by Coe, Stephens and Tatlow (107).

In separate experiments, chlorotrifluoroethylene and tetrafluoroethylene was added in excess to a solution of pentafluorophenyl lithium in a Carius tube cooled in liquid nitrogen. The tube was sealed and allowed to warm to about 0°, at which point it was unsealed and the contents hydrolyzed with dilute hydrochloric acid. Inspection of the ether layer indicated the presence of pentafluorobenzene as the only significant product in both cases.

Reaction Between Pentafluorophenylmagnesium Bromide and Chlorotrifluoroethylene

a. In tetrahydrofuran. Bromopentafluorobenzene (5.0 g.) was added to a stirred mixture of magnesium (0.6 g.) in tetrahydrofuran (15 cc.). The reaction was initiated with iodine and refluxed for 2 hours. The solution was filtered through glass wool into a Carius tube cooled to -78°. Chlorotrifluoroethylene (2.7 g.) was added and the tube sealed. The tube was allowed to warm up to room temperature and shaken for 16 hours. The tube was unsealed and the contents poured into a stirred solution of sulphuric acid (2N, 25 cc.). Diethyl ether (50 cc.) was added and the ethereal layer separated. Analytical gas chromatography (D.N.P. and Si gum packings) indicated only ether and tetrahydrofuran. No pentafluorobenzene was present. Evaporation of the solvents gave a mobile gum.

The infrared spectrum of the gum had no C-H bond absorption but had absorptions at 1500 - 1540 cm^{-1} consistent with an aromatic nucleus and between 1000 - 1300 cm^{-1} consistent with C-F bonds.

b. In ether. The above experiment was repeated in a similar manner except that diethyl ether was used as solvent. On hydrolysis, pentafluorobenzene was formed, no other product being present.

Preparation of 1,2-Bis(pentafluorophenyl)tetrafluorocyclo-1-butene

a. With pentafluorophenyllithium. Pentafluorophenyllithium (from

C_6F_5Br (5 g.) in ether solution (ca. 50 cc.) was added to a solution of hexafluorocyclobutene (4.0 g.) at -50°. Reaction was immediately apparent. The solution was warmed to reflux point, cooled and worked up by usual procedures. Analytical gas chromatography of the product on a silicon gum packing showed one product of long retention time and no trace of C_6F_5H, indicating that all pentafluorophenyllithium has been used in the reaction. Evaporation of the solvent followed by sublimation gave a white waxy solid (1.5 g.). There was considerable polymeric residue. Recrystallization (pet. ether 30 - 60°) of the sublimed material gave 1,2-bis-(pentafluorophenyl)-tetrafluorocyclo-1-butene. m.p. 106 - 7° (Analysis Found: C, 41.74; H, none; F, 58.33. $C_{16}F_{14}$ requires C, 41.92; H, 0.00; F, 58.08%).

Infrared absorptions at 1655 cm^{-1} and at 15.25 and 1500 cm^{-1} are consistent with the olefinic and aromatic, respectively.

The nuclear magnetic resonance spectra were entirely consistent with the proposed structure.

b. <u>With pentafluorophenylmagnesium bromide</u>. V.p.c. analysis showed that with diethyl ether as solvent slight reaction occurred; however, the main compound present was pentafluorobenzene from the hydrolysis of the unreacted Grignard. The ratio of 1,2-di(pentafluorophenyl)tetrafluorocyclobutene and pentafluorobenzene was 1:5. Total reaction occurred with THF as solvent as no pentafluorobenzene was present after hydrolysis; however, on evaporation of the solvent a black gum was formed. Both reaction mixtures were combined and sublimed at 100° to give a white crystalline material (1.0 g.) 1,2-di(pentafluorophenyl)tetrafluorocyclobutene.

Vinylmagnesium Chloride and 1,1-Dichlorodifluoroethylene

1,1-Dichlorodifluoroethylene (0.05 mole, 7.0 g.) was added to a stirred solution of vinylmagnesium chloride in tetrahydrofuran (0.05 mole, 15.5 ml.) at 0° and stirring continued for one hour. The solution hydrolyzed (2N, H_2SO_4, 25 ml.) and the organic layer shown by analytical gas chromatography to contain only tetrahydrofuran and the original olefin.

Vinyllithium and 1,1-Dichlorodifluoroethylene

1,1-Dichlorodifluoroethylene (0.05 mole, 7.0 g.) was added to a stirred solution of vinyllithium (0.05 mole in 85 ml. of diethyl ether). After two hours at room temperature, the mixture was hydrolyzed (H_2SO_4, 2N, 50 ml.). The ethereal layer was shown by analytical gas chromatography to contain solvent and some unreacted olefin. Evaporation of the solvent gave a tar (5.0 g.).

Allylmagnesium Bromide and Fluoroölefins

a. Reaction with Chlorotrifluoroethylene, Bromotrifluoroethylene, Hexafluoropropene, 1,1,2-Trifluorobutadiene, and unsym-Dichlorodifluoroethylene

Allylmagnesium bromide in diethyl ether (150 ml., 0.25 mole) was placed in a three-necked flask with a stirrer and an acetone-dry ice condenser. The fluoroölefin (0.25 mole) was added to the cooled solution (-78°) over 0.5 hours and then allowed to warm to room temperature; stirring was continued for a further hour. The solution was hydrolyzed with sulfuric acid (100 ml. of *ca.* 6N) and the ether layer was separated, dried (Drierite), and distilled to obtain a new fluorodiolefin. The distillates were checked for purity by analytical vapor phase chromatography using a silicone elastomer column at 100°.

b. Reaction with Hexafluorocyclobutene

A reaction similar to the above gave 19 g. of the recovered butene (0.124 mole) and 15 g. of a brittle, black residue (36.89% fluorine) which was recovered from the reaction mixture by steam distillation.

c. Reaction with 1,1,2-Trifluoro-4-bromo-1-butene (17)

Run at half scale (0.125 mole), the reaction was stirred for 70 hours at room temperature. A similar reaction in tetrahydrofuran was refluxed for 5 hours before hydrolysis.

d. Reaction with Tetrafluoroethylene and Trifluoroethylene and the Reaction of Allylmagnesium Chloride with Tetrafluoroethylene

The olefin (0.125 mole) was vacuum condensed into a Fischer-Porter compatibility tube containing the Grignard reagent in diethyl ether (75 ml., 0.125 mole). The tube was sealed and shaken under the following conditions (temperature, time): (1) $CF_2=CF_2$ + $CH_2=CHCH_2MgBr$, room temperature, 17 hours; (2) $CF_2=CFH$ + CH_2CHCH_2MgBr, room temperature, 3 hours, 100°, 2 hours; (3) $CF_2=CF_2$ + $CH_2=CHCH_2MgCl$, room temperature, 65 hours.

The solutions were cooled and any unreacted gas condensed and identified by vapor phase chromatography. In the second reaction, 9.0 g. of trifluoroethylene (0.11 mole) was recovered. The solutions were then hydrolyzed with sulfuric acid (50 ml. of ca. 6N) and the ether layers were worked up as previously indicated.

Bromination of 3,4-Difluoro-1,3,6-heptatriene

The olefin (1.0 g.) was dissolved in carbon tetrachloride (5 ml.) and treated slowly with bromine until a slight excess was present. After washing with dilute sodium hydroxide and water, drying and evaporating the solvent, the product was identified as 1,2,6,7-tetrabromo-3,4-difluoro-3-heptene. Absorption peaks in the infrared spectrum at 5.77 and 5.90μ were associated with the cis and trans -CF=CF- group.

(Analysis Calcd. for $C_7H_8Br_4F_2$: C, 18.66; H, 1.78; Br, 71.11; F, 8.45. Found: C, 18.73; H, 1.75; Br, 71.47; F, 8.73%).

Benzylmagnesium Bromide and Fluoroölefins

(1) Benzylmagnesium bromide in diethyl ether (200 ml. 0.25 mole) was treated with chlorotrifluoroethylene (29.1 g., 0.25 mole) at room temperature for 36 hours. Chlorotrifluoroethylene (19.8 g., 0.17 mole) was recovered. After hydrolysis (100 ml. of 6N H_2SO_4), vapor phase chromatographic analysis showed the only product to be toluene.

(2) Benzylmagnesium bromide in diethyl ether (125 ml., 0.125 mole) was allowed to react with hexafluorocyclobutene (20.2 g., 0.125 mole). After stirring for 3 hours at room temperature, the solution was refluxed for 5 hours and worked up as indicated above.

Crotonylmagnesium Bromide and Chlorotrifluoroethylene

Crotonylmagnesium bromide in diethyl ether (200 ml., 0.25 mole) was refluxed with chlorotrifluoroethylene (29.1 g., 9.25 mole) for 36 hours.

The solution was processed as described above.

Anhydrous Magnesium Bromide and Fluoroölefins

Anhydrous magnesium bromide (7.5 g.), prepared by heating an equimolecular amount of $MgBr_2.6H_2O$ and ammonium bromide, was placed in a Carius tube with diethyl ether (50 ml.). Tetrafluoroethylene (12 g.) was vacuum transferred and the tube sealed. No reaction occurred after shaking at 70° for 72 hours. A similar experiment using 1,1,2-trifluoro-1,4-pentadiene (6.1 g.) and magnesium bromide (9.2 g.) was also unsuccessful.

The Reaction of Allylmagnesium Bromide with Pairs of Fluoroölefins

The two olefins (0.15 mole) were vacuum condensed into a Fischer-Porter compatibility tube containing allylmagnesium bromide (40 ml ; 0.15 mole), sealed and shaken at room temperature for between 16 and 20 hours.

The solution was cooled and any unreacted olefins condensed out and identified by v.p.c. The ether layer was separated and after hydrolysis with sulfuric acid (100 ml. of 6N) and dried (Drierite) and fractionated. The products were analyzed by v.p.c. and identified by their infrared spectrum. The results are shown in Table XII. The pressure reactions were carried out on the sample scale using an autoclave: nitrogen was introduced such that a pressure of 450 lb./in^2 was obtained.

Solubility of the Fluoroölefins in Ether

The pairs of fluoroölefins (0.15 mole each) were vacuum condensed into a Fischer-Porter tube containing ether (35 ml.), sealed and shaken at room temperature for 2 hours. The tube was turned upside down and some of the liquid condensed into a cold trap. This was analyzed by v.p.c. and the results shown in Table XI.

2. Preparation of Isopropenyl Lithium

Reaction of Trifluoropropene, Butyllithium and Acetone

Trifluoropropene (10 g., 0.104 mole) in diethyl ether (120 ml.) was cooled to -90° under dry nitrogen. Butyllithium in pentane (60 ml.) ether (60 ml.), precooled to -78°, was added over 10 minutes while the temperature was maintained at -95° ± 2° for an additional one hour.

chlorotetrafluoroacetone (dropwise) under a dry ice condenser. After all the acetone had been added, the mixture was allowed to warm to room temperature and then hydrolyzed with dilute hydrochloric acid. The ethereal solution was separated, dried ($MgSO_4$) and fractionally distilled. In each case an azeotrope of the appropriate ether and the carbinol was obtained. Final purification was achieved by preparative gas chromatography, with the carbinols from sym-dichlorotetrafluoroacetone separation on a silicone gum packing and with those derived from hexafluoroacetone on a dinonylphtalate packing. Table XVIII gives the reactants and results.

b. Reaction Between 4-Bromo-1,1,2-trifluoro-1-butene, Magnesium, and Trimethylchlorosilane

(1) 4-Bromo-1,1,2-trifluorobut-1-ene (11.9 g.) was added dropwise to a suspension of magnesium (3.0 g.) in diethyl ether (100 cc.) at room temperature. After the reaction appeared to have been initiated, chlorotrimethylsilane (5 g.) was added. Eventually a gummy material formed around the remaining magnesium and reaction ceased. Fresh magnesium was added but no further reaction was apparent. The ether solution was inspected by analytical gas chromatography which indicated the formation of two products, neither having the retention time of the desired trimethyl-3,4,4-trifluoro-but-3-enylsilane which was apparently not formed. The supernatent ether solution was poured off and the gummy residue washed with ether, the ether was poured off and combined with the original solution. The ether solution was fractionally distilled to remove excess ether. The residue was separated by preparative gas chromatography (Si gum: Chromosorb) to give 1,1,2,7,8,8-Hexafluoroocta-1:7-diene (2.6 g., 38.2%) b.p. 132°, n_D^{19} 1.3615 (Analysis Found: C, 44.24; H, 3.82. $C_8H_8F_6$ requires C, 44.03; H, 3.67%). Infrared and ^{19}F NMR spectra were consistent with the proposed structure.

(2) The above experiment was repeated on 1/5 scale using tetrahydrofuran as solvent for the reaction. Analytical gas chromatography indicated that the same two products were formed. Also, a third product in low yield, having the same retention time as trimethyl-3,4,4-trifluorobut-3-enyl-

TABLE XVII

YIELDS AND PROPERTIES OF CARBINOLS FORMED BY REACTION OF FLUORINE-CONTAINING VINYL GRIGNARD REAGENTS WITH CARBONYL COMPOUNDS

	Ketone	Organometallic Reagent	Solvent	Carbinol	b.p. Azeotrope	Yield %
A	$(CF_2Cl)_2CO$	$CF_2:CFMgBr$	THF	$CF_2:CF.C(CF_2Cl).OH$	$55^{\circ}/2$ mm.	55
B	$(CF_3)_2CO$	$CF_2:CFMgBr$	THF	$CF_2:CFC(CF_3)_2.OH$	106 - 108	65
C	$(CF_3)_2CO$	$CF_2:CHMgBr$	THF	$CF_2:CH{\cdot}C(CF_3)_2{\cdot}OH$	99 - 100	5-10

Analytical and Physical Data

	Found C	Found H	Found F	Theory C	Theory H	Theory F	b.p.	n_D^t	Infrared Olefin absorption	NMR
A	21.17	0.45	47.11	21.35	0.43	47.4	121°	$1.3666^{20.5}$	5.63	consistent
B	24.19	0.29	68.72	24.2	0.4	68.95	68°	$1.2965^{20.5}$	5.59	consistent
C	not obtained pure enough for analysis NMR detected impurity						...	....	5.67	consistent

silane, was observed. In the third experiment on the same scale as the above, in the absence of chlorotrimethylsilane, analytical gas chromatography indicated the formation of the two products observed in the first experiment.

c. Attempted Preparation of Perfluoroallyl Lithium

Reaction of Perfluoroallyl Bromide with Methyllithium

Methyllithium (10 ml., 0.91 mole 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. V.p.c. 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 v.p.c. (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 v.p.c. 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.

d. Preparation of 2,2-Difluorovinyl Lithium and Reactions of Various Carbonyl Compounds and Triethylchlorosilane

A solution of butyllithium (0.077 mole) in the appropriate solvent

(40 ml.) was cooled to -78° and then added dropwise in four aliquots to a cooled, (-78 to -105°), solution of 2,2-difluorovinyl bromide (0.077 mole) in ether (40 to 100 ml.). After the addition of each of the above aliquots, dropwise addition of one quarter of a solution of the appropriate carbonyl compound or silane (0.077 mole) in ether (40 ml.) was executed. The solution was stirred while allowing to warm up to room temperature. With the carbonyl compound, the solution generally became colored around room temperature (yellow → red).

In the cases of triethylchlorosilane and acetyl chloride, a white solid which was precipitated, (probably LiCl), was filtered off and the solutions dried over $CaSO_4$. In reactions involving carbonyl compounds, however, any lithium salts formed were hydrolyzed by addition of water (20 ml.) followed by 6N hydrochloric acid (20 ml.). Usually a white solid was formed which redissolved on stirring. The organic layers were separated and dried over $MgSO_4$ or $CaSO_4$. Further work-up procedures are described below.

(1) Benzaldehyde

Solvents and butyl bromide (30%) were removed from the dried organic layer by distillation. V.p.c. of the residue indicated the presence of benzaldehyde and three other high-boiling products. Benzaldehyde was removed by dissolving the residue in a little ether and shaking with a saturated solution of sodium bisulphite (3 X 17 ml.). Attempts to separate by gas-liquid preparative chromatography were unsuccessful. The experiment was repeated several times under varying conditions of temperature and rates of addition of the reactants but in no case did one product predominate nor was any separation possible. Maximum yield of butyl bromide was 30%.

(2) Acetone

Attempted product separation by distillation resulted in obvious product decomposition as the residue darkened considerably and a smell of hydrogen fluoride was observed along with some glass etching. The residual mixture was shaken with 10% aqueous sodium bicarbonate (3 X 30 ml.)

and the aqueous layer acidified and extracted with ether. The latter was removed by distillation after drying ($MgSO_4$). The residue was an off-white solid which, on vacuum sublimation, gave white needles m.p. 66 - 68°. β,β-Dimethylacrylic acid has m.p. 69°(108). Yield 7 - 10% (2 exp.). The original organic residue was distilled, affording only butyl bromide (16%).

(3) Cyclohexanone

V.p.c. of the yellow organic solution indicated the presence of two products A and B with an A:B peak area ratio of 6:1. The retention times of A and B were inconsistent with the theory that A was due to the desired alcohol and B to the n-butyl adduct of cyclohexanone. About half of the solvents were removed by distillation. The residual solution had turned purple in color. The remaining solvents and butyl bromide were removed by vacuum distillation and the purple residue allowed to stand at room temperature for a few minutes. Heat was generated in the flask and hydrogen fluoride was evolved. GLC of the residue showed that the A:B peak area ratio was 1:1 at that stage, thus indicating the decomposition of the product giving peak A.

The residue was dissolved in a little ether (10 ml.) and shaken with saturated sodium bicarbonate solution (3 X 30 ml.). The latter was separated and acidified. The precipitated solid was removed by filtration and recystallized (hexane) to give white needles m.p. 90°, thus indicating that the product was cyclohexylidine acetic acid (lit.(109) 90 - 91°). The acid was obtained in 25% yield.

Fractionation of the original distillate afforded butyl bromide in 34% yield.

(4) Acetyl Chloride

Solvents were removed by distillation and the residual products separated by GLPC. This afforded ethyl acetate (9%), and butyl bromide (13%). The two products were identified by comparison of their infrared spectra and v.p.c. retention times with those of authentic samples.

(5) Triethylchlorosilane

V.p.c. of the solution indicated the presence of butyl bromide, a considerable amount of unreacted triethylchlorosilane and a small amount of a product (C) of intermediate retention time. The solvents were removed by distillation under vacuum. Considerable darkening of the residual solution indicated that product (C) was decomposing even at room temperature and this was confirmed since the peak due to C had disappeared on the v.p.c. trace. The distillate was fractionated, giving butyl bromide (24%), and fractionation of the residue afforded only unreacted triethylchlorosilane (47%).

e. Preparation of 2,2-Difluorovinylmagnesium Bromide and Its Reaction with Trimethylchlorosilane

(1) 2-Bromo-1,1-difluoromethylene (42 g.) was bubbled slowly into a well-stirred suspension of magnesium (10 g.) in anhydrous tetrahydrofuran (250 cc.). After initiation of the reaction the flask was cooled in an acetone/dry ice bath at -25°. The temperature of the bath was kept between -20 and -25° throughout the experiment. The mixture was stirred at -20° for 30 minutes after all the ethylene had been added. Trimethylchlorosilane (12 g.) in tetrahydrofuran (50 ml.) was quickly added to the cooled solution, and after addition the solution was allowed to warm up to room temperature. Water (20 cc.) was added and the mixture fractionally distilled. In the fraction boiling between 30° and 66°, three main components were observed consistent with 2-bromo-1,1-difluoroethylene, a product and tetrahydrofuran. The fraction was washed with water twice to remove the tetrahydrofuran and then separated by preparative scale gas chromatography to give:

(i) 2-Bromo-1,-difluoroethylene (not collected)

(ii) Trimethyl-(2,2-difluorovinyl)silane (2.3 g., 5.0%) (Analysis Found: C, 44.22; H, 7.56. $C_5H_{10}F_2Si$ requires: C, 44.1; H, 7.36%) b.p. 58.5°, n_D^{19} 1.3664. Infrared and ^{19}F NMR spectra were consistent with this structure.

(2) The above experiment was repeated in a similar fashion except

that trimethylchlorosilane was added before the addition of 2-bromo-1,1-difluoroethylene. The quantities used were as before and the reaction gave trimethyl-2,2-difluorovinylsilane (7.8 g., 17.5%).

f. Attempted Preparation of 1-Fluorovinylmagnesium Bromide

(1) 1-Bromo-1-fluoroethylene (5 g.) was bubbled into a well-stirred suspension of magnesium (4.5 g.) in tetrahydrofuran (150 cc.), activated by a few drops of ethylene dibromide. No reaction could be induced at this stage. A further 10 g. of 1-bromo-1-fluoroethylene was bubbled into the solution which was simultaneously heated to reflux. No reaction occurred.

(2) A similar reaction using methyl bromide (1 g.) to initiate the reaction failed to cause any reaction between magnesium and 1-bromo-1-fluoroethylene.

g. Attempted Preparation of 1-Fluorovinyl Lithium via an Exchange Reaction Involving Butyllithium and 1-Fluorovinylbromide. Reaction of the above Lithium Reagent with Ethylmethyl Ketone and Triethylchlorosilane

(1) Preparation of 1,2-Dibromo-1-fluoroethane

Vinyl fluoride was bubbled into bromine (100 g., 0.625 mole) at a rate sufficient to ensure complete olefin consumption. During this process the reaction flask was irradiated with light and the contents stirred. When all the bromine had reacted, the solution became light yellow in color. The product was distilled b.p. 121 - 122° (lit.(110) 122.5°). Weight = 115 g. (88% yield).

(2) Reaction of 1,2-Dibromo-1-fluoroethane with Alkali

The above dibromide (103 g., 0.5 mole) was added dropwise to potassium hydroxide pellets (100 g., 1.8 mole). No reaction was observed until the flask was heated (vigorous stirring) to 60°. Heating was continued at 60 - 80° until no more gaseous product was evolved (3 hours). The volatile products were condensed in a dry ice-acetone cooled trap which necessarily contained an inhibitor (α-pinene) to prevent polymerization. Phosphorus pentoxide was added to the contents of the trap and an attempt was made to distill the product. This was achieved only with difficulty since there was presumably some monofluoroacetylene present which decomposed with accompanying minor explosions, flashes and carbon deposition. Consequently, the yield of 1-fluorovinyl bromide b.p. 6 - 8° (lit.[111] 6.8°) from successive runs varied considerably. Attempts to repeat this experiment using mineral oil (150 ml.) as a solvent gave similar results.

1-Fluorovinyl bromide was not isolated when 1,2-dibromo-1-fluoroethane was treated with potassium hydroxide in refluxing ethanol for 6 hours.

h. Preparation of 1-Fluorovinyllithium and Reaction with Ethyl Methyl Ketone

A cooled (-78°) solution of butyllithium (0.075 mole) in hexane was added dropwise in four aliquots to a solution of 1-fluorovinylbromide (0.75 mole) in ether (100 ml.) which was also maintained at -78°. Following the addition of each of the above aliquots, one quarter of a solution of ethyl methyl ketone (0.075 mole) in ether (30 ml.) was added dropwise. On addition of the first aliquot of the ketone solution, a milky white suspension was formed. This disappeared following the addition when the temperature had reached -3°. At room temperature, water (20 ml.) and hydrochloric acid (20 ml., 6N) were added. A small amount of white precipitate formed and redissolved. The organic layer was separated, dried ($CaSO_4$), and the solvents removed by distillation. Further distillation afforded butyl bromide, (24%) and five other products which were inseparable either by distillation of GLPC.

The reaction was repeated adding the butyllithium and ketone solutions at -30 → -25° with similar results.

i. Reaction of 1-Fluorovinyllithium with Triethylchlorosilane

1-Fluorovinyllithium (0.075 mole) was prepared as described in the previous experiment, except that a solution of butyllithium in a mixed solvent (pentane 50 ml. - ether 50 ml.) was employed. In this case, all the butyllithium solution was added before any of the triethylchlorosilane. After the addition of all of the organometallic reagent, a white cloudiness developed. The mixture was allowed to stand for 30 minutes and a solution of triethylchlorosilane (0.075 mole) in ether (50 ml.) was then added dropwise. The white cloudiness persisted. The solution was permitted to warm up to room temperature overnight during which time a white water soluble, precipitate formed. The latter was removed by filtration, the filtrate dried over $CaSO_4$ and the organic solvents were removed by distillation. GLC of the green colored residue indicated the presence of butyl bromide, an unknown product, and unreacted triethylchlorosilane. Water was added to hydrolyze the latter product to render GLPC separation of the desired product easier. A sample of the unknown compound was isolated by this means and was shown to be triethyl ethynyl silane, $(CH_3CH_2)_3SiC\equiv CH$. The infrared and ^1H NMR spectra were consistent with this structure. (Analysis Calcd. for $(CH_3CH_2)_3SiC\equiv H$: C, 68.52; H, 11.42. Found: C, 68.80; H, 11.61%) n_D^{23} 1.4325, lit. (112) n_D^{20} 1.4302. Product yields from GLC; -butyl bromide (36%); triethylethynylsilane (30%).

Preparation and Reactions of Trifluoro-isopropenyl Lithium

j. Preparation of Trifluoro-isopropenyl Bromide

Potassium hydroxide pellets (100 g.) were placed in a 3-necked flask fitted with a dropping funnel, stirrer, and distillation apparatus. Trifluorodibromopropane (100 g., 0.39 mole) was dropped onto the stirred potassium hydroxide which was cooled in an ice-bath. When all the dibromide was added, the ice-bath was replaced by a water bath and the temperature increased until the product began to distill out of the reaction vessel. Occasional immersion of the flask in the ice-bath was required to control the rate of reaction.

Wt. of product, $CF_3CBr=CH_2$, was 68 g., 0.38 mole (99%)
b.p. 33° (Lit. (83) b.p. 33°)

k. Attempted Metallation of Trifluoro-isopropenyl Bromide Followed by Carbonation

Trifluoro-isopropenyl bromide (4.3 g., 0.025 mole) and dry diethyl ether (10 ml.) were placed in a 3-necked flask, fitted with a dropping funnel, gas-lead and drying tube, and cooled to -78° under an atmosphere of dry nitrogen. Butyllithium (0.025 mole) in mixed solvent (ether (10 ml.)

/hexane (15.5 ml.)) was added over 30 minutes to the bromo-olefin solution at -78°. The mixture was allowed to stand for 50 minutes at -78°, then warmed to -60°, when dry carbon dioxide was bubbled into the reaction which was allowed to warm to room temperature with the continuous passage of carbon dioxide. The reaction mixture was treated with hydrochloric acid (1:1) (20 ml.), the solution was made alkaline with dil. sodium hydroxide solution, and the layers separated. The organic layer was further extracted with sodium hydroxide solution. The aqueous extracts were combined, acidified with hydrochloric acid and extracted with ether. These ether extracts were dried ($CaSO_4$) and the solvent removed by distillation, leaving a viscous oil (0.1 g.) as residue, which was not the desired carboxylic acid.

The original organic solution from the reaction contained an insoluble white solid (1.00 g.), which was shown to be lithium fluoride together with organic polymeric material.

1. <u>Attempted Metallation of Trifluoro-isopropenyl Bromide Followed by Reaction with Benzaldehyde</u>

Butyllithium (0.025 mole) in mixed solvent (ether (20 ml.)/hexane (17.3 ml.)) was cooled to -78° under an atmosphere of dry nitrogen. Trifluoroisopropenyl bromide (5 g., 0.0285 mole) in diethyl ether (10 ml.) was added dropwise with stirring. The reaction temperature was maintained at -78° for 30 minutes and then benzaldehyde (3.1 g., 0.025 mole) in diethyl ether (10 ml.) was added. The temperature was allowed to warm slowly to that of the room and hydrochloric acid (1:1) (20 ml.) was added. A white insoluble solid in the aqueous layer was filtered (0.45 g.) and the aqueous layer extracted with ether. The combined ethereal solutions were dried ($CaSO_4$) and the solvent removed by distillation. V.p.c. analysis showed that butyl bromide had been produced together with a small amount (~5%) of high-boiling compound. Unreacted benzaldehyde was also present. The high-boiling product was separated by preparative scale v.p.c. and infrared spectroscopy suggested that it was not a carbinol but probably a fluoroolefin containing a butyl group, e.g., $CF_2=CBr-CH_2-C_4H_9$.

The insoluble solid was shown to be LiF, produced in 60 - 65% yield.

m. Reaction of Trifluoro-isopropenyllithium with Benzaldehyde

Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in dry diethyl ether (50 ml.) was cooled to -95° under dry nitrogen. Butyllithium (0.057 mole) in mixed solvent (hexane (34.6 ml.)/ether (50 ml.)), precooled to -78°, and benzaldehyde (6.2 g., 0.057 mole) in ether (15 ml.) were added alternatively in four aliquots each, the benzaldehyde solution being added immediately after the butyllithium solution. After the final addition the temperature was maintained between -90° and -95° for 2 hours and then allowed to warm very slowly to room temperature. Water (15 ml.) was added, causing a dense white precipitate to form, followed by aqueous hydrochloric acid (1:1) (15 ml.) which redissolved the solid to give a pale green solution. The organic layer was separated, dried, and most of the solvent removed by distillation. V.p.c. showed the presence of butyl bromide, together with an approximately equimolar amount of high-boiling product as well as a small quantity of much higher boiling material. No benzaldehyde was present in the reaction product. Fractionation, at atmospheric pressure, gave: butyl bromide (2.6 g., 0.0190 mole, 33% yield), and at reduced pressure, (a) α-(trifluoro-isopropenyl) benzyl alcohol, b.p. 122°/21 mm. Hg, $n_D^{22.5}$ 1.4746 (3.7 g., 32% yield). (Analysis Found: C, 59.65; H, 4.6; F, 27.96. $C_{10}H_9F_3O$ requires C, 59.4; H, 4.45; F, 28.2%.) The infrared ^1H and ^{19}F NMR spectra were consistent with this structure. and,

(b) α-butyl benzyl alcohol, b.p. 95°/1 mm. Hg., (1.2 g., 13%) (Analysis Found: C, 80.44; H, 8.7. $C_{11}H_{16}O$ requires C, 80.5; H, 9.7%)

n. Reaction of Trifluoro-isopropenyl Lithium with Acetone

Trifluoro-isopropenyl bromide (15 g., 0.085 mole) in diethyl-ether (30 ml.) was cooled to -90° under dry nitrogen. Butyllithium (0.085 mole) in mixed solvent (hexane (51.9 ml.)/ether (50 ml.)) and acetone (5 g., 0.085 mole in ether (10 ml.) were added aternatively, dropwise, with stirring, in five aliquots each. The temperature was maintained at -90° → -80° for a further one and one-half hours and then allowed to warm slowly to that of the room. Water (10 ml.), followed by hydrochloric acid (1:1) (20 ml.) were added. The organic layer was separated and the aqueous layer extracted with ether. The combined organic solutions were dried ($CaSO_4$) and analyzed by v.p.c. Butyl bromide and an approximately equivalent amount of product were present, together with a very small quantity (~2%) of a high-boiling compound. Fractional distillation gave: butyl bromide, 5. 5., (43%), and dimethyl(trifluoro-isopropenyl) carbinol, b.p. 116 - 117°, $n_D^{22.5}$ 1.3773. (Analysis Found: C, 46.92; H, 6.00; F, 36.83. $C_6H_9F_3O$ requires C, 46.7; H, 5.85; F, 37.0%.) The infrared ^{1}H and ^{19}F NMR spectra were consistent with the structure.

Dehydration of Dimethyl(Trifluoro-isopropenyl) Carbinol

Dimethyl(trifluoro-isopropenyl) carbinol (1.3 g., 0.00845 mole) was dropped onto excess phosphorus pentoxide at 0°, in a distillation apparatus. The mixture was heated slowly to 120° during which time a colorless liquid distilled out of the reaction flask. V.p.c. showed this product to be 97% pure. Redistillation from phosphorus pentoxide gave pure 2-trifluoromethyl-3-methyl-butadiene, b.p. 64 - 65°, (0.56 g., 49%). (Analysis Found: C, 52.88; H, 5.02; F, 41.82. $C_6H_7F_3$ requires C, 53.0; H, 5.15; F, 41.9%.) The infrared, ^{1}H and ^{19}F NMR spectra were consistent with this structure. A sample was sealed in a tube and after several days at room temperature gave a solid elastomeric material.

c. Reaction of Trifluoro-isopropenyl Lithium With Acetaldehyde

Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in diethyl ether (50 ml.) was cooled to -100° under dry nitrogen. Butyllithium (0.057 mole) in mixed solvent (hexane (34.6 ml.)/ether (50 ml.)), precooled to -78° and acetaldehyde (2.5 g., 0.057 mole) in ether (20 ml.) were added alternatively with stirring in four aliquot portions each. The temperature was maintained at -100° ± 2° for a further 30 minutes and then allowed to warm to -78°, where it was maintained for 4 hours before allowing it to rise to that of the room. Water (20 ml.) followed by hydrochloric acid(1:1) (40 ml.) were added and the organic layer separated and dried ($CaSO_4$). The solvent was removed by distillation and v.p.c. analysis showed the presence of butyl bromide together with an approximate equivalent amount of product. The product was isolated by prep. scale v.p.c. (D.N.P. 100°) and shown to be 2-trifluoromethyl-but-1-en-3-ol, b.p. 110 - 111°, $n_D^{22.5}$ 1.3646, (3.5 g., 44% yield). (Analysis Found: C, 42.57; H, 4.93; F, 40.54. $C_5H_7F_3O$ requires C, 42.8; H, 5.0; F, 40.75%). The infrared, ^{1}H and ^{19}F NMR spectra were consistent with this structure.

Dehydration of 2-Trifluoromethyl-but-1-en-3-ol

2-Trifluoromethyl-but-1-en-3-ol (1.1 g., 0.00846 mole) was dropped onto phosphorus pentoxide cooled to 0° in a distillation apparatus. The temperature was increased slowly to 110°, causing a colorless liquid product to distill from the reaction flask.

Redistillation gave 2-trifluoromethylbutadiene, b.p. 34 - 35°. (lit. b.p. 35 - 35.5°). (0.8 g., 84% yield). The infrared, ^{1}H and ^{19}F NMR spectra were consistent with this structure.

p. Reaction of Trifluoro-isopropenyl Lithium and Ethyl Methyl Ketone

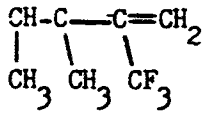
Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in diethyl ether (100 ml.) was cooled to -90° under dry nitrogen. Butyllithium (0.057 mole) in hexane (34.6 ml.)/ether (60 ml.), precooled to -78°, and ethyl methyl ketone (4.16 g., 0.057 mole) in ether (50 ml.), added alternatively in four aliquots each while maintaining the temperature at -90°. The mixture was allowed to warm to -78° and was maintained here for 3 hours before warming to room temperature. The reaction mixture became orange colored but clear. Water (25 ml.) was added to give a white precipitate which dissolved on stirring. Hydrochloric acid (1:1) (20 ml.) was added and the layer separated. The aqueous layer was extracted with ether, the ethereal solutions combined, dried ($CaSO_4$), and the solvent removed by distillation. Analytical v.p.c. showed the presence of butyl bromide and one higher boiling product. Fractional distillation yielded, butyl bromide, 6.9 g., (88.5%) and ethyl methyl (trifluoro-isopropenyl) carbinol, b.p. 130 - 131°, 4.0 g., (42%). (Analysis $C_7H_{11}OF_3$ requires C, 50.0; H, 6.55; F, 33.9%. Found: C, 50.16; H, 6.70; F, 33.86%. The infrared, ^{1}H and

^{19}F NMR spectra were consistent with this structure.

Dehydration of Ethyl Methyl (trifluoro-isopropenyl) Carbinol

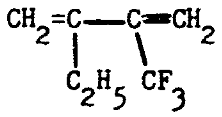
Ethyl methyl(trifluoro-isopropenyl) carbinol (1.0 g., 0.006 mole) was dropped onto phosphorus pentoxide at 0°. The mixture was heated slowly to 130°, causing a liquid to distill between 70 - 90°.

This product was shown by infrared, ^1H and ^{19}F NMR spectroscopy to be a 3:2 isomeric mixture of butadienes,



$\underset{CH_3}{CH}-\underset{CH_3}{C}-\underset{CF_3}{C}=CH_2$

and



$CH_2=\underset{C_2H_5}{C}-\underset{CF_3}{C}=CH_2$

Yield of product 0.7 g. (78%)

(Analysis $C_7H_9F_3$ requires C, 56.0; H, 6.0; F, 38.0% Found: C, 55.74; H, 5.7; F, 38.23%).

q. Reaction of Trifluoro-isopropenyl Lithium and Acetophenone

Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in diethyl ether (150 ml.) was cooled to -110° $\pm$ 3° under dry nitrogen. Butyllithium (0.057 mole) in pentane (35 ml.)/ether (40 ml.), precooled to -78°, was added over 5 minutes. After a further 10 minutes, during which the reaction temperature was allowed to attain -100°, acetophenone (6.84 g., 0.057 mole) in ether (20 ml.) was added and the temperature allowed to rise slowly to that of the room. Aqueous hydrochloric acid (1:1) (40 ml.) was added, the layers separated, the aqueous layer extracted with ether, the ethereal solutions combined, dried ($CaSO_4$), and the solvent removed by distillation. Analytical v.p.c. showed some unreacted acetophenone together with a major and a minor product of greater retention times.

The mixture was separated by prep. scale v.p.c. (Carbowax, 200°) to give: Butyl bromide, 6.0 g. (77%), acetophenone 0.9 g. (13%) and the major product, phenylmethyl(trifluoro-isopropenyl) carbinol b.p. 210 - 211°, 6.2 g. (51%). (Analysis $C_{11}H_{11}OF_3$ requires C, 61.2; H, 5.1; F, 26.4%. Found: C, 61.06; H, 5.1; F, 26.63%). The infrared, ^1H and ^{19}F NMR spectra were consistent with this structure.

The minor product (<5% yield) gave an infrared spectrum which suggested it might be butylphenylmethyl carbinol.

Dehydration of Phenylmethyl(trifluoro-isopropenyl) Carbinol

Phenylmethyl(trifluoro-isopropenyl) carbinol (1.2 g., 0.00556 mole) was heated with phosphorus pentoxide in vacuum (0.5 mm. Hg) to 160° for 30 minutes. The product was distilled from the system. This process was repeated three times to give 2-trifluoromethyl-3-phenyl-butadiene, b.p. approx. 190° (decomp.), 0.9 g. (82%). (Analysis $C_{11}H_9F_3$ requires C, 66.7; H, 4.55; F, 28.8. Found: C, 66.58; H, 4.70; F, 29.05%).

r. Reaction of Trifluoro-isopropenyl Lithium with Trifluoroacetone

Trifluoro-isopropenyl bromide (20 g., 0.114 mole) in diethyl ether (150 ml.) was cooled to -115° ± 3° under dry nitrogen. Butyllithium (0.114 mole) in pentane (70 ml.) precooled to -78° was added over 10 minutes while maintaining the temperature at -115° ± 3°. After allowing the reaction to attain -105° during 15 minutes, trifluoroacetone (12.8 g., 0.114 mole) in ether (30 ml.) was added, and the mixture allowed to warm slowly to room temperature. Hydrochloric acid (1:1) (40 ml.) was added, the ethereal layer separated, dried, and the solvent removed by distillation. Analytical v.p.c. showed two products as well as butyl bromide. Fractionation, followed by prep. scale v.p.c., to give pure samples, yielded a. butyl bromide 6.2 g., (45%). b. 1,1,1,5,5,5-hexafluoro-2-methyl-pentan-4-on-2-ol, 2.6 g. (16.3%) (Analysis $C_6H_6O_2F_6$ requires C, 32.18; H, 2.68; F, 50.80. Found: C, 32.38; H, 2.80; F, 50.68%). c. butylmethyltrifluoromethyl carbinol, b.p. 135 - 6°, 2.6 g., (10%) (Analysis $C_7H_{13}OF_3$ requires C, 49.4; H, 7.65; F, 33.4. Found: C, 49.18; H, 7.65; F, 38.20%). d. crude pyran derivative (0.1 g.), which on recrystallization from pentane gave m.p. 94 - 95°. The infrared, ^1H and ^{19}F NMR spectra were consistent with the above structures.

Preparation of 1,1-Difluoroallene

Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in diethyl ether (30 ml.) was cooled to -90° under dry nitrogen. Butyllithium (0.057 mole) in mixed solvent (hexane (34.6 ml.)/ether (40 ml.)) was added dropwise with stirring and the temperature maintained at -90 ± 2° for a further 30 minutes, before allowing the reaction to warm to room temperature. The over-gases were condensed in an acetone/dry ice trap. The reaction mixture became dark-colored at approximately -30° and precipitation of a solid material increased as the temperature rose.

At room temperature, water (40 ml.) was added and the mixture filtered to give the solid (1.4 g.) which was shown to be lithium fluoride (~95%) together with some polymeric organic material.

The organic layer was separated and the aqueous layer extracted with ether. The ethereal solutions were combined and dried ($CaSO_4$). V.p.c. showed only the presence of ether, hexane and butyl bromide. Fractional distillation gave butyl bromide (5.8 g., 74%).

The condensed over-gases were distilled at low temperatures to give difluoroallene, b.p. -20° → -21°. (lit. -20°), (3.1 g., 72%).

The infrared spectrum of this compound was identical to that of an authentic sample of difluoroallene.

A small amount of difluoroallene was sealed in a tube and allowed to stand at room temperature for several days to give a viscous polymeric semi-solid material.

s. Reaction of Trifluoro-isopropenyl Lithium with Carbon Dioxide

Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in diethyl ether (150 ml.) was cooled to -110° ± 3° under dry nitrogen. Butyllithium (0.057 mole) in pentane (35 ml.)/ether (40 ml.), precooled to -78°, was added over 5 minutes while maintaining the temperature at -110° ± 3°. The reaction mixture was allowed to warm to -100° over 15 minutes and dry carbon dioxide bubbled into the system. The introduction of carbon dioxide was continued until the temperature attained -78°, and the temperature allowed to rise to that of the room. Hydrochloric acid (1:1) (40 ml.) was added and the layers separated. The aqueous layer was extracted with ether (3 X) and the total ethereal solutions combined and dried. Distillation gave butyl bromide, 5.3 g., (68%) and a white crystalline residue of crude acid, 4.5 g., (56%). A pure sample of the acid was obtained by prep. scale v.p.c. (Silicone elastomer, 140°) and shown to be 2-trifluoromethyl-acrylic acid, m.p. 50 - 1° (lit. 50.2°).

The infrared, ^{1}H and ^{19}F NMR spectra were consistent with this structure.

t. Reaction of Trifluoro-isopropenyl Lithium and Triethylchlorosilane

Trifluoro-isopropenyl bromide (10 g., 0.057 mole) in diethyl ether (150 ml.) was cooled to -110° ± 3° under nitrogen. Butyllithium (0.057 mole) in pentane (35 ml.)/ether (45 ml.), precooled to -78°, was added over 5 minutes while maintaining the temperature at -110° ± 3°. The mixture was allowed to warm to -100° over 20 minutes, and triethylchlorosilane (8.58 g., 0.057 mole) in ether (40 ml.) was added over 5 minutes, while maintaining the temperature at -100°. The reaction mixture was then allowed to attain room temperature. A dense white precipitate formed, was filtered, dried and weighed (1.6 g.). This solid was boiled with water, the insoluble component filtered, dried and re-weighed (0.9 g.). This was shown to be lithium fluoride (61%). The aqueous solution contained lithium chloride (29%). The ethereal reaction mixture was distilled to give: a. butyl bromide 5.9 g. (~16%) b. impure product 0.8 g. (~11%) and unreacted triethyl chlorosilane 5.9 g. (69%). A pure sample of the product was obtained by prep. scale v.p.c. (Silicone gum rubber, 110°) and shown to be triethylfluorosilane, b.p. 109° (lit. b.p. 109 - 110°). This compound had an infrared spectrum identical to that of an authentic sample of triethylfluorosilane. The ^{1}H and ^{19}F NMR spectra were consistent with this structure.

u. Preparation and Reactions of 3,3,3-Trifluoropropynyl Lithium

Preparation of 1,1,1-Trifluoropropyne

The above acetylene was prepared in high yield (70 - 80%) by zinc dust dehalogenation of 1,1,2-trichloro-3,3,3-trifluoropropene-1 in dimethylacetamide (93).

v. Preparation of 3,3,3-Trifluoropropynyl Lithium and Reaction with Carbonyl Compounds or Triethylchlorosilane

A cooled (-78°) solution of butyllithium (0.05 mole) in a mixed solvent (pentane 32 ml., ether 32 ml.) was added dropwise to a solution of

1,1,1-trifluoropropyne (0.05 mole) in ether (120 ml.) at -78°. The reaction mixture was stirred for 30 minutes at this temperature and then warmed to -30° before being recooled to -78°. At this stage, a solution of the carbonyl compound (0.05 mole)* in ether (30 ml.) was added and the reaction mixture allowed to warm slowly to room temperature.

Water (20 ml.) and 6N hydrochloric acid (20 ml.) were added. The white precipitate usually formed initially and redissolved on stirring. The organic layer was separated, dried over calcium sulphate, and the solvents removed by distillation. The desired product was usually obtained by further distillation.** A pure sample was isolated using preparative scale v.p.c.

*Carbon dioxide (Xs) was bubbled into the reaction flask after passing through a calcium sulphate drying tube. When using ethyl acetate or acetyl chloride, a 2:1 ratio of 3,3,3-trifluoropropynyl lithium to carbonyl compound was employed.

**4,4,4-trifluorobut-2-ynoic acid was isolated by extraction with a saturated sodium bicarbonate solution after solvent removal. Acidification of the latter afforded the acid which was extracted in ether. The extracts were dried ($CaSO_4$) and the solvent removed. A pure sample of the acid, m.p. 40 - 42°, was obtained by vacuum sublimation. The S-benzyl thiouronium salt was prepared, m.p. 147°, and submitted for analysis.

The yields and properties of the compounds obtained are given in Table XVIII.

TABLE XVIII

REACTIONS OF 3,3,3-TRIFLUOROPROPYNYL LITHIUM WITH VARIOUS CARBONYL COMPOUNDS AND TRIETHYL CHLOROSILANE

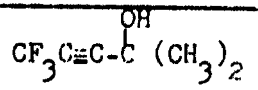
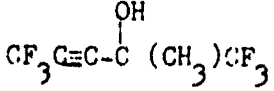
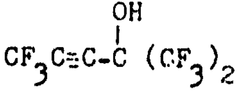
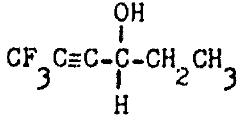
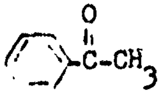
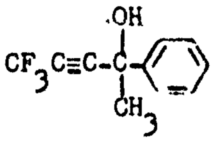
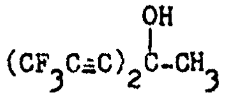
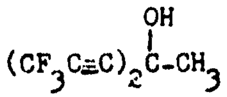
Reactant	Product (a)	Yield (%)	b.p. or m.p.	Refractive Index	Analysis or Literature Values
CO_2	$CF_3C\equiv CCOOH$	65	m.p. 40-42°	....	$C_4HF_3O_2$ requires C, 34.78; H, 0.73; F, 41.30
$(CH_3CH_2)_3SiCl$	$(CH_3CH_2)_3SiC\equiv CCF_3$	81	b.p. 160°	n_D^{24} 1.3542	Reqd. for $C_9H_{15}F_3Si$: C, 51.92; H, 7.25; F, 27.34. Found: C, 50.89; H, 7.41; F, 29.45% Analysis to be repeated
CH_3COCH_3	 $CF_3C\equiv C-\overset{OH}{C}(CH_3)_2$	70	b.p. 110-112°	n_D^{27} 1.3642	lit. (95) 110-111°; n_D^{20} 1.3229
CH_3COCF_3	 $CF_3C\equiv C-\overset{OH}{C}(CH_3)CF_3$	55		n_D^{24} 1.3230	Reqd. for $C_6H_4F_6O$: C, 34.95; H, 1.94; F, 55.34. Found: C, 34.72; H, 1.98; F, 55.51%
CF_3COCF_3	 $CF_3C\equiv C-\overset{OH}{C}(CF_3)_2$	25		n_D^{24} 1.3000 (∽1.2950)	Reqd. for C_6HF_9O: C, 27.68; H, 0.39; F, 65.78. Found: C, 27.74; H, 0.53; F, 65.43%
CH_3CH_2CHO	 $CF_3C\equiv C-\underset{H}{\overset{OH}{C}}-CH_2CH_3$	54		n_D^{24} 1.3679	Reqd. for $C_6H_7F_3O$: C, 47.37; H, 4.60; F, 37.50. Found: C, 47.29; H, 4.82; F, 37.27%

TABLE XVIII (continued)
REACTIONS OF 3,3,3-TRIFLUOROPROPYNYL LITHIUM WITH VARIOUS CARBONYL COMPOUNDS AND TRIETHYL CHLOROSILANE

		69	m.p. 71-73°	.....	Reqd. for $C_{11}H_9F_3O$: C, 61.68; H, 4.21; F, 26.63. Found: C, 61.90; H, 4.49; F, 26.32%
$CH_3COOCH_2CH_3$	 $(CF_3C\equiv C)_2\overset{\overset{OH}{\vert}}{C}-CH_3$	25	b.p. 130°	n_D^{24} 1.3540	Reqd. for $C_8H_4F_6O$: C, 41.47; H, 1.74; F, 49.57. Found: C, 41.55; H, 1.87; F, 49.87%
CH_3COCl	 $(CF_3C\equiv C)_2\overset{\overset{OH}{\vert}}{C}-CH_3$	54	b.p. 130°		

(a) Infrared, and ^1H and ^{19}F NMR spectra were consistent with these structures

IV. REFERENCES

1. W. T. Miller, *U. S. Pat.*, 2, 733, 277, (Jan. 31, 1956)
2. P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 77, 2783, (1955)
3. A. Posta and O. Paleta, *Czech. Pat.*, 106, 812, (March 15, 1963)
4. A. H. Fainberg and W. T. Miller Jr., *J. Amer. Chem. Soc.*, 79, 4170 (1957)
5. W. T. Miller Jr., E. W. Fager and P. H. Griswold, *J. Amer. Chem. Soc.*, *70*, 431, (1948)
6. J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, *J. Amer. Chem. Soc.*, *70*, 1550, (1948)
7. P. Tarrant and H. C. Brown, *J. Amer. Chem. Soc.*. 73, 1781, (1951)
8. E. S. Lo, *U. S. Pat.*, 2, 856, 435, (Oct. 14, 1958)
9. E. S. Lo, *U. S. Pat.*, 2, 975, 163, (March 14, 1961)
10. D. D. Coffman, R. Cramer and G. W. Rigby, *J. Amer. Chem. Soc.*, 71, 979, (1949)
11. A. Posta and O. Paleta, *Czech. Pat.*, 105, 966, (Dec. 15, 1962)
12. H. Nadai and R. Mueller, *J. Prakt. Chem.*, 19, 83, (1962)
13. A. L. Henne and M. S. Newman, *J. Amer. Chem. Soc.*, 60, 1697, (1938) W. T. Miller Jr., *J. Amer. Chem. Soc.*, 62, 993, (1940). W. T. Miller Jr., et al *J. Amer. Chem. Soc.*, 72, 705, (1950). W. T. Miller Jr., et al., *U. S. Pat.*, 2, 598, 411, (May 27, 1952)
14. J. D. Park and J. R. Lacher, *Univ. of Colorado*, Contract Report, U. S. Army, October 1964 - April 1965, p. 74
15. G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry" McMillan Co., New York, 1964, (a) p. 31, (b) p. 39, (c) p. 56
16. P. Tarrant and A. M. Lovelace, *J. Amer. Chem. Soc.*, *76*, 3466, (1954), *idem. ibid.*, *77*, 768, (1955)
17. P. Tarrant and E. G. Gillman, *J. Amer. Chem. Soc.*, *76*, 5423, (1954)
18. M. S. Kharasch, O. Reinmuth and W. H. Urry, *J. Amer. Chem. Soc.*, *69*, 1105, (1947)

19. P. Tarrant and H. Muramatsu, J. Org. Chem., 29, 1795, (1964)

20. I. L. Knunyants et al., J. Acad. of Sc., U. S. S. R., 359, (1965)

21. P. Tarrant and E. C. Stump, J. Org. Chem., 26, 4646, (1961)

22. P. Tarrant and E. C. Stump, J. Org. Chem., 29, 1198, (1964)

23. W. S. Friedlander, A. C. S., Abstract of Paper, April 1958, p. 18N

24. W. S. Friedlander. Gen. 109849, September 29, 1958

25. D. Seyferth, T. Wada and G. E. Hacial, Inorg. Chem., 1, 232, (1962)

26. A. H. Lovelace, A. R. Douglas and W. Postelnek, "Aliphatic Fluorine Compounds", A. C. S. Monograph Series, Reinhold Publishing Corp., New York, 1958

27. Handbook of Chemistry and Physics, 40th Edition, Chemical Rubber Publishing Company, Cleveland, Ohio, 1958

31. A. K. Barbour, M. H. Buxton, P. L. Coe, R. Stephens and J. C. Tatlow, J. Chem. Soc., 808, (1961)

32. J. H. Antonucci and L. A. Wall, Amer. Chem. Soc., Polymer Reprints, 3, 364, (1962)

33. K. Okuhara, H. Baba, and R. Kojima, Bull. Chem. Soc., Japan, 35, 532, (1962). Chem. Abstr., 57, 5784, (1962)

34. S. Dixon, J. Org. Chem., 21, 400, (1956) N. P. Gambanyan et al, Chem. Abstr., 63, 16202 g, (1965)

35. F. E. Bentley, PhD. Diss., Univ. of Florida (1957)

36. P. A. Claret, J. Coulson and G. H. Williams, Chem and Ind., (5) (22) (1965)

37. J. D. Park, R. W. Lamb and J. R. Lacher, Bull. Chem. Soc., Japan 37, 946, (1964)

38. E. S Huyser and E. Bedard, J. Org. Chem., 29, 1588, (1964)

39. J. D. Park, W. R. Lycan and J. R. Lacher, J. Amer. Chem. Soc., 73, 711, (1951)

40. J. Heyes, Private communication

41. W. T. Miller, J. H. Fried and H. Goldwhite, J. Amer. Chem.,Soc., 82, 3091, (1960)

42. W. T. Miller and R. Becker, 145th A.C.S. Meeting, New York (1963) p. 14M

43. L. Schumerling, P. J. Luvisi and R. W. Welch, J. Amer. Chem. Soc., 78, 2819, (1956)

44. E. T. McBee, C. G. Hsu, O. R. Pierce and C. W. Roberts, J. Amer. Chem. Soc., 77, 915, (1955)

45. P. D. Bartlett, L. K. Montgomery and B. Seidel, J. Amer. Chem. Soc., 86, 616, (1964)

46. R. N. Hazeldine, J. Chem. Soc., 2504, (1952)

47. J. D. Park, A. P. Stephani and J. R. Lacher, J. Org. Chem., 26, 3319, (1961)

48. J. D. Park, A. P. Stephani and J. R. Lacher, J. Org. Chem., 26, 4017 (1961)

49. F. J. Piscayne, PhD. Diss., Univ. of Florida

50. D. E. Barr and R. N. Hazeldine, J. Chem. Soc., 3416, (1956)

51. E. I. DuPont de Nemours, Brit. Pat., 904, 877, (Sept. 5, 1962)

56. H. E. Summan and D. W. Wiley, J. Amer. Chem. Soc., 82, 2288, (1960)

57. I. L. Knunyants, N. P. Gambaryan, Ch'ing-Yen Ch'en and Rohklin, Izvest Akad. Nauk U. S. S. R., Otdtel. Khim. Nauk, 684, (1962)

58. R. Calas and N. Duffant, C. R. Acad. Sci., Paris, 247, 906, (1957) quoted in Eaborn, "Organosilicon Compound", Academic Press Inc., London, (1960), p. 213

59. B. G. Tucker and E. Whittle, Proc. Chem. Soc., 93, (1963)

60. D. Seyferth and T. Wada, Inorg. Chem., 1, 78, (1962)

61. R. N. Sterlin, I. L. Knunyants, L. N. Pinkince and R. D. Yatsenko, Izv. Akad. Nauk U. S. S. R., Otd Khim. Nauk, 1492 (1959)

62. D. Seyferth, K. A. Brandle and G. Raab, Angew. Chem., 72, 77, (1960)

63. D. Seyferth, D. E. Welch, and G. Raab, J. Amer. Chem. Soc., 84, 4266, (1962)

64. P. Tarrant and D. A. Warner, J. Amer. Chem. Soc., 76, 1624, (1954)

65. C. Tomasino, PhD. Diss., Univ. of Florida (1959)

66. P. Tarrant and J. Heyes, J. Org. Chem., 0, 1485, (1965)

67. T. D. Coyle, S. L. Stafford and F. G. A. Stone, J. Chem. Soc., 3103, (1961)

68. D. C. England, L. R. Melby, H. A. Dietrich and R. V. Lindsay Jr., J. Amer. Chem. Soc., 82, 5116, (1960)

69. P. Tarrant, J. Savory and E. S. Iglehart, J. Org. Chem., 29, 2009, (1964)

70. P. Tarrant, P. Johncock and J. Savory, J. Org. Chem., 28, 839, (1963)

71. W. J. Pummer and L. A. Wall, J. Res. N. B. S., 63A, 167, (1959)

72. E. J. P. Fear, J. Thrower and M. A. White, Royal Aircraft Establishment (Farnborough), Tech Note CPM 26: August 1963

73. M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances", Prentice-Hall Co., Inc., New York, N. Y. (1954), p. 1154 - 57

74. M. Gaudemar, Bull. Soc. chim, France, 1475, (1958)

75. J. E. Nordlander, W. C. Young, and J. D. Roberts, J. Amer. Chem. Soc., 83, 494, (1961)

76. G. M. Whitesides, J. E. Nordlander and J. D. Roberts, Discussions Society, 34, 185, (1962)

77. W. C. Young and J. D. Roberts, J. Amer. Chem. Soc., 68, 649, (1946)

78. U. S. Army Contract, Quarterly Report No. 34034, Sept. - Mar., 1960

79. R. N. Sterlin, R. D. Yatsenko and I. L. Knunyants, Chem. Abstr., 53, 4195, (1959)

80. P. Tarrant and R. D. Richardson, Abstracts of Papers, 138th National Meeting of the A. C. S., New York, (1960), p. 17M

81. C. Eabom, "Organosilicon Compounds", Academic Press Inc., New York (1960)

82. W. J. Middleton and W. H. Sharkey, J. Amer. Chem. Soc., 81, 803, (1959)

83. A. L. Henne and M. J. Nager, J. Amer. Chem. Soc., 73, 1042, (1951)

84. P. Tarrant and R. E. Taylor, J. Org. Chem., 24, 1888, (1959)

85. A. T. Blomquist and D. T. Langone, J. Amer. Chem. Soc., 79, 4981, (1957)

86. Peninsular Chem. Research, Inc., Authentic sample

87. Ref. 81, p. 133

88. R. Fontanelli and D. Sianisi, Chem. Abstr., 64, 1, 578

89. G. Köbrich and K. Flory, Chem. Ber., 99, (6), 1773, (1966) Chem. Abstr., 65, 7203d, (1966)

90. H. Gilman and H. A. Haubein, J. Amer. Chem. Soc., 67, 1420 (1945)

91. S. J. Cristol and R. S. Bly, J. Amer. Chem. Soc., 83, 4027, (1961)

92. J. Normant, Bull. Soc. Chim, 1876, (1963)

93. W. G. Finnegan and W. P. Norris, J. Org. Chem., 28, 1139, (1963)

94. R. N. Hazeldine, Nature, 165, 152, (1950)

95. A. L. Henne and M. Nager, J. Amer. Chem. Soc., 74, 650 (1952)

96. M. W. Buxton, M. Stacey, and J. C. Tatlow, J. Chem. Soc., 366, (1954)

97. Ibid, idem, 31, 3292, (1966)

98. B. D. H. Pat. Appl. for Neth. 6504, 377, Chem. Abstr., 64, 8266 (1966)

99. W. R. Cullen and W. R. Leeder, Inorg. Chem., 5, 1004, (1966)

100. D. Y. Curtin and J. W. Crump, J. Amer. Chem. Soc., 80, 1922, (1958)

101. W. T. Miller Jr., U. S. Pat., 2, 671, 799, (March 9, 1954)

102. H. Bernstein, Can. J. Res., 288, 132, (1950)

103. R. J. Haper, E. J. Soloski and C. Tamborski, J. Org. Chem. 29, 2385, (1964)

104. D. Seyferth and M. A. Weiner, Chem and Ind., 402, 1959

105. W. I. Patinode and D. F. Wisicox, J. Amer. Chem. Soc., 68, 358, (1946)

106. E. R. H. Jones, L. Skattebal and M. C. Whiting, J. Chem. Soc., 4765, (1956)

107. P. L. Coe, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 3227 (1962)

108 A. A. Horton, et al., J. Amer. Chem. Soc., 67, 2224, (1945)

109. R. P. Linstead, J. Chem. Soc., 355, (1927)

110. F. Sewarts, Bull. Acad. Roy. Belg., 728, (1909)

111. F. Sewarts, Bull. Acad. Roy. Belg., 563, (1911)

112. L. L. Shcukovskaya and A. D. Petrov, Inzvest. Akad. Nauk U. S. S. R. Otdel. Khim. Nauk, 101 - 14, (1958) Chem. Abstr., 53, 1119 (1959)

DOCUMENT CONTROL DATA - R & D

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

1 ORIGINATING ACTIVITY (Corporate author)
The University of Florida
Department of Chemistry
Gainesville, Florida 32601

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3 REPORT TITLE
Research on Synthesis of Unsaturated Fluorocarbon Compounds

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Report

5 AUTHOR(S) (First name, middle initial, last name)
Tarrant, Paul; Stewart, O.J.; Drakesmith, F.G.
Sayers, D.; Heyes, J.; Oliver, W.; Wright, A.C.
Perry, D.; Tandon, J; Wright, A.; Misaki, S.

6 REPORT DATE March 31, 1967	7a. TOTAL NO. OF PAGES 184	7b. NO. OF REFS 112

8a. CONTRACT OR GRANT NO
DA19-129-AMC-79(N)

b. PROJECT NO
1C024401A329

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
67-79-CM; C&OM-33

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

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
U. S. Army Natick Laboratories
Natick, Massachusetts 01760

13 ABSTRACT

Synthesis of a variety of fluorine-containing compounds was studied. A convenient synthesis of perfluoroallyl halides was developed. Lewis acid catalyzed addition of haloalkanes to olefins resulted in new fluoroölefins. A series of fluorine monomers were prepared for polymerization studies. A number of partially fluorinated norbornadienes were prepared by the reaction of cyclopentadiene with haloölefins and subsequent dehalogenation. Several new fluorinated nitroso monomers were prepared. A series of compounds of the general structure $(CH_3)_3SiCF{=}CFR$ were synthesized utilizing organolithium reagents. Alcoholysis of these compounds provides a convenient route to 1,2-difluoroölefins. Several other unsaturated fluoro-organometallic compounds were prepared and their reactions studied. It was found that they could be reacted with carbonyl compounds to produce alcohols which on dehydration gave fluorinated dienes.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Preparation (Formulation)	8					
Synthesis (Chemistry)	8					
Fluorochemicals	1,2		9			
Unsaturated	0		0			
Elastomers	4		9			
Nitroso rubber	4		9			
Chemical properties			8			
Physical properties			8			