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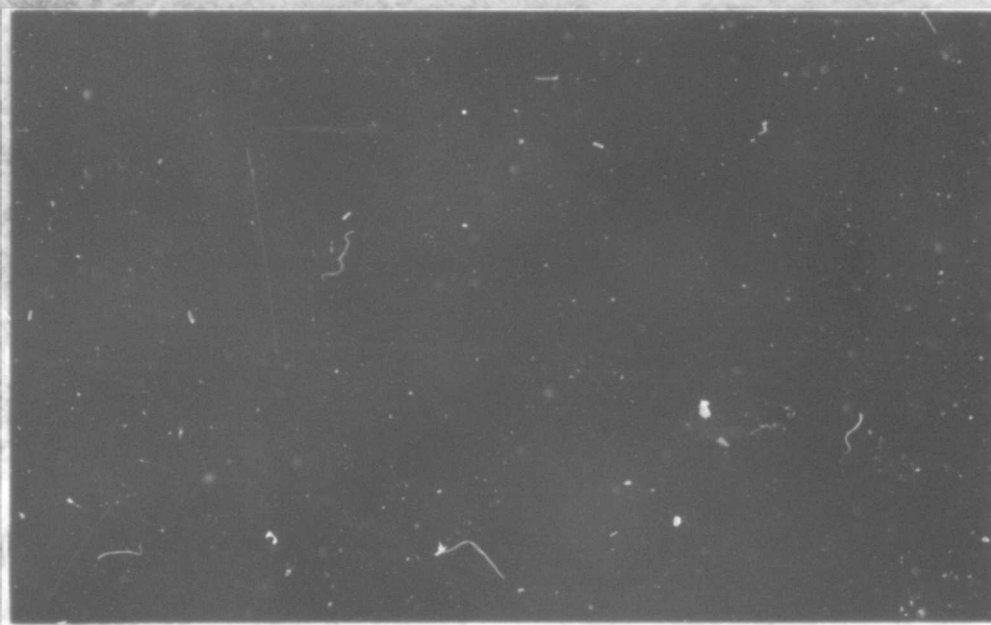


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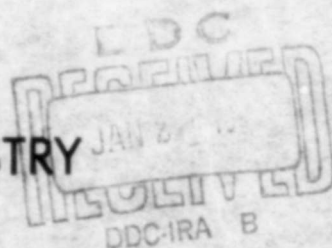
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DEPARTMENT OF CHEMISTRY

UNIVERSITY OF FLORIDA

GAINESVILLE, FLORIDA



RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS

Contract DA-19-129-AMC-79(N)

Between

U. S. Army Natick Laboratories

and

The University of Florida

Semiannual Report 5: April 1, 1965 - September 30, 1965

By: Paul Tarrant
Doug Ferry
Jai Tandon
Alan Wright
Susumu Misaki

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I. INTRODUCTION

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

It is estimated that 80% of the work has been completed to date and that 80% of the estimated costs have been incurred to date.

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 DA-44-109-QM-1469 and DA-19-129-QM-500.

This is the 5th report under the contract but the 52nd since the project was initiated in 1951.

II. SUMMARY OF CURRENT PROGRESS

The preparation of perfluoroallyl chloride has been improved and this compound was treated with various alkoxide ions to produce saturated and unsaturated ethers.

Lewis acid catalysed additions of polyhaloalkanes to haloolefins were continued.

In an attempt to prepare fluoronitroso compounds carrying other functional groups, nitrosyl chloride was allowed to react with unsaturated fluoroesters and ethers.

The investigation of the radical addition of haloalkyl chlorides and bromides with various olefins was continued.

Attempts have been made to react radicals from $\text{CF}_2\text{BrCFClBr}$ and $\text{CF}_2\text{ClCFClI}$ with aromatic nuclei.

III. DISCUSSION

Perfluoroallyl Systems

Work has been continued on the preparation of perfluoroallylchloride (PFAC) as previously described¹, namely, the addition of CFCl_3 to $\text{CFCl}=\text{CFCl}$ in the presence of aluminum chloride, and the subsequent fluorination and dehalogenation of the $\text{C}_3\text{Cl}_5\text{F}_3$ fraction. The preparation of $\text{C}_3\text{Cl}_5\text{F}_3$ has been perfected to give 68% yields in 6 hours. A small amount of $\text{C}_3\text{Cl}_6\text{F}_2$ is also formed by the replacement of one of the fluorines in $\text{C}_3\text{Cl}_5\text{F}_3$ by chlorine. The optimum conditions for the fluorination of $\text{C}_3\text{Cl}_5\text{F}_3$ have been found to be about 12 hours at 190–200°C. in an autoclave with antimony trifluoride and chlorine. Under these conditions all the starting material is converted into chiefly $\text{C}_3\text{Cl}_3\text{F}_5$ with some $\text{C}_3\text{Cl}_4\text{F}_4$ present, depending on the reaction time. Dehalogenation of the $\text{C}_3\text{Cl}_3\text{F}_5$, which has been shown to be a mixture of $\text{CF}_2\text{ClCFClCF}_2\text{Cl}$ (71%) and $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$ (25%), gives PFAC in 80% yield. Detailed NMR analysis has shown this to be the only olefinic isomer present.

Attempts to fluorinate $\text{C}_3\text{Cl}_5\text{F}_3$ with SbF_3Cl_2 in glass equipment at atmospheric pressure resulted in a 66% yield of $\text{C}_3\text{Cl}_4\text{F}_4$ but further fluorination did not occur. It was concluded that more vigorous conditions are required for this last step. When $\text{C}_3\text{Cl}_4\text{F}_4$ was used as the starting material it was recovered unchanged even after refluxing for 4 hours over SbF_3Cl_2 .

As a continuation² of the study of nucleophilic additions to fluoro-olefins, PFAC was treated with allyl alcohol/KOH, methanol/sodium methoxide, sodium methoxide/dioxane, and ethanol/sodium ethoxide. The reaction of PFAI with ethanol/KOH was reported previously². In the present case however the major product has not been positively identified yet.

The product from the addition of CFCl_3 to $\text{CFCl}=\text{CFCl}$, namely $\text{C}_3\text{Cl}_5\text{F}_3$, was treated with AlCl_3 in an attempt to elucidate the changes in the isomer ratio, if any. Instead of isomerization, a gas was produced (which was shown by infrared to be a complex mixture containing CF_2Cl_2 and $\text{CF}_2=\text{CFCl}$) and a liquid containing 6% CCl_4 , 52% $\text{CCl}_2=\text{CCl}_2$, 7% $\text{C}_3\text{Cl}_5\text{F}_3$, and 36% $\text{C}_3\text{Cl}_6\text{F}_2$. Similar cleavage reactions in the presence of AlCl_3 have been reported in the chlorocarbon field⁴. The replacement product, $\text{C}_3\text{Cl}_6\text{F}_2$, was shown by NMR to be ca. 95% $\text{CF}_2\text{ClCCl}_2\text{CCl}_3$ and ca. 5% $\text{CCl}_3\text{CF}_2\text{CCl}_3$. However, the $\text{C}_3\text{Cl}_6\text{F}_2$ produced as a by-product in the initial reaction of CFCl_3 with $\text{CFCl}=\text{CFCl}$ (in ca. 5% yield) consisted of 74% $\text{CFCl}_2\text{CFClCCl}_3$ and 26% $\text{CF}_2\text{ClCCl}_2\text{CCl}_3$.

In Table I the results of some of the addition reactions of alkanes to olefins are reported.

An attempt was made to study the effect of fluoride ion on this type of reaction by conducting the addition of CFCl_3 to $\text{CFCl}=\text{CFCl}$ 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% $\text{C}_3\text{Cl}_5\text{F}_3$ was formed. Since it was difficult to obtain pure anhydrous potassium fluoride, sodium fluoride was used in a series of three runs (see Table II), each having 0.313 moles CFCl_3 , 0.203 moles $\text{CFCl}=\text{CFCl}$, and 0.067 moles AlCl_3 . The sodium fluoride used was 0.190 moles. 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, $\text{C}_3\text{Cl}_6\text{F}_2$, increases.

An attempt was made to add carbon tetrachloride to $\text{CF}_2=\text{CFCl}$ in the presence of AlCl_3 without an autoclave⁵⁻⁷ but no $\text{C}_3\text{Cl}_5\text{F}_3$ was formed either at room temperature or at reflux. This agrees with the many

TABLE I

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%)
	$CF_2=CFCl^a$	64	$C_3Cl_4F_4$	$CF_3CFClCCl_3$ (51), $CF_2ClCF_2CCl_3$ (37), $CFCl_2CF_2CFCl_2$ (8)
	$CF_2=CCL_2^a$	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.	—	—
$CHCl_2$	$CF_2=CFCl$	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), $CF_2ClCH_2CCl_3$ (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)
	$CF_2=CFCl^a$	17	$C_3Cl_4F_4$	$CF_2ClCF_2CCl_3$ (44), $CF_3CFClCCl_3$ (38), $CFCl_2CF_2CFCl_2$ (11)

a. Experimental details in Semiannual report 4, Oct. 1964 - March, 1965.

TABLE II

The Effect of F (NaF) on the Reaction of $CFCl_3$ with $CFCl=CFCl$ in the Presence of $AlCl_3$

Run	NaF	Time (hrs.)	Yield (%)		$C_3Cl_5F_3$ Isomers (NMR%)				
			$C_3Cl_5F_3$	$C_3Cl_6F_2$	$CF_2ClCFClCCl_3$	$CF_2CCl_2CCl_3$	$CFCl_2CFClCFCl_2$	$CFCl_2CF_2CCl_3$	None
1	No	6.50	75	5.8	70	2	24		
2	Yes	6.25	66	5.5	74	2	21		
3	Yes	35	65	9.3	76	3	18		

observations that no CCl_4 adduct is formed in the various reactions of CFCl_3 with olefins.

The adduct of CFCl_3 with $\text{CF}_2=\text{CFBr}$ was shown by NMR to be $\text{CF}_3\text{CFBrCCl}_3$ (56%) and $\text{CF}_2\text{BrCF}_2\text{CCl}_3$ (44%). This material was treated with zinc dust in ethanol to give $\text{CF}_3\text{CF}=\text{CCl}_2$ in 45% yield.

So far attempts to extend the scope of this reaction to alkanes other than CFCl_3 and CHFCl_2 have failed. Instead, rearrangement or replacement reactions of the starting alkane occurred. With CF_2Br_2 and $\text{CFCl}=\text{CFCl}$ no reaction occurred at room temperature, and, after heating for five days at about 60° , a complex mixture was obtained but no one product predominated. With CCl_4 and $\text{CFCl}=\text{CFCl}$ the product mixture contained 46% $\text{CCl}_2=\text{CCl}_2$, 8% $\text{C}_3\text{Cl}_5\text{F}_3$, and 46% $\text{C}_3\text{Cl}_7\text{F}$. When CBrCl_3 was treated with AlCl_3 it disproportionated to give CBr_2Cl_2 and CCl_4 . This also was the only reaction when CBrCl_3 was treated with $\text{CFCl}=\text{CFCl}$ and AlCl_3 . Benzotrichloride and $\text{CFCl}=\text{CFCl}$ gave no reaction at all.

This addition reaction also seems restricted to haloethylenes⁸. Table III gives the pertinent data for several attempts using various fluoroolefins. The structures given were determined from the NMR and infrared spectra.

The high boiling product previously⁹ obtained from the reaction of perfluorocyclobutene with CFCl_3 in the presence of AlCl_3 has been shown to be a mixture of hexachlorobutadiene-1,3 and hexachlorocyclobutene. Since this mixture contained both liquid and solid phases at room temperature, a sample of the solid was recrystallized from *n*-hexane to give white crystals, m.p. $50-2^\circ$, with a strong infrared band at 6.10μ , indicative of the cyclobutene. However, since the original mixture had infrared bands at 6.12μ and 6.41μ , it was concluded that the cyclobutene rearranged to the butadiene on distillation.¹⁰

TABLE III

Reaction of Alkane and Olefin in the Presence of AlCl_3

<u>Alkane</u>	<u>Olefin</u>	<u>Products</u>
CFCl_3	$\begin{array}{c} \text{CF}_2-\text{CF}^a \\ \quad \\ \text{CF}_2-\text{CF} \end{array}$	$\begin{array}{c} \text{CFCl}-\text{CCl} \\ \quad \\ \text{CFCl}-\text{CCl} \end{array}$ or $\begin{array}{c} \text{CF}_2-\text{CCl} \\ \quad \\ \text{CCl}_2-\text{CCl} \end{array}$ and $\begin{array}{c} \text{CCl}_2-\text{CCl} \\ \quad \\ \text{CCl}_2-\text{CCl} \end{array}$
None	" a	$\begin{array}{c} \text{CF}_2-\text{CCl} \\ \quad \\ \text{CF}_2-\text{CF} \end{array}$ and $\begin{array}{c} \text{CF}_2-\text{CCl} \\ \quad \\ \text{CF}_2-\text{CCl} \end{array}$
CFCl_3	$\text{CF}_3\text{CF}=\text{CFCF}_3$	$\text{CF}_3\text{CF}=\text{CClCF}_3$ and $\text{CF}_3\text{CCl}=\text{CClCFCl}_2$
CFCl_3	$\text{CF}_3\text{CF}=\text{CF}_2$	$\text{CF}_3\text{CF}=\text{CFCl}$ and $\text{CF}_3\text{CF}=\text{CCl}_2$
None	$\begin{array}{c} \text{CCl}-\text{CF}_2 \\ \quad \diagup \\ \text{CCl}-\text{CF}_2 \quad \text{CF}_2 \end{array}$	Cyclo- $\text{C}_5\text{Cl}_x\text{F}_{8-x}$, $x = 3, 4, 5, 6$
CFCl_3	'	', $x = 4, 6, 8$

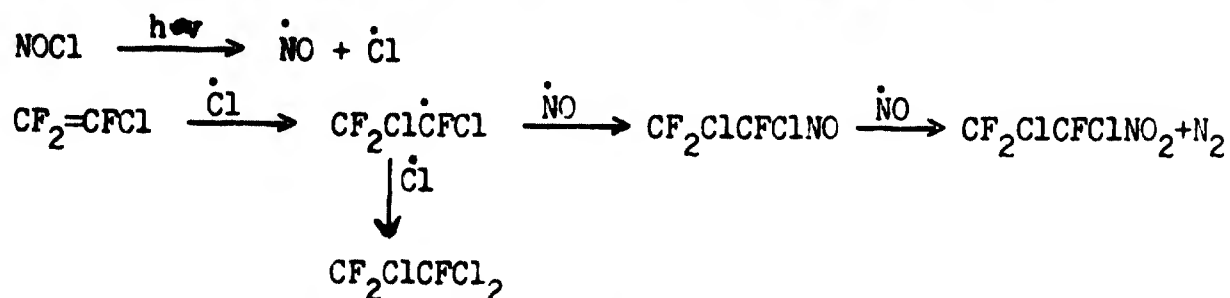
Structures of Cyclo- $\text{C}_5\text{Cl}_x\text{F}_{8-x}$

$x = 3$	$\begin{array}{c} \text{CCl}-\text{CF}_2 \\ \quad \diagup \\ \text{CCl}-\text{CF}_2 \quad \text{CFCl} \end{array}$	and	$\begin{array}{c} \text{CCl}-\text{CF}_2 \\ \quad \diagup \\ \text{CCl}-\text{CFCl} \quad \text{CF}_2 \end{array}$	ca. 50:50
$x = 4$	$\begin{array}{c} \text{CCl}-\text{CF}_2 \\ \quad \diagup \\ \text{CCl}-\text{CF}_2 \quad \text{CCl}_2 \end{array}$	and	$\begin{array}{c} \text{CCl}-\text{CF}_2 \\ \quad \diagup \\ \text{CCl}-\text{CCl}_2 \quad \text{CF}_2 \end{array}$	22:78
$x = 6$	$\begin{array}{c} \text{CCl}-\text{CCl}_2 \\ \quad \diagup \\ \text{CCl}-\text{CCl}_2 \quad \text{CF}_2 \end{array}$			
$x = 8$	$\begin{array}{c} \text{CCl}-\text{CCl}_2 \\ \quad \diagup \\ \text{CCl}-\text{CCl}_2 \quad \text{CCl}_2 \end{array}$			

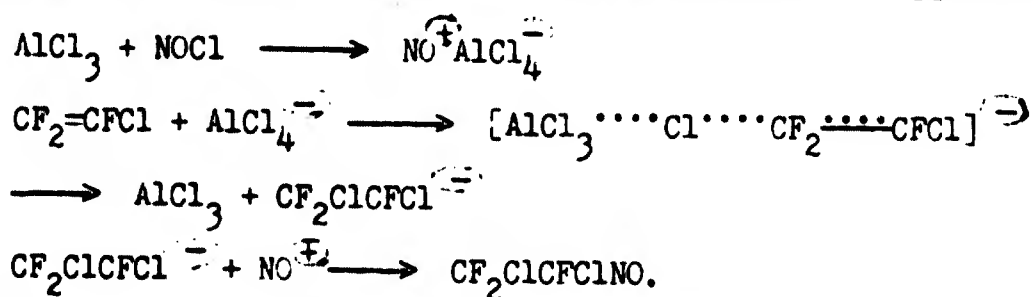
a. Experimental details in Semiannual report 4, Oct. 1964 - March 1965.

Fluoronitroso Compounds

The preparation of fluoronitroso compounds by the addition of nitrosyl chloride to fluorodlefins has been reported^{11,12,13} 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 fluorodlefins 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:



Park^{11,12} 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 fluorodlefins react in a suspension of aluminum chloride and dimethylformamide¹³. The following mechanism was suggested:



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

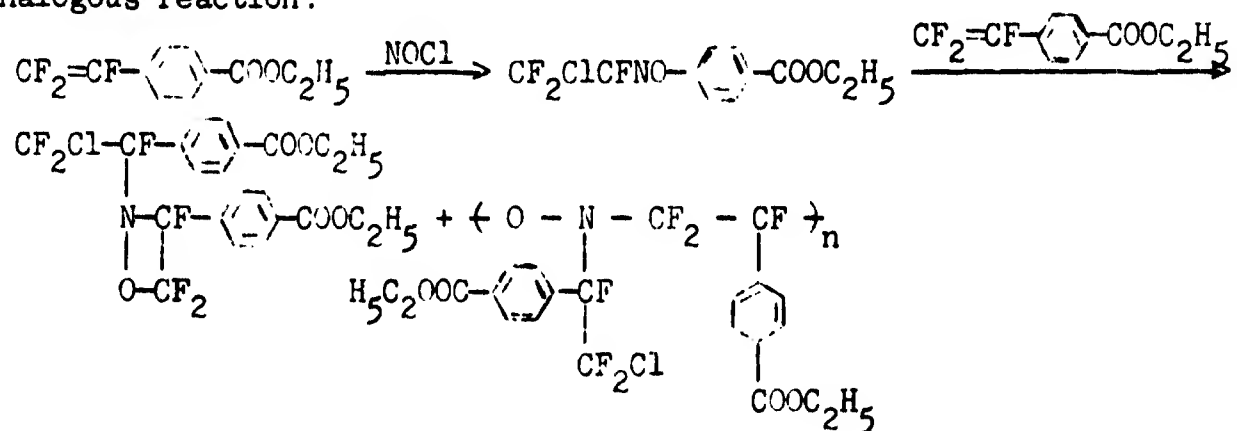
Preparation of p-Trifluorovinyl Ethyl Benzoate and Reaction with Nitrosyl Chloride

The preparation of trifluorovinyl benzoic acid has been investigated.¹⁴ Trifluorovinyl ethyl benzoate was prepared via this method¹⁴ 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

$$\begin{array}{c} \text{CF}_2-\text{CF}-\langle \text{C}_6\text{H}_4 \rangle-\text{COOEt} \\ | \\ \text{CF}_2-\text{CF}-\langle \text{C}_6\text{H}_4 \rangle-\text{COOEt} \end{array}$$

for this compound. The reaction of trifluorovinyl ethyl benzoate with nitrosyl chloride was carried out at 0° using the method reported¹³. The reaction product was a light green viscous oil which decomposed at room temperature after ca. 7 hours. An attempt was made to separate the product by alumina chromatography. The light green compound which was collected was not the expected nitroso compound but a mixture of two compounds, as on standing at 0° a white solid crystallised out. Olefins and nitroso compounds have reacted to form oxazetidines and polymers¹⁵ 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.

Reaction of the Unsaturated Fluoroesters with Nitrosyl Chloride

$\text{CF}_2=\text{CF}-\text{CF}_2-\text{COOC}_2\text{H}_5$, $\text{CF}_2=\text{CF}-\text{CF}_2-\text{COOCH}_3$ and $\text{CF}_2=\text{CF}-\text{COOC}_2\text{H}_5$ were used as the esters. In each case, the blue nitroso compounds were separated from the chloro derivatives by VPC. The nitroso products decomposed below their boiling points.

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 $CH_2=CHCH_2OCF_2CFClH$ and $CH_3COOCH_2CH=CH_2$ did not give blue nitroso products.

Radical Addition of Haloalkyl Halides to Olefins

Trifluorovinyl bromide was dimerised to 1,2-dibromohexafluorocyclobutane in 40% yield. Hexafluorocyclobutene only reacted with bromine under prolonged UV irradiation. A preliminary reaction of 1,2-dibromohexafluorocyclobutane with ethylene gave only a poor yield of product, but this reaction is to be further investigated.

$CF_3CFBrCF_2Br$ reacted with ethylene in the presence of benzoyl peroxide to give a single isomer which is suspected $CF_2Br(CF_3)CFCH_2CH_2Br$. Dehydrohalogenation of this product gave one major product.

Fluorination of $CF_3CFBrCF_2Br$ was attempted in an effort to produce a monobromide for this work but no reaction occurred.

The reaction between acrylonitrile and $CF_2BrCFClBr$ in the presence of benzoyl peroxide in various ratios gave only a white polymer and VPC did not show any simple adducts.

Addition of CF_2BrCF_2Br to ethylene in the presence of benzoyl peroxide gave a 1:1 adduct in 20% yield and trace amounts of higher boiling products. $CH_2BrCH_2CF_2CF_2CH_2CH_2Br$ was not detected; this result is consistent with the reaction of $CFClBrCFClBr$ with ethylene¹⁶. The 1:1 adduct was dehydrohalogenated to yield $CF_2BrCF_2CH=CH_2$.

The 1:1 addition of benzotrichloride to ethylene in the presence of benzoyl peroxide could not be effected at 100° at atmospheric pressure, or in an autoclave, although in the latter experiment a polymerisation may have occurred.

product showed no high boiling product by VPC, but on distillation to remove starting materials followed by VPC separation, bromobenzene and suspected $C_6H_5CFC1CF_2Br$ (infrared and H^1 and F^{19} NMR spectra were consistent) were isolated in 0.25% yield.

In an attempt to isolate the known compound $p-CF_2BrCFC1C_6H_4COOH$, benzoic acid in benzene solution and $CF_2BrCFC1Br$ 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 peroxide¹⁷. Therefore, bromobenzene and $CF_2BrCFC1Br$, 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 VPC 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 VPC retention time to suspected $C_6H_5.CFC1CF_2Br$ 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 $CF_2BrCFC1Br$. 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 peroxide¹⁸, but ultraviolet irradiation of pentafluorobenzene with $\text{CF}_2\text{BrCFClBr}$ 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 $\text{CF}_2\text{BrCFClBr}$ and have been exposed to sunlight. The latter experiment gave no apparent reaction on VPC 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 $\text{CF}_2\text{BrCFClBr}$ or inefficiency of ultraviolet light in producing those radicals.

Pyrolysis Experiments with $\text{CF}_2\text{BrCFClBr}$

$\text{CF}_2\text{BrCFClBr}$ has been pyrolysed in a platinum tube at 500° and 600° and the products isolated¹⁹. The proposed initiation mechanism is 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 $\text{CF}_2\text{BrCFClBr}$ was pyrolysed at various temperatures. The optimum temperature of pyrolysis appeared to be 400–500° when minor products of longer VPC retention time were observed, but there was no product of retention time similar to suspected $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Br}$ obtained from the ultraviolet irradiation energised

reaction. There appeared to be very little inter-reaction of $\text{CF}_2\text{BrCFClBr}$ and benzene, as benzene was the only major product in experiments at all temperatures.

Pyrolysis of bromobenzene and $\text{CF}_2\text{BrCFClBr}$ 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. These high boiling components, two of which corresponded by VPC to the products isolated from the ultraviolet initiated reaction, were still very minor products and bromobenzene appeared to be largely unchanged. Similarly, both pentafluorobenzene and bromopentafluorobenzene on pyrolysis with $\text{CF}_2\text{BrCFClBr}$ gave only traces of high-boiling products.

A preliminary experiment on pyrolysis of $\text{CF}_2\text{BrCFClBr}$ with olefins using a mixture of olefins showed a major product of longer VPC retention time than starting materials, but as this was off the main course of the investigation, it was not pursued.

A mixture of $\text{CF}_2\text{BrCFClBr}$ and bromine was pyrolysed in an effort to obtain more $\text{CF}_2\text{BrCFBr}_2$ in the pyrolysis product than that obtained from pyrolysis of $\text{CF}_2\text{BrCFClBr}$ alone. This would give a convenient route to the preparation of the monomer, vinyl bromide. A pyrolysis of the mixture at 400° gave a 26% yield of the suspected tribromotrifluoroethane compared to 8% on pyrolysis of $\text{CF}_2\text{BrCFClBr}$ alone. Also in an attempt to prepare vinyl bromide a mixture of bromine and $\text{CF}_2=\text{CFCl}$ was pyrolysed, but the bromine reacted with the olefin before pyrolysis occurred.

Attempted Formation of a Radical from $\text{CF}_2\text{ClCFClI}$ and its Reaction in situ with Aromatic Nuclei

Recently it has been shown that trifluoromethyl iodide will react with monohalobenzenes to yield trifluoromethylmonohalobenzenes²⁰.

This work has been adapted in an attempt to produce potential difunctional monomers. Benzene was reacted with $\text{CF}_2\text{ClCFClI}$ under conditions used in the reference but there was considerable decomposition to carboneous material and only 5% of the substituted benzene was formed. Under milder conditions the amount of decomposition decreased and the yield of suspected $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$ increased to 24%. $\text{CF}_2\text{ClCFClH}$ (6% yield) was also identified²¹. The structure of $\text{C}_6\text{H}_5\text{CFClCF}_2$ was based on consistent infrared, H^1 and F^{19} NMR, and ultraviolet spectra.

It seems that even milder conditions for the reaction above may increase the yield of $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$, but there is an optimum as an experiment in which benzene and $\text{CF}_2\text{ClCFClI}$ were refluxed for 140 hours gave very little reaction.

Although dechlorination of $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$ will only yield the known α, β, β -trifluorostyrene, which has been polymerised, the same radical reaction may be effected using substituted benzene derivatives and $\text{CF}_2\text{ClCFClI}$ to yield monomers through which cross linking is possible. Thus bromobenzene was reacted with $\text{CF}_2\text{ClCFClI}$. The product of long retention time is suspected to be $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$ (14% yield). It was of interest to note that in addition to suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$, a product whose VPC retention time corresponded to $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$ was present in the ratio $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}:\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}::8:1$. This ratio was reversed by effecting the reaction in the presence of copper dust.

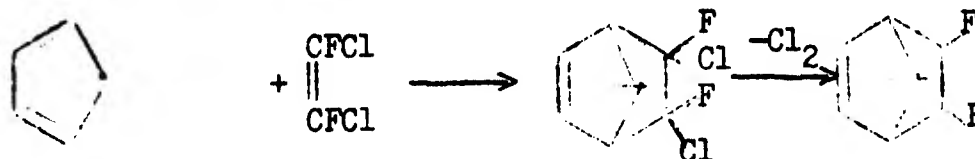
Refluxing bromobenzene with $\text{CF}_2\text{ClCFClI}$ at a liquid temperature of ca. 115° gave a 13% conversion (by VPC peak area) to suspected $\text{C}_6\text{H}_4\text{CFClCF}_2\text{Cl}$ after 90 hours. This indicates that the ideal temperature for liberation of radicals from $\text{CF}_2\text{ClCFClI}$ is $>115^\circ$ and $<165^\circ$.

Reaction of pentafluorobenzene with $\text{CF}_2\text{ClCFClI}$, which would have given a facile preparation of perfluorostyrene, could not be effected.

Initial experiments between phenol and $\text{CF}_2\text{ClCFClI}$ and nitrobenzene and $\text{CF}_2\text{ClCFClI}$ indicate, by VPC, a poor conversion to the haloethyl substituted products.

Attempted Preparation of Partially Fluorinated Norbornadienes

The hydrocarbon norborna-2,5-diene has been prepared by Diels-Alder addition of *sym*-dichloroethylene to cyclopentadiene, followed by dechlorination²². 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-difluoronorborna-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. Work will continue on this topic.

IV. EXPERIMENTAL

Preparation and Reactions of Perfluoroallyl Chloride

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

CFCl_3 (348 g., 2.53 mole), $\text{CFCl}=\text{CFCl}$ (273 g., 2.05 mole), and AlCl_3 (26 g., 0.195 mole) were combined in a flask at 0° . After

stirring for 22 min. AlCl_3 (10 g., 0.075 mole) was added and the mixture was stirred for 3.5 hours during which time the temperature rose to 45° . AlCl_3 (6 g., 0.045 mole) was added and then the mixture stirred for 2 hours. Normal work-up procedure consisted of washing with cold dilute HCl , then ice water, separation of the organic layer, and drying over Drierite. This gave a material (589 g.) which was distilled to give pure $\text{C}_3\text{Cl}_5\text{F}_3$ (380 g., 68% yield).

Fluorination of $\text{C}_3\text{Cl}_5\text{F}_3$

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. $\text{C}_3\text{Cl}_5\text{F}_3$ (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 $185-190^\circ$ due to a thermocouple malfunction. After further heating at $190-200^\circ$ for 2.5 hours the mixture was left overnight at ambient. VPC indicated only a small amount of fluorination had occurred so the mixture was re-heated at $190-200^\circ$ for 7 hours. Work-up gave a material (113 g.) which on distillation yielded $\text{C}_3\text{Cl}_3\text{F}_5$ (99 g., 74% yield).

Preparation of Perfluoroallylchloride (PFAC)

$\text{C}_3\text{Cl}_3\text{F}_5$ (94 g., 0.39 mole) in ethanol (50 ml.) was added dropwise over a period of 1.25 hour to a suspension of zinc (32 g., 0.49 mole) in gently refluxing ethanol (100 ml.). The mixture was refluxed for 1.5 hour 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., 80% yield).

Fluorination of $\text{C}_3\text{Cl}_5\text{F}_3$ with SbF_3Cl_2 in Glass Apparatus

Chlorine was passed slowly over the surface of freshly ground

SbF_3 (65 g., 0.363 mole) for 0.5 hour. The dark brown semi-liquid mixture was heated and $\text{C}_3\text{Cl}_5\text{F}_3$ (59.8 g., 0.220 mole) was added during 1 hour. Nothing distilled into the receiver. After heating for 1 hour the coagulated SbF_3 was broken up and chlorine passed in for 20 minutes with heating. After leaving at room temperature overnight, VPC showed that $\text{C}_3\text{Cl}_4\text{F}_4$ was formed but no $\text{C}_3\text{Cl}_3\text{F}_5$. More chlorine and SbF_3 (30 g.) were added and after heating for 1.5 hour material distilled from the flask at $105-8^\circ$. This milky white liquid (44 g.) was washed with ice/HCl to give a material (41 g.) which was 10% unreacted $\text{C}_3\text{Cl}_5\text{F}_3$ and 90% $\text{C}_3\text{Cl}_4\text{F}_4$, a 66% yield of the latter.

Addition of $\text{CH}_2=\text{CHCH}_2\text{OH}$ to $\text{CF}_2=\text{CFCF}_2\text{Cl}$ with KOH

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 $68-70^\circ$ for 1.5 hour. 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 VPC contained 3% PFAC, 19% D, 14% A-1, 36% A-2, 8% unknown, and 20% A-3.

The experiment was repeated using a flask equipped 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 was 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 VPC 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 5.57 μ . 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 5.62 μ , 5.84 μ , and 6.08 μ . 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 6.08 μ . Analysis calcd. for $C_9H_{11}F_5O_2$, $CH_2=CHCH_2OCF_2CHFCF_2OCH_2CH=CH_2$: Calcd.: 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 5.66 μ and a weak band at 6.09 μ . Analysis calcd. for $C_9H_{11}F_3O_3$, $CH_2=CHCH_2OCF_2CHFCOCH_2CH=CH_2$: F, 25.43. Found: F, 22.90; Cl, 3.46.

Addition of CH_3OH to $CF_2=CFCF_2Cl$ with CH_3ONa

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) via 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.

VPC 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 5.56 μ and a weak shoulder at 5.67 μ , hence ²³CH₃OCF₂CF=CF₂.

C: b.p. 78-9° (micro), $n_D^{20.5}$ 1.3305, with broad infrared band at 5.83 μ . Analysis calcd. for C₄H₃ClF₄O, CH₃OCF₂CF=CFCl and/or CH₃OCF=CFCF₂Cl: 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.. Analysis calcd. for C₅H₇F₅O₂, CH₃OCF₂CHFCF₂OCH₃: C, 30.94; H, 3.64. Found: C, 30.75; H, 3.19.

Reaction of CF₂=CFCF₂Cl with CH₃ONa in Dioxane

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 CH₃OCF₂CF=CF₂ (b.p. ca. 55-6°, n_D^{21} ca. 1.30, and strong infrared band at 5.65 μ by comparison with previous experiments.

Lewis Acid Catalysed Additions of Haloalkanes to Haloolefins

Attempted Addition of CFCl₃ to CFCl=CFCl Catalyzed by SbF₃

Boron trifluoride was bubbled slowly through a mixture of

$\text{CFCl}=\text{CFCl}$ (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. VFC showed no adduct formed. Boron trifluoride fumes were still present at the end of the reaction.

Attempted Addition of CFCl_3 to $\text{CFCl}=\text{CFCl}$ Catalyzed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$

CFCl_3 (35.5 g., 0.258 mole), $\text{CFCl}=\text{CFCl}$ (26.0 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 $\text{CFCl}=\text{CFCl}$ Catalyzed by HgCl_2

A Fischer-Porter tube was charged at 0° with CFCl_3 (32 g., 0.23 mole), $\text{CFCl}=\text{CFCl}$ (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.

Cleavage of $\text{C}_3\text{Cl}_5\text{F}_3$ by AlCl_3

$\text{C}_3\text{Cl}_5\text{F}_3$ (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 $\text{CF}_2=\text{CFCl}$. Washing gave a liquid (31 g.) which contained 6% CCl_4 , 52% A, 7% $\text{C}_3\text{Cl}_5\text{F}_3$, and 36% $\text{C}_3\text{Cl}_6\text{F}_2$. Compound A had $n_D^{19.5}$ 1.5048 and was identified by infrared as $\text{CCl}_2=\text{CCl}_2$. The $\text{C}_3\text{Cl}_6\text{F}_2$ had b.p. $65-6^\circ/4.5$ mm. (b.p. $203-3^\circ/760$ mm.) and m.p. $44.0-45.5^\circ$.

Addition of CFCl_3 to $\text{CF}_2=\text{CF}_2$ Catalyzed by AlCl_3

CFCl_3 (60 g., 0.44 mole) and AlCl_3 (5 g., 0.06 mole) were placed in a Fischer-Porter tube at 0° . $\text{CF}_2=\text{CF}_2$ (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% $\text{C}_3\text{Cl}_3\text{F}_5$ and 4% higher boiling material. The yield was 55%. Distillation and VPC gave a pure sample of $\text{C}_3\text{Cl}_3\text{F}_5$, b.p. $72-3^\circ$ (micro), $n_D^{20.0}$ 1.3535, and d_4^{24} 1.648 g./cc.

Addition of CFCl_3 to $\text{CF}_2=\text{CFBr}$ Catalyzed by AlCl_3

CFCl_3 (130 g., 0.94 mole) and AlCl_3 (7 g.) were placed in a flask at -30° . $\text{CF}_2=\text{CFBr}$ (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 hour. Normal work-up gave a product (150 g.) which was distilled to give $\text{C}_3\text{BrCl}_3\text{F}_4$ (54.2 g., 76%), b.p. $127-8^\circ$, $n_D^{20.0}$ 1.4238, and d_4^{25} 1.9693 g./cc.

Addition of CFCl_3 to $\text{CFCl}=\text{CCl}_2$ Catalyzed by AlCl_3

CFCl_3 (41.0 g., 0.30 mole), $\text{CFCl}=\text{CCl}_2$ (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 VPC showed was 49% CCl_4 , 40% $\text{CCl}_2=\text{CCl}_2$, and 11% $\text{C}_3\text{Cl}_6\text{F}_2$. Distillation and recrystallization from petroleum ether gave a pure white solid, $\text{C}_3\text{Cl}_6\text{F}_2$ (9% yield), m.p. $47.5-49.5^\circ$, b.p. $63^\circ/7.2$ mm. $-55^\circ/3.7$ mm. (189-194°/760 mm.).

Addition of CFCl_3 to $\text{CHF}=\text{CF}_2$ Catalyzed by AlCl_3

AlCl_3 (7 g., 0.052 mole) was added to CFCl_3 (151 g., 1.10 mole) at -72° and $\text{CF}_2=\text{CHF}$ (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 hour, then the material which had collected in the cold trap was re-cycled 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 methanol²⁴. 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 $\text{CCl}_2=\text{CCl}_2$ Catalyzed by AlCl_3

CFCl_3 (134 g., 0.97 mole), $\text{CCl}_2=\text{CCl}_2$ (109 g., 0.66 mole), and AlCl_3 (6 g., 0.045 mole) were stirred at $24-30^\circ$ for 1 hour, then AlCl_3 (3 g., 0.022 mole) was added and the mixture heated at 80° for 2 hours. After leaving at room temperature overnight, the mixture was again heated at $91-2^\circ$ for 1.5 hour, CFCl_3 (54 g.) added and stirred for 2 hours more. Normal work-up gave a material (189 g.) containing $\text{CCl}_2=\text{CCl}_2$ (100 g., 92% recovery). No adduct was formed.

Attempted Addition of CFCl_3 to $\text{CHCl}=\text{CCl}_2$ Catalyzed by AlCl_3

CFCl_3 (42 g., 0.305 mole), $\text{CHCl}=\text{CCl}_2$ (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 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 b.p. $43-44/30$ mm ($133-44/760$ mm.), $n_D^{21.0}$ 1.4816, d_4^{24} 1.531 g./cc. and a M.W. of 165. Analysis calcd. for $\text{C}_2\text{H}_2\text{Cl}_4$, $\text{CH}_2\text{ClCCl}_3$: Cl, 84.49. Found: Cl, 84.60. This was positively identified by comparison of the infrared spectrum with that in the literature²⁵. The residue could not be vacuum distilled.

Addition of CHFCl_2 to $\text{CF}_2=\text{CFCl}$ 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 $\text{CF}_2=\text{CFCl}$ (60 g., 0.51 mole). AlCl_3 (5 g., 0.037 mole) was added and the mixture stirred up to 0° during 1.25 hour. 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 hour. 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 $\text{C}_3\text{HCl}_3\text{F}_4$ (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 $\text{CF}_2=\text{CFCl}$ (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 $\text{CF}_2=\text{CCl}_2$ 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 $\text{CF}_2=\text{CCl}_2$ (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 VPC purification gave $\text{C}_3\text{HCl}_4\text{F}_3$ (18%), b.p. $131-3^{\circ}$, $n_D^{20.0}$ 1.4180, and d_4^{23} 1.656 g./cc..

Addition of CHFCl_2 to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3

CHFCl_2 (32 g., 0.31 mole) and $\text{CFCl}=\text{CFCl}$ (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 $\text{C}_3\text{HCl}_4\text{F}_3$ (17.2 g., 61%), b.p. $125-6^{\circ}$, $n_D^{20.0}$ 1.4184, and $d_4^{23.5}$ 1.683 g./cc..

Addition of CHFCl_2 to $\text{CCl}_2=\text{CCl}_2$ Catalyzed by AlCl_3

$\text{CCl}_2=\text{CCl}_2$ (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 $\text{C}_3\text{HCl}_6\text{F}$ (40% yield) and the replacement product C_3HCl_7 (34% yield). Distillation gave pure $\text{C}_3\text{HCl}_6\text{F}$, b.p. $70^{\circ}/5$ mm. ($206^{\circ}/760$ 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. $30-1^{\circ}$.

Addition of CHFCl_2 to $\text{CF}_2=\text{CFBr}$ 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 $\text{CF}_2=\text{CFBr}$ (67.0 g., 0.416 mole) was bubbled in at -35° to -32° over 20 minutes. During 1 hour the mixture warmed to $+8^\circ$ 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 re-cycled 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 $\text{C}_3\text{HBrCl}_2\text{F}_4$ (86.5 g., 79%), b.p. $110-2^\circ$, $n_D^{20.0}$ 1.4009, and d_4^{25} 1.9088 g./cc.

Addition of CHFCl_2 to $\text{CFCl}=\text{CCl}_2$ Catalyzed by AlCl_3

CHFCl_2 (36 g., 0.35 mole), $\text{CFCl}=\text{CCl}_2$ (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 $\text{C}_3\text{HCl}_5\text{F}_2$ (22 g., 44%), b.p. $79'/39$ mm. - $76'/35$ mm. ($168-170^\circ/760$ mm.), $n_D^{21.0}$ 1.4601, and d_4^{25} 1.710 g./cc..

Addition of CF_2Cl_2 to $\text{CF}_2=\text{CFCl}$ Catalyzed by AlCl_3

CF_2Cl_2 (87 g., 0.72 mole), $\text{CF}_2=\text{CFCl}$ (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 $\text{C}_3\text{Cl}_4\text{F}_4$ (32 g., 17%), b.p. $113-5^\circ$. Analysis calcd. for $\text{C}_3\text{Cl}_4\text{F}_4$: Cl, 55.86. Found: Cl, 53.61. No expected $\text{C}_3\text{Cl}_3\text{F}_5$ was formed.

Addition of CFCl_3 to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3 , in Presence of KF

CFCl_3 (36 g., 0.26 mole), $\text{CFCl}=\text{CFCl}$ (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 VPC indicated was 94% unreacted material, 4% CCl_4 , and only 2% $\text{C}_3\text{Cl}_5\text{F}_3$.

Addition of CFCl_3 to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3 , in Presence of NaF

Reference reaction

CFCl_3 (43 g., 0.313 mole), $\text{CFCl}=\text{CFCl}$ (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 $\text{C}_3\text{Cl}_5\text{F}_3$ (41 g., 75%) b.p. $149-150^\circ$ and $n_D^{21.0}$ 1.4394. Also obtained was $\text{C}_3\text{Cl}_6\text{F}_2$ (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 $\text{C}_3\text{Cl}_5\text{F}_3$ (36 g., 66%), b.p. $144.0-146.5^\circ$ and $n_D^{20.0}$ 1.4398. Also formed was $\text{C}_3\text{Cl}_6\text{F}_2$ (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 $\text{C}_3\text{Cl}_5\text{F}_3$ (35.6 g., 65%), b.p. $147-150^\circ$ and $n_D^{20.0}$ 1.4396. Also formed was $\text{C}_3\text{Cl}_6\text{F}_2$ (5.4 g., 9.3%).

Attempted Addition of CCl_4 to $\text{CF}_2=\text{CFCl}$ Catalyzed by AlCl_3

CCl_4 (235 g., 1.53 mole) and AlCl_3 (10 g., 0.075 mole) were combined in a flask at room temperature then $\text{CF}_2=\text{CFCl}$ (76 g., 0.65 mole) was bubbled in during 1 hour. Since most of the olefin was collected in the dry ice/acetone trap at the end of the reflux condenser this was re-cycled five times during 3.75 hours, then the mixture was left overnight. No adduct was formed. Some polymerization of the olefin occurred.

CCl_4 (111 g., 0.72 mole) and AlCl_3 (6 g., 0.045 mole) were refluxed gently then $\text{CF}_2=\text{CFCl}$ (56 g., 0.48 mole) was bubbled slowly through the mixture over 0.75 hours. The olefin was re-cycled three times in 2.5 hours, then the mixture was refluxed for 0.25 hour. No adduct was formed.

Dehalogenation of $\text{C}_3\text{BrCl}_3\text{F}_4$

A suspension of zinc dust (10.6 g., 0.162 mole) in absolute ethanol (70 ml.) was heated and $\text{C}_3\text{BrCl}_3\text{F}_4$ (32.6 g., 0.109 mole) was added dropwise over 1.25 hour. After refluxing for 3 hours, the mixture was washed with dilute HCl and ice water to give a liquid (15.0 g.) containing product (60%). Chromatographic purification (S.E. column, 78-80°, 3 x 0.8 ml.) gave pure $\text{C}_3\text{Cl}_2\text{F}_4$ (45%), b.p. 46-7° (micro), $n_D^{21.0}$ 1.3510, and d_4^{24} 1.4972 g./cc.

Attempted Addition of CF_2Br_2 to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3

CF_2Br_2 (66 g., 0.31 mole), $\text{CFCl}=\text{CFCl}$ (26 g., 0.195 mole), and AlCl_3 (8 g., 0.06 mole) were combined in a Fischer-Porter tube at 0° then rocked at room temperature for ca. 3 days. Since VPC showed only traces of higher boiling material, AlCl_3 (4 g., 0.03 mole) was added and the mixture was rocked for 6.5 hours. Work-up gave chiefly unreacted material (78 g.).

The product above was combined in a tube with AlCl_3 (6 g., 0.045 mole) and heated overnight at 72° , 4 hours at 52° , overnight at 56° , then 4 days at $55-60^\circ$. Work-up gave a material (63 g.) containing at least ten components, but no one major product.

Addition of CCl_4 to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3

CCl_4 (59 g., 0.38 mole), $\text{CFCl}=\text{CFCl}$ (21 g., 0.16 mole), and AlCl_3 (6 g., 0.045 mole) were combined in a Fischer-Porter tube at 0° . After 5 days at room temperature AlCl_3 (6 g., 0.045 mole) was added and rocked for 1.5 days. Work-up gave a material (67 g.) consisting of 65% CCl_4 , 16% unknown, 3% $\text{C}_3\text{Cl}_5\text{F}_3$, and 16% high boiling material. Distillation gave a pure sample of the unknown component which had b.p. $114-5^\circ$, n_D^{20} 1.5014, and an infrared identical with $\text{CCl}_2=\text{CCl}_2$. Vacuum distillation of the residue gave pure $\text{C}_3\text{Cl}_7\text{F}$, b.p. $81^\circ/3.5$ mm. - $85^\circ/3.8$ mm., (b.p. $230-3^\circ/760$ mm.), $n_D^{19.8}$ 1.5188, and d_4^{23} 1.847 g./cc.. No $\text{C}_3\text{Cl}_6\text{F}_2$ was detected.

Reaction of CBrCl_3 with AlCl_3

CBrCl_3 (44 g., 0.22 mole) and AlCl_3 (5 g., 0.037 mole) were placed in a Fischer-Porter tube and rocked for 3 hours at room temperature, then overnight. Normal work-up gave a material (39 g.) containing 40% CCl_4 , 46% unreacted CBrCl_3 , and 14% material believed to be CBr_2Cl_2 .

Attempted Addition of CBrCl_3 to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3

CBrCl_3 (46 g., 0.23 mole), $\text{CFCl}=\text{CFCl}$ (21 g., 0.16 mole), and AlCl_3 (6 g., 0.045 mole) were combined at 0° in a Fischer-Porter tube then rocked at room temperature for 9 hours. VPC showed no adduct formed. AlCl_3 (5 g., 0.037 mole) was added and left at ambient for 1.5 days. Work-up gave only the expected CCl_4 , unreacted olefin (18 g.) and

CBrCl_3 , and CBr_2Cl_2 . No higher boiling material was formed.

Attempted Addition of $\text{C}_6\text{H}_5\text{CCl}_3$ to $\text{CFCl}=\text{CFCl}$ Catalyzed by AlCl_3

$\text{C}_6\text{H}_5\text{CCl}_3$ (42 g., 0.215 mole), $\text{CFCl}=\text{CFCl}$ (26 g., 0.195 mole), and AlCl_3 (5 g., 0.037 mole) were combined in a Fischer-Porter tube at 0° then rocked at room temperature for 4.5 hours. AlCl_3 (4 g., 0.030 mole) was added and the mixture left for 3 hours. Work-up gave a material (52 g.), which contained none of the desired adduct.

Attempted Addition of CFCl_3 to $\text{CF}_3\text{CF}=\text{CF}_3$ 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 re-cycled. VPC 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 VPC contained 6% unreacted material, 12% low boiling component, 28% CCl_4 , and 46% high boiling component. Chromatographic purification gave material believed to be $\text{CF}_3\text{CF}=\text{CClCF}_3$, b.p. 32° , with weak infrared bands at 6.04μ and 6.23μ , and $\text{CF}_3\text{CCl}=\text{CClCFCl}_2$, b.p. $140-1^\circ$ (micro), $n_D^{21.0}$ 1.4304, d_4^{24} 1.692 g./cc., with strong infrared band at 6.12μ .

Attempted Addition of CFCl_3 to $\text{CF}_3\text{CF}=\text{CF}_2$ Catalyzed by AlCl_3

CFCl_3 (50 g., 0.36 mole), $\text{CF}_3\text{CF}=\text{CF}_2$ (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 compounds²⁶ and CCl_4 . The infrared spectrum of the mixture had strong bands at 5.80μ and 6.01μ , indicative of $\text{CF}_3\text{CF}=\text{CFCl}$ and $\text{CF}_3\text{CF}=\text{CCl}_2$. No higher boiling components were formed.

Reaction of Cyclo- $\text{C}_5\text{Cl}_2\text{F}_6$ with AlCl_3

Cyclo- $\text{C}_5\text{Cl}_2\text{F}_6$ (43 g., 0.175 mole) and AlCl_3 (3 g., 0.0225 mole) were placed in a Fischer-Porter tube and left overnight at room temperature. AlCl_3 (3 g., 0.0225 mole) was added and the mixture left for 1 day, then worked-up to give a material (40 g.) which contained five components, A, B, C, D, and E; but was chiefly unreacted olefin A. Distillation and VPC purification (S.E. column, $125-30^\circ$) gave pure B, identified as cyclo- $\text{C}_5\text{Cl}_3\text{F}_5$; b.p. $123-4^\circ$ (micro), $n_D^{20.0}$ 1.4076, with a strong infrared band at 6.16μ characteristic of $-\text{CCl}=\text{CCl}-$, and pure C, identified as cyclo- $\text{C}_5\text{Cl}_4\text{F}_4$; b.p. $155-6^\circ$ (micro), $n_D^{20.0}$ 1.4440, with a strong infrared band at 6.19μ . Components D and E were not isolated but were tentatively assumed to be cyclo- $\text{C}_5\text{Cl}_5\text{F}_3$ and cyclo- $\text{C}_5\text{Cl}_6\text{F}_2$ respectively.

Attempted Addition of CFCl_3 to Cyclo- $\text{C}_5\text{Cl}_2\text{F}_6$ Catalyzed by AlCl_3

CFCl_3 (42 g., 0.30 mole), olefin (40 g., 0.16 mole), and AlCl_3 (6 g., 0.047 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 VPC 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. $70^\circ/2.8$ mm. - $72^\circ/3.0$ mm. ($220-1^\circ/760$ mm.), $n_D^{20.5}$ 1.5175, d_4^{23} 1.778 g./cc., with a strong infrared band at 6.20μ , identified as cyclo- $\text{C}_5\text{Cl}_6\text{F}_2$. A small amount of higher boiling residue was present which solidified, m.p. $34-6^\circ$, and had a strong infrared band at 6.19μ . Recrystallization from absolute ethanol-water gave white crystals, m.p. $36.5 - 37.5^\circ$, identified²⁷ as cyclo- C_5Cl_8 .

Fluoronitroso Compounds

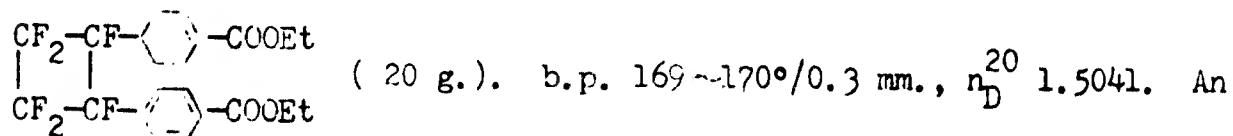
Preparation of p-Trifluorovinyl Ethyl Benzoate

Benzoyl peroxide (60.5 g., 0.25 mole) was added in 5 g. aliquots to stirred, refluxing $\text{CF}_2\text{BrCFClBr}$ (138 g., 0.5 mole) over a period of 3 hours. The reaction mixture was extracted with 12% aqueous sodium bicarbonate (4 x 50 ml.). The aqueous solution was acidified to yield crude $\text{CF}_2\text{BrCFClC}_6\text{H}_4\text{COOH}$. The reaction was carried out six times and the total yield of $\text{CF}_2\text{BrCFClC}_6\text{H}_4\text{COOH}$ 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 $\text{CF}_2\text{BrCFClC}_6\text{H}_4\text{COOC}_2\text{H}_5$ (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 $\text{CF}_2=\text{CFC}_6\text{H}_4\text{COOC}_2\text{H}_5$ (34.5 g., 47.5%) and viscous oil (24.2 g.). $\text{CF}_2=\text{CFC}_6\text{H}_4\text{COOC}_2\text{H}_5$, b.p. $80^\circ/15$ mm., n_D^{20} 1.4966, d^{20} 1.274. The infrared spectrum showed $\text{CF}_2=\text{CF}-$ and $-\text{COOC}_2\text{H}_5$ absorption at 5.69μ ,

and 5.81μ : NMR data showed the compound had a $\text{CF}_2=\text{CF}-$ group para to the ester group. Redistillation of viscous oil gave



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

Reaction of $\text{CF}_2=\text{CFC}_6\text{H}_4\text{COOC}_2\text{H}_5$ with NOCl

Dimethylformamide (100 ml.) was added slowly to cooled aluminum chloride (3.5 g., 0.002 mole). After the suspension became cool, $\text{CF}_2=\text{CFC}_6\text{H}_4\text{COOC}_2\text{H}_5$ (11.5 g., 0.054 mole) was added and NOCl bubbled into the mixture at 0° . After ca. 2 hours VPC 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 $\text{C}_{22}\text{H}_{18}\text{ClF}_6\text{NO}_5$: 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 $\text{C}_{22}\text{H}_{18}\text{ClF}_6\text{NO}_5$: 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 H^1 and F^{19} NMR spectra were consistent with proposed structure.

Preparation of $\text{CF}_2=\text{CFCF}_2\text{COOEt}$ and its Reaction with NOCl

A mixture of ethanol (55.2 g., 1.2 mole), and $\text{CF}_2\text{ClCFClCF}_2\text{COONa}$ (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 $\text{CF}_2\text{ClCFClCF}_2\text{COOC}_2\text{H}_5$ (90 g., 87%): b.p. $66^\circ/20$ mm., n_D^{20} 1.3741, (lit. b.p. $64^\circ/20$ 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 $\text{CF}_2=\text{CFCF}_2\text{COOC}_2\text{H}_5$ (31.8 g., 46%): b.p. 109° , n_D^{20} 1.3403, d^{20} 1.3450. MR_D : calcd.: 31.36. Found: 31.98.

$\text{CF}_2=\text{CFCF}_2\text{COOC}_2\text{H}_5$ (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 VPC peak areas was $\text{CF}_2\text{ClCFNOCF}_2\text{COOC}_2\text{H}_5$ 6.2 g. (51.7%) and $\text{CF}_2\text{ClCFClCF}_2\text{COOC}_2\text{H}_5$ 4.2 g. (37.5%). An analytical sample which was separated by VPC had the following properties: No definite boiling point. Color became faint at ca. 140° . Analysis calcd. for $\text{C}_6\text{H}_5\text{ClF}_5\text{NO}_3$: C, 26.75; H, 1.86. Found: C, 26.96; H, 2.37.

Reaction of $\text{CF}_2=\text{CFCF}_2\text{COOCH}_3$ with NOCl

$\text{CF}_2=\text{CFCF}_2\text{COOCH}_3$ (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 VPC was $\text{CF}_2\text{ClCFNOCF}_2\text{COOCH}_3$ 5.3 g. (41.6%) and $\text{CF}_2\text{ClCFClCF}_2\text{COOCH}_3$ 2.8 g. (21.5%). An analytical sample which was separated by VPC had the following properties: No definite boiling point. Color became faint at about 125° . Analysis calcd. for $\text{C}_5\text{H}_3\text{ClF}_3\text{NO}_3$: C, 23.51; H, 1.18. Found: C, 24.64; H, 1.98.

Preparation of $\text{CF}_2=\text{CFCOOC}_2\text{H}_5$ and its Reaction with NOCl

$\text{CF}_2\text{BrCFClCH}=\text{CH}_2$ (56.2 g., 0.25 mole) was added to a solution of KMnO_4 (18 g., 0.75 mole) and water (600 ml.) at $60-65^\circ$ over the period of two hours. The mixture was stirred for six hours at 60° and cooled to 0° , acidified with dil. H_2SO_4 , treated with NaHSO_3 solution, and extracted with ether. Distillation gave $\text{CF}_2\text{BrCFClCOOH}$ (19.0 g., 32.1%): b.p. $71-72^\circ/4.5$ mm., n_D^{20} 1.4213, (lit. b.p. $78-80^\circ/5.0$ mm., n_D^{20} 1.4180).

A solution of $\text{CF}_2\text{BrCFClCOOH}$ (19.6 g., 0.08 mole), ethanol (40 g.) and conc. H_2SO_4 (2 ml.) was refluxed for 5 hours. $\text{CF}_2\text{BrCFClCOOC}_2\text{H}_5$ (12.5 g., 58%) was obtained; b.p. $82-3^\circ/45$ mm. (lit. $83-4^\circ/60$ mm.).

To a refluxing mixture of ether (100 ml.), Zn (12.3 g., 0.19 mole), and ZnCl_2 (1.0 g.), $\text{CF}_2\text{BrCFClCOOC}_2\text{H}_5$ (25.1 g., 0.093 mole) was added dropwise over the 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 $\text{CF}_2=\text{CFCOOC}_2\text{H}_5$ (2.8 g., 19.5%) was obtained; b.p. $101-102^\circ$, n_D^{20} 1.3656 (lit. b.p. $100-101^\circ$, n_D^{25} 1.3618).

$\text{CF}_2=\text{CFCOOC}_2\text{H}_5$ (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 VPC was $\text{CF}_2\text{ClCFNOCOOC}_2\text{H}_5$ 1.0 g. (25.3 %) and $\text{CF}_2\text{ClCFClCOOC}_2\text{H}_5$ 0.3 g. (7.4%). An analytical sample was separated by VPC. It had no definite boiling point and the color became faint at about 90° . Analysis calcd. for $\text{C}_5\text{H}_5\text{ClF}_3\text{NO}_3$: C, 27.39; H, 2.30. Found: C, 27.99; H, 2.74.

Preparation of $\text{C}_6\text{H}_5\text{-O-CF}=\text{CCl}_2$ 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). $\text{CF}_2=\text{CCl}_2$ (133 g., 1.0 mole) was added over the period of 3 hours. After the 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 VPC 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.

Free Radical Additions of Haloalkylhalides to Olefins

Preparation of 1,2-Dibromohexafluorocyclobutane and its Attempted Addition to Ethylene

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. 1,2-Dibromohexafluorocyclobutane (73.7 g., 0.23

mole), benzoyl peroxide (0.5 g.), and ethylene (2.8 g., 0.1 mole) were heated in an autoclave at 100° for 12 hours. Unreacted ethylene (1 g.) was recovered on venting. Distillation of the liquid yielded pure BTFE and a few grams residue of a complex mixture. This is to be repeated.

Preparation of $\text{CF}_3\text{CFBrCF}_2\text{Br}$ and its Reaction with Ethylene

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 $\text{CF}_3\text{CFBrCF}_2\text{Br}$ (236 g.).

$\text{CF}_3\text{CFBrCF}_2\text{Br}$ (236 g., 0.76 mole), benzoyl peroxide (1 g.) and ethylene (7 g., 0.25 mole) were heated in an autoclave at 100° for 6 hours. Distillation of the product yielded $\text{CF}_2\text{Br}(\text{CF}_3)\text{CFCH}_2\text{CH}_2\text{Br}$ (43 g., 51%) b.p. 145°, n_D^{21} 1.4017, d^{20} 1.992. Analysis calcd. for $\text{C}_5\text{H}_4\text{Br}_2\text{F}_6$: MR_D , 41.27; C, 17.75; H, 1.18; Br, 47.34; F, 34.00. Found: MR_D , 40.82; C, 18.11; H, 1.26; Br, 49.67; F, by difference, 30.96. The proton and F^{19} NMR spectra were consistent with the proposed structure.

$\text{CF}_2\text{Br}(\text{CF}_3)\text{CFCH}_2\text{CH}_2\text{Br}$ (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 $\text{CF}_2\text{Br}(\text{CF}_3)\text{CFCH}=\text{CH}_2$, b.p. 79°, n_D^{22} 1.3469, d^{21} 1.663. Analysis calcd. for $\text{C}_5\text{H}_3\text{BrF}_6$: MR_D , 32.67; Br, 31.17. Found: MR_D , 32.99; Br, 31.58.

Fluorination of $\text{CF}_3\text{CFBrCF}_2\text{Br}$

Chlorine was passed into heated SbF_3 (25 g.) with stirring until the whole mass became liquid. $\text{CF}_3\text{CFBrCF}_2\text{Br}$ (44 g.) was added slowly to the heated stirred SbCl_2F_3 and the reaction was continued for a

further 2 hours. The organic layer was separated, but VPC indicated the absence of any fluorinated product.

Free Radical Addition of $\text{CF}_2\text{BrCF}_2\text{Br}$ to Ethylene

$\text{CF}_2\text{BrCF}_2\text{Br}$ (78 g., 0.3 mole), benzoyl peroxide (0.5 g.), and ethylene (3.1 g.) were heated in an autoclave at 100° for 4 hours. The product was distilled to yield an adduct (6 g., 20% based on ethylene) and a residue (2 g.). The adduct had the following properties: b.p. $72^\circ/80$ mm., n_D^{22} 1.4167, d^{21} 1.9702. Analysis calcd. for $\text{C}_4\text{H}_4\text{Br}_2\text{F}_4$, $\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CH}_2\text{Br}$: MR_D , 36.13; Br, 55.56. Found: MR_D , 35.83; Br, 55.81.

Dehydrohalogenation of $\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CH}_2\text{Br}$

$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CH}_2\text{Br}$ (21 g.), potassium hydroxide (8 g.), and ethanol (20 ml.) were heated in a flask fitted with a fractionation column. $\text{CF}_2\text{BrCF}_2\text{CH}=\text{CH}_2$ (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 $\text{C}_4\text{H}_3\text{BrF}_4$: MR_D , 27.98; Br, 38.65. Found: MR_D , 28.14; Br, 38.44.

Attempted Addition of Benzotrichloride to Ethylene

Ethylene was passed into benzotrichloride (135 g.) and benzoyl peroxide (1.5 g.) at 100° for 3 hours. No reaction was indicated by VPC.

Benzotrichloride (300 g.), benzoyl peroxide (1 g.) and ethylene (16 g.) were heated in an autoclave at 100° for 6 hours. The pressure rose to 450 p.s.i. and then dropped to 200 p.s.i. The autoclave was vented to yield a gaseous material (9 g.) which was chiefly hydrogen chloride. The liquid residue was washed with aqueous sodium bicarbonate and water and dried over CaCl_2 . Distillation gave pure benzotrichloride. The solid residue (10 g.) was not very soluble in acetone.

Reaction of $\text{CF}_3\text{CF}_2\text{CCl}_3$ and $\text{CF}_2\text{BrCF}_2\text{Br}$ with $\text{CF}_2=\text{CFCl}$

$\text{CF}_3\text{CF}_2\text{CCl}_3$ (215 g., 0.9 mole), benzoyl peroxide (1.5 g.) and $\text{CF}_2=\text{CFCl}$ (31.0 g., 0.3 mole) were heated in an autoclave at 100° for 12 hours. On venting the autoclave a product (6 g.) which was chiefly $\text{CF}_2=\text{CFCl}$ was obtained. The residue showed no higher boiling product by VPC, but it had a suspension of white polymeric material.

$\text{CF}_2\text{BrCF}_2\text{Br}$ (176 g.), benzoyl peroxide (1 g.) and $\text{CF}_2=\text{CFCl}$ (21 g.) were heated in an autoclave at 100° for 12 hours. On venting the autoclave a gaseous material (1 g.) was collected. No 1:1 adduct was present in the residue as shown by VPC, but a white solid, m.p. ca. 250° , was obtained.

Attempted Hydrolysis of >CCl_2 to >C=O

$\text{CF}_3\text{CF}_2\text{CCl}_2\text{CH}_2\text{CHClCH}_3$ (11 g.) and conc. sulfuric acid (17 g.) were heated to 200° . The product was washed with water and the organic product isolated, showed no reaction by VPC.

$\text{CF}_3\text{CF}_2\text{CCl}_2\text{CH}_2\text{CHClCH}_3$ (6.5 g.), mercuric oxide (5 g.) and water (2 g.) were heated in a sealed tube at 200° for 2 hours. The organic product showed no reaction by VPC.

$\text{CF}_3\text{CF}_2\text{CCl}_2\text{CH}_2\text{CHClCH}_3$ (1 g.), fuming sulfuric acid (3 g.) and mercuric and mercurous sulfate (20 mg.) were heated in a sealed tube at 200° for 1 hour. The tube was cooled in dry ice/acetone, but during opening the sealed tube exploded.

$\text{CF}_3\text{CF}_2\text{CCl}_2\text{CH}_2\text{CHClCH}_3$ (2 g.), fuming sulfuric acid (4 g.), mercuric sulfate (10 mg.) and mercurous sulfate (10 mg.) were heated at 200° for 1 hour. Some gaseous product condensed into a cold trap, but could not be identified. The liquid showed no reaction by VPC.

Attempted Formation of Radicals from the Haloalkanes and their
Reaction in situ with Aromatic Nuclei

Ultraviolet Irradiation of Benzene with $\text{CF}_2\text{BrCFClBr}$

Benzene (56.2 g., 0.72 mole) and $\text{CF}_2\text{BrCFClBr}$ (200 g., 0.716 mole) were irradiated in quartz apparatus with a mercury vapor 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 VPC examination, was fractionated to remove most of the starting materials. The residue (18.3 g.) was further distilled to remove more $\text{CF}_2\text{BrCFClBr}$ (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 VPC (Si gum at 115°) to yield (i) $\text{CF}_2\text{BrCFClBr}$ (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 $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Br}$ (0.5 g., 0.25% yield). The F^{19} NMR spectrum, which showed a doublet and triplet, the H^1 NMR spectrum and the infrared spectrum were consistent with the proposed structure. The NMR spectra showed ca. 5% impurity present; (b) three components (0.27 g.) corresponding to (a) and two longer retained components.

Ultraviolet Irradiation of Benzoic Acid with $\text{CF}_2\text{BrCFClBr}$

Benzoic Acid (16.3 g.) was dissolved in the minimum volume of dry benzene (ca. 50 ml.), $\text{CF}_2\text{BrCFClBr}$ (44.8 g.) was added and the mixture irradiated with a mercury vapor lamp for 65 hours at ca. 75°. The product was washed out with benzene and most of the benzene fractionated off. The residue was repeatedly treated with hot water, which extracted

benzoic acid (14.7 g., 90% recovery) only.

Ultraviolet Irradiation of Bromobenzene with $\text{CF}_2\text{BrCFClBr}$

Bromobenzene (73.8 g.) and $\text{CF}_2\text{BrCFClBr}$ (138.5 g.) were irradiated in a quartz apparatus with a mercury vapor lamp for 70 hours at ca. 90°. The products were washed out with ether and fractionated, finally under reduced pressure to remove most of the starting materials. The residue (4.6 g.) was separated by VPC (Si gum 120°) to yield (i) bromobenzene, (ii) two overlapping long retained components (2.47 g.) which have not been separated.

Ultraviolet Irradiation of Pyridine with $\text{CF}_2\text{BrCFClBr}$

Pyridine (102.3 g.) and $\text{CF}_2\text{BrCFClBr}$ (22.0 g.) were irradiated in a quartz apparatus with a mercury vapor lamp for 72 hours at ca. 90°. Fractionation etc. of the product revealed no higher boiling product (by VPC) consistent with a substituted pyridine, but there was a large residual tar.

Ultraviolet Irradiation of Pentafluorobenzene with $\text{CF}_2\text{BrCFClBr}$

Refluxing pentafluorobenzene (27.6 g.) and $\text{CF}_2\text{BrCFClBr}$ (16.8 g.) were irradiated for 150 hours with ultraviolet irradiation from a Pen-Ray lamp inserted into the thermometer pocket of the flask.

Examination of the product by VPC showed the presence of starting materials only. The mixture was fractionated to leave a residue (5.0 g.) which also showed starting materials only by VPC. Evaporation on a rotary vacuum pump gave a brown tar residue (0.09 g.).

Sunlight Irradiation of Benzoic Acid and $\text{CF}_2\text{BrCFClBr}$

A mixture of benzoic acid (0.53 g.) in benzene (2.1 g.) and

$\text{CF}_2\text{BrCFClBr}$ (7.7 g.) has been exposed to sunlight since 5/3/65.

Sunlight Irradiation of Pentafluorobenzene with $\text{CF}_2\text{BrCFClBr}$

A mixture of pentafluorobenzene (6.1 g.) and $\text{CF}_2\text{BrCFClBr}$ (10.0 g.) was exposed to sunlight for 87 days. A trace of solid, insufficient for an infrared spectrum, was deposited on the flask wall. The organic liquid showed only starting materials present by VPC as did the small residue obtained from the distillation.

Pyrolysis of $\text{CF}_2\text{BrCFClBr}$

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 pyrolysed was added dropwise over a slow stream of nitrogen (ca. 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.

$\text{CF}_2\text{BrCFClBr}$ (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 VPC showed seven peaks in the following percentages: (1) 4%; (2) 17%; (3) 3%; (4) 10%; (5) 31%; (6) 27% ($\text{CF}_2\text{BrCFClBr}$); and (7) 8% (suspected $\text{CF}_2\text{BrCFBr}_2$).

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% $\text{CF}_2\text{BrCFClBr}$. 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 $\text{CF}_2\text{BrCFClBr}$

Using the same procedure and apparatus as in the previous experiment, an intimate mixture of benzene (2.06 g.) and $\text{CF}_2\text{BrCFClBr}$ (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 VPC 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.

Pyrolysis of Bromobenzene with $\text{CF}_2\text{BrCFClBr}$

Passage of a mixture of bromobenzene (2.02 g.) and $\text{CF}_2\text{BrCFClBr}$ (2.2 g.) through the pyrolysis tube at 400° over a period of 60 minutes gave a product (2.03 g., 48% recovery) which by VPC showed a complex mixture of at least 14 products. The main product ca. 70% corresponded to bromobenzene by VPC but there were two overlapping minor peaks of long retention time which corresponded to the products of the ultra-violet initiated reaction of bromobenzene and $\text{CF}_2\text{BrCFClBr}$.

A similar pyrolysis at 500° gave a lower recovery (36.5%) and the complexity of products was reduced, but the long retained material was still produced. A pyrolysis at 330° gave no high boiling products.

Pyrolysis of Pentafluorobenzene with $\text{CF}_2\text{BrCFClBr}$

Passage of a mixture of pentafluorobenzene (3.02 g.) and $\text{CF}_2\text{BrCFClBr}$ (2.01 g.) through the pyrolysis tube at 400° over a period

of 15 minutes gave a product (4.79 g., 95% recovery) which by VPC appeared to be unchanged pentafluorobenzene and the products of $\text{CF}_2\text{BrCFClBr}$ pyrolysis.

Pentafluorobenzene (2.02 g.) and $\text{CF}_2\text{BrCFClBr}$ (2.00 g.) on pyrolysis at 500° gave 59.5% recovery, which was ca. 95% pentafluorobenzene.

Pyrolysis of Bromopentafluorobenzene with $\text{CF}_2\text{BrCFClBr}$

Passage of a mixture of bromopentafluorobenzene (2.01 g.) and $\text{CF}_2\text{BrCFClBr}$ (2.09 g.) through the pyrolysis tube at 400° over a period of 60 minutes gave a liquid (3.6 g., 88%) which by VPC showed no product of longer retention time than bromopentafluorobenzene.

A similar experiment at 500° gave a 46% recovery which showed a trace of high boiling product.

Pyrolysis of an Olefin Mixture with $\text{CF}_2\text{BrCFClBr}$

Passage of a mixture of the olefins $\text{CF}_3\text{CH=CHBr}$ and $\text{CF}_3\text{CBr=CH}_2$ (2.02 g.) and $\text{CF}_2\text{BrCFClBr}$ (2.05 g.) through the pyrolysis tube at 400° over a period of 45 minutes gave a liquid (1.5 g., 37% recovery) which by VPC showed a complex mixture containing mainly starting olefins, but no addition products.

As the pyrolysis gave decomposition and a poor recovery the experiment was repeated at 330° , when a 61% recovery was achieved, which consisted of starting materials and a main product of longer VPC retention time.

Pyrolysis of $\text{CF}_2\text{BrCFClBr}$ in the Presence of Bromine

Passage of a mixture of $\text{CF}_2\text{BrCFClBr}$ (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 VPC showed nine peaks in the following

percentages: (1), (2) and (3) 1.5%; (4) 7%; (5) 23%; (6) 35% ($\text{CF}_2\text{BrCFClBr}$); (7) 25.5% (suspected $\text{CF}_2\text{BrCFBr}_2$); (8) 3%; and (9) 3%. The peak numbering corresponds to that in the pyrolysis of $\text{CF}_2\text{BrCFClBr}$ alone (see p. 43). (8) and (9) were not detected in the pyrolysis of $\text{CF}_2\text{BrCFClBr}$ alone.

A repeat experiment produced only 14% of the suspected $\text{CF}_2\text{BrCFBr}_2$.

Pyrolysis of $\text{CF}_2=\text{CFCl}$ with Bromine

Bromine (2.23 g.) was dropped into a tube heated at 53° . A stream of nitrogen and $\text{CF}_2=\text{CFCl}$ 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 $\text{CF}_2\text{BrCFClBr}$ and there was no increase in the yield of suspected $\text{CF}_2\text{BrCFBr}_2$.

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

1,2-Dichloro-1,2,2-trifluoroiodoethane as a Source of Radicals

Reaction of Benzene with $\text{CF}_2\text{ClCFClI}$

(a) $\text{CF}_2\text{ClCFClI}$ was washed with aqueous sodium bisulfite, and water and dried (Drierite) and distilled.

Dry benzene (1.6 g.) and $\text{CF}_2\text{ClCFClI}$ (2.8 g.) were sealed in a hard glass tube at 0° 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 VPC 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 VPC (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 $\lambda_{max.}$ 214 $m\mu$ ($\epsilon_{max.}$ 6860), $\lambda_{max.}$ 256 $m\mu$ ($\epsilon_{max.}$ 559), $\lambda_{max.}$ 262 $m\mu$ ($\epsilon_{max.}$ 686), $\lambda_{max.}$ 268 $m\mu$ ($\epsilon_{max.}$ 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 VPC (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 F^{19} 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. VPC examination of the product showed only a trace of a product corresponding to $C_6H_5CFICF_2Cl$.

Reaction of Bromobenzene with $CF_2ClCFClI$

(a) Bromobenzene (3.14 g., 0.02 mole) and $CF_2ClCFClI$ (2.79 g., 0.01 mole) were sealed in a 100 ml. Fischer-Porter tube and heated on an oil bath at 180°-190° for 26.5 hours. Hydrogen halide was evolved on opening the tube. The liquid product was washed out with ether and the ethereal solution was washed with aqueous sodium bisulfite and water

and examined by VFC. There was a long retained product, suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$, which formed 15% of the mixture by peak area, and also a small peak corresponding to $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$.

(b) An experiment using exactly the same quantities and reaction temperature, but a reaction time of 90 hours gave a product which was 24% suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$. The ratio of peak areas of suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$ to that corresponding to $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$ was 8:1.

The products of (a) and (b) were combined and separated by VFC (Si gum 125°) into three fractions, which should have been:

(1) ether, $\text{CF}_2\text{ClCFClI}$, and bromobenzene, (2) suspected $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$, (3) suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$. Experimentally, bromobenzene which was a major component overlapped with suspected $\text{C}_6\text{H}_5\text{CFClCF}_2\text{Cl}$ and a second separation of (1) and (2) will have to be performed to purify the minor peak so that an infrared spectrum can be measured. Fraction (3) of suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$ (1.05 g.) was contaminated with a longer retained peak, which may be isomer(s) of the major product. The identification of products is continuing.

(c) Bromobenzene (3.01 g.) and $\text{CF}_2\text{ClCFClI}$ (3.17 g.) were refluxed under nitrogen for 90 hours. The liquid temperature on refluxing was ca. 115°. The vapor phase chromatogram showed that suspected $\text{BrC}_6\text{H}_4\text{CFClCF}_2\text{Cl}$ formed 13% of the product. The other 87% was starting material.

Reaction of Bromobenzene with $\text{CF}_2\text{ClCFClI}$ in the Presence of Copper Dust

Bromobenzene (1.6 g., 0.01 mole), $\text{CF}_2\text{ClCFClI}$ (2.79 g., 0.01 mole), and electrolytic copper dust (3.2 g., 0.05 mole) were sealed in a Fischer-Porter tube and heated on an oil bath at 180°-190° for 25.5 hours.

The product was washed out with ether, filtered to remove copper powder and insoluble material, dried, and evaporated on a rotary

vacuum pump to remove most of the ether. VPC examination of the product showed the peaks corresponding to $C_6H_5CFClCF_2Cl$ and suspected $BrC_6H_4CFClCF_2Cl$ in the ratio of ca. 10:1 respectively.

Reaction of Pentafluorobenzene with $CF_2ClCFClI$

Pentafluorobenzene (3 g.) and $CF_2ClCFClI$ (2 g.) were sealed in a Fischer-Porter tube and heated on an oil bath at 180°-190° for 96 hours. The product, which showed a deep violet iodine coloration, showed only starting materials present on VPC examination.

Reaction of Phenol with $CF_2ClCFClI$

Phenol (1.41 g., 0.015 mole) and $CF_2ClCFClI$ (4.19 g., 0.015 mole) were sealed in a Fischer-Porter tube and heated on an oil bath at 180°-190° for 22 hours. The product appeared mainly carbeneous and a large amount of hydrogen halide was evolved. The product was crushed and washed with ether and filtered. The ethereal solution was washed with aqueous sodium bisulfite, and water and dried (Drierite). Most of the ether was evaporated on a rotary vacuum pump to yield a residue which by VPC showed a small amount of long retained material and $CF_2ClCFClI$ as the major product, but no phenol.

This was a preliminary experiment.

Reaction of Nitrobenzene with $CF_2ClCFClI$

Nitrobenzene (1.23 g., 0.01 mole) and $CF_2ClCFClI$ (4.19 g., 0.015 mole) were sealed in a Fischer-Porter tube and heated on an oil bath at 190-200° for 25 hours. During the reaction the lower half of the vapor was violet in color and the upper half brown. VPC examination of the product showed a minor long retained product and large percentages of starting materials.

The reaction was continued at 190–210° for a further 94 hours but there was no appreciable increase of high boiling material on VPC examination.

Diels–Alder Addition of Cyclopentadiene and $\text{CFCl}=\text{CFCl}$

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 solid (2.85 g.) which was filtered off. The ethereal solution was dried (Drierite) and evaporated under reduced pressure to leave a brown gum. The gum did not separate on an alumina column and was not affected by decolorising 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 VPC 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 VPC pure ethanol and a residue which by VPC showed no appreciable change from starting material.

V. FUTURE WORK

Research shall be continued to find synthetic methods for the preparation of nitroso compounds containing other functional groups.

For example, the reaction of $\text{CF}_2\text{CFCH}_2\text{CH}=\text{CH}_2$ and NOCl will be carried out to make $\text{CF}_2\text{ClCFNOCH}_2\text{CH}=\text{CH}_2$.

The reaction of $\text{CF}_2\text{BrCF}_2\text{CH}=\text{CH}_2$ and $\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CH}_2\text{Br}$ will be studied.

A study will be made of the Diels-Alder reactions of perfluorocyclopentadiene with fluorolefins to obtain products of interest to Dr. Douglas Relyea.

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13. ABSTRACT The preparation of perfluoroallyl chloride has been improved and this compound was treated with various alkoxide ions to produce saturated and unsaturated ethers. Lewis acid catalysed additions of polyhaloalkanes to haloolefins were continued. In an attempt to prepare fluoronitroso compounds carrying other functional groups, nitrosyl chloride was allowed to react with unsaturated fluoroesters and ethers. The investigation of the radical addition of haloalkyl chlorides and bromides with various olefins was continued. Attempts have been made to react radicals from $CF_2BrCFC1Br$ and $CF_2ClCFC1I$ with aromatic nuclei.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Preparation (formulation)	8					
Fluorochemicals	1,2					
Elastomers	2					
Nitroso rubber	2					
Unsaturated	0					

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