

THE SYNTHESIS OF SOME  
FLUORINE-CONTAINING CYCLOBUTANES  
BY CYCLOALKYLATION

By  
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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF  
THE UNIVERSITY OF FLORIDA  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA  
June, 1959

## TABLE OF CONTENTS

	Page
LIST OF TABLES . . . . .	iii
ACKNOWLEDGMENTS . . . . .	iv
I. INTRODUCTION . . . . .	1
II. DISCUSSION . . . . .	4
III. INFRARED SPECTRA . . . . .	15
IV. GENERAL CONSIDERATIONS . . . . .	17
V. EXPERIMENTAL . . . . .	24
A. Reactions of 1,3-Butadiene with Fluoroölefins . . . . .	25
B. Reactions of Styrene with Fluoroölefins . . . . .	36
C. Reactions of Chlorotrifluoroethylene with Olefins . . . . .	41
D. Miscellaneous Addition Reactions . . . . .	54
E. Reactions of Addition Products . . . . .	58
VI. SUMMARY . . . . .	63
VII. BIBLIOGRAPHY . . . . .	64
BIOGRAPHICAL DATA . . . . .	66

LIST OF TABLES

Table	Page
I. Properties of the Compounds Prepared	19
II. Analyses of the Compounds Prepared	22

## ACKNOWLEDGMENTS

"From the nature of things, ideas do not come from prosperity, affluence and contentment, but rather from the blackness of despair, not in the bright light of day or in the footlight's glare but rather in the quiet, undisturbed hours of midnight or early morning when one is alone to think!".....

Dr. Frederick Banting

The author wishes to express his appreciation to many people for their contributions to the completion of this research problem. He gratefully acknowledges the advice and assistance of Dr. Paul Tarrant, chairman of the Supervisory Committee and director of this research. Special thanks is given to Dr. W. S. Brey, Jr. for interpretation of the NMR data. For their valuable suggestions and building certain apparatus, thanks are due to Mr. P. J. Thompson and Mr. Calvin Workinger.

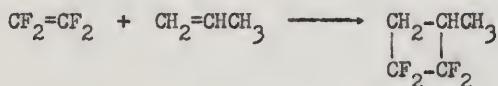
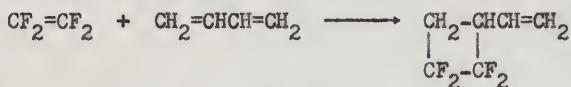
This research was carried out under a grant financed by the Office of the Quartermaster General, U.S. Army, whose support the author now acknowledges.

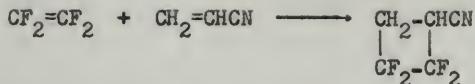
## I INTRODUCTION

The Office of the Quartermaster General established and is currently sponsoring a long-range Arctic Rubber Program for the purpose of discovering and developing elastomers which have the desired low-temperature properties, resistance to swelling when in contact with hydrocarbon fuels and resistance to deterioration by oxidizing agents.

Fluorine-containing compounds such as polytetrafluoroethylene and polychlorotrifluoroethylene have shown extraordinary inertness and range of usefulness. Several fluorobutadienes, when polymerized, have shown remarkable low temperature flexibility along with good solvent resistance. The most promising of these are homopolymers of 1,1,2-trifluorobutadiene and 1,1,3-trifluorobutadiene and a copolymer of the two dienes.

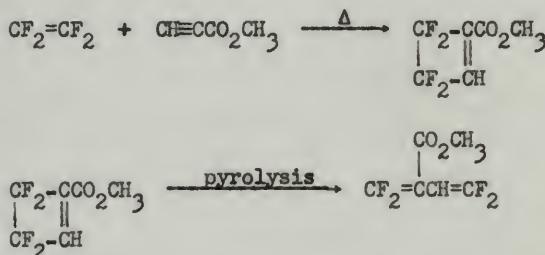
In looking for new methods for preparing fluorobutadienes attention was directed to work done by Coffman and by Anderson. Coffman (7) prepared a series of cyclobutane derivatives in which tetrafluoroethylene was reacted with a variety of olefins. Some typical reactions are as follows:



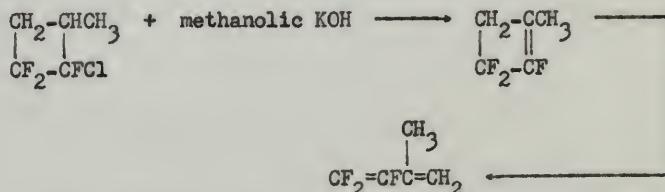
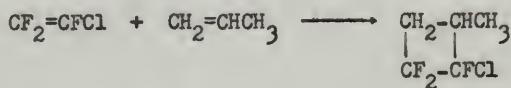


It was observed that the co-dimerization reaction occurred at a lower temperature than the dimerization of tetrafluoroethylene and without the formation of open-chain polymers.

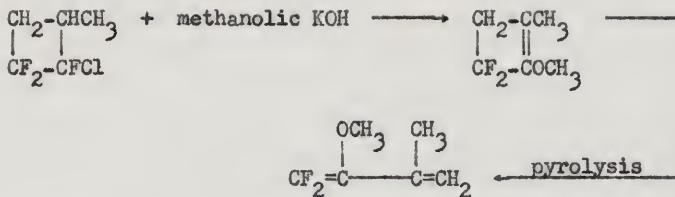
Anderson (1) has prepared fluorinated butadienes containing functional groups by the novel method illustrated below:



These methods of preparation can also be applied to a number of compounds reported in this dissertation. Typical examples are as follows:



By using excess alcoholic potassium hydroxide, ethers could be prepared:

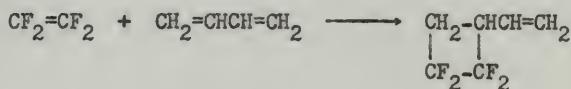


Because of the variety and usefulness of compounds that are obtained from the co-dimerization of fluoroolefins with hydrocarbon olefins, it seemed desirable to prepare a series of such compounds and to study their mode of formation. The products of the co-dimerization reactions are substituted cyclobutanes and in some cases substituted cyclohexenes are also formed.

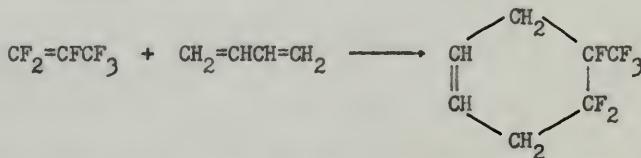
The co-dimerization reactions reported in this dissertation are all thermal initiated reactions in the temperature range of 100-310°, and when necessary, in the presence of a polymerization inhibitor.

## II DISCUSSION

In the course of some investigations on the reactions of fluoroolefins with dienes, it was observed that either a four-membered or a six-membered ring was produced. For example, Coffman (7) reacted tetrafluoroethylene with butadiene and obtained only the cyclobutane derivative:



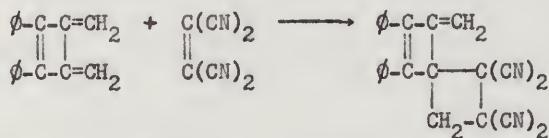
McBee (19), on the other hand, reacted perfluoropropene with butadiene and reported that the reaction proceeded in a Diels-Alder fashion to give a cyclohexene derivative:



Many other olefins have been reacted with butadiene to give the Diels-Alder product, a substituted cyclohexene. However, no reaction has been reported in which both a four-membered and a six-membered ring were formed simultaneously in the reaction.

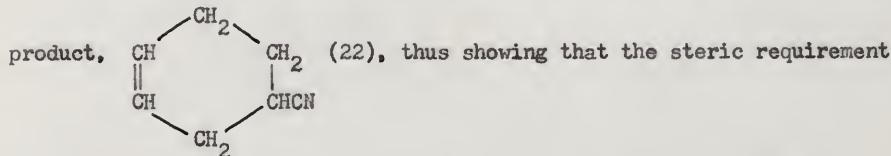
The following are some observations on the formation of four-membered versus six-membered rings. Ethylene reacts with butadiene to give cyclohexene (15). Tetrafluoroethylene reacts with butadiene to give 1-vinyl-2,2,3,3-tetrafluorocyclobutane (7). Considering only these two reactions, it appears that cyclobutane

formation should be favored if the hydrogens on ethylene were replaced by strong electronegative groups. This observation seems to be only partly true. The other criterion appears to be steric in nature. For example, tetracyanoethylene,  $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ , reacts with butadiene to give a substituted cyclohexene instead of forming the cyclobutane derivative (20). However, when the system demands it, the cyclobutane ring is formed (4).



As can be seen, if the cyclohexene were formed then the highly unstable cyclobutadiene would have formed simultaneously.

Acrylonitrile reacts with butadiene to give only the Diels-Alder



alone does not suffice in the formation of the cyclobutane ring. Like ethylene, it reacts with butadiene to form a six-membered ring.

However, acrylonitrile forms a cyclic dimer,  $\begin{array}{c} \text{CH}_2-\text{CHCN} \\ | \\ \text{CH}_2-\text{CHCN} \end{array}$ , when heated to

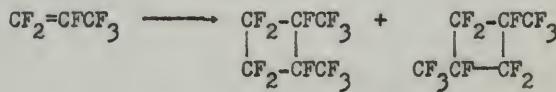
$190-300^\circ$  in the presence of a polymerization inhibitor (8), whereas neither ethylene nor tetracyanoethylene (6) form cyclic dimers when heated to temperatures even greater than this.

It has also been observed that the co-dimerization of tetrafluoroethylene with reactants containing a terminal methylene group occurs more readily than with 1,2-disubstituted ethylenes such as 2-butene or trichloroethylene (7).

Thus, from the preceding discussion, it seems that in order to form the cyclobutane ring from a cycloalkylation reaction in reasonable yields, the following steric requirement must be met:

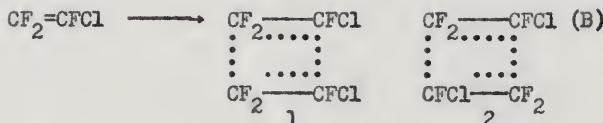
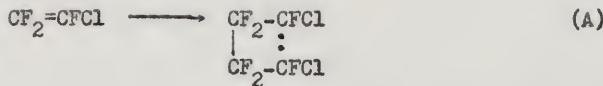
Only hydrogen or fluorine atoms can be attached to the double-bonded terminal carbon of both olefins; for example, both of the reactants must have one of the groups present:  $\text{CH}_2=\text{C}$ ,  $\text{CHF}=\text{C}$ ,  $\text{CF}_2=\text{C}$ .

It has also been observed in cyclic dimerization reactions that some dimers were formed only in a head-to-head manner (13) while other dimers were formed both in a head-to-head and in a head-to-tail manner (12):



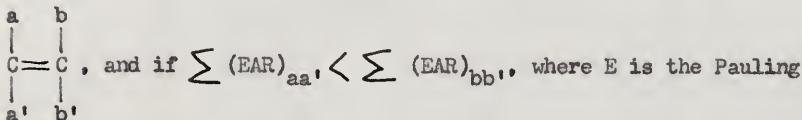
Essentially two types of transition state have been proposed for the process:

An open chain diradical structure (A) in which the most stable diradical would be formed (28) and a cyclic delocalized (four centered) structure (B) (14).

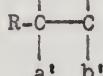


Transition state (A) should be favored over that of (B) because of the following reason. Only one product is formed, that being 1,2-dichloroperfluorocyclobutane (13). If the reaction proceeded through transition state (B) it would seem likely that some 1,3-dichloroperfluorocyclobutane from structure 2 would have formed. Increasing the reaction temperature, which would favor a more random formation, causes only a break-down of the cyclobutane ring without any of the 1,3-type structure being observed (21).

The more stable free radical can be predicted on the basis of an empirical rule (17). If the radical R· is added to the olefin



electronegativity and AR is the atomic refraction of a, a', b, b', then the orientation will be  $\begin{array}{c} \text{a} & \text{b} \\ | & | \\ \text{R}-\text{C} & -\text{C} \\ | & | \\ \text{a}' & \text{b}' \end{array}$ . The radical R· attacks the



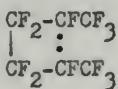
olefinic carbon with the lowest  $\sum (\text{EAR})$  of its substituents and thus forms the more stable free radical. Listed below are the EAR values of some of the common elements:

Atom	H	F	Cl	B	I	C
EAR	2.31	4.80	18.0	24.9	33.4	6.0

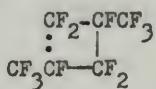
The  $\sum$  (EAR) for  $-CFCl\cdot$  is 22.8 compared to 9.6 for  $-CF_2\cdot$ .

This indicates that the  $-CFCl\cdot$  is much more stable than the  $-CF_2\cdot$ .

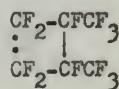
In the dimerization of perfluoropropene, it has been observed that both the head-to-head and head-to-tail structures are formed (12). Only the open-chain diradical transition state will be considered in accounting for the observed products. The three transition states for this dimerization are:



(A)



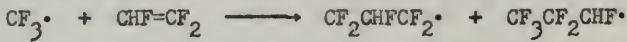
(B)



(C)

The  $\sum$  (EAR) for  $-CFCF_3$  is 10.8 compared to 9.6 for  $-CF_2\cdot$ , a difference of only 1.2. Therefore, the stabilities of the diradicals would be approximately equal. Transition state (A) would be slightly favored over (B), which in turn, would be slightly favored over (C).

Transition states (A) and (C) would give rise to the same product, a 1,2-type structure, while (B) would give a 1,3-type structure. Even when the difference of the  $\sum$  (EAR) values is as much as 2.5, as in the following example, two different free radicals are formed (11):



EAR 7.1 9.6

80%

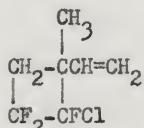
20%

Thus, in the dimerization of perfluoropropene, it is not too surprising even at the lower temperatures that both the 1,2- and the 1,3-type structures are formed with the 1,2-type structure predominating.

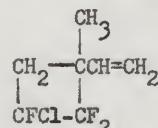
Higher temperatures favor a more random type of attack and the more stable product, and the 1,3-type structure is predominately formed (12).

The above discussions were presented as a basis for the mode of formation for this type of reaction and in discussing the structures of products presented herein, frequent use of the term "mode of formation" will be made.

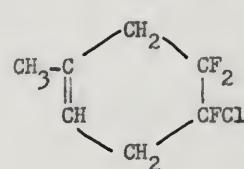
The addition of chlorotrifluoroethylene to isoprene can give rise to six different products (not counting cis-trans isomers):



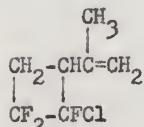
Xa



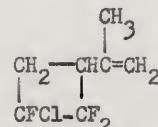
Xb



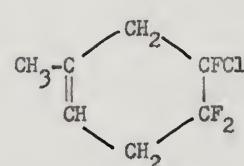
Xc



Xd



Xe



Xf

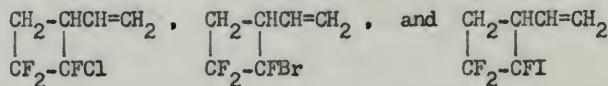
Only structure Xa fits all of the experimental data. Its failure to react with alcoholic potassium hydroxide is a strong indication that there is no hydrogen on the carbon atom adjacent to the carbon atom holding the chlorine. NMR results show the absence of a six-membered ring and the presence of two kinds of four-membered ring structures which are cis-trans isomers of structure Xa.

1,1-Dichlorodifluoroethylene reacted with butadiene to give only the cyclobutane structure. NMR results show that only one kind of four-membered ring structure was present. This material has been assigned the structure  $\begin{array}{c} \text{CH}_2-\text{CHCH=CH}_2 \\ | \\ \text{CF}_2-\text{CCl}_2 \end{array}$ , IV, on the basis that it would

arise from the more stable diradical as previously discussed, and because of its similarity to Xa.

A series of fluoroolefins of the type  $\text{CF}_2=\text{C}\text{FX}$ , where X was Cl, Br, I, CN,  $\text{CF}_3$ ,  $\text{CH}_2\text{CH}_2\text{Br}$  and H, were reacted with butadiene and the mode of formation studied. The ease of reaction seemed to vary with the electronegativity of X, the order of decreasing reactivity being  $\text{Cl} > \text{CN} > \text{Br} > \text{I} > \text{CF}_3 > \text{CH}_2\text{CH}_2\text{Br} > \text{H}$ . This approximate order of reactivity is based on the conversion to products when these fluoroolefins were reacted with butadiene and styrene.

Chlorotrifluoroethylene, bromotrifluoroethylene and iodotri-fluoroethylene reacted with butadiene to give only the cyclobutane structure. For each of these reaction products NMR results show the presence of two kinds of cyclobutane structures, which are probably cis-trans isomers of the 1,2-type structure. This would be expected since the 1,2-type structure arises from the more stable diradical. These materials have been assigned the structures



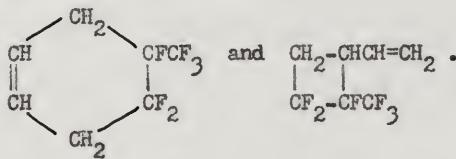
I

II

III

Perfluoropropene, perfluoroacrylonitrile and 4-bromo-1,1,2-trifluoro-1-butene reacted with butadiene to give in each case both the cyclohexene ring and the cyclobutane ring structures. NMR results show that only one kind of cyclobutane structure was present.

The addition products of perfluoropropene to butadiene have been assigned the structures

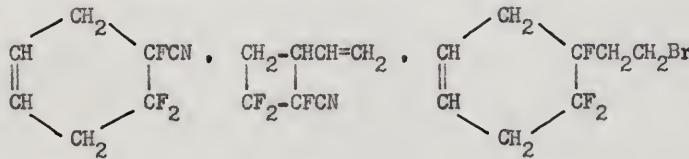


Va

Vb

The 1,2-type structure is preferred over the 1,3-type structure since it arises from the more stable diradical. Since there is only one kind of four-membered ring structure, Vb exists either with the trifluoromethyl group cis or trans to the vinyl group. No reason can be given here as to which structure is present or why a cyclohexene ring was formed in this case.

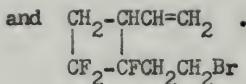
The addition products of perfluoroacrylonitrile to butadiene and of 4-bromo-1,1,2-trifluoro-1-butene to butadiene have been assigned the structures



VIIa

VIIb

VIIc

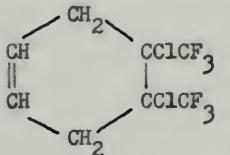


## VIIb

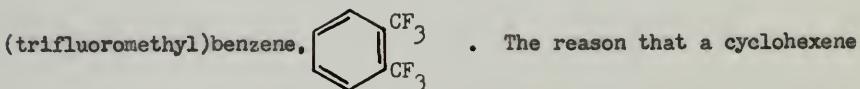
The 1,2-type structures for VIIb and VIIb are preferred over the 1,3-type structure for reasons previously given.

The addition of trifluoroethylene to butadiene gave a mixture of two components as shown by its gas chromatogram. One peak has been identified as being due to 4-vinylcyclohexene, a product of the Diels-Alder dimerization of butadiene. The other peak has not been identified since the 4-vinylcyclohexene interferes with the methods of analysis used in identifying compounds of similar structure.

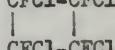
The addition of 2,3-dichlorohexafluoro-2-butene to butadiene gave a material, IX, which has been assigned the structure



with alcoholic potassium hydroxide to give the known (5) 1,2-bis-



ring was formed in preference to a cyclobutane ring was probably due to steric effects. The dimerization of 1,2-dichlorodifluoroethylene does not give  $\text{CFCl}-\text{CFCl}$ , but rather an open chain dimer,



$\text{CFCl}_2\text{CFClCF}=\text{CFCl}$  (10). This is not due to the instability of the

cyclic dimer because it has been prepared by a different route.

The addition of chlorotrifluoroethylene to isobutylene gave a material, XIX, which has been assigned the structure

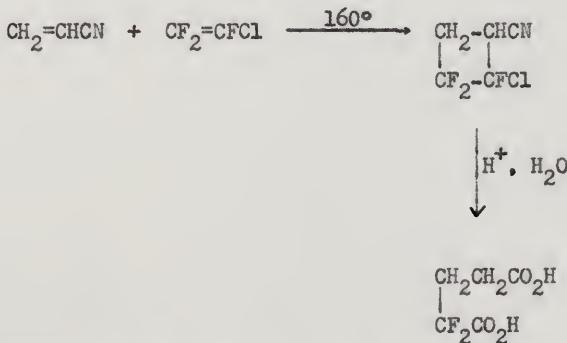
$$\begin{array}{c} \text{CH}_2-\text{C}(\text{CH}_3)_2 \\ | \\ \text{CF}_2-\text{CFCl} \end{array}$$

on the basis of its mode of formation, NMR spectrum and its failure to react with alcoholic potassium hydroxide. A structure in which a hydrogen on a carbon atom adjacent to a carbon holding the chlorine would be expected to react with alcoholic potassium hydroxide.

The addition of chlorotrifluoroethylene to acrylonitrile gave a material, XXII, which has been assigned the structure

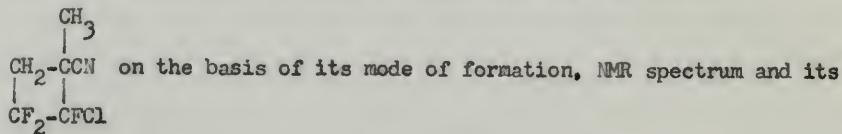
$$\begin{array}{c} \text{CH}_2-\text{CHCN} \\ | \\ \text{CF}_2-\text{CFCl} \end{array}$$

on the basis of its mode of formation, NMR spectrum and its ease of reaction with alcoholic potassium hydroxide. Further evidence supporting this structure is found in the work of Barney and Cairns (2). They carried out the following reactions:



No acid containing chlorine was found as would be expected if a 1,3-type structure were present.

The addition of chlorotrifluoroethylene to methacrylonitrile gave a material, XXIII, which has been assigned the structure



failure to react with alcoholic potassium hydroxide. A structure in which a hydrogen on a carbon atom adjacent to a carbon holding the chlorine would be expected to react with alcoholic potassium hydroxide.

Other reactions and structure proofs are given in the Experimental section of this dissertation.

### III INFRARED SPECTRA

One of the most valuable means of detection of double bonds through infrared spectra is the examination of the region near 3.3 microns. Tallent (27) reported data for the =CH stretching bands for several representative olefinic systems using sodium chloride optics. He assigned the peak at 3.23-3.25 microns to the =CH stretch for a terminal methylene and the peak at 3.29-3.32 microns to the =CH stretch in a six-membered system. In the present investigation for compounds assigned the general structure  $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}=\text{CH}_2 \\ | \qquad | \\ \text{CF}_2-\text{CFX} \end{array}$ , a peak occurs at 3.20 microns which is believed to be due to the =CH stretch for a terminal methylene. There is also a peak at 3.28-3.29 microns possibly due to the =CH stretch in a six-membered ring. However, on bromination of this material the peak at 3.20 microns disappears while the one at 3.28-3.29 microns is still present. Roberts (24) has shown that the frequencies of the  $\text{CH}_2$  bands increase as the ring size becomes smaller. He examined the  $\text{CH}_2$  vibrations of three-, four-, five- and six-membered rings substituted with a single chlorine, and found that the value for the six-membered ring was normal, 3.43 microns, for the five-membered ring very nearly so, 3.39 microns, for the four-membered ring the wavelength decreased to 3.34 microns, while for the three-membered ring the wavelength decreased considerably to 3.24 microns. Thus, the band at 3.28-3.29 may be due to  $\text{CH}_2$  vibrations

of the cyclobutane systems presented herein. However, it has also been observed for the compound,  $\text{CF}_2\text{BrCH}_2\text{CFBrCH}_3$ , that there is a shift of the CH stretching frequency toward lower wavelengths and this compound absorbs in this region at 3.35 microns. It would be difficult to make positive assignments in this region for the cyclobutane system until a number of closely related materials have been examined using a high-dispersion lithium fluoride prism.

Wilson (29) assigned band at 10.87 and 11.07 microns in cyclobutane to two  $\text{CH}_2$  rocking frequencies. Derfer (9) made the observation that seven substituted cyclobutanes all absorbed in the narrow range 10.87-10.99 microns. They pointed out that if the assignment to  $\text{CH}_2$  modes was correct, this band would not be expected to appear in fully substituted materials. Reid (23) examined a series of eight substituted cyclobutanes in which all the carbon atoms were substituted and found all of these to absorb between 11.26 and 11.52 microns. Morrison (18) has pointed out that neither methylene-nor perfluorocyclobutane absorbs in the 10.87-10.99 microns region.

Most of the compounds described in the Experimental section that are believed to have the cyclobutane structure absorb in the range 10.90-11.10 microns.

#### IV GENERAL CONSIDERATIONS

All temperatures reported in this dissertation are on the Centigrade scale and are uncorrected. The distillations were carried out using a 25 centimeter electrically-heated jacketed column packed with one-eighth inch glass helices. Pressures during distillation under 10 millimeters were determined by a McLeod gauge; pressures above 10 millimeters were read from a Zimmerli gauge.

Refractive indices were determined with an Abbe refractometer at the temperatures indicated. Densities were determined at the temperature indicated using a one milliliter pycnometer calibrated against water at 20° Centigrade and corrected to water at 4° Centigrade. Molar refractions were calculated using the Lorenz-Lorentz equation. The values for the atomic refractions were taken from Lange's "Handbook of Chemistry," sixth edition, page 1025. In all cases the value 1.1000 was used for the atomic refraction of fluorine.

The gas chromatography apparatus was built by Mr. Calvin Workinger, Mr. Eugene Barker and the author. The detector, a thermal conductivity cell, Model 9285, was purchased from the Gow-Mac Instrument Company. The column, 20 feet of one-fourth inch aluminum tubing packed with material prepared from 0.6 gram dinonyl phthalate per 1.0 gram Johns-Manville Chromosorb, 35-80 mesh size. The tubing was then coiled; the diameter of the coil was about 5 inches. Helium was used as the carrier gas in all cases.

The infrared spectra were obtained by a Perkin-Elmer Model 21 double beam, recording, infrared spectrophotometer.

The nuclear magnetic resonance spectra were obtained by a Varian High Resolution Nuclear Magnetic Resonance Spectrometer operating at 56.4 megacycles and were interpreted by Dr. W. S. Brey, Jr.

The autoclave used in this research was obtained from the American Instrument Company.

All analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee and by Drs. G. Weiler and F. B. Strauss of Oxford, England.

TABLE I  
PROPERTIES OF THE COMPOUNDS PREPARED

Compd. Number	Reactants	% Conversion	B.P. (°C)	Pressure (mm. Hg)	t	$\eta_D^t$	$d_4^t$
I	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFCl}$	92.2	115	760	21	1.3960	1.2282
II	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFBr}$	60.8	70	89	22	1.4209	1.5323
III	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFI}$	55.6	88-89	82	21	1.4700	1.7851
IV	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CCl}_2$	75.5	144	760	21	1.4352	1.3131
V	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFCF}_3$	29.0	97	760	22	1.3447	1.3171
VI	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFCN}$	38.0	140	760	21	1.3885	1.1705
VII	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}$	35.4	100	37	21	1.4471	1.4476
VIII	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CHF}$	11.7	110-118	760	--	--	--
IX	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_3\text{CCl}=\text{CClCF}_3$	21.5	106	71	m.p. 46°		
X	$\text{CH}_2=\text{CHCH=CH}_2 + \text{CF}_2=\text{CFCl}$	63.5	134	760	20	1.4049	1.2210
XI	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{CF}_2=\text{CFCl}$	67.0	109-110	20	21	1.4829	1.3071
XII	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{CF}_2=\text{CFBr}$	43.0	55	0.5	21	1.5026	1.5313
XIII	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{CF}_2=\text{CFI}$	33.3	82-83	0.5	21	1.5408	1.7346
XIV	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{CF}_2=\text{CFCN}$	56.6	75	3.0	22	1.4743	1.2340

TABLE I (continued)

Compd. Number	Reactants		% Conversion	B.P. (°C)	Pressure (mm. Hg)	t	n <sub>D</sub> <sup>t</sup>	d <sub>4</sub> <sup>t</sup>
XV	CH <sub>2</sub> =C=CH <sub>2</sub>	+ CF <sub>2</sub> =CFCl	7.3	97	760	22	1.3853	1.2950
XVI	CH <sub>2</sub> =C=CH <sub>2</sub>	+ 2 CF <sub>2</sub> =CFCl	19.0	150	760	22	1.4030	1.6675
XVII	CH <sub>2</sub> =CH-CH <sub>3</sub>	+ CF <sub>2</sub> =CFCl	35.4	99-100	760	21	1.3702	1.2582
XVIII	CH <sub>2</sub> =CH-CH <sub>3</sub>	+ CF <sub>2</sub> =CCl <sub>2</sub>	16.6	131	760	21	1.4170	1.3175
XIX	CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub>	+ CF <sub>2</sub> =CFCl	20.2	114-115	760	25	1.3827	1.2140
XX	CH <sub>2</sub> =CH-CH <sub>2</sub> Cl	+ CF <sub>2</sub> =CFCl	7.8	142-144	760	21	1.4130	1.4275
XXI	CH <sub>2</sub> =CH-CO <sub>2</sub> CH <sub>3</sub>	+ CF <sub>2</sub> =CFCl	47.4	82	42	19	1.3980	1.3947
XXII	CH <sub>2</sub> =CH-CN	+ CF <sub>2</sub> =CFCl	65.0	82	40	20	1.4012	1.4332
		CH <sub>3</sub>						
XXIII	CH <sub>2</sub> -C-CN	+ CF <sub>2</sub> =CFCl	30.6	80	34	20	1.4013	1.3513
XXIV	CF <sub>2</sub> =CF-CN		63.6	75-78	760	20	1.3328	1.4809

TABLE I (continued)

Compd. Number	Reactants	% Conversion	B.P. (°C)	Pressure (mm. Hg)	t	n <sub>D</sub> <sup>t</sup>	d <sub>4</sub> <sup>t</sup>
XXV	I + Br <sub>2</sub>	72.2	96-98	8	22	1.4898	1.9836
XXVI	III + Br <sub>2</sub>	70.0	84.85	1.5	23	1.5503	2.3748
XXVII	IV + Br <sub>2</sub>	64.1	83	3	22	1.5198	1.9897
XXVIII	V + Br <sub>2</sub>	65.0	75-79	7	21	1.4351	1.9715
XXIX	VII + Br <sub>2</sub>	28.7	96-98	10	22	1.4874	1.9690
XXX	I + Methanolic KOH	62.2	84-110	760	polymerized		
XXXI	VII + Methanolic KCH	41.2	132-134	760	21	1.4048	1.0912
XXXII	IX + Methanolic KOH	39.8	141	760	21	1.3938	1.4225
XXXIII	XI + Methanolic KOH	30.2	181	760	19	1.4290	1.2654

TABLE II  
ANALYSES OF THE COMPOUNDS PREPARED

Compd. Number	MR <sub>D</sub>		% Carbon		% Hydrogen	
	[Calcd.]	[Found]	[Calcd.]	[Found]	[Calcd.]	[Found]
I	32.59	33.35	42.25	42.12	3.55	3.72
II	35.49	35.65	33.51	33.94	2.81	3.06
III	40.52	40.95	27.50	28.06	2.31	2.81
IV	37.46	37.20	38.53	38.55	3.23	3.11
V	32.34	32.88	41.19	43.11	2.64	3.76
VI	32.09	32.45	52.18	52.41	3.75	3.96
VII	44.72	44.80	39.53	40.20	4.15	4.55
VIII	-----	-----	52.94	60.35	5.18	6.76
IX	-----	-----	33.47	33.64	2.11	2.22
X	37.21	37.02	45.55	45.97	4.37	4.47
XI	47.93	48.21	54.44	54.63	3.64	3.91
XII	50.82	51.10	45.31	45.48	3.04	3.41
XIII	55.86	56.28	38.48	39.34	2.58	2.68
XIV	47.43	48.09	62.56	62.58	3.82	4.05
XV	27.97	28.34	-----	-----	-----	-----
XVI	40.82	39.97	-----	-----	-----	-----
XVII	28.44	28.55	37.87	37.74	3.81	3.85
XVIII	33.30	33.41	34.31	34.53	3.46	3.68
XIX	33.06	33.05	41.75	41.57	4.68	4.84
XX	33.30	33.71	31.11	31.79	2.61	2.91
XXI	34.71	34.90	35.57	36.14	2.98	3.26
XXII	28.19	28.75	35.42	35.77	1.78	1.90

TABLE II (continued)

Compd. Number	MR <sub>D</sub> [Calcd.] [Found]		% Carbon [Calcd.] [Found]		% Hydrogen [Calcd.] [Found]	
XXIII	33.81	33.01	39.26	39.54	2.75	2.94
XXIV	27.69	28.88	-----	-----	-----	-----
XXV	48.59	48.25	21.81	22.28	1.83	1.94
XXVI	56.51	56.74	17.08	17.62	1.43	1.53
XXVII	52.97	53.01	20.78	20.80	1.74	2.03
XXVIII	48.34	48.25	-----	-----	-----	-----
XXIX	43.24	43.25	24.35	24.48	2.38	2.74
XXX	-----	-----	53.75	51.86	3.73	3.43
XXXI	36.48	36.55	59.25	59.03	5.59	5.92
XXXII	35.54	35.90	44.87	44.80	1.88	2.16
XXXIII	35.63	36.44	47.19	47.18	4.53	4.68

## V EXPERIMENTAL

In general all cycloalkylation reactions were carried out in either a three-tenths liter stainless steel reaction vessel fitted with a valve, pressure gauge, and blow-out assembly or in a 120 ml., sealed, thick-walled Pyrex glass tube. The polymerization inhibitor was in all cases p-tertbutylcatechol. If the reactants were gases at room temperature, they were condensed either in a thick-walled glass tube and weighed or were condensed in a cold trap cooled to Dry Ice temperature, weighed and poured into the autoclave which was cooled to Dry Ice temperature. The autoclave was then sealed, fitted with a high pressure valve, rocked and heated at the desired temperature. After the heating process, the reaction vessel was cooled and opened, and any unreacted material was collected in a cold trap cooled to Dry Ice temperature. The remaining liquid material was subjected to fractional distillation.

Ozonolysis reactions were carried out as follows:

About 4-5 drops of the sample was dissolved in exactly 5 ml. of the ethyl acetate-acetic acid solution. The solution was cooled to about -20° (by means of an ice-hydrochloric acid mixture in a Dewar flask), and ozone was passed through the solutions for fifteen to twenty minutes. A 2 ml. aliquot of this solution was placed in a 250 ml. flask containing a solution of 30 ml. of the fuchsin-aldehyde reagent and either 15 ml. of 24% hydrochloric acid solution and 45 ml. of water or 60 ml. water.

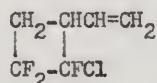
This is a method for determining methylene groups by ozonolysis (26). The resulting ozonide is reductively cleaved in a fuchsin-aldehyde reagent containing excess sulfur dioxide. The color produced by the resulting formaldehyde is compared with that produced by similar treatment of a compound known to have a terminal methylene group. The fuchsin-aldehyde reagent used is desensitized by the addition of hydrochloric acid and does not give a color with aldehydes other than formaldehyde.

#### A. Reactions of 1,3-Butadiene with Fluoroolefins

##### 1. Chlorotrifluoroethylene (3)

The autoclave was charged with 60 g. (0.52 mole) of chlorotrifluoroethylene, 35 g. (0.65 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for twenty hours at 100°. Fractional distillation of the resulting liquid material gave 81 g. (92% conversion) of material, I, b.p. 115°,  $n_D^{21}$  1.3960,  $d_4^{21}$  1.2282. Anal. Calcd. for  $C_6H_6F_3Cl$ :  $M_R D$ . 32.59; %C, 42.25; %H, 3.55. Found:  $M_R D$ . 33.35; %C, 42.12; %H, 3.72.

##### Proposed Structure of I



Evidence supporting proposed structure:

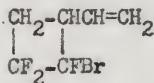
1. Mode of formation and elemental analyses.
2. Infrared absorptions.

- (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group present.
  - (c) Band at  $11.05\mu$ ; cyclobutane structure present.
  - (d) Dibromide of I gave band at  $11.05\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of I gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  group present.
- (4) I with alcoholic potassium hydroxide gave a material that polymerized on standing thus indicating a conjugated diene was formed. This supports the above 1,2-type structure.
- (5) A gas chromatogram of I showed only one peak. NMR results show the absence of the cyclohexene structure and the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure.

## 2. Bromotrifluoroethylene

The autoclave was charged with 80 g. (0.50 mole) of bromotrifluoroethylene, 30 g. (0.56 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for twenty hours at  $140^\circ$ . Fractional distillation of the resulting liquid material gave 65 g. (61% conversion) of material, II, b.p.  $70^\circ/89 \text{ mm.}$ ,  $n_D^{22} 1.4209$ ,  $d_4^{22} 1.5323$ . Anal. Calcd. for  $\text{C}_6\text{H}_6\text{F}_3\text{Br}$ :  $M_R$ <sub>D</sub> 35.49; %C, 33.51; %H, 2.81. Found:  $M_R$ <sub>D</sub> 35.65; %C, 33.98; %H, 3.36.

Proposed Structure of II



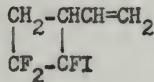
Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\swarrow$  group present.
  - (c) Band at  $10.97\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of II gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\swarrow$  group present.
- (4) A gas chromatogram of II showed only one peak. NMR results show the absence of the cyclohexene structure and the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure.

### 3. Iodotrifluoroethylene

A mixture of 20 g. (0.097 mole) of iodotrifluoroethylene, 8 g. (0.15 mole) of butadiene and 1 g. of inhibitor was heated in a sealed tube for sixteen hours at  $125^\circ$ . Fractional distillation of the resulting liquid material gave 14 g. (56% conversion) of material, III, b.p.  $88-89^\circ/82$  mm.,  $n_D^{21}$  1.4700,  $d_4^{21}$  1.7851. Anal. Calcd. for  $\text{C}_6\text{H}_6\text{F}_3\text{I}$ :  $\text{MR}_D$ , 40.52; %C, 27.50; %H, 2.31. Found:  $\text{MR}_D$ , 40.95; %C, 28.06; %H, 2.81.

Proposed Structure of III



Evidence supporting proposed structure:

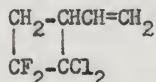
- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group present.
  - (c) Band at  $11.04\mu$ ; cyclobutane structure present.
  - (d) Dibromide of III gave a band at  $11.00\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of III gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  group present.
- (4) A gas chromatogram of III showed two peaks. The ratio of the areas under the peaks was about 3:2. NMR results show the absence of the cyclohexene structure and the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure.

4. 1,1-Dichloro-2,2-difluoroethylene

The autoclave was charged with 65 g. (0.49 mole) of 1,1-dichloro-2,2-difluoroethylene, 30 g. (0.56 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at  $125^\circ$ . Fractional distillation of the

resulting liquid material gave 69 g. (76% conversion) of material, IV.  
 $b.p.$   $144^\circ$ ,  $n_D^{21}$  1.4352,  $d_4^{21}$  1.3131. Anal. Calcd. for  $C_6H_6F_2Cl_2$ :  
 $M_R$ <sub>D</sub>, 37.46; %C, 38.53; %H, 3.23. Found:  $M_R$ <sub>D</sub>, 37.20; %C, 38.55;  
%H, 3.11.

#### Proposed Structure of IV



Evidence supporting proposed structure:

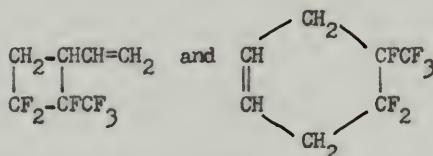
- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.80\mu$ ;  $\text{CF}_2=\text{CCl}_2$ - group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group present.
  - (c) Band at  $10.98\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of IV gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  group present.
- (4) A gas chromatogram of IV showed only one peak. NMR results show the absence of the cyclohexene structure and the presence of one kind of four-membered ring structure. No cis-trans isomerization is possible for the above structure.

#### 5. Perfluoropropene (19)

The autoclave was charged with 60 g. (0.40 mole) of

perfluoropropene, 30 g. (0.56 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at 175°. Fractional distillation of the resulting liquid material gave 21 g. (26% conversion) of material, V, b.p. 97°,  $n_D^{22}$  1.3447,  $d_4^{22}$  1.3171.

### Proposed Structures of V



Evidence supporting proposed structures:

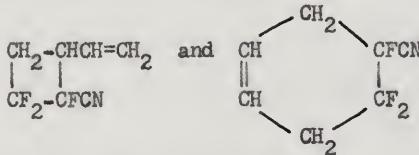
- (1) Mode of formation and physical properties which agreed with compound of known composition.
- (2) Infrared absorptions and interpretations.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group present.
- (3) Ozonolysis of V gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  group present.
- (4) A gas chromatogram of V showed two peaks. The ratio of the areas under the peaks was about 2:1. NMR results show the presence of both the cyclohexene structure and the cyclobutane structure in the amount of one part cyclohexene to three parts cyclobutane. It was also noted that only one kind of four-membered ring structure was present. It could not be determined from the NMR

spectrum whether the trifluoromethyl group was cis or trans with respect to the vinyl group.

### 6. Perfluoroacrylonitrile (16)

A mixture of 14 g. (0.13 mole) of perfluoroacrylonitrile, 10 g. (0.19 mole) of butadiene and 0.5 g. of inhibitor was heated in a sealed tube for fifteen hours at 150°. Fractional distillation of the resulting liquid material gave 8 g. (38% conversion) of material, VI, b.p. 140°,  $n_D^{21}$  1.3885,  $d_4^{21}$  1.1705. Anal. Calcd. for  $C_7H_6F_3N$ :  $MR_D$ , 32.09; %C, 52.18; %H, 3.75. Found:  $MR_D$ , 32.45; %C, 52.41; %H, 3.96.

#### Proposed Structures of VI



Evidence supporting proposed structures:

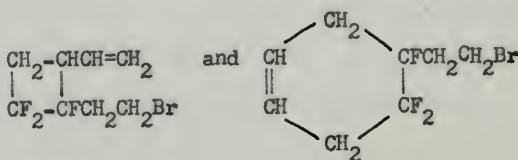
- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.19\mu$ ;  $\text{CH}_2=\text{C}\swarrow$  group present.
  - (c) Band at  $10.91\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of VI gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\swarrow$  group present.

(4) A gas chromatogram of VI showed two peaks. The ratio of the areas under the peaks was about 3:2. NMR results show the presence of both the cyclohexene structure and the cyclobutane structure in the ratio of 1:1. It was also noted that only one kind of four-membered ring structure was present. It could not be determined from the NMR spectrum whether the cyanide group was cis or trans with respect to the vinyl group.

#### 7. 4-Bromo-1,1,2-trifluoro-1-butene

The autoclave was charged with 95 g. (0.50 mole) of 4-bromo-1,1,2-trifluoro-1-butene, 30 g. (0.56 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for nineteen hours at 160°. Fractional distillation of the resulting liquid material gave 43 g. (35% conversion) of material, VII. b.p. 100°/37 mm.,  $n_D^{21}$  1.4471,  $d_4^{21}$  1.4476. Anal. Calcd. for  $C_8H_{10}F_3Br$ :  $\text{MR}_D$ , 44.72; %C, 39.53; %H, 4.15. Found:  $\text{MR}_D$ , 44.80; %C, 40.20; %H, 4.63.

#### Proposed Structure of VII



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.

## (2) Infrared absorptions.

- (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group present.
  - (c) Band at  $11.02\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of VII gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  group present.
- (4) A gas chromatogram of the dehydrobrominated material, XXXI, showed two peaks. The ratio of the areas under the peaks was about 3:2. NMR results on XXXI show the presence of both the cyclohexene structure and the cyclobutane structure in the ratio of 1:1. It was also noted that only one kind of four-membered ring structure was present. It could not be determined from the NMR spectrum whether one vinyl group was cis or trans with respect to the other vinyl group.

8. Trifluoroethylene

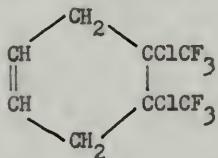
The autoclave was charged with 41 g. (0.50 mole) of trifluoroethylene, 27 g. (0.50 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for twelve hours at  $150^\circ$ . Fractional distillation of the resulting liquid material gave 8 g. of material, VIII, b.p.  $110$ - $118^\circ$ . A gas chromatogram of this material showed two peaks, one of which was due to 4-vinylcyclohexene. The other peak was assumed to be due to the addition product from the fluoroolefin and butadiene. NMR results were inconclusive concerning

the structures of this material.

**9. 2,3-Dichlorohexafluoro-2-butene**

The autoclave was charged with 116.5 g. (0.50 mole) of 2,3-dichlorohexafluoro-2-butene, 32 g. (0.59 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for twenty-four hours at 140-150°. Fractional distillation of the resulting liquid material gave 31 g. (22% conversion) of material, IX, b.p. 106°/71 mm., m.p. 46°. Anal. Calcd. for  $C_8H_6F_6Cl_2$ : %C, 33.47; %H, 2.11. Found: %C, 33.64; %H, 2.22.

### Proposed Structure of IX

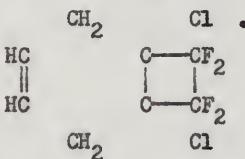


#### Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
  - (2) Infrared absorptions.
    - (a) Band at  $3.25\mu$ ; C=C in cyclohexene present.
    - (b) No band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group absent.
  - (3) Ozonolysis of IX failed to give  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  absent.
  - (4) IX reacted with alcoholic potassium hydroxide to give XXXII, the structure of which was proven to be 1,2-bis-(trifluoromethyl)benzene (5).

10. 1,2-Dichlorotetrafluorocyclobutene

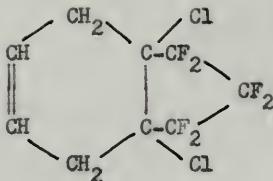
A mixture of 18 g. (0.093 mole) of 1,2-dichlorotetrafluorocyclobutene, 11 g. (0.20 mole) of butadiene and 1 g. of inhibitor was heated in a sealed tube for sixteen hours at 180°. Fractional distillation of the resulting liquid material gave 0.5 g. of material, b.p. 160-190°. Upon fusing with sodium, a positive test for chloride ion was obtained. This is the only evidence supporting that addition took place to give the probable product.



11. 1,2-Dichlorohexafluorocyclopentene

A mixture of 4 g. (0.016 mole) of 1,2-dichlorohexafluorocyclopentene, 5 g. (0.093 mole) of butadiene and 1 g. of inhibitor was heated in a sealed tube for sixteen hours at 160°. The unreacted material was distilled off leaving 6.5 g. higher boiling material which contained a considerable amount of 4-vinylcyclohexane. The higher boiling material was treated with excess alcoholic potassium hydroxide, washed with water several times, and dried over calcium chloride. The wash water was acidified and gave a positive test for chloride ion with silver nitrate. The organic material was diluted with iso-octane and its ultraviolet absorption spectrum showed a maximum at 280.5 $\mu$ . This is the region in which substituted benzenes absorb. Therefore, there is some indication that addition took place and that the compound formed

was



### 12. 2-Chloro-1,1-difluoroethylene

The autoclave was charged with 60 g. (0.61 mole) of 2-chloro-1,1-difluoroethylene, 30 g. (0.56 mole) of butadiene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at 175°. Fractional distillation of the resulting liquid material gave 32 g. of material, b.p. 125-129°. A gas chromatogram showed two peaks. The ratio of the areas under the peaks was about 9:1. The larger peak was found to be due to 4-vinylcyclohexene. The other peak was assumed to be due to the addition product from the fluoroölefin and butadiene.

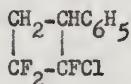
## B. Reactions of Styrene with Fluoroölefins

### 1. Chlorotrifluoroethylene (25)

The autoclave was charged with 50 g. (0.43 mole) of chlorotrifluoroethylene, 50 g. (0.48 mole) of styrene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for twenty-two hours at 100°. Fractional distillation of the resulting liquid material gave 63.5 g. (67% conversion) of material, XI, b.p. 109-110°/20 mm.,  $n_D^{21}$  1.4829,  $d_4^{21}$  1.3071. Anal. Calcd. for  $C_{10}H_8F_3Cl$ : MR<sub>D</sub> 47.93; %C, 54.44; %H, 3.64. Found: MR<sub>D</sub>, 48.21;

%C, 54.63; %H, 3.91.

### Proposed Structure of XI



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.6\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $11.05\mu$ ; cyclobutane structure present.
- (3) NMR spectrum of XI is in agreement with the proposed structure; however, because of several additional peaks that were present and were not due to the above 1,2-type structure, XI may be a mixture of the 1,2- and 1,3-type structures. Roberts (25) mentioned only the 1,2-type structure and gives some chemical evidence supporting it but makes no mention of the 1,3-type structure.

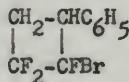
No gas chromatogram was obtained from XI because of its high boiling point.

### 2. Bromotrifluoroethylene

The autoclave was charged with 80.5 g. (0.50 mole) of bromotrifluoroethylene, 52 g. (0.50 mole) of styrene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking

for sixteen hours at 125°. Fractional distillation of the resulting liquid material gave 57 g. (43% conversion) of material, XII, b.p. 65°/0.5 mm.,  $n_D^{21}$  1.5026,  $d_4^{21}$  1.5312. Anal. Calcd. for  $C_{10}H_8F_3Br$ : MR<sub>D</sub>, 50.82; %C, 45.31; %H, 3.04. Found: MR<sub>D</sub>, 51.10; %C, 45.48; %H, 3.41.

#### Proposed Structure of XII



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.6\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $11.10\mu$ ; cyclobutane structure present.
- (3) Because of its similarity to XI, XII is also believed to have the 1,2-type structure with the possibility that some 1,3-type structure is also present.

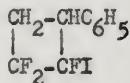
No gas chromatogram was obtained from XII because of its high boiling point.

#### 3. Iodotrifluoroethylene

A mixture of 20 g. (0.097 mole) of iodotrifluoroethylene, 20 g. (0.19 mole) of styrene and 1 g. of inhibitor was heated in a sealed tube for sixteen hours at 125°. Fractional distillation of the

resulting liquid material gave 10 g. (33% conversion) of material, XIII, b.p. 82-83°/0.5 mm.,  $n_D^{21}$  1.5408,  $d_4^{21}$  1.7346. Anal. Calcd. for  $C_{10}H_8F_3I$ : MR<sub>D</sub>, 55.86; %C, 38.48; %H, 2.58. Found: MR<sub>D</sub>, 56.28; %C, 39.34; %H, 2.68.

#### Proposed Structure of XIII



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.6\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $11.14\mu$ ; cyclobutane structure present.
- (3) Because of its similarity to XI, XIII is also believed to have the 1,2-type structure with the possibility that some 1,3-type structure is also present.

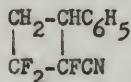
No gas chromatogram was obtained from XIII because of its high boiling point.

#### 4. Perfluoroacrylonitrile

A mixture of 8.5 g. (0.079 mole) of perfluoroacrylonitrile, 20 g. (0.19 mole) of styrene and 1 g. of inhibitor was heated in a sealed tube for fourteen hours at 100°. Fractional distillation of the resulting liquid material gave 9.5 g. (57% conversion) of

material, XIV, b.p. 75-76°/3 mm.,  $n_D^{22}$  1.4743,  $d_4^{22}$  1.2340. Anal. Calcd. for  $C_{11}H_8F_3N$ :  $M_R D$ . 47.43; %C. 62.56; %H. 3.82. Found:  $M_R D$ . 48.09; %C. 62.58; %H. 4.05.

#### Proposed Structure of XIV



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.6\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $10.98\mu$ ; cyclobutane structure present.
  - (c) Band at  $4.48\mu$ ;  $-\text{C}\equiv\text{N}$  group present.
- (3) Because of its similarity to XI, XIV is also believed to have the 1,2-type structure with the possibility that some 1,3-type structure is also present.

No gas chromatogram was obtained from XIV because of its high boiling point.

#### 5. Perfluoropropene

A mixture of 15 g. (0.10 mole) of perfluoropropene, 17 g. (0.16 mole) of styrene and 1 g. of inhibitor was heated in a sealed tube for fourteen hours at 125°. There were recovered 14 g. of perfluoropropene and 17 g. of viscous material (polystyrene).

Thus, perfluoropropene failed to react with styrene under above conditions.

#### 6. Trifluoroethylene

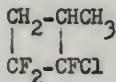
The autoclave was charged with 45 g. (0.55 mole) of trifluoroethylene, 25 g. (0.24 mole) of styrene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at 125°. There were recovered 40 g. of trifluoroethylene, 22 g. of styrene and 3 g. of viscous material remained in the distillation pot. Thus, trifluoroethylene failed to react with styrene under the above conditions.

### C. Reactions of Chlorotrifluoroethylene with Olefins

#### 1. Propene

The autoclave was charged with 18 g. (0.43 mole) of propene, 55 g. (0.47 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for eighteen hours at 275°. Fractional distillation of the liquid material from two identical runs gave 48 g. (35% conversion) of material, XVII, b.p. 99-100°,  $n_D^{21}$  1.3702,  $d_D^{21}$  1.2582. Anal. Calcd. for  $C_5H_6F_3Cl$ : MR<sub>D</sub>, 28.44; %C, 37.87; %H, 3.81. Found: MR<sub>D</sub>, 28.55; %C, 37.74; %H, 3.85.

Proposed Structure of XVII



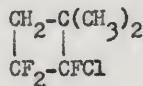
Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) No band in the region of  $6.10\mu$ ;  $\text{C}=\text{C}$  absent.
  - (c) Band at  $10.94\mu$ ; cyclobutane structure present.
- (3) NMR results show the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure. Because of its similarity to XIX, XVII is also believed to have only the 1,2-type structure.

## 2. Isobutylene

The autoclave was charged with 15 g. (0.31 mole) of isobutylene, 30 g. (0.26 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for three hours at  $310^\circ$ . Fractional distillation of the resulting liquid material gave 9 g. (20% conversion) of material, XIX, b.p.  $114\text{-}115^\circ$ ,  $n_D^{25}$  1.3827,  $d_4^{25}$  1.2140. Anal. Calcd. for  $\text{C}_6\text{H}_8\text{F}_3\text{Cl}$ :  $\text{MR}_D$ , 33.06; %C, 41.75; %H, 4.68. Found:  $\text{MR}_D$ , 33.05; %C, 41.57; %H, 4.84.

Proposed Structure of XIX



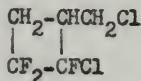
Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) No band in the region of  $6.10\mu$ ;  $\text{C}=\text{C}$  absent.
  - (c) Band at  $11.07\mu$ ; cyclobutane structure present.
- (3) NMR spectrum of XIX is in agreement with the proposed structure and indicates that no other structures are present.
- (4) XIX failed to react with alcoholic potassium hydroxide, thus indicating that the  $-\text{CH}_2-$  group is not adjacent to the  $-\text{CFCl}-$  group.

3. Allyl Chloride

The autoclave was charged with 25.5 g. (0.33 mole) of allyl chloride and 40 g. (0.34 mole) of chlorotrifluoroethylene. The autoclave was then sealed and heated while rocking for two hours at  $240^\circ$ . Some charring occurred and hydrochloric acid was evolved upon opening the autoclave. Fractional distillation of the resulting liquid material gave 5 g. (7.8% conversion) of material, XX, b.p.  $142-144^\circ$ ,  $n_D^{21} 1.4130$ ,  $d_4^{21} 1.4275$ . Anal. Calcd. for  $\text{C}_5\text{H}_5\text{F}_3\text{Cl}_2$ :  $\text{MR}_D$  33.30; %C, 31.11; %H, 2.61. Found:  $\text{MR}_D$  33.71; %C, 31.79; %H, 2.91.

Proposed Structure of XX



Evidence supporting proposed structure:

- (1) Mode of formation and molar refraction.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) No band in the region of  $6.10\mu$ ;  $\text{C}=\text{C}$  absent.
  - (c) Band at  $10.87\mu$ ; cyclobutane structure present.
- (3) Because of its similarity to XIX, XX is also believed to have only the 1,2-type structure.

4. Allyl Alcohol

The autoclave was charged with 29 g. (0.50 mole) of allyl alcohol, 60 g. (0.52 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for eighteen hours at  $180^\circ$ . Upon distillation of the resulting liquid residue no material boiling higher than allyl alcohol was obtained. Thus, chlorotrifluoroethylene failed to react with allyl alcohol under the above conditions.

5. cis-2-Butene

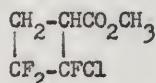
The autoclave was charged with 17.5 g. (0.31 mole) of cis-butene and 34 g. (0.29 mole) of chlorotrifluoroethylene. The autoclave was then sealed and heated while rocking for four hours at  $250^\circ$ .

Upon distillation of the resulting liquid residue no material boiling higher than the dimer of chlorotrifluoroethylene was obtained. Thus, chlorotrifluoroethylene failed to react with cis-2-butene under the above conditions.

#### 6. Methyl Acrylate

The autoclave was charged with 43 g. (0.50 mole) of methyl acrylate, 60 g. (0.52 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for eighteen hours at 140°. Fractional distillation of the resulting liquid material gave 48 g. (47% conversion) of material, XXI, b.p. 82°/42 mm.,  $n_D^{19}$  1.3980,  $d_4^{19}$  1.3947. Anal. Calcd. for  $C_6H_6F_3ClO_2$ :  $MR_D$ , 34.71; %C, 35.57; %H, 2.98. Found:  $MR_D$ , 34.90; %C, 36.14; %H, 3.26.

#### Proposed Structure of XXI



Evidence supporting proposed structures:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $5.70\mu$ ;  $>\text{C=O}$  group present.
  - (c) Band at  $11.05\mu$ ; cyclobutane structure present.

(3) XXI reacted readily with alcoholic potassium hydroxide.

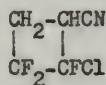
This would be expected if the hydrogen atom being eliminated is activated by a group such as a carbonyl. This observation is in agreement with the proposed structure.

(4) NMR results show the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure. Because of its similarity to XIX, XXI is also believed to have only the 1,2-type structure.

### 7. Acrylonitrile (2)

The autoclave was charged with 25 g. (0.47 mole) of acrylonitrile, 55 g. (0.47 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for eighteen hours at 155°. Fractional distillation of the resulting liquid material gave 52 g. (65% conversion) of material, XXII, b.p. 82°/40 mm.,  $n_D^{20}$  1.4012,  $d_4^{20}$  1.4332. Anal. Calcd. for  $C_5H_3ClN$ :  $\text{MR}_D$ , 28.19; %C, 35.42; %H, 1.78. Found:  $\text{MR}_D$ , 28.75; %C, 35.77; %H, 1.90.

#### Proposed Structure of XXII



Evidence supporting proposed structure:

(1) Mode of formation and elemental analyses.

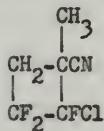
## (2) Infrared absorptions.

- (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $4.43\mu$ ;  $-\text{C}\equiv\text{N}$  group present.
  - (c) Band at  $11.00\mu$ ; cyclobutane structure present.
- (3) XXII reacted readily with alcoholic potassium hydroxide. This would be expected if the hydrogen atom being eliminated is activated by a group such as a nitrile. This observation is in agreement with the proposed structure.
- (4) NMR results show the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure. Because of its similarity to XIX, XXII is also believed to have only the 1,2-type structure.

8. Methacrylonitrile

The autoclave was charged with 33.5 g. (0.50 mole) of methacrylonitrile, 60 g. (0.52 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at 140-150°. Fractional distillation of the resulting liquid material gave 28 g. (31% conversion) of material, XXIII, b.p.  $80^\circ/34 \text{ mm.}$ ,  $n_D^{20} 1.4013$ ,  $d_4^{20} 1.3513$ . Anal. Calcd. for  $\text{C}_6\text{H}_5\text{F}_3\text{ClN}$ :  $\text{MR}_D$ , 32.81; %C, 39.26; %H, 2.75. Found:  $\text{MR}_D$ , 33.01; %C, 39.54; %H, 2.94.

Proposed Structure of XXIII



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $4.43\mu$ ;  $-\text{C}\equiv\text{N}$  group present.
  - (c) Band at  $11.02\mu$ ; cyclobutane structure present.
- (3) XXIII failed to react with alcoholic potassium hydroxide. This would be expected if there were no hydrogen atom on the carbon adjacent to the  $-\text{CFCl}-$  group. This observation is in agreement with the proposed structure and thus eliminates the possibility of the 1,3-type structure being present.
- (4) NMR results show the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure.

9. Maleic Anhydride

The autoclave was charged with 25 g. (0.26 mole) of maleic anhydride, 55 g. (0.47 mole) of chlorotrifluoroethylene and 50 ml. of benzene. The autoclave was then sealed and heated while rocking for sixteen hours at  $175^\circ$ . The volatile material was removed

under reduced pressure leaving 24 g. of unreacted maleic anhydride, m.p. 55-56°. Thus, chlorotrifluoroethylene failed to react with maleic anhydride under the above conditions.

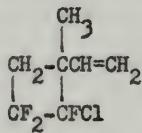
#### 10. Cinnamic Acid

The autoclave was charged with 20 g. (0.14 mole) of cinnamic acid, 55 g. (0.47 mole) of chlorotrifluoroethylene and 60 ml. of glacial acetic acid. The autoclave was sealed and heated while rocking for sixteen hours at 175°. There were recovered 48 g. of unreacted chlorotrifluoroethylene and 20 g. of cinnamic acid, m.p. 297-298°. Thus, chlorotrifluoroethylene failed to react with cinnamic acid under the above conditions.

#### 11. Isoprene

The autoclave was charged with 34 g. (0.50 mole) of isoprene, 60 g. (0.52 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for twelve hours at 125°. Fractional distillation of the resulting liquid material from three identical runs gave 175 g. (64% conversion) of material, X, b.p. 134°,  $n_D^{20}$  1.4049,  $d_4^{20}$  1.2210. Anal. Calcd. for  $C_7H_8F_3Cl$ :  $M_R D$ . 37.21; %C. 45.55; %H. 4.37. Found:  $M_R D$ . 37.02; %C. 45.97; %H. 4.47.

Proposed Structure of X



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $3.20\mu$ ;  $\text{CH}_2=\text{C}\backslash$  group present.
  - (c) Band at  $11.09\mu$ ; cyclobutane structure present.
- (3) Ozonolysis of X gave  $\text{CH}_2\text{O}$ , thus showing  $\text{CH}_2=\text{C}\backslash$  group present.
- (4) X failed to react with alcoholic potassium hydroxide, thus favoring the 1,2-type structure and showing that no 1,3-type structure was present.
- (5) NMR results show the absence of the cyclohexene structure and the presence of two kinds of four-membered ring structures which are cis-trans isomers of the above 1,2-type structure.

**12. 1,3-Cyclopentadiene**

A mixture of 11 g. (0.17 mole) of cyclopentadiene, 20 g. (0.17 mole) of chlorotrifluoroethylene and 1 g. of inhibitor was heated in a sealed tube for sixteen hours at  $115^\circ$ . Nineteen grams

of unreacted chlorotrifluoroethylene was recovered from the reaction mixture. Thus, chlorotrifluoroethylene failed to react with cyclopentadiene under the above conditions.

13. Furan

A mixture of 13 g. (0.19 mole) of furan, 14 g. (0.12 mole) of chlorotrifluoroethylene and 1 g. of inhibitor was heated for sixteen hours at 125°. Fourteen grams of unreacted chlorotrifluoroethylene was recovered from the reaction mixture. Thus, chlorotrifluoroethylene failed to react with furan under the above conditions.

14. Anthracene

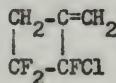
A mixture of 3 g. (0.169 mole) of anthracene, 12 g. (0.10 mole) of chlorotrifluoroethylene and 20 ml. of benzene was heated in a sealed tube for sixteen hours at 200°. Ten grams of unreacted chlorotrifluoroethylene was recovered. The benzene was evaporated off and the remaining solid was recrystallized from aqueous ethanol to give 0.1 g. of an orange solid, m.p. 164-165°. Upon fusion with sodium, a negative test for chloride ion was obtained. No further attempt to identify this material was made.

15. Allene

The autoclave was charged with 20 g. (0.50 mole) of allene and 41 g. (0.35 mole) of chlorotrifluoroethylene. The autoclave was then sealed and heated for twelve hours at 125-150°. Fractional

distillation of the resulting liquid material gave 4 g. (7.3% conversion) of material, XV, b.p. 96-98°,  $n_D^{22}$  1.3853,  $d_4^{22}$  1.2950, and 9 g. (19% conversion) of material, XVI, b.p. 150-152°,  $n_D^{22}$  1.4030,  $d_4^{22}$  1.6675. Anal. Calcd. for  $C_5H_4F_3Cl$ :  $\text{MR}_D$ , 27.97. Found:  $\text{MR}_D$ , 28.97. Calcd. for  $C_7H_4F_6Cl_2$ :  $\text{MR}_D$ , 40.82. Found:  $\text{MR}_D$ , 39.97.

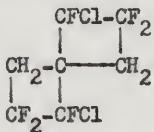
#### Proposed Structure of XV



Evidence supporting proposed structure:

- (1) Mode of formation and molar refraction.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.6\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.
  - (b) Band at  $5.90\mu$ ;  $\text{CH}_2=$  attached to a four-membered ring.
  - (c) No band in the region of  $11\mu$ ; it has been reported that methylene cyclobutane does not absorb in this region either.
- (3) Because of its similarity to XVII, XV is also believed to have only the 1,2-type structure.

Proposed Structure of XVI



Evidence supporting proposed structure:

- (1) Mode of formation and molar refraction.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.6\mu$ ;  $\text{CF}_2=\text{CF}$ - group absent.
  - (b) Band at  $11.13\mu$ ; cyclobutane structure present.
  - (c) Weak band  $5.96\mu$ ; probably due to impurity from XV.
- (3) Because of its similarity to XV, XVI is also believed to have only the 1,2-type structure.

**16. 1,1,3-Trifluoro-1,3-butadiene**

A mixture of 11 g. (0.10 mole) of 1,1,2-trifluoro-1,3-butadiene, 12 g. (0.10 mole) of chlorotrifluoroethylene and 2 g. of inhibitor was heated in a sealed tube for twelve hours at  $100^\circ$ . Distillation of the resulting liquid material gave 10 g. of material b.p.  $90-120^\circ$ . A gas chromatogram of this material showed four major peaks, three of which were due to the dimer of the diene as was shown from an independent experiment. No further attempt was made to identify the separate components of the mixture.

### 17. 2,3-Dichlorohexafluoro-2-butene

A mixture of 20 g. (0.086 mole) of 2,3-dichlorohexafluoro-2-butene and 20 g. (0.17 mole) of chlorotrifluoroethylene was heated in a sealed tube for sixteen hours at 225°. Upon distillation no material boiling higher than 2,3-dichlorohexafluoro-2-butene was obtained.

### 18. Cyclohexene

The autoclave was charged with 41 g. (0.50 mole) of cyclohexene and 60 g. (0.52 mole) of chlorotrifluoroethylene. The autoclave was then sealed and heated while rocking for sixteen hours at 175°. Upon distillation no material boiling higher than cyclohexene was obtained.

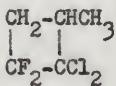
## D. Miscellaneous Addition Reactions

### 1. 1,1-Dichloro-2,2-difluoroethylene with Propene

The autoclave was charged with 21 g. (0.50 mole) of propene, 70 g. (0.53 mole) of 1,1-dichloro-2,2-difluoroethylene and 2 g. of inhibitor. The autoclave was then sealed and heated while rocking for sixteen hours at 225°. The resulting liquid was reacted with 63.5 g. (1 g. atom) of zinc dust in 200 ml. of dioxane in order to remove 1,1,2,2-tetrachlorotetrafluorocyclobutane from the reaction mixture. This material and the desired product have similar boiling points. The mixture was then filtered to remove the solid material, the remaining liquid washed several times with water to remove the

dioxane and dried over calcium chloride. Fractional distillation gave 14.5 g. (17% conversion) of material, XVIII, b.p. 131°,  $n_D^{21}$  1.4170,  $d_4^{21}$  1.3175. Anal. Calcd. for  $C_5H_6F_2Cl_2$ : MR<sub>D</sub>, 33.30; %C, 34.31; %H, 3.46. Found: MR<sub>D</sub>, 33.41; %C, 34.53; %H, 3.68.

#### Proposed Structure of XVIII



Evidence supporting proposed structure:

- (1) Mode of formation and elemental analyses.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.80\mu$ ;  $\text{CF}_2=\text{CCl}_2$ - group absent.
  - (b) No band in the region of  $6.10\mu$ ; C=C absent.
  - (c) Band at  $11.02\mu$ ; cyclobutane structure present.
- (3) NMR results show the presence of only one kind of four-membered ring structure. Because of its similarity to XIX, XVIII is also believed to have the 1,2-type structure ( $-\text{CCl}_2-$  group adjacent to the  $-\text{CHCH}_3-$  group).

#### 2. Chlorotrifluoroethylene with Nitrosobenzene

The autoclave was charged with 40 g. (0.37 mole) of nitrosobenzene, 55 g. (0.47 mole) of chlorotrifluoroethylene and 2 g. of inhibitor. The autoclave was sealed and at about room temperature a violent reaction occurred blowing the rupture disc. The remaining

material in the autoclave was carbon.

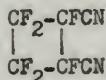
### 3. Chlorotrifluoroethylene with Benzonitrile

The autoclave was charged with 53 g. (0.52 mole) of benzonitrile and 50 g. (0.43 mole) of chlorotrifluoroethylene. The autoclave was then sealed and heated while rocking for eighteen hours at 180°. Forty-eight grams of unreacted chlorotrifluoroethylene and 53 g. of benzonitrile were recovered. Thus, chlorotrifluoroethylene failed to react with benzonitrile under the above conditions.

### 4. Perfluoroacrylonitrile Dimer (16)

Eleven grams (0.10 mole) of perfluoroacrylonitrile was heated in a sealed tube for eight hours at 225°. A considerable amount of carbonized material was noted inside the tube. Fractional distillation of the resulting liquid material gave 7 g. (64% conversion) of material, XXIV. b.p. 75-78°,  $n_D^{20}$  1.3328,  $d_4^{20}$  1.4809.  $MR_D$ , calcd. for  $C_6F_6N_2$ : 27.69. Found: 28.88.

#### Proposed Structure of XXIV



Evidence supporting proposed structure:

- (1) Mode of formation and molar refraction.
- (2) Infrared absorptions.
  - (a) No band in the region of  $5.60\mu$ ;  $\text{CF}_2=\text{CF}-$  group absent.

- (b) Band at  $4.44\mu$ ;  $\text{-C}\equiv\text{N}$  group present.
- (3) NMR results show the presence of two kinds of four-membered ring structures which are probably cis-trans isomers of the above 1,2-type structure.

#### 5. 1,1,2-Trifluoro-1,3-butadiene Dimer

A mixture of 15 g. (0.14 mole) of 1,1,2-trifluoro-1,3-butadiene and 2 g. of inhibitor was heated in a sealed tube for twelve hours at  $100^\circ$ . Eleven grams of a rubbery polymer and 4 g. of material, b.p.  $100-130^\circ$ , were obtained. A gas chromatogram of this material gave three major peaks, all of which were assumed to be due to various isomers of the dimer. No further attempt was made to identify the separate components of the mixture.

#### 6. Thermal Reaction of 2-Chloropentafluoropropene

The autoclave was charged with 65 g. (0.39 mole) of 2-chloropentafluoropropene. The autoclave was then sealed and heated while rocking for eighteen hours at  $350^\circ$ . Upon distillation of the resulting liquid material 8.5 g. of material, b.p.  $54-78^\circ$ , was obtained. A gas chromatogram of this material showed six major peaks. No further attempt was made to identify the separate components of the mixture.

#### 7. Thermal Reaction of 2-Chloro-1,2-difluorovinyl Methyl Ether

The autoclave was charged with 30 g. (0.23 mole) of 2-chloro-1,2-difluorovinyl methyl ether and 2 g. of inhibitor. The

autoclave was then sealed and heated while rocking for twelve hours at 190°. Fractional distillation of the resulting liquid material gave 5 g. of material, b.p. 110-117°. This material upon standing produced a white solid which was not identified.

#### E. Reactions of Addition Products

##### 1. I with Bromine

A solution of I (10 g., 0.058 mole) in carbon tetrachloride (10 ml.) was placed in a 100 ml., three-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel. The flask was cooled in a Dry Ice-acetone bath maintained at -20° to -10°. A solution of 9.6 g. (0.06 mole) of bromine in 10 ml. of carbon tetrachloride was added slowly. After addition was complete, the reaction mixture was brought to room temperature and stirred for one hour. The excess bromine was then removed by shaking with sodium thiosulfate solution. The organic layer was separated, washed with water, dried over calcium chloride and distilled under reduced pressure to give 14 g. (72.2% conversion) of material, XXV, b.p. 96-98°/8 mm.,  $n_D^{22}$  1.4898,  $d_4^{22}$  1.9836. Anal. Calcd. for  $C_6H_4FClBr_2$ :  $MR_D$ , 48.59; %C, 21.81; %H, 1.83. Found:  $MR_D$ , 48.25; %C, 22.28; %H, 1.94.

##### 2. III with Bromine

In the manner described above 6.0 g. (0.038 mole) of bromine in 5 ml. of carbon tetrachloride was added to a solution of III

(4.0 g., 0.015 mole) in 5 ml. of carbon tetrachloride. Distillation gave 4.5 g. (70.0% conversion) of material, XXVI, b.p. 84-85°/1.5 mm.,  $n_D^{23}$  1.5503,  $d_4^{23}$  2.3748. Anal. Calcd. for  $C_6H_6F_3IBr_2$ :  $MR_D$ , 56.51; %C, 17.08; %H, 1.43. Found:  $MR_D$ , 56.74; %C, 17.62; %H, 1.53.

### 3. IV with Bromine

In the manner previously described 7.0 g. (0.044 mole) of bromine in 5 ml. of carbon tetrachloride was added to a solution of IV (8.0 g., 0.043 mole) in 5 ml. of carbon tetrachloride. Distillation gave 9.5 g. (64.1% conversion) of material, XXVII, b.p. 83°/3 mm.,  $n_D^{22}$  1.5198;  $d_4^{22}$  1.9897. Anal. Calcd. for  $C_6H_6F_2Cl_2Br_2$ :  $MR_D$ , 52.97; %C, 20.78; %H, 1.74. Found:  $MR_D$ , 53.01; %C, 20.80; %H, 2.03.

### 4. V with Bromine

In the manner previously described 12.0 g. (0.075 mole) of bromine in 10 ml. of carbon tetrachloride was added to a solution of V (12.5 g., 0.061 mole) in 10 ml. of carbon tetrachloride. Distillation gave 14.5 g. (65.0% conversion) of material, XXVIII, b.p. 75-79°/7 mm.,  $n_D^{21}$  1.4351,  $d_4^{21}$  1.9715. The physical constants agree with those reported by McBee (19).

### 5. VIII with Bromine

In the manner previously described 18.0 g. (0.113 mole) of bromine in 15 ml. of carbon tetrachloride was added to a solution of VIII (9.0 g., 0.066 mole) in 10 ml. of carbon tetrachloride.

Distillation gave 5.5 g. (28.7% conversion) of material, XXIX, b.p. 96-98°/10 mm.,  $n_D^{22}$  1.4874,  $d_4^{22}$  1.9690. Anal. Calcd. for  $C_6H_7F_3Br_2$ : MR<sub>D</sub> 43.24; %C, 24.35; %H, 2.38. Found: MR<sub>D</sub> 43.25; %C, 24.48; %H, 2.74.

#### 6. I with Methanolic Potassium Hydroxide

To a 100 ml. three-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel was added 30 g. (0.176 mole) of I. Potassium hydroxide (10 g., 0.175 mole) dissolved in 60 ml. of methyl alcohol was added dropwise while the reaction flask was cooled in an ice bath. After addition was complete, the reaction mixture was poured into 500 ml. of cold water. The organic layer was separated, washed with water, dried over calcium chloride and distilled to give 14 g. (62.2% conversion) of material, XXX, b.p. 84-110°. Anal. Calcd. for  $C_6H_5F_3$ : %C, 53.75; %H, 3.73. Found: %C, 51.86; %H, 3.43.

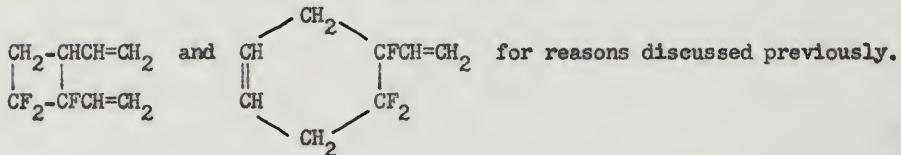
This material polymerized upon standing and the monomer has been assigned the structure  $\begin{array}{c} \text{CH}_2-\text{C}\equiv\text{CH}-\text{CH}_2 \\ | \\ \text{CF}_2-\text{CF} \end{array}$  for reasons discussed previously.

#### 7. VII with Methanolic Potassium Hydroxide

To a 100 ml. three-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel was added 25 g. (0.103 mole) of VII. Potassium hydroxide (7.0 g., 0.125 mole) dissolved in 50 ml. of methyl alcohol was added dropwise while the reaction flask was heated to 70-80°. After addition was complete, the reaction mixture

was poured into 500 ml. of cold water. The organic layer was separated, washed with water, dried over calcium chloride and distilled to give 7 g. (41.9% conversion) of material, XXXI, b.p. 132-134°,  $n_D^{21}$  1.4048,  $d_4^{21}$  1.0912. Anal. Calcd. for  $C_8H_9F_3$ :  $M_R D$ . 36.48; %C, 59.25; %H, 5.59. Found:  $M_R D$ . 36.55; %C, 59.03; %H, 5.92.

This material has been assigned the structures



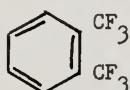
### 8. IX with Ethanolic Potassium Hydroxide

A solution of IX (18 g., 0.063 mole) in 95% ethyl alcohol (20 ml.) was placed in a 100 ml., three-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel. The mixture was heated to reflux and a solution of potassium hydroxide (15 g., 0.268 mole) dissolved in 50 ml. of 95% ethyl alcohol was added slowly. After addition was complete, the reaction mixture was poured into 500 ml. of cold water. The organic layer was separated, washed with water, dried over calcium chloride and distilled to give 5.5 g.

(39.8% conversion) of material, XXXII, b.p. 141°,  $n_D^{21}$  1.3938,  $d_4^{21}$  1.4225.

Anal. Calcd. for  $C_8H_4F_6$ :  $M_R D$ . 35.54; %C, 44.87; %H, 1.88. Found:  $M_R D$ . 35.90; %C, 44.80; %H, 2.16.

This material is the known (5) 1,2-bis(trifluoromethyl)-benzene.



### 9. XXI with Methanolic Potassium Hydroxide

To a 250 ml., three-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel was added 30 g. (0.148 mole) of XXI. Potassium hydroxide (17 g., 0.30 mole) dissolved in 100 ml. of methyl alcohol was added dropwise while the reaction flask was maintained at 30-40°. After addition was complete, the reaction mixture was poured into 500 ml. of cold water. The organic layer was separated, washed with water, dried over calcium chloride and distilled to give 8 g. (30.2% conversion) of material, XXXIII, b.p. 181°,  $n_D^{19}$  1.4290,  $d_4^{19}$  1.2654. Anal. Calcd. for  $C_7H_8F_2O_3$ :  $M_R D$ . 35.63; %C, 47.19; %H, 4.53; %F, 21.33. Found:  $M_R D$ . 36.44; %C, 47.18; %H, 4.68; %F, 21.12.

This material has been assigned the structure  
$$\begin{array}{c} \text{CH}_2-\text{CCO}_2\text{CH}_3 \\ || \\ \text{CF}_2-\text{COCH}_3 \end{array}$$
 on the basis of its composition, mode of formation and infrared spectrum.

## VI SUMMARY

A study has been made of the reactions of chlorotrifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, 1,1-dichlorodifluoroethylene, perfluoropropene, perfluoroacrylonitrile, 4-bromo-1,1,2-trifluoro-1-butene and 2,3-dichlorohexafluoro-2-butene with butadiene. Chlorotrifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene and 1,1-dichlorodifluoroethylene reacted with butadiene to give only compounds containing the cyclobutane ring. However, perfluoropropene, perfluoroacrylonitrile and 4-bromo-1,1,2-trifluoro-1-butene reacted with butadiene to give in each case both the cyclobutane ring and the cyclohexene ring. 2,3-Dichlorohexafluoro-2-butene reacted with butadiene to give only the cyclohexene ring.

Chlorotrifluoroethylene and a number of other fluoroolefins were added to various hydrocarbon olefins and dienes and a study was made of their mode of formation.

Evidence was presented for a diradical transition state for most of these cycloalkylation reactions.

Structures have been assigned for most of the products and were based on both chemical and physical evidence. Several of the assigned structures have been definitely established by means of NMR spectroscopy.

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## BIOGRAPHICAL DATA

Robert William Johnson, Jr. was born on October 9, 1927, in Jacksonville, Florida where he attended local schools and was graduated from Andrew Jackson High School in June, 1945.

He enlisted in the U.S. Navy in September, 1945, and served in both the Atlantic and Pacific Areas until his discharge in October, 1948. He entered the University of Florida in February, 1949 and received the B.S. in Chemistry in June, 1953. The author began graduate study at Purdue University in September, 1953, and was awarded the M.S. degree in January, 1956. The author re-entered the University of Florida in February, 1956 and undertook the program leading to the Ph.D. degree in Fluorine Chemistry. He held a teaching assistantship at Purdue University, and at the University of Florida he held a research assistantship sponsored by the Office of the Quartermaster General, U.S. Army.

The author is a member of Alpha Chi Sigma, Gamma Sigma Epsilon, Sigma Xi, American Chemical Society and the American Association for the Advancement of Science. He is married and has one child.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 8, 1959

A.H. Gropf

Dean, College of Arts and Sciences

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Dean, Graduate School

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