FLUOROCARBON DERIVATIVES OF ARSENIC, SULFUR AND NITROGEN

by

PRITAM SINGH DHALIWAL

B.Sc. (Hons.) University of British Columbia

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in the Department of Chemistry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

July, 1966
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date August 8, 1968
The University of British Columbia

FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

PRITAM SINGH DHALIWAL

B.Sc. (Hons.), The University of British Columbia, 1963

FRIDAY, AUGUST 5, 1966 AT 3:30 P. M.

IN ROOM 261, CHEMISTRY BUILDING

COMMITTEE IN CHARGE

Chairman: I. McT. Cowan

W. R. Cullen
C. A. McDowell
L. W. Reeves

A. Storr
R. C. Thompson
G. B. Turrell

Research Supervisor: W. R. Cullen
External Examiner: F. G. A. Stone

Department of Inorganic Chemistry
School of Chemistry
University of Bristol
Bristol, England
FLUOROCARBÓN DERIVATIVES OF ARSENIC, SULFUR AND NITROGEN

ABSTRACT.

The disulfides \( \text{RSSR} \) (\( R = \text{C}_2\text{H}_5, \text{C}_6\text{H}_{11}, \text{and CF}_3 \)) react with the diarsines \( \text{R}'\text{As-AsR'}_2 \) (\( R' = \text{CH}_3, \text{CF}_3 \)) to give the compounds \( \text{R}'\text{As-SR}. \) Dimethylarsine readily cleaves As-S and As-N bonds to yield a diarsine and the corresponding thiol and amine respectively. Unsymmetrical disulfides are obtained from the reaction of trifluoromethanesulfenylchloride with compounds containing arsenic-sulfur bonds. Trifluoromethanesulfenylchloride is readily reduced by dimethylarsine to yield chlorodimethylarsine and trifluoromethanethiol. Tetramethylidarsine is readily cleaved by trifluoromethanesulfenylchloride and trifluoromethanesulfenyldimethylarsine respectively, in addition to chlorodimethylarsine. Tetramethylidarsine also reacts with methanesulfonanhydride to yield dimethylarsinomethanesulfonate.

The cyclic fluoro-olefins \( \text{RC}=\text{CR'CF}(\text{CF}_2)_n \) (\( n = 1, R = R' = F, R = R' = C1, R = C1, R' = H, \) and \( n = 2, R = R' = C1, R = C1, R' = H \)) react with secondary amines and arsines to give the compounds \( \text{R}''\text{C}=\text{CR'CF}(\text{CF}_2)_n \) (\( R'' = (\text{C}_2\text{H}_5)_2\text{N}, (\text{CH}_3)_2\text{As} \)). Methane thiol also reacts with these cyclic fluoro-olefins (\( n = 1, R = R' = F, R = R' = \text{C1} \)) to yield the compounds \( \text{CH}_3\text{SC}=\text{CR'CF}(\text{CF}_2)_2 \) (\( R' = F, \text{C1} \)). With 1-H-2-chlorotetrafluorocyclobutene, methane thiol affords a 1:1 adduct, which fails to eliminate hydrogen halide even at 150°. With 1-H-2-chlorohexafluorocyclopentene and methane thiol, double bond migration occurs to yield 1-chloro-5-H-5-methylthiopentafluorocyclopentene. 1-Ethyl-2-chlorotetrafluorocyclobutene affords 1-ethyl-2-methylthietrafluorocyclobutene and 1-ethyl-2-dimethylarsinotetrafluorocyclobutene when heated with methane thiol and dimethylarsine respectively. The rates of the above reactions are dependent on the nucleophilicity of the attacking nucleophile, the size of the fluoro-olefin ring and the electronegativity of the groups attached to the double bond.
The chelating properties of the new ditertiary arsine, 1,2-dimethylarsino-tetrafluorocyclobutene (difars) have also been investigated. Reaction with Fe(CO) and Mo(CO) under mild conditions yields the stable crystalline complexes \[(\text{difars}) \text{Fe(CO)}_\text{3}\] and \[(\text{difars}) \text{Mo(CO)}_\text{4}\], and under vigorous conditions all the carbon monoxide can be displaced from Mo(CO)\_6. Difars displaces all the carbon monoxide from Ni(CO)\_4 at 25\(^\circ\), but attempts to obtain coordination complexes of difars with Ni(II) salts have been unsuccessful. Platinum and palladium salts react with difars to yield stable crystalline complexes which can be formulated as \[(\text{difars}) \text{PtCl}_\text{2}\] and \[(\text{difars}) \text{PdCl}_\text{2}\]. Rhodium trichloride trihydrate affords the complex \[(\text{Rh (difars)}_\text{2} \text{Cl}_\text{2})\text{Cl}\]. Mercuric chloride and cadmium bromide yield the unstable complexes \[(\text{difars}) \text{HgCl}_\text{2}\] and \[(\text{difars}) \text{CdBr}_\text{2}\].

G R A D U A T E  S T U D I E S

Field of Study: Inorganic Chemistry

Seminar in Chemistry
Topics in Physical Chemistry
Spectroscopy and Molecular Structure

The Chemistry of Organometallic Compounds
Topics in Inorganic Chemistry

Advanced Inorganic Chemistry
Topics in Organic Chemistry

Physical Organic Chemistry
Organic Reaction Mechanisms

N. Bartlett
J. A. R. Coope
A. V. Bree
E. J. Wells
C. Reid
L. W. Reeves
K. B. Haryey
G. B. Porter
D. G. L. James
H. C. Clark
W. R. Cullen
R. C. Thompson
D. E. McGreer
J. P. Kutney
F. McCapra
R. Stewart
R. E. Pincock


PRITAM SINGH DHALIWAL. FLUOROCARBON DERIVATIVES OF ARSENIC, SULFUR AND NITROGEN.
Supervisor: Dr. W. R. Cullen.

ABSTRACT

The disulfides \( \text{RSSR} (R = \cdot \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{and CF}_3) \) react with the diarsines \( \text{R'}_2\text{As-AsR'}_2 (R' = \cdot \text{CH}_3, \text{CF}_3) \) to give the compounds \( \text{R'}_2\text{As-SR} \). Dimethylarsine readily cleaves As-S and As-N bonds to yield a diarsine and the corresponding thiol and amine respectively. Unsymmetrical disulfides are obtained from the reaction of trifluoromethanesulfenylchloride with compounds containing arsenic-sulfur bonds. Trifluoromethanesulfenylchloride is readily reduced by dimethylarsine to yield chlorodimethylarsine and trifluoromethanethiol. Tetramethyldiarsine is readily cleaved by trifluoromethanesulfenylchloride and trifluoromethanesulfenyldimethylarsine and yields trifluoromethythiodimethylarsine and trifluoromethanesulfenyldimethylarsine respectively, in addition to chlorodimethylarsine. Tetramethyldiarsine also reacts with methanesulfonlanhydride to yield dimethylarsinomethanesulfonate.

The cyclic fluoro-olefins \( \text{RC} = \text{CR}^\cdot \text{CF}_2(\text{CF}_2)_n \) \( (n = 1, R = R' = F, R = R' = \cdot \text{Cl}, R = \cdot \text{Cl}, R' = \cdot \text{H}, \text{and} n = 2, R = R' = \cdot \text{Cl}, R = \cdot \text{Cl}, R' = \cdot \text{H}) \) react with secondary amines and arsines to give the compounds \( \text{R''C} = \text{CR'}\text{CF}_2(\text{CF}_2)_n \) \( (R'' = \cdot \text{C}_2\text{H}_5)_2\text{N}, (\text{CH}_3)_2\text{As}) \). Methane thiol also reacts with these cyclic fluoro-olefins \( (n = 1, R = R' = F, R = R' = \cdot \text{Cl}) \) to yield the compounds \( \text{CH}_3\text{SC} = \text{CR'}\text{CF}_2\text{CF}_2(R', = F, \cdot \text{Cl}) \). With 1-H-2-chlorotetrafluorocyclobutene, methane thiol affords a 1:1 adduct, which fails to eliminate hydrogen halide even at 150°. With 1-H-2-chlorohexafluorocyclopentene and methane thiol, double bond migration occurs to yield 1-chloro-5-H-5-methylthiohexafluorocyclopentene. 1-Ethyl-2-chlorotetrafluorocyclobutene affords 1-ethyl-2-methylthiotetrafluorocyclobutene and 1-ethyl-2-dimethylarsinotetrafluorocyclobutene when heated with methane thiol and dimethylarsine respectively. The rates of the above reactions are dependent on the nucleophilicity of the.
attaching nucleophile, the size of the fluoro-olefin ring and the electronegativity of the groups attached to the double bond.

The chelating properties of the new ditertiary arsine, 1,2-dimethylarsinotetrafluorocyclobutene (difars) have also been investigated. Reaction with Fe(CO)$_5$ and Mo(CO)$_6$ under mild conditions yields the stable crystalline complexes (difars) Fe(CO)$_3$ and (difars) Mo(CO)$_4$, and under vigorous conditions all the carbon monoxide can be displaced from Mo(CO)$_6$. Difars displaces all the carbon monoxide from Ni(CO)$_4$ at 25°, but attempts to obtain coordination complexes of difars with Ni(II) salts have been unsuccessful. Platinum and palladium salts react with difars to yield stable crystalline complexes which can be formulated as [(difars) PtCl$_2$] and [(difars) PdCl$_2$]. Rhodium trichloride trihydrate affords the complex [Rh(difars) Cl$_2$]Cl. Mercuric chloride and cadmium bromide yield the unstable complexes (difars) HgCl$_2$ and (difars) CdBr$_2$. 
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td></td>
</tr>
<tr>
<td>General Introduction</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER I. Derivatives of Compounds Containing Arsenic Bonded to Both Carbon and Sulphur</td>
<td>4</td>
</tr>
<tr>
<td>Introduction</td>
<td>4</td>
</tr>
<tr>
<td>Experimental</td>
<td>7</td>
</tr>
<tr>
<td>I. Apparatus and Techniques</td>
<td>7</td>
</tr>
<tr>
<td>II. Synthesis of Starting Materials</td>
<td>8</td>
</tr>
<tr>
<td>III. Synthesis of Derivatives of As-S Bonds</td>
<td>9</td>
</tr>
<tr>
<td>Discussion</td>
<td>22</td>
</tr>
<tr>
<td>(1) Results</td>
<td>22</td>
</tr>
<tr>
<td>(2) Structures and Spectroscopic Properties of the New Compounds</td>
<td>26</td>
</tr>
<tr>
<td>(3) Postulated Mechanisms</td>
<td>27</td>
</tr>
<tr>
<td>CHAPTER II. Derivatives of Fluorinated Cyclobutenes</td>
<td>29</td>
</tr>
<tr>
<td>Introduction</td>
<td>29</td>
</tr>
<tr>
<td>Experimental</td>
<td>36</td>
</tr>
<tr>
<td>I. Starting Materials</td>
<td>36</td>
</tr>
<tr>
<td>(b) Synthesis of Additional Starting Materials</td>
<td>36</td>
</tr>
<tr>
<td>II. Reactions of the Cyclobutenes, Cyclopentenes and Cyclohexenes</td>
<td>37</td>
</tr>
<tr>
<td>Discussion</td>
<td>53</td>
</tr>
<tr>
<td>(1) Results</td>
<td>53</td>
</tr>
<tr>
<td>(2) Structures and Spectroscopic Properties of the New Compounds</td>
<td>62</td>
</tr>
<tr>
<td>A. N.M.R. Spectra</td>
<td>63</td>
</tr>
<tr>
<td>(1) $^{19}$F Spectra</td>
<td>63</td>
</tr>
<tr>
<td>(2) $^1$H Spectra</td>
<td>68</td>
</tr>
</tbody>
</table>
CHAPTER III.
Reactions of 1,2-Dimethylarsinotetrafluorocyclobutene ("Difars") with Transition Metal Carbonyls and Halides

Introduction

Experimental
A. Reaction with Metal Carbonyls
B. Reaction with Metal Halides

Discussion

Results
A. Reactions of 1,2-Dimethylarsinotetrafluorocyclobutene ("Difars") with Transition Metal Carbonyls
B. Reactions with Metal Halides
C. Structures and Spectroscopic Properties of the New Compounds

BIBLIOGRAPHY
### LIST OF TABLES

| Chapter I | Table I: Data for Reactions of Diarsines with Disulfides | 22 |
| Chapter II | I. Data for Reactions of Arsines with Fluorocarbon Cyclobutenes | 53 |
| Chapter II | II. Data for Reactions of Amines with Fluorinated Cycloalkenes | 57 |
| Chapter II | III. Data for Reactions of Methane Thiol with Fluorinated Cyclobutenes | 58 |
| Chapter II | IV. $^{19}$F N.M.R. Chemical Shifts | 64 |
| Chapter II | V. Chemical Shifts for Vinylic Protons in Cyclobutenes and Cyclopentenes | 69 |
| Chapter II | VI. Double Bond Stretching Frequencies of the Cyclobutenes | 71 |
| Chapter II | VII. Double Bond Stretching Frequencies of Cyclopentenes | 72 |
| Chapter II | VIII. Double Bond Stretching Frequencies of Disubstituted Cyclobutenes and Cyclopentenes | 73 |
| Chapter II | IX. Comparison of Hydrocarbon and Fluorocarbon Cycloalkene Double Bond Stretching Frequencies | 73 |
| Chapter III | Table I: Products from the Reactions of Difars and Diars with Metal Carbonyls | 96 |
| Chapter III | II. Data concerning the Reactions of Difars with Metal Halides | 100 |
I would like to express deep gratitude to Dr. W. R. Cullen for his advice and encouragement during the course of this investigation. I would also like to thank Dr. L. D. Hall and Dr. L. W. Reeves and their respective students for assistance in obtaining some of the $^{19}$F nmr. spectra. My appreciation is also extended to Miss B. M. Dominique for preparation of the typescript.

It is a pleasure to record here my gratitude to friends outside the University for their unstinting contributions towards the realization of this thesis.

Financial assistance from the National Research Council (1964-66) and the University of British Columbia Graduate Scholarship programme is gratefully acknowledged.
That certain unsaturated organic compounds will react with transition metal compounds has been known for more than one hundred years (1,2). The demand for synthetic gasolines in the 1920's (3), and for large quantities of stable polymeric materials such as synthetic rubber during World War II, provided the basis for investigations into the possibility of obtaining polymeric or other useful products from the reactions of unsaturated organic compounds with transition metal complexes or organometallic compounds. The discovery by Reppe (4) of the catalytic ability of transition metal phosphine complexes for polymerizing acetylenes, and the discovery by Ziegler and coworkers that ethylene could be polymerized by lithium or aluminum alkyls (5,6) has provided an added incentive for the synthesis of organometallic compounds, and an investigation of their properties.

\[
\text{HC} = \text{CH} + \text{Ni(P(C}_6\text{H}_5)_3)_2(\text{CO})_2 \rightarrow \text{C}_6\text{H}_6
\]

\[
\text{LiC}_2\text{H}_5 + n\text{C}_2\text{H}_4 \rightarrow \text{Li}[\text{C}_2\text{H}_4]_n\text{C}_2\text{H}_5
\]

\[
>\text{AlR} + n\text{C}_2\text{H}_4 \rightarrow >\text{Al}[\text{C}_2\text{H}_4]_n\text{R}
\]

The characterization of transitional metal complexes with pseudo-aromatic properties such as Ferrocene (7), and the observed high temperature stability of organosilicones (8), coupled with the continued industrial demand for polymeric materials, has stimulated additional work on organo-derivatives of the metals and metalloids in the last two decades.

At the same time, successful use of a number of fluorocarbons in the polymer, refrigeration and aerosol industries, has resulted in an increased activity in the synthesis of new organo-fluorine compounds. In this area the greatest commercial impetus was provided by the polymerization of
tetrafluoroethylene (Teflon) to yield polymers which withstand high temperatures and are extremely resistant to solvents. It was thus expected that chemists would attempt to bring about a union of fluorocarbon and organometallic chemistry in the synthesis of fluorocarbon derivatives of the elements (9), and that a study would be made of their properties in relation to the corresponding hydrocarbon derivatives.

A number of fluorocarbon derivatives of arsenic, nitrogen and sulfur have been previously synthesized (10,11,12) but much new work remains to be done. The first chapter of this thesis is concerned with some new derivatives of arsenic and sulfur, such as tetrakistrifluoromethylarsine, bistrifluoromethylidisulfide, trifluoromethanesulfenylchloride and trifluoromethanesulfonylechloride, and their reactions with diarsines and arsines to yield compounds containing arsenic sulfur bonds.

The second chapter of this thesis deals with the synthesis and properties of arsenic, sulfur and nitrogen derivatives of the cyclic fluoroolefins, hexafluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene, 1,2-dichlorohexafluorocyclopentene and 1,2-dichlorooctafluorocyclohexene. The reactions of some cyclic fluoroolefins with nucleophilic reagents, such as amines, alcohols and thiols have been investigated (11,13,14) but very little systematic information is available on the reactions of substituted cyclic fluoroolefins. Moreover, there is no information in the literature concerning the reactions of organic arsenic compounds with cyclic fluoroolefins. It is the aim of this investigation to obtain at least a qualitative idea on the reactivity of substituted cyclic fluoroolefins with amines, arsines and thiols, and an understanding of their spectroscopic properties.

The third chapter of this thesis is concerned with the synthesis and properties of transition metal carbonyl and halide derivatives of the new chelating ditertiary arsine, 1,2-dimethylarsinotetrafluorocyclobutene.
(Difars). There is considerable information on the coordination properties of the ditertiary arsine o-phenylenebisdimethylarsine with a number of transition metal compounds provided by Chatt (15), Mann (15) and Nyholm and their coworkers (15). This diarsine stabilizes a wide range of oxidation states and unusual coordination numbers of the metals. It was the object of this investigation, to examine the coordinating ability of 1,2-dimethylarsinotetrafluorocyclobutene in relation to o-phenylenebisdimethylarsine, and to study the effect of the tetrafluorocyclobutene ring as compared with the benzene ring, on the availability of the lone pair electrons on the arsenic atoms for coordination to metal ions or atoms.
CHAPTER I

Derivatives of Compounds containing Arsenic Bonded to both Carbon and Sulphur

Introduction

Since the synthesis of the first organoarsenic sulfide, "dimethylarsenious sulfide", by Bunsen (16)

\[
\text{H}_2\text{S} + (\text{CH}_3)_2\text{As(O)OH} \rightarrow (\text{CH}_3)_2\text{As-S-As(CH}_3)_2 + \text{H}_2\text{O}
\]

the formation and reactions of organic compounds containing As-S bonds have been the subject of numerous investigations. A variety of synthetic routes have been developed but most compounds have been prepared by one of the following general reactions (17).

1. Those in which the elimination of a hydrogen halide results in the formation of the As-S bond.

\[
\text{RAsCl}_2 + 2\text{RSH} \rightarrow \text{RAs(SR)}_2 + 2\text{HCl}
\]

2. Those in which the elimination of metal halide results in the formation of the As-S bond.

\[
\text{RAsCl}_2 + \text{RSNa} \rightarrow \text{RAs(SR)}_2 + \text{NaCl}
\]

3. Those in which the elimination of water results in the formation of As-S bond.

\[
\text{RAsO} + \text{HSR} \rightarrow \text{RAs(SR)}_2 + \text{H}_2\text{O}
\]

A few less common methods for synthesizing As-S bonds are as follows (18):

4. By reaction of tertiary arsines with sulfur

\[
(\text{C}_2\text{H}_5)_3\text{As} + \text{S} \rightarrow (\text{C}_2\text{H}_5)_3\text{As=S}
\]

5. By reaction of secondary arsines with sulfur
5

\[
(\text{CH}_3)_2\text{AsH} + 2\text{S} \rightarrow (\text{CH}_3)_2\text{As-S-As(}\text{CH}_3\text{)}_2 + \text{H}_2\text{S}
\]

6. **By reaction of diarsines with sulfur**

\[
(\text{C}_6\text{H}_5)_2\text{As-As(}\text{C}_6\text{H}_5\text{)}_2 + \text{S} \rightarrow (\text{C}_6\text{H}_5)_2\text{As-As(}\text{C}_6\text{H}_5\text{)}_2
\]

7. **By cleavage of aminoarsines with thiols**

\[
\text{CH}_3\text{As(N(}\text{CH}_3\text{)}_2)_2 + 2\text{HSC}_2\text{H}_4\text{C}_2\text{H}_5 \rightarrow \text{CH}_3\text{As(}\text{C}_2\text{H}_4\text{C}_2\text{H}_5\text{)}_2 + (\text{CH}_3\text{)}_2\text{NH}
\]

In recent years, due to the availability of suitable starting materials, a number of workers have studied the reactions and properties of fluoro-carbon derivatives of organic compounds containing As-S bonds. Thus Emeléus and Pugh (19) using method 2, reacted bistrifluoromethylmercury and arsenic trichloride and obtained a variety of organoarsenic sulfides.

\[
(\text{CF}_3\text{S}_2\text{)}_2\text{Hg} + \text{AsCl} \rightarrow \text{CF}_3\text{SAsCl} + (\text{CF}_3\text{S})_2\text{AsCl} + (\text{CF}_3\text{S})_3\text{As}
\]

Emeléus and Nabi (20) reacted trifluoromethanesulfonylchloride and arsine in an attempt to eliminate hydrogen chloride thus forming the As-S bond (compare method 1). However, reduction of the sulphenyl chloride occurred and the thiol was the only product identified.

As a result of the work of Abel (21), who cleaved Si-S bonds with alkyl iodides, and in view of the ready cleavage of As-As bonds by alkyl and perfluoroalkyl iodides, Cullen (22,23) studied the cleavage of As-S bonds with perfluoroalkyl iodides. Reaction of ethylthiodimethylarsine with trifluoroiodomethane produced dimethyltrifluoromethylarsine and diethyl disulfide presumably by the following reactions.

\[
(\text{CH}_3)_2\text{As-S-C}_2\text{H}_5 + \text{CF}_3\text{I} \rightarrow (\text{CH}_3)_2\text{AsCF}_3 \text{I} + \text{ISC}_2\text{H}_5
\]

\[
2\text{ISC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{SSC}_2\text{H}_5 + \text{I}_2
\]
However, not all compounds containing As-S bonds react in this way; since bistrifluoromethylarsenious sulfide reacts with trifluoriodomethane to produce low yields of iodobistrifluoromethylarsine and bistrifluoromethyltrifluoromethylthioarsine.

\[(\text{CF}_3)_2\text{As-S-As(CF}_3)_2 + \text{CF}_3\text{I} \rightarrow (\text{CF}_3)_2\text{AsI} + \text{CF}_3\text{SAs(CF}_3)_2\]

It would thus appear that the reactivity of the As-S bond is dependent on the groups attached, and the direction of addition of organic iodides to this bond is a function of the induced polarity of the bond.

The present investigation was initiated for the purpose of studying the chemical properties of known derivatives and to find new synthetic routes. In particular it was desirable to explore the reductive capabilities of dimethylarsine in view of the results, that triphenyltinhydride (24) and lithium aluminum hydride (25) reduce disulfides and sulfonyl halides. Furthermore, some compounds containing the As-As bond are readily cleaved by sulfur, iodomethane, iodotrifluoromethane and trifluoroacetylchloride; a further examination of the reactions of diarsines with compounds containing sulfur-sulfur and sulfur-chlorine bonds seemed warranted. The results of these studies are presented in the following experimental and discussion sections.
EXPERIMENTAL

I Apparatus and General Techniques

For the three chapters of this thesis, the following description summarizes the apparatus and experimental techniques used in the experimental part of the present investigation.

Vacuum techniques were used for volatile reactants and products, and unless otherwise indicated, the reactions were carried out in sealed thick walled Pyrex Carius tubes. An inert atmosphere chamber was used for identification and purification of suitable volatile compounds and the column used for a particular separation is indicated in the text.

The $^1$H nmr. spectra were obtained on a Varian A-60 spectrometer and chemical shifts are reported in p.p.m. relative to external tetramethylsilane (negative values to lower field). The $^{19}$F nmr. spectra were obtained on a Varian HR-60 (56.4 Mc/s) spectrometer and chemical shifts are reported relative to external trifluoroacetic acid indicated in the text by (A); other $^{19}$F spectra were run on a Varian HR-100 (94.6 Mc/s) and these chemical shifts are reported relative to external trichlorofluoromethane, indicated in the text by (B). Infrared spectra were obtained on Perkin-Elmer 21, and 410 spectrophotometers and are reported in cm$^{-1}$. For those spectra reported in microns (µ), a calibrated Perkin-Elmer 137 instrument was used. The microanalysis were carried out by Schwartzkopf microanalytical Laboratory, Woodside 77, N.Y., U.S.A. and Alfred Bernhardt Mikroanalytisches Laboratorium in Max-Planck-Institut, Mulheim (Ruhr) Kaiser-Wilhelm-Platz 1, Germany. Microanalysis for which only carbon, hydrogen and nitrogen are reported were carried out by Mrs. Jenkins and
II Synthesis of Starting Materials

a. Tetramethyldiarsine. The diarsine was prepared by the reduction of dimethylarsinic acid with excess hypophosphorous acid in 2.5N hydrochloric acid (26). A fraction which distilled at 74° (46mm) was collected. Its identity and purity were checked by its $^1$H nmr. spectrum which showed a single peak at -1.13 ppm.

b. Dimethylarsine. This arsine was prepared by the reduction of dimethylarsinic acid with an excess of zinc and 12N hydrochloric acid in ethanolic solution (27). The dimethylarsine was purified by exposing it to potassium hydroxide to remove any hydrogen chloride and dried over phosphorous pentoxide. The identity of dimethylarsine was established by its strong As-H absorption at 4.8 $\mu$. The $^1$H nmr. spectrum showed two sets of resonances; one, a doublet centred at 0.87 ppm. ($J = 6.7$ c.p.s.) and the other, a septet centred at -2.29 ppm. ($J = 6.8$ c.p.s.) of relative area 1:5.9 (Calc. 1:6.0) in agreement with Styan (28).

c. Bis(trifluoromethyl)disulfide. This disulfide was prepared by the reaction of trifluoroiodomethane and excess sulfur at 200° for three days (29). The fraction distilling at 32°-33° (760 mm) (lit. value 32°) was collected and identified by means of its known infrared spectrum.

d. Chlorodimethylarsine. This arsine was prepared by the reduction of dimethylarsinic acid with hypophosphorous acid in 2.5N hydrochloric acid (30). The arsine was purified by distillation and the fraction distilling at 107° (760 mm) (lit. value 108°) was collected and identified by means of
its known infrared spectrum (liquid film).

e. Bis(trifluoromethylthio)mercury. This mercurial was prepared by the fluorination of carbon disulfide with mercuric fluoride at 150° for six hours (31). Its purity and identity was established by m.p. 40° (lit. value 39°) and infrared spectrum.

f. Tetrakis(trifluoromethyl)diarsine. Iodobis(trifluoromethyl)arsine was prepared by the reaction of trifluoroiodomethane and arsenic metal at 200° for 14 days (10). The iodobis(trifluoromethyl)arsine was then reduced with mercury at 20° for three days to the corresponding diarsine (10). The diarsine was recovered from a trap at 64° and its purity and identity were established by means of its known infrared spectrum.

g. Dimethylaminodimethylarsine. This arsine was prepared by the reaction of iododimethylarsine and dimethylamine at 20° for 24 hours (32, 35, 36). The arsine was purified by distillation at atmospheric pressure and the fraction b.p. 114° was collected (lit. value 112°) and was identified by means of its known infrared spectrum.

III. Synthesis of Derivatives of As-S bonds

A. Reactions of Tetramethyl(diarsine)

1. With Bistrifluoromethyl(disulfide). Bistrifluoromethyl(disulfide) (6.3 g) and the diarsine (3.2 g) were miscible at 20° and were left at this temperature for one week. Bistrifluoromethyl(disulfide) (4.0 g) which went through a trap at -64° was recovered. The fraction (5.5 g, 86%) which condensed in a trap at -64° was identified as trifluoromethylthiodimethylarsine b.p. 115° (760 mm) Anal. Found: As, 36.23, F, 27.88%, S, 15.5%. Calc. for
C₃H₆AsF₃S: As, 36.4, F, 27.7, S, 15.6%. Infrared spectrum (liquid film):
3000W, 2920W, 1342W, 1273W, 1226W, 1158VS, 1117VS, 900VW, 840W, 757 cm⁻¹
Nmr. spectrum: the ¹H spectrum showed a singlet at -1.32 p.p.m.

2. With Bistrifluoromethyldithetene. Bistrifluoromethyldithetene (7.2 g)* and the diarsine (6.4 g) were left at 20° for six days. After one day at this temperature a red tinge was imparted to the solution. Bistrifluoromethyldithetene (0.3 g) was recovered. The involatile liquid product b.p. 92-95° (10⁻³ cm) was identified as 2,3-thiodimethylarsino-hexa-fluorobutene-2, a reddish air sensitive liquid obtained in quantitative yield. Anal. Found: C, 22.22; H, 2.88; As, 34.2; F, 26.10; S, 14.56%.
Calc. for C₈H₁₂As₂S₂F₆: C, 22.08; H, 2.52; As, 34.4; F, 26.1; S, 14.7%.

3. With Deethyl Disulfide. Diethyl disulfide (3.7 g)† and the diarsine (3.5 g) were left at 20° for 30 days. The reaction product, ethylthiodimethylarsine was identified by means of its known ¹H nmr. spectrum (33). The yield was found to be quantitative by ¹H nmr. analysis of the reaction mixture.

4. With Diphenyl Disulfide. Diphenyl disulfide† (1.6 g) and the

*gift of Dr. W. R. Cullen.
†Diethyl disulfide and diphenyl disulfide were obtained from K & K Chemical Laboratories and used without further purification.
diarsine (2.0 g) were immiscible at 20°. The reaction tube was heated to 100° to obtain complete dissolution of the diphenyl disulfide in the arsine and was then left at this temperature for nine days. Unreacted diarsine (0.5 g) was pumped into the vacuum system. The reaction product was an involatile colourless liquid which remained in the tube was found to be phenylthiodimethylarsine b.p. 88° (2 mm) (2.5 g, 89%). Anal. Found: C, 45.68; H, 5.75%. Calc. for C₈H₁₁AsS: C, 45.3; H, 5.14%. Infrared spectrum (liquid film): 3.21S, 3.41S, 6.34VS, 6.8VS, 7.0VS, 7.19S, 7.72W, 8.02S, 8.03S, 9.23S, 9.38S, 9.78VS, 11.15S, 11.95S, 13.50VS, 14.5VS microns. Nmr. spectrum: the ¹H spectrum showed two sets of peaks; one a singlet at -1.03 ppm. and the other a multiplet centred at -7.10 ppm. of relative area 6:4.9 (Calc. 6:5).

B. Reactions of Tetrakis(trifluoromethyl) diarsine

1. With Diethyl Disulfide. The diarsine (0.7 g) and a slight excess of diethyl disulfide (1.9 g) were miscible at 20° and were left at this temperature for two weeks. The gas phase infrared spectrum of the reaction mixture showed a predominance of the diarsine bands indicating incomplete reaction. The reaction mixture was then heated at 100° for four days. A small amount of unreacted diarsine which passed through a trap at -22° was recovered and was identified by means of its known infrared spectrum. The fraction (2.9 g) which condensed in a trap at -22° was found to contain only two components which were separated by v.p.c. (silicone column at 160°) and identified as diethyl disulfide of known infrared spectrum and ethylthiobistrifluoromethylarsine, b.p. 129° (760 mm). Anal. Found: C, 17.31, H, 1.79; As, 27.3; F, 41.7%. Calc. for C₄H₅AsF₆S: C, 17.5; H, 1.3; As, 27.4;
F, 41.6%. Infrared spectrum (liquid film): 2980W, 1457W, 1435VW, 1383VW, 1283S, 1090VS, 1175VS, 965W, 735S cm$^{-1}$. Nmr. spectrum: the $^1$H spectrum showed two sets of peaks; one a quartet centred at -2.7 ppm. (J = 7.0 c.p.s.) and the other a triplet centred at -1.19 ppm. (J = 7.0 c.p.s.) of relative area triplet: quartet 2:3 (Calc. 2:3).

2. With Bistrifluoromethyl Disulfide. Bistrifluoromethyl disulfide (1.63 g) and tetrakis(trifluoromethyl)diarsine (1.3 g) were miscible at 20° and were left at this temperature for two weeks. The infrared spectrum of the fraction which condensed in a trap at -64° and had passed through a trap at -46° exhibited bands similar to those of trifluoromethylthiobistrifluoromethylarsine of known infrared spectrum (34). The infrared spectrum of the fraction which condensed in a trap at -46° showed a predominance of the diarsine bands indicating incomplete reaction. The fractions were then mixed and heated to 95° for four days. Trap to trap distillation yielded a fraction (1.7 g) which stopped in a trap at -64° and which was found to be trifluoromethylthiobistrifluoromethylarsine of known infrared spectrum (34). The yield of the arsine was quantitative.

C. The reaction of Bistrifluoromethylthiomercury and Chlorodimethylarsine

Chlorodimethylarsine (2.9 g) and a slight excess of bistrifluoromethylthiomercury (11.3 g) were not completely miscible at 20° and were left at this temperature for two days. During this period a white solid precipitated. The volatile contents of the tube were taken into the vacuum system and the fraction stopping in a trap at -66° (3.1 g, 85%) was identified as trifluoromethylthiodimethylarsine by means of its known infrared and $^1$H Nmr. spectra and b.p. 115° (760 mm). The fraction (1.3 g)
which passed through a trap at -64° and condensed in a trap at -135° was identified as a mixture of bistrifluoromethyl disulfide and silicon tetrafluoride and other unidentifiable compounds by means of infrared spectra.

D. Reactions of Dimethylarsine

1. With Ethylthiodimethylarsine. Dimethylarsine (1.5 g) and ethylthiodimethylarsine (4.4 g) were heated to 100° for four days. Trap to trap distillation yielded a fraction (1.0 g) which passed through a trap at -64° and was found to contain dimethylarsine (0.05 g) and ethanethiol (0.95 g) of known $^1$H nmr. spectra (33). A fraction (4.6 g) which condensed in a trap at -64° was found to contain only two components which were identified as ethylthiodimethylarsine (2.72 g) and tetramethyldiarsine (1.88 g) by means of their known $^1$H nmr. spectra. The yield of tetramethyldiarsine was quantitative based on the quantity of dimethylarsine consumed in the reaction.

2. With Dimethylaminodimethylarsine. Dimethylaminodimethylarsine (3.6 g) and dimethylarsine (2.0 g) were miscible at 20° and were left at this temperature for 21 days. Trap to trap distillation yielded a fraction (0.71 g) which passed through a trap at -64° and was identified as dimethylamine by means of its known infrared spectrum. A fraction (3.0 g) which condensed in a trap at -64° was found to contain dimethylaminodimethylarsine (0.8 g) and tetramethyldiarsine (2.7 g) of known $^1$H nmr. spectra. The yield of tetramethyldiarsine was quantitative based on the quantity of dimethylarsine consumed in the reaction.

3. With Diethyl Disulfide. Dimethylarsine (4.2 g) and diethyl disulfide (3.0 g) were heated to 100° for 24 hours. Trap to trap distillation yielded
a fraction (3.5 g) which stopped in a trap at -22°. This fraction was found to contain only two components which were identified as tetramethyl-
diarsine (2.12 g) and ethylthiodimethylarsine (1.3 g) by means of their known ¹H nmr. spectra (33). A fraction (2.0 g) which passed through a trap at -22° was found to contain dimethylarsine (0.24 g) and ethanethiol (1.76 g) of known ¹H nmr. spectra (33).

4. With Bistrifluoromethyl Disulfide. Dimethylarsine (1.0 g) and bistrifluoromethyl disulfide (1.8 g) were left at 20° for one day (although a vigorous exothermic reaction took place immediately upon mixing well below this temperature). Trap to trap distillation yielded a fraction (1.84 g) which stopped in a trap at -64° and was found to contain only two components. These were identified as tetramethyldiarsine (0.14 g) and trifluoromethylthiodimethylarsine (1.7 g) by means of their known ¹H nmr. spectra. The thioarsine was also identified by means of its known infrared spectrum (See A-1). A more volatile fraction (0.6 g) which stopped in a trap at 135° was identified as trifluoromethanethiol of known infrared spectrum (33). The yield of the thiol was quantitative.

E. Reactions of Trifluoromethanesulfenylchloride

1. With Tetramethyldiarsine. Trifluoromethanesulfenylchloride (2.2 g) and tetramethyldiarsine (3.8 g) were left at 20° for 9 days. A minute quantity of unidentified white solid remained at the bottom of the Carius tube after the volatiles were condensed into the vacuum system. Trap to trap distillation of the volatiles yielded a fraction (4.0 g) which stopped in a trap at -64° and which contained only two components by v.p.c. (silicone column at 125°). These were identified after separation by v.p.c. as
1. Chlorodimethylarsine (3.06 g) and trifluoromethylthiodimethylarsine (1.53 g) by means of their known $^1$H nmr. and infrared spectra (See A-l). Trifluoromethanesulfenylchloride (0.483 g) of known infrared spectrum (33) was recovered condensed in a trap at -96°.

2. With Dimethylarsine. Trifluoromethanesulfenylchloride (3.0 g) and dimethylarsine (2.0 g) were left at 20° for seven days. A small quantity of unidentified white solid remained behind in the Carius tube after the volatiles were condensed into the vacuum system. Trap to trap distillation of the volatiles, yielded a fraction (2.81 g) which stopped in a trap at -66° and separated into two components by v.p.c. (silicone column at 125°). These were identified as trifluoromethylthiodimethylarsine and chlorodimethylarsine (in the weight ratio 1:10) by means of their known $^1$H nmr. and infrared spectra. Trifluoromethanethiol (1.30 g) of known infrared spectrum was recovered from a trap at -135°.

3. With Dimethylphenylthioarsine. Trifluoromethanesulfenylchloride (7.11 g) and dimethylphenlthioarsine (1.5 g) were left at 20° for two days. A vigorous reaction took place forming a white solid immediately upon mixing well below this temperature. Trifluoromethanesulfenylchloride (5.21 g) was recovered. The reaction product which condensed in a trap at -23° was distilled under reduced pressure and identified as trifluoromethylphenyl disulfide b.p. 110° (70 mm). Anal. Found: C, 40.0; H, 2.46; F, 27.0; S, 30.4%. Calc. for C$_7$H$_5$F$_3$S$_2$: C, 40.0; H, 2.38; F, 27.2; S, 30.4%. Infra-red spectrum (liquid film): 3100S, 1583S, 1482S, 1445S, 1380VW, 1297VW, 1152VS, 1100VS, 1022S, 1000W, 900W, 830VW, 805W, 739VS, 698W(Sh), 658 cm$^{-1}$. The yield of the disulfide was quantitative. After the volatiles had been taken
into the vacuum system, a white solid remained in the Carius tube. Analysis of the solid gave an empirical formula of $\text{CH}_3\text{AsCl}_2\text{F}_0.6$ however, since the solid slowly decomposed on standing, the analytical result may not be very reliable.

4. **With Ethylthiodimethylarsine.** Trifluoromethanesulfenylchloride (5.4 g) and ethylthiodimethylarsine (3.2 g) reacted vigorously upon mixing forming a white solid. After twelve hours, the white solid had decomposed forming a liquid. After 3 days at 20° trifluoromethanesulfenylchloride (0.9 g) was recovered condensed in a trap at -96°. A fraction (7.11 g) which condensed in a trap at -64° was examined by v.p.c. (silicone column at 110°) and found to contain two main components and one minor involatile one. The two main components were identified as chlorodimethylarsine of known infrared spectrum and ethyltrifluoromethyl disulfide b.p. 91° (760 mm).

Anal. Found: C, 22.3; H, 3.3; F, 35.0; S, 39.8%. Calc. for $\text{C}_3\text{H}_5\text{F}_3\text{S}_2$: C, 22.2; H, 3.1; F, 35.2; S, 39.5%. Infrared spectrum (liquid film): 2940W, 1455S, 1382S, 1258S, 1130VS (broad), 1048W, 970W, 750S cm$^{-1}$. The yield of the disulfide was quantitative.

5. **With Chlorodimethylarsine.**

a. **Excess Trifluoromethanesulfenylchloride.** Trifluoromethanesulfenylchloride (5.2 g) and chlorodimethylarsine (3.6 g) reacted vigorously on mixing forming a white solid. The tube was left at 20° for three days. The volatiles were pumped into the vacuum system leaving a white solid behind. Trifluoromethanesulfenylchloride (4.3 g) which passed through a trap at -78° was recovered, together with chlorodimethylarsine (1.9 g) which condensed in a trap at -64°. The solid was left under a nitrogen atmosphere and
decomposed overnight into a colourless liquid, b.p. 74° (110 mm) which was identified as dichloromethylarsine of known infrared spectrum (33).

b. **Excess Chlorodimethylarsine.** Chlorodimethylarsine (6.2 g) and trifluoromethanesulfonylchloride (2.2 g) were left at 20° for four months. The initially produced white solid was stable under these conditions. In an attempt to decompose the solid, the tube was heated to 150° for three days. The volatiles were pumped into the vacuum system. A fraction (4.5 g) which condensed in a trap at -64° was separated by v.p.c. and identified as a mixture of dichloromethylarsine and chlorodimethylarsine (4:6 weight ratio) of known infrared spectra. A fraction which had passed through a trap at -135° was identified as a mixture of silicon tetrafluoride and carbon dioxide of known infrared spectra. The fractions of intermediate volatility which condensed in traps at -78°, -96° and -135° respectively could not be identified on the basis of infrared spectra. There was no evidence in the infrared spectra for the presence of trifluoromethyldimethyl sulfide.

F. **Reactions of Methanesulfonylchloride:**

1. (a) **With Tetramethyldiarsine.** Methanesulfonylchloride (10.9 g) and tetramethyldiarsine (4.0 g) were left at 20° for 10 days. The volatiles were pumped into the vacuum system. A fraction (2.2 g) which condensed in a trap at -64° was identified as chlorodimethylarsine b.p. 107°10° (760 mm) of known infrared spectrum. The remaining product, an air sensitive

---

* Methanesulfonylchloride was obtained from Eastman Organic Chemicals and was used without further purification.
involatile liquid (3.0 g) distilled in the range 67-110° (10 mm). An examination of the \( ^1 \)H nmr. spectra of the different fractions showed that a pure product was not obtained. Attempts to obtain infrared spectra (liquid film) of the fractions were unsuccessful due to the air sensitivity of the liquid. Attempts to purify the fractions by v.p.c. (Dinonyl phthalate column at 170°) were also unsuccessful due to decomposition.

\begin{enumerate}
\item Reaction in an Nmr. Tube. Methanesulfonylchloride (0.4 g) and tetramethyldiarsine (0.75 g) were left at 20° in an Nmr. tube. After 12 hours the \( ^1 \)H Nmr. spectrum showed singlets at -3.81, -3.37, -2.72 and -1.72 p.p.m. of relative area 8:10:9:95. After 7 days, the \( ^1 \)H nmr. spectrum showed singlets at -3.32, -2.70, -2.42, -1.70 p.p.m. of relative area 8:10:9:95. After 6 weeks, the volatiles were taken into the vacuum system. A fraction (0.78 g) which condensed in a trap at -46° was identified as chlorodimethylarsine of known infrared spectrum. There were no other volatile fractions. The white solid, which remained behind was insoluble in common laboratory solvents and upon exposure to air quickly turned into an oil.

\item With Dimethylarsine. Methanesulfonylchloride (9.5 g) and dimethylarsine (5.1 g) were miscible at 20° and were left at this temperature for 23 days. Trap to trap distillation yielded a fraction (5.0 g) which condensed in a trap at -46° and was identified as chlorodimethylarsine of known infrared spectrum. No other arsenic compounds were detected. The \( ^1 \)H nmr. spectrum of the involatile liquid product showed peaks at -3.79 (methanesulfonylchloride), -2.92, -2.43 and a very small peak due to chloro(dimethylarsine at -1.68 p.p.m. On distillation of this liquid at (10\(^{-2}\) mm) a small fraction (~0.3 g) b.p. 140° was obtained whose \( ^1 \)H nmr. spectrum
showed the presence of some methane sulfonylchloride. The peak at -2.92
ing the original mixture now appeared at -2.97 p.p.m. and the peak originally
at -2.43 p.p.m. was absent. In the distillation pot, a charred white solid
remained which was sublimed at 120° under vacuum, m.p. 248-50°. Infrared
spectrum (KBr pellet): 2900VW, 1260W, 1194W, 1049S, 793VS cm⁻¹. This solid
was not analyzed.

G. Additional Reactions of Tetramethyldiarsine

1. Trifluoromethanesulfonyl Chloride*

   a. Excess Diarsine. Trifluoromethanesulfonyl chloride (4.2 g) and
tetramethyldiarsine (7.9 g) reacted vigorously upon mixing forming a small
quantity of white solid and were left at 20° for one day. Tetramethyldiarsine
(1.0 g) which condensed in a trap at -23° was recovered. A fraction (3.8 g)
which condensed in a trap at -64° was identified as chlorodimethylarsine of
known infrared spectrum. The product, an involatile liquid (5.5 g), which
distilled at 105° (47 mm) was identified as trifluoromethanesulfonyldimethyl-
arsine. Anal. Found: C, 16.3; H, 3.26; As, 33.2; F, 25.1; S, 14.0%. Calc.
for C₃H₅AsF₃SO₂: C, 15.1; H, 2.52; As, 31.5; F, 24.0; S, 13.5%. Infrared
spectrum (liquid film): 3030VW, 2930 W, 2240W, 1420S, 1260W, 1150VS, 1072VS,
1012VS, 901VS, 855VS, 795VS cm⁻¹. The H Nmr. spectrum showed a single
peak at -1.64 p.p.m.

   b. Excess Trifluoromethanesulfonyl Chloride. Trifluoromethanesulfonyl
chloride (8.31 g) and tetramethyldiarsine (2.89 g) reacted vigorously upon
mixing forming a large quantity of white solid and were left at 20° for

* Trifluoromethanesulfonyl Chloride was obtained from Penninsular Chem.
Research Inc., Gainsville, Florida and used without further purification.
four months. A fraction (1.4 g) which condensed in a trap at -64° was separated into two components by v.p.c. (silicone column at 110°). The major component was dichloromethylarsine of known infrared spectrum, and a minor part was due to an unidentifiable substance which contained C-H, C-F, $SO_2$ bands in its infrared spectrum. Trifluoromethanesulfonyl chloride (6.3 g) which passed through a trap at -64° was recovered.

This trifluoromethanesulfonyl chloride (6.3 g) was then left with tetramethylarsine (5.6 g) at 20° for 2 days. A fraction (8.1 g) which condensed in a trap at -64° was separated into two components by v.p.c. (silicone column at 110°). These were identified as trifluoromethylthiodimethylarsine and chlorodimethylarsine of known infrared spectra. A fraction (1.6 g) which passed through a trap at -64° was recovered (mixture of trifluoromethanesulfonyl chloride and trifluoromethanesulfonyl chloride). An involatile liquid product (1.0 g) was identified as trifluoromethanesulfonyldimethylarsine of known infrared spectrum. (1 a).

2. **Methanesulfonyl Anhydride** Methanesulfonyl anhydride (4.7 g) and tetramethylarsine (5.0 g) were miscible at 20° and were left at this temperature for one week. No volatile products were obtained. The product, an involatile liquid, was distilled under reduced pressure and a fraction b.p. 137° ($10^{-2}$ mm) (4.2 g, 82% based on diarsine consumed) was identified as dimethylarsinomethanesulfonate. Anal. Found: C, 18.2; H, 4.63; As, 37.4; S, 15.9%. Calc. for $C_3H_9AsO_3S$: C, 18.0; H, 4.5; As, 37.5; S, 16.0%.

Infrared spectrum (liquid film): 3020W, 2900W, 1417W, 1333S, 1200S, 1165VS, 910W, 850VW, 790VS cm$^{-1}$. The $^1$H nmr. spectrum showed two peaks, one at -1.8 and the other at -3.1 p.p.m. of relative area 2:1 (Calc. 2:1).

---

*Methanesulfonyl Anhydride was obtained from Eastman Organic Chemicals, Rochester, New York, and used without further purification.*
3. Methanesulfonyl Fluoride* Methanesulfonyl fluoride (6.8 g) and tetramethyldiarsine (4.8 g) were miscible at 20° and were left at this temperature for 7 days. At the end of this period, there was no evidence of a reaction. The entire contents of the reaction tube could be taken into the vacuum system, involatile liquid being left in the reaction tube.

* Methanesulfonyl fluoride was obtained from Eastman Organic Chemicals, Rochester, New York, and used without further purification.
DISCUSSION

Arsines and Diarsines have been found to react with disulfides, sulfonyl and sulfenylchlorides to yield compounds containing As-S bonds.

A. Reactions of Diarsines with Disulfides

Diarsines react with disulfides to yield organic derivatives of arsenic sulfides. Table I summarizes the results of a number of experiments which can be represented by the following general equation.

\[
R_2\text{As-AsR}_2 + R'-\text{S-S-R'} \rightarrow 2R_2\text{As-S-R'}
\]

**TABLE I**

Data for Reactions of Diarsines with Disulfides

<table>
<thead>
<tr>
<th>Diarsine</th>
<th>Disulfide</th>
<th>Product</th>
<th>RX.T. (°C)</th>
<th>RX.Time (days)</th>
<th>B.P. (°C) (mm)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = CH₃</td>
<td>R' = CF₃</td>
<td>(CH₃)₂As-S-CF₃</td>
<td>20</td>
<td>7</td>
<td>115</td>
<td>70</td>
</tr>
<tr>
<td>R = CH₃</td>
<td>CF₃-C=C-CF₃</td>
<td>CF₃-C = C-CF₃</td>
<td>20</td>
<td>6</td>
<td>92-95 (10⁻² mm)</td>
<td>100</td>
</tr>
<tr>
<td>R = CH₃</td>
<td>R' = C₂H₅</td>
<td>(CH₃)₂As-S-C₂H₅</td>
<td>20</td>
<td>30</td>
<td>145-8 (a)</td>
<td>100</td>
</tr>
<tr>
<td>R = CH₃</td>
<td>R' = C₆H₅</td>
<td>(CH₃)₂As-S-C₆H₅</td>
<td>100</td>
<td>9</td>
<td>88 (2)</td>
<td>83</td>
</tr>
<tr>
<td>R = CF₃</td>
<td>R' = C₂H₅</td>
<td>(CF₃)₂As-S-C₂H₅</td>
<td>100</td>
<td>4</td>
<td>129</td>
<td>100</td>
</tr>
<tr>
<td>R = CF₃</td>
<td>R' = CF₃</td>
<td>(CF₃)₂As-S-CF₃</td>
<td>95</td>
<td>4</td>
<td>63 (b)</td>
<td>100</td>
</tr>
</tbody>
</table>

(a) See reference (22)
(b) See reference (34)
RX = Reaction
Tetramethyldiarsine also reacts with trifluoromethanesulfonylchloride at 20° (9 days) to yield chlorodimethylarsine and trifluoromethylthiodimethylarsine.

\[
\text{CF}_3\text{SCl} + (\text{CH}_3)_2\text{As-As(CH}_3)_2 \xrightarrow{20°} (\text{CH}_3)_2\text{AsCl} + \text{CF}_3\text{-S-As(CH}_3)_2
\]

Similarly tetramethyldiarsine reacts with methanesulfonylchloride at 20° (10 days) to yield chlorodimethylarsine and an involatile liquid. Attempts to purify the involatile liquid by vacuum distillation and v.p.c. were unsuccessful, due to considerable decomposition.

\[
(\text{CH}_3)_2\text{As-As(CH}_3)_2 + \text{CH}_3\text{SO}_2\text{Cl} \rightarrow (\text{CH}_3)_2\text{AsCl} + ?
\]

Attempts to react tetramethyldiarsine with methanesulfonylfluoride at 20° (7 days) were unsuccessful; only starting materials were obtained.

\[
(\text{CH}_3)_2\text{As-As(CH}_3)_2 + \text{CH}_3\text{SO}_2\text{F} \rightarrow \text{NO Reactions}
\]

Reaction of tetramethyldiarsine with methanesulfonyl anhydride at 20° (7 days) yields dimethylarsinomethanesulfonate b.p. 137° (10⁻² mm).

There was no evidence in the distillate of the other expected product, methanesulfonyldimethylarsine.

Reaction of trifluoromethanesulfonylchloride with excess tetramethyldiarsine at 20° (1 day) yields trifluoromethanesulfonyldimethylarsine b.p. 105° (47 mm) and chlorodimethylarsine.

\[
(\text{CH}_3)_2\text{As-As(CH}_3)_2 + \text{CF}_3\text{SO}_2\text{Cl} \rightarrow (\text{CH}_3)_2\text{AsSO}_2\text{CF}_3 + (\text{CH}_3)_2\text{AsCl}
\]

Reaction of excess trifluoromethanesulfonylchloride and tetramethyl-
diarsine at 20° yields a white solid which slowly decomposes (4 months) into dichloromethylarsine and an unidentified substance. The excess trifluromethanesulfonylchloride from this reaction was then reacted with more tetramethyldiarsine at 20° (2 days) and yielded trifluoromethylthiodimethylarsine b.p. 117° (760) and a small quantity of trifluoromethanesulfonyldimethylarsine, in addition to chlorodimethylarsine.

\[
(CH_3)_2As-As(CH_3)_2 + CF_3SO_2Cl \rightarrow \text{[white solid]} \quad 4 \text{ months} \quad CH_3AsCl_2 + ?
\]

\[
CF_3SO_2Cl + (CH_3)_2As-As(CH_3)_2 \rightarrow (CH_3)_2AsCl + CF_3SO_2As(CH_3)_2 + CF_3-S-As(CH_3)_2
\]

B. Reaction of Arsines with Compounds containing As-S, As-N, S-S and S-Cl Bonds

Dimethylarsine has been found to cleave As-S, As-N, S-S and S-Cl bonds. In Table II are summarized the results of some experiments involving dimethylarsine.

**TABLE II**

Data for Reactions of Dimethylarsine with Compounds containing As-S, As-N, S-S and S-Cl bonds

<table>
<thead>
<tr>
<th>Reactants, Compounds containing As-S, As-N, S-S, S-Cl bonds</th>
<th>Products</th>
<th>RX.T. (°C)</th>
<th>RX.Time (days)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2H_5-S-As(CH_3)_2)</td>
<td>((CH_3)_2As-As(CH_3)_2 + C_2H_5SH)</td>
<td>100</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>((CH_3)_2N-As(CH_3)_2)</td>
<td>((CH_3)_2As-As(CH_3)_2 + (CH_3)_2NH)</td>
<td>20</td>
<td>21</td>
<td>100</td>
</tr>
<tr>
<td>(C_2H_5-S-S-C_2H_5)</td>
<td>(C_2H_5-S-As(CH_3)_2 + C_2H_5SH)</td>
<td>100</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>(CF_3-S-S-CF_3)</td>
<td>(CF_3-S-As(CH_3)_2 + CF_3SH)</td>
<td>20</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>(CF_3SCl)</td>
<td>(CF_3SH + (CH_3)_2AsCl + CF_3SAs(CH_3)_2)</td>
<td>20</td>
<td>7</td>
<td>90⁷</td>
</tr>
</tbody>
</table>

^a is the yield of chlorodimethylarsine based on quantity of dimethylarsine used.
Dimethylarsine also reacts with methanesulfonylchloride at 20° (23 days) to yield chlorodimethylarsine and an unidentified solid.

\[
(CH_3)_2AsH + CH_3SO_2Cl \longrightarrow (CH_3)_2AsCl + \text{white solid}
\]

C. Reactions of Trifluoromethanesulfonylchloride with Compounds containing As-S, and As-Cl bonds.

Trifluoromethanesulfonylchloride has been found to cleave As-S bonds. Thus the reaction of trifluoromethanesulfonylchloride with phenylthiodimethylarsine yields phenyltrifluoromethyl disulfide b.p.110° (70 mm), chlorodimethylarsine and a white solid of empirical formula CH₃AsCl₂F₀.₆

\[
C_6H_5-S-\text{As(Ch₃)}_2 + \text{CF}_3\text{SCl} \longrightarrow \text{CF}_3-S-S-C_6H_5 + (\text{CH}_3)_2\text{AsCl}
\]

Trifluoromethanesulfonylchloride also reacts with ethylthiodimethylarsine at 20° (1 day) to yield chlorodimethylarsine and ethyltrifluoromethyl-disulfide.

\[
C_2H_5-S-\text{As(Ch₃)}_2 + \text{CF}_3\text{SCl} \longrightarrow C_2H_5-S-S-CF_3 + (\text{CH}_3)_2\text{AsCl}
\]

In the above reactions, wherever chlorodimethylarsine is a reaction product in the presence of trifluoromethanesulfonylchloride, a white solid is always produced. In an attempt to elucidate the composition of this solid, chlorodimethylarsine was reacted with trifluoromethanesulfonylchloride to yield this white solid.

\[
(CH_3)_2AsCl + \text{CF}_3\text{SCl} \longrightarrow \text{[white solid]}
\]

The white solid decomposes overnight in a drybox into a liquid which was found to be dichloromethylarsine b.p. 74° (110 mm).

\[
\text{[White solid]} \longrightarrow \text{CH}_3\text{AsCl}_2 + ?
\]
In an attempt to determine the other component of this decomposition, chlorodimethylarsine and trifluoromethanesulfonyl chloride, which immediately produced the white solid, were left at 20° for 4 months. The initially produced solid was stable under these conditions. In an attempt to decompose the solid, the tube was heated to 150° (3 days). Although dichloromethylarsine was produced there was no evidence in the volatile components for the other anticipated product of decomposition - methyltrifluoromethylsulfide.

\[
\text{[White solid]} \quad \text{CH}_3\text{AsCl}_2 + \ (\text{CF}_3\text{S-CH}_3)\ ?
\]

The white solid is believed to be a five coordinate species of arsenic with empirical formula \( \text{C}_3\text{H}_6\text{AsCl}_2\text{F}_3\text{S} \). Due to its instability, analysis results are unreliable. One such result gave the empirical formula as \( \text{CH}_3\text{AsCl}_2\text{F}_{0.6} \) indicating that the anticipated product \( \text{CF}_3\text{SCH}_3 \) had been eliminated. Two of the four possible isomers of the white solid are:

- \( \text{As-SCF}_3 \)
- \( \text{CH}_3\text{Cl} \)

**Structures and Spectroscopic Properties of the New Compounds**

The structures of these compounds were determined by chemical analysis (See Experimental Section), \(^1\text{H} \) nmr. and Infrared spectroscopy. The presence of methyl, ethyl or phenyl groups attached to arsenic or sulfur were corroborated by their characteristic resonance frequency in their \(^1\text{H} \) nmr. spectra. Thus in the case of trifluoromethylthiodimethylarsine, the methyl groups are readily accounted for by the appearance of the expected single peak at -1.32 p.p.m. The other compounds were similarly identified. The presence of C-H,
SO$_2$ and C-F groups in these compounds were confirmed by means of their characteristic absorption in their infrared spectra in the regions 3000 cm$^{-1}$ (C-H), 1425-1250 cm$^{-1}$ (SO$_2$) and 1200-1000 cm$^{-1}$ (C-F).

Postulated Mechanisms

For the reaction of diarsines with disulfides, two mechanisms seem likely. The first, a free radical mechanism, involves the homolytic scission (37) of the S-S bond.

$$R-S-S-R \quad \rightarrow \quad RS^*$$

$$RS^* + (R')_2As-As(R')_2$$

$$\rightarrow \quad (R')_2As-S-R + (R')_2As^*$$

$$(R')_2As^* + RSSR \quad \rightarrow \quad (R')_2As-S-R + RS^*$$

$$RS^* + (R')_2As^*$$

$$\rightarrow \quad (R')_2As-S-R$$

The second possible mechanism involves nucleophilic attack by arsenic on to sulfur, resulting in heterolytic cleavage of the S-S bond.

$$R-S-S-R$$

$$\delta^-$$

$$(R')_2As-As(R')_2 + RSSR \quad \rightarrow \quad \text{As}^+\text{As}(R')_2$$

$$\delta^+$$

$$(R')_2As-As(CH_3)_2 \quad \rightarrow \quad R-S-As(R')_2$$

However, evidence is not available at present to distinguish between the two possibilities.

For the reaction of tetramethyldiarsine with trifluoromethanesulfenylchloride, a mechanism, involving an electrophilic attack by the sulfenylchloride on to the arsenic resulting in a heterolytic cleavage of the As-As bond to form the observed products, is postulated.

$$\text{CF}_3\text{SCl} + (\text{CH}_3)_2\text{As-As(}\text{CH}_3)_2 \quad \rightarrow \quad \text{As}^+\text{S-Cl}^-$$

$$\quad \rightarrow \quad (\text{CH}_3)_2\text{AsSCF}_3 + (\text{CH}_3)_2\text{AsCl}$$
The reaction of trifluoromethanesulfenylchloride with compounds containing As-S bonds is believed to involve an electrophilic attack, by the sulfur of the trifluoromethanesulfenylchloride on the sulfur of the As-S bond to yield the observed products.

Mechanisms, similar to the above reactions of diarsines, can be suggested to account for the observed products, in the reactions of dimethylarsine with disulfides and sulfenylchlorides.

The reactions of dimethylarsine with compounds containing As-S, and As-N bonds, are postulated to occur by means of a nucleophilic attack by the arsenic atom of the dimethylarsine on the arsenic atom of the As-N, or As-S bond. Thus for the reaction of dimethylarsine with dimethyamino-dimethylarsine, we have

\[
(\text{CH}_3)_2\text{AsH} + (\text{CH}_3)_2\text{N-As(CH}_3\text{)}_2 \rightarrow (\text{CH}_3)_2\text{As-As(CH}_3\text{)}_2 + (\text{CH}_3)_2\text{NH}
\]
CHAPTER II

Derivatives of Fluorinated Cyclobutenes

Introduction

In recent years, the base catalyzed addition of alcohols to fluorinated cyclobutenes and cyclopentenes has been studied by a number of workers (38,39). Mono, di and trisubstituted derivatives have been obtained depending on the reaction conditions, nature of R, and the cycloalkene used, for example:

\[
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \quad \text{ROH} \quad \text{KOH} \\
\end{align*}
\]

Substituted derivatives are also formed as a result of attack at an allylic position (40).

For cyclobutenes which do not contain an activated double bond, attack occurs
exclusively at the allylic positions (41).

The reactions of metal-carbon bonds with fluorinated cycloalkenes have been investigated extensively by a number of workers. Thus Dixon (42) studied the reactions of lithium alkyls and aryls, and Park (43) investigated alkyl and aryl Grignard reagents. Both mono and disubstituted derivatives have been obtained depending on reaction conditions, the nature of R and the cycloalkene used, for example:

\[
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \quad \text{RLi} \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad \rightarrow \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \quad \text{LiF}

R = \text{alkyl}

\[
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \quad \text{ArLi} \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad \rightarrow \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \quad \text{RMgBr}

\[
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \quad \text{ArMgBr} \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad \rightarrow \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + \\
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F} & \quad \text{F} \\
\end{align*}
\quad + 

Ar = \text{Aryl}
For cyclobutenes containing vinyl bromine or iodine, Park (44) observed a "halogen-metal exchange reaction with Grignard reagents" in the following manner.

However, if B = F and A = Br, a competing reaction takes place giving a small yield of ethylsubstituted product.

The addition of amines to fluorinated cycloalkenes has also been the subject of numerous investigations. Thus Pruett and coworkers (11) reacted primary and secondary amines with hexafluorocyclobutene. The structures of the primary amine derivatives of general formula $(RN=)$$_2$C$_4$F$_3$H were not well established due to their instability. With secondary amines however, more stable derivatives were obtained.
Diphenylamine failed to react. Surprisingly, however, triethylamine reacted with hexafluorocyclobutene to produce a white solid of unknown structure.

Parker (45) and Mill et al (46) studied the reactions of cyclopentenes with amines. Thus Parker reacted 1,2-dichlorohexafluorocyclopentene-1 with ammonia, primary and secondary amines. With secondary amines monosubstituted products were obtained.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*}
\]

\[+ R_2NH \rightarrow \text{Cl} \quad \text{Cl} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\]

However, ammonia and primary amines yielded derivatives of 1-amino-2-chloro-3-iminotetrafluorocyclopentene-1.

Mill et al obtained similar results for the reactions of 1-chloro-2-carboxamidohexafluorocyclopentene with ammonia and primary amines. Thus they observed that this molecule underwent selective substitution by one or two molecules of ammonia or aniline, for example:
The base catalyzed addition of thiols to fluorinated cycloalkenes has also been reported by a number of workers. Thus Rapp et al (14) obtained both mono and disubstituted cyclobutene derivatives as well as a disubstituted cyclobutane adduct, which was unstable, and liberated hydrogen fluoride on distillation.

\[
\begin{align*}
\text{F}_2 & \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{RSH} \\
\text{F}
\end{array} \\
\text{Cl} & \quad \begin{array}{c}
\text{F} \\
\text{C}_6\text{H}_5 \\
\text{F}
\end{array}
\end{align*}
\]

\[
\text{RS} + \text{RCF}_2 \rightarrow \text{SR} + \text{RCF}_2
\]

Cuprous mercaptides have also been reacted with cycloalkenes by Ferretti and Tesi (47) to produce disubstituted derivatives.

\[
\begin{align*}
\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2
\end{align*}
\]

The reaction of tetramethyldiarsine with hexafluorocyclobutene has been reported by Cullen and Hota (48) to yield monosubstituted derivatives.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{As-As(CH}_3\text{)}_2 + & \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F}
\end{array} \\
\text{(CH}_3\text{)}_2\text{As} + & \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\end{align*}
\]
The reaction of sodium manganesepentacarbonyl with hexafluorocyclobutene has also been reported by Stone et al (49).

\[
\text{NaMn(CO)}_5^+ + 2F_2 + \text{NaF} \rightarrow \text{(CO)}_5\text{Mn}^+ + \text{F}_2 \text{C}_2\text{H}_5\text{N}_3 + \text{RSH}
\]

To account for the reactions of nucleophilic reagents with fluorinated cycloalkenes, two possible mechanisms have been suggested by a number of workers. These involve addition-elimination or direct substitution. Work by \text{Rapp et al.}(14) employing thiols produced a cyclobutane derivative which eliminates hydrogen fluoride on heating to yield the corresponding cyclobutene derivative.

Thus indicating an addition elimination mechanism for the reaction. Most workers seem to favour this alternative over the other mechanism. However, Park et al (41) have proposed a direct substitution mechanism to account for the attack at the allylic position in the cyclobutenes and cyclopentenes.
Cullen and Styan (50) have also obtained similar adducts of the cyclobutene by using trimethylgermanium hydride and trimethyltin hydride.

\[
\text{(CH}_3\text{)}_3\text{GeH} + \text{C}_{2}\text{H}_5\text{Cl} \rightarrow \text{Ge(CH}_3\text{)}_3 \text{Cl} + \text{(CH}_3\text{)}_3\text{GeCl} + \text{HCl}
\]

\[
\text{(CH}_3\text{)}_3\text{SnH} + \text{F}_2\text{C}_2\text{H}_5 \rightarrow \text{F}_2\text{C}_2\text{H}_5\text{H} + \text{(CH}_3\text{)}_3\text{SnF}
\]

The present investigation was initiated for the purpose of studying the reactivities of alkyl substituted fluorinated cycloalkenes with amines, thiols and arsines, and to examine the chemical and spectral properties of the resulting derivatives. It was also of interest to investigate fairly extensively reactions of the cycloalkenes with diarsines and arsenic hydrides. The results of this investigation are presented in the following experimental and discussion sections.
EXPERIMENTAL

The general experimental technique and apparatus were described in Chapter I, page 7.

I Starting Materials

Hexafluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene, 1,2-dichlorohexafluorocyclopentene and 1,2-dichlorooctafluorocyclohexene were obtained from Peninsular Chemresearch Inc., Gainsville, Florida. Diethylamine, dimethylamine, triethylamine, and methanethiol were obtained from Eastman Organic Chemical Distillation Products Industries, Rochester, New York. They were all used without further purification. The preparation of tetramethyldiarsine and dimethylarsine were described in Chapter I.

b Synthesis of Additional Starting Materials

1. \textbf{1-H-2-chlorotetrafluorocyclobutene}. 1,1-Dihydro-2,2-dichlorotetrafluorocyclobutane was prepared by the thermal dimerization of 1,1-dihydro-2,2-dichloroethylene and tetrafluoroethylene at 150° for 15 hours (51). The butane was then added to a slurry of potassium hydroxide in heavy mineral oil (41). A fraction, b.p. 58-59 (760 mm) (lit. value 52-3°) (634 mm) was identified as 1-hydro-2-chlorotetrafluorocyclobutene, by means of its b.p. and known infrared spectrum (52). The H nmr spectrum showed a multiplet centred at -6.19 ppm.

2. \textbf{1-H-2-chlorohexafluorocyclopentene}. Sodium borohydride was added to 1,2-dichlorohexafluorocyclopentene in diglyme (52). The product, 1-H-2-chlorohexafluorocyclopentene b.p. 79° (760 mm) (lit. value 78-9°) was separated by v.p.c. (silicone column at 110°) and identified by means of its b.p. and known infrared spectrum. The H nmr spectrum showed a multiplet
at -6.21 ppm.

3. 1-Ethyl-2-chlorotetrafluorocyclobutene. 1,2-Dichlorotetrafluorocyclobutene was added to an ethereal solution of ethylmagnesiumbromide (43). A fraction, b.p. 102 (760 mm) (lit. value 98°) (634 mm) was identified as 1-ethyl-2-chlorotetrafluorocyclobutene by means of its b.p.

4. 1-Methoxy-2-chlorotetrafluorocyclobutene. 1,2-Dichlorotetrafluorocyclobutene was added to a solution of potassium hydroxide in methanol (40). A fraction b.p. 117° (760 mm) (lit. value 116° (630 mm)) was identified as 1-methoxy-2-chlorotetrafluorocyclobutene, by means of its b.p.

II. Reactions of the Cyclobutenes, Cyclopentenes and Cyclohexenes

A. Reactions of Hexafluorocyclobutene:

1a. With Dimethylarsine. Dimethylarsine (5.9 g) and hexafluorocyclobutene (11.9 g) were miscible at 20° and were left at this temperature for one week. After 2 days, etching was observed on the sides of the reaction tube, indicating the production of hydrogen fluoride. Hexafluorocyclobutene (8.3 g) was recovered. The least volatile fraction (4.6 g, 94%) which condensed in a trap at -46° was recovered and identified as 1-dimethylarsinopentafluorocyclobutene by means of its b.p. 124° (760) (lit. value 125° (760)) and its known infrared spectrum (48). N.m.r. spectra: the H spectrum showed a single peak at -1.00 ppm. The 19F spectrum showed multiplets at 28.9, 33.7 and 39.4 ppm. of relative area 1:2:2 (a).

lb. Reaction of 1-Dimethylarsinopentafluorocyclobutene and Diethylamine.

The arsine (5.6 g) and diethylamine (10.9 g) reacted vigorously on warming to 20°; the reactants were left for 24 hours at this temperature.
Diethylamine which condensed in a trap at -64° was recovered. The product, a colourless involatile liquid, (4.0 g, 59%) was identified as 1-dimethylarsino-2-diethylaminotetrafluorocyclobutene, b.p. 68° (10⁻² mm.). Anal. Found: C, 39.9; H, 5.22; As, 24.8; F, 25.4; N, 4.70%. Calc. for C₁₀H₁₆AsF₄N: C, 39.8; H, 5.30; As, 24.9; F, 25.3; N, 4.65%. Infrared spectrum (liquid film): 2980S, 2910S, 1637VS, 1465S, 1455S, 1418S, 1383S, 1365S, 1330S, 1297VS, 1270VS, 1262VS, 1220VS, 1200VS, 1165VS, 1153VS, 1100VS, 1055VS, 1030VS, 960S, 935W, 895S, 801S, 830VS, 807S, 792S, 751W, 744VW, 690VW cm⁻¹. The ¹H nmr spectrum showed a quartet centred at -3.15, a triplet at -3.00, and a singlet at -3.05 ppm. The relative area of singlet and triplet to quartet is 12:4 (Calc. 12:4).

2. With Diethylamine. (a) Diethylamine (8.2 g) and hexafluorocyclobutene (5.3 g) reacted vigorously on mixing well below 0°. The reactants were left at 20° for 24 hours. The product, a colourless liquid, recovered from a trap at -23° (6.0 g, 86%) was identified as the known (11) 1-diethylaminopentafluorocyclobutene b.p. 80° (55 mm). Anal. Found: C, 44.0; H, 4.8; N, 6.6%. Calc. for C₈H₁₆F₅N: C, 44.6; H, 4.65; N, 6.5%. Infrared spectrum (liquid film): 3015W, 2950W, 2905W, 1750S, 1485S, 1380S, 1342VS, 1300S, 1258S, 1210VS, 1180S, 1150W, 1070VS, 1035VS, 965VS, 927VS, 850S, 816S, 785W, 657W cm⁻¹. N.m.r. spectra: the ¹H spectrum showed a quartet centred at 3.24 and a triplet centred at -1.18 ppm. of relative area 2:3 $J_{C-H} = 7$ cps). The ¹⁹F nmr showed multiplets at 32.9, 37.4 and 79.5 ppm. of relative area 2:2:1 (Calc. 2:2:1)

(b) Reaction of Diethylaminopentafluorocyclopentene and Tetramethyldiarsine.

The cyclobutene (5.0 g) and the diarsine (3.0 g) were left at 20° for one week. The entire contents of the reaction tube were volatile enough to be
taken into the vacuum system, and could not be separated by trap to trap
distillation. A $^1$H nmr spectrum, showed peaks due only to the starting
materials.

3. **With Dimethylamine.** Dimethylamine (6.2 g) and hexafluorocyclobutene
(4.0 g) reacted vigorously on mixing well below 0°. The reactants were left
at 20° for 24 hours. The product, an involatile liquid, (4.2 g 92%) was
identified as 1-dimethylaminopentafluorocyclobutene, b.p. 88° (117.5 mm).
Anal. Found: C, 38.8; H, 3.34; N, 7.7%. Calc. for C$_6$H$_5$F$_5$N: C, 38.5;
H, 3.2; N, 7.49%. Infrared spectrum (liquid film): 3.33S, 5.64VS, 6.0W,
6.72S, 6.8VS, 7.09VS, 7.43VS, 7.65S, 8.10VS, 8.35S, 8.75W, 9.-VS, 9.35VS,
9.90VS, 10.45VS, 11.55VS, 11.85VS, 13.75WV microns. Nmr spectra: the $^1$H
spectra showed a single peak at -2.9 ppm. The $^{19}$F spectrum showed multiplets
at 33.0, 38.1 and 79.8 ppm. of relative area 2:2:1 (Calc. 2:2:1) (A)

4. **With Methanethiol.** Hexafluorocyclobutene (10.9 g) and methanethiol
(4.3 g) and triethylamine (1.3 g) were heated to 80° for 3 days. A mixture
of hexafluorocyclobutene and methanethiol (5.5 g) was recovered. The mix­
ture passed through a trap at -78° and could not be separated by trap to
trap distillation. A fraction (2.0 g) was recovered from a trap at -64°
and identified as 1-methylthiopentafluorocyclobutene, b.p. 104° (760 mm).
Anal. Found: C, 31.6; H, 1.58; F, 50.0; S, 16.8%. Calc. for C$_5$H$_3$F$_5$S:
C, 31.4; H, 1.74; F, 49.9; S, 16.8%. Infrared spectrum (liquid phase):
2930W, 1670VS, 1435VS, 1375VS, 1325VS, 1286VS, 1217VS, 1190W, 1122VS, 990S,
948VS, 855VS, 809W, 700W, 651W cm$^{-1}$. Nmr spectra: the $^{19}$F spectrum showed
multiplets at 37.4, 39.0 and 45.2 ppm. of relative area 2:2:1 (Calc. 2:2:1). An
involatile fraction (3.0 g) which remained in the tube was identified as
1,2-methylthiotetrafluorocyclobutene, b.p. 85° (14 mm). Anal. Found: C, 33.1;
H, 2.72; F, 35.0; S, 29.2%. Calc. for C_{6}H_{6}F_{8}S_{2}: C, 32.9; H, 2.74; F, 34.7; S, 29.4%. Infrared spectrum (liquid film): 2983, 1550, 1435, 1326, 1300, 1240, 1158, 1095, 979, 961, 852, 845, 755, 700 cm^{-1}. The mixture of methanethiol and hexafluorocyclobutene (5.5 g) was reacted with excess diethylamine (8.0 g). Methanethiol (1.9 g) which had passed through a trap at -78° was recovered. Thus 2.4 g of methanethiol were consumed in the original reaction.

B. Reactions of 1,2-Dichlorotetrafluorocyclobutene:

1. With Tetramethyldiarsine. Excess 1,2-dichlorotetrafluorocyclobutene (10.1 g) and the diarsine (4.0 g) were miscible at 20° and were left at this temperature (21 days). A fraction (7.9 g) recovered from a trap at -64° was distilled at atmospheric pressure and separated into 1,2-dichlorotetrafluorocyclobutene b.p. 66-7° (4.4 g) and chlorodimethylarsine b.p. 107-8° (2.8 g), both compounds being of known infrared spectra. The product, an involatile liquid, (4.5 g, 81.5%) distilled at 154° (760 mm) and was identified as 1-dimethylarsino-2-chlorotetrafluorocyclobutene. Anal. Found: C, 27.5; H, 2.32; As, 28.3; Cl, 13.3; F, 28.7%. Calc. for C_{6}H_{6}AsClF_{4}

C, 27.2; H, 2.26; As, 28.2; Cl, 13.4; F, 28.7%. Infrared spectrum (liquid film): 3025, 2940, 1576, 1426, 1328, 1270, 1245, 1176, 1115, 902, 860, 810, 725 cm^{-1}. Nmr. spectra: the ^{1}H spectrum showed a single peak at -1.17 ppm. The ^{19}F spectrum showed multiplets at 31.7 and 37.4 ppm. of relative area 1:1 (Calc. 1:1)^{A}.

2. With Methylphenylarsine. Excess 1,2-dichlorotetrafluorocyclobutene (5.9 g) and methylphenylarsine (2.2 g) were heated to 130° (3 days). 1,2-dichlorotetrafluorocyclobutene (3.4 g) was recovered. The product,
involatile liquid (3.8 g, 86%), was identified as 1-methylphenylarsino-2-chlorotetrafluorocyclobutene, b.p. 133° (21 mm). Anal. Found: C, 40.5;
H, 2.5; As, 23.1, Cl, 11.0; F, 23.3%. Calc. for C₁₁H₈AsClF₄: C, 40.4,
H, 22.2; As, 22.9; Cl, 10.9; F, 23.2%. Infrared spectrum (liquid film):
3095W, 3050W, 2935VW, 1575VS, 1489S, 1443S, 1423VW, 1326VS, 1246VS, 1187VW,
1123VS, 1080S, 1025S, 1002S, 855VS, 810S, 738VS, 726W, 694VS, 668W cm⁻¹.
Nmr. spectra: the ¹H spectrum showed a multiplet at -7.00 and a singlet at
-1.15 ppm. of relative area 5.25:3.1 (Calc. 5.0:3.0). The ¹⁹F spectrum
showed multiplets at 31.2 and 37.2 ppm. of relative 1:1 (Calc. 1:1). The
¹H spectrum also showed an impurity peak at -1.32 ppm. (10-15%) which was
supposed to be due to chloromethylphenylarsine. On addition of an authentic
sample of chloromethylphenylarsine, peak enhancement at -1.32 ppm. was
observed.

3 With Diethylamine. (a) The cyclobutene (8.3 g) and excess amine
(10.0 g) were left at 20° (3 days). The volatiles were taken into the
tube system. The product, an involatile liquid, (9.2 g, 90%) was identified
as 1-chloro-2-diethylaminotetrafluorocyclobutene, b.p. 112° (46 mm). Anal.
Found: C, 41.4; H, 4.54; Calc. for C₈H₁₀ClF₄N: C, 41.5; H, 4.33%.
Infrared spectrum (liquid film): 3020VW, 2980W, 2910VW, 1696VS, 1473S,
1458S, 1415VS, 1388S, 1333VS, 1305VS, 1287VS, 1245S, 1204VS, 1163S, 1149S,
1117S, 1080VS, 1034VS, 965S, 938W, 855VS, 838S, 803S, 677VW cm⁻¹. The ¹⁹F
nmr. spectrum showed multiplets at 110.7 and 114.4 ppm. of relative area
1:1 (Calc. 1:1).

(b) Reaction of 1-chloro-2-diethylaminotetrafluorocyclobutene and
Dimethylarsine. The cyclobutene (3.5 g) and dimethylarsine (5.5 g)
were heated at 100° (3 days). The volatile contents of the tube were
pumped into the vacuum system. Dimethylarsine (1.0 g) was recovered. A charred solid remained behind, and no isolable products were obtained.

4 With Methanethiol. 1,2-Dichlorotetrafluorocyclobutene (12.0 g) and methanethiol (3.7 g) and triethylamine (0.2 g) were heated at 100° (8 days). The entire contents of the reaction tube were taken into the vacuum system. Methanethiol (2.2 g) and 1,2-dichlorotetrafluorocyclobutene (6.0 g) were recovered. The least volatile liquid, (5.5 g, 85%, based on cyclobutene used) condensed in a trap at -46° and was identified as 1-chloro-2-methylthio-
tetrafluorocyclobutene, b.p. 134.5° (760 mm). Anal. Found: C, 29.0; H, 1.63; Cl, 17.0; F, 36.6; S, 15.5%. Calc. for C₅H₃ClF₄S: C, 29.6; H, 1.45; Cl, 17.0; F, 36.9; S, 15.5%. Infrared spectrum (liquid film): 2930νW, 2850νW, 1587νS, 1437νS, 1335νS, 1316νS, 1254νS, 1115νS, 961νW, 855νS, 758νW cm⁻¹. Nmr. spectra: the ¹H spectrum showed a single peak at -2.43 ppm. The ¹F spectrum showed multiplets at 112.5 and 115.2 ppm. of relative area 1:1 (Calc. 1:1).

C Reactions of 1,2-Dichlorohexafluorocyclopentene

1. With Tetramethyldiarsine. (a) The diarsine (5.0 g) and the cyclo-
pentene (8.6 g) were left at 20° (21 days). A fraction (7.1 g) which condensed in a trap at -46° was recovered. This material which distilled at 89-93°, was identified as 1,2-dichlorohexafluorocyclopentene, and a fraction (2.9 g) which distilled at 107-109°, identified as chlorodimethylarsine. The product, an involatile liquid (4.7 g, 64%) was identified as 1-chloro-
2-dimethylarsinohexafluorocyclopentene b.p. 108° (103 mm). Anal. Found:
C, 26.9; H, 2.01; As, 23.8; Cl, 11.4; F, 36.2%. Calc. for C₇H₆AsClF₆:
C, 26.8; H, 1.92; As, 23.8; Cl, 11.3; F, 36.2%. Infrared spectrum (liquid film): 3020νW, 2930νW, 1590νW, 1426S, 1332νS, 1282νS, 1262S, 1233νS, 1200νS,
$^{1}$H spectrum showed a single peak at -1.25 ppm. The $^{19}$F spectrum showed multiplets at 29.9, 40.8 and 67.6 ppm. of relative area 1:1:1 (Calc. 1:1:1). 

(b) Reaction of 1-Chloro-2-Dimethylarsino-hexafluorocyclopentene with Diethylamine. The arsine (6.0 g) and excess diethylamine (10.0 g) were heated at 100° (3 days). The volatile contents of the tube were taken into the vacuum system. The involatile liquid product which remained in the tube distilled at 80-100° (10^{-3} \text{ cm}). The infrared spectrum indicated it to be a mixture of 1-chloro-2-dimethylarsino-hexafluorocyclopentene and 1-diethylamino-2-dimethylarsino-hexafluorocyclopentene. Infrared spectrum (liquid film): 2930W, 1630S, 1593S, 1427Sh, 1422S, 1385W, 1330S, 1278VS, 1232VS, 1193S, 1145VS, 1117Sh, 1094S, 1063SH, 998VS, 965W, 899W, 873VS, 798W cm^{-1}.

2. With Diethylamine. (a) Diethylamine (6.0 g) and 1,2-dichloro-hexafluorocyclopentene (10.0 g) were left at 20° (48 hours). 1,2-Dichloro-hexafluorocyclopentene (3.0 g) was recovered from a trap at -46°. A fraction (6.1 g, 86%) which condensed in a trap at -23° was recovered, and identified as 1-chloro-2-diethylaminohexafluorocyclopentene b.p. -104° (28 mm). Anal. Found: C, 38.4; H, 3.56; N, 4.70%. Calc. for C_{9}H_{10}ClF_{6}N: C, 38.3; H, 3.55; N, 4.98%. Infrared spectrum (liquid film): 2990S, 2935W, 1632VS, 1475S, 1455S, 1428S, 1387S, 1369S, 1335S, 1317S, 1298S, 1268VS, 1208VS, 1120VS, 1182VS, 1120VS, 1062VS, 995VS, 868VS, 834S, 808S, 785W, 685W cm^{-1}.

(b) Reaction of 1-chloro-2-diethylaminohexafluorocyclopentene (6.1 g) and dimethylarsine (6.1 g) were left at 20° (1 week). The volatile contents of the tube were pumped into the vacuum system. An infrared spectrum of the involatile material indicated incomplete reaction. The entire mixture was
then heated to 80° (34 hours). Dimethylarsine (3.0 g) was recovered from a trap at -78°. The product, an involatile liquid (4.0 g, 65%) distilled at 80-85° (10⁻³ cm) (∼1.3 g). The infrared spectrum of this indicated that although it contained 1-chloro-2-diethylaminotetrafluorocyclobutene, the other product was not the same as the product in 1b. Infrared spectrum (liquid film): 2970W, 2919W, 1630S, 1586S, 1468W, 1453S, 1415S, 1382S, 1363W, 1346W, 1306S, 1282W, 1236S, 1164S, 1085S, 1015S, 987W, 875S, 860S, 842W, 828W, 798S, 745 W cm⁻¹.

D. Reactions of 1-Hydro-2-chlorotetrafluorocyclobutene.

1. With Dimethylarsine. Dimethylarsine (9.2 g) and 1-hydro-2-chlorotetrafluorocyclobutene (8.1 g) were heated at 150° (3 days). A fraction (3.0 g) was recovered from a trap at -46°, and was separated into two components by vpc (Silicone column at 125°). The first peak (50% by wt) was identified as chlorodimethylarsine of known infrared spectrum, the second peak was identified as 1-H-2-dimethylarsinotetrafluorocyclobutene b.p. 153° (760 mm). Anal. Found: C, 31.3; H, 3.03; As, 32.4; F, 33.2%. Calc. for C₆H₇AsF₄: C, 31.3; H, 3.04; As, 32.6; F, 33.3%. Infrared spectrum (liquid film): 3025W, 2940W, 1548W, 1425S, 1385VW, 1328VS, 1263VS, 1158VS, 1100VS, 897S, 848S, 803S, 738S cm⁻¹. Nmr. spectra: the ¹H spectrum showed a triplet of multiplets (JₕF = 10 cps) at -6.68 and a singlet at -1.03 ppm. of relative area 0.95:6 (Calc. 1:6). The ¹⁹F spectrum showed multiplets at 108.3 and 109.4 ppm. of relative area 1:1 (Calc. 1:1). An examination of the more volatile fractions showed that the reaction was not complete.

2. With Diethylamine. 1-Hydro-2-chlorotetrafluorocyclobutene (2.30 g) and diethylamine (2.6 g)
reacted vigorously on mixing well below 20° and were left at 20° for 24 hours. A fraction (1.4 g, 50%) was recovered from a trap at -23° and identified as 1-hydro-2-diethylaminotetrafluorocyclobutene b.p. 112° (59 mm).

Anal. Found: C, 47.3; H, 5.67; N, 7.69%. Calc. for C₉H₁₁F₄N\( \text{C}, 48.7; \text{H}, 5.58; \text{N}, 7.10\% \). Infrared spectrum (liquid film): 3010W, 2900W, 1668VS, 1628S, 1472S, 1458S, 1418VW, 1390S, 1322VS, 1294VS, 1248VS, 1205VS, 1178VS, 1138VS, 1102VS, 1058VS, 1027VS, 958VS, 827VS, 755S, 745VS, 674VW cm\(^{-1}\). The \(^1\)H nmr spectrum showed a triplet centred at -0.8, a quartet at -2.9 and a triplet of triplets at -4.55 ppm. (\(J_{HF} = 11\) cps) of relative area 6:4:1 (Calc. 6:4:1).

3. With Methanethiol. Methanethiol (5.6 g) and the cyclobutene (3.0 g) and a catalytic quantity of triethylamine were heated at 150° (6 days). A fraction (2.5 g) recovered from a trap at -46° was separated into two components by vpc (silicone column at 110°). The first component (66% by weight) was identified as dimethyl disulfide of known infrared spectrum, and the second (30% by weight) was identified as 1-chloro-1,2-dihydro-2-methylthiotetrafluorocyclobutane b.p. 138-39° (760). Anal. Found: C, 29.2; H, 2.48; Cl, 17.1; F, 27.9; S, 15.7%. Calc. for C₅H₅CIF₄S: C, 28.8; H, 2.40; Cl, 16.8; F, 36.5; S, 15.4%. Infrared spectrum (liquid film): 2960W, 1440S, 1368VS, 1332VW, 1284VS, 1185VS, 1130VW, 1111VS, 1090VS, 1017VS, 990W, 945VS, 846VS, 814VS, 772S, 718VW, 705W cm\(^{-1}\). Nmr. spectra: the \(^1\)H spectrum showed a singlet at -2.15, and multiplets at 3.53 and -4.10 ppm. of relative area 3:0.95:1 (Calc. 3:1:1). The \(^19\)F spectrum showed multiplets at 107.0 and 126.7 ppm. of relative area 1:1 (Calc. 1:1).\(^B\)

Examination of the more volatile fractions, showed that the reaction was incomplete.
E Reactions of 1-Hydro-2-chlorohexafluorocyclopentene

1. With Dimethylarsine. Dimethylarsine (3.7 g) and 1-hydro-2-chlorohexafluorocyclopentene (2.6 g) were heated at 100° (9 days). A fraction (3.0 g) was found to contain only two components by v.p.c. (dinonylphthalate column at 165°). The first component (45% by wt.) was identified as chloro-dimethylarsine of known infrared spectrum and the second (55% by wt.) was identified as 1-hydro-2-dimethylarsino-hexafluorocyclopentene b.p. 95° (100 mm). Anal. Found: C, 30.1, H, 2.63; As, 26.6; F, 40.7%. Calc. for C₇H₇AsF₆: C, 30.0, H, 2.50; As, 26.8; F, 40.7%. Infrared spectrum (liquid film): 3010W, 2940VW, 1600S, 1428S, 1348VS, 1302VS, 1258VS, 1193VS, 1158VS, 1132VS, 1077VS, 978VS, 900S, 872W, 852S, 806S, 714S, 635W cm⁻¹. Nmr. spectrum: the ¹H spectrum showed a singlet at -1.05 and a multiplet at -6.28 of relative area 6:1 (Calc. 6:1). The more volatile fraction which passed through a trap at -64° was mainly dimethylarsine and a small quantity of fluorocarbon.

2. With Diethylamine. Diethylamine (3.2 g) and the cyclopentene (2.6 g) were left at 20° (18 hours). The volatile contents of the tube were taken into the vacuum system. The product, an involatile liquid (2.6 g, 83%), was identified as 1-hydro-2-diethylaminohexafluorocyclopentene b.p. 108-109° (35 mm). Anal. Found: C, 43.3; H, 4.77; N, 5.81%. Calc. for C₉H₁₁F₆N: C, 43.7; H, 4.45; N, 5.66%. Infrared spectrum (liquid film): 2975W, 2880W, 1698W, 1630VS, 1472VW, 1455W, 1385Sh, 1362VS, 1310W, 1294W, 1267S, 1232W, 1208S, 1195S, 1185Sh, 1156VS, 1120VS, 1070S, 1045S, 1010S, 995VS, 852S, 826VW, 810VW, 767VW, cm⁻¹. The ¹H Nmr. spectrum showed a triplet at -0.85, a quartet at -3.0 and a multiplet at -4.4 ppm. of relative area 6:4:1 (Calc. 6:4:1).
3. With Methanethiol. Methanethiol (4.6 g) and the cyclopentene (3.2 g) and triethylamine (1.1 g) were heated at 140° (10 days). A fraction (3.0 g) recovered from a trap at -46° was purified by v.p.c. (dinonylphthalate column at 135°) and identified as 1-chloro-5-hydro-5-methylthiopentafluorocyclopentene b.p. 155° (760). Anal. Found: C, 30.2; H, 1.52; Cl, 14.1; F, 39.7; S, 13.3%. Calc. for C₆H₄ClF₅S: C, 31.2; H, 1.68; Cl, 14.7; F, 39.9; S, 13.5%. Infrared spectrum (liquid film): 2940W, 1692VS, 1443Sh, 1435S, 1368VS, 1308VS, 1258W, 1243W, 1210S, 1130VS, 1096VS, 1045VS, 1018VS, 973S, 855VS, 810VS, 730S, 708W, 684W cm⁻¹. The ¹H nmr. spectrum showed a singlet at -2.02 and a multiplet at -3.91 ppm. of relative area 3:1 (Calc. 3:1).

F. Reactions of 1-Ethyl-2-Chlorotetrafluorocyclobutene

1. With Dimethylarsine. Dimethylarsine (4.6 g) and the cyclobutene (5.6 g) were heated at 140° (8 days). 1-Ethyl-2-chlorotetrafluorocyclobutene (1.5 g) which passed through a trap at -46° was recovered. A fraction (5.0 g, 83%) recovered from a trap at -46° was identified as 1-ethyl-2-dimethylarsinotetrafluorocyclobutene b.p. 102° (59 mm). Anal. Found: C, 37.2; H, 4.32; As, 29.0; F, 29.6%. Calc. for C₈H₁₁AsF₄: C, 37.2; H, 4.26; As, 29.1; F, 29.5%. Infrared spectrum (liquid film): 3015W, 2945W, 1612W, 1467W, 1426W, 1387Sh, 1345VS, 1325VS, 1288VS, 1268S, 1250S, 1185VS, 1158VS, 1098VS, 990W, 899S, 880S, 863S, 848W, 809S cm⁻¹. The ¹H nmr. spectrum showed an unresolved quartet at -2.2 and a singlet superimposed on a triplet at -1.07 ppm. of relative area, quartet to rest, 2:9 (Calc. 2:9).

2. With Diethylamine. Diethylamine (4.7 g) and the cyclobutene (6.2 g) were left at 20° (24 hours). The cyclobutene (1.0 g) was recovered from a trap at -64°. The product (6.0 g), recovered from a trap at -46° was
distilled at reduced pressure and a fraction (4.0 g) which distilled at 100° (45 mm) was obtained. Although this fraction seemed to consist of only one compound (single peak on a number of v.p.c. columns), the infrared and nmr. spectra could not be reconciled with any likely reaction product. Infrared spectrum (liquid film): 3000W, 2920W, 1651VW, 1626VW, 1475VW, 1460W, 1390S, 1340VS, 1280VS, 1210S, 1175S, 1140Sh, 1104VS, 1035W, 997VW, 935VW, 922VW, 870S, 860S, 796W, 755W, 742W, 720W cm⁻¹. The ¹H nmr. spectrum showed a triplet centred at -6.25, each component of the triplet split into an approximate quartet, a broad absorption at -3.45, a quartet centred at -2.20, a triplet at -0.85 superimposed on another triplet at -0.75 ppm. of relative area 2.5:2.5:9:21.

3. With Dimethylamine. Dimethylamine (7.7 g) and the cyclobutene (6.4 g) reacted vigorously on mixing and were left at 20° (36 hours). Dimethylamine (3.6 g) was recovered from a trap at -95°. The product, recovered from a trap at -46° was distilled under reduced pressure and a fraction (5.0 g) which distilled at 110-12° (57 mm) was obtained. This was not identified for analogous reasons to 2.

4. With Methanethiol. Methanethiol (4.5 g), the cyclobutene (5.8 g) and triethylamine (0.2 g) were heated at 140° (1 week). The cyclobutene, (4.0 g) which passed through a trap at -46° was recovered. The product, (1.2 g, 70% on cyclobutene consumed) was recovered from a trap at -46° and purified by v.p.c. (PFAFF column at 130°) and identified as 1-ethyl-2-methylthiotetrafluorocyclobutene b.p. 158° (760 mm). Anal. Found: C, 42.1; H, 4.15; F, 38.0; S, 15.9%. Calc. for C₇H₈F₄S: C, 42.0; H, 4.01; F, 38.0; S, 16.0%. Infrared spectrum (liquid film): 3020W, 2980W, 1622W,
1470S, 1444S, 1389Sh, 1325VS, 1255VS, 1199VS, 1147VS, 1095VS, 998S, 964W
882VS, 850VS, 700VW, 635VW, cm⁻¹. The ¹H nmr. spectrum showed a singlet at
-2.20, a quartet at -2.0 and a triplet at -0.9 p.p.m. of relative area
3:2:3 (Calc. 3:2:3).

G. Reactions of 1-chloro-2-methoxytetrafluorocyclobutene
1. With Tetramethyldiarsine. The cyclobutene (8.2 g) and tetramethyl
diarsine (4.8 g) were heated at 110° (7 days). A black charred solid was
obtained. The solid was insoluble in common organic solvents and sublimed
at 120-35° with partial decomposition. The sublimate, m.p. 118°-23°
dissolved readily in water. Infrared spectrum (KBr Pellet): 2970VS, 2390VW,
1650W, 1410W, 1280W, 1160W, 1120VW, 1018VW, 925S, 910Sh, 850W, 765S, 735VS
cm⁻¹. The ¹H spectrum showed two peaks of equal intensity at -2.35 and
-2.25 p.p.m.

No starting materials were recovered, and no evidence was obtained
for the production of chlorodimethylarsine.

2. With Dimethylarsine. 1-Methoxy-2-chlorotetrafluorocyclobutene (6.4 g)
and dimethylarsine (3.6 g) were heated at 130° (7 days). Considerable
charring occurred. A fraction (4.7 g) which condensed in a trap at -46°
was found to be a mixture of chlorodimethylarsine (2.4 g) and 1-methoxy-2-
chlorotetrafluorocyclobutene (2.3 g) by an examination of its ¹H nmr. spectrum
A fraction (~0.1 g) which passed through a trap at -64° showed in its ¹H
nmr. spectrum a triplet centred at -5.86 p.p.m. An involatile yellow liquid
(~0.4 g) showed two peaks of relative area 1:1 at -1.18 and -1.23 p.p.m. in
its ¹H nmr. spectrum. Infrared spectrum (liquid film): 3.29S, 3.38S, 5.55VS,
6.08VW, 6.18VW, 6.65W, 6.72VS, 7.02VS, 7.68VS, 8.03VS, 8.31S, 8.62BS, 8.9VS,
9.30VS, 11.02VS, 11.50VS, 12.1S, 12.31S, 12.8VS, 13.2VS, 13.68S, 14.45S μ.
3. With Methylphenylarsine. The cyclobutene (5.4 g) and methylphenylarsine (5.0 g) were heated at 130° (7 days). Considerable charring occurred. An involatile liquid (2.0 g) was identified as chloromethylphenylarsine, b.p. 106° (10 mm) by means of its known infrared spectrum. No identifiable product was obtained from the charred solid and there was no evidence of a reduction product of the 1-methoxy-2-chlorotetrafluorocyclobutene in the small volatile fraction.

4. With Diethylamine. The cyclobutene (6.0 g) and diethylamine (2.4 g) reacted vigorously on mixing well below 20° and were left at 20° for 20 hours. The volatile contents of the reaction tube were taken into the vacuum system and unreacted cyclobutene (2.2 g) was recovered from a trap at -64°. The product, an involatile liquid was distilled under reduced pressure and a fraction (2.7 g, 59%) which distilled at 112° (10⁻³ cm) was identified as 1-chloro-2-diethylamino-3,3-difluoro-4-cyclobutenone. Anal. Found: C, 46.6; H, 4.96; F, 18.9; N, 6.39%. Calc. for C₆H₁₀ClF₂NO: C, 47.6; H, 5.7; F, 20.5; N, 6.16%. Infrared spectrum (liquid film): 3.35S, 5.5VS, 6.1VS, 6.85S, 7.21S, 7.39S, 7.45W, 7.55S, 7.81VS, 8.05VS, 8.39VS, 8.79S, 9.11Sh; 9.35VS, 10.11W, 10.61W, 11.70S, 12.01VS, 12.40S, 12.75S, 13.45S μ. The ¹H nmr. spectrum showed a triplet at -1.09 and a quartet at 3.32 p.p.m. of relative area 3:2 (Calc. 3:2).

5. With Methanethiol. The cyclobutene (5.3 g) and methanethiol (4.7 g) were heated at 130° (7 days). An oily yellow liquid and a white solid were obtained. The liquid was distilled at reduced pressure and a fraction, (1.5 g, 30%) which distilled at 107° (10 mm) was identified as 1-chloro-2-methylthio-3,3-difluoro-4-cyclobutenone. Anal. Found: C, 32.7; H, 1.80; Cl, 19.3; F, 20.5 S, 17.3%. Calc. for C₅H₃ClF₂OS: C, 32.4; H, 1.68; Cl, 19.2;
A second fraction (1.1 g) distilled at 146-50° (10 mm). An infrared spectrum of this fraction showed it to be a mixture of 1-chloro-2-methylthio-3,3-difluoro-4-cyclobutenone and another compound, probably the disubstituted analog. Attempts to separate this fraction by v.p.c. (Ucon Polar Column at 200°) were unsuccessful. Decomposition was observed at this temperature and at lower column temperatures, the compound failed to come off the column.

An unsuccessful attempt was made to purify the solid product by sublimation. On heating, the solid charred extensively, a small quantity of sublimate was obtained, but it was contaminated by a yellow liquid which distilled on to the cold finger. Attempts to purify the solid by fractional recrystallization were also unsuccessful, because of the difficulty of dissolving the sample. The infrared spectrum indicated the absence of C-F groups. (KBr pellet): 3010VW, 1445W, 1438W, 1065VW, 1044W, 941W, 735VS cm⁻¹.

b. Reaction of 1-chloro-2-methylthio-3,3-difluoro-4-cyclobutenone with Methanethiol. The ketone (1.5 g) and methanethiol (5.9 g) were heated at 110° (16 days). Methanethiol (5.4 g) was recovered, a viscous oily liquid (∼0.75 g) and a charred solid were obtained. Attempts to distill this liquid under reduced pressure were unsuccessful, decomposition occurred on heating and a charred solid was obtained.

6. With Tri(n-butyl)silane. The cyclobutene (6.0 g) and tri(n-butyl) silane (4.0 g) were heated at 230° (24 hours). Some charring was observed. The cyclobutene (5.7 g) was recovered from the vacuum system, tri(n-butyl)silane (3.3 g) was recovered from the reaction tube. Infrared analysis of
the silane fraction did not show any peaks, indicative of a reaction product.

H. Reaction of 1,2-Dichloroperfluorocyclohexene and Diethylamine

Diethylamine (8.3 g) and 1,2-dichloroperfluorocyclohexene (12.7 g) were left at 20° for one month. Diethylamine (6.2 g) and 1,2-dichloroperfluorocyclohexene (5.0 g) were recovered. The product condensed in a trap at -23° and was distilled under reduced pressure to yield 1-diethylamino-2-chloroperfluorocyclohexene b.p. 64-66° (9 mm) (6.8 g). Anal.

Found: C, 36.3; H, 3.16; H, 4.41%.  Calc. for C<sub>10</sub>H<sub>10</sub>ClF<sub>8</sub>N: C, 36.2; H, 3.01; N, 4.23%. Infrared spectrum (liquid film): 2980VS, 2930Sh, 2870Sh, 1595VS, 1453S, 1415S, 1363VW, 1339VS, 1302VS, 1280S, 1236VS, 1183VS, 1100VS, 1022VS, 996VS, 960VS, 935VW, 858VS, 803VW, 890VW, 660S, 638 cm<sup>-1</sup>.
DISCUSSION

A. Reactions of Arsines with Fluorinated Cycloalkenes

Table I is a summary of the results of a number of experiments which can be represented by the following general equation.

\[ \text{R(CH}_3\text{)AsH + } \text{F}_2 \rightarrow \text{R(CH}_3\text{)As} + \text{HX} \]

**TABLE I**

Data for Reactions of Arsines with Fluorocarbon Cyclobutenes

<table>
<thead>
<tr>
<th>Reactants</th>
<th>*RX.T.</th>
<th>*RX.Time</th>
<th>B.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = CH(_3), X = Cl, Y = CH(_2)H(_5)</td>
<td>140</td>
<td>8</td>
<td>102 (59)</td>
</tr>
<tr>
<td>R = CH(_3), X = Cl, Y = C(_2)H(_5)</td>
<td>130</td>
<td>3</td>
<td>133 (21)</td>
</tr>
<tr>
<td>R = CH(_3), X = Y = F</td>
<td>20</td>
<td>7</td>
<td>94</td>
</tr>
</tbody>
</table>

*RX = Reaction

Chlorodimethylarsine (45%) is also produced in the reaction of dimethylarsine with 1-H-2-chlorotetrafluorocyclobutene.

\[ \text{(CH}_3\text{)}_2\text{AsH + Cl} \rightarrow \text{F}_2 \rightarrow \text{(CH}_3\text{)}_2\text{AsH} + \text{HCl} + \text{(CH}_3\text{)}_2\text{AsCl} \]

However, attempts to isolate the reduction product 1,2-dihydrotetrafluoro-
were unsuccessful. Reduction is also observed in the reaction of methylphenylarsine with 1,2-dichlorotetrafluorocyclobutene. Chloromethylphenylarsine (~ 15%) is obtained in addition to the main product, 1-methylphenylarsino-2-chlorotetrafluorocyclobutene. Here again, attempts to isolate the reduction product of the 1,2-dichlorocyclobutene were unsuccessful.

\[
\text{(CH}_3\text{)}\text{(C}_6\text{H}_5\text{)}\text{AsH} \cdot + \cdot \cdot\text{C}_1\text{Cl} \rightarrow \text{(CH}_3\text{)}\text{As(C}_6\text{H}_5\text{)}\text{Cl} + \text{HCl} + \text{(CH}_3\text{)}\text{(C}_6\text{H}_5\text{)}\text{AsCl}
\]

Dimethylarsine also reacts with 1-H-2-chlorohexafluorocyclopentene at 100° (9 days) and yields 1-H-2-dimethylarsinohexafluorocyclopentene b.p. 95° (100 mm) in 55% yield. In addition, chlorodimethylarsine (~ 45%) is produced as a result of the reduction of the 1-H-2-chlorohexafluorocyclopentene. However, the expected, 1,2-dihydroperfluorocyclopentene was not isolated.

\[
\text{(CH}_3\text{)}_2\text{AsH} + \text{(CH}_3\text{)}_2\text{AsCl} \rightarrow \text{HCl} + \text{HCl} + \text{(CH}_3\text{)}_2\text{AsCl}
\]

Reaction of dimethylarsine with 1-chloro-2-methoxytetrafluorocyclobutene at 130° (7 days) yields a mixture of chlorodimethylarsine and the starting cyclobutene. In addition, there is also produced a small quantity of an involatile liquid whose infrared and \text{^1H} nmr. spectra indicate that it is the cyclic ketone 1-chloro-2-dimethylarsino-3,3-difluoro-4-cyclobutenone. This compound is similar to the ketones produced by the reaction of diethylamine and methane thiol with 1-chloro-2-methoxytetrafluorocyclobutene.
Styan has found (53, 54) that methylphenylarsine reacts with perfluorocyclobutene to yield 1-methylphenylarsinopentafluorocyclobutene.

Similarly dimethylarsine has also been found to react with 1,2-dichlorotetra-fluorocyclobutene and 1,2-dichlorohexafluorocyclopentene to yield 1-dimethylarsino-2-chlorotetrafluorocyclobutene and 1-dimethylarsino-2-chlorohexafluorocyclopentene respectively (53, 54).

From the results obtained in all the above experiments, it appears that the reaction of arsines with fluorinated cycloalkenes, yields mono-substituted products under mild conditions. The reaction also proceeds to completion regardless of the nature of (R, X, and Y, see Table I) and the ring size. The yields obtained are in general excellent, and in some cases quantitative.
B. Reactions of Diarsines with Fluorinated Cycloalkenes

Diarsines also react with cyclobutenes and cyclopentenes to yield the same products as the arsines. Thus tetramethyldiarsine reacts with 1,2-dichlorotetrafluorocyclobutene at 20° (21 days) affording 1-dimethylarsino-2-chlorotetrafluorocyclobutene b.p. 156° (760 mm) in 82% yield.

\[
\text{F}_2\text{Cl} + (\text{CH}_3)_2\text{As-As}(\text{CH}_3)_2 \rightarrow \text{F}_2\text{Cl} + (\text{CH}_3)_2\text{AsCl} 
\]

The same diarsine also reacts with 1,2-dichlorohexafluorocyclopentene at 20° (21 days) and yields 1-dimethylarsino-2-chlorohexafluorocyclopentene b.p. 108° (103 mm), in 64% yield.

\[
\text{F}_2\text{Cl} + (\text{CH}_3)_2\text{As-As}(\text{CH}_3)_2 \rightarrow \text{F}_2\text{Cl} + (\text{CH}_3)_2\text{AsCl} 
\]

Cullen and Hota (48) had discovered previously that tetramethyldiarsine reacts with hexafluorocyclobutene to yield 1-dimethylarsinopentafluorocyclobutene.

\[
\text{F}_2\text{Cl} + (\text{CH}_3)_2\text{As-As}(\text{CH}_3)_2 \rightarrow \text{F}_2\text{Cl} + (\text{CH}_3)_2\text{AsF} 
\]

C. Reactions of Amines with Fluorinated Cycloalkenes

Amines react with fluorinated cycloalkenes in an analogous manner to arsines affording monosubstituted derivatives. Table II, summarizes the results of a number of experiments which can be represented by the following
general equation.

\[ R_2NH + \left(\text{CF}_2\right)_n C = C \xrightarrow{Y} \xrightarrow{HX} R_2N (\text{CF}_2)_n C = C Y \]

### TABLE II

Data for Reactions of Amines with Fluorinated Cycloalkenes

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Ring Size n</th>
<th>Product</th>
<th>*RX. T. (^\circ\text{C})</th>
<th>*RX. Time (hours)</th>
<th>Yield (%)</th>
<th>B.P. (\text{mm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R = \text{C}_2\text{H}_5) (X = Y = \text{F})</td>
<td>2</td>
<td>(Y = \text{F})</td>
<td>20</td>
<td>24</td>
<td>86</td>
<td>80 (55)</td>
</tr>
<tr>
<td>(R = \text{CH}_3) (X = Y = \text{F})</td>
<td>2</td>
<td>(Y = \text{F})</td>
<td>20</td>
<td>24</td>
<td>92</td>
<td>88 (117)</td>
</tr>
<tr>
<td>(R = \text{C}_2\text{H}_5) (X = Y = \text{Cl})</td>
<td>2</td>
<td>(Y = \text{Cl})</td>
<td>20</td>
<td>72</td>
<td>90</td>
<td>112 (46)</td>
</tr>
<tr>
<td>(R = \text{C}_2\text{H}_5) (X = \text{Cl}, Y = \text{H})</td>
<td>2</td>
<td>(Y = \text{H})</td>
<td>20</td>
<td>24</td>
<td>50</td>
<td>112 (59)</td>
</tr>
<tr>
<td>(R = \text{C}_2\text{H}_5) (X = Y = \text{Cl})</td>
<td>3</td>
<td>(Y = \text{Cl})</td>
<td>20</td>
<td>48</td>
<td>86</td>
<td>104 (28)</td>
</tr>
<tr>
<td>(R = \text{C}_2\text{H}_5) (X = \text{Cl}, Y = \text{H})</td>
<td>3</td>
<td>(Y = \text{H})</td>
<td>20</td>
<td>18</td>
<td>83</td>
<td>108 (35)</td>
</tr>
<tr>
<td>(R = \text{C}_2\text{H}_5) (X = Y = \text{Cl})</td>
<td>4</td>
<td>(Y = \text{Cl})</td>
<td>20</td>
<td>1 mth.</td>
<td>80</td>
<td>64-6 (9)</td>
</tr>
</tbody>
</table>

(a) Previously known compound (see reference (11)).

*RX = Reaction

In contrast with the reactions shown in Table II, diethylamine interacts with 1-chloro-2-methoxytetrafluorocyclobutene to yield the cyclic ketone, 1-chloro-2-diethylamino 3,3-difluoro-4-cyclobutenone.
During the course of the present investigation, Dreir and coworkers (55) independently reported the preparation of the same ketone, in a study of the reactions of fluorinated alkoxy cycloalkenes with diethylamine.

Diethylamine and 1-ethyl-2-chlorotetrafluorocyclobutene react vigorously at 20° (24 hours), the product b.p. 100° (45 mm) although appearing to be pure (gives one peak on a number of v.p.c. columns) was not identified. The 1H nmr. spectrum was much more complicated than would be expected for 1-ethyl-2-diethylaminotetrafluorocyclobutene. A similar result was obtained from reaction of dimethylamine and 1-ethyl-2-chlorotetrafluorocyclobutene.

D. Reactions of Thiols with Fluorinated Cycloalkenes

Thiols react with fluorinated cycloalkenes in a manner analogous to amines and arsines. In Table III, are summarized the results of some experiments involving methane thiol. Triethylamine was used as a catalyst in the reaction described by the following general equation.

\[
\text{CH}_3\text{SH} + \begin{array}{ccc} \text{F}_2 & \text{F}_2 \\
\text{X} & \text{Y} \end{array} \xrightarrow{(\text{C}_2\text{H}_5)\text{3N}} \begin{array}{ccc} \text{F}_2 & \text{F}_2 \\
\text{CH}_3\text{S} & \text{Y} \end{array} + \text{HX}
\]

<table>
<thead>
<tr>
<th>Reactant Cyclobutene</th>
<th>Product</th>
<th>*RX T. (°C)</th>
<th>*RX. Time (days)</th>
<th>Yield %</th>
<th>b.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = Y = F</td>
<td>Y = F</td>
<td>80</td>
<td>3</td>
<td>100</td>
<td>104</td>
</tr>
<tr>
<td>C = Y = C1</td>
<td>Y = Cl</td>
<td>100</td>
<td>8</td>
<td>85</td>
<td>134</td>
</tr>
<tr>
<td>X = Cl, Y = C\text{2H}_5</td>
<td>Y = C\text{2H}_5</td>
<td>140</td>
<td>7</td>
<td>70</td>
<td>158</td>
</tr>
</tbody>
</table>

*X = Reaction
The reaction of methanethiol with hexafluorocyclobutene, also yields the disubstituted product, 1,2-methylthiotetrafluorocyclobutene, b.p. 85° (14 mm), in addition to the monosubstituted product indicated in Table III.

\[
3\text{CH}_3\text{SH} + \begin{array}{c}
\text{C}_2\text{H}_5\text{F}_2\text{C}_2\text{H}_5\text{F}_2\text{C}_2\text{H}_5\text{F}_2
\end{array} \rightarrow \text{CH}_3\text{SCH}_2\text{F}_2\text{F}_2\text{F}_2 + 3\text{HF}
\]

Reaction of methanethiol with 1-H-2-chlorotetrafluorocyclobutene and 1-H-2-chlorohexafluorocyclopentene yields products which are not the simple "addition-elimination" cyclobutene or cyclopentene derivatives. Thus the reaction of methane thiol with 1-H-2-chlorotetrafluorocyclobutene at 150° (6 days) yields the 1:1 addition product, 1-methylthio-1,2-dihydro-2-chlorotetrafluorocyclobutane, b.p. 138-9°.

\[
\text{CH}_3\text{SH} + \begin{array}{c}
\text{Cl} \text{H} \text{Cl}
\end{array} \xrightarrow{150°} \text{C}_2\text{H}_5\text{N}_3 \rightarrow \text{F}_2\text{F}_2\text{F}_2\text{F}_2\text{Cl}\text{SCH}_3 + 3\text{HF}
\]

No evidence was obtained for the elimination of hydrogen halide to form a cyclobutene. On the other hand, reaction of methanethiol with 1-H-2-chlorohexafluorocyclopentene at 140° (10 days) yields 1-chloro-5-methylthio-5-H-pentafluorocyclopentene b.p. 155°.

\[
\text{CH}_3\text{SH} + \begin{array}{c}
\text{F}_2\text{F}_2\text{F}_2\text{F}_2
\end{array} \xrightarrow{140°} \text{C}_2\text{H}_5\text{N}_3 \rightarrow \text{F}_2\text{F}_2\text{F}_2\text{F}_2\text{Cl}\text{SCH}_3 + \text{HF}
\]

It is worth noting, that in this reaction hydrogen fluoride elimination occurs in preference to the expected hydrogen chloride elimination.
Reaction of methanethiol with 1-chloro-2-methoxytetrafluorocyclobutene at 130° (7 days) yields 1-chloro-2-methylthio-3,3-difluoro-4-cyclobutenone b.p. 107° (10 mm) 30% yield.

\[
\begin{align*}
\text{CH}_3\text{SH} + \text{F}_2\text{C} = \text{CF}_2 \xrightarrow{130°} \text{CH}_3\text{S} + \text{HF} \\
\text{CH}_3\text{O} & \quad \text{C}1 \\
\end{align*}
\]

A white solid, which is also produced was not identified. Attempts to purify it by sublimation and fractional recrystallization were unsuccessful. Attempts to prepare the disubstituted derivative by heating the cyclobutenone with excess methanethiol at 110° (16 days) were also unsuccessful.

From the results obtained for the reaction of arsines, amines and thiols with fluorinated cycloalkenes, the ease of reaction seems to be a function of the electronegativity of the atoms attached to the double bond. Thus, the more electronegative atoms withdraw electronic charge from the double bond through inductive effects, and leaving it susceptible to nucleophilic attack by the amine, arsine or thiol. From this argument, it appears that the ease of reaction should depend on the relative basicity or nucleophilicity of the attacking species. Qualitatively, this has been found to be so, in that amines react much faster than arsines which in turn react faster than thiols. The results, from a study (54) of the reaction of dimethylarsine with perfluorocyclobutene and 1,2-dichlorocyclobutene, where it was found that the former reaction was much faster than the latter, are in agreement with the above arguments. In the present investigation, the relatively slow reaction of methylphenylarsine with perfluorocyclobutene and the 1,2-dichlorocyclobutene compared to the reaction of dimethylarsine with these butenes, can be explained by the decrease in availability of the arsenic.
lone pair electrons due to the inductive and possible resonance effects of the phenyl group; thus making methylphenylarsine a weaker nucleophile than dimethylarsine.

For the reaction of dimethylarsine with substituted cyclobutenes of the type RC = CC1CF2CF2(R = H, C2H5), it was found that the ease of reaction decreased, as the ability of the group or atom R to donate electronic charge into the double bond increased, thus making the double bond less susceptible to nucleophilic attack. The reaction of dimethylarsine with 1-H-2-chlorotetrafluorocyclobutene was faster than with 1-ethyl-2-chlorotetrafluorocyclobutene, but both reactions were extremely slow, compared to the reactions with the perfluoro- and 1,2-dichloro compounds (see Table I). This is in agreement with the arguments set forth above. Analogous conclusions can be drawn from the reactions of diethylamine and methanethiol with the same cyclobutenes. (See Tables II and III).

E. Synthesis of 1,2-Disubstituted Derivatives of Cyclobutenes and Cyclopentenes

With substituted cyclobutenes and cyclopentenes, replacement of the second fluorine or chlorine atom is very difficult. The reaction of diethylamine with 1-dimethylarsinopentafluorocyclobutene, to yield 1-dimethylarsino-2-diethylaminotetrafluorocyclobutene b.p. 68° (10⁻³ cm) proceeds very much slower than the reaction of diethylamine with hexafluorocyclobutene.

Attempts to prepare the same disubstituted compound from tetramethyldiarsine
and 1-diethylaminopentafluorocyclobutene and from 1-diethylamino-2-chloro-
tetrafluorocyclobutene and dimethylarsine were unsuccessful. Only starting 
materials were recovered from the former reaction and the latter gave, after 
2 days at 100° an intractable charred solid.

\[
\text{(CH}_3\text{)}_2\text{As-As(CH}_3\text{)}_2 + (\text{C}_2\text{H}_5\text{)}_2\text{NH -} \rightarrow \text{NO Reaction}
\]

\[
\text{(CH}_3\text{)}_2\text{AsH} + \text{Cl} + \text{N(C}_2\text{H}_5\text{)}_2\text{F}_2 \rightarrow \text{charred solid}
\]

Reaction of 1-dimethylarsino-2-chlorohexafluorocyclopentene with 
diethylamine at 100° (3 days) yields an inseparable mixture of 1-dimethyl-
arsino-2-diethylaminohexafluorocyclopentene and the starting cyclopentene.

No reaction is observed between 1-diethylamino-2-chlorohexafluoro-
cyclopentene and dimethylarsine at 20°. However, at 80° (34 hours) reaction 
proceeds smoothly and also yields an inseparable mixture of the starting 
cyclopentene and a product b.p. 80° (10^{-3} \text{cm}) which does not appear to be 
the same as the 1-dimethylarsino-2-diethylaminohexafluorocyclopentene 
obtained above.

Structures and Spectroscopic Properties of the New Compounds

The structures of all the compounds described above are established
on the basis of their chemical analysis (See Experimental Section). $^{19}\text{F}$ nmr. (Table IV), $^1\text{H}$ nmr. (Table V) and infrared spectra (Tables VI-IX).

NMR. Spectra ($^{19}\text{F}$ spectra)

The $^{19}\text{F}$ nmr. spectrum of 1-diethylaminopentafluorocyclobutene is shown in figure 1. It is seen that although the spectrum is complex, absorptions due to three different types of fluorine atoms occur in well defined regions. The high field region is associated with the vinylic fluorine atom (C) (area = 1 unit) and the other two regions A and B (each of area = 2 units) with the allylic fluorine atoms. The spectra of the other cyclobutene derivatives are similar and their $^{19}\text{F}$ nmr. chemical shifts are presented in Table IV.

From the $^{19}\text{F}$ nmr. spectra, it is seen that the areas of A and B are equal and that of C, when present ($X = \text{F}$), is equal to one half of this. Therefore, there are four allylic fluorine atoms present in each compound. It is worth noting that the chemical shift of these atoms does not change markedly as a result of the change of atoms attached to the carbon atom of the double bond. However, the chemical shift of the vinylic fluorine atom shifts considerably as a result of substitution of different atoms at the other end of the double bond. It seems (Table IV) that the nature of the substituents on that atom do not have a great effect on the resonance frequency of the vinylic fluorine atom, as it is readily seen for the compounds $XC = \text{CRCF}_2\text{CF}_2$, ($X = \text{F}$, $R = \text{As(CH}_3\text{)}_2$, $\text{As(CH}_3\text{)(C}_6\text{H}_5$), $\text{N(CH}_3\text{)}_2$, $\text{N(C}_2\text{H}_5\text{)}_2$).

Spectroscopic studies by Stone and coworkers (56), show that the $^{19}\text{F}$ spectra of perfluorovinyl derivatives of metals and metalloids show a much smaller variation of chemical shift on changing the central atom. Stone and coworkers (49) also studied some perfluorocyclobutenyl derivatives of iron, manganese, and rhenium carbonyls and found that there is no significant
<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_2\text{H}_5)\text{N}) (\text{F})</td>
<td>33.0</td>
<td>38.1</td>
<td>79.8</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)\text{N}) (\text{F})</td>
<td>32.9</td>
<td>37.4</td>
<td>79.5</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)\text{As}) (\text{F})</td>
<td>33.7</td>
<td>39.7</td>
<td>28.9</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)\text{N} (\text{C}_6\text{H}_5)\text{As}) (\text{F})</td>
<td>33.7</td>
<td>39.7</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{S})</td>
<td>37.4</td>
<td>39.0</td>
<td></td>
<td>45.2</td>
</tr>
<tr>
<td>((\text{CH}_3)\text{As})</td>
<td>31.7</td>
<td>37.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)\text{N} (\text{C}_6\text{H}_5)\text{As})</td>
<td>31.1</td>
<td>37.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)\text{N}) (\text{Cl})</td>
<td>110.7</td>
<td>114.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)\text{As})</td>
<td>108.3</td>
<td>109.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{S})</td>
<td>112.5</td>
<td>115.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\pi\text{-C}_6\text{H}_5\text{Fe(CO)}\text{F})</td>
<td>117.6</td>
<td>117.6</td>
<td>122.5</td>
<td></td>
</tr>
<tr>
<td>(\text{Mn(CO)}\text{F})</td>
<td>123.4</td>
<td>119.1</td>
<td>124.1</td>
<td></td>
</tr>
<tr>
<td>(\text{Re(CO)}\text{F})</td>
<td>123.7</td>
<td>117.7</td>
<td>118.6</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{F}\) upfield from external trifluoroacetic acid, p.p.m.
\(\text{b}\) upfield from external trichlorofluoromethane, p.p.m.
\(\text{c}\) from reference (49).
$^{19}$F nmr. for (C$_2$H$_5$)$_2$N-C=CFCF$_2$CF$_2$

\[
\begin{align*}
\text{F}_2\text{C} & \quad \text{CF}_2 \\
(C_2\text{H}_5)_2\text{N-C} & \quad \text{C} \\
\end{align*}
\]
change in the chemical shift of either the vinylic fluorine atom or the allylic fluorine atoms on changing the central metal atom. (Table IV). However, in the corresponding perfluorocyclohexenyl derivatives, significant changes in the chemical shift of the vinylic fluorine atom and the other fluorine atoms were observed. Studies by Taft and coworkers (65,66,67) on monofluorinated benzenes, showed that the chemical shift of the fluorine atom changes considerably depending on the relative ability of substituents on the ring to withdraw or donate electronic charge.

The $^{19}$F nmr. spectrum of 1-methylthio-1,2-dihydro-2-chlorotetrafluorocyclobutane shows the maximum eight lines, expected for an AA' BB' (61) system of a tetrafluorocyclobutane, at 107.1, 109.3; 110.6; 112.8, and 126.7, 127.7, 128.9, 130.1 p.p.m. upfield from trichlorofluoromethane. The four upfield lines at 126.7, 127.7, 128.9 and 130.1 can be assigned as due to one set of geminal fluorine atoms, and the other four lines at 107.1, 109.3, 110.6, and 112.8, to be the other set of geminal fluorine atoms. It is not possible to say unequivocally, which set of geminal fluorine atoms a particular set of four lines belongs to. The spectrum is similar to the spectra obtained by Phillips (57) for a series of substituted tetrafluorocyclobutanes. The present spectrum shows no measurable vicinal fluorine-fluorine coupling and can be assigned on a first order basis. The resolution of the spectrum was not sufficient to show the effect of H-F couplings.

The $^{19}$F nmr. spectrum of 1-dimethylarsino-2-chlorohexafluorocyclopentene shows three well defined absorption of equal intensity at 29.9, 40.8 and 67.6 p.p.m. in agreement with the assigned structure. Examination of the chemical shifts of allylic fluorine atoms in the cyclobutenes of Table IV, allows one to assign the two low field bands in the spectrum of the cyclopentene, to the fluorine atoms adjacent to the double bond, and the high field band to the
remaining pair of fluorine atoms. Supporting evidence for this assignment is obtained from the spectra of the compounds $\text{XC} = \text{CXCF}_2\text{CF}_2\text{CF}_2$ (58) where the approximate chemical shifts for F' and F'' respectively are 35 and 51 p.p.m. (X = Cl) and 41 and 53 p.p.m. (X = F).

The chemical shift $\delta$, can be defined in terms of the electronic screening constant $\sigma$. Thus $\sigma$ and $\sigma r$ are respectively the screening constants of the fluorine atom (or proton) to be measured and that of the reference fluorine atom (or proton), then

$$\delta = \sigma - \sigma r$$

Therefore, a positive value of $\delta$ corresponds to higher electronic screening for the fluorine atom that is being measured, than for the reference fluorine atom. Thus as the electronic charge density (or electronic screening) increases at the fluorine atom bonded to carbon, the resonance generally appears at higher field, or at lower field if electronic charge density is withdrawn from the fluorine atom (65, 66, 67). It is seen from Table IV, that for compounds of the type $\text{RC} = \text{CFCF}_2\text{CF}_2$, the chemical shift of the vinylic fluorine atom is dependent on the nature of R. From an examination of these compounds it appears that there are two possible explanations for the observed change in chemical shifts. One is based on inductive effects depending on the electronegativity of the atom or group R. The other on resonance effects, depending on the amount of overlap between the $p^\pi$ orbitals of the double bond carbon atom and the atom attached to it. In the case of the amine contributions from resonance hybrids such as $\text{R}_2\text{N}^+ = \text{C} - \text{CFCF}_2\text{CF}_2$ would result in an upfield shift of the resonance of the vinylic fluorine atom. Structures such as these would make a smaller contribution in the case of the arsines and sulfides. Although more delocalization of the $p^\pi$ electrons into empty d-orbitals could have the
effect of shifting the resonance downfield. Normally both resonance and inductive effects are operating in compounds of this type, and unfortunately, it is difficult if not impossible to determine the contribution of each effect to the total chemical shift. It may be possible to estimate the chemical shift due to resonance effects only by comparing the compounds R = CF₃ and Cl. The electronegativity of CF₃ and chlorine are almost the same (59) but the possibility of resonance effects due to the presence of the CF₃ group is unlikely where they could occur for R = Cl.

II. ¹H nmr. Spectra

The ¹H nmr. spectra of these compounds offers further corroborative evidence for the structures suggested above. Thus in the case of 1-diethylaminopentafluorocyclobutene, the ethyl groups are readily accounted for by the appearance of the expected quartet at -3.24 p.p.m. due to the resonance of the methylene protons and a triplet at -1.18 p.p.m. due to the resonance of the methyl protons, relative area quartet to triplet 2:3. The other compounds containing methyl, ethyl, or phenyl substituents on arsenic, sulfur or nitrogen were similarly identified.

The ¹H nmr. spectrum of 1-H-2-dimethylarsinotetrafluorocyclobutene shows the expected single peak at -1.03 p.p.m. (As(CH₃)$_2$) and a downfield signal consisting of a triplet ($J = 10$ c.p.s.) split into multiplets at -6.68 p.p.m., which is assigned as being due to the resonance of the vinylic proton. The downfield signal in the spectrum of 1-H-2-diethylaminotetrafluorocyclobutene at -4.55 p.p.m. consists of a triplet of triplets ($J = 11$ c.p.s.). In the spectrum of the arsine and the amine, the triplet with the greater coupling constant is probably due to coupling of the hydrogen atom with the two fluorine atoms across the ring. Thus in the case of the amine $J_{H-F_3}$ is probably $11$ c.p.s. whilst $J_{H-F_4}$ is $3$ c.p.s. This is in agreement with the
The findings of J. D. Roberts (60), who examined similar fluorinated cyclobutenes.

The $^1$H nmr. spectrum of 1-H-2-chlorotetrafluorocyclobutene, shows a down field multiplet (7 peaks) due to the resonance of the vinyl proton at -6.9 p.p.m. In Table V are listed the proton chemical shifts of the 1-H-cyclobutene and 1-H-cyclopentene and derivatives.

### Table V

<table>
<thead>
<tr>
<th>R</th>
<th>Chemical Shift of Cyclobutene (PPM)</th>
<th>Chemical Shift of Cyclopentene (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-6.19</td>
<td>-6.12</td>
</tr>
<tr>
<td>(CH$_3$)$_2$As</td>
<td>-6.68</td>
<td>-6.22</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_2$N</td>
<td>-4.55</td>
<td>-4.42</td>
</tr>
</tbody>
</table>

(a) measured on neat liquids relative to external tetramethylsilane.

It is seen from Table V, that the chemical shift of the vinylic hydrogen atom in the compounds $RC = CX(CF_2)_n$ ($n = 2,3; X = H$), like the vinylic fluorine atom ($X = F$) described above, shifts considerably on substitution of different atoms at the other end of the double bond. The same qualitative explanation of the change in the chemical shift of the vinylic
fluorine atom as different atoms are substituted at the other end of the double bond, can be applied to the shift of the vinylic hydrogen atom. The relative change in chemical shift, however, is very much smaller for hydrogen atoms, probably due to its inability to form π bonds or π interactions with the double bonded carbon atom (61).

The ¹H nmr. spectrum of 1-methyl-1,2-dihydro-2-chlorotetrafluorocyclobutane shows the expected singlet (CH₃S) at -2.15 p.p.m. and multiplets at -3.53 and -4.10 p.p.m. of relative area 3:1:1. The resolution of the spectrum was not sufficient to permit an accurate assignment of coupling constants. On the basis of the ¹H nmr. and ¹⁹F nmr. it is possible to say that there is only one isomer present, but the structure cannot be established on the available evidence.

The spectrum of 1-chloro-5H-5-methylthiopentafluorocyclopentene shows the expected single peak at -2.02 p.p.m. (CH₃S) and a downfield signal in the allylic region at -3.91 p.p.m. The resolution of the spectrum, however, was not sufficient to permit an accurate assignment of coupling constants.

Infrared Spectra

The infrared spectra of the cyclobutene and cyclopentene derivatives show absorptions in the region 3000 cm⁻¹ (C-H), 1800-1600 cm⁻¹ (C = C), 1300-1000 cm⁻¹ (C-F) and some absorptions in the region 1000-650 cm⁻¹ which are due to skeletal absorptions. A few striking features of the spectra are the high intensity absorptions which are usually associated with stretching vibrations of highly polar linkages. The C-F stretching vibrations which absorb in the range 1300-1000 cm⁻¹, lie in a region where other molecular modes (skeletal stretching) occur and thus result in very complex absorption patterns which are difficult to interpret. The C=C bonds of
these compounds absorb in the range 1800-1600 cm\(^{-1}\) and useful correlations, which appear to be dependent on the nature of groups attached to the cyclobutene or cyclopentene skeleton can be obtained. A discussion of the double bond absorption frequencies of these compounds, which are listed in Tables VI-IX, is presented below.

### TABLE VI

Double Bond Stretching Frequencies of the Cyclobutenes

<table>
<thead>
<tr>
<th>R</th>
<th>X = F</th>
<th>X' = Cl</th>
<th>X = C(_2)H(_5)</th>
<th>X = H</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>1799 (a)</td>
<td></td>
<td></td>
<td>1682 (a)</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>1765 (a)</td>
<td>1726 (a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C(_2)H(_5))(_2)N</td>
<td>1750</td>
<td>1696</td>
<td></td>
<td>1668</td>
</tr>
<tr>
<td>Alkyl</td>
<td>1720-30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)S</td>
<td></td>
<td>1670</td>
<td>1587</td>
<td>1622</td>
</tr>
<tr>
<td>(CH(_3))(C(_6)H(_5))As</td>
<td>(1695)</td>
<td>1576</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH(_3))(_2)As</td>
<td>1659</td>
<td>1576</td>
<td>1612</td>
<td>1548</td>
</tr>
<tr>
<td>Cl</td>
<td>1620 (a)</td>
<td></td>
<td></td>
<td>1596 (b)</td>
</tr>
</tbody>
</table>

(a) See reference (62)
(b) See reference (52)
(c) See reference (39)

From Table VI, it seems that the change in double bond stretching frequencies of the cyclobutenes, as a result of the change of atoms attached
to the carbon atoms of the double bond is due to more than just a change in mass of the vibrating atoms (See column 1). For the first, second and fourth columns ($X = F, Cl, H$) as $R$ changes from fluorine down to $(\text{CH}_3)_2\text{As}$, the fall in double bond stretching frequency, can be qualitatively correlated with the decrease in electronegativity of the central atom. There appears to be an exception to the above generalization, in that the $\text{C=C}$ stretching frequency changes from 1659 to 1695 cm$^{-1}$, as $R$ changes from $(\text{CH}_3)_2\text{As}$ to $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{As}$ for the compound ($X = F$); whereas for ($X = Cl$) it remains unaltered as $R$ changes from $(\text{CH}_3)_2\text{As}$ to $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{As}$.

### TABLE VII

Double Bond Stretching Frequencies of Cyclopentenes

<table>
<thead>
<tr>
<th>$R$</th>
<th>$X = F$</th>
<th>$X = Cl$</th>
<th>$X = H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>1771 (a)</td>
<td>1708 (c)</td>
<td>1695</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}$</td>
<td>1727 (a)</td>
<td>1666 (c)</td>
<td>1630</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_2N$</td>
<td>1632</td>
<td>1630</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{As}$</td>
<td>1590</td>
<td>1615 (c)</td>
<td>1635 (b)</td>
</tr>
</tbody>
</table>

It seems, that similar conclusions apply to the cyclopentene derivatives as is seen from Table VII. Thus there appears to be a correlation between the fall in double bond stretching frequency, and the decrease in electronegativity of the central atom when $X = Cl$. However, for $X = H$, there appears to be no obvious correlation with the electronegativity.
### TABLE VI.1

**Double Bond Stretching Frequencies for Disubstituted Cyclobutenes and Cyclopentenes**

<table>
<thead>
<tr>
<th>Substitution</th>
<th>Frequency (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = Y = F</td>
<td>1799</td>
<td></td>
</tr>
<tr>
<td>X = Y = OCH₃</td>
<td>1750</td>
<td></td>
</tr>
<tr>
<td>X = Y = Cl</td>
<td>1620</td>
<td></td>
</tr>
<tr>
<td>X = Y = (CH₃)₂As</td>
<td>1613</td>
<td></td>
</tr>
<tr>
<td>X = (CH₃)₂As, Y = (CH₂H₅)₂N</td>
<td>1637, 1630</td>
<td></td>
</tr>
<tr>
<td>X = (CH₂H₅)₂N, Y = OCH₃</td>
<td>1750</td>
<td></td>
</tr>
</tbody>
</table>

In the above Table (VIII), for 1,2-disubstituted cyclobutene derivatives, there does not appear to be any obvious dependence of the change in double bond stretching frequency, to the change in electronegativity of the groups attached to the carbon atoms of the double bond; whereas for the cyclopentene derivatives, there appears to be a dependence.

### TABLE IX

**Comparison of Hydrogen and Fluorocarbon Cycloalkene Double Bond Stretching Frequencies**

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Fluorocarbon Perfluoro</th>
<th>1-Methoxy</th>
<th>1-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>1646</td>
<td>1746</td>
<td>1705</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>1611</td>
<td>1771</td>
<td>1727</td>
</tr>
<tr>
<td>Cyclobutene</td>
<td>1571</td>
<td>1799</td>
<td>1765</td>
</tr>
</tbody>
</table>

See Reference (62)
In Table IX, it is seen that there is a sharp contrast in the behaviour of the C=C stretching frequencies of the perfluorocycloalkenes, to their hydrocarbon counterparts. In the former, there is an increase in stretching frequency with a decrease in ring size; whereas in the latter, there is an increase with increasing ring size. The 1-methoxy derivatives of the fluoro compounds also follow the same trend; whereas the 1-H-derivatives follow the same trend as the hydrocarbons.

The structures of the disubstituted derivatives of the cyclobutenes and cyclopentenes (Table VIII) are assigned on the basis of their infrared spectra, in addition to chemical analysis. The new dimercaptocyclobutene, 1,2-methylthiotetrafluorocyclobutene, shows only a weak double bond absorption at 1550 cm\(^{-1}\). Thus the structure is the symmetrical 1,2-methylthiotetrafluorocyclobutene and not the 1,3-disubstituted derivative. The latter compound would be expected to show an intense absorption in its infrared spectrum due to asymmetry.

The structures of 1-dimethylarsino-2-diethylaminotetrafluorocyclobutene and 1-dimethylarsino-2-diethylaminohexafluorocyclopentene were assigned by utilization of the following argument. The starting cyclobutene, 1-dimethylarsinopentafluorocyclobutene, exhibits a double bond absorption at 1695 cm\(^{-1}\), on substitution of the vinylic fluorine atom by the diethylamino group, the double bond frequency is shifted to 1637 cm\(^{-1}\) probably due to the lower electronegativity of the nitrogen atom. If the product was a 1,3-disubstituted derivative, then the change in double bond frequency would not be as large (62). Similarly for the disubstituted cyclopentene derivative, the starting cyclopentene, 1-dimethylarsino-2-chlorohexafluorocyclopentene, shows a double bond absorption at 1586 cm\(^{-1}\), and on substitution of the vinylic chlorine by a diethylamino group, the double bond frequency is shifted
to 1625 cm\(^{-1}\). Therefore the structure is probably 1-dimethylarsino-2-diethylaminohexafluorocyclopentene since this increase in the double bond frequency is not likely for other structures such as the 1,3; 1,4; or 1,5 disubstituted derivatives.

The structure of 1-chloro-5-hydro-5-methylthiopentafluorocyclopentene (prepared from 1-H-2-chlorohexafluorocyclopentene and methanethiol) was assigned on the basis of its \(^1\)H nmr. and infrared spectra. The double bond showed an absorption at 1710 cm\(^{-1}\) which is in excellent agreement with 1708 cm\(^{-1}\) for the double bond of 1-chloroheptafluorocyclopentene (39). The presence of a resonance at -3.91 p.p.m. in the \(^1\)H nmr. spectrum in the region of the allylic protons, lends further support to the assigned structure.

In a study of the reaction of 1-chloro-2-methoxytetrafluorocyclobutene with diethylamine, methanethiol and dimethylarsine, cyclic ketone derivatives were obtained, instead of the expected 1-chloro-2-(amino, thio, or arsino)tetrafluorocyclobutene compounds. The structures of these new ketones were assigned on the basis of chemical analysis, and the appearance of very intense bands in the C = O and C = C stretching frequency regions.

The structure of 1-chloro-2-diethylamino-3,3-difluoro-4-cyclobutenone (prepared from 1-chloro-2-methoxytetrafluorocyclobutene and diethylamine) was assigned on the basis of its infrared spectrum, which showed a carbonyl absorption at 1780 cm\(^{-1}\) and a double bond absorption at 1615 cm\(^{-1}\) (lit. values 1777 and 1600 cm\(^{-1}\)(55)). Similarly 1-chloro-2-methylthio-3,3-difluoro-4-cyclobutenone had a carbonyl bond at 1793 cm\(^{-1}\) and a double bond absorption at 1530 cm\(^{-1}\).

The reaction of dimethylarsine with 1-chloro-2-methoxytetrafluorocyclobutene yields a product in very low yield which exhibits absorptions
at 1801 and 1618 cm\(^{-1}\) in its infrared spectrum. From the similarity of this spectrum to the spectra of the above ketones, the structure is postulated as 1-chloro-2-dimethylarsino-3,3-difluoro-4-cyclobutenone.

C. Possible Mechanisms for the above Reactions

The different reactions are determined by the thermodynamic stability of the intermediate carbanion. Sequence (1) to form addition products is most common for fluoroethylens, and the tendency toward (2) to form unsaturated products increases for higher fluoro-olefins and cyclic fluoro-olefins for example, perfluoroisobutene and perfluorocyclobutene. It should be pointed out that sequence (2) is a compromise between direct vinyl sub-
stitution of the fluorine atom (SN2) and the formation of a saturated product followed by elimination of hydrogen fluoride. "addition-elimination". Both of these mechanisms have been postulated to account for the observed products but from available evidence it is not possible to distinguish between the two possibilities. Sequence (3) is the tendency for polyfluorohalogen compounds to undergo SN2 displacement of allylic halogen rather than direct displacement by halide ions, and is believed to occur for the following reactions which were investigated by Miller and coworkers (64).

\[ X^- + CF_2=CHCCl_2F \rightarrow X-CF_2CH = CClF + Cl^- \]

\((X = Cl, F \text{ or } I)\)

One of the more convincing evidence for an addition-elimination mechanism, is the isolation of the cyclobutane, 1,2-n-butylthio-1-hydro-pentafluorocyclobutane, from the reaction of butanethiol with perfluorocyclobutene (14).

\[ \begin{align*} n-C_4H_9SH + & \rightarrow \quad C_4H_9S \quad + \quad HF \\
\begin{array}{c}
F_2 \\
\text{C}_4\text{H}_9\text{S} \\
F_2 \\
F_2
\end{array} & \quad \begin{array}{c}
F_2 \\
H \\
C_4H_9S \\
F_2 \\
F_2
\end{array} + C_4H_9SH & \rightarrow \quad C_4H_9S \quad + \quad HF \\
\begin{array}{c}
F_2 \\
\text{SC}_4\text{H}_9 \\
\text{C}_4\text{H}_9\text{S} \\
F_2
\end{array}
\]

This cyclobutane is unstable and decomposes on distillation to yield 1,2-butylthiotetrafluorocyclobutene.
In the present investigation, the reaction of methanethiol with 1-H-2-chlorotetrafluorocyclobutene, catalyzed by triethylamine yields a cyclobutane,

\[
\begin{array}{c}
\text{F}_2 \\
\text{Cl} \\
\text{H} \\
\text{F}_2
\end{array} + \text{CH}_3\text{SH} \xrightarrow{(\text{C}_2\text{H}_5)_3\text{N} \, 150^\circ} \begin{array}{c}
\text{F}_2 \\
\text{Cl} \\
\text{CH}_3\text{S} \\
\text{F}_2
\end{array}
\]

which fails to eliminate hydrogen halide under the reaction conditions (150°, 6 days). This is in sharp contrast with the reaction of 1,2-dichlorotetrafluorocyclobutene and methanethiol which eliminates hydrogen chloride very readily to yield the cyclobutene derivative.

For the reaction of 1-H-2-chlorohexafluorocyclopentene and methanethiol, elimination of hydrogen fluoride is observed instead of the expected hydrogen chloride elimination.

\[
\begin{array}{c}
\text{F}_2 \\
\text{Cl} \\
\text{C}_1 \text{H} \\
\text{F}_2
\end{array} + \text{CH}_3\text{SH} \xrightarrow{(\text{C}_2\text{H}_5)_3\text{N}} \begin{array}{c}
\text{F}_2 \\
\text{Cl} \\
\text{H} \\
\text{F}_2
\end{array} \rightarrow \begin{array}{c}
\text{F}_2 \\
\text{Cl} \\
\text{CH}_3\text{S} \\
\text{F}_2
\end{array}
\]

Similar mechanisms of "addition-elimination" have been proposed by other workers for the reactions of perfluorocyclobutene with amines (11), Grignard reagents (43), alcohols (38), and thiols (14). Thus for the Grignard reagents, Park and coworkers (43) favor the following addition-elimination mechanism.
For the reaction of perfluorocyclobutene with alcohols, Barr and coworkers (38) postulated on addition-elimination mechanism.

\[
\begin{array}{c}
\text{ROH} + \text{F}_2\text{C}_2\text{F}_2 \rightarrow \text{ROF}_2 + \text{HF} \\
\end{array}
\]

Whereas, Park and coworkers (13,40) favour a SN₂ substitution of the vinylic fluorine atom by the alcohol. However, sufficient evidence is not available to distinguish between the two possibilities.

For the reaction of arsines and amines with perfluorocyclobutene a possible mechanism is as follows.

1. nucleophilic attack at the double bond carbon atom

\[
\begin{array}{c}
\text{R}_2\text{EH} + \text{F}_2\text{C}_2\text{F}_2 \\
\end{array}
\]

2. intermolecular cleavage of E-H bond to give the addition product.
(3) rapid elimination of hydrogen fluoride to yield the observed products.

A similar mechanism is favoured for the reaction of tetramethylarsine with perfluorocyclobutene.

Dreir and coworkers (55) have postulated a mechanism for the reaction of diethylamine with 1-chloro-2-methoxyhexafluorocyclopentene and 1-chloro-2-methoxytetrafluorocyclobutene. In a study of the reactions of alkoxide ion with the cyclopentene and cyclobutene, using NMR to distinguish between the trialkoxy olefins [I and II],

the authors found that in every case isomer [II] was found, indicating that the reaction proceeds by a series of addition elimination reactions. This result requires that the amine react with the 1-chloro-2-methoxyhexafluorocyclopentene to give a 2-methoxy-2-alkylamino intermediate addition product.
[III]. These authors, then propose that either concurrent with or subsequent to reaction with more amine, [III] undergoes internal elimination of a secondary or tertiary amine to form a carbonyl group.

\[
\begin{align*}
\text{CH}_3O & \quad \text{F} \\
\text{C}_2\text{H}_5\text{NH} & \quad \text{F} \\
\text{C}_2\text{H}_5\text{NH} & \quad \text{CH}_3O
\end{align*}
\]

\[
\begin{align*}
\text{+ (C}_2\text{H}_5\text{H}_2\text{NH} & \quad \text{C}_2\text{H}_5\text{NH} \quad \text{F} \\
\text{+ (C}_2\text{H}_5\text{H}_2\text{NH} & \quad \text{F} \\
\text{+ (C}_2\text{H}_5\text{H}_2\text{NH} & \quad \text{C}_2\text{H}_5\text{NH}
\end{align*}
\]

Similarly for the cyclobutene.

A similar mechanism can be suggested for the reaction of methane thiol with the cyclobutene.

\[
\begin{align*}
\text{CH}_3\text{SH} & \quad \text{C}_2\text{H}_5\text{H}_2\text{N} \\
\text{C}_2\text{H}_5\text{NH} & \quad \text{CH}_3\text{SH}
\end{align*}
\]
CHAPTER III

Reaction of 1,2-Dimethylarsinotetrafluorocyclobutene ("Difars") with Transition Metal Carbonyls and Halides

INTRODUCTION

Since Hoffman's (68) synthesis of complexes of platinum and gold containing triethyl-phosphine, arsine and stibine ligands, the synthesis and properties of coordination compounds of the transition metals has been the subject of a large number of investigations. In the last two decades, advances in the theoretical interpretation of the powerful spectroscopic methods of u.v., i.r., n.m.r., e.s.r. spectroscopies and X-ray crystallography have stimulated an enormous interest in the synthesis, identification and structural studies of these compounds. In the field of coordination complexes of the transition metal salts and carbonyls with phosphines, arsines and stibine ligands, considerable contributions have been made by Mann (15), Nyholm (15), Chatt (15) and Hieber (15) and their respective coworkers. These workers have synthesized compounds containing mono-arsines, phosphines and stibine ligands, diarsines and diphosphines as well as the chelating ligands o-phenylenebisdimethylarsine, "Diars" (15), o-phenylenebisdiethylphosphine "Diphos", and 1,2-diphenylphosphinoethane.

A. Carbonyl Complexes

The reactions of metal carbonyls with phosphines and arsines yield a variety of products of which the following are typical. The reaction of nickel tetracarbonyl with phosphines (4) or arsines (4,69), affords compounds in which one or two molecules of carbon monoxide are normally replaced to form derivatives of the type \( [\text{Ni(CO)}_3\text{L}] \) and \( [\text{Ni(CO)}_2\text{L}_2] \) where \( \text{L} \) is the ligand \( \text{R}_3\text{P} \) or \( \text{R}_3\text{As} \), (\( \text{R} = \text{alkyl or aryl} \)) for example

\[
\text{Ni(CO)}_4 + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow \text{Ni(CO)}_3(\text{C}_6\text{H}_5)_3 + \text{Ni(CO)}_2(\text{P(}\text{C}_6\text{H}_5)_3)_2
\]
Replacement of all four carbon monoxide molecules is not known with either alkyl or aryl phosphines or with arsines; however, by using phosphorous trichloride it is possible to replace all four carbon monoxide molecules (70).

\[ \text{PCl}_3 + \text{Ni( CO)}_4 \rightarrow \text{Ni( PCl}_3)_4 + \text{CO} + \text{Ni( CO)}_n \text{( PCl}_3)_4-n \]

\[ n = 1, 2, 3. \]

Reaction of the product, with phosphorous trifluoride yields the corresponding tetra(trifluorophosphine)nickel (0), in addition to other products (71).

\[ \text{PF}_3 + \text{Ni( PCl}_3)_4 \rightarrow \text{Ni( PF}_3)_4 + \text{Ni( PCl}_3)_n \text{( PF}_3)_4-n \]

\[ n = 1, 2, 3. \]

It is also possible to replace all four carbon monoxide molecules from nickel tetra Carboxyl by using ditertiary phosphines \( \alpha\)-C\(_6\)H\(_5\)(P(C\(_2\)H\(_5\))\(_2\))\(_2\) and (C\(_6\)H\(_5\))\(_2\)PC\(_2\)H\(_5\)P(C\(_6\)H\(_5\))\(_2\) (72, 73).

\[ \text{Ni( CO)}_4 + \alpha\text{-C}_6\text{H}_5\text{( P(C}_2\text{H}_5)_2)_2} \rightarrow \text{Ni[\alpha\text{-C}_6\text{H}_5\text{( P(C}_2\text{H}_5)_2)_2]}_2 + \text{CO} \]

However, with the "Diarsine" (74) only two carbon monoxide molecules are replaced even under vigorous reflux.

\[ \text{Ni( CO)}_4 + \text{Diarsine} \rightarrow \text{Ni( CO)}_2 \text{ (Diars)} \]

With iron pentacarbonyl, direct substitution of more than two carbon monoxide molecules by monodentate phosphines, arsines or stibines is not known, but by using the chelating ditertiary arsine "Diars", it is possible to replace four carbon monoxide molecules to yield the product \([\text{Fe( CO)( Diars)}_2] \) (75).

\[ \text{Fe( CO)}_5 + \text{"Diars"} \rightarrow [\text{Fe( CO)( Diars)}_2] \]

However, by using olefin derivatives of iron carbonyls, substitution of three
carbon monoxide molecules is possible with monodentate phosphines. Thus the reaction of cycloheptatrienyltricarbonyliron with triphenylphosphine yields tristriphenylphosphinedicarbonyliron (76).

\[ \text{[Fe(CO)}_3\text{(Cycloheptatriene)}] + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow \text{Fe(CO)}_2(\text{P(C}_6\text{H}_5)_3)_3 \]

With carbonyls of chromium, molybdenum and tungsten, it is possible to substitute four carbon monoxide molecules by using the chelating ligands "Diarsine" and "Diphos" (77,78,79,80,81,82).

\[ \text{M(CO)}_6 + \text{Diarsine} \rightarrow \text{M(CO)}_2(\text{Diars})_2 \quad \text{M = Cr, Mo, W} \]

Although total substitution of the carbonyls of Cr, Mo, and W by direct action of phosphines or arsines cannot be affected, products of the formula [M("Diphosphine") ] have been obtained by other methods. Thus naphthenide in [Mo(CH}_3}_2\text{PC}_2\text{H}_4\text{P(CH}_3}_2)_3] can be obtained from di-π-benzenemolybdenum and the diphosphine (83). \[ \text{[W((CH}_3}_2\text{PC}_2\text{H}_4\text{P(CH}_3}_2)_2}_3] \] and the chromium analogue are made by the reduction of the metal trichloride by sodium in the presence of the diphosphine (84,85).

For diphosphines and diarsines of the type \( R}_2\text{E-E-R}_2 (E=\text{As, P, R = alkyl or aryl}), reactions with molybdenum, chromium and tungsten carbonyls yield phosphido and arsenido bridged carbonyl complexes of structure I, involving a metal-metal bond, and diphosphine and diarsine bridged carbonyl complexes of structure II, depending on the conditions of the reaction (86,87,88).

\[ \text{M(CO)}_6 + \text{R}_2\text{EER}_2 \rightarrow (\text{CO})_4\text{M} -> \text{M(CO)}_4 + (\text{OC})_5\text{M} \quad \text{M = Cr, Mo, W} \]

\[ \text{I} \quad \text{II} \]
B. Halide Complexes of the Transition Metals with the "Diarsine"

Using the chelating bidentate ligands "Diars" and "Diphos", it has been possible to prepare a large number of complexes of the transition metal halides in which both usual and unusual oxidation states of metals are stabilized. Nyholm has reacted "diars" with transition metal halides and found that it possesses a marked capacity for affecting electron pairing in transition metal atoms and for stabilization of a wide variety of both common Ni (II) and uncommon Ni (III) and Ni (IV) valency states in addition to forming complexes of unusual coordination numbers. Thus the diarsine reacts with titanium tetrachloride (89) to form an eight coordinate complex \( \text{TiCl}_4(\text{Diars})_2 \), which has been shown by X-ray crystallography to be in the form of a duodecahedron (90).

\[
\text{TiCl}_4 + \text{As(CH}_3\text{)}_2 \rightarrow \text{TiCl}_4(\text{Diars})_2
\]

Similarly, zirconium tetrachloride and hafnium tetrachloride react with the diarsine to yield \( \text{ZrCl}_4(\text{diars})_2 \) and \( \text{[HfCl}_4(\text{diars})_2 \) respectively (89,90).

An analogous compound \( \text{[VCl}_4(\text{diars})_2 \) which possesses an unpaired electron has been shown to be isostructural with the zirconium, hafnium and titanium analogues (89,90).

With metals of Group VII, manganese, technetium and rhenium the diarsine has been found to stabilize a wide variety of valency states. Thus for technetium, Nyholm and Fergusson (91,92) have prepared Tc (III) complexes \( \text{[TcX}_2(\text{Diars})_2 \) \( (X = \text{Cl,Br,I}) \), which may be reversibly reduced to Tc (II) complexes \( \text{[TcX}_2(\text{Diars})_2 \) and oxidized to the Tc (V) complex \( \text{TcCl}_4(\text{Diars})_2\text{Cl} \). Like their technetium analogues, the rhenium (II) complexes \( \text{[ReX}_2(\text{Diars})_2 \) are also produced by the reduction of the corresponding rhenium (III) complexes.
[ReX₂(Diars)_2]X (93). With manganese halides, the diarsine forms the Mn (II) complex [MnX₂(Diars)_2] (in dioxane) possessing five unpaired electrons. A Mn (III) complex is also known, [MnCl₂(Diars)_2H₂O](ClO₄), prepared from manganic acetate, perchloric acid and hydrochloric acid in the presence of the diarsine (94).

\[
\text{Mn (OAc)}_3 + \text{Diarsine} + \text{HClO}_4 \rightarrow [\text{MnCl}_2(\text{Diars})_2\text{H}_2\text{O}](\text{ClO}_4)
\]

For the metals of Group VIII diarsine has also been found to stabilize various oxidation states of these metals. Some of the compounds reported with the diarsine are: [FeX₂(Diars)_2] (93, 75), prepared from ferrous halide and the diarsine. Ferric chloride forms the complex [FeCl₃(Diars)_2] [FeCl₄], which can be oxidized to the Fe (IV) complex [Fe^{IV}Cl₂(Diars)_2] [Fe^{III}Cl₄] (96). The complexes [MX₂(Diars)_2] where M = Os or Ru (97, 98) are readily oxidized to [MX₂(Diars)_2]X, having one unpaired electron. Further oxidation of the Os (III) complex yields [OsX₂(Diars)_2](ClO₄)₂ but the corresponding Ru IV complex has not been obtained. With nickel halides, the diarsine stabilizes the (II, III and IV) oxidation states. The Ni (II) complex [NiX₂(Diars)_2] (99) can be readily oxidized to the Ni (III) complex [NiX₂(Diars)_2]X. For Ni (IV) there is only one compound isolated; the complex [NiCl₂(Diars)_2]Cl is oxidized by nitric acid in the presence of perchloric acid to yield [NiCl₂(Diars)_2](ClO₄)₂ (100). Similar types of complexes with Pd (II), Pt (II), (IV) have also been obtained.

The diarsine also forms chelate complexes with cuprous, argentous and aurous halides. Thus the complexes [Cu(Diars)_2]X, [Cu(diars)_2] [CuX₂] (101), [Ag(Diars)_2]X, [Ag(Diars)_2] [AgX₂] (102), and [Au(Diars)_2]X (103) are formed from the metal halide and diarsine. The latter compound of gold [Au(Diars)_2]X can be oxidized to a gold (III) complex [Au(Diars)_2]X₃-. 
have also been described.

The present investigation was initiated for the purpose of studying the chemical and physical properties of the complexes obtained by reacting the new ditertiary arsine-1,2-dimethylarsinotetrafluorocyclobutene, (Difars) with a variety of transition metal halides and carbonyls. In view of the work of Nyholm and coworkers with the "Diars" described above, it was of interest to study the effect of the tetrafluorocyclobutene ring on the availability of the arsenic lone pair electrons for coordination with metal atoms. The results of these studies are presented in the following experimental and discussion sections.
The general experimental technique and apparatus were described in Chapter 1, page 7.

A. Reaction with Metal Carbonyls

1. Reaction with Molybdenum Hexacarbonyl (a) mild conditions. Molybdenum carbonyl (0.5 g) and the diarsine (0.4 g) were heated to gentle reflux in tetrahydrofuran (40 ml). After two hours, the solution was dark blue and the reaction was stopped. The product, a greenish blue needle-like crystalline solid, was recrystallized from tetrahydrofuran and identified as 1,2-dimethylarsinotetrafluorocyclobutenemolybedenum tetracarbonyl m.p. 147°. Anal. Found: C, 27.2; H, 2.42; As, 27.8; F, 13.8; Mo 17.9%. Calc. for C_{12}H_{12}As_{2}F_{4}O_{4}Mo: C, 26.6; H, 2.22; As, 27.7; F, 14.0; Mo, 17.9%. (M.W. Found: 542. Calc. 511). Infrared spectrum (KBr pellet): 2940W, 2930W, 2025VS, 1940VS, 1930VS, 1918VS, 1892VS, 1420S, 1390VW, 1315VW, 1296VS, 1273VS, 1264VS, 1234VS, 1004VS, 969VW, 906VS, 888W, 874VS cm^{-1}. Nmr. spectra: the ^{1}H nmr. spectrum showed a single peak at -1.12 p.p.m. and the ^{19}F spectrum showed a peak at 109.5 p.p.m. (b). Both spectra were measured in nitrobenzene solution.

(b). Reaction under more vigorous conditions. Excess diarsine (3.5 g) and molybedenum carbonyl (1.5 g) were heated to a vigorous reflux in tetrahydrofuran. After twelve hours a red microcrystalline deposit was observed, and after thirty-six hours the red solid had changed to a pink form. The pink solid was insoluble in a wide range of polar and non-polar solvents. Infrared spectrum (dried crude product) (KBr pellet): 2920S, 1760W, 1712S, 1650S, 1405S, 1170S, 1158VS, 1134S, 1125S, 800VS (broad), 690 cm^{-1}. However, the pink solid showed a limited solubility in dimethylsulfoxide and was recrystallized from it accompanied with some decomposition. On heating
the pink solid underwent a gradual colour change from the pink to a blue form, which became darker as the temperature was raised above 300°. Anal. Found: C, 12.3; H, 2.65; As, 25.6; F, 9.59%. This analysis, however, cannot be related to either the tetrasubstituted or the hexasubstituted derivatives of molybdenum carbonyl, which require much higher values for C, H, As, F.

Infrared spectrum (KBr pellet): 2900S, 1710W, 1635VW, 1448S, 1403VS, 1370W, 1348VW, 1260S, 1178VW, 1051VS, 1024VS, 965VS, 945S, 910VS, 810VS (broad), 725VS, 690VS, 640W cm⁻¹.

On exposure to air for two days at 20°, the pink form changes to a blue form, which can also be obtained by heating the pink form in dimethylsulfoxide above 80° for five minutes. The blue solid was recrystallized from ethanol m.p. 321-2° (decomp.) Anal. Found: C, 12.2; H, 3.03; As, 24.3; F, 2.89%. This analysis also cannot be related to the tetrasubstituted or the hexasubstituted derivatives which require much higher values of C, H, As, F. Infrared spectrum (KBr pellet): 2930S, 1710VW, 1658S, 1407S, 1217S, 1115S, 840VS (broad), 658VW cm⁻¹.

2. Reaction with Nickel Tetracarbonyl. The diarsine (1.5 g) and an excess of nickel carbonyl (5.0 g) were left in a benzene solution (40 ml) at 20°. After twelve hours a small quantity of yellow solid separated out of the solution, and after ten days a sufficient quantity of this solid was obtained for chemical investigations. The product, after drying under vacuum, was a greyish yellow amorphous powder m.p. >360 which was insoluble in a wide range of polar and non-polar solvents. Anal. Found: C, 16.72; H, 3.48; As, 15.2; F, 11.4; Ni, 20.8%. This analysis cannot be related to either the disubstituted or tetrasubstituted derivatives of nickel carbonyl, which require much higher values of C, H, As, F. Infrared spectrum (KBr pellet): 3300VS, (broad), 1760S, 1600VS, 1500S, 1410S, 1290S, 1242VW, 1140S,
Attempts to purify the solid by vacuum sublimation were unsuccessful. The solid was then washed with acetone and dried under vacuum. Anal. Found. C, 17.7; H, 3.29; As, 18.0; F, 9.14%. This analysis also cannot be reconciled with the disubstituted or tetrasubstituted derivatives which require much higher values of C, H, As, F. Infrared spectrum (KBr pellet): 3400VS, 1765S, 1613VS, 1410S, 1288W, 1244S, 1163S, 983W, 825VS, cm$^{-1}$.

3. Reaction with Iron pentacarbonyl. The diarsine (2.5 g) and an excess of iron pentacarbonyl (8.0 g) were refluxed in benzene (50 ml) (40 hours). The product, a red solid, was sublimed under vacuum at 150-180°, yielding reddish-orange crystals, which were then recrystallized from acetone and identified as 1,2-dimethylarsino-tetrafluorocyclobuteneiron tricarbonyl, m.p. 220°. Anal. Found: C, 27.7; H, 2.41; As, 31.9; F, 16.3%. Calc. for C$_{11}$H$_{12}$As$_2$F$_4$FeO$_3$: C, 27.8; H, 2.53; As, 31.6; F, 16.6%. Infrared spectrum (KBr pellet): 2960VW, 2063VS, 2015VS, 1995VS, 1988VS, 1935VS, 1420W, 1293VS, 1275S, 1260VW, 1250W, 1215S, 1100VS, 1092VS, 904S, 871W, 825VS, 812S, 650S, 625W cm$^{-1}$.

B. Reaction with Metal Halides

1. Reaction with Ammonium hexachloroplatinate. An acetone solution (10 ml) of the diarsine (0.7 g) was added to an aqueous solution (50 ml) of ammonium hexachloroplatinate (0.2 g) at 20°. The reddish-yellow colour of the ammonium hexachloroplatinate immediately disappeared and a yellow microcrystalline solid precipitated out. The acetone was evaporated off and the yellow solid was filtered from the aqueous solution and heated under vacuum in a rotary evaporator at 95°. After one hour, the yellow colour disappeared and a white microcrystalline solid was obtained which was...
recrystallized from acetone, m.p. 286.8° (decomposition). Analysis indicates that the empirical formula of the solid was approximately [(Difars) Pt Cl₂]

\[ \text{C}_8\text{H}_{12}\text{As}_2\text{Cl}_2\text{F}_4\text{Pt}. \]

Anal. Found: C, 16.7; H, 2.14; As, 23.8; Cl, 13.6; F, 12.6; Pt, 32.4%. Calc. for \( \text{C}_8\text{H}_{12}\text{As}_2\text{Cl}_2\text{F}_4\text{Pt} \): C, 16.0; H, 2.0; As, 25.0; Cl, 11.8; F, 12.7; Pt, 32.5%. Infrared spectrum (KBr pellet): 3040W, 2940W, 1645W, 1408S, 1276W, 1237S, 1139VS, 1124VS, 930S, 895S, 828S, 810S, 695W, cm⁻¹. Nmr. spectra: the \(^1\text{H}\) spectrum showed a single peak at -1.60 p.p.m. and the \(^19\text{F}\) spectrum showed a single peak at 109.5 p.p.m.

(b). Both spectra were measured in benzonitrile solution due to insolubility of the substance in acetone.

2. Reaction with Potassium Tetrachloroplatinite. An acetone solution (8 ml) of the diarsine (0.5 g) was added to an aqueous solution (45 ml) of potassium tetrachloroplatinite (0.4 g). The reddish brown colour of the potassium tetrachloroplatinite immediately disappeared and a reddish yellow microcrystalline solid precipitated out. The crystals were filtered, and heated under vacuum in a rotary evaporator at 95°. After one hour, the reddish yellow colour disappeared, and a white microcrystalline solid was obtained, which was recrystallized from acetone, m.p. 285-7 (decomposition).

Analysis indicates that the empirical formula of this compound was [(Difars) Pt Cl₂] \( \text{C}_8\text{H}_{12}\text{As}_2\text{Cl}_2\text{F}_4\text{Pt}. \)

Calculated for \( \text{C}_8\text{H}_{12}\text{As}_2\text{Cl}_2\text{F}_4\text{Pt} \): C, 16.0; H, 2.0; As, 25.0; Cl, 11.8%. Infrared spectrum (KBr pellet): 3030W, 2940W, 1410S, 1333VW, 1306VS, 1276W, 1233VS, 1142S, 1125VS, 893VS, 827VS, 810S, 695S cm⁻¹. Nmr. spectra: the \(^1\text{H}\) spectrum showed two overlapping peaks of equal intensity at -1.38 and -1.53 ppm, both spectra were measured in nitrobenzene solution due to insolubility of the substance in acetone.
3. Reaction with Platinum Tetrachloride. The diarsine (4.3 g) was added to an acetone solution (40 ml) of platinum tetrachloride (1.1 g). The red colour of the platinum tetrachloride immediately disappeared and a yellow microcrystalline solid precipitated out. The yellow solid redissolved on refluxing after two hours producing a colourless solution. The solution was then refluxed for a further ten hours, evaporated to dryness and a white microcrystalline solid was obtained which was recrystallized from acetone m.p. 286-7° (decomposition). Analysis indicates that this solid has the approximate empirical formula \([\text{Difars Pt Cl}_2 \text{C}_8\text{H}_1_2\text{As}_2\text{Cl}_2\text{F}_4\text{Pt}]\). Anal. Found: C, 19.14; H, 2.42; As, 25.4; Cl, 11.8; F, 12.0; Pt, 28.8%. M.W. 600. Calc. for \(\text{C}_8\text{H}_1_2\text{As}_2\text{Cl}_2\text{F}_4\text{Pt}\): C, 16.0; As, 25.0; Cl, 11.8; F, 12.7; Pt, 32.5%. Infrared spectrum (KBr pellet): 3020W, 2940W, 1708VS, 1418S, 1360W, 1305VS, 1278VW, 1238VS, 1231VS, 1127VS, (broad), 930VS, 890VS, 829VS, 810VS, 696S cm\(^{-1}\).

4. Reaction with Rhodium Trichloride Trihydrate. The diarsine (4.5 g) was added to an ethanol solution (55 ml) of rhodium trichloride trihydrate (1.0 g). On refluxing for a half hour, the solution changed from reddish orange to yellow. The solution was refluxed overnight, then evaporated to dryness and a yellow microcrystalline solid was obtained, which was recrystallized from ethanol and identified as dichlorodi-(1,2-dimethylarsino-tetrafluorocyclobutene)-rhodium (III) chloride. Anal. Found: C, 21.1; H, 2.89; As, 34.4; Cl, 12.3; F, 17.4; Rh, 11.5%. Calc. for \(\text{C}_8\text{H}_1_2\text{As}_2\text{Cl}_2\text{F}_8\text{Rh}\): C, 22.0; H, 2.74; As, 34.3; Cl, 12.1; F, 17.4; Rh, 11.5%. On heating, the solid changes from yellow to orange at 200° and chars at higher temperatures. Infrared spectrum (KBr pellet): 2900W, 1633W, 1415S, 1306VS, 1268VW, 1230VS, 1140VS, 1131VS, 925S, 878VS, 824W, 815S, 690S cm\(^{-1}\). Nmr. spectra: the \(^1\)H
spectrum showed a single peak at -2.06 p.p.m. and the $^{19}$F spectrum showed a single peak at 109.5 p.p.m. Both spectra were measured in sym-1,3-dichloro-tetrafluoro-2, 2-deutero-propanediol (C1CF$_2$QD – C – CF$_2$Cl), due to insolubility of the solid in ethanol.

5. **Reaction with Ammonium Tetrachloropalladate.** An acetone solution (6 ml) of the diarsine (0.8 g) was added to an aqueous solution (40 ml) of ammonium tetrachloropalladate (0.5 g). The reddish brown colour of the ammonium tetrachloropalladate immediately disappeared and red crystals precipitated out. The crystals were filtered, recrystallized from acetone then from chloroform, and dried under vacuum where their colour changed from red to yellow. The product, a yellow crystalline substance, was identified as 1,2-dimethylarsinotetrafluorocyclobutenepalladium dichloride m.p. 220°. Anal. Found: C, 19.4; H, 2.61; As, 29.3; Cl, 13.9; F, 14.0; Pd, 20.8%. Calc. for C$_8$H$_{12}$As$_2$Cl$_2$F$_4$Pd: C, 18.8; H, 2.35; As, 29.4; Cl, 13.9; F, 14.9; Pd, 20.7%. (M.W. Found 560 Calc. 511). Infrared spectrum (KBr pellet): 2930VW, 1630VW, 1415S, 1303VS, 1270S, 1224VS, 1115VS, 917VS, 882VS, 805VS, 700W cm$^{-1}$.

6. **Reaction with Palladium Dichloride.** The diarsine (1.5 g) was added to an acetone solution (20 ml) of palladium dichloride (0.5 g). On heating to a gentle reflux, the reddish brown colour of palladium dichloride immediately disappeared and red crystals precipitated out. The crystals were filtered, recrystallized from acetone, then from chloroform, and dried under vacuum and were shown to be identical with the product obtained from ammonium tetrachloropalladate and the diarsine, by means of m.p., infrared spectrum and chemical analysis.
7. **Reaction with Mercuric Chloride.** (a) An acetone solution (25 ml) of mercuric chloride (0.5 g) and the diarsine (0.9 g) were left at 20° and after one hour, a white crystalline solid separated out. After forty hours the white crystalline solid was filtered and recrystallized from acetone, m.p. 123°, and identified as 1,2-dimethylarsinetetrafluorocyclobutenemercuric chloride. Anal. Found: C, 13.8; H, 2.42; As, 24.2; Cl, 12.9; F, 9.50; Hg, 37.0%. Calc. for C₈H₁₂As₂Cl₂F₄Hg: C, 15.8; H, 1.98; As, 24.8; Cl, 11.6; F, 12.6; Hg, 33.1%. Infrared spectrum (KBr pellet): 3040W, 2950W, 1414S, 1307VS, 1280VS, 1265S, 1230VS, 1217S, 1127VS, 925S, 895VS, 806VS, 697S cm⁻¹.

(b). **Reaction Under Vigorous Conditions.** The diarsine (2.0 g) and mercuric chloride (2.0 g) were refluxed in acetone, a white crystalline solid quickly precipitated out. After ten hours the solid was filtered, and recrystallized from acetone, m.p. 215°. Anal. Found: C, 13.4; H, 1.65; As 18.8; Cl, 22.4; F, 5.83; Hg, 38.0%. This analysis cannot be correlated with the 1:1 addition product, which requires higher values of C, H, As, F. Infrared spectrum (KBr pellet): 2920VW, 1407S, 1300 VS, 1224VS, 1120VS, 920VS, 882VS, 797VS, 700S cm⁻¹.

8. **Reaction with Cadmium Bromide.** The diarsine (1.8 g) and cadmium bromide (1.1 g) were refluxed in ethanol for ten hours. The product, a white crystalline solid, was recrystallized from acetone, m.p. >360°, and could not be identified on the basis of chemical analysis due to loss of the diarsine on standing at 20°. However, from the similarity of its infrared spectrum to the spectra of the corresponding mercury, platinum and palladium compounds, the compound is suggested to be 1,2-dimethylarsinetetrafluorocyclobutene cadmium bromide. Infrared spectrum (KBr pellet):
9. Miscellaneous Reactions. The diarsine was refluxed with solutions of nickel nitrate, nickel chloride in ethanol, acetone, dilute and glacial acetic acid for two days and no reaction was observed. With nickel nitrate in refluxing dioxane, a red colour, indicative of complex formation was observed immediately on addition of the diarsine, however no isolable products were obtained. The diarsine and zinc chloride failed to react in refluxing acetone (40 hours). Attempts to complex the diarsine with silver iodide in saturated potassium iodide solution (reflux two days) were unsuccessful. With ferric chloride hexahydrate and the diarsine in ethanol, reduction appeared to occur on refluxing (40 hours) yielding a green solution indicative of ferrous chloride. Ferrous chloride tetrahydrate and the diarsine in ethanol failed to yield any isolable products even after refluxing for one week, although a slight red colour was imparted to the solution.
DISCUSSION

A. Reactions of 1,2-Dimethylarsinotetrafluorocyclobutene (Difars) with Metal Carbonyls

Table I lists the products obtained from the reactions of Difars and o-phenylenebisdimethylarsine (Diars) with metal carbonyls.

**TABLE I**

Products from the reactions of Difars and Diars with Metal Carbonyls

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Carbonyl</th>
<th>Product</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Difars</td>
<td>Fe(CO)$_5$</td>
<td>(Difars)Fe(CO)$_3$</td>
<td>220</td>
</tr>
<tr>
<td>Diars</td>
<td>Fe(CO)$_5$</td>
<td>(Diars)Fe(CO)$_3$, (Diars)$_2$Fe(CO)</td>
<td>131, 150$^a$</td>
</tr>
<tr>
<td>Difars</td>
<td>Mo(CO)$_6$</td>
<td>(Difars)Mo(CO)$_4$</td>
<td>147</td>
</tr>
<tr>
<td>Diars</td>
<td>Mo(CO)$_6$</td>
<td>(Diars)Mo(CO)$_4$, (Diars)$_2$Mo(CO)$_2$</td>
<td>158, 231$^b$</td>
</tr>
<tr>
<td>Difars</td>
<td>Ni(CO)$_4$</td>
<td>Ni(Difars)$_2$</td>
<td>&gt;360</td>
</tr>
<tr>
<td>Diars</td>
<td>Ni(CO)$_4$</td>
<td>(Diars)Ni(CO)$_2$</td>
<td>125$^c$</td>
</tr>
</tbody>
</table>

(a) See reference (75)
(b) See reference (81, 82)
(c) See reference (74)

Suggested Structures of the New Compounds

Difars reacts with iron pentacarbonyl in refluxing benzene to yield a red crystalline solid of empirical formula Fe(Difars)(CO)$_3$. 
From the empirical formula it is possible to suggest four possible structures, involving a five coordinate iron (0) complex with two chelating arsenic atoms. For a five coordinate complex, two types of geometrical configurations are possible, trigonal bipyramid (structures A and B) and square base pyramid (structures C and D).

Structure A, involves coordination of the arsenic atoms at equatorial positions of the pseudo trigonal bipyramidal structure of the complex. In
structure B, the arsenic atoms occupy equatorial and axial positions. Structure C, involves coordination of the arsenic atoms at equatorial positions of a square based pyramid and in Structure D, the arsenic atoms occupy equatorial and apical positions. The infrared spectrum of this complex which shows five strong carbonyl bands could not be correlated with any one of the structures A, B, C or D, each one of which should show a maximum of three carbonyl bands in its infrared spectrum (110). It is possible that this complex is either a mixture of the isomers A, B, C or D, or an entirely new type of compound or that the chemical analysis is not reliable. In view of these difficulties and the scarcity of information concerning five coordinate iron complexes, it seemed worthwhile to determine the crystal structure of this complex. This would also give information concerning the geometry of the chelating ligand "difars" in its coordinated state.

After the above complex had been standing for six months, it was sublimed under vacuum and recrystallized from acetone and its crystal structure determined. The molecular weights from X-ray density measurements (607) and mass spectrometry (612) did not agree with the original formulation of the complex as \([\text{Fe(CO)}_3\text{difars}]\) m.w. (473). The X-ray crystal structure (109) showed that the new complex could be correctly formulated as \([(\text{Fe(CO)}_3)_2\text{difars}]\) m.w. (614), which is in excellent agreement with the experimental molecular weights. The structure of this new complex is shown below.
This new complex, contains two arsenic atoms and two iron atoms, which are tetrahedrally arranged. The structure is unusual in that it contains one iron atom which is octahedrally coordinated while the other is situated in the middle of a trigonal bipyramid.

The complex obtained from the reaction of difars with molybdenum hexacarbonyl is formulated as \([\text{Mo(CO)}_6 \text{Difars}]\).

\[
\text{Mo(CO)}_6 + (\text{CH}_3)_2\text{As} + (\text{As(CH}_3)_2)(\text{CH}_3)_2 \rightarrow (\text{CH}_3)_2\text{As} + \text{As(CH}_3)_2 + \text{Mo(CO)}_4
\]

From symmetry considerations of the geometry of this complex, it is possible to suggest only one structure in which the arsenic atoms occupy equatorial positions of the octahedron.

Under more vigorous conditions, the reaction of difars with molybdenum carbonyl (reflux 36 hours), yields a pink microcrystalline solid, which is insoluble in a wide range of polar and non-polar solvents. The yellow solid, obtained from the reaction of nickel carbonyl and difars, is also insoluble in polar and non-polar solvents. The infrared spectra of both solids, show an absence of carbonyl absorptions, and therefore it is possible to suggest formulations for the complexes as \([\text{Mo(Difars)}_3]\) and \([\text{Ni(Difars)}_2]\) which involves the total substitution of the carbonyls on the molybdenum and
nickel by arsine groups respectively. The chemical analysis of both solids cannot be reconciled with the above formulations, but this discrepancy, however, may be due to difficulty in completely decomposing the complexes, thus leading to the observed low values of carbon, hydrogen, arsenic and fluorine.

B. Reactions of Difars with Metal Halides

1,2-Dimethylarsinotetrafluorocyclobutene "Difars" forms complexes of the type \([M \text{ (Difars)}X_n]\) when treated with metal halides. Table II, summarizes the results of a number of experiments of this sort.

**TABLE II**

<table>
<thead>
<tr>
<th>Metal Halide</th>
<th>Product</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{PdCl}_2)</td>
<td>([\text{Pd(Difars)}\text{Cl}_2])</td>
<td>220</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{PdCl}_4)</td>
<td>([\text{Pd(Difars)}\text{Cl}_2])</td>
<td>220</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{PtCl}_6)</td>
<td>([\text{Pt(Difars)}\text{Cl}_2])</td>
<td>286-8</td>
</tr>
<tr>
<td>(\text{K}_2\text{PtCl}_4)</td>
<td>([\text{Pt(Difars)}\text{Cl}_2])</td>
<td>285-7</td>
</tr>
<tr>
<td>(\text{PtCl}_4)</td>
<td>([\text{Pt(Difars)}\text{Cl}_2])</td>
<td>286-7</td>
</tr>
<tr>
<td>(\text{HgCl}_2)</td>
<td>([\text{Hg(Difars)}\text{Cl}_2])</td>
<td>123</td>
</tr>
<tr>
<td>(\text{CdBr}_2)</td>
<td>([\text{Cd(Difars)}\text{Br}_2])</td>
<td>&gt;360</td>
</tr>
<tr>
<td>(\text{RhCl}_3\cdot 3\text{H}_2\text{O})</td>
<td>([\text{Rh(Difars)}_2\text{Cl}_3])</td>
<td>charrs</td>
</tr>
</tbody>
</table>

C. Structures and Spectroscopic Properties of the New Compounds

The infrared spectra of the compounds show that the cyclobutene ring is still present in each compound. Table III, shows the main bands of the infrared spectra of these compounds and as would be expected, there are very
close correlations.

TABLE III

Infrared Data for Complexes Obtained from the Reaction of Difars with Transition Metal Compounds

<table>
<thead>
<tr>
<th>Difars</th>
<th>(NH₄)₂PtCl₆</th>
<th>K₂PtCl₄</th>
<th>PtCl₄(a)</th>
<th>PtCl₄(b)</th>
<th>(NH₄)₂PdCl₄</th>
<th>RhCl₃</th>
<th>HgCl₂</th>
<th>CdBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1420</td>
<td>1408</td>
<td>1410</td>
<td>1418</td>
<td>1410</td>
<td>1415</td>
<td>1415</td>
<td>1414</td>
<td>1420</td>
</tr>
<tr>
<td>1300</td>
<td>1310</td>
<td>1306</td>
<td>1305</td>
<td>1305</td>
<td>1303</td>
<td>1306</td>
<td>1307</td>
<td>1305</td>
</tr>
<tr>
<td>1263</td>
<td>1276</td>
<td>1276</td>
<td>1278</td>
<td>1275</td>
<td>1270</td>
<td>1268</td>
<td>1265</td>
<td>1263</td>
</tr>
<tr>
<td>1225</td>
<td>1237</td>
<td>1233</td>
<td>1231</td>
<td>1235</td>
<td>1224</td>
<td>1230</td>
<td>1230</td>
<td>1225</td>
</tr>
<tr>
<td>1154</td>
<td>1139</td>
<td>1142</td>
<td>1127*</td>
<td>1142</td>
<td>1115*</td>
<td>1140</td>
<td>1152</td>
<td></td>
</tr>
<tr>
<td>1130</td>
<td>1124</td>
<td>1125</td>
<td>1127</td>
<td></td>
<td></td>
<td>1131</td>
<td>1127</td>
<td>1133</td>
</tr>
<tr>
<td>1084</td>
<td>930</td>
<td>928</td>
<td>930</td>
<td>932</td>
<td>917</td>
<td>925</td>
<td>925</td>
<td></td>
</tr>
<tr>
<td>897</td>
<td>895</td>
<td>893</td>
<td>890</td>
<td>894</td>
<td>882</td>
<td>878</td>
<td>895</td>
<td>900</td>
</tr>
<tr>
<td>803</td>
<td>810</td>
<td>810</td>
<td>810</td>
<td>810</td>
<td>805</td>
<td>815</td>
<td>806</td>
<td>800</td>
</tr>
<tr>
<td>695</td>
<td>695</td>
<td>696</td>
<td>695</td>
<td></td>
<td>700</td>
<td>690</td>
<td>697</td>
<td></td>
</tr>
</tbody>
</table>

(a) (Difars) PtCl₂ (acetone)ₓ

(b) (Difars) PtCl₂

*Main bands only

(broad)

Difars reacts with platinum tetrachloride, ammonium hexachloroplatinate and potassium hexachloroplatinate to yield complexes of approximate empirical formula [Pt(Difars)Cl₂].

\[
\text{PtCl}_4^+ + \text{As(}\text{CH}_3\text{)}_2 \xrightarrow{\text{As(}\text{CH}_3\text{)}_2} \text{[Pt(Difars)Cl}_2\text{]} (1)
\]
It is interesting to note that reduction of Pt(IV) to Pt(II) occurs in reactions one and two. The complexes obtained from the three reactions show only one peak in the $^{19}$F spectra, corresponding to the equivalent CF$_2$ groups of the cyclobutene ring. Complexes from reaction two and three are non-conducting in nitrobenzene and have identical infrared spectra. The infrared spectrum of the complex from reaction one is the same as the other two, but in addition, it has an intense peak in the carbonyl region at 1708 cm$^{-1}$. The complex from reaction three shows two overlapping peaks in its $^1$H nmr. spectrum indicative of two different types of dimethylarsino groups; whereas the other two complexes show only one peak. X-ray powder photographs of all three compounds are different.

From the above experimental data, in conjunction with molecular weights, it is possible to rule out a structure of the type [Pt(Difars)$_2$] [PtCl$_4$], since the complexes are non-conducting in nitrobenzene. Structures for the complexes obtained from the three reactions are presented below, together with supporting experimental data.

A molecular species involving four coordinate platinum is suggested for the structure of the complex obtained from reaction two. In this structure the CF$_2$ groups of the cyclobutene ring and the dimethylarsino groups are equivalent and thus account for the single peak in the $^{19}$F nmr.
and $^1\text{H}$ nmr spectra.

The covalent nature of the platinum-chlorine bonds of the complex in this structure account for its non-conductance in nitrobenzene. The presence of the cyclobutene ring is also corroborated by its infrared spectrum.

For the complex obtained from reaction three, a covalent chlorine bridged complex is suggested. In this structure there are two different types of dimethylarsino groups, one coordinated and the other is free, thus accounting for the two overlapping peaks in the $^1\text{H}$ nmr spectrum. The covalent nature of the platinum chlorine bond in this structure accounts for the non conducting behaviour of the complex in nitrobenzene. This complex has a similar melting point to the above complex from reaction two, and it is possible to suggest that this complex breaks down on heating to the monomeric four coordinate complex.
For the complex obtained from reaction one, a six coordinate structure can be suggested, involving coordination by acetone, to account for the intense band in the carbonyl region at 1708 cm\(^{-1}\). This compound gradually loses acetone on standing at 20°, and after six months the peak at 1708 cm\(^{-1}\) has almost entirely disappeared. On heating to 130° (4 hours), the peak at 1708 cm\(^{-1}\) is completely removed, and the infrared spectrum is identical with the spectra of the product obtained from reaction two.

Nyholm and coworkers (107) have studied the reactions of the ditertiary arsine "Diars", with platinum (II) salts, and found that 1:1 and 2:1 complexes are formed. Thus with sodium platinite and "Diars", the compounds [Pt(Diars)\(_2\)] [PtCl\(_4\)]; [Pt(Diars)Cl\(_2\)]; and [Pt(Diars)\(_2\)Cl\(_2\)] have been isolated.

\[
\text{As(CH}_3\text{)}_2 + \text{Na}_2\text{PtCl}_4 \rightarrow [\text{Pt(Diars)}] \text{[PtCl}_4\text{]} \xrightarrow{\text{heating}} [\text{Pt(Diars)Cl}_2] \\
\downarrow \text{Diars} \\
[\text{Pt(Diars)}] \text{Cl}_2
\]

Chatt and Mann (108) have prepared 1:1 and 2:1 complexes of the types [PdCl\(_2\)(Diars)] and [PdCl\(_2\)(Diars)\(_2\)] from the reaction of "Diars" with palladium (II) salts. They claim that on mixing a palladium (II) salt and "Diars" the salt [Pd(Diars)\(_2\)] (PdCl\(_4\)) is first formed, which breaks down on heating to the 1:1 complex, the latter coordinating with further "Diars" to form the 2:1 complex.

\[
\text{As(CH}_3\text{)}_2 + (\text{NH}_4\text{)}_2\text{PdCl}_4 \rightarrow [\text{Pd(Diars)}] \text{[PdCl}_4\text{]} \xrightarrow{\text{heat}} [\text{Pd(Diars)Cl}_2] \\
\downarrow \text{Diars} \\
[\text{Pd(Diars)}] \text{Cl}_2
\]
In the present investigation, in the reaction of "difars" with palladium chloride or ammonium tetrachloropalladate, only \([\text{Pd}(\text{difars})\text{Cl}_2]\) was obtained. A structure involving four coordinate covalent palladium is suggested for this complex to account for its molecular weight (Found: 560. Calc. 511).

The structure of the complex obtained from the reaction of difars with rhodium trichloride trihydrate is suggested as

\[ \text{RhCl}_3 \cdot 3\text{H}_2\text{O} + (\text{CH}_3)_2\text{As} \rightarrow \text{Rh} \begin{array}{c} \text{Cl}_2 \\ \text{As} \\ (\text{CH}_3)_2 \end{array} \]

in view of an analogous compound obtained by Nyholm and coworkers (106) using the ditertiary arsine "Diars". These authors suggest the structure of the complex obtained from "Diars" on the basis of its behaviour as a uni-univalent electrolyte in nitrobenzene.

For the complex obtained from difars and mercuric chloride a covalent structure involving four coordinate mercury is suggested.

\[ \text{F}_2 \begin{array}{c} \text{As} \\ (\text{CH}_3)_2 \end{array} \rightarrow \text{Hg} \begin{array}{c} \text{Cl} \\ \text{F}_2 \end{array} \]
A similar structure is suggested for the complex obtained from the reaction of cadmium dibromide and difars.

\[
\text{Cd} \quad \text{(CH}_3\text{)}_2 \quad \text{As} \quad \text{F}_2
\]

The chemical analysis of the mercury complex is approximately \([\text{Hg(Difars)Cl}_2]\), but the mercury and chlorine percentages are slightly high. This may be due to either a loss of difars from the complex during recrystallization from acetone, or incomplete coordination resulting in some free mercuric chloride. The structure of this complex, however, is also indicated by the similarity of its infrared spectrum to the corresponding platinum and palladium complexes (See Table III). Under more vigorous conditions, difars and mercuric chloride yield a white crystalline complex m.p. 215°, whose chemical analysis indicates that it may be of a polymeric nature.

The chemical analysis of the complex obtained from the reaction of difars and cadmium bromide indicates that nearly all of the difars is lost during recrystallization from ethanol. The infrared evidence (Table III) supports its formulation.

As mentioned in the introduction, Nyholm and coworkers have used the "diars" to complex many first row transition metal halides (15). But attempts to obtain complexes of "difars" with the first row transition metal halides have been unsuccessful. For example, with nickel chloride and nitrate no reaction was observed with difars in ethanol, acetone, glacial and dilute acetic acid even after refluxing for many days. However, in dioxane, nickel nitrate does appear to complex, a red colour developed
immediately upon addition of the "difars" but no isolable product could be obtained.

In conclusion, it appears that although difars is not as versatile a coordinating ligand as "diars" with transition metal halides, with metal carbonyls it is as good if not better than "Diars".


33. Infrared spectra available in laboratory.


