ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to his major professor, Dr. Lewis C. Sams, for his advice and encouragement during the entire period of his graduate studies. The author is also grateful to his graduate committee, Drs. Lyman R. Caswell, Carlton T. Wendel, Walter Hamilton, and James E. Hardcastle for their suggestions in the preparation of this dissertation.

The author wishes to express his appreciation to the Texas Woman's University for financial support in the form of teaching and research assistantships.

The author wishes to express his appreciation to his typist, Thelma Ayers, for her assistance in the preparation of this dissertation.

A special acknowledgment is extended to his wife, Giti Emtiazi, for her courage and patience during the period of his graduate studies.

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CHAPTER I

INTRODUCTION

There have been several reports describing the preparation of iodine (III) and iodine (V) compounds (1-4) of the types RIF_2 (R=CF_3 and other C_nF_{2n+1} groups, C_6F_5, or Ph and substituted Ph groups) and RIF_4 (R=C_nF_{2n+1} where n > 2, Ph, or $C_6H_4CH_3$). Perfluoroalkyliodine (V) tetrafluorides are of interest in connection with a study of substituted derivatives of high oxidation state fluorides. The R_F group may be used as an NMR probe to follow the replacement of fluorine bound to iodine (V) by other ligands. Preparation and properties of trifluoromethyliodine (V) tetrafluoride and an NMR study of the replacement of fluoro-by methoxo-ligands has been reported (5). Trifluoromethyliodide has been oxidized by chlorine trifluoride in $\underline{n}$-C_6F_{14} at -78°C to give trifluoromethyliodine (V) tetrafluoride. Evidence for the formation of trifluoromethyliodine (III) difluoride has also been obtained. CF_3IF_4 decomposes readily at 20°C but is more stable in this respect than CF_3IF_2. Other R_FIF_4 (R_F= C_2F_5, $(CF_3)_2CF$, or n-C_4F_9) compounds are more stable with respect to decomposition than CF_3IF_4. Trifluoromethyl-

iodine (V) tetrafluoride (CF_3IF_4) reacts (6,7) with methylmethoxysilanes (Me_3SiOMe or $Me_2Si(OMe)_2$) at 20°C to give $CF_3IF_{4-n}(OMe)_n$ (n=1-4).

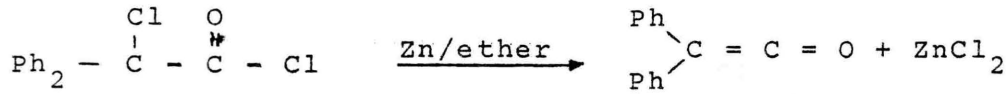
There have been reports describing the preparation of chlorine (III), chlorine (V), bromine (III) and bromine (V) compounds of the types $RClF_2$, $RClF_4$, $RBrF_2$ and $RBrF_4$ where R=C_6F_5 group. Pentafluorophenylchlorine (III) difluoride ($C_6F_5ClF_2$), pentafluorophenylchlorine (V) tetrafluoride ($C_6F_5ClF_4$), pentafluorophenylbromine (III) difluoride ($C_6F_5BrF_2$) and pentafluoro-bromine (V) tetrafluoride ($C_6F_5BrF_4$) have been prepared (8-11) by the oxidation of pentafluorophenyl chloride or bromide using elemental fluorine, chlorine trifluoride as fluorinating agents.

No aliphatic interhalogen compounds containing either chlorine or bromine (R_FXF_2 or R_FXF_4 where R_F= C_nF_{2n+1} and X=Cl or Br) have been synthesized. It should be possible to prepare perfluoroalkylbromine (V) tetrafluoride (R_FBrF_4 where $R_F=C_nF_{2n+1}$). This is the subject of a part of this dissertation.

Halogenated ketenes are defined as ketenes which have at least one halogen atom attached directly to the ketene functionality.

$$\begin{matrix} H \\ X \end{matrix}\!\!>\!C = C = O \qquad \begin{matrix} X \\ X \end{matrix}\!\!>\!C = C = O \ (X=F,Cl,Br)$$

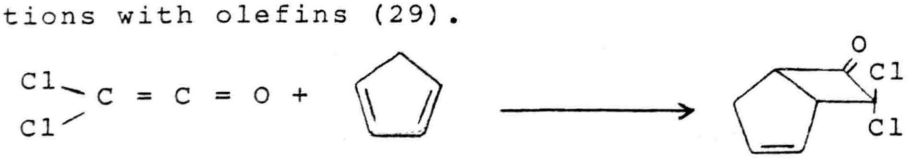
There are several available methods for the synthesis of ketenes, but the most general method is the activated zinc dehalogenation of an α-haloacid halide in ether or ethyl acetate solution. This method was used to prepare diphenylketene by Staudinger in 1905 (12).



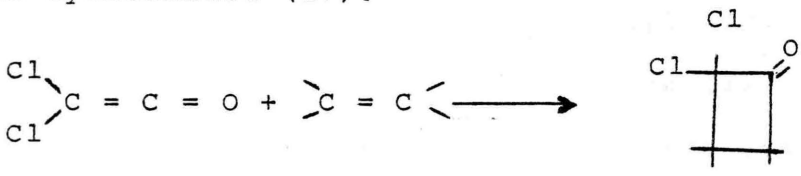
Another widely used method for the synthesis of ketenes is the triethylamine dehydrohalogenation of an appropriately substituted acid halide in hydrocarbon solvent (13).

Many ketenes are unstable and cannot be isolated and are generated from stable precursors and trapped by a suitable substrate to yield a cycloaddition product. Most of the halogenated ketenes are not isolable (17).

Dihaloketenes are well known to undergo cycloaddition reactions with unsaturated compounds. The (2+2) cycloaddition is a synthetically useful reaction to prepare the four-membered ring (17). One of the most reactive ketenes is dichloroketene, which, in spite of the tendency to polymerize, enters readily into cycloaddition reactions with olefins (29).



Recently, an improved procedure has been discovered in which the dihaloketene is generated by zinc dehalogenation in a very dilute ether solution. Trihaloacetylchloride is introduced by the substrate over a long period of time to deter polymerization of ketene at the expense of the cycloadduct (17).



Since there are no reports in the literature on the cycloaddition of dihaloketenes with siloxyolefins, it was proposed to investigate the cycloaddition reactions of dihaloketenes with various types of siloxyolefins.

CHAPTER II

HISTORICAL

1. Perfluoroalkylbromine (V) Tetrafluorides

The syntheses of several perfluoroalkyliodine fluorides have been reported. The perfluoroalkyliodine fluorides were first prepared using a perfluoroalkyl iodide and either elemental fluorine or chlorine trifluoride (1).

In 1968, Rondestvedt (2) reported the preparation and properties of several perfluoroalkyliodine fluorides using chlorine trifluoride as fluorinating agent:

$$2C_nF_{2n+1}I + 2ClF_3 \longrightarrow C_nF_{2n+1}IF_4 + C_nF_{2n+1}IF_2 + Cl_2 \qquad n = 2,3,4,6,10$$

He also reacted bromine trifluoride and bromine pentafluoride with perfluoroalkyl iodides (3):

$$2C_nF_{2n+1}I + 2BrF_3 \longrightarrow C_nF_{2n+1}IF_4 + C_nF_{2n+1}IF_2 + Br_2$$

$$3C_nF_{2n+1}I + 2BrF_5 \longrightarrow 2C_nF_{2n+1}IF_4 + C_nF_{2n+1}IF_2 + Br_2$$

In 1970, Schmeisser, Dahmen and Sartori (4) prepared pentafluorophenyliodine (III) difluoride by reaction of pentafluoroiodobenzene with elemental fluorine. $C_6F_5IF_2$ was hydrolyzed to give a colorless product assumed to be iodosopentafluorobenzene.

Chambers, Oates and Winfield (5) in 1972 reported the preparation of trifluoromethyliodine (V) tetrafluoride by the oxidation of trifluoromethyl iodide with chlorine trifluoride. They also prepared pentafluorophenyliodine (V) tetrafluoride in a similar way. The stability of perfluoroalkyliodine (V) tetrafluorides with respect to decomposition increased in the order of $CF_3IF_4 < (CF_3)_2CFIF_4 < C_6F_5IF_4$. Pentafluorophenyliodine (V) tetrafluoride was formed to be stable indefinitely at 20°C. Trifluoromethyliodine (V) tetrafluoride and pentafluorophenyliodine (V) tetrafluoride were more stable than the analogous iodine (III) difluoride compounds.

In 1973, Baumanns, Deneken, Naumann and Schmeisser(6) prepared trifluoromethyliodine (III) difluoride by the direct fluorination of trifluoromethyl iodide at -78°C.

Oates and Winfield (7) in the same year oxidized trifluoromethyl iodide with chlorine trifluoride in perfluorohexane at -78°C to give trifluoromethyliodine (V) tetrafluoride in addition to trifluoromethyliodine (III) difluoride.

In 1980, Obaleye and Sams reported the first aromatic interhalogen compound containing either chlorine or bromine. Pentafluorophenylbromine (V) tetrafluoride (8) was prepared by the oxidation of pentafluorophenyl bromide at

128°C with elemental fluorine. Pentafluorophenylbromine (III) difluoride (9) was prepared by the reaction of pentafluorobromobenzene and fluorine. Preparation of $C_6F_5ClF_4$ (10) and $C_6F_5ClF_2$ (11) was reported by the reaction of pentafluorophenyl chloride with elemental fluorine.

2. Dihaloketene Cycloadducts

Ketenes have been known since the synthesis of diphenylketene by Staudinger in 1905 (12). This new class of compounds was extensively studied during the next twenty years. During these investigations, attempts were made to prepare haloketenes; dichloro-, ethylchloro-, methylbromo-, and ethylbromoketenes (13-15). These ketenes could not be detected and were described as unstable compounds which polymerize readily even at very low temperatures.

Investigations in the two decades following Staudinger's work resulted in the industrial development of the parent compound, ketene. This development resulted in a thorough study of the chemistry of ketene itself. A comprehensive review on preparative ketene chemistry (16), including halogenated ketenes, appeared in 1968.

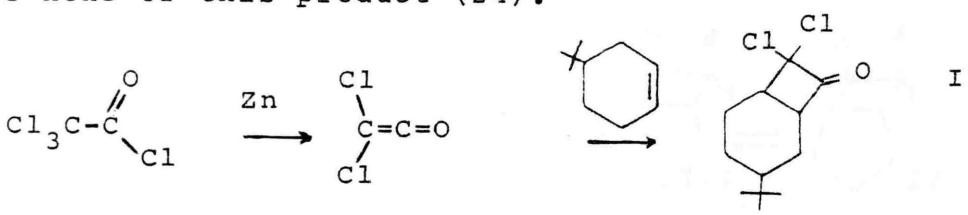
Despite the publication of many papers on halogenated ketenes, they still cannot be isolated but are usually generated <u>in situ</u> by dehalogenation or dehydrohalogenation (17). Halogenated ketenes are indeed very susceptible to polymerization and reactions involving them are

usually accompanied by the formation of tarry by-products.

The preparation of difluoroketene was first reported in 1957 (18), but several attempts to repeat this work have been unsuccessful (19). More recently, however, difluoroketene has been successfully prepared by dehalogenation of bromodifluoroacetyl halides with zinc (20). Difluoroketene dissociates above 35°C forming carbon monoxide and tetrafluoroethylene (21). Dichloroketene was first prepared in 1966 by the addition of trichloroacetyl bromide to activated zinc dust in ether or ethyl acetate. Other workers have prepared dichloroketene by dehydrochlorination of dichloroacetyl chloride with triethylamine. Since the dehydrohalogenation method gives higher yields and more reproducible results, it is considered to be a superior method of preparation (22).

However, while generation of dichloroketene by dehalogenation of trichloroacetyl chloride by zinc in the presence of ketones results in the formation of oxetanones, dichloroketene does not undergo cycloaddition to simple ketones when it is generated by dehydrochlorination of dichloroacetyl chloride by triethylamine, unless zinc or zinc chloride is also added to the reaction mixture. It has been suggested that either zinc or zinc chloride activate the carbonyl group of the ketone and thus facilitate the cycloaddition reaction (23). Similarly, while

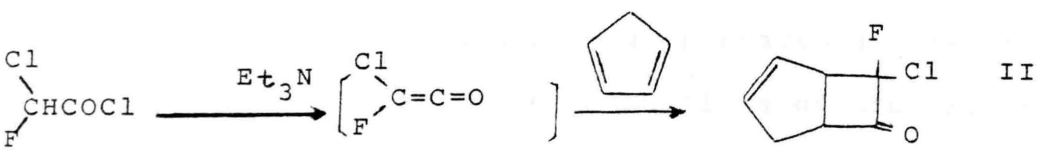
generation of dichloroketene by dehalogenation in the presence of 4-t-butylcyclohexene produced the expected adduct I, generation of the ketene by dehydrohalogenation gave none of this product (24).



I

Chlorofluoroketene has been prepared by dehydrochlorination of chlorofluoroacetyl chloride (25). The adduct II, formed in the presence of cyclopentadiene, decomposed on heating to give volatile products, which fumed in air and reacted with ethanol to give ethyl fluorochloroacetate. Bromochloroketene has also been generated *in situ* by dehydrochlorination of bromochloroacetyl chloride.

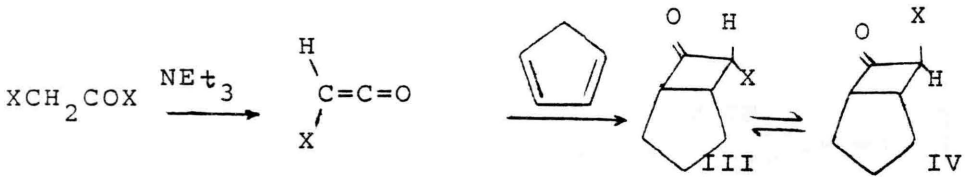
Dibromoketene itself has been prepared by both of the methods (26).



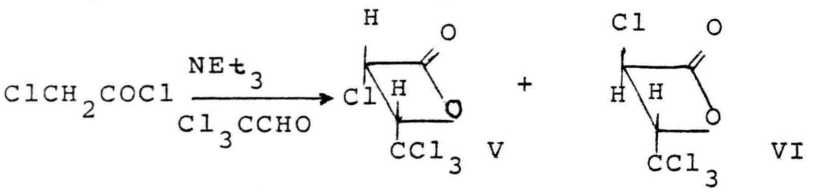
II

The dehydrohalogenation of haloacetyl halides in the presence of cyclopentadiene produces the corresponding 1,2-cycloadducts of fluoro-, chloro-, and bromoketenes (27,28). The unsymmetrically substituted ketenes undergo cycloaddition to cyclopentadiene to give only

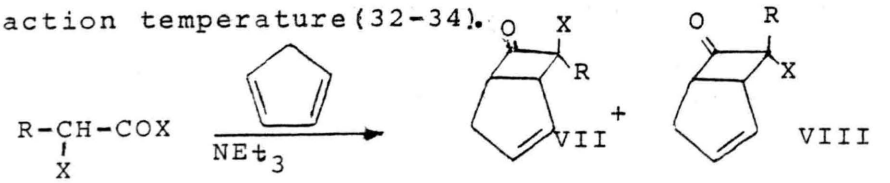
the endo isomer III, but in the presence of excess triethylamine some of the more stable exo isomer IV is also produced, probably as a result of isomerization via the enol tautomer of the initial adduct (29).



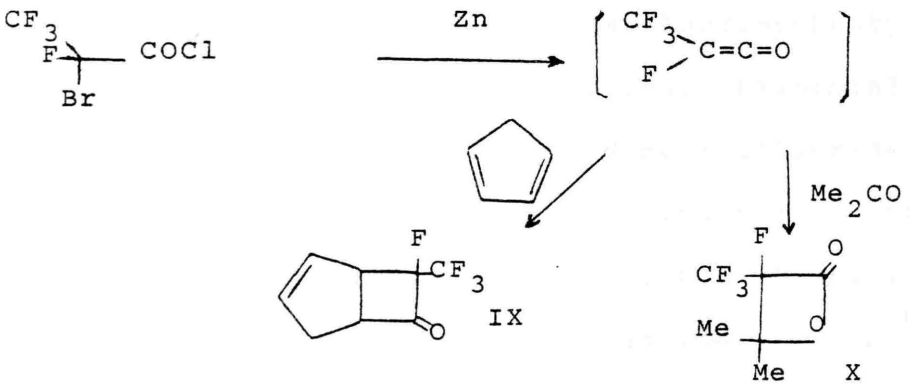
When chloroketene is generated by dehydrohalogenation of chloroacetyl chloride, in the presence of chloral, a mixture of the cis and trans oxetanones V and VI is obtained (30). However, when the chloroketene is generated by dehalogenation of dichloroacetyl chloride, in the presence of chloral, it reacts preferentially with the acyl halide to give a dichlorovinyl ester.



Alkylhaloketenes have also been prepared and reacted in situ with alkenes (31). The proportions of the exo and endo isomers obtained are strongly dependent upon the solvent polarity, the substituents attached to the ketene and the reaction temperature (32-34).



Evidence for the transitory existence of trifluoromethylfluoroketene during the dehalogenation of 2-bromo-2,3,3,3-tetrafluoro propionyl chloride is also provided by the formation of an adduct X with acetone in 6% yield (35).



CHAPTER III

EXPERIMENTAL

1. Perfluoroalkylbromine (V) Tetrafluorides

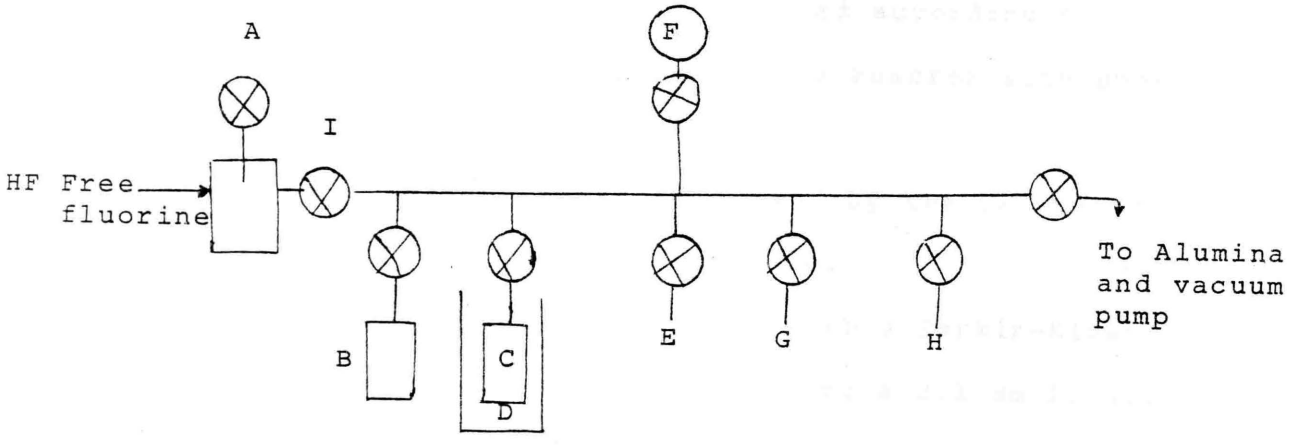
A. General

Perfluoro-n-propyl bromide and perfluoro-n-heptyl bromide were bought from PCR, Incorporated. Elemental fluorine, chlorine trifluoride and bromine trifluoride were purchased from Air Products, Inc. Elemental fluorine was passed through a tower filled with sodium fluoride pellets to remove traces of hydrogen fluoride. Chlorine trifluoride and bromine trifluoride were used as received.

A vacuum manifold (figure 1) was used to condense perfluoroalkyl bromide and fluorinating agent into a previously evacuated Monel reactor.

Reaction products were analyzed, using a Varian 90P-3 gas chromatograph fitted with a 3/8 inch x 20-foot column packed with 30% SE-30 on Chromosorb P. Separations were performed using 80°C and 100°C and helium flow rates of 80 and 65 mL/min, respectively. The appropriate peaks from the gas chromatograph were trapped with the aid of a U-tube held at -78°C.

The reactor used for the fluorination was Monel, Hoke 69H 1695, W.P. 5000 PSI; volume 392 mL.



A. Pressure regulator

B. Substrate metering tube

C. Monel pressure reactor

D. Dewar containing liquid nitrogen

E. Connection point for sample bottle

F. 0-1500 Torr pressure gauge for fluorine service

G. Connection point for helium gas

H. Connection point for other fluorinating agent

I. Valve

Figure I. Line Diagram of Manifold

The Monel manifold was constructed according to Figure 1, which was used for loading the reactor with substrates and fluorinating agents.

Elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra were recorded with a Perkin-Elmer Model 225 infrared spectrophotometer using a 0.1 mm liquid cell fitted with polyethylene windows.

Fluorine nuclear magnetic resonance spectra were obtained with a Varian EM-390 spectrometer operating at 84.67 MHz using fluorotrichloromethane as an internal reference.

Mass spectra were obtained with a Consolidated Electrodynamics Corporation (CEC) Model 21-104 single-focus mass spectrometer with an electron-multiplier detector.

The oxidation equivalents of perfluoroalkylbromine(V) tetrafluorides were determined by standard solutions of KI, in which the iodide ion was oxidized to iodine, and the iodine was titrated using a standard solution of sodium thiosulfate and starch as an indicator.

B. General Procedure for the Synthesis of Perfluoroalkylbromine (V) Tetrafluorides: Perfluoro-n-propylbromine (V) Tetrafluoride.

A series of experiments were carried out to determine the optimum fluorinating conditions based on percent yield of perfluoro-n-propylbromine (V) tetrafluoride. During the course of the investigation, the following typical procedures were followed on a routine basis. The vacuum manifold was used to condense 10 mmol of perfluoro-n-propyl bromide, 25 mmol of perfluoro-n-hexane as a solvent and 20 mmol of elemental fluorine into a previously evacuated and cooled (-196°C) Monel reactor. The reactor was closed and placed in an ice bath while stirring magnetically for 15 hours. At the completion of the reaction period, the reactor was reconnected to the manifold, cooled to -196°C, and evacuated. Additional perfluoro-n-hexane was vacuum distilled into the reactor to dissolve the products, and dry nitrogen gas was used to pressurize the reactor. The reactor was separated from the manifold and inverted. The reddish-brown liquid products were transferred into a nitrogen flushed sample holder through a septum. Moisture was vigorously excluded during sample handling by working in the nitrogen atmosphere. The product, perfluoro-n-propylbromine (V) tetrafluoride ($n\text{-}C_3F_7BrF_4$) was isolated by trapping the appropriate peak from a gas chromatograph. Similar reactions were carried out using chlorine trifluoride, bromine trifluoroide and

bromine pentafluoride as fluorinating agents. ^{19}F NMR: δ_{CFCl_3} = 141.8(4F,-BrF_4), -80.1(3F,CF_3), -123.1(2F,C-CF_2-C) and -63.2(2F,CF_2-Br). Mass spectrum: m/e 326(30), 324(30), 169(100). IR: 1340(s), 1250(vs), 1145(s), 1080(s), 685(vs).

Anal. Calcd. for $C_3F_7BrF_4$: C,11.07; F,64.30; Br, 24.61. Found: C,10.58; F,64.14; Br,24.05.

C. Synthesis of perfluoro-n-heptylbromine (V) tetrafluoride.

By the above procedure 10 mmol of perfluoro-n-heptyl bromide, 20 mmol of elemental fluorine and 25 mmol of perfluoro-n-hexane as a solvent was condensed into a previously evacuated and cooled (-196°C) Monel reactor. The product, perfluoro-n-heptylbromine (V) tetrafluoride was isolated by GC.

Similar reactions were run using BrF_3, BrF_5, and ClF_3 as fluorinating agents. ^{19}F NMR: δ_{CFCl_3} = +140.2 (4F,-BrF_4), -65.3(2F,Fα), -127.5(2F,F_β), -123.8(2F,Fα), -122.9(2F,F_δ), -122.0(2F,F_ε), -118.4(2F,F_ζ) and -82.8 (3F,CF_3)(CF_3-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-BrF_4). Mass spectrum: m/e 526(3), 524(3), 469(12), 467(12), 69(100). IR: 1230(s), 1200(vs), 1147(s), 1115(m), 680(s), 570(vs).

Anal. Calcd. for $C_7F_{15}BrF_4$: C,16.0; F,68.8; Br,15.2. Found: C,16.2; F,68.6; Br,14.8.

D. Typical Procedure for the Reactions of Perfluoroalkylbromine (V) Tetrafluorides with Cycloalkenes: Perfluoro-n-heptylbromine (V) Tetrafluoride with 1,2-Dichlorohexafluorocyclopentene.

The vacuum manifold was used to condense 10 mmol of perfluoro-n-heptylbromine (V) tetrafluoride and 22 mmol of 1,2-dichlorohexafluorocyclopentene into a previously evacuated and cooled (-196°C) Monel reactor. The reactor was closed and placed in an oven for eight hours at 120°C. At the completion of the reaction period, the reactor was reconnected to the manifold, cooled to -196°C, evacuated, and dry nitrogen gas was used to pressurize the reactor. The reactor was separated from the manifold and inverted. The products were transferred into a sample holder. The product, 1,2-dichlorooctafluorocyclopentane ($C_5Cl_2F_8$) was isolated by distillation and gas chromatography. ^{19}F NMR: δ_{CFCl_3} = -139.0(2F), -126.7(1F), -125.4(1F), -124.0(2F), -117.1(2F).

Anal. Calcd. for $C_5Cl_2F_8$: C,21.20; F,53.71. Found: C,20.78; F,53.60.

E. Reaction of Perfluoro-n-heptylbromine (V) Tetrafluoride with 1,2-Dichlorooctafluorocyclohexene.

The reaction of perfluoro-n-heptylbromine (V) tetrafluoride (0.4 mmol) with an excess of 1,2-dichlorooctafluorocyclohexene (10 mmol) was carried out at 140°C for

eight hours, using the above procedure. The product, 1,2-dichlorodecafluorocyclohexane ($C_6Cl_2F_{10}$) was isolated and characterized. ^{19}F NMR: δ_{CFCl_3} = -132.0(2F), -128.2(2F), -124.6(2F), -120.5(2F), -116.8(2F).

Anal. Calcd. for $C_6Cl_2F_{10}$= C,21.62; F,57.05. Found: C,21.91; F,56.73.

2. Dihaloketene-Siloxyolefin Cycloadducts

A. General

Trichloroacetyl chloride and chlorodifluoroacetyl chloride were purchased from Aldrich Chemical Company, Inc., and Columbia Organic Chemicals Company, Inc., respectively. Tribromoacetic acid was bought from Fluka Chemical Corp.

The fluorine and proton nuclear magnetic resonance spectra were recorded on Varian EM-390 spectrometer using fluorotrichloromethane and tetramethylsilane as internal references, respectively.

Analytical samples were obtained, where possible, by vapor phase chromatography on a Varian 90P-3 gas chromatograph fitted with a 3/8 inch x 20 foot column packed with 30% SE-30 on Chromosorb P.

Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Indiana.

Glassware was dried at 100°C and cooled under nitrogen before use.

Dry ether, ethyl acetate, hexane, heptane and acetone were commercially available and were used as received, under a nitrogen atmosphere prior to each run. Triethylamine was commercially available and was dried over sodium metal and distilled prior to use.

The zinc was activated by a standard procedure (36) and was always stored and used under a nitrogen atmosphere.

Tribromoacetyl chloride was prepared from tribromoacetic acid and either thionyl chloride or oxalyl chloride. The acid halides were freshly distilled prior to each dihaloketene preparation.

B. Preparation of 1,2-Bis(trimethylsiloxy)cyclobutene (37).

A 3 L, 3-neck, round-bottomed flask fitted with a condenser, mechanical stirrer and a dropping funnel equipped with a pressure-equalizing side arm was charged with 2.57 mol(59.2g) of freshly cut sodium and 460 mL of dry toluene under a nitrogen atmosphere. By means of an oil bath (115-120°), the toluene was heated to reflux with vigorous stirring until the sodium was melted and fully dispersed. To the Na dispersion was added dropwise a solution of 0.6 mol(104.4g) of diethyl succinate, 2.81 mol (305.0g) of trimethylchlorosilane and 150 mL of dry toluene

through the dropping funnel over a period of 3.5 hours while maintaining the oil bath temperature at 105-110°C. After refluxing with stirring for an additional 16 hours, the reaction mixture was allowed to cool to room temperature and filtered. The purple precipitate was washed thoroughly with dry toluene. The filtrate and toluene washings were combined and the solvent removed with a rotary evaporator at 50°C. The residue was distilled in vacuo through a Claisen distilling head to give 127.0 g (92%) of 1,2-bis(trimethylsiloxy)cyclobutene (37) as a colorless liquid, b.p. = 56-59°C(0.6 Torr). ^{1}H NMR (CCl_4; TMS external reference): δ = 0.1(s,18H,$Si(CH_3)_3$, 2.01(t,4H). IR: 760, 850, 950, 1085, 1260, 1320, 1730, 2860 and 2970 cm^{-1}.

C. Preparation of 1,2-Bis(trimethylsiloxy)cyclopentene (38).

Using the previous procedure, 2.57 mol(59.2 g) of freshly cut sodium and 460 mL of dry toluene with 0.6 mol (112.8 g) of diethyl glutarate, 2.81 mol (305 g) of trimethylchlorosilane at 120°C gave 139.3 g (95%) of 1,2-bis (trimethylsiloxy)cyclopentene (38) as a colorless liquid, b.p. = 90-93°C(9-14 Torr). ^{1}H NMR(CCl_4; TMS external reference): δ = 0.08(s,18H,$Si(CH_3)_3$), 1.65(m,2H), 1.0 (m,4H). IR: 760, 870, 930, 1095, 1260, 1346, 1712, 2864, 2918 and 2987 cm^{-1}.

D. Preparation of 1,2-Bis(trimethylsiloxy)cyclohexene (39).

A 3.04 mol(70.0 g) of sodium and 50.0 mL of dry toluene with 1.0 mol(202 g) of diethyl adipate, 3.50 mol (379.9 g) of trimethylchlorosilane at 115°C and using the same procedure as before gave 240.0 g (93%) of 1,2-bis(trimethylsiloxy)cyclohexene (39) as a colorless liquid, b.p. = 98-101°C(10-13 Torr). ^{1}H NMR(CCl_4; TMS external references) δ = 0.05(s,18H,$Si(CH_3)_3$), 1.75(m,4H), 2.20(m,4H). IR: 757, 852, 910, 1130, 1220, 1238, 1350, 1700, 2845, 2942 and 2970 cm^{-1}.

E. General Procedure for Cycloaddition of Dihaloketenes with Siloxyolefin: Difluoroketene-1,2-Bis(trimethylsiloxy) cyclohexene.

A 500 mL, 1-neck, round-bottomed flask fitted with a condenser, magnetic stirrer and a dropping funnel equipped with a pressure-equalizing side arm was charged with 25 mmol(6.45 g) of 1,2-bis(trimethylsiloxy)cyclohexene in 200 mL ethyl acetate and 7.0 g of activated zinc under a nitrogen atmosphere. A solution of 25 mmol(3.72 g) of chlorodifluoroacetyl chloride in 200 mL of dry ethyl acetate was added very slowly (10-12 hours) to the stirred mixture at 40-45°C. At the completion of reaction period, the excess of zinc was filtered. The solution was con-

centrated to about 10 mL by means of a rotary evaporator, the residue was dissolved in 50 mL of dry hexane, decanted, vacuum distilled through a short-path distillation apparatus and further characterized. After distillation at 52-55°C at 0.4 Torr, yielded 4.62 g (55%). IR: 2980, 1795 (C=O) and 1150 cm^{-1}. ^{1}H NMR (with CCl_4 as a solvent and $SiMe_4$ as a reference): δ = 1.91(m,4H), 1.52(m,4H), 0.4 (m,9H), 0.15(m,9H). ^{19}F NMR: δ_{CFCl_3} = 63.5(d,1F), 64.5 (d,1F) with respect to $CFCl_3$ as an internal reference. Mass spectra, m/e 336 (2.7), 263 (9.6), 73 (100).

Anal. Calcd. for $C_{14}H_{26}O_3F_2Si_2$: C,50.0; H,7.74. Found: C,50.23; H,7.92.

F. 7,7-Difluoro-1,5-bis(trimethylsiloxy)bicyclo[3.2.0] heptane-6-one.

By the above procedure, a 25 mmol(3.72 g) portion of chlorodifluoroacetyl chloride, 7.0 g of activated zinc and 25 mmol(6.10 g) of 1,2-bis(trimethylsiloxy)cyclopentene in 400 mL of dry ethyl acetate after distillation at 48-50°C at 0.35 Torr, yield 3.94 g (47%). IR: 3000, 1800 (C=O), broad band at 1160 and 985 cm^{-1}. ^{1}H NMR: δ = 1.9(t,4H), 1.4(m,2H), 0.4(m,9H,$Si(CH_3)_3$), 0.1(m,9H,$Si(CH_3)_3$). ^{19}F NMR: δ = 63.2(d,1F), 64.1(d,1F) with respect to $CFCl_3$ as internal standard. Mass spectra, m/e 322 (3.2), 307 (11.4), 233 (7.8), 79 (95), 73 (100).

Anal. Calcd. for $C_{13}H_{24}O_3F_2Si_2$: C,48.44; H,7.45. Found: C,48.60; H,7.65.

G. 6,6-Difluoro-1,4-bis(trimethylsiloxy)bicyclo[2.2.0] hexane-5-one.

By the above procedure, 25 mmol(3.72 g) portion of chlorodifluoroacetyl chloride, 7.0 g of activated zinc and 25 mmol(5.75 g) of 1,2-bis(trimethylsiloxy)cyclobutene in 400 mL of dry ethyl acetate after distillation at 41-45°C at 0.3 Torr, yield 2.62 g (34%). IR: 2995, 1800 (C=O), 1165 cm^{-1}. ^1H NMR: δ = 2.0(m,4H), 0.45(m,9H,Si-$(CH_3)_3$), 0.2(m,9H,Si$(CH_3)_3$). ^{19}F NMR: δ_{CFCl_3} = 65(d,1F), 65.8(d,1F). Mass spectra, m/e 308 (5.4), 293 (21), 73 (100).

Anal. Calcd. for $C_{12}H_{22}O_3F_2Si_2$: C,46.75; H,7.14. Found: C,46.36; H,6.73.

H. 8,8-Dichloro-1,6-bis(trimethylsiloxy)bicyclo[4.2.0] octane-7-one.

By the above procedure, 25 mmol(4.65 g) of trichloroacetyl chloride, 7.0 g of activated zinc and 25 mmol(6.45 g) of 1,2-bis(trimethylsiloxy)cyclohexene in 400 mL of dry ether after distillation at 105°C (0.35 Torr) yield 6.0 g (65%). IR: 2980, 1795 (C=O) and 1150 cm^{-1}. ^1H NMR: δ = 2.00(m,4H), 1.63(m,4H), 0.45(m,9H), 0.20(m,9H,Si$(CH_3)_3$).

Anal. Calcd. for $C_{14}H_{26}O_3Cl_2Si_2$: C,45.51; H,7.09. Found: C,45.27; H,7.13.

I. 7,7-Dichloro-1,5-bis(trimethylsiloxy)bicyclo[3.2.0] heptane-6-one.

By the above procedure, 25 mmol(4.65 g) of trichloroacetyl chloride, 7.0 g of activated zinc and 25 mmol(6.03 g) of 1,2-bis(trimethylsiloxy)cyclopentene in 450 mL of ether after distillation at 72-76°C(0.3 Torr), yield 6.65 g (75%). IR: 2960, 1750 (C=O), 1260, 850 cm^{-1}. ^1H NMR: δ = 2.0 (m,4H), 1.7(m,2H), 0.2(m,9H,$Si(CH_3)_3$), 0.03(m,9H),$Si(CH_3)_3$).

Anal. Calcd. for $C_{13}H_{24}O_3Cl_2Si_2$: C,43.88; H,6.75. Found: C,43.50; H,6.82.

J. 6,6-Dichloro-1,4-bis(trimethylsiloxy)bicyclo[2.2.0] hexane-5-one.

This cycloadduct was prepared by cycloaddition of 25 mmol(4.65 g) of trichloroacetyl chloride, 7.0 g of activated zinc and 25 mmol(5.75 g) of 1,2-bis(trimethylsiloxy)cyclobutene in 450 mL of dry ether. After distillation at 60-64°C(0.4 Torr), yield was 4.69 g (55%). IR: 2980, 1790 (C=O), 1150 cm^{-1}. ^1H NMR: δ = 1.9(m,4H), 0.15(m,9H,$Si(CH_3)_3$), 0.03(m,9H,$Si(CH_3)_3$).

Anal. Calcd. for $C_{12}H_{22}O_3Cl_2Si_2$: C,42.23; H,6.45. Found: C,42.56; H,6.71.

K. 8,8-Dibromo-1,6-bis(trimethylsiloxy)bicyclo[4.2.0] octane-7-one.

By the use of general procedure, 25 mmol (7.88 g) of

tribromoacetyl chloride (m.p. = 45°C), 7.0 g of activated zinc and 25 mmol(6.45 g) of 1,2-bis(trimethylsiloxy)cyclohexene in 450 mL of dry ether after distillation at 95°C (0.2 Torr), yield was 7.1 g (82%). IR: 2970, 1750 (C=O), 1270, 785 cm^{-1}. ^1H NMR: δ = 1.95(m,4H), 1.50(m,4H), 0.3 (m,9H,$Si(CH_3)_3$), 0.06(m,9H,$Si(CH_3)_3$).

Anal. Calcd. for $C_{14}H_{26}O_3Br_2Si_2$: C,36.68; H,5.68. Found: C,37.12; H,5.84.

L. 7,7-Dibromo-1,5-bis(trimethylsiloxy)bicyclo[3.2.0] heptane-6-one.

By the typical procedure, 25 mmol(7.88 g) of tribromoacetyl chloride (m.p. = 45°C), 7.0 g of activated zinc and 25 mmol(6.10 g) of 1,2-bis(trimethylsiloxy)cyclopentene after distillation at 82-85°C(0.25 Torr), yield was 8.21 g (74%). IR: 2975, 1765 (C=O), 1270, 780 cm^{-1}. ^1H NMR: δ = 1.80(m,4H), 1.63(m,2H), 0.2(m,9H,$Si(CH_3)_3$), 0.03(m,9H,$Si(CH_3)_3$).

Anal. Calcd. for $C_{13}H_{24}O_3Br_2Si_2$: C,35.13; H,5.40. Found: C,35.44; H,5.69.

M. 6,6-Dibromo-1,4-bis(trimethylsiloxy)bicyclo[2.2.0] hexane-5-one.

By the general procedure, 25 mmol(7.88 g) of tribromoacetyl chloride (m.p. = 45°C), 7.0 g of activated zinc and 25 mmol(5.75 g) of 1,2-bis(trimethylsiloxy)cyclobutene after distillation at 66-69°C(0.25 Torr), yield was

45%. IR: 2970, 1780 (C=O), 1165 cm^{-1}. ^1H NMR: δ = 1.68 (m,4H), 0.15(m,9H), 0.00(m,9H,$Si(CH_3)_3$).

Anal. Calcd. for $C_{12}H_{22}O_3Br_2Si_2$: C,33.49; H,5.12. Found: C,33.86; H,5.37.

3. General Procedure for the Preparation of Silylated Ketene Acetals: Tris(trimethylsiloxy)ethene (40).

To a stirred solution of 1.52 mol(245 g) of 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) in 1.2 L of THF was added, over 1.5 hour under nitrogen, at 0°, 650 mL of 2.4 M n-butyllithium in hexane. The solution was then maintained at 45°C for 30 min. The solution was cooled to -78°C, and 1.25 mol(275 g) of trimethylsilyl trimethylsiloxyacetate (40) was added dropwise over a 30 min. period. After the solution was stirred an additional 30 min., 1.9 mol(205 g) of Me_3SiCl was added dropwise. The solution was allowed to warm up to room temperature. The solution was poured into 1 L of petroleum ether and filtered through Celite. The solvent was removed and the residue was redissolved in petroleum ether. The solvent was removed, and the residue was distilled (62-65°C) at 0.4 Torr to give 360 g (100%) of tris(trimethylsiloxy)ethene. ^1H NMR ($CDCl_3$): δ = 5.42(s,1H,CH), 0.00(s,9H,$Si(CH_3)_3$), 0.03(s,9H,$Si(CH_3)_3$), 0.06(s,9H,$Si(CH_3)_3$)($CHCl_3$; Me_4Si as external reference).

Anal. Calcd. for $C_{11}H_{26}O_3Si_3$: C,45,15; H,9.65.

Found: C,45,30; H,9.82.

A. 2-Phenoxy-1,1-bis(trimethylsiloxy)ethene.

By the above procedure, 0.40 mol(90.0 g) of trimethylsilylphenoxyacetate gave 110.0 g (95%) of 2-phenoxy-1,1-bis(trimethylsiloxy)ethene after distillation (120-125°C) at 0.6 Torr. ^{1}H NMR: δ = 7.05(m,5H,C_6H_5), 5.95 (s,1H,CH), 0.27(s,9H,$Si(CH_3)_3$), 0.21(s,9H,$Si(CH_3)_3$)($CHCl_3$; Me_4Si as external reference.

Anal. Calcd. for $C_{14}H_{24}O_3Si_2$: C,56.71; H,8.16. Found: C,56.46; H,8.35.

B. 2-Methoxy-1,1-bis(trimethylsiloxy)ethene

By the above procedure, 0.68 mol(110 g) of trimethylsilylmethoxyacetate gave 140.0 g (81%) of 2-methoxy-1,1-bis (trimethylsiloxy)ethene after distillation at 65-70°C at 10 Torr: ^{1}H NMR: δ = 6.1(s,1H,CH), 3.16(s,3H,OCH_3), 0.03(s,9H,$Si(CH_3)_3$), 0.00(s,9H,$Si(CH_3)_3$).

Anal. Calcd. for $C_9H_{22}O_3Si_2$: C,46.11; H,9.46. Found: C,45.96; H,9.51.

C. General Procedure for <u>in situ</u> silylated ketene Acetals-Dihaloketene Cycloaddition: Difluoroketene with Tris(trimethylsiloxy)ethene.

A 1 L, 1 neck, round-bottomed flask with a condenser, magnetic stirrer and a dropping funnel equipped with a pressure-equalizing side arm was charged with a 25 mmol

(7.3 g) of tris(trimethylsiloxy)ethene in 250 mL of dry ethyl acetate and 7.0 g of activated zinc, under a nitrogen atmosphere. A solution of 25 mmol(3.72 g) of chlorodifluoroacetyl chloride in 250 mL of dry ethyl acetate was added slowly (4-6 hours) to the stirred mixture at 46-50°C. At the completion of reaction period, the excess of zinc was filtered. The solution was concentrated to about 10 mL and dissolved in 35 mL of dry heptane, decanted, vacuum distilled through a short-path distillation apparatus. After distillation at 67-70°C(0.4 Torr), yield was 3.89 g (40%). ^{1}H NMR: δ = 4.0(t,1H), 0.03(s,9H), 0.00(s,9H), -0.10(s,9H), and δ = 4.7(s,1H), 0.2(s,9H), 0.15(s,9H), 0.1 (s,9H). ^{19}F NMR: δ_{CFCl_3} = 65.5(m).

Anal. Calcd. for $C_{13}H_{28}O_4F_2Si_3$: C,42.16; H,7.52. Found: C,42.45; H,7.71.

D. Cycloadduct of Difluoroketene with 2-Phenoxy-1,1-bis(trimethylsiloxy)ethene.

This adduct was prepared (procedure 3-C) from 25 mmol (12.5 g) of 2-phenoxy-1,1-bis(trimethylsiloxy)ethene and 25 mmol(3.72 g) of chlorodifluoroacetyl chloride at 48-51°C for four hours. After distillation at 99-104°C(0.1 Torr), yield was 5.80 g (62%). ^{1}H NMR: δ = 4.50(t,1H), 6.35(m,5H, C_6H_5), 0.28(s,9H,$Si(CH_3)_3$), 0.21(s,9H,$Si(CH_3)_3$) and δ = 5.13(s,1H,CH), 6.87(m,5H,C_6H_5), 0.36(s,9H), 0.29(s,9H).

^{19}F NMR: δ_{CFCl_3} = 64.3(m).

Anal. Calcd. for $C_{16}H_{24}O_4F_2Si_2$: C,51.34; H,6.42. Found: C,50.98; H,6.51.

E. Cycloadduct of Difluoroketene with 2-Methoxy-1,1-bis(trimethylsiloxy)ethene.

This adduct was prepared (procedure 3-C) from 25 mmol (5.85 g) of 2-methoxy-1,1-bis(trimethylsiloxy)ethene and 25 mmol(3.72 g) of chlorodifluoroacetyl chloride at 44-46°C for four hours. After distillation at 70-74°C(4 Torr), yield was 2.8 g (36%). ^1H NMR: δ_{Me_4Si} = 3.90(t,1H,CH), 3.03(s,3H,OCH_3), 0.09(s,9H,$Si(CH_3)_3$, 0.06(s,9H,$Si(CH_3)_3$ and δ_{Me_4Si} = 4.62(s,1H,CH), 3.19(s,3H,OCH_3), 0.1(s,9H,Si-$(CH_3)_3$), 0.08(s,9H,$Si(CH_3)_3$). ^{19}F NMR: δ_{CFCl_3} = 66.5(m).

Anal. Calcd. for $C_{11}H_{22}O_4F_2Si_2$: C,42.30; H,7.05. Found: C,41.96; H,7.22.

F. Cycloadduct of Dichloroketene with Tris(trimethylsiloxy)ethene.

This adduct was prepared (procedure 3-C) from 25 mmol (7.3 g) of tris(trimethylsiloxy)ethene and 25 mmol(4.65 g) of trichloroacetyl chloride in 500 mL ether at 45-47°C for five hours. After distillation at 63-65°C(0.2 Torr), yield was 4.74 g (45%). ^1H NMR: δ_{Me_4Si} = 5.16(s,1H,CH), 4.57 (s,1H,CH), 0.3(s,9H,$Si(CH_3)_3$), 0.2(s,9H,$Si(CH_3)_3$), 0.08 (3,9H,$Si(CH_3)_3$), 0.25(s,9H), 0.15(s,9H), 0.00(s,9H).

IR: 1790 (C=O) cm^{-1}.

Anal. Calcd. for $C_{13}H_{28}O_4Cl_2Si_3$: C,38.71; H,6.95. Found: C,38.85; H,6.82.

G. Cycloadduct of Dichloroketene with 2-Phenoxy-1,1-bis(trimethylsiloxy)ethene.

By using the procedure 3-C, 25 mmol(12.5 g) of 2-phenoxy-1,1-bis(trimethylsiloxy)ethene, and 25 mmol(4.65 g) of trichloroacetyl chloride in 500 mL ether at 45-47°C for five hours, after distillation at 120-123°C(0.1 Torr), yield was 3.83 g (38%). ^1H NMR: δ_{Me_4Si} = 7.00(m,5H,C_6H_5), 5.62(s,1H,CH), 0.22(s,9H,$Si(CH_3)_3$), 0.18(s,9H,$Si(CH_3)_3$). IR: 1760 cm^{-1} (C=O).

Anal. Calcd. for $C_{16}H_{24}O_4Cl_2Si_2$: C,47.17; H,5.90. Found: C,47.29; H,5.95.

H. Dichloroketene-2-Methoxy-1,1-bis(trimethylsiloxy) ethene Cycloadduct.

By the procedure 3-C, 25 mmol (5.85 g) of 2-methoxy-1,1-bis(trimethylsiloxy)ethene and 25 mmol(4.65 g) of trichloroacetyl chloride in 500 mL ether after distillation at 71-75°C(1,2 Torr), yield was 3.53 g (41%). ^1H NMR: δ_{Me_4Si} = 4.90(s,1H,CH), 3.12(s,3H,OCH_3), 0.08(s,9H), 0.03 (s,9H,$Si(CH_3)_3$). IR: 1765 cm^{-1} (C=O).

Anal. Calcd. for $C_{11}H_{22}O_4Cl_2Si_2$: C,38.26; H,6.38. Found: C,38.49; H,6.45.

I. Dibromoketene-Tris(trimethylsiloxy)ethene Cycloadduct.

By the procedure 3-C, 25 mmol(7.3 g) of Tris(trimethylsiloxy)ethene and 25 mmol(7.88 g) of tribromoacetyl chloride (m.p. = 45°C) after distillation at 70-73°C (0.1 Torr), yield was 8.12 g (66%). ^{1}H NMR: δ_{Me_4Si} = 4.98 (s,1H,CH), 0.20(s,9H,$Si(CH_3)_3$), 0.16(s,9H,$Si(CH_3)_3$), 0.1 (s,9H,$Si(CH_3)_3$) and δ_{Me_4Si} = 5.24(s,1H,CH), 0.23(s,9H), 0.18(s,9H), 0.13(s,9H). IR: 1770 cm^{-1} (C=O).

Anal. Calcd. for $C_{13}H_{28}O_4Br_2Si_3$: C,31.70; H,5.69. Found: C,31.87; H,5.75.

J. Dibromoketene-2-Phenoxy-1,1-bis(trimethylsiloxy) ethene Cycloadduct.

By the procedure 3-C, 25 mmol(12.5 g) of 2-phenoxy-1,1-bis(trimethylsiloxy)ethene and 25 mmol(7.88 g) of tribromoacetyl chloride after distillation at 128-130°C(0.1 Torr), yield was 3.35 g (27%). ^{1}H NMR: δ_{Me_4Si} = 7.1(m,5H, C_6H_5), 5.75(s,1H,CH), 0.28(s,9H), 0.20(s,9H) and δ_{Me_4Si} = 6.82(m,5H,C_6H_5), 5.48(s,1H,CH), 0.15(s,9H), 0.12(s,9H). IR: 1770 cm^{-1} (C=O).

Anal. Calcd. for $C_{16}H_{24}O_4Br_2Si_2$: C,38.70; H,4.84. Found: C,39.16; H,4.90.

K. Dibromoketene-2-Methoxy-1,1-bis(trimethylsiloxy) ethene Cycloadduct.

By the procedure 3-C, 25 mmol(5.85 g) of 2-methoxy-

1,1-bis(trimethylsiloxy)ethene and 25 mmol(7.88 g) of tribromoacetyl chloride after distillation at 75-78°C(0.3 Torr), yield was 4.23 g (39%). ^{1}H NMR: δ_{Me_4Si} = 5.03(s,1H, CH), 3.20(s,3H,OCH_3), 0.10(s,9H), 0.08(s,9H) and δ_{Me_4Si} = 4.75(s,1H,CH), 3.0(s,3H,OCH_3), 0.05(s,9H), 0.00(s,9H).

Anal. Calcd. for $C_{11}H_{22}Br_2O_4Si_2$: C,30.41; H,5.07. Found: C,30.65; H,4.84.

4. General Procedure for Selective Fluorination of Cycloadducts.

To a stirred solution of 20 mmol of cycloadduct in a 25 mL two-necked flask equipped with a dropping funnel with side-arm, and a reflux condenser connected to a nitrogen flow, all of which was dried before use, was added 40 mmol of phenyltetrafluorophosphorane (49) ($PhPF_4$) in a period of one hour at room temperature. Three major products were detected by gas chromatography as follows: $(CH_3)_3SiF$,$PhPF_4$ and difluoroadduct.

A. 1,6,8,8-Tetrafluorobicyclo[4.2.0]octane-7-one.

This fluorocycloadduct showed IR: 1795 cm^{-1} (C=O); ^{19}F NMR: δ_{CFCl_3} = 162.5 ppm(d,2F), 158.0(m,2F); ^{1}H NMR: δ_{Me_4Si} = 2.35(m).

Anal. Calcd. for $C_8H_8F_4O$: C,48.98; H,4.08. Found: C,48.51; H,4.26.

B. 1,5,7,7-Tetrafluorobicyclo[3.2.0]heptane-6-one.

This difluorocycloadduct showed: IR: 1800 cm^{-1} (C=O): ^{19}F NMR: δ_{CFCl_3} = 163.0(m,2F), 128.5(d,2F).

Anal. Calcd. for $C_7H_6F_4O$: C,46,15; H,3.30. Found: C,46.41; H,3.52.

C. 8,8-Dichloro-1,6-difluorobicyclo[4.2.0]octane-7-one.

This difluorocycloadduct showed: IR: 1790 cm^{-1} (C=O); ^{19}F NMR: δ_{CFCl_3} = 151(m); ^{1}H NMR: δ_{Me_4Si} = 1.95(m,4H), 2.58(m,4H).

Anal. Calcd. for $C_8H_8Cl_2F_2O$: C,41.92; H,3.49. Found: C,42.21; H,3.61.

CHAPTER IV

RESULTS AND DISCUSSION

1. Perfluoro-n-propylbromine (V) Tetrafluoride

A. Preparation

Perfluoro-n-propylbromine (V) tetrafluoride was synthesized by allowing perfluoro-n-propyl bromide and fluorinating agent (elemental fluorine, chlorine trifluoride, bromine trifluoride and bromine pentafluoride) to react in a Monel reactor, using perfluoro-n-hexane as solvent, at $0^{\circ}C$ for fifteen hours. The reaction products were dissolved in additional perfluoro-n-hexane and a colorless liquid was isolated from the reddish-brown solution by G.C. This colorless product was identified as perfluoro-n-propylbromine (V) tetrafluoride ($n\text{-}C_3F_7BrF_4$) on the basis of elemental analysis, mass spectra, fluorine NMR and its ability to oxidize four equivalents of KI per mole.

B. Mass Spectrum

The mass spectrum, detailed in Table I, consists of molecular ions at m/e 324 and 326 and expected fragment ions. The expected isotope patterns (1:1) for ^{79}Br and ^{81}Br were observed and the peak at m/e 169 was assigned to $C_3F_7^+$ as the base peak.

TABLE I

Mass Spectrum of $C_3F_7BrF_4$

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
326	30	$C_3BrF_{11}^+$	286	6	$C_3BrF_9^+$
324	30	$C_3BrF_{11}^+$	257	19	$C_2BrF_8^+$
307	23	$C_3BrF_{10}^+$	255	19	$C_2BrF_8^+$
305	23	$C_3BrF_{10}^+$	169	100	$C_3F_7^+$
288	6	$C_3BrF_9^+$	69	70	CF_3^+

C. ^{19}F NMR Spectra

A comparison of the NMR spectra of $\underline{n}$-C_3F_7Br and $\underline{n}$-$C_3F_7BrF_4$ is given in Table II. The integration of the +141.8 ppm signal is consistent with four fluorines in the same magnetic environment, similar to the equatorial fluorines of BrF_5. The R_F(R_F=$\underline{n}$-C_3F_7 group) chemical shifts are as expected in comparison with perfluoro-$\underline{n}$-propyl bromide.

D. IR Spectrum

The liquid phase infrared spectrum consists of absorption bands at 1340(s), 1250(vs), 1145(s), 1080(s), 910(w), 710(m), 685(vs), 665(s), 640(m), 620(m), 550(m) and 475(s) cm^{-1}. IR spectra of $\underline{n}$-$C_3F_7BrF_4$ contained bands comparable to those of the C_3F_7 group (41) and a strong band at 685 cm^{-1} which is comparable to the 683 cm^{-1} band of BrF_5 (42).

E. Elemental Analysis and Stability

Perfluoro-$\underline{n}$-propylbromine (V) tetrafluoride decomposes slowly at room temperature in contact with air (decomposition was detectable by F-NMR after 30 minutes). Under dry helium at -30°C the compound was stable for a month.

TABLE II

The ^{19}F-NMR spectra of perfluoro-n-propylbromine(V) tetrafluoride

Compound	Chemical Shifts (ppm)*				Coupling Constants (Hz)		
	CF_3	CF_2	CF_2	BrF_4	J(FBrCF)	J(FBrCCF)	Others**
$n\text{-}C_3F_7Br$	-80.0	-121.8	-58.6	--	--	--	
$n\text{-}C_3F_7BrF_4$	-80.1	-123.1	-63.2	+141.8	32.0	32.0	$J(F_1F_2)$ 32.0
							$J(F_1F_3)$ 11.8
							$J(F_2F_3)$ 1.2

*From CCl_3F as internal references, upfield is negative to CCl_3F.

**^{19}F nuclei in C_3F_7 numbered from the alpha-position.

Perfluoro-n-propylbromine (V) tetrafluoride hydrolyzes and NMR analysis of the hydrolysis products showed that fluorines attached to bromine in n-$C_3F_7BrF_4$ were liberated.

Analysis: Found: C,10.58; F,64.14; Br,24.05; $C_3F_7BrF_4$ requires C,11.07; F,64.30; Br,24.61.

2. Perfluoro-n-heptylbromine (V) tetrafluoride

A. Preparation

Perfluoro-n-heptylbromine (V) tetrafluoride was synthesized by allowing n-$C_7F_{15}Br$ and fluorinating agent to react in a Monel cylinder at 0°C for eighteen hours. The reaction products were dissolved in n-C_6F_{14} and a colorless liquid was isolated from the reddish-brown solution by gas chromatography. It oxidized four equivalents of KI per mole:

$$\text{n-}C_7F_{15}BrF_4 + 4KI \longrightarrow \text{n-}C_7F_{15}Br + 2I_2 + 4\ KF$$

B. Mass Spectrum

The mass spectrum, detailed in Table III, consists of molecular ions at m/e 524 and 526 and expected fragment ions. The expected isotope pattern (1:1) for ^{79}Br and ^{81}Br was observed for fragments containing Br, and the peak at m/e 69 was assigned to CF_3^+ as the base peak.

TABLE III

Mass Spectrum of $\underline{n}$-$C_7F_{15}BrF_4$

m/e	Relative Abundance	Ion
526	3	$[C_7BrF_{19}]^+$
524	3	$[C_7BrF_{19}]^+$
469	12	$[C_7BrF_{16}]^+$
467	12	$[C_7BrF_{16}]^+$
369	75	$[C_7F_{15}]^+$
281	45	$[C_4BrF_8]^+$
279	43	$[C_4BrF_8]^+$
169	80	$[C_3F_7]^+$
157	40	$[BrF_4]^+$
155	38	$[BrF_4]^+$
69	100	$[CF_3]^+$

C. ^{19}F NMR Spectra

A comparison of the NMR spectra of $\underline{n}$-$C_7F_{15}Br$ and $\underline{n}$-$C_7F_{15}BrF_4$ is given in Table IV. The integration of the +140.2 ppm signal is consistent with four fluorines (relative to fluorines of the α-CF_2 group) in the same magnetic environment, similar to the equatorial fluorines of BrF_5. The R_F (R_F=n-C_7F_{15} group) chemical shifts are as expected by comparison with perfluoro-$\underline{n}$-heptyl bromide.

TABLE IV

The ^{19}F-NMR spectra of n-$C_7F_{15}Br$ and n-$C_7F_{15}BrF_4$

$CF_3-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-Br$

ξ ε δ γ β α

$CF_3-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-BrF_4$

ξ ε δ γ β α

	Chemical Shifts (ppm)[a]			Coupling Constant (Hz)		
	$\delta(CF_3)$	$\delta(CF_2)$	$\delta(BrF_4)$	J(FBrCF)	J(FBrCCF)	Others
n-$C_7F_{15}Br$	-81.3	-63.1(F_α)[b]	-	-	-	-
		-126.7 F_β				
		-123.0 F_γ				
		-122.2 F_δ				
		-121.3 F_ε				
		-117.7 F_ξ				
n-$C_7F_{15}BrF_4$	-82.8	-65.3(F_α)[b]	+140.2	28	28	$J(CF_\alpha-CF_3)$28
		-127.5 F_β				
		-123.8 F_γ				
		-122.9 F_δ				
		-122.0 F_ε				
		-118.4 F_ξ				

[a] From CCl_3F as internal reference, upfield is negative.

[b] First order spectra.

D. IR Spectra

The liquid phase infrared spectrum consists of absorption bands at 1230(s), 1200(vs), 1147(s), 1115(m), 978(m), 820(w), 720(w), 700(m), 680(s), 648(m), 570(vs), and 530(m) cm^{-1}. This spectrum is comparable with that of other $\underline{n}$-C_7F_{15} groups (41) and the strong bands at 680 and 570 cm^{-1} are comparable to the 683 and 587 cm^{-1} bands of bromine pentafluoride (42). This spectrum is also comparable with the IR of $C_6F_5BrF_4$.

E. Elemental Analysis

Analysis showed the product to be 38% $C_7F_{15}BrF_4$, 30% $C_7F_{15}Br$ and 32% unidentified. Anal. Calcd. for $C_7F_{15}BrF_4$: C,16.0; F,68.8; Br,15.2. Found: C,16.2; F,68.6; Br,14.8.

F. Stability and Hydrolysis

Perfluoro-$\underline{n}$-heptylbromine (V) tetrafluoride decomposes slowly at room temperature, giving a mixture of $\underline{n}$-$C_7F_{16}Br_2$, and $\underline{n}$-$C_7F_{15}Br$. It hydrolyzes and ^{19}F NMR analysis of the hydrolysis products showed the presence of $\underline{n}$-$C_7F_{15}Br$ and HF.

G. Reaction with $C_5F_6Cl_2$

When an excess of 1,2-dichlorohexafluorocyclopentene (43) ($C_5F_6Cl_2$) was allowed to react with $\underline{n}$-$C_7F_{15}BrF_4$ in a Monel reactor at 120°C for 8 hours, NMR and mass spectra

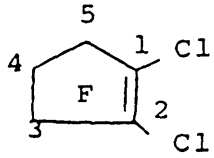
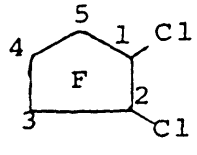
that 1,2-dichlorooactafluorocyclopentane ($C_5F_8Cl_2$) and $\underline{n}$-$C_7F_{15}Br$ has been formed according to the equation:

$$2C_5F_6Cl_2 + \underline{n}\text{-}C_7F_{15}BrF_4 \longrightarrow 2C_5F_8Cl_2 + \underline{n}\text{-}C_7F_{15}Br$$

The NMR data for $C_5F_6Cl_2$ and $C_5F_8Cl_2$ are given in Table V.

TABLE V

The Chemical Shifts of $C_5F_6Cl_2$ and $C_5F_8Cl_2$

Compound	Structure	^{19}F nucleus	Chemical Shifts*
$C_5F_6Cl_2$		3,5	-115.0
		4	-131.0
$C_5F_8Cl_2$		3,5-eq	-117.1
		3,5-ax	-124.0
		4-eq	-125.4
		4-ax	-126.7
		1,2-ax	-139.0

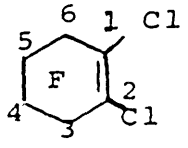
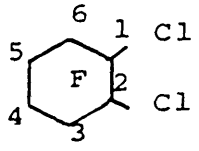
*In ppm from $CFCl_3$ as internal references, upfield is negative.

H. Reaction with $C_6F_8Cl_2$

Excess 1,2-dichlorooctafluorocyclohexene ($C_6F_8Cl_2$) was allowed to react with $\underline{n}$-$C_7F_{15}BrF_4$ in a Monel reactor at 140°C for eight hours. The product was isolated by GC. The NMR and mass spectra showed that 1,2-dichlorodecafluorocyclohexane ($C_6F_{10}Cl_2$) and $\underline{n}$-$C_7F_{15}Br$ had been formed. The NMR data for $C_6F_8Cl_2$ (44,45) and $C_6F_{10}Cl_2$ (46) are given in Table VI.

TABLE VI

The Chemical Shifts of ^{19}F nuclei in $C_6F_8Cl_2$ and $C_6F_{10}Cl_2$

Compound	Structure	^{19}F nucleus	Chemical Shifts*
$C_6F_8Cl_2$		3,3',6,6'	-110.0
		4,4',5,5'	-133.5
$C_6F_{10}Cl_2$		3,6-eq	-116.8
		3,6-ax	-120.5
		4,5-eq	-124.6
		4,5-ax	-128.2
		1,2-ax	-132.0

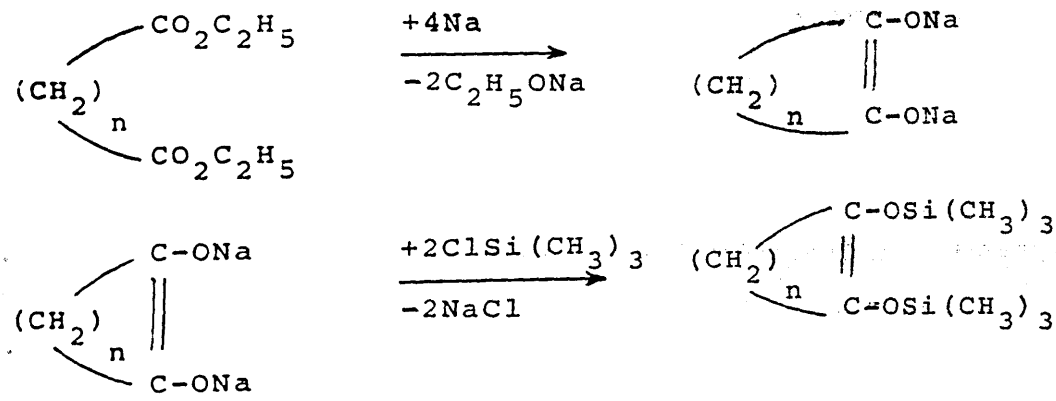
*In ppm from $CFCl_3$ as internal references, upfield is negative.

A comparison of observed ^{19}F NMR data of $C_6F_{10}Cl_2$ and $C_5F_8Cl_2$ with the literature values (46) showed them to be cis isomers.

3. Dihaloketene-Siloxyolefin Cycloadducts

A. Preparation of Reagents

The siloxyolefins 17-19 shown in Table VII was prepared by the addition of esters 11-13 to dry toluene solution of sodium at 115°C, followed by addition of trimethylchlorosilane (Me_3SiCl). The spectral data obtained for these siloxyolefins are shown in Table VIII.



17: n=2 18: n=3 19: n=4

The silylated ketene acetals 20-22 shown in Table VII was prepared by addition of esters 14-16 to a tetrahydrofurane solution of lithio-1,1,1,3,3,3-hexamethyldisilazane at -78°C, followed by quenching of the resulting enolate with chlorotrimethylsilane (Me_3SiCl). The silylated esters 14-16 were prepared by the silylation of the corresponding carboxylic acids, using a 2:1 mixture of 1,1,1,3,3,3-hexamethyldisilazane [HMDS] and Me_3SiCl in pyridine or pridine-tetrahydrofurane mixtures:

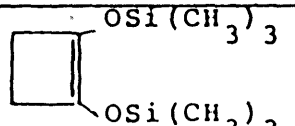
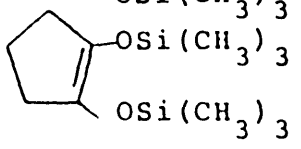
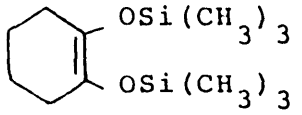
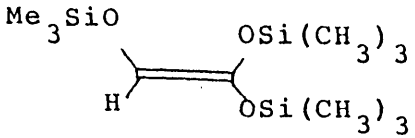
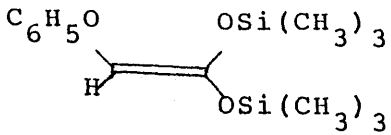
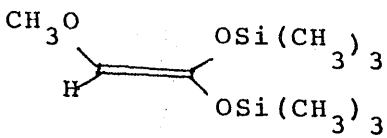
TABLE VII

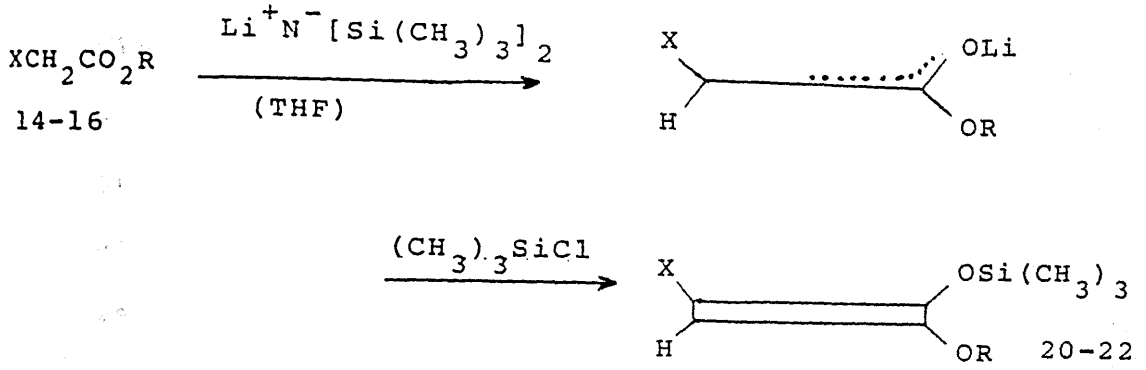
Siloxyolefins Prepared

esters		Siloxyolefin		b.p.°C (Torr)	% yield
$C_2H_5CO_2CH_2CH_2CO_2C_2H_5$	11	$C_{10}H_{22}O_2Si_2$	17	56-59(0.6)	92
$C_2H_5CO_2CH_2CH_2CH_2CO_2C_2H_5$	12	$C_{11}H_{24}O_2Si_2$	18	90-93(10)	95
$C_2H_5CO_2CH_2(CH_2)_2CH_2CO_2C_2H_5$	13	$C_{12}H_{26}O_2Si_2$	19	98-101(10)	93
$(CH_3)_3SiOCH_2CO_2Si(CH_3)_3$	14	$C_{11}H_{28}O_3Si_3$	20	62-65(0.4)	100
$C_6H_5OCH_2CO_2Si(CH_3)_3$	15	$C_{14}H_{24}O_3Si_2$	21	120-125(0.6)	95
$CH_3OCH_2CO_2Si(CH_3)_3$	16	$C_9H_{22}O_3Si_2$	22	65-70(10)	81

TABLE VIII

Spectral Data of Siloxyolefins

Siloxyolefin	Empirical Formula	Structure	NMR	IR, cm^{-1} C=C
17	$C_{10}H_{22}O_2Si_2$		δ=2.01(t,4H,CH_2)	1730
18	$C_{11}H_{24}O_2Si_2$		δ=2.1(m,4H,CH_2) 1.65(m,4H,CH_2) 0.08(s,18H,$Si(CH_3)_3$)	1712
19	$C_{12}H_{26}O_2Si_2$		δ=2.20(m,4H) 1.75(m,4H) 0.05(s,18H)	1700
20	$C_{11}H_{28}O_3Si_3$		δ=5.4(s,1H,CH) 0.06(s,9H) 0.03(s,9H) 0.00(s,9H)	1708
21	$C_{14}H_{24}O_3Si_2$		δ=7.05(m,5H,C_6H_5) 5.85(s,1H,CH) 0.27(s,9H) 0.21(s,9H)	1700
22	$C_9H_{22}O_3Si_2$		δ=6.1(s,1H,CH) 3.16(s,3H,OCH_3) .03(s,9H) .00(s,9H)	1710



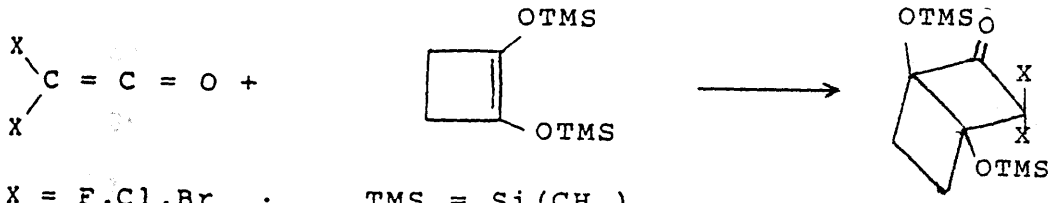
The spectral data obtained for these silylated ketene acetals are shown in Table VIII.

B. Synthesis and Analysis of Cycloadducts

The in situ cycloaddition of siloxyolefins 17-22 with dihaloketene generated from corresponding acetyl chloride by activated zinc dehalogenation in dry ether or ethyl acetate under a nitrogen atmosphere, were found to yield [2+2] cycloaddition. The optimum conditions for effecting this cycloaddition are in refluxing ethyl acetate for difluoroketene cycloaddition and in refluxing ether for dichloro- and dibromoketene. A slow addition of acid halide to the zinc and olefin in ethyl acetate (difluoroketene) or ether (dichloro and dibromo) to minimize the formation of the α-halovinyl esters (47,48).

The in situ cycloaddition of difluoroketene and siloxyolefins 17-22, occur in low yield (Table IX) because the low boiling point of chlorodifluoroacetyl chloride (difluoroketene) dictates a lower reaction temperature.

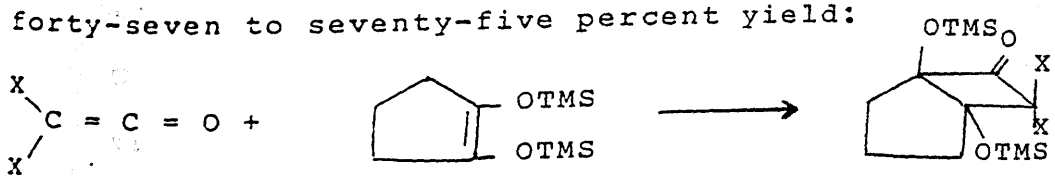
The addition of equimolar quantities of dihaloketene and 1,2-bis(trimethylsiloxy)cyclobutene under a nitrogen atmosphere (Table IX-XI) resulted in a thirty-four to sixty-five percent yield of the 6,6-dihalo-1,4-bis(trimethylsiloxy)bicyclo[2.2.0]hexane-5-one:



X = F,Cl,Br ; TMS = $Si(CH_3)_3$

The infrared spectra of the above adducts revealed the carbonyl band at 1780-1800 cm^{-1} and the ^1H NMR spectra (Table XII-XIV) multiplets at 1.60-2.00 ppm, 0.15-0.45 ppm, and 0.00-0.20 ppm. The mass spectra and elemental analysis were consistent with the structure.

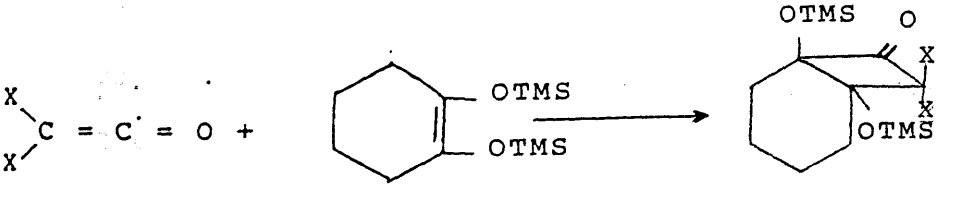
The cycloaddition of dihaloketenes with 1,2-bis-(trimethylsiloxy)cyclopentene was allowed to proceed overnight and 7,7-dihalo-1,5-bis(trimethylsiloxy)bicyclo [3.2.0]heptane-6-one (Table IX-XI) were isolated in forty-seven to seventy-five percent yield:



X = F,Cl,Br ; TMS = $Si(CH_3)_3$

The infrared spectra of the above adducts showed the carbonyl band at 1750-1800 cm^{-1} and the ^{1}H NMR spectra (Table XII-XIV) multiplets at 1.80-2.0 ppm, 1.40-1.70 ppm, 0.20-0.40 ppm, and 0.03-0.1 ppm. The mass spectra and elemental analysis were in agreement with the structure.

The addition of equimolar quantities of dihaloketenes and 1,2-bis(trimethylsiloxy)cyclohexene under a nitrogen atmosphere after 12 hours afforded 8,8-dihalo-1,6-bis(trimethylsiloxy)bicyclo[4.2.0]octane-7-one (Table IX-XI):

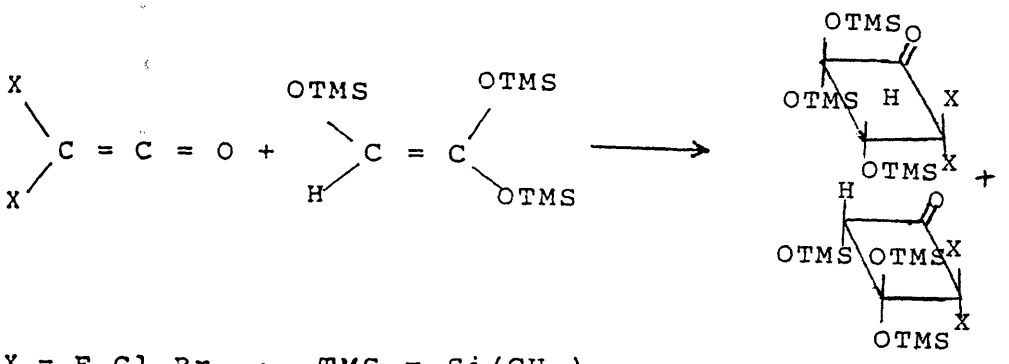


X = F,Cl,Br ; TMS = $Si(CH_3)_3$

An infrared spectra of the adducts revealed the carbonyl band at 1750-1795 cm^{-1} and the ^{1}H NMR spectra (Table XII-XIV) multiplets at 1.91-2.0 ppm, 1.50-1.63 ppm, 0.30-0.45 ppm, and 0.06-0.20 ppm. The mass spectra and elemental analysis were consistent with the structure.

When an equimolar mixture of dihaloketenes and tris(trimethylsiloxy)ethene were treated in dry ether or ethyl acetate under a nitrogen atmosphere, 4,4-dihalo-2,2,3-tris(trimethylsiloxy)cyclobutanone and 4,4-dihalo-2,3,3-tris(trimethylsiloxy)cyclobutanone (Table IX-XI)

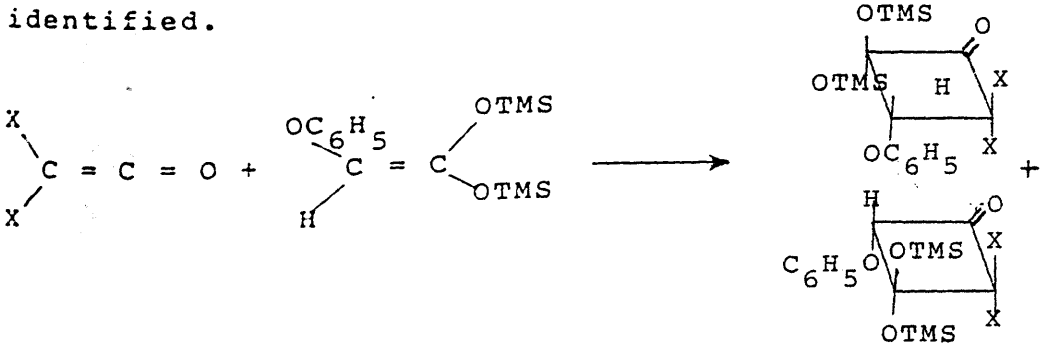
were isolated in quantitative yield.



X = F,Cl,Br ; TMS = $Si(CH_3)_3$

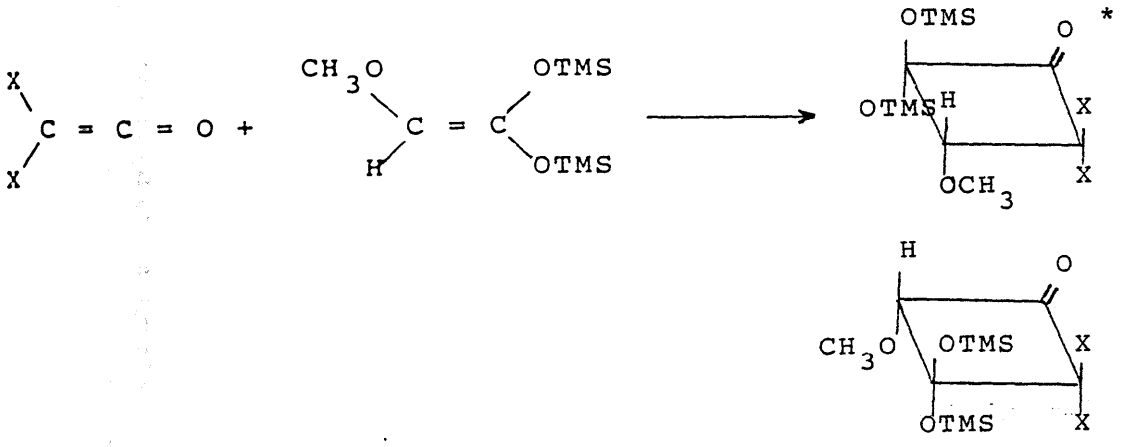
The spectral data (Table XV-XVII), infrared spectra, ^1H NMR spectra, mass spectra and elemental analysis were in agreement with the structure.

Treatment of equimolar quantities of dihaloketenes with 2-phenoxy-1,1-bis(trimethylsiloxy)ethene under a nitrogen atmosphere, 4,4-dihalo-3-phenoxy-2,2-bis(trimethylsiloxy)cyclobutanone and 4,4-dihalo-2-phenoxy-3,3-bis(trimethylsiloxy)cyclobutanone (Table IX-XVII) were identified.



X = F,Cl,Br ; TMS = $SiMe_3$

The addition of dihaloketenes and 2-methox-1,1-bis-(trimethylsiloxy)ethene afforded 4,4-dihalo-3-methoxy-2,2-bis(trimethylsiloxy)cyclobutanone and 4,4-dihalo-2-methoxy-3,3-bis(trimethylsiloxy)cyclobutanone (Table IX-XVII).



4. Fluorination of Cycloadducts

Treatment of cycloadducts with $PhPF_4$ resulted in replacement of $OSiMe_3$ groups with fluorines.

*Since the GC showed the presence of two compounds, also using the ^1H NMR data, the cycloadducts assumed to be mixture of cis and trans isomers.

TABLE IX

Difluoroketene-Siloxyolefin Cycloadducts Synthesized

dihaloketene	Siloxyolefin	Product No.	Empirical Formula	b.p.°C (Torr)	%yield
$F_2C=C=O$	$C_{10}H_{22}O_2Si_2$	23	$C_{12}H_{22}F_2O_3Si_2$	41-45(0.3)	34
$F_2C=C=O$	$C_{11}H_{24}O_2Si_2$	24	$C_{13}H_{24}F_2O_3Si_2$	48-50(0.35)	47
$F_2=C=O$	$C_{12}H_{26}O_2Si_2$	25	$C_{14}H_{26}F_2O_3Si_2$	52-55(0.4)	55
$F_2C=C=O$	$C_{11}H_{28}O_3Si_3$	26,27	$C_{13}H_{28}F_2O_4Si_3$	67-70(0.4)	40
$F_2C=C=O$	$C_{14}H_{24}O_3Si_2$	28,29	$C_{16}H_{24}F_2O_4Si_2$	99-104(0.1)	62
$F_2C=C=O$	$C_9H_{22}O_3Si_2$	30,31	$C_{11}H_{22}F_2O_4Si_2$	70-74(4)	36

TABLE X

Dichloroketene-Siloxyolefin Cycloadduct Synthesized

Dichloroketene	Siloxyolefin	Product No.	Empirical Formula	b.p °C (Torr)	%yield
$Cl_2C=C=O$	$C_{10}H_{22}O_2Si_2$	32	$C_{12}H_{22}Cl_2O_3Si_2$	105-107(0.35)	65
$Cl_2C=C=O$	$C_{11}H_{24}O_2Si_2$	33	$C_{13}H_{24}Cl_2O_3Si_2$	72-76(0.3)	75
$Cl_2C=C=O$	$C_{12}H_{26}O_2Si_2$	34	$C_{14}H_{26}Cl_2O_3Si_2$	60-64(0.4)	55
$Cl_2C=C=O$	$C_{11}H_{28}O_3Si_3$	35,36	$C_{13}H_{28}Cl_2O_4Si_3$	63-65(0.2)	45
$Cl_2C=C=O$	$C_{14}H_{24}O_3Si_2$	37,38	$C_{16}H_{24}Cl_2O_4Si_2$	120-123(0.1)	38
$Cl_2C=C=O$	$C_9H_{22}O_3Si_2$	39,40	$C_{11}H_{22}Cl_2O_4Si_2$	71-75(1.2)	41

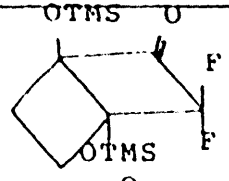
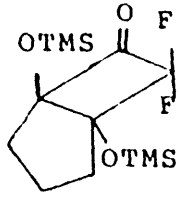
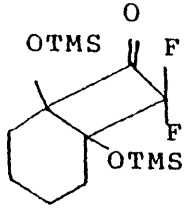
TABLE XI

Dibromoketene-Siloxyolefin Cycloadduct Synthesized

dibromoketene	siloxyolefin	Adduct	Empirical formula	b.p.° (Torr)	% yield
$Br_2C = C = O$	$C_{10}H_{22}O_2Si_2$	41	$C_{12}H_{22}Br_2O_3Si_2$	66-69(0.25)	45
$Br_2C = C = O$	$C_{11}H_{24}O_2Si_2$	42	$C_{13}H_{24}Br_2O_3Si_2$	82-85(0.25)	74
$Br_2C = C = O$	$C_{12}H_{26}O_2Si_2$	43	$C_{14}H_{26}Br_2O_3Si_2$	95(0.2)	82
$Br_2C = C = O$	$C_{11}H_{28}O_3Si_3$	44,45	$C_{13}H_{28}Br_2O_4Si_3$	70-73(0.1)	66
$Br_2C = C = O$	$C_{14}H_{24}O_3Si_2$	46,47	$C_{16}H_{24}Br_2O_4Si_2$	128-130(0.1)	27
$Br_2C = C = O$	$C_9H_{22}O_3Si_2$	48,49	$C_{11}H_{22}Br_2O_4Si_2$	75-78(0.3)	39

TABLE XII

Spectral Data of Difluorocycloadducts

Adduct No.	Empirical formula	Structure	^{1}H NMR: δ_{Me_4Si}	^{19}F NMR: δ_{CFCl_3}	IR, cm^{-1} C=O
23	$C_{12}H_{22}F_2O_3Si_2$		2.00(m,4H,CH_2) 0.45(m,9H,$SiMe_3$) 0.20(m,9H),$SiMe_3$)	65.0(d,1F) 65.8(d,1F)	1800
24	$C_{13}H_{24}F_2O_3Si_2$		1.90(t,4H,CH_2) 1.40(m,2H,CH_2) 0.4(m,9H,$SiMe_3$) 0.1(m,9H,$SiMe_3$)	63.2(d,1F) 64.1(d,1F)	1800
25	$C_{14}H_{26}F_2O_3Si_2$		1.91(m,4H,CH_2) 1.52(m,4H,CH_2) 0.4(m,9H,$SiMe_3$) 0.15(m,9H,$SiMe_3$)	63.5(d,1F) 64.5(d,1F)	1795

*From CCl_3F as internal reference, upfield is positive.

TABLE XIII

Spectral Data of Dichlorocycloadducts

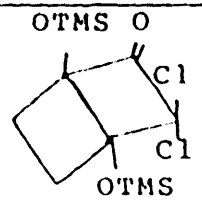
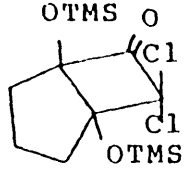
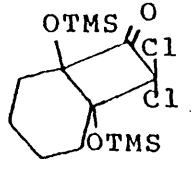
Adduct No.	Empirical formula	Structure	H-NMR: δ_{Me_4Si}	IR, cm^{-1} C=O
32	$C_{12}H_{22}Cl_2O_3Si_2$		1.9(m,4H,CH_2) 0.15(m,9H,$SiMe_3$) 0.03(m,9H,$SiMe_3$)	1790
33	$C_{13}H_{24}Cl_2O_3Si_2$		2.0(m,4H,CH_2) 1.7(m,2H,CH_2) 0.2(m,9H,$SiMe_3$) 0.03(m,9H,$SiMe_3$)	1750
34	$C_{14}H_{26}Cl_2O_3Si_2$		2.0(m,4H,CH_2) 1.63(m,4H,CH_2) 0.45(m,9H,$SiMe_3$) 0.20(m,9H,$SiMe_3$)	1795

TABLE XIV

Spectral Data of Dibromoadducts

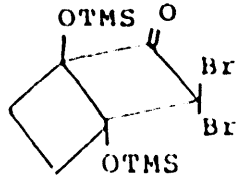
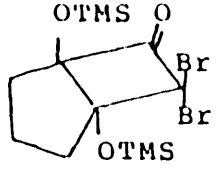
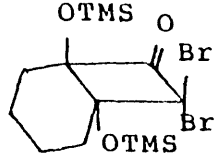
Adduct No.	Empirical formula	Structure	H-NMR: δ_{Me_4Si}	IR, cm^{-1} (C=O)
41	$C_{12}H_{22}Br_2O_3Si_2$		1.60(m,4H,CH_2) 0.15(m,9H,$SiMe_3$) 0.00(m,9H,$SiMe_3$)	1780
42	$C_{13}H_{24}Br_2O_3Si_2$		1.80(m,4H,CH_2) 1.63(m,2H,CH_2) 0.20(m,9H,$SiMe_3$) 0.03(m,9H,$SiMe_3$)	1765
43	$C_{14}H_{26}Br_2O_3Si_2$		1.95(m,4H,CH_2) 1.50(m,4H,CH_2) 0.30(m,9H,$SiMe_3$) 0.06(m,9H,$SiMe_3$)	1750

TABLE XV

Spectral Data of Difluorocycloadduct

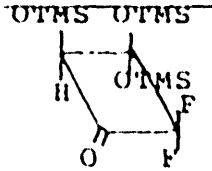
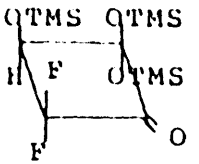
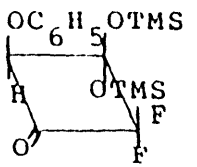
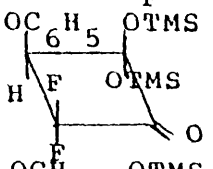
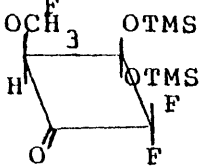
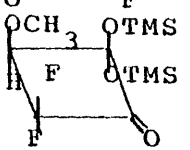
Adduct No.	Structure	^{1}H NMR: δ_{Me_4Si} ppm
26		4.7(s,1H,CH), 0.15(s,9H,$SiMe_3$) 0.2(s,9H,$SiMe_3$), 0.1(s,9H,$SiMe_3$)
27		4.0(t,1H,CH), 0.00(s,9H,$SiMe_3$) 0.03(s,9H,$SiMe_3$),-0.10(s,9H,$SiMe_3$)
28		5.13(s,1H,CH), 0.36(s,9H,$SiMe_3$) 6.87(m,5H,C_6H_5), 0.29(s,9H,$SiMe_3$)
29		4.50(t,1H,CH), 0.28(s,9H,$SiMe_3$) 6.35(m,5H,C_6H_5), 0.21(s,9H,$SiMe_3$)
30		4.62(s,1H,CH), 0.1(s,9H,$SiMe_3$) 3.19(s,3H,OCH_3), 0.08(s,9H,$SiMe_3$)
31		3.90(t,1H,CH), 0.09(s,9H,$SiMe_3$) 3.03(s,3H,OCH_3), 0.06(s,9H,$SiMe_3$)

TABLE XVI

Spectral Data of Dichlorocycloadducts

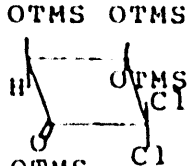
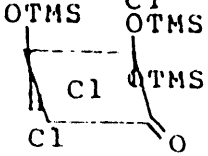
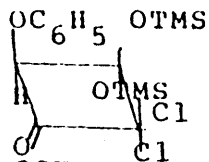
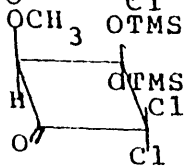
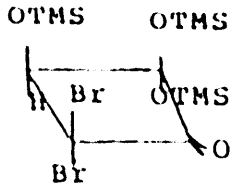
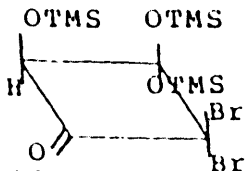
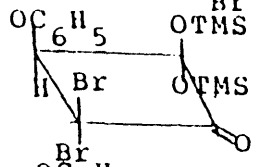
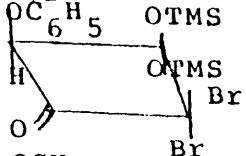
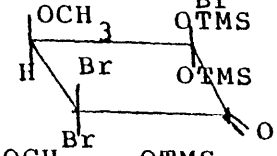
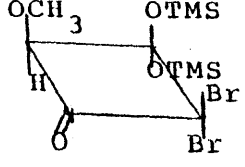
Adduct No.	Empirical formula	Structure	^{1}H NMR: δ_{Me_4Si} = ppm
35	$C_{13}H_{28}Cl_2O_4Si_3$		5.16(s,1H,CH), 0.2(s,9H) 0.3(s,9H,$SiMe_3$), 0.08(s,9H)
36	$C_{13}H_{28}Cl_2O_4Si_3$		4.57(s,1H,CH), 0.15(s,9H) 0.25(s,9H), 0.00(s,9H)
37	$C_{16}H_{24}Cl_2O_4Si_2$		7.00(m,5H,C_6H_5), 0.22(s,9H) 5.62(s,1H,CH) 0.18(s,9H)
38	$C_{11}H_{22}Cl_2O_4Si_2$		4.90(s,1H,CH), 0.08(s,9H) 3.12(s,3H,OCH_3), 0.03(s,9H)

TABLE XVII

Dibromocycloadduct's Spectral Data

Adduct No.	Structure	^{1}H NMR: δ_{Me_4Si} = ppm
44		5.24(s,1H,CH), 0.18(s,9H) 0.23(s,9H), 0.13(s,9H)
45		4.98(s,1H,CH), 0.16(s,9H) 0.20(s,9H), 0.10(s,9H)
46		6.1(m,5H,C_6H_5), 0.28(s,9H) 5.75(s,1H,CH), 0.20(s,9H)
47		6.82(m,5H, C_6H_5, 0.15(s,9H) 5.48(s,1H,CH), 0.12(s,9H)
48		5.03(s,1H,CH), 0.10(s,9H) 3.20(s,3H,OCH_3), 0.08(s,9H)
49		4.75(s,1H,CH), 0.05(s,9H) 3.00(s,3H,OCH_3), 0.00(s,9H)

CHAPTER V

SUMMARY AND CONCLUSION

A. Perfluoroalkylbromine (V) tetrafluorides

Perfluoro-n-propylbromine (V) tetrafluoride, perfluoro-n-heptylbromine (V) tetrafluoride are new classes of aliphatic derivatives of bromine pentafluoride. They were prepared by the oxidation of perfluoro-n-propyl bromide and perfluoro-n-heptyl bromide with elemental fluorine, chlorine trifluoride, bromine trifluoride and bromine pentafluoride. The reactions of perfluoro-n-heptylbromine (V) tetrafluoride (n-$C_7F_{15}BrF_4$) with 1,2-dichlorohexafluoropentene ($C_5F_6Cl_2$) and 1,2-dichlorooctafluorocyclohexene ($C_6F_8Cl_2$) were used to demonstrate in the fluorinating ability of n-$C_7F_{15}BrF_4$.

B. Dihaloketene-Siloxyclycloolefin Cycloadducts

The (2+2) cycloaddition of difluoro, dichloro, and dibromoketene with 1,2-bis(trimethylsiloxy)cyclobutene, 1,2-bis(trimethylsiloxy)cyclopentene, and 1,2-bis(trimethylsiloxy)cyclohexene were found to yield the corresponding cyclobutanones in dry ether or ethyl acetate and under a nitrogen atmosphere.

C. Dihaloketene-Silylated Ketene Acetal Cycloadducts

The cycloaddition of difluoro, dichloro, and

dibromoketenes with tris(trimethylsiloxy)ethene, 2-phenoxy-1,1-bis(trimethylsiloxy)ethene, and 2-methoxy-1,1-bis(trimethylsiloxy)ethene under a nitrogen atmosphere afforded the corresponding cyclobutanones.

D. Fluorination of Cycloadducts

Treatment of cycloadducts with $PhPF_4$ resulted in replacement of $OSiMe_3$ groups with fluorines.

APPENDIX

Chemical	Source
n-Butyl lithium	Aldrich
Cupric sulfate	J. T. Baker
Dichlorophenylphosphine	Aldrich
Diethyl adipate	Aldrich
Diethyl glutarate	Aldrich
Diethyl succinate	Aldrich
Ether anhydrous	MC/B
Ethyl acetate	MC/B
Glycolic acid	Aldrich
Hexamethyldisilazane	Aldrich
n-Hexane	Aldrich
n-Pentane	Aldrich
Petroleum ether	J. T. Baker
Phenoxy acetic acid	Aldrich
Sulfur tetrafluoride	Union carbide
Tetrahydrofuran	J. T. Baker
Thiony chloride	MC/B
Toluene	MC/B
Trimethylchlorosilane	Aldrich
Zinc metal	Fisher Scientific

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