

UNCLASSIFIED

AD 408 975

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

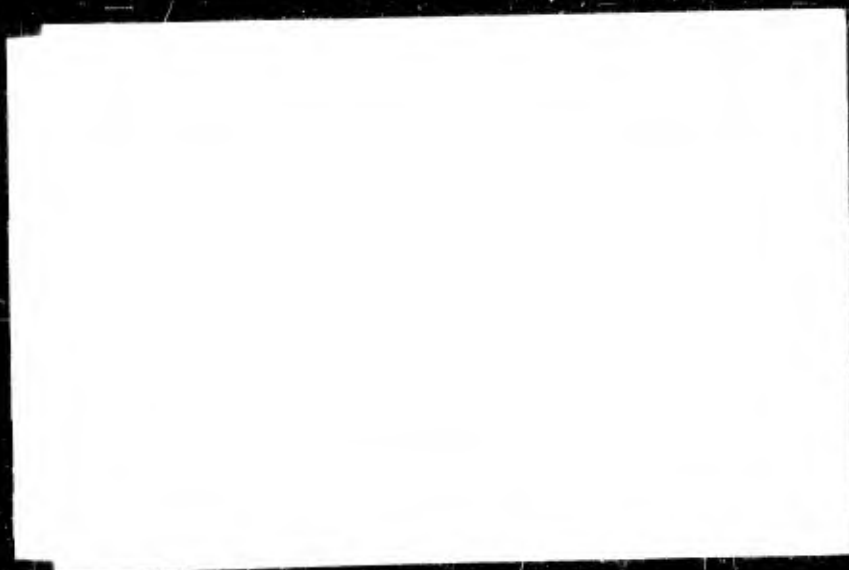
CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

408 975



N-63-4-2

THE SYNTHESIS OF UNSATURATED FLUOROCARBONS

Supported in part by Wright Air Development Division
U. S. Air Force: MIPR 339(616)-5701
Project Number 7-93-15-004: Contract DA-19-129-QM-500

Between
The Office of the Quartermaster General
and
The University of Florida

Final Report: March 31, 1963

By Paul Tarrant
John Savory
David Sayers
Ward Oliver
Ed Iglehart

JUN 24 1963

I. INTRODUCTION

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

It is estimated that 100% of the work has been completed and 99.9% of the estimated costs have been incurred to date.

This research is authorized under Contract Number DA-19-129-QM-500 and is a further continuation of the work initiated under DA-44-109-QM-522 and continued under DA-44-109-QM-1469. The Wright Air Development Center has contributed funds for the operation of the project in part since September 13, 1956, under MIPR 33(616)-5701.

This is the 30th report under the contract but the 47th since the project was initiated in 1951.

II. SUMMARY OF CURRENT PROGRESS

The reaction of $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ [I] and $\text{CF}_2=\text{CFSi}(\text{CH}_3)_3$ [II] with butadiene has been studied. A cyclobutyl derivative was formed from the butenylsilane. Nitrosyl chloride reacted with I to give $\text{CF}_2\text{ClCFNOCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$. I also formed a cyclobutyl dimer on heating.

Trifluoroacetophenone was treated with ethylene chlorohydrin to give 2-trifluoromethyl-2-phenyl-1,3-dioxolane.

Lithium methylacetylide has been found to react with a number of fluoro-olefins to give compounds containing both double and triple bonds. Yields were generally good, $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CFCl}$ having been realized in 73% yield from $\text{CH}_3\text{C}\equiv\text{CH}$ and $\text{CF}_2=\text{CFCl}$. Tetrafluoroethylene gave the di-yne-ene, $\text{CH}_3\text{C}\equiv\text{C}-\text{CF}=\text{CF}-\text{C}\equiv\text{CCH}_3$, while 1,1,2-trifluorobutadiene gave the di-ene-yne $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CFCH}=\text{CH}_2$.

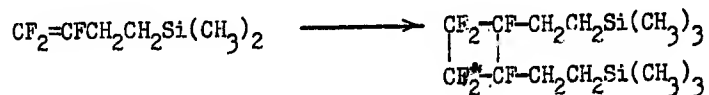
A preliminary study has been made of the chemical behavior of the ene-yne.

III. DISCUSSION

Silane Studies

The syntheses of $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ [I] and $\text{CF}_2=\text{CFSi}(\text{CH}_3)_3$ [II] were described in the last quarterly report. Additional research has been carried out in this area to gain an understanding of the chemical behavior of these compounds.

One typical reaction of compounds containing the $\text{CF}_2=\text{CX}_2$ grouping with olefins is the formation of cyclobutane derivatives. The silanes were found to undergo these reactions as shown below:



The reaction was carried out at 210° for a period of 47 hours in a sealed tube to give a product in 33% yield, b.p. $68-74^\circ$ at 0.8 mm. Anal. Calc'd for $\text{C}_{14}\text{H}_{26}\text{F}_6\text{Si}_2$: C, 46.12; H, 7.19; F, 31.26. Found: C, 46.31, H, 7.19; F, 31.52.

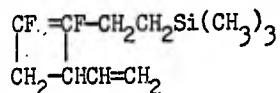
The NMR spectra were consistent with the structure shown above.

Allyltrimethylsilane was heated with I and a small amount of high boiling material was obtained. Analytical results indicated a mixture of components with the dimer of I as the predominant product.

Similar results were obtained when vinyltrimethylsilane and I were heated.

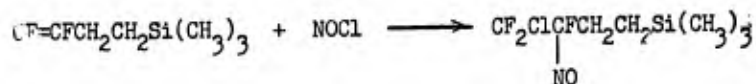
Butadiene has also been heated with I and II. In the case of $\text{CF}_2=\text{CFSi}(\text{CH}_3)_3$ [II] only a thick oil was obtained which was not resolved by gas

chromatographic separation. More success was obtained with I and a 33% yield of adduct was obtained. It has been assigned the structure



on the basis of NMR and IR data. Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{F}_3\text{Si}$: C, 55.88; H, 8.11. Found: C, 56.87; H, 8.11.

Nitrosyl chloride has also been added to $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ [I] to give the blue nitroso adduct.



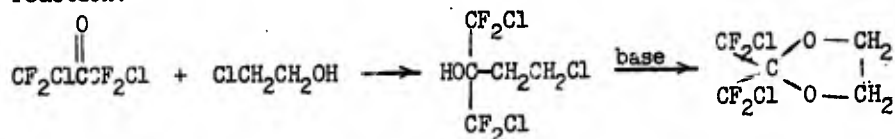
The nitroso compound was separated by partition through an alumina column with pentane as the eluting agent. The yield of adduct was 13%. Anal. Calcd for $\text{C}_7\text{H}_{13}\text{F}_3\text{ClSiNO}$: C, 33.89; H, 5.29. Found: C, 33.76; H, 5.43.

NMR indicated the structure as shown but also indicated it was present to the extent of 50%. Very probably this result was due to the elapsed time of a week between preparation of the sample and determination of the spectrum during which considerable decomposition could have occurred.

It was anticipated that $\text{CF}_2=\text{CFCH}_2\text{Si}(\text{CH}_3)_3$ could be made by coupling $\text{CF}_2=\text{CFMgBr}$ with $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$; however, only polymeric material was produced.

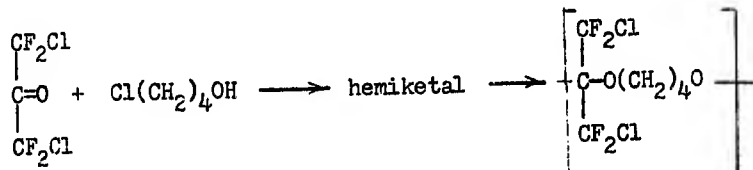
Ketal Studies

Some reactions of α -fluoroketones with chloro alcohols have been studied. Simons and Wiley [J. Am. Chem. Soc. 82, 2288 (1960)] reported the following reaction:



3-Chloro-1-propanol reacted to give the corresponding dioxane.

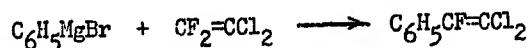
It was anticipated that polymers might be obtained by proper choice of a chloro alcohol which would not give a 5- or 6- membered ring.



4-Chloro-1-butanol was treated with dichlorotetrafluoroacetone and the mixture refluxed until the exothermic reaction had subsided. Potassium carbonate was added and reflux continued several hours. Inspection of the reaction mixture by V.P.C. indicated the presence of 3 high boiling components but no high molecular weight polymer was present.

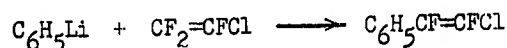
Trifluoroacetophenone was reacted with ethylene chlorohydrin to give a product separated by the preparative scale chromatographic apparatus and identified as 2-trifluoromethyl-2-phenyl-1,3-dioxolane. Physical constants are b.p. 218-9°, n_D^{25} 1.4575. Anal. Calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_2$: C, 55.1; H, 4.3. Found: C, 55.9; H, 4.2. The yield was 48%. NMR and IR data support the assigned structure.

Trifluoroolefins containing the $\text{CF}_2=\text{CF}$ group are susceptible to attack by nucleophilic reagents. Earlier work in these laboratories have shown that the Grignard reagent will attack a fluoroolefin to give a longer chain fluoroolefin. [Tarrant and Warner, J. Am. Chem. Soc. 76, 1624 (1954).] Thus phenylmagnesium bromide reacts with difluorodichloroethylene to give fluorodichlorostyrene in 65% yield:



McGrath and Levine [J. Am. Chem. Soc. 77, 4168 (1955)] and Dixon [J. Org. Chem. 21, 400 (1956)] have also shown that lithium reagents react with

fluoroolefins in a similar manner.



It was of some interest to determine if acetylenic compounds would also react with fluoroolefins, particularly in view of the suspected reactivity of the resulting compounds which should contain both a double and a triple bond.

Methylacetylene was selected as the acetylenic compound to add because it is conveniently handled and has only one active hydrogen atom. It was found to react readily with a number of fluoroolefins to give the expected products in yields from 17 to 73%. The reactions were carried out by passing the olefin into a slurry of lithium methylacetylide, prepared from methylacetylene and methyllithium, in tetrahydrofuran at either 0° or -22°. The white mixture gradually turned black as the fluoroolefin was added.

The following table shows the products from the reactions.

Table I. Products of the Reaction of $\text{MeC}\equiv\text{CLi}$ with Fluoroolefins

Olefin	Product %	Yield	cis-trans ratio	wt. of Polymer Formed g.
$\text{CF}_2=\text{CCL}_2$	IV. $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CCL}_2$	51		9.0
$\text{CF}_2=\text{CFCl}$	V. $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CFCl}$	73	4/1	2.0
$\text{CF}_2=\text{CFBr}$	VI. $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CFBr}$	56	7/3	1.5
$\text{CF}_2=\text{CFCF}_3$	VII. $\text{CH}_3\text{C}\equiv\text{CF}=\text{CFCF}_3$	17	all trans	15.0
$\text{CF}_2=\text{CFCH}=\text{CH}_2$	VIII. $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CFCH}=\text{CH}_2$	64	all trans	4.5
$\text{CF}_2=\text{CF}_2$	IX. $\text{CH}_3\text{C}\equiv\text{C}-\text{CF}=\text{CF}-\text{C}\equiv\text{CCH}_3$	35		4.0
$\text{CF}_2=\text{CHF}$	None			
CF_2CH_2	None			
$\text{CF}_2\text{CF}_2\text{CF}=\text{CF}$	None			

It will be noted that the presence of hydrogen in the fluoroethylene series prevented reaction from taking place. Both $\text{CHF}=\text{CF}_2$ and CH_2CF_2 are

low boiling but $\text{CF}_2=\text{CF}_2$ is also a low boiling material, indicating that the lack of reactivity is not caused by this factor. It may be that these hydrogen atoms are sufficiently acidic to react with the acetylide to regenerate methylacetylene and form either $\text{FC}\equiv\text{CF}$ or $\text{FC}\equiv\text{CH}$. We are unable to account for the unreactivity of the perfluorocyclobutene.

The reaction with tetrafluoroethylene is interesting since the product contained two acetylene units per $-\text{CF}=\text{CF}-$ group. The formation of this product demonstrates the unusual reactivity of the $\text{CF}_2=$ group.

It is also interesting that 1,1,2-trifluorobutadiene, $\text{CF}_2=\text{CF}-\text{CH}=\text{CH}_2$ also reacted with methylacetylene to give a compound with a triple bond and two double bonds.

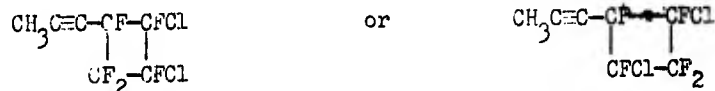
The reaction product of methylacetylene and chlorotrifluoroethylene, $\text{CH}_3\text{C}\equiv\text{C}-\text{CF}=\text{CFCl}$ [V] was prepared in considerable quantity for a study of its chemical behavior.

It was treated with bromine to give $\text{CH}_3\text{CBr}=\text{CBrCF}=\text{CFCl}$ which was identified by IR and elemental analysis. Normally the double bond is more susceptible to attack by bromine and this behavior once again demonstrates the unexpected character of fluorolefins.

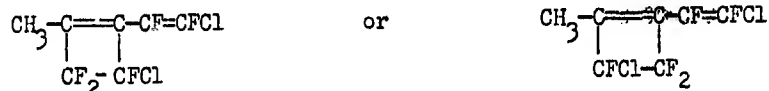
Normally acetylenic hydrocarbons react with hydrogen fluoride to give vinylic fluorides or difluorides in clean-cut reactions. However, when $\text{CH}_3\text{C}\equiv\text{CCF}=\text{CFCl}$ [V] was treated with HF, fourteen (14) compounds were produced according to gas chromatographic analysis.

Attempts were made to add ethyl alcohol across the triple bond of $\text{CH}_3\text{C}\equiv\text{C}-\text{CF}=\text{CFCl}$ but none of the expected $\text{CH}_3\text{C}(\text{OC}_2\text{H}_5)=\text{CHCF}=\text{CFCl}$ was obtained.

Chlorotrifluoroethylene reacted with V to give 3 different products which were separated on the preparative scale V.P.C. The lower boiling isomer was shown to be either



while the higher boiling material is tentatively assigned the structure



V reacted with water to give a mixture of isomeric ketones, $\text{CH}_3\text{COCH}_2\text{CF}=\text{CFCl}$ and $\text{CH}_3\text{CH}_2\overset{\text{O}}{\text{C}}\text{CF}=\text{CFCl}$ thus indicating that no appreciable difference exists between the polarized forms $\text{CH}_3\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{C}}-\text{CF}=\text{CFCl}$ and $\text{CH}_3\overset{\ominus}{\text{C}}=\overset{\oplus}{\text{C}}-\text{CF}=\text{CFCl}$.

The absence of attack on the $\text{CFCl}=\text{C}$ group probably indicates the small contribution made by the resonance form $\text{CH}_3-\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{C}}(\text{F})-\overset{\oplus}{\text{C}}(\text{Cl})$.

IV. EXPERIMENTAL

Preparation of Cyclobutylsilanes

The conditions reported by Park, Groves, and Lacher [J. Org. Chem. 25, 1628 (1960)] reacting $\text{Me}_3\text{SiCH}=\text{CH}_2$ with $\text{CF}_2=\text{CFCl}$ were used for these reactions.

(1) Into a glass tube containing a pinch of hydroquinone was placed 4.8 g. $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$ (0.026 mole) and 3.06 g. $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (0.026 mole). The tube was evacuated and sealed and heated in an oil bath at 200° for 36 hours. The tube was then opened and the reaction mixture distilled. A small amount of product (0.62 g.) was collected at $66^\circ/0.8 \text{ mm.}$, $n_D^{20} 1.4133$.

Anal. Calculated for $\text{C}_{13}\text{H}_{27}\text{F}_3\text{Si}$: C, 52.25; H, 9.19; F, 19.20. Found: C, 49.04; H, 8.37; F, 30.39.

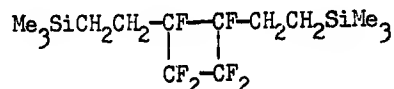
These data indicate that the product is mainly the dimer of $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$. (Calcd for $\text{C}_{14}\text{H}_{26}\text{F}_6\text{Si}_2$: C, 46.12; H, 7.19; F, 41.26).

(2) A similar reaction was run, using $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$ and $\text{Me}_3\text{SiCH}=\text{CH}_2$ (0.026 moles of each). A sample (0.83 g.) boiling between $57^\circ\text{--}69^\circ/0.8\text{mm.}$ was collected, n_D^{20} 1.4253. The similarity of b.p. to the previous product indicated another mixture, and the sample was not further investigated.

(3) A tube containing $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$ (24.6 g., 0.135 mole) was sealed under nitrogen and heated at 210° for 47 hours. The reaction mixture was distilled and 8.02 g. product (32.6%) was obtained, b.p. $68^\circ\text{--}74/0.8\text{mm.}$ n_D^{20} 1.4059.

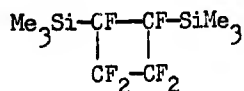
Anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{F}_6\text{Si}_2$: C, 46.12; H, 7.19; F, 31.26. Found: C, 46.31; H, 7.19; F, 31.52.

NMR spectra (Dr. Brey) was consistent with the structure,



containing cis and trans isomers.

(4) A tube containing $\text{Me}_3\text{SiCF}=\text{CF}_2$ (7.04 g.) was heated for 46 hours in an oil bath. Distillation yielded 0.27 g. (3.8%) of a product assumed to be



Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{F}_6\text{Si}_2$: c, 38.94; H, 5.88; F, 36.96. Found: C, 39.19; H, 6.07; F, 37.22.

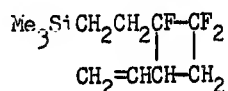
There was insufficient material for an NMR spectra.

(5) Samples of $\text{Me}_3\text{SiCF}=\text{CF}_2$ (6.7 g., 0.044 mole) and $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$ (8.2 g., 0.045 mole) were put into separate thick-walled glass tubes. Each tube was then charged with 1,3-butadiene (4.8 g., 0.09 mole) and sealed under nitrogen.

The two tubes were heated in an oil bath at 200° for 24 hours. Both tubes contained a solid (even at 200°) which was assumed to be polybutadiene.

The liquid portions were removed from the tubes. V.P.C. analysis indicated a well defined product from the reaction with $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$, but not from the reaction with $\text{Me}_3\text{SiCF}=\text{CF}_2$. The latter was a very thick oil.

Distillation of the former sample yielded 3.75 g. (33.6%) product boiling at $38^\circ/0.8$ mm, which was assigned the structure



from IR and NMR data.

IR: 3095 cm^{-1} (w); 2957 (s) cm^{-1} (s); 1645 cm^{-1} (m).

Calcd for $\text{C}_{11}\text{H}_{19}\text{F}_3\text{Si}$: c, 55.88; H, 8.11. Found (ave. of two): C, 56.87; H, 8.11.

Reaction of $\text{CF}_2=\text{CFMgBr}$ with $\text{Me}_3\text{SiCH}_2\text{Cl}$

$\text{CF}_2=\text{CFMgBr}$ was prepared by the conventional method in THF at about 0° , using $\text{CF}_2=\text{CFBr}$ (22.5 g., 0.14 mole) and magnesium (8 g.). Upon completion of reaction $\text{Me}_3\text{Si}-\text{CH}_2\text{Cl}$ (17 g., 0.14 mole) was slowly added. No obvious reaction took place, so the mixture was heated for 30 minutes. Upon removal from the heat, it was noted that a brown gelatinous mass was formed. This hardened later to a lumpy solid.

Preparation of $\text{Me}_3\text{SiCH}_2\text{CH}_2-\text{CF}(\text{NO})\text{CF}_2\text{Cl}$

A 300 ml. 3-necked R.B. flask was fitted with an inlet tube, reflux condenser, and stirrer. To the flask was added AlCl_3 (11 g., 0.082 mole) and DMF (160 ml.). When the contents cooled, $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$ (10.9 g., 0.06 mole) was added and NOCl bubbled in with stirring.

The reaction began immediately with evolution of heat. NOCl was bubbled in periodically until no further reaction was evident (about 2 hours). About 50 ml. of the mixture was put in a column containing activated alumina

(Fischer Reagent, acid) and pentane. The DMF was found not to be soluble in the pentane and the blue material floated on the DMF. The mixture was then removed from the column and extracted with pentane. The pentane layer became very blue, and this layer was passed through the column. The blue material was then collected and the pentane evaporated via aspirator, then vacuum pump.

A product (2.44 g., 12.9% yield) was obtained. NMR indicated the expected compound, but with about 50% impurities. Since a period of over a week elapsed between preparation and the running of the NMR spectra, this was probably due to decomposition. This is very likely due to the close agreement of elemental analysis.

Anal. Calcd for $C_7H_{13}F_3ClSiNO$: C, 33.89; H, 5.29. Found: C, 33.76; H, 5.43.

IR Data: Medium peaks at 3.40, 6.37, 10.0, 11.0 (sh), 13.1, and 14.5 μ . Strong peaks at 8.04, 8.50, 8.80, 9.48, and 11.6-11.9 μ .

Preparation of 2-Trifluoromethyl-2-phenyl-1,3-dioxolane

2-Chloroethanol (0.60 g.) was added to trifluoroacetophenone (1.30 g.) and the mixture stirred for 15 minutes, when the initial exothermic reaction had subsided. Pentane (5cc) and potassium carbonate (1.05 g.) were added and the mixture vigorously stirred under reflux for 4 hrs. The mixture was poured into water, separated, the water layer extracted with pentane and separated. The pentane layers were combined, dried ($MgSO_4$) and excess pentane removed by distillation. V.P.C. inspection of the residue indicated a high boiling component and some trifluoroacetophenone.

Separation by preparative scale V.P.C. (Silicone Elastomer/Celite; 140°) gave:

I. Trifluoroacetophenone (0.31 g.)

II. 2-Trifluoromethyl-2-phenyl-1,3-dioxolane

(0.78 g; 48%); b.p., 213-9°; n_D^{25} 1.4575; (Found: C, 55.9; H, 4.2; $C_{10}H_9F_3O_2$ requires: C, 55.1; H, 4.3). U.V. absorption maxima: λ , 2660 Å; E max 265; λ , 2615 Å, E max 272 (sh); λ , 2600 Å, E max 352; λ , 2560 Å, E max 289; λ , 2540 Å, E max 284; λ , 2500 Å, E max 215; λ , 2480 Å, E max 197 (sh).

The F_{19} and proton NMR spectra were entirely consistent with the proposed structure. The infrared spectrum was consistent with the structure.

Attempted Reaction between 4-Chlorobutanol and Trifluoroacetophenone

4-Chlorobutanol (1.0 g.) was added to trifluoroacetophenone (1.5 g.) and stirred for 30 mins. No exothermic reaction was observed. Pentane (5 cc) and potassium carbonate (1.0 g.) were added and the mixture was refluxed, while stirring was continued, for 4 hrs. The mixture was filtered and excess pentane was removed by distillation. Inspection of residual solution by analytical V.P.C. indicated only starting materials, pentane and some degradation products; no higher boiling material was indicated. The solution was vacuum distilled, no involatile polymeric residue was obtained.

Preparation of Propynyllithium

Methylacetylene from a cylinder was slowly passed into a stirred solution of methyllithium in ether (143 mls., 0.2 mole). A white precipitate of propynyllithium [III] was soon formed and methane was evolved from the solution. The reaction was continued for 6 hours with the addition of more ether as required.

Reaction of [III] with Fluoro-Olefins

General Procedure

The propynyllithium (see above) was allowed to settle overnight and the supernatant liquid was drawn off. Anhydrous tetrahydrofuran (THF) (175 mls)

was then added and was sufficient to dissolve most of [III]. Reactions were then carried out immediately with this solution since any delay might cause unnecessary cleavage of the THF by [III].

The solution of [III] in THF was cooled to 0°C or -22°C and slowly treated with the desired fluoroolefin. The reactions were exothermic and the solution immediately turned black. In most of the reactions the olefin was a gas and was passed into the reaction mixture three times in order to ensure complete reaction. Hydrolysis of unreacted [III] was effected by pouring the reaction mixture into ice cold 3N hydrochloric acid (50 mls). This whole mixture was steam distilled when a residual black tar was obtained. The organic layer from the steam distillation was separated and the aqueous layer extracted with ether (3 x 25 mls). Due to the extreme solubility of THF in water there was still some THF left in the aqueous layer. An analytical V.P.C. check, however, showed that the ether extraction had removed all reaction product from this aqueous portion. The combined organic extracts were dried over calcium chloride and the ether and THF removed by distillation through either an 18" Vigreux or 24" Heliplate packed column. The residue consisted of product and THF. The last traces of the latter were removed by repeated washing with water. A check by analytical V.P.C. showed no product to be in the aqueous layer. The organic product was dried over calcium chloride and phosphoric anhydride and was vacuum distilled.

1,1-Dichloro-2-fluoropent-1-en-3-yne [IV]

Reaction of 1,1-dichlorodifluoroethylene (40 g., 0.3 mole, 50% excess) with [III] gave 15.7 g. (51%) of [IV], b.p. 141.5°C, n_D^{25} 1.4850.

Anal. Calcd for: $C_5H_3Cl_2F$: C, 39.25; H, 1.96; F, 12.42. Found: C, 39.16; H, 2.21; F, 12.67.

An infrared spectrum of [IV] had strong bands at 4.49 ($C\equiv C$), 7.76, 9.50 (C-F stretching), 10.25, 12.30 μ , and a medium strong band at 6.15 μ ($C=C$).

The ultraviolet spectrum (CH_3OH) had λ max 228, 233 and 245 μ (E , 12,550; 13,730; and 12,060 respectively).

The F^{19} NMR spectrum showed a single absorption at 22.3 ppm relative to external CF_3COOH which was split by coupling into a quartet of 4.8 c.p.s. which is consistent with the proposed structure for [IV].

A black tarry material (9.0 g.) was also formed in the reaction.

1-Chloro-1,2-difluoropent-1-en-3-yne [V]

Reaction of chlorotrifluoroethylene (35 g., 0.3 mole, 50% excess) with [III] gave 20.0 g. (73%) of [V], b.p. 97°C , n_D^{25} 1.4300.

Anal. Calcd for $\text{C}_5\text{H}_3\text{ClF}_2$: C, 44.00; H, 2.20; F, 27.84. Found: C, 44.29; H, 2.42; F, 27.55.

An infrared spectrum of [V] had strong bands at 4.48 ($\text{C}\equiv\text{C}$), 5.90 ($\text{C}=\text{C}$) 7.70, 8.45, 9.51 ($\text{C}-\text{F}$ stretching) and 11.15 μ .

The ultraviolet spectrum (CH_3OH) had λ max 212, 222, and 232 μ with intensities in the region expected for enynes. The F^{19} NMR spectrum showed four peaks corresponding to a mixture of cis (F-F) and trans isomers in the ratio of 4:1 respectively. The cis isomer showed absorptions at 17.3 and 45.9 ppm relative to external CF_3COOH . The trans isomer, which was easily identified by the large trans F-F coupling constant of 120 cps showed absorptions at 35.3 and 61.4 ppm relative to external CF_3COOH .

Separation of [V] into its cis and trans isomers could be effected to a very limited extent on analytical V.P.C. (dinonylphthalate on 80/100 mesh chromosorb, 120°C). The two peaks were merged together almost completely and attempts to separate the two compounds by preparative scale V.P.C. were unsuccessful.

A similar reaction was carried out using [III] (1.3 moles) and chlorotrifluoroethylene (151.5 g., 1.3 moles) and resulted in the formation of 123 g. of [V] 69.5% and 10 g. of tar.

1-Bromo-1,2-difluoropent-1-en-3-yne [VI]

Reaction of bromotrifluoroethylene (48 g., 0.3 mole, 50% excess) with [III] gave 20.0 g. (55.5%) of [IV]. b.p. 122.0°C, n_D^{25} 1.4590.

Anal. Calcd for $C_5H_3BrF_2$: C, 33.18; H, 1.66; F, 20.99. Found: C, 32.89; H, 1.86; F, 21.22.

Vapor phase chromatography of [VI] showed that two compounds were present with very similar retention times. The F^{19} NMR spectrum showed 4 peaks corresponding to a mixture of cis (F-F), and trans isomers in the ratio of 3:1 respectively. The cis isomer showed absorptions at 17.3 and 45.9 ppm relative to external CF_3COOH . The trans isomer which was easily identified by the large trans F-F coupling constant of 120 cps showed absorption at 35.3 and 61.4 ppm relative to external CF_3COOH . The cis isomer, b.p. 122.0°C, n_D^{25} 1.4589 was isolated in the pure form by preparative scale V.P.C. by collecting a limited amount of material as the peaks first emerged from the column. An infrared spectrum of [VI A] had strong bands at 4.48 ($C\equiv C$), 5.98 ($C=C$), 7.72, 8.50 (sh), 8.60, 9.70, 11.20 and 11.40 μ . The ultraviolet spectrum (CH_3OH) had λ max 224 and 234 $m\mu$ (E 14,280 and 10,440 respectively) with a shoulder at 213 $m\mu$.

An infrared spectrum of the mixture of [VI A] and [VI B] had strong bands at 4.48 ($C\equiv C$), 5.45, 5.74, 5.98 ($C=C$), 7.72, 8.50, 8.60, 9.70, 11.20, and 11.40. The ultraviolet spectrum of this mixture was essentially the same as obtained from the cis isomer.

1,1,1,2,3-Pentafluorohex-2-en-4-yne [VII]

Reaction of hexafluoropropene (45 g., 0.3 mole, 50% excess) with [III] (0.2 mole) at -22°C gave 5.7 g. of [VII] (17%) b.p. 79.5°-80°C, n_D^{21} 1.3591.

Anal. Calcd for $C_6H_3F_5$: C, 42.36; H, 1.76; F, 55.89. Found: C, 42.55; H, 1.95; F, 56.17.

An infrared spectrum of [VII] had strong bands at 4.46 ($C\equiv C$), 5.90 ($C=C$) 7.25, 7.80, 8.30, 8.49, 8.70 and 9.43 μ . The ultraviolet spectrum (CH_3OH) had λ 221 $m\mu$ (E 14,880) with a shoulder at 228 $m\mu$. The F^{19} NMR spectrum showed absorptions at 7.9 ppm, 61.9 ppm and 89.6 ppm relative to external CF_3COOH . The relative areas were in accord with the above structure with only one trans isomer present. The two up field peaks exhibited the characteristic trans (F-F) coupling.

Black tarry material (15 g.) was formed in the reaction. Separation of [VII] from the THF was accomplished using a 24 plate spinning band column and a final purification was carried out using preparative scale V.P.C.

3,4-Difluorohept-1,3-diene-5-yne [VIII]

Reaction of 1,1,2-trifluorobutadiene (27.0 g., 0.25 mole) with [III] (0.2 mole) gave 16.4 g. of [VIII] (64%) b.p. (decomp. at 86°C), n_D^{21} 1.4970.

Anal. Calcd for $C_7H_6F_2$: C, 65.66; H, 4.68; F, 29.67. Found: C, 65.44; H, 4.72; F, 29.92.

An infrared spectrum of [VIII] had strong bands at 4.50 ($C\equiv C$), 0.01 ($C=C$) 7.55, 8.05, 9.22, 9.91, 10.20 and 10.90 μ . The ultraviolet spectrum (CH_3OH) had λ max 260 $m\mu$ (E 24,570).

The F^{19} NMR spectrum showed absorptions at 71.5 ppm and 79.0 ppm relative to external CF_3COOH . The peaks exhibited the characteristic trans (F-F) coupling at 120 cpm.

A black solid polymer (4.5 g.) was also formed in the reaction.

[VIII] was colorless when pure but rapidly turned black at room temperature in the presence of air.

4,5-Difluorooct-2,6-diyne-4-ene [IX]

Reaction of tetrafluoroethylene (30 g., 0.3 mole) with [III] gave, after removal of the THF by distillation and washing with water, 4.9 g. of [IX] (35%) m.p. 76-78°C which was purified by sublimation.

Anal. Calcd for $C_8H_6F_2$: C, 68.60; H, 4.28; F, 27.13. Found: C, 68.71; H, 4.50; F, 27.44.

An infrared spectrum of [IX] showed strong bands at 4.50 ($C\equiv C$), 7.85, 8.95, 9.05 and 12.51 μ with a medium strong band at 4.38. No band in the double bond region was present.

The ultraviolet spectrum (CH_3OH) had λ max 249 and 260 $m\mu$ (ϵ 32,690, and 30,350 respectively) with a shoulder at 240 $m\mu$.

The F^{19} NMR spectrum exhibited a single peak at 65.1 ppm relative to external CF_3COOH . The 2 fluorines were equivalent and therefore no characteristic trans F-F coupling would be shown.

Tar (4.0 g.) was obtained.

Attempted reactions of [III] with other Fluorodlefins

Trifluoroethylene

Reaction of trifluoroethylene (24.6 g., 0.3 mole) with [III] (0.2 mole) at 0°C gave only 8.0 g. of a black solid.

Hexafluorocyclobutene

Reaction of hexafluorocyclobutene (18.5 g., 0.114 mole) with [III] gave 25 g. of a black solid.

1,1-Difluoroethylene

No reaction was observed when 1,1-difluoroethylene was passed into a solution of [III] at either -78°C, -22°C, 0°C or 25°C. No discoloring of the solution occurred and most of the 1,1-difluoroethylene was recovered.

Bromination of [V]

[V] (15.0 g., 0.11 mole) was stirred at room temperature and slowly treated with bromine (17.5 g., 0.11 mole). The red liquid formed was shown by analytical V.P.C. to contain no [V]. Vacuum distillation gave 30.0 g. of

2,4-dibromo-1-chloro-1,2-difluoropent-1,3-diene (92.5%) b.p. 182-183°C, n_D^{21} 1.5192.

Anal. Calcd for $C_5H_3Br_2ClF_2$: C, 20.42; H, 1.01; F, 12.82. Found: C, 20.51; H, 1.19; F, 13.09.

An infrared spectrum showed strong bands at 5.85 and 6.15 (C=C) and in the region 7 μ to 10 μ (C-F stretching). There was no absorption between 4 μ and 5 μ (C=C) thus showing that additions had occurred only to the triple bond.

The NMR data on this compound are not yet available.

Addition of Water to [V]

[V] (20.0 g., 0.147 mole) was stirred and refluxed for 18 hours with 100 mls of 10% aqueous sulfuric acid containing mercuric sulfate (5.0 g.). A brown inorganic solid (4.0 g.) was formed during the reaction. Organic material (16.0 g.) was separated from the water and distilled at reduced pressure (50 mm) through a 18" spinning band column into fraction 1, b.p. 34-37°, 5.2 g.; fraction 2, b.p. 50-58°, 1.8 g.; fraction 3, b.p. 65-75°C, 2.5 g.; leaving a residue 1.3 g. Fraction 1 was starting material. Fraction 2 was identified as 1-chloro-1,2-difluoro-1-ene-3-one (11%) b.p. 122.0°C n_D^{28} 1.4148.

Anal. Calcd. for $C_5H_5ClF_2O$: C, , 38.88; H, 3.24. Found: C, 39.12; H, 3.28.

An infrared spectrum showed strong bands at 5.80 (C=C), 6.12 (C=O in α , β unsaturated ketone), 7.95, 8.45, 9.15, 9.44, 11.29. C-H stretching showed at 3.35, 3.40, 3.44, 3.47 μ indicating CH_3 and CH_2 .

The ultraviolet spectrum and the NMR data are not yet available.

Fraction 2 was shown to consist of a single component some of which was present in fraction 3. Preparative scale V.P.C. was used to isolate this compound which was identified as 1-chloro-1,2-difluoropent-1-ene-4-one, (3.8 g., 23%) b.p. 148-149°C, n_D^{21} 1.4154.

Anal. Calcd for $C_5H_5ClF_2O$: c, 38.88; H, 3.24; Found: C, 39.27; H, 3.15.

An infrared spectrum showed strong bands at 5.74 and 5.76 (doublet C=C and C=O) and in the region 7.0-10.0 μ (C-F stretching).

The ultraviolet and NMR Data for this compound are not yet available.

Some higher boiling material (0.6 g.) was also isolated from fraction 3, but an infrared spectrum gave no indication of the structure.

Reaction of [V] with Chlorotrifluoroethylene

A 335 ml stainless steel autoclave was charged with [V] (19.5 g., 0.143 mole) chlorotrifluoroethylene (52 g, 0.446 mole) and shaken at 190° for 7 hours. Unreacted chlorotrifluoroethylene (35 g.) was vented from the autoclave leaving behind 26 g. of liquid product. Fractional distillation at atmospheric pressure afforded 12.1 g. of 1,2-dichlorohexafluorocyclobutane, b.p. 59-60° (lit. 58.5-59.5), 6.7 g. of recovered [V] (65.5% conversion). The black residue was vacuum distilled leaving 3.5 g. of tar. The distillate was shown by analytical V.P.C. to contain 3 components. Preparative scale V.P.C. (silicone elastomer 125°C) afforded 1.5 g. of $\text{CH}_3\text{-C}(\text{O})\text{-CF-CFCl}$ (6.5%) or its 1,3-dichlorocyclobutyl isomer, CF_2CFCl
 b.p. 148.5°C; n_D^{20} 1.4064.

Anal. Calcd for $\text{C}_7\text{H}_3\text{Cl}_2\text{F}_5$: C, 33.16; H, 1.19; F, 37.55. Found: C, 33.01; H, 1.43; F, 37.79. An infrared spectrum showed strong bonds at 4.44 (C=C) and 7.5 to 9.1 μ (C-F). Ultraviolet and NMR data are not yet available on this compound.

The second peak was isolated and identified as $\text{CH}_3\text{-C}(\text{O})\text{-CF}=\text{CFCl}$ or its cyclobutenyl isomer (6.9 g.). CF_2CFCl
 b.p. 163.5-164°C, n_D^{20} 1.4419.

Anal. Calcd for $\text{C}_7\text{H}_3\text{Cl}_2\text{F}_5$: C, 33.16; H, 1.19; F, 37.55. Found: C, 33.09; H, 1.39; F, 37.87. An infrared spectrum showed strong bands at 5.94 and 6.14 μ (C=C) and 7.15 to 8.85 μ (C-F). Ultraviolet and NMR data for this compound have not yet been completed.

The third component has not yet been identified.

A similar experiment carried out at 150° for 12 hours gave very little reaction of [V] with chlorotrifluoroethylene.

UNCLASSIFIED

UNCLASSIFIED