TECHNICAL REPORT
C&OM-4

SYNTHESIS OF HIGH-STRENGTH CHEMICAL RESISTAN ELASTOMERS FOR EXTREME TEMPERATURE SERVICE

by

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FMC CORPORATION

Chemical Research and Development Center
Princeton, New Jersey

Contract No. DA19-129-AMC-147(N)

January 1965

U. S. Army Materiel Command
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts

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FOREWORD

High-strength chemical resistant rubber serviceable at temperature extremes is needed for fabricating many types of military items. A research program is conducted by the Army to develop rubbers having these special properties, for the rigorous requirements of the global operations imposed on the special military items far exceed commercial needs. From information based on past research effort, the fluorine-containing materials offer the greatest promise of success.

The work covered by this report, performed by the FMC Corporation under U. S. Army Contract DA19-129-AMC-147(N), reflects a concentration of effort in the field of fluorine-containing rubbers. Studies toward the preparation of high-strength chemical resistant rubbers that are serviceable at low temperatures (down to -65°F) and high temperatures (600°F and above) have been made through investigations of random and stereoregulated fluorine-containing high polymers.

The U. S. Army Natick Laboratories Project Officer was Mr. C. B. Griffis and the Alternate Project Officer was Mr. A. F. Wilson. Both are from the Rubber Technology Section, Clothing and Organic Materials Division.

S. J. KENNEDY
Director
Clothing & Organic Materials Division

Approved:

DALE H. SIELING, Ph.D.
Scientific Director

W. W. VAUGHAN
Brigadier General, USA
Commanding

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I SUMMARY

The synthesis of new fluorinated elastomers servicable at low temperatures is described. Hexafluoroacetone and hydrogen-containing olefins have been found to form both low polymers and hydrogen-containing oxetanes on actinic irradiation. Evidence is presented to show that the intermediate is a biradical. A new elastomer system has been discovered involving the condensation of a polyfluorinated diol with a fluorocarbon diene. This unique fluorinated polyether has been found to have a very low T_g (-54° C). Evidence has also been found that a polyfluorinated diol will condense with hexafluorobenzene. Polyurethane polymers have been successfully formed by condensation of a polyfluorinated diol with phosphorous containing diisocyanates. Several new monomers are described.

II. INTRODUCTION

A. Objectives

The objectives of this program have been the development of high-strength chemical-resistant rubbers servicable at low temperatures (down to -65° F) and chemical resistant rubbers that have high strength and rubber-like properties at high temperature (600° F and above), through the investigation of random and stereoregulated fluorine-containing high polymers.

B. Program

Initially, considerable difficulty was experienced in obtaining sufficient quantities of monomers to permit intensive investigation and the entire research program was critically curtailed for the whole of the first half of the contract period. However, a subsequent contract modification permitted synthesis of monomers in adequate quantities by established procedures. Polymer research was sustained by the end of the third quarter of the contract period. Also, the two cooperating Universities, in addition to their development of new synthetic procedures, submitted small quantities of potential monomers from time to time.

In order to achieve the above objectives, a broad program was planned embracing (a) the development of block copolymers and (b) the synthesis of fluorocarbon polymers containing a nitrogen, sulfur, or oxygen heteroatom in the backbone of the macromolecule. The latter program was subdivided into two broad areas: vinyl polymers and condensation polymers.

Development of block copolymers followed two lines: (a) fluorocarbon units alternating with fluoroalkyl siloxane units and (b) polyurethanes by condensation of fluorinated diols with phosphorus-and sulfur-containing diisocyanates. The hydroxyl-terminated liquid prepolymers so often obtained from fluorinated diol condensations would, of course, be the most desirable comonomers for polyurethane formation, but initial experiments utilized low molecular weight diols for feasibility studies.

The vinyl polymer program had the objectives of improving existing polymer systems by incorporation of selected termonomers and long-range exploratory research toward the utilization of new potential monomers, i. e., 2-azaperfluoropropene and hexafluoroacetone. Low molecular weight polyethers were made for the first time from hexafluoroacetone and hydrogen-containing olefins.

The objective of the condensation polymer program was to develop new polymers by utilizing classical reactions and new difunctional fluorinated monomers. The particular system selected for study was the base catalyzed addition of fluorinated diols to unsaturated fluorinated compounds, that is, the addition of hexafluoropentanediol to 4-chloroperfluoroheptadiene and hexafluorobenzene. In the former instance a rubbery polymer was successfully synthesized and found to retain its rubbery characteristics down to remarkably low temperatures (T_g, -54° C). The polycondensation of hexafluoropentanediol and hexafluorobenzene yielded a heavy grease with good lubricity.

III. DISCUSSION OF RESULTS

A. Monomer Procurement

The following monomers and precursors were obtained during the period of this report:

Monomer Number	Monomer of Precursors	Amt.	Supplier
	Bromopentafluorobenzene	550 g.	Imperial Smelting Corp.
	Pentafluorobenzene	25 g.	Imperial Smelting Corp.
519	Hexafluorobenzene	1050 g.	Imperial Smelting Corp.
	Pentafluoroaniline	300 g.	Imperial Smelting Corp.
	Pentafluorothiophenol	1 kg.	Imperial Smelting Corp.
	Pentafluorophenyl hydrazine	250 g.	Imperial Smelting Corp.
	4, 4'Diaminooctafluorobiphenyl	100 g.	Imperial Smelting Corp.
	Pentafluorophenol	1 kg.	Imperial Smelting Corp.
	C-7 Fluoroalcohol	1 lb.	E. I. duPont deNemours Co.
	C-9 Fluoroalcohol	1 lb.	E. I. duPont deNemours Co.
	C-11 Fluoroalcohol	1 lb.	E. I. duPont deNemours Co.
	Difluorotetrachloroethane (Freon 112)	1 gal.	E. I. duPont deNemours Co.
2	Vinylidene fluoride (Freon 1132A)	18 lbs.	E. I. duPont deNemours Co.
	Methyldichlorosilane	2 lbs.	Dow Corning
	Dimethylchlorosilane	13 lbs.	Dow Corning
	Dimethyldichlorosilane	1 lb.	Dow Corning
	Diallyldimethylsilane	100 g.	Columbia Organic Chemicals, Inc.
	3, 4, 4-Trifluoro-4-bromo-3-chlorobutene-1	4. 9 kg.	Columbia Organic Chemicals, Inc.
	Kel-F Acid No. 8114	3 lbs.	Columbia Organic Chemicals, Inc.
	Kel-F Acid No. 8114	10 lbs.	3M Company
14	Hexafluoropropylene	5 lbs.	Columbia Organic Chemicals, Inc.
108	Perfluorobutene-2	2 lbs.	Halocarbon Products Corp.
	2, 2, 3, 3-Tetrachlorohexafluorobutane	3 lbs.	Halocarbon Products Corp.
1	Chlorotrifluoroethylene (Genetron 1113)	24 lbs.	Allied Chemical Corp. General Chemical Div.
	Kel-F Acid No. 683	10 lbs.	3M Company
	p-Aminotetrafluorobenzoic acid	100 g.	Imperial Smelting Corp.

Monomer Number	Monomer or Precursors	Amt.	Supplier
511	Perfluoroglutaryl dichloride	2 lbs.	Hooker Chemical Corp.
508	2, 2, 3, 3, 4, 4-Hexafluoro-pentanediol-1, 5	325 g.	Aldrich Chemical Co.
	Bromotrifluoromethane (Freon 13B1)	6 lbs.	E. I. duPont deNemours Co.
40	Vinyl fluoride	3 lbs.	E. I. duPont deNemours Co.
9	1, 1-Dichlorodifluoro-ethylene (Genetron 1112a)	1 lb.	Allied Chemical Corp. General Chemical Div.
	1, 2-Dichlorotetrafluoro-cyclobutene	100 g.	Columbia Organic Chemicals, Inc.
512	Hexafluoroacetone (6FK)	5 lbs.	Allied Chemical Corp. General Chemical Div.
	Pentafluorobenzoic acid	200 g.	Imperial Smelting Corp.
	Dibromodifluoromethane	5 kg.	Columbia Organic Chemicals, Inc.
507	2-Azaperfluoropropene	60 g.	Peninsular Chem Research
	Dibromotetrafluoroethane	17 lbs.	E. I. duPont deNemours Co.
	1-Iodo-1, 2-dichloro-trifluoroethane	200 g.	Peninsular ChemResearch
	FC-43	8 lbs.	3M Company

The following monomers or precursors were obtained from the cooperating contractors:

35	3, 3, 3-Trifluoropropene-1	113 g.	J. D. Park, University of Colorado
204	Trifluorovinyldimethyl-ethoxysilane	50 g.	P. Tarrant, University of Florida
302	4-Chlorperfluoro-heptadiene-1, 6	32 g.	J. D. Park, University of Colorado
301	Bis(2, 3, 3-trifluoro-bicyclobutenyl-1)	13 g.	J. D. Park, University of Colorado
205	1, 1, 2, 5, 6, 6-Hexafluoro-hexadiene-1, 5	19. 3 g.	P. Tarrant, University of Florida
206	Perfluorostyrene	12. 7 g.	P. Tarrant, University of Florida
200	3, 4, 4-Trifluoro-3-butenyl-trimethyl silane	15 g.	P. Tarrant, University of Florida
201	Trifluorovinyltrimethyl-silane	15 g.	P. Tarrant, University of Florida
202	Bis(3, 4, 4-trifluoro-3-butenyl dimethyl)-disiloxane	10 g.	P. Tarrant, University of Florida
203	Perfluoroacetophenone	10 g.	P. Tarrant, University of Florida

Monomer Number	Monomer or Precursors	Amt.	Supplier
407	1, 3, 5-trimethyl-1, 3, 5-tris(3, 3, 4, 4, 4-pentafluorobutyl)cyclotrisiloxane	110 g.	E. C. Stump, Peninsular ChemRes.
408	1, 3, 5, 7-tetramethyl-1, 3, 5, 7, -tetrakis(3, 3, 4, 4 4-pentafluorobutyl) cyclotetrasiloxane	75 g.	E. C. Stump, Peninsular ChemRes.
300	1-Vinyl-2-chloro-2, 3, 3-trifluorocyclobutane	56 g.	J. D. Park, University of Colorado
207	1, 1, 2-Trifluoropentadiene-1, 4	10 g.	P. Tarrant, University of Florida
415	1, 4-Dibromotetrafluorobenzene	25 g.	P. Tarrant, University of Florida

The following monomers have been prepared by FMC:

202	1, 3-Bis(3, 4, 4-Trifluoro-3-butenyl)-1, 1-3, 3-tetramethyl disiloxane	485 g.
302	4-Chloroperfluoroheptadiene-1, 6	345 g.
500	2, 2, 3-Trifluoro-3, 4, 4-(trifluoromethyl)oxetane	100 g.
504	1, 1-Bis(trifluoromethyl)oxetane	25 g.
505	1, 1-Bis(trifluoromethyl)-3, 3-difluoroöxetane	50 g.
506	1, 1-Bis(trifluoromethyl)-2, 2-difluoroöxetane	50 g.
509	cis-Perfluoroheptatriene-1, 3, 6	25 g.
510	trans-Perfluoroheptatriene-1, 3, 6	25 g.
513	1, 1-Bis(trifluoromethyl)-2-fluoroöxetane	10 g.
514	1, 1-Bis(trifluoromethyl)-3-fluoroöxetane	10 g.
515	Phosphorous triisocyanate	12 g.
516	Butyl Phosphonic diisocyanate	15 g.
517	Phenyl phosphonic diisocyanate	29 g.

B. Monomer Master List

A complete list of monomers considered under previous Quartermaster contracts with M. W. Kellogg and subsequently with 3M is presented in Appendix I of this report. It has been decided to extend the system of assigning numbers to new monomers in a systematic fashion which would allow each of the present contractors to the Army Natick Laboratories to make assignments to monomers which are prepared for the first time in their own laboratories.

The system decided upon by the Army Natick Laboratories involved assigning a block of 100 numbers to the contractors as follows:

Originating Laboratory	Assigned Number Block
University of Florida	200 through 299
University of Colorado	300 through 399
Peninsular ChemResearch	400 through 499
FMC Corporation	500 through 599
Thiokol Chemical Corporation	600 through 699
U. S. Army Natick Laboratories	700 through 799

Those monomers and the appropriate number assignments of which FMC has been advised are present in Appendix II.

In order to avoid confusion it has been agreed that only those monomers which do not appear elsewhere with a prior number assignment will be given an assigment under the block assignment system.

C. Polymerization Research

It is generally recognized that a useful technique for preserving elastomer flexibility at low temperature extremes is to incorporate hetroatoms in the polymer chain. If, in addition, the elastomer is to have high solvent resistance, then a large number of fluorine substituents should also be incorporated so as to present an effective electrostatic shield towards any foreign molecule. It is then axiomatic that the most promising area of research would be heteroatomic fluorinated systems.

For pragmatic reasons the research effort has been divided into two broad areas of classification: vinyl polymers and condensation polymers.

With vinyl polymers the effort has generally been to either improve existing polymer systems or to investigate entirely new systems based on materials not previously available or studied.

On the other hand, the study of condensation polymerization has been determined not by restrictions of reactivity but by consideration of the availability of difunctional compounds from the cooperating Universities.

1. Vinyl Polymerization

a. Modification of Vinylidene Fluoride/Hexafluoropropylene Emulsion Polymerization System

Improvement in low temperature flexibility and solvent resistance of vinylidene fluoride/hexafluoropropylene elastomer was sought by modification of this emulsion polymerized system with novel fluorinated vinyl monomers.

The following fluoroölefins were investigated as potential termonomers:

$[CF_2{=}CFCH_2CH_2Si(CH_3)_2]_2O$

I

$$\begin{array}{l} CF_2-CFCl \\ |\qquad\quad | \\ CH_2-CH-CH{=}CH_2 \end{array}$$

II

Terpolymerization of disiloxane (I) was attempted with high system pressures (*ca.* 630 psig) at 70°C by charging the disiloxane into the aqueous phase. The elastomeric product appeared to be identical to the control copolymer (70/30% $CH_2{=}CF_2/C_3F_6$) by IR analysis, but had a slightly lower T_g value (-26°C. *vs.* -21°C). Silicon analysis of pentene extracted elastomer was erratic. Evidently, the sample was inhomogeneous. It must be concluded that no terpolymer was formed.

Disiloxane (I) was also mechanically incorporated in Viton A gum stock by milling. The stock was then vulcanized with benzoyl peroxide. Unfortunately, the disiloxane could be recovered intact from the compounded stock by extraction. The glass transition temperature of the compounded stock as measured (prior to extraction) with a Gehman torsional stiffness tester, was -21°C, which is almost identical to the value reported for unplasticized Viton A.

Incorporation of vinylcyclobutane (II) into a vinylidene fluoride/hexafluropropylene emulsion polymerization system was examined.

At 35° C. and 25 psig a low conversion to a white, brittle powder was achieved which contained 58% fluorine and 0.25% chlorine. The product appeared to be largely a polymer of vinylidene fluoride with incorporation of a minor proportion of the fluorine-containing vinylcyclobutane.

With a higher temperature and pressure of 70° C and 610 psig a 10% conversion to a yellow brittle powder was realized. This powder evidently was a homopolymer of the fluorine-containing vinylcyclobutane. Moreover, a partial dehydrochlorination of the monomer probably occurred in the alkaline emulsion medium to form the polymerizable vinylcyclobutane (III), as the polymeric product analyzed for 32% fluorine and 12.4% chlorine (theory: 33.4% fluorine and 20.8% chlorine for polyvinylcyclobutane).

III

b. Polyethers from Hexafluoroacetone and Olefins

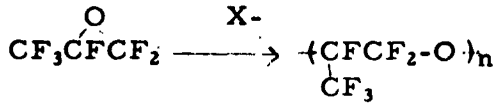
One of the most interesting and, at the same time, elusive class of fluorocarbon elastomers is the polyethers, best exemplified by the hypothetical parent polyether IV. This class would combine the advantage of a solvent resistant fluorocarbon backbone with the flexibilizing influence of the ether linkages. Further modification of this basic structure would be expected to enhance the desirable properties this class is believed to possess. For example, the inclusion of trifluoromethyl pendant groups would be expected to decrease crystallinity in the polymer and thus enhance the low temperature properties desired. It should also be noted that the perfluorinated polyethers would be expected to show high thermal stability.

$$-\!\left[O(CF_2)_m\right]_n\!-$$

IV

There are only a few cases known where perfluoropolyethers have been successfully made. DuPont workers have disclosed the preparation of polymers from hexafluoropropylene oxide (Eq. 1) although details are lacking.[1]

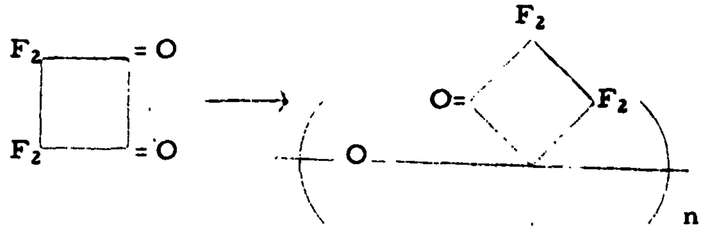
(1)



$$\mathrm{CF_3\overset{O}{\overbrace{CFCF_2}}} \xrightarrow{X^-} -\!\!\left(\underset{\mathrm{CF_3}}{\mathrm{C}}\mathrm{FCF_2\text{-}O}\right)_n$$

England[2] has disclosed a polymer of perfluorocyclobutadione-1,2 (Eq. 2),

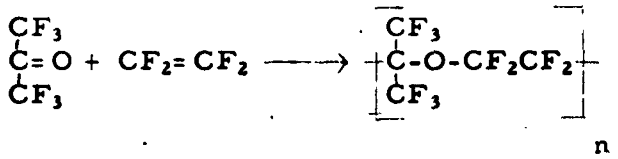
(2)



although, because of the particular structure of this polymer, it is thermally unstable.

The recent availability of hexafluoroactone makes attractive the possibility of its copolymerization with fluorinated ethylenes (Eq. 3). To this end, an examination of the literature concerned

(3)

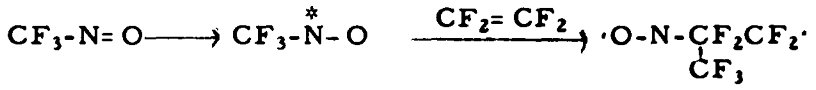


$$\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}\mathrm{=O} + \mathrm{CF_2{=}CF_2} \longrightarrow \left[-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}\mathrm{-O-CF_2CF_2}-\right]_n$$

with fluorinated carbonyl compounds reveals several interesting parallels to the fluorinated nitroso compounds[3].

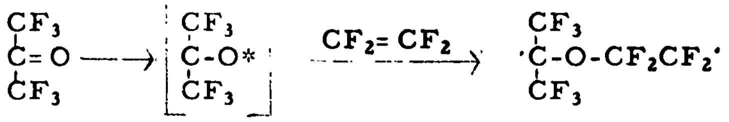
Because the copolymerization of nitrosotrifluoromethane with tetrafluoroethylene is initiated by an n_N-π^* transition (Eq. 4), a similar n_O-π^* transition with hexafluoroacetone might be expected

(4)



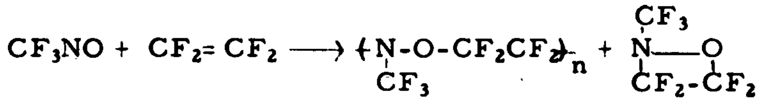
$$\mathrm{CF_3\text{-}N{=}O} \longrightarrow \mathrm{CF_3\text{-}\overset{*}{N}\text{-}O} \xrightarrow{\mathrm{CF_2=CF_2}} \cdot\mathrm{O\text{-}\underset{CF_3}{N}\text{-}CF_2CF_2}\cdot$$

to lead to the same type of copolymerization (Eq. 5).

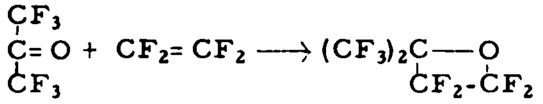
(5) 

$$(CF_3)_2C{=}O \longrightarrow \left[(CF_3)_2C\text{-}O^*\right] \xrightarrow{CF_2=CF_2} \cdot C(CF_3)_2\text{-}O\text{-}CF_2CF_2\cdot$$

However, while the fluorinated nitrosoalkanes produce both the cyclic product (oxazetidines) and the linear elastomer on reaction with olefins (Eq. 6), hexafluoroacetone has only been reported to produce the cyclic adduct (oxetanes) (Eq. 7).

(6) 

$$CF_3NO + CF_2{=}CF_2 \longrightarrow \left(N(CF_3)\text{-}O\text{-}CF_2CF_2\right)_n + \underset{CF_2-CF_2}{\overset{CF_3}{N\text{—}O}}$$

(7) 

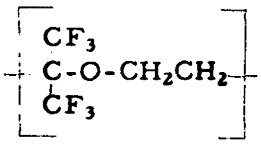
$$(CF_3)_2C{=}O + CF_2{=}CF_2 \longrightarrow \underset{CF_2-CF_2}{(CF_3)_2C\text{—}O} \qquad \text{only}$$

Several preliminary syntheses were conducted with fluorinated olefins in order to determine the nature of the reaction. With hexafluoropropylene, oxetane formation was observed to be complete in 12 hours. Several photosensitizers, namely benzophenone and diacetyl, were then used to determine if the reaction rate could be increased. The results were inconclusive, as the photolysis was conducted in the vapor phase and a significant concentration of photosensitizer was probably not available in this phase.

Photolysis of hexafluoroacetone with perfluorobutene-2 was also examined. Mass spectrographic analysis suggested that the product is mainly perfluorodiisopropyl or a similar compound along with a small amount of the desired oxetane. Evidently, the π-π^* transition for the butene is energetically more favorable than the n_O-π^* transition for hexafluoroacetone, and inter-system crossing occurred.

A prior discussion with Dr. J. D. Park had revealed that hydrogen-containing olefins such as 3, 3, 3-trifluoropropylene might provide a good point of departure for the synthesis of intermediate oxetanes that may be opened more readily; furthermore, a review of the literature in this area disclosed that no hydrogen-containing olefins had been previously utilized in this reaction.

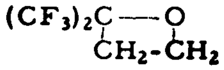
Vinylidene fluoride, vinyl fluoride, ethylene, and octadiene-1, 7 were selected as model compounds for study. With vinylidene fluoride, vinyl fluoride, and ethylene, photolysis with hexafluoroacetone yielded viscous oils along with oxetanes. Analysis of the oils revealed that the fluorine content was close to that calculated for a 1:1 CF_3COCF_3/olefin polymer. The oil from photolysis of CF_3COCF_3/C_2H_4 has an average molecular weight of 570, while the $CF_3COCF_3/CH_2=CF_2$ oil has an average molecular weight of 612. Both of these values agree approximately with a calculated molecular weight for three repeating carbonyl-olefins units. NMR analysis of the CF_3COCF_3/C_2H_4 oil suggests that methylene groups alpha and beta to an ether linkage are present, in accordance with the anticipated structure (V). The ratio of the two different methylenes does not appear to be quite the 1:1 expected for this structure, however.



$$\left[-\overset{CF_3}{\underset{CF_3}{C}}-O-CH_2CH_2- \right]$$

V

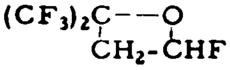
The oxetane (VI) produced by photolysis of hexafluoroacetone with ethylene was identified by its NMR spectrum. A triplet centered at τ 7.06 (J=8.0 cps) arises from the methylene beta to



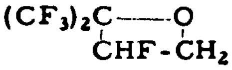
VI

oxygen while a triplet centered at τ 5.31 (J= 8.0 cps) arises from the methylene alpha to the ether linkage.

Two oxetanes (VII and VIII) are isolable from the photolysis of hexafluoroacetone with vinyl fluoride. The proton NMR spectrum of oxetane (VII) showed a sextuplet from the tertiary proton at τ 3.96 and a multiplet from the methylene protons at τ 6.91; while oxetane (VIII) had a sextuplet at τ 4.37 from the



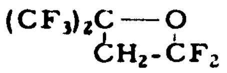
VII



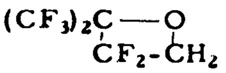
VIII

tertiary proton and a multiplet at τ 5.11 from the methylene protons. The oxetanes were produced in a 1.6:1 (VII: VIII) ratio.

Two oxetanes (IX and X) can be isolated from the photolysis of hexafluoroacetone with vinylidene fluoride.



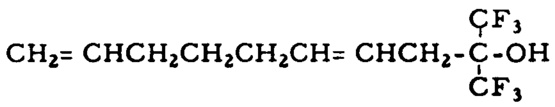
IX



X

Oxetane (IX) was identified by a triplet centered at τ 6. 59 (J= 7. 0 cps) on its NMR spectrum, while oxetane (X) displayed a triplet centered at τ 5. 00 (J= 12. 2 cps). Interestingly, oxetane (IX) was formed in larger amounts than the isomeric adduct (X), the ratio being about 1. 3: 1.

Rather different and unexpected results were obtained from the photolysis of hexafluoroacetone with octadiene-1, 7. Instead of the oxetane, an unsaturated alcohol was obtained (XI). This alcohol was only tentatively identified by its gross proton NMR



$$CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2\text{-}\overset{CF_3}{\underset{CF_3}{C}}\text{-}OH$$

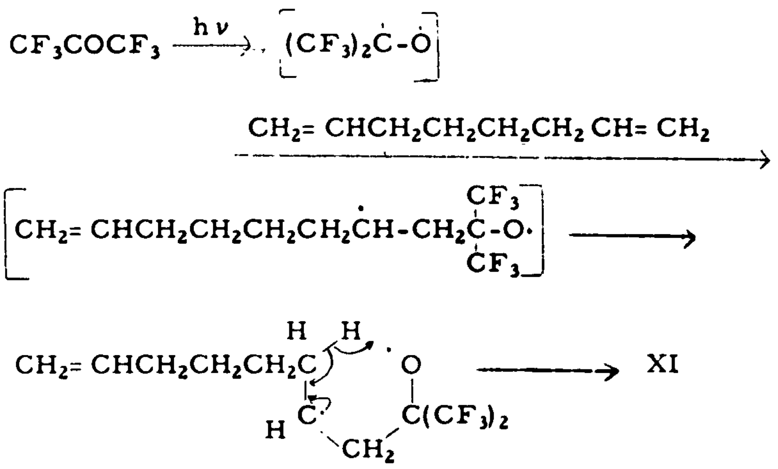
XI

spectrum, as the spectrum could not be completely resolved line-for-line because of its complexity.

While further evidence is needed to establish conclusively that the structure proposed is correct, there is at present no basis for proposing any other structure.

It appears quite reasonable that the mechanistic pathway involved is as described in (Eq. 8).

(8)



The most important observation is, of course, that the reaction as formulated goes through a biradical intermediate Proton abstraction that occurs through a six-membered cyclic transition state reminiscent of the Barton Reaction.

This is the first evidence that photolysis of hexafluoroacetone with olefins proceeds through a discrete biradical intermediate rather than operating through a concerted process. This is naturally very encouraging from a polymerization-minded view point, and lends credence to the earlier declared objective of the copolymerization of hexafluoroacetone with olefins by actinic initiation.

2. Condensation Polymerization

The ever advancing art of fluorocarbon monomer synthesis now enables condensation polymerization techniques to be an attractive research area for the synthesis of fluorinated elastomers. The recently published review by Knunyants and his co-workers[4] on fluorinated bifunctional compounds as potential monomers highlights many of the possibilities existent in this area.

Also, the extension of well-known condensation reactions of fluorocarbon chemistry to bifunctional moieties for polymerization research is a short range program. The most difficult problem is of course, not the polymerization step but the availability of desirable monomers.

a. Addition of Highly Fluorinated Diols to Highly Fluorinated Dienes

A basic tenet of this polymer research program is the desirability of incorporating heteroatoms, such as nitrogen or oxygen, in a polymer backbone. One example of this concept is the class of perfluorinated polyethers (IV) mentioned previously. Long range research towards the preparation of these polyethers is described elsewhere in this report, but the additional possibility of synthesizing highly fluorinated elastomers by condensation techniques cannot be overlooked. Of course, these condensation polymers should a priori be useful polymers in their own right, but the economics of large scale production would normally be expected to favor the vinyl-type polymers.

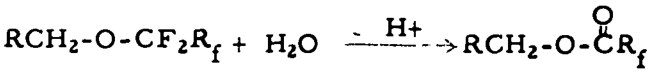
One of the oldest known and best studied reactions of fluorine chemistry is the nucleophilic attack of alkoxides, amines, halide, etc., on unsaturated fluorocarbons. The nucleophiles most thoroughly studied, particularly by Park and co-workers, are the potassium alkoxides. (Eq. 9):

$$(9)\qquad RO^- + CF_2{=}CFR_f \xrightarrow{ROH} \begin{array}{l} \nearrow RO{-}CF_2CFHR_f \\ \quad\text{or} \\ \searrow RO{-}CF{=}CFR_f \end{array}$$

The product, either the β-hydroether or the vinyl ether, is determined by the availability of a proton in the reaction medium and by the basicity of the intermediate carbanion relative to the nucleophile employed. For terminal fluoroolefins, generally, the saturated ether is the expected product (except under aprotic conditions).

The hydrolytic stability of these saturated ethers varies over a tremendous range. On one hand are those ethers of the type $RCH_2{-}O{-}CF_2R_f$ which are hydrolytically very unstable (Eq. 10); on the other hand 3M's "FC-75" (a perfluorinated cyclic ether) **and the recently discovered perfluorinated oxetanes, examples of the type $R_fCF_2{-}O{-}CF_2R_f$, are extremely stable to hydrolysis.**

(10).



$$RCH_2{-}O{-}CF_2R_f + H_2O \xrightarrow{H+} RCH_2{-}O{-}\overset{O}{\overset{\|}{C}}R_f$$

$$R_fCF_2{-}O{-}CF_2R_f + H_2O \xrightarrow{H+} N.\,R.$$

$$R_fCH_2{-}O{-}CF_2R_f + H_2O \xrightarrow{H+} N.\,R.$$

R= hydrocarbon radical
R_f= fluorocarbon radical

It is obvious that, whatever the reason, the location of perfluorinated segments on both sides of the ether oxygen greatly enhances the resistance of these compounds to hydrolysis. Larson[5] has recently demonstrated that electron-withdrawing substituents markedly stabilize halogenated ethers to hydrolysis.

One could expect then, that the preparation of a polyether from a highly fluorinated diol and a perfluorinated diene should produce an interesting elastomer.

The recent availability of several fluorinated dienes from Professor Park at the University of Colorado, in particular 4-chloroperfluorophetadiene-1, 6 (Monomer 302), and the availability of 2, 2, 3, 3, 4-hexafluoropentanediol-1, 5 from Aldrich Chemical Company has now allowed examination of this system (Eq. 11).

$$\text{(11)}\quad CF_2{=}CFCF_2CFClCF_2CF{=}CF_2 + HO\text{-}CH_2CF_2CF_2CF_2CH_2\text{-}OH \xrightarrow{KOH}$$

XII XIII

Polymer chain:

$$\left(O\text{-}CH_2CF_2CF_2CF_2CH_2\text{-}O\text{-}CF_2CFHCF_2CFClCF_2CFHCF_2\right)_n$$

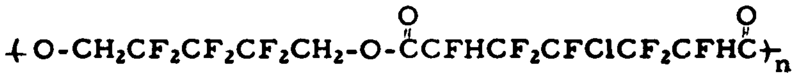
XIV

$$\left(O\text{-}CH_2CF_2CF_2CF_2CH_2\text{-}O\text{-}CF{=}CFCF_2CFClCF_2CF{=}CF\right)_n$$

XV

$$\left(O\text{-}CH_2CF_2CF_2CF_2CH_2\text{-}O\text{-}CF_2CF{=}CFCFClCF{=}CFCF_2\right)_n$$

XVI



$$\left(O\text{-}CH_2CF_2CF_2CF_2CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}CFHCF_2CFClCF_2CFH\overset{O}{\overset{\|}{C}}\right)_n$$

XVII

Terminal groups:

$$\text{-}O\text{-}CH_2CF_2CF_2CF_2CH_2\text{-}OH$$

XVIII

$$CF_2{=}CFCF_2CFClCF_2CFHCF_2\text{-}$$

XIX

The most likely structures are listed. Polyether (XIV) the product of simple addition of the alcohol across the double bond, is the anticipated product (vida supra). The unsaturated polyethers (XV and XVI), products of substitution, would normally be expected to be present in significant amounts only under aprotic conditions. Polyester (XVII) would be the hydrolysis product of polyether (XIV) but is not likely to play an important role because of the expected hydrolytic stability of the highly fluorinated polyether.

One can envision either unreacted alcohol(XVIII) or olefin (XIX) as terminal groups.

The polymerization was investigated in several solvents and at several temperatures. Both polar solvents and elevated temperatures materially increased the reaction rate. This observation is entirely consistent with an ionic mechanism.

Although the rubber swells in acetone, it was found to be insoluble in all solvent systems investigated including carbon tetrachloride, ethyl ether, hexane, toluene, Freon 113, FC-43 and FC-75 (perfluorinated solvents of 3M Co.) and Fluorolube FS-5 (perhalogenated solvent of Hooker Chemical Corp.). Lower molecular weight fractions, all oils, were soluble in a number of solvents.

Physical methods of structural determination were then generally confined to the lower molecular weight fractions because of solubility considerations.

Because of the limited number of protons in decidedly different environments for each possible structure, proton NMR offered the greatest opportunity for elucidation of structure.

The NMR spectra of several samples of the oil displayed a triplet centered at τ 5.58 attributable to the protons alpha to an oxygen, and a triplet centered at τ 5.97, attributable to the protons alpha to a hydroxyl oxygen.

Additionally, the tertiary proton of the polyether (XIV) would be expected to show a doublet from the alpha fluorine further split into two pentuplets by the beta fluorines. An incompletely resolved peak appears to be one-half of this requirement the other half being obscured by methylene resonance lines. Should this be the case, the tertiary proton resonance absorption is centered at about τ 5.0, a shift that is anticipated for such a system. Also, one sample displays what appears to be a triplet centered at about τ 5.25 attributable to the methylene group as in polyether (XV) although the methylene group of polyether (XIV) is 10 times more abundant.

There is no evidence observed in these samples of any proton resonance affected by an ester group such as polyester (XVII).

Succinctly then, it appears likely that the rubbery polymer is mainly polyether (XIV) with a minor amount (probably less than 10%) of polyvinyl ether (XV or XVI). Pendant terminal groups may be either unreacted olefin (XIX) or alcohol (XVIII). As the ratio of ether - methylene groups to hydroxyl-methylene groups of the oils varies from 1:1 to 2:1; it would appear that the unreacted hydroxyl groups predominate.

It is possible to measure several physical properties of the elastomer with the Perkin-Elmer Differential Scanning Calorimeter, notably phase transitions and decomposition temperatures.

Some variation of the T_g observed was noted with various samples ranging from -44°C to -57°C; the most reliable value appears to be -54°C.

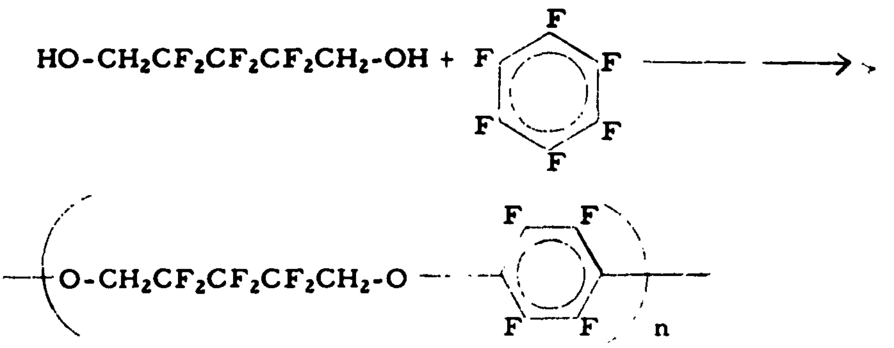
The Differential Scanning Calorimeter spectra show a strong endotherm at about -22° C along with a smaller endotherm at about -30°C. It is doubtful that these endotherms are a true T_m, but rather appear to be a possible loss of hydrogen bonding in the polymer.

The samples studied appear generally to decompose slightly at about 200°C and extensively at about 300°C. The decomposition at the lower temperature is endothermic and well defined; it appears to be loss of hydrogen fluoride.

b. Addition of Highly Fluorinated Diols to Hexafluorobenzene

A single exploratory experiment was conducted utilizing hexafluorobenzene as the unsaturated component in a condensation polymerization similar to the previously mentioned technique (Eq. 12).

(12)



A tacky semisolid was obtained; suggesting that the system merits further study.

c. Copolymerization of $[CF_2{=}CFCH_2CH_2Si(CH_3)_2]_2O$ with $(CF_2{=}CFCF_2)_2CFCl$

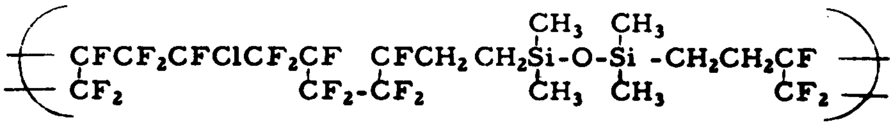
The initial investigations conducted under this contract arose from a suggestion of Dr. Tarrant where a novel block-copolymer could be formed by the polymeric cyclocodimerization of an alpha, omega fluorinated diene with a difunctional fluoroolefinic disiloxane:

(13)

$$CF_2{=}CFCF_2CFClCF_2CF{=}CF_2 + CF_2{=}CFCH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2CH_2CF{=}CF_2$$

XII

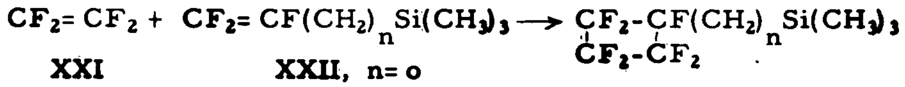
I



XX

Initial studies of this system utilized two model compounds, silanes (XXII and XXIII). The coreactant selected for this preliminary study was tetrafluorethylene, known to participate in similar cycloadditions with a variety of olefins[6] (Eq. 14).

(14)



$$CF_2{=}CF_2 + CF_2{=}CF(CH_2)_nSi(CH_3)_3 \longrightarrow \underset{CF_2\text{-}CF_2}{CF_2\text{-}CF(CH_2)_nSi(CH_3)_3}$$

XXI

XXII, n= o

XXIII, n=2

XXIV, n= o

XXV, n= 2

For this model study equimolar quantities of silane (XXII or XXIII) and tetrafluoroethylene were heated under autogenous pressure for ca. 17 hours. Simple distillation was used to estimate the degree of conversion to the expected product. Examination of the experimental details (see Table III) shows that while reaction commenced at 150°C, optimum conversion was obtained at 200°C.

Product identity was confirmed by absence of double bond adsorption in the infrared spectra and by elemental analysis.

Condensation copolymerization of equimolar quantities of disiloxane (I) and heptadiene (XII) was conducted initially in a stainless steel autoclave at 150 and 200°C. At the lower temperature a mixture of lower molecular weight oils was obtained while only a viscous tar could be recovered from the higher temperature run.

In collateral experiments, the behavior of the individual monomers was studied under the desired conditions of copolymerization.

Obviously, these difunctional monomers could cyclize by themselves to dimers, trimers and possibly homopolymers. Accordingly, a sample of the disiloxane alone was heated in a stainless-steel reactor at 150° C for 20 hours. Unfortunately, violent decomposition left only a dense carbonized residue. Further attempts to study this potentially hazardous instability more completely in a glass tube with stainless stell filings from the steel reactor did not lead to decomposition and the disiloxane was recovered unchanged. Heating the disiloxane alone in a sealed glass tube at 150° C for 50 days also failed to reveal any thermal instability.

Thermal reaction of the heptadiene (XII) alone was also investigated; it was unchanged after heating at 150° C for 20 hours, but a brittle amber solid was recovered in low conversion (ca. 2%) after 20 hours at 200° C. Examination of the infrared spectrum of this solid disclosed the presence of trifluorovinyl groups in the product.

Subsequent studies of the copolymerization of the disiloxane (I) with the heptadiene (III) were attempted concurrently with controls of the respective monomers alone. All of the runs were carried out for 52 days at 150° C and the results were compared.

The material obtained from a 1:1 molar mixture of disiloxane and heptadiene was examined by VPC analysis after removal of unreacted heptadiene and was shown to be a complex mixture of low molecular weight oils in ca. 20% conversion. Moreover, this mixture proved to be essentially identical to the mixture produced by heating the disiloxane alone under the same conditions (conversion ca. 60%). Thus, little copolymerization occurred and the preponderant reactions were of the disiloxane with itself.

Thermal reaction of the heptadiene alone at 150° C for 52 days produced only ca. 5% yield of a viscous liquid product with the remainder being unchanged starting material.

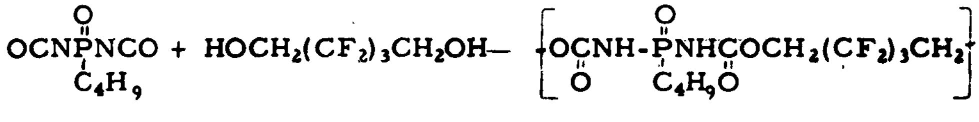
d. Condensation of Phosphorous-Containing Diisocyanates with 2, 2, 3, 3, 4, 4-Hexafluoropentanediol-1, 5

Condensation reactions of butyl and phenylphosphonic diisocyanate (XXVI) and (XXVII) with hexafluoropentanediol (XIII) were explored in an attempt to obtain unique properties from polymers containing phosphorous in the backbone of the polymer alternating with fluorocarbon moieties.

The presence of phosphorous in the system was expected to confer thermal stability and solvent resistance and it was ultimately envisioned that synthetic elastomers composed of a polyurethane structure would be prepared from hydroxyl terminated polyethers possessing fluorocarbon units in the chain and phosphorous-containing diisocyanates.

Several exploratory runs were conducted with $C_4H_9-P(O)(NCO)_2$ and $HOCH_2(CF_2)_3CH_2OH$ in an effort to establish reaction conditions for the formation of polyurethanes.

(15)



$$OCN\overset{O}{\underset{C_4H_9}{P}}NCO + HOCH_2(CF_2)_3CH_2OH \longrightarrow \left[O\underset{O}{C}NH-\overset{O}{\underset{C_4H_9}{P}}NH\underset{O}{C}OCH_2(CF_2)_3CH_2 \right]$$

XXVI XIII XXVIII

Two methods of polymerization were studied, (a) a low temperature solution polycondensation employing acetone as solvent and (b) melt polycondensation at elevated temperatures.

The former method was employed by refluxing equimolar quantities of the reagents in dried acetone (temperature= 65 °C) for various time periods as shown in Table V. The principal products obtained were viscous liquids; some side-reaction of the diisocyanate with adventitious quantities of water evidently upset the reactant balance. Presence of unreacted pentanediol (XIII) was concluded from NMR spectra of the samples. Furthermore the infrared spectra suggested that some cyclic homopolymerization of the diisocyanate had occurred. No catalyst was used so as to minimize the many other side-reactions which diisocyanates can undergo, e. g. , dimerization, trimerization, etc.

Melt polycondensation technique was more successful in forming polyurethane polymers. Heating equimolar mixtures of the reactants in the absence of catalysts at elevated temperatures (175-195°C) was usually satisfactory. In one instance, some decomposition of the molten polymer inadvertently occurred. The products were glassy or horny solids possessing urethane linkages as shown by infrared analysis. A glassy specimen was of very low molecular weight M_n= 700 and readily soluble in acetone. The horny solid was insoluble in acetone and the molecular weight was unknown.

Thermal stability of the solid polymers was measured; except for some decomposition at ca. 200° C, the specimens were stable to above 400° C where extensive decomposition ensued.

D. Monomer Synthesis

1. Preparation of Fluorinated Olefins

a. 4-Chloroperfluoroheptadiene-1, 6 (Monomer 302) and cis-trans Perfluoroheptatriene-1, 3, 6 (Monomers 509 and 510)

The synthesis of 4-chloroperfluoroheptadiene-1, 6 followed the procedure of Park and Lacher[7] (Eq. 16).

$$(16)\quad \underset{\text{XXIX}}{Cl(CF_2\text{-}CFCl)_3CF_2CO_2H} \longrightarrow Cl(CF_2\text{-}CFCl)_3CF_2CO_2Na \longrightarrow$$

$$\underset{\text{XXX}}{Cl(CF_2\text{-}CFCl)_2CF_2CF{=}CF_2} \longrightarrow \underset{\text{XII}}{CF_2{=}CFCF_2CFClCF_2CF{=}CF_2}$$

The final step of the sequence, the dechlorination, was invariably attended by unusually low yields for a supposedly simple elimination. Employment of several different solvents did not increase the yield of heptadiene. However, it was noted that the dehalogenated products invariably contained lower boiling material which reached significant amounts when higher boiling solvents were employed.

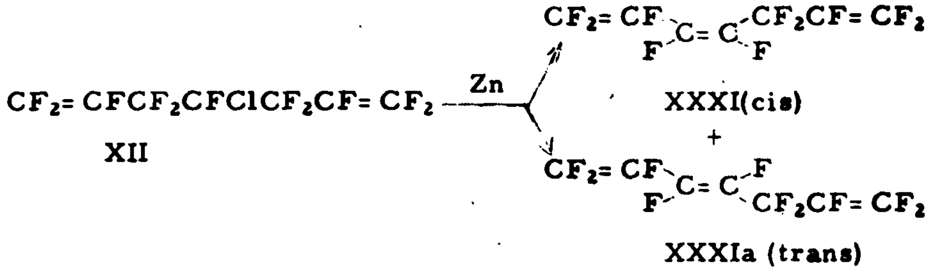
Accordingly, the low boiling materials were analyzed further. VPC analysis indicated that this material was mainly composed of two compounds in essentially equimolar quantities. These two compounds were cleanly separated and isolated with a Wilkins Instrument Co. Autoprep (automatic preparative gas chromatograph).

Examination of the infrared spectra of these two compounds reveals that the low-boiling (81.5° C) compound has an absorption of strong intensity in the double bond stretching region at 1765 cm^{-1} and a second band of lesser intensity at 1705 cm^{-1}, while this latter band is absent in the high-boiling (86° C) isomer. Now, terminal fluoroölefins absorb at about 1750 cm^{-1} and internal fluoroölefins at 1700-1720 cm^{-1}. Furthermore, double bonds having an approximate center of symmetry are infrared inactive, while those lacking such a symmetry element are active. Clearly the low-boiling isomer is cis-perfluoroheptatriene while the high-boiling isomer is trans-perfluoroheptatriene.

Furthermore, the boiling points of both isomers are close to the value calculated for such a system (82 °C). Elemental analysis supports the formula C_7F_{10}.

Undoubtedly, cis-and trans-perfluoroheptatriene (XXI and XXXIa) were formed by further dehalogenation of 4-chloroperfluoroheptadiene-1, 6, (XII) (Eq. 17). It is, however, somewhat unusual for dechlorofluorination to occur; as only a few examples are known, all involving hydrogen-containing compounds[8].

(17)



$$CF_2{=}CFCF_2CFClCF_2CF{=}CF_2 \xrightarrow{Zn} \underset{\text{XXXI(cis)}}{CF_2{=}CF(F)C{=}C(F)CF_2CF{=}CF_2} + \underset{\text{XXXIa (trans)}}{CF_2{=}CF(F)C{=}C(F)CF_2CF{=}CF_2}$$

XII

XXXI(cis)

XXXIa (trans)

The utilization of high-boiling solvents and long reaction times is advantageous for formation of heptatrienes at the expense of heptadiene; in one such instance, there was a 27% yield of triene and only a 16% yield of diene. This may be considered a satisfactory synthetic procedure for the preparation of perfluoroheptatriene, a potentially interesting monomer.

The boiling point of the heptadiene was determined to be 100 °C (760mm). This value agrees well with the value of 103°C (630mm) reported by Park[7] in contrast to Wall's[9] value of 122°C (760mm).

b. Perfluoropentadiene (Monomer 100)

The synthetic approach to this monomer (Eq. 18), following the same general method used for preparing the heptadiene, has been

$$(18)\quad \underset{\text{XXXII}}{CF_2ClCFClCF_2CFClCF_2CO_2H} \rightarrow CF_2ClCFClCF_2CFClCF_2CO_2Na \rightarrow$$

$$\underset{\text{XXXIII}}{CF_2ClCFClCF_2CF{=}CF_2} \longrightarrow \underset{\text{XXXIV}}{CF_2{=}CFCF_2CF{=}CF_2}$$

described by Park and Lacher[1]. The preparation of the sodium salt was slightly modified by utilizing pure acid and concentrated sodium hydroxide solution and eliminated the necessity of evaporating large volumes of water.

Several preliminary dechlorinations of the pentene (XXXIII) were performed using different solvents. The yields, however, were not very high, as dehalogenation occurred only at higher temperatures where the starting pentene (XXXIII) codistilled with pentadiene (XXXIV). The pentadiene could undoubtedly be gotten with higher yields by employing a fractionating column on the pot to return unreacted material. Physical properties agree with those reported by Park[1].

c. 3, 3, 4, 4-tetrafluorohexadiene-1, 5 (Monomer 501)

Several synthetic approaches to this hexadiene were attempted (Eqs. 19 and 20)

$$(19)\quad CF_2Br_2 + CH_2{=}CH_2 \longrightarrow \underset{\text{XXXV}}{CF_2BrCH_2CH_2Br} \xrightarrow{-HBr}$$

$$\underset{\text{XXXVI}}{CF_2BrCH{=}CH_2} \xrightarrow[\text{Zn or Mg}]{} \underset{\text{XXXVII}}{CH_2{=}CHCF_2CF_2CH{=}CH_2}$$

$$(20)\quad \underset{\text{XX}}{CF_2{=}CF_2} + I_2 \longrightarrow \underset{\text{XXXVIII}}{CF_2ICF_2I} \xrightarrow{C_2H_4}$$

$$\underset{\text{XXXIX}}{CH_2ICH_2CF_2CF_2CH_2CH_2I} \xrightarrow{-2HI} \text{XXXVII}$$

Synthesis of propane (XXXV) in scheme (19) was initially carried out by the benzoyl peroxide-initiated addition of dibromodifluoromethane to ethylene originally described by Tarrant[11] and later by Bloomquist[12] and their co-workers. There are several disadvantages to this method, however. Generally conversions of the order of 74% and yields of 25-35% of consumed starting material are realized. In addition, the addition is strongly exothermic under these conditions and is potentially uncontrollable.

Accordingly, the reaction was modified to take advantage of the photolysis of the carbon-bromine bond under ultraviolet irradiation[13]. Vapor phase photolysis of equimolar amounts of dibromodifluoromethane and ethylene with a quartz, high pressure, mercury resonance lamp gave about 50% yields of the desired propane (XXXV).

This is a significant improvement over the older method. Recently, Tarrant and Stump[14] have also expressed preference for ultraviolet initiation over the earlier peroxide technique.

An attempt to modify further the experimental technique to a flow system did not lead to any improvment, as the fine flow control necessary could not be realized with the equipment on hand. As a result, the static system was preferred for the preparative runs.

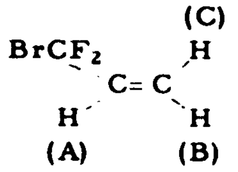
Initial attempts to dehydrobrominate the propane (XXXV) to the propene (XXXVI) in hot aqueous potassium hydroxide according to the method of Tarrant and his co-workers[15] were not successful, apparently because the starting propane (XXXV) steam distilled without reacting. Therefore, several alternate methods of dehydrobromination were investigated. Cold ethanolic potassium hydroxide was found to be the most satisfactory.

Although the propene (XXXVI) has been described, evidence was not presented to establish the correct structure (XXXVI or XL, Eq. 21). That the correct structure is (XXXVI) was readily determined by proton NMR spectroscopy.

(21) $CF_2BrCH_2CH_2Br \rightarrow CF_2BrCH{=}CH_2$ and/or $CF_2{=}CHCH_2Br$

XXXV XXXVI XL

The spectrum displays a typical ABC pattern consistent with the proposed structure.



XLI

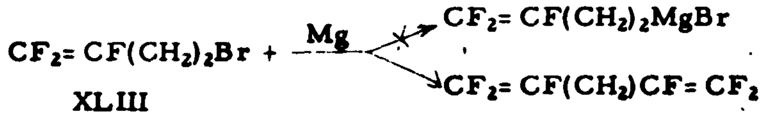
Proton A gives rise to a multiplet centered at ca. $\tau 3.97$; proton B gives a quadruplet centered at $\tau 4.32$; proton C gives a quadruplet centered at $\tau 4.62$. Coupling values were determined to be:

J_{AB}: ca. 10.3 c/s; J_{AC}: ca. 17.0 c/s; J_{BC}: ca. 1.0 c/s; J_{AF}: ca. 8.0 c/s.

A weak resonance signal at $\tau 5.85$ may have been caused by a small amount ($< 4\%$) of either the isomeric propene (XL) or the starting propane (XXXV). In light of these observations, it is surprising to find an account by Maramatsu and Tarrant[16] stating that the starting propane with ethanolic potassium hydroxide gives, not the propene (XXXVI) but the isomeric propene (XL); they conclude that... "the choice of solvent seems to be an important factor (in determining direction of elimination)". It is not possible to verify their results. But, as they did not show their structural proof, the problem cannot be further resolved.

The final step in the sequence, coupling of the propene to form the hexadiene (XXXVII) (Eq. 17), was patterned after the recent finding of Tarrant, et. al[17]. These workers, attempting to form the Grignard of 4-bromo-1,1,2-trifluorobutene-1, (XLII), discovered only the coupled product, 1,1,2,7,8,8-hexafluorooctadiene (XLIII) (Eq. 22).

(22)



$$\mathrm{CF_2{=}CF(CH_2)_2Br} + \xrightarrow{\mathrm{Mg}} \begin{cases} \not\rightarrow \mathrm{CF_2{=}CF(CH_2)_2MgBr} \\ \rightarrow \mathrm{CF_2{=}CF(CH_2)CF{=}CF_2} \end{cases}$$

XLIII

XLIII

In the present case, reaction with magnesium was attempted in ethyl ether, butyl ether, and tetrahydrofuran. Only with tetrahydrofuran did a reaction occur. The product could not be separated from the reaction medium, however, because of the similarity of boiling points.

Zinc-promoted intermolecular dehalogenation, an older and better known process, was also investigated. Several of the media employed by earlier workers included acetic acid, methylene chloride, and dioxane (Ref. 2, p. 319 ff.). An attempt using dioxane in the present case failed.

The other synthesis (Eq. 18) of hexadiene (XXXVII) investigated was first disclosed by Brace[18], and later by Knunyants, et. al.,[19] who described the synthesis from tetrafluoroethylene diiodide and ethylene. Tetrafluoroethylene diiodide, previously synthesized from tetrafluoroethylene and iodine[20], defied present synthetic attempts; the reactants invariably corroded the autoclave walls. Previous experimenters had utilized silver or Hastelloy-lined apparatus, not available for the present work.

d. 1, 3-Bis(3, 4, 4-Trifluoro-3-butenyl)-1, 1, 3, 3-tetramethyl disiloxane (Monomer 202)

The preparation of this disiloxane (XXL Eq. 23) followed the precedure of Tarrant, *et. al.* (Ref. 17, , 8).

(23)
$$\underset{\text{XLIV}}{CF_2BrCFClCH{=}CH_2} + HSi(CH_3)_2Cl \longrightarrow$$

$$\underset{\text{XLV}}{CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl} \xrightarrow{H_2O}$$

$$\underset{\text{XLVI}}{[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O} \xrightarrow{Zn} \underset{\text{I}}{[CF_2{=}CFCH_2CH_2Si(CH_3)_2]_2O}$$

The initial step, chloroplatinic acid catalyzed addition of chlorodimethylsilane to butene (XLIV), was found not to be clean. Significant amounts of hydrogen and dichlorodimethylsilane were obtained and undoubtedly accounted for the only moderate yields of silane (XLV). Reasoning that chlorodimethylsilane disproportionated under the reaction conditions[21], the synthesis was modified so that aliquots could be added during the course of the reaction; the yields were moderately increased (55% *vs.* 40%). An autoclave was also found unnecessary; the addition proceeded readily at reflux in isopropyl alcohol.

Hydrolysis of chlorosilane (XLV) to disiloxane (XLVI) was straight forward, providing good yields (55-88%). Dehalogenation of disiloxane (XLVI) to the unsaturated monomer (I) also occurred without difficulty. Utilization of tetrahydrofuran as solvent enabled realization of product in *ca.* 70% yield.

Physical properties of the monomer disiloxane (I) agreed only moderately well with the values reported by Tarrant (Ref. 17, p. 8). However, VPC comparison of the FMC preparation with a sample submitted by University of Florida researchers demonstrated that the former was 90 mole % pure while the latter only 73% pure.

A total of 458 g. of disiloxane (I) was synthesized; about 25 g. of highly purified (99. 7 mole %) material was isolated by preparative gas chromatographic techniques for polymerization studies.

e. Hexafluoroisobutylene (Monomer 114)

The synthetic approach to hexafluoroisobutylene (XLIX) envisioned was a simple extention of earlier work by Knunyants, et. al. on Grignard reagent addition to hexafluoroacetone[22] and dehydration of the resultant alcohol[23] (Eq. 24);

$$(24)\quad \underset{\text{XLVII}}{(CF_3)_2C=O} + CH_3MgBr \longrightarrow \xrightarrow{H_3O\,+}$$

$$\underset{\text{XLVIII}}{(CF_3)_2COHCH_3} \longrightarrow \underset{\text{XLIX}}{(CF_3)_2C=CH_2}\ .$$

However, only an exploratory synthesis of alcohol (XLVIII) was done. The Grignard addition, conducted in ethyl ether successfully gave 1, 1-bis(trifluoromethyl) ethanol (XLVIII) which could be readily identified by its NMR spectrum. A single reasonance line at τ 5. 32 arises from the hydroxyl proton; a heptuplet at τ 8. 46 ($J = 1$ c/s) is undoubtedly from the methyl group. Reasonance absorption lines attributable to ethyl ether are also present and intergration of the spectrum suggests a dietherate. It is likely that ethyl ether azeotropes with this alcohol, as earlier observed by Knunyants and his co-workers[22]. This problem could be avoided in the future by either utilizing butyl ether or washing the reaction product with sulfuric acid.

2. Preparation of Phosphorus and Sulfuryl Isocyanates

a. Phosphorus Triisocyanate (Monomer 515)

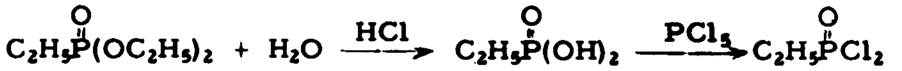
Phosphorus triisocyanate (L) was prepared by the reaction of phosphorus trichloride and silver cyanate in benzene[24]. The product polymerized while standing in the refrigerator before it could be used.

$$(25)\quad PCl_3 + 2AgNCO \longrightarrow \underset{\text{L}}{P(NCO)_3} + 3AgCl$$

A description of the properties of the compound has been published.[24]

b. Alkyl and Arylphosphonic Diisocyanates (Monomers 516 and 517)

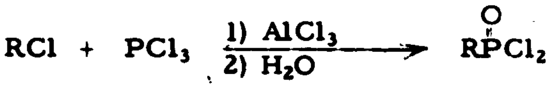
Ethylphosphonic dichloride (LI) was prepared by the method of Kosolapoff[25] from diethyl ethylphosphonate. It was not converted to the diisocyanate.

(26) 

$$C_2H_5\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + H_2O \xrightarrow{HCl} C_2H_5\overset{O}{\overset{\|}{P}}(OH)_2 \xrightarrow{PCl_5} C_2H_5\overset{O}{\overset{\|}{P}}Cl_2$$

LI

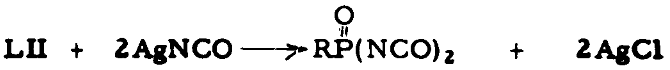
Butylphosphonic dichloride (LII, R= C_4H_9) was prepared by the reaction of phosphorus trichloride, 1-chlorobutane and aluminum chloride[26]. Spectral evidence indicates that the product is probably the 2-butyl derivative.

(27) 

$$RCl + PCl_3 \xrightarrow[2)\ H_2O]{1)\ AlCl_3} R\overset{O}{\overset{\|}{P}}Cl_2$$

LII

Butyl-and phenylphosphonic diisocyanates (XXVI, R= C_4H_9 ; XXVII, R= C_6H_5) were prepared from the corresponding dichlorides with silver cyanate according to published methods[27, 28]. The compounds are apparently stable although they react rapidly with moisture. The undistilled products do not keep, however.

(28) 

$$LII + 2AgNCO \longrightarrow R\overset{O}{\overset{\|}{P}}(NCO)_2 + 2AgCl$$

XXVI, R= C_4H_9
XXXVII, R= C_6H_5

c. Sulfuryl Diisocyanate

A two-step synthesis of sulfuryl diisocyanate (LIV) has been reported[29, 30] in which chlorosulfonyl isocyanate (LIII) is prepared from sulfur trioxide and cyanogen chloride. Reaction with silver cyanate then gives sulfuryl diisocyanate. Attempts were made to

$$(29)\quad SO_3 + ClCN \longrightarrow ClSO_2NCO \xrightarrow{AgNCO} SO_2(NCO)_2$$

LIII LIV

prepare the latter directly from sulfuryl chloride and silver cyanate. With benzene as a solvent, no reaction occurred. With acetonitrile as the solvent, a solid identified as cyanuric acid was formed.

IV. EXPERIMENTAL

A. Polymerization Research

1. Vinyl Polymerizations

a. Modification of Vinylidene Fluoride/Hexafluoropropylene Emulsion Polymerization System

Emulsion Polymerization of $CF_2=CH_2/CF_3CF=CF_2$

The following procedure is typical for the emulsion polymerization runs tabulated in Table I.

D-871-143 A 110 ml. Aminco bomb was charged with 42g. of 3.8% aqueous potassium persulfate solution, 17.6 g. of 9.1% disodium hydrogen phosphate solution and 20 g. of 10% sodium perfluoroöctanate solution. The bomb was then closed, cooled in dry ice and evacuated. Then, 20 g. of $CF_2=CH_2$(70 mole %) and 20 g. of $CF_3CF=CF_2$(30 mole %) were charged to a 75 ml. stainless steel cylinder by gaseous transfer in vacuo and the 75 ml. cylinder was attached to the Aminco bomb via an oxygen regulator. The cylinder valve was opened at 50 °C (50 psig) and the reducing value was set to deliver 450 psig to the Aminco bomb (also heated to 50 °C). The assembly was rocked for 17 hrs. at which time the pressure had dropped to 300 psig. The bomb was cooled, unreacted monomers vented and the product (a bluish latex) was decanted. The latter was coagulated with a 10% aqueous aluminum sulfate solution and a white elastomeric product was recovered by filtration. After thorough washing with water and drying in an oven at 60 °C. overnight, 6.7g. of product was obtained, representing a 17% conversion based on the total monomer charge of 40 g.

Attempted Curing of Viton A with $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$

D-871-152 The following ingredients were blended on a cold rubber mill with Viton A elastomer (vinylidene fluoride/hexafluoropropylene 80/20 mole %):

Ingredient	Parts by weight
Viton A	100
Magnesium oxide	15
$[CF_2=CFCH_2CH_2Si(CH_3)_2]_2$	10
Benzoyl peroxide	2

The stock was molded 30 min. at 300° F into four 6-in. square plaques. All four plaques contained bubbles upon opening the molds. Two of the plaques were passed again through the rubber mill. One of the plaques was then molded for 15 min. at 230° F and the other was molded by gradually increasing the mold temperature from 80° F to 230° F and applying 40 tons pressure for 5 min. before cooling. The molded specimens were then oven cured by gradually increasing the temperature from 200° F to 350° F over a 6 hr. period. Finally, the upper temperature (350° F) was maintained for 18 hrs.

One specimen was then cut into small pieces and subjected to a pentane extraction overnight in a Soxhlet apparatus. After drying in an oven at 50° C overnight the specimen was analyzed for silicon but the results were negative. A glass transition temperature (T_g) measurement performed on the unextracted specimen in the Gehman apparatus showed the sample to have T_g -20° C. A similar measurement performed on a differential scanning calorimeter resulted in a T_g -23° C. A sample of gum Viton A was found to have T_g -22° C.

b. Copolymerization of Hexafluoroacetone with Olefins

Pertinent proton NMR data of the oxetanes synthesized is given in Table II.

Preparation of 2, 2, 3(and4)-Tris(trifluoromethyl)perfluorooxetane

C-1129-30 The apparatus employed in this preparation was a 12 liter round-bottom flask equipped with an outlet connected to a Hg manometer, an inlet for charging and evacuating, and a Hanovia water-jacketed quartz immersion well with a 450 watt high pressure Hg ultraviolet lamp. The flask was evacuated and then charged with 300 mm. $CF_3CF{=}CF_2$ and 300 mm. CF_3COCF_3. During the irradiation the pressure drop was followed as a function of time. When the pressure dropped to a value of 1/2 of the total original charge the lamp was extinguished and the flask evacuated through a dry-ice cooled trap. The contents of the trap were rectified to give 44.5g. of product boiling at 48-55° C. A wide boiling range was collected to insure that both possible isomers would be collected. VPC analysis indicated that the product consisted of 90% of one isomer, presumably the 2, 2, 3 isomer and 5% of another isomer, presumably the 2, 2, 4 isomer.

C-1129-30 The flask employed in the above preparation was utilized for this preparation. 1 g. benzophenone was added to the flask which was then evacuated and charged with 300 mm. of CF_3COCF_3 and 300 mm. $CF_3CF=CF_2$, as before. The pressure drop during irradiation was followed as a function of time and was virtually identical to the above experiment. After irradiation the flask was evacuated and the material collected in the trap distilled to give 45.0 g. of product boiling at 48-55° C (Lit.[7] b.p. 51-52° C).

Preparation of 2, 2, 3, 4-Tetrakis(trifluoromethyl)perfluoro-oxetane

C-1129-34 Into the 12 liter round-bottom flask used before was charged 300 mm. hexafluoroacetone and 300 mm. $CF_3CF=CFCF_3$ After irradiating 16 hours no pressure drop was recorded. The flask was evacuated through a dry-ice cooled trap and the material collected in the trap distilled to give 7.5 g. of material boiling 60-63° C.

C-1481-2 Into the evacuated flask mentioned above was charged 302 mm. CF_3COCF_3 and 302 mm. $CF_3CF=CFCF_3$. After irradiating for 18 hours a pressure drop of 4 mm. was observed. A small amount of liquid had collected and the flask was pumped down through a dry-ice cooled trap. The material collected in the trap was distilled and 8 g. of material boiling at 58-64° C collected.

IR analysis failed to show carbonyl or double bond absorption. Mass spectrographic analysis suggested perfluorodiisopropyl contaminated with a small amount of the desired oxetane.

1, 1-bis(trifluoromethyl)oxetane and polymer

C-1129-43 Into an evacuated 12 liter 3-neck flask containing a Hanovia 450 watt high pressure Hg lamp in a quartz insert was charged 300 mm. hexafluoroacetone and 300 mm ethylene. After 8 hours irradiation the pressure decreased 180 mm. and the lamp was extinguished. The flask was pumped down and the liquid products thus stripped off were separated directly by means of preparative VPC. The oxetane accounted for about 80% of the product; another compound, accounting for the remainder of the volatile product was not identified.

The IR spectrum of the oxetane, b.p. 85.5° C, 761 mm. (micro), is reproduced in Figure 5.

A nonvolatile oil remaining in the flask analyzed for 55.5%F, and had an average molecular weight of 570 (vapor pressure Osmometer, benzene solution).

1,1-bis(trifluoromethyl)-2-fluoroöxetane, 1,1-bis(trifluoromethyl)-3-fluoroöxetane and polymer

C-1129-81 The above procedure was followed with vinyl fluoride and hexafluoroacetone.

Two compounds comprised the major amount of product and were separated and isolated by preparative VPC. 1,1-bis(trifluoromethyl)-2-fluoroöxetane, b.p. 88.6° C, 764 mm. (micro), IR spectrum, Figure 5; 1,1-bis(trifluoromethyl)-3-fluoroöxetane, b.p. 78.8° C, 764 mm. (micro), IR spectrum Figure 6. Complete analysis of the nonvolatile oil, which was orange colored, was not conducted.

1,1-bis(trifluoromethyl)-2,2-difluorooxetane, 1,1-bis(trifluoromethyl)-3,3-difluoroöxetane, and polymer

C-1129-52 The same procedure with vinylidene fluoride and hexafluoroactone was followed as in the above examples.

The volatile liquid product was washed with water, dried over sodium sulfate, and distilled, b.p. 58-62° C. The two isomers were separated and isolated by preparative VPC. 1,1-bis(trifluoromethyl)-2,2-difluoroöxetane, b.p. 65.2° C, 761 mm. (micro), IR spectrum, Figure 3. 1,1-bis(trifluoromethyl)-3,3-difluoroöxetane, b.p. 58.0° C, 761 mm. (micro), IR spectrum, Figure 4.

The white opaque nonvolatile oil remaining in the flask analyzed for 62% F, and had an average molecular weight of 612 (vapor pressure Osmometer, methanol solution).

1,1-bis(trifluoromethyl)nonadiene-3,7-ol-1

C-1129-76 A modified Soxhlet apparatus was employed to maintain a reasonable concentration of octadiene-1,7 (Columbia Carbon Co.) vapors in proximity to the ultraviolet lamp while a slight positive pressure of hexafluoroäcetone was introduced to the apparatus. After conclusion of irradition, the liquid was distilled; of the 135 g. octadiene charged, 104 g. was recovered.

The major component of the pot residue was then isolated by preparative VPC techniques and identified by proton NMR as 1, 1-bis(trifluoromethyl)nonadiene-3, 7-ol-1, b.p. 192.0-192.4° C, 764 mm. (micro), IR spectrum, Figure 8.

2. Condensation Polymerizations

a. Copolymerization of 4-Chloroperfluoroheptadiene-1, 6 with 2, 2, 3, 3, 4, 4-Hexafluoropentanediol-1, 5

The following experiment is typical of those carried out. All are tabulated in Table III.

C-1129-71 To 11 g. (50 mmole) of the pentanediol in 20 ml. acetone was added 3.0 g. potassium hydroxide. This mixture was then rapidly poured into 16 g. of the heptadiene contained in a 250 ml. Erlenmeyer flask and the resultant mixture stirred magnetically. The light yellow color, which formed immediately, slowly darkened and, after 72 hours, tan to brown polymer was found in the flask along with a viscous oil. The oil was dissolved in acetone, the solution decanted, and the polymer washed with acetone. The polymer was leached in a Soxhlet extractor overnight with acetone and then dried in a vacuum oven.

Several modifications were investigated; solvent, temperature, and base. Succinctly, the results were,polar solvents are much more effective than non-polar solvents (acetone vs. hexane-benzene); the rate of polymerization is highly temperature dependent (minutes at 50° C vs. hours at 25° C); strong bases are required (sodium bicarbonate was not effective).

b. Copolymerization of 2, 2, 3, 3, 4, 4-Hexafluoropentanediol-1, 5 with Hexafluorobenzene

C-1129-78 A solution of 9.0 g. (0.10 mole) 2, 2, 3, 3, 4, 4-hexafluoropentanediol-1, 5, 9.3 g. (0.10 mole) hexafluorobenzene and 5.6 g. (0.10 mole) potassium hydroxide in 25 ml acetone was stirred at reflux for 1 month. The resultant paste was washed with water, dissolved in acetone, and then reprecipitated by slowly adding the acetone solution to a large volume of stirred, ice-cooled water. There was obtained 13.7 g. of tacky semi-solid.

c. Copolymerization of 1, 3-Bis(3, 4, 4-trifluoro-3-butenyl)-1, 1, 3, 3-tetramethyldisiloxane with 4-Chloroperfluoroheptadiene-1, 6

Reaction of Tetrafluoroethylene with 3, 4, 4-Trifluoro-3-butenyltrimethylsilane and Trifluorovinyltrimethylsilane

Several reactions were done under different conditions to determine optimum conditions for cyclodimerization. The following is typical (all are tabulated in Table III):

D-971-64-B A 75 ml. stainless steel cylinder was charged with 10. 0 g. of $CF_2=CFCH_2CH_2Si(CH_3)_3$ and 0. 03 g. of $(C_4H_9)_3N$. The bomb was then fitted with a Hoke needle valve, cooled with liquid nitrogen, evacuated and charged with 5. 5 g. of $CF_2=CF_2$ from a gas transfer system. The sealed bomb was then allowed to remain at 150 °C for 17 hours in a barricaded Aminco rocker. Upon completion of the reaction, the bomb was cooled in liquid nitrogen, the unreacted $CF_2=CF_2$ allowed to escape and the liquid mixture remaining decanted from the bomb and placed in an apparatus for simple distillation; 4. 4 g. distilled at 116-120 °C. and 0. 4 g. was collected at 130-149 °C. Infrared analyses indicated that both fractions were almost identical.

The following procedure is typical for the thermal reactions of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ and $CF_2=CFCF_2CFClCF_2CF=CF_2$ (tabulated in Table IV).

C-1529-3 A 30 ml. Pyrex tube equipped with a Teflon needle valve was charged with a mixture of 5. 00 g of $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ (0.014 mole) and 5. 68 g. (0. 014 mole) of $CF_2=CFCF_2CFClCF_2CF=CF_2$. The tube was then placed in liquid nitrogen, evacuated, closed and placed in a thermostated oil bath at 150 °C for 52 days (as there was little change in viscosity). The reaction mixture was stripped of unreacted heptadiene at atmospheric pressure, by simple distillation with a maximum pot temperature of 160 °C. The concentrate was then analyzed by VPC and was shown to consist of a complex mixture of products with ca. 38% unreacted disiloxane present. The concentrate was then vacuum distilled to 170 °C/ 1 mm. to remove unreacted disiloxane. VPC analysis of the residue showed that the latter was a complex mixture of high boilers present in the original reaction mixture (after removal of heptadiene).

d. Condensation of Phosphorous-Containing Diisocyanates with 2, 2, 3, 3, 4, 4-Hexafluoropentanediol-1, 5

Several condensations of n-butyl phosphonic diisocyanate were performed; all are tabulated in Table V. The following two experiments are examples of a solution and a melt condensation.

C-1529-33 A dry 50 ml. round-bottom flask equipped with a reflux condenser, drying tube, and magnetic stirrer was charged with 1.65 g. (0.0087 mole) of n-butyl phosphonic diisocyanate dissolved in 15 ml. of acetone (%H_2O undetermined) and then charged with 1.82 g. (0.0087 mole) of 2, 2, 3, 3, 4, 4-hexafluoropentanediol-1, 5 dissolved in 15 ml. of acetone. The reaction mixture was refluxed (65°C) for 2 hours and then allowed to remain overnight at room temperature.

About 0.1 g. of white solid, m.p. 212-214°C, was isolated by filtration of the reaction mixture and the filtrate was then stripped of acetone at atmospheric pressure whereupon 0.1 g. more of white solid was isolated from the concentrate.

The reaction mixture was finally stripped in vacuo (ca. 25 mm Hg) with a maximum pot temperature of 80°C. The residue was an orange colored, viscous liquid. The sample exhibited an absorption at 1695-1725 cm^{-1} in the infrared which would be consistent with a carbonylamide group indicating some cyclic homopolymerization of the butyl phosphonic diisocyanate.

C-1529-40 A dry 10 ml. round-bottom flask equipped with a helium gas inlet tube, an air condenser with drying tube, and a magnetic stirrer was charged with 1.07 g. (0.0050 mole) of 2, 2, 3, 3, 4, 4-hexafluoropentanediol-1, 5, and the latter was melted with an oil bath maintained at ca. 80°C. Then, 0.95 g. (0.0050 mole) of n-butyl phosphonic diisocyanate was added at once to the molten diol and the reaction flask was heated gradually to 170-175°C and maintained at that temperature for 1.5 hours. The molten reaction mixture was extremely viscous and on cooling to room temperature the mass consisted of a brittle glass which was readily soluble in acetone.

The product possessed a number-average molecular weight of 705, measured in acetone in an osmometer.

The presence of urethane groups was observed as a broad band at 1724-1754 cm^{-1} in the infrared spectra. Differential thermal analysis of the specimen revealed that some decomposition started at 197°C and an endothermic reaction commenced at 212°C and was completed at 232°C. Afterwards, a gradual decomposition ensued up to 431°C whereupon a strong exotherm was noted leaving a carbonaceous residue at 461°C.

B. Monomer Synthesis

1. Synthesis of Fluorinated Olefins

a. Preparation of 4-Chloroperfluoroheptadiene-1, 6

Preparation of $Cl(CF_2CFCl)_3CF_2CO_2Na$

D-798-134 To a solution of 37.5 g. (0.937 mole) of sodium hydroxide in 100 ml. of water was added 449 g. (0.937 mole) of $Cl(CF_2CFCl)_3CF_2COOH$ over a 1-hour period with stirring. The mixture turned into a thick paste. Most of the water was removed by drying on a steam bath. Drying was completed by heating to 125 °C in an oven at a pressure of about 1 mm. The yield of slightly gray powder was 457 g. (99.1% of theory).

The above preparation was repeated twice, on 250 and 500 gram scales (C-1129-1, C-1129-8, respectively). In these runs, the final drying was carried out, in vacuo, over phosphorus pentoxide. **Yields** in both cases were virtually quantitative.

Preparation of 4, 6, 7-Trichloroperfluoroheptene-1

C-1129-3 Exactly 267 g. of $Cl(CF_2CFCl)_3CF_2COONa$ was transferred to a 1-liter round-bottom flask equipped with a distilling adaptor, Friedrich condenser, vacuum adapter, and receiver. The system was evacuated through a dry-ice cooled trap to approximately 1 mm. pressure and then heated to approximately 150° C. Decarboxylation commenced within approximately 15 minutes and the pressure increased to ca. 10 mm. because of carbon dioxide evolution. The heptene came over smoothly to the ice-cooled receiver and was washed once with water, once with 10% aqueous sodium carbonate, once again with water, and dried over sodium sulfate. There was obtained 180.5 g. of crude product. Infrared analysis of this showed a strong adsorption band at 1770 cm^{-1} indicating a terminal fluoroolefin and an adsorption band at 1720 cm^{-1} indicating a small contaminant of internal olefin. There was no adsorption in the range 3500-2500 cm^{-1} indicative of carbon-hydrogen bonding which would be expected of a possible contaminant (due to incomplete drying of starting material). Distillation of this crude material gave 159 g. of pure heptene boiling at 161-162°C, 75% of the theoretical possible yield from the starting $Cl(CF_2CFCl)_3CF_2COOH$.

D-798-137 A 605 g. (1.23 mole) quantity of $Cl(CF_2CFCl)_3CF_2COONa$ (D-798-134) was divided in two equal portions. Each was pyrolyzed by slowly heating to 370° C at a pressure of 4 mm. The distillate was collected in an ice-cooled receiver followed by a dry-ice/acetone cooled trap. The total yield was 461 g. The distillate was washed first with 5% aqueous sodium bicarbonate solution and then with water and dried over magnesium sulfate. The product was distilled through a 15 cm. Vigreux column, giving a 427 g. yield (87.0%) of the desired product, b.p. 65-70° C (20 mm) n_D^{25} 1.3639, d_4^{25} 1.78. VPC analysis indicated that the product was 92.3% pure.

One additional run (C-1129-9) was carried out to yield an additional 315 g. of heptene, b.p. 160-163° C (760 mm.) (Yield 74.5% from starting acid. (Lit.[31] b.p. 156-157° C (760 mm), n_D^{25} 1.3639, and d_4^{20} 1.800).

Preparation of 4-Chloroperfluoroheptadiene-1,6

D-798-141 To a stirred refluxing mixture of 16 g. (0.25 mole) of zinc dust, 1 g. of zinc chloride, and 25 ml. of isopropanol was added 39.9 g. (0.1 mole) of 4,6,7-trichloroperfluoro-1-heptene (D-798-137) over a 6 hour period. After refluxing an additional 0.5 hour, the mixture was filtered from unreacted zinc and the filtrate diluted with several volumes of water. The organic layer was taken up in methylene chloride, water washed several times, and dried over magnesium sulfate. Distillation gave 11.3 g. of product, b.p. 97-112° C (761 mm.), n_D^{25} 1.311. The purity by gas chromatography was 67.5%. The yield of crude product based on heptene actually consumed was 40.9%. Unreacted material recovered was 6.5 g. (16.3% of the amount charged).

The physical constants reported by Park and Lacher[7] are: b.p. 103-103.5° C (630 mm.) and n_D^{23} 1.3326. Fearn and Wall[9], however, report 122° C (760 mm). In their reports, Park and Lacher claim to have confirmed the structure by means of NMR spectroscopy.

This zinc dechlorination reaction was repeated several times, using other solvents; the best run was carried out in isopropanol solvent and utilized recovered heptene. In run D-798-146, the procedure described above was modified to the extent that the reaction was carried out at 100° C (88 mm) with a short Vigreux column and a still head added to the apparatus, and heptadiene removed as it formed. The crude product so obtained was redistilled.

Some details of this series of reactions are summarized in Table II.

About 12 g. of the heptadiene was isolated in 98 mole percent purity by preparative VPC for use as a highly purified monomer.

b. Preparation of cis-and trans-Perfluoroheptatriene-1, 3, 6

These two isomeric trienes were isolated from the 82-98° C fraction obtained in experiment C-1129-10. A total of 58.2 g. of the two heptatrienes were present in equimolar amounts, the yield being 27% from the heptenes charged. Cis-perfluoroheptatriene: b.p. 81.5° C, 761 mm. (micro) IR spectrum; Figure 1: trans-perfluoroheptatriene: b.p. 86° C, 761 mm. (micro); IR spectrum; Figure 2.

c. Preparation of Perfluoropentadiene-1, 4

C-1129-42 To two 505 g. (2.78 mole total) portions of $CF_2ClCFClCF_2CFClCF_2CO_2H$ in a 2-liter beaker was rapidly added with stirring 60 g. sodium hydroxide in 60 ml. water to each. There was considerable heat generated, evolving most of the water as steam. The two pasty fractions were combined and further dehydrated in a vacuum oven. The solid was then pulverized and dried over phosphorous pentoxide. About 1 week and 5 changes were required. There was obtained 1048 g. (2.72 mole) of finely powdered, free flowing, white sodium salt in 98% yield.

C-1129-51 In a 1-liter round-bottomed flask, 433g, (1.13 mole) $CF_2ClCFClCF_2CFClCF_2CO_2Na$ was pyrolyzed at about 150° C. The pentene was pumped off into a cooled receiver as it formed. Distillation afforded 223.4 g. (0.789 mole) of the pentene, b.p. 92-3° C, 756 mm (Lit^1, 86° C, 630 mm) in 70% yield. There were mechanical losses from the powdered sodium salt being carried away by the rapid carbon dioxide evolution.

Dechlorination of perfluoropentadiene was not completed.

d. Preparation of 3-Bromo-3, 3-difluoropropene

Preparation of 1, 3, -Dibromo-3, 3-difluoropropane

A number of runs were conducted towards the preparation of this compound. The following are typical:

C-1129-32 A 2 liter Aminco Bomb was charged with 15 g. benzoyl peroxide, evacuated, purged with bone-dry nitrogen, further evacuated, and finally charged with 550 g. (2.62 moles) CF_2Br_2. The bomb was placed in a barricaded rocker, charged with 350 psig CP ethylene while rocking, and was then rapidly heated to 90° C. Very shortly thereafter, an exotherm occurred raising the bomb temperature to 120° C momentarily, with a pressure rise to 900 psig. Immediately thereafter, the pressure fell to 200 psig and there remained. Heating was continued at 90° C for 2 hours (4 half-lives of the initiator). The bomb was cooled to room temperature and the volatiles collected in a dry-ice cooled trap. The liquid product was steam distilled, the lower organic layer separated, and dried over sodium sulfate. Distillation gave 203 g. (0.966 mole) of unreacted $CF_2Br_2$and 135 g. (0.567 mole) of dibromodifluoropropane boiling at 125-126° C (760 mm.) (Lit.[11] 81.5-82° C (173 mm). Thus, 63% of the CF_2Br_2 charged into the bomb was consumed with 35% of the consumed CF_2Br_2 producing the desired product (the overall yield of product is 23% of total reactant charged into the bomb). The bomb runs made according to the above procedure are summarized in Table III.

C-1129-39 A 12-liter flask equipped with a quartz immersion well containing a 450-watt high pressure Hg lamp was intermittently charged with equibaric amounts of dibromodifluoromethane and ethylene. After a total of 179 g. (0.895 mole) dibromodifluoromethane had been charged, the liquid product was isolated, washed twice with water, and dried over sodium sulfate. The fraction b.p. 110-133° C was collected, 54.6 g. (0.417 mole), 47% yield.

Several later modifications were attempted in order to obtain a flow system. A 5-liter flask with a stopcock on the bottom for liquid removal was employed. This system was not as satisfactory, however, because of the necessity of a finely controlled, stable rate of introduction of the reactants. This could not be achieved without continuous monitoring. Also, it appeared that an optimum rate of introduction and reactant temperature would have to be determined for highest yields.

Preparation of 3-Bromo-3,3-difluoropropene

C-1491-13 The following methods of dehydrobromination of 1,3-dibromo-1,1-difluoropropane were examined:

α. Use of hot aqueous potassium hydroxide

Following the method of Tarrant [15], 47.6 g. (0.2 mole) of 1,3-dibromo-1,1-difluoropropane was added over 0.5 hours to a hot (80° C) stirred solution of 56 g. of 85% potassium hydroxide in 100 ml. of water. A heavy organic liquid distilled with a little water. This distillate was recycled in an attempt to insure maximum conversion. The organic layer in the second distillation was separated, dried, and distilled. Only 3.1g. of liquid distilled at 40-42° C, the expected boiling point of the product. Most came over at a much higher temperature and was presumably unreacted starting material.

β. Use of Tributylamine

To93 g. (0.5 mole) of tributylamine at 125° C was added 47.6 g. (0.2 mole) of 1,3,-dibromo-1,1difluoropropane over 1.0 hour. At the end of the addition, a vigorous exothermic reaction occurred and 3.0 g. of colorless liquid distilled, which although quite impure, contained some of the desired product according to its infrared spectrum. No more product could be removed from the black liquid in the pot, even after dissolving in dilute hydrochloric acid.

γ. Use of hot aqueous sodium hydroxide

Experiment (α) was repeated using 50% sodium hydroxide solution at 130° C. No reaction occurred.

δ. Use of cold ethanolic potassium hydroxide

A solution of 18 g. (0.27 mole) of potassium hydroxide in 125 ml. of ethanol was added to 59.5 g. (0.25 mole) of 1,3-dibromo-1,1-difluoropropane in 25 ml of ethanol over 2.0 hours while keeping the temperature at 15° C. A heavy white precipitate formed. After stirring an additional 0.5 hours, the mixture was diluted with 200 ml. of water, the organic layer separated, and the aqueous layer (still alkaline) extracted with tetrachloroethane. After drying, the product was distilled over potassium hydroxide to give 16.8 g. (53.5%) of colorless liquid, b.p. 40-41° C (762 mm.), n_D^{25} 1.3751. (Lit. [15] b.p. 42° C, n_D^{25} 1.3773).

e. Preparation of 1, 3-Bis(3, 4, 4-Trifluoro-3-butenyl)-1, 1, 3, 3-tetramethyl disiloxane

Preparation of $CF_2BrCFClCH_2CH_2Si(CH_3)_2Cl$

D-871-108 A 2. 7 liter Aminco Bomb was charged with 473 g. (5 moles) of $HSi(CH_3)_2Cl$, 1117. 5 g. (5 moles) of $CH_2=CHCFClCF_2Br$ and 10 cc. of 0. 1M H_2PtCl_6 in isopropanol in an air atmosphere. The bomb contents were then rocked at 75° C for 11 hours. At the conclusion of the heating period, the bomb was cooled, vented, and the contents decanted. Distillation at atmospheric pressure through a a 14" insulated Vigreux column gave two fractions: The first distilling at 60-90° C and weighing 805 g. and the second distilling at 180-185°C. and weighing 606 g. (38% yield of the desired product). The first fraction was redistilled in a Fenske-helices packed column with the following results:

BP° C	Weight	Identity
20-70	56 g.	-
70-73	276 g.	$(CH_3)_3SiCl_2$
73-77	84 g.	-
77-84	87 g.	-
84-96	43 g.	-
96-98. 5	161 g.	$CH_2=CHCFClCF_2Br$
Residue	94 g.	-

The $(CH_3)_2SiCl_2$ was identified by vapor phase chromatography employing commercially available material as a reference compound.

The $CH_2=CHCFClCF_2Br$ recovered was identified by its boiling point and chemical properties; 52% of the butene was accounted for in the product and as unchanged starting material.

D-798-145 A mixture of 1117 g. (5. 0 moles) of $CH_2=CHCFClCF_2Br$ 709 g. (7. 5 moles) of dimethylchlorosilane, and 10 ml. of an 0. 1 molar solution in chloroplatinic acid in isopropanol was heated at reflux with stirring. After 3. 5 hours, another 100 g. (1. 06 moles) of the silane, added. After another 3. 5 hours of refluxing, another 100 g. (1. 06 moles) of the silane was added. Stirring under reflux was continued for a total of twenty-four hours. The dark fuming liquid was distilled through a 15 cm Vigreux column to give 914 g. (57. 4%) of the desired product, b. p. 71-95° C (16 mm), n_D^{25}, 1. 4358, d_4^{25} 1. 42.

Preparation of $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$

This was carried out by heating at reflux temperature a mixture of the silane with an excess of water overnight. Then, the organic phase was water washed until acid-free, dried over magnesium sulfate and distilled. The results of several such preparative runs are summarized in Table IV.

Preparation of $[CF_2{=}CFCH_2CH_2Si(CH_3)_2]_2O$

D-798-144 To a stirred refluxing mixture of 58.6 g. (0.9 mole) of zinc dust and 2 g. of zinc chloride in 400 mls of tetrahydrofuran was added 209 g. (0.36 mole) of $[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$ (D-798-142) over two hours. The reaction commenced almost immediately. After stirring an additional two hours at reflux, the mixture was filtered from the unreacted zinc. The filtrate was diluted with water and the organic phase taken up in methylene chloride. The organic layer was washed several times with water to remove zinc salts and dried over magnesium sulfate. Distillation gave an 85.9 g. yield (68.2%) of the desired product, b.p. 60-65 °C (0.5 mm.), n_D^{25} 1.3924, d_4^{25} 1.05. According to VPC analysis, the product was 90.1% pure.

D-798-149 A larger scale reaction was carried out, starting with 727 g. (1.25 moles) of the halogenated disiloxane, giving 319 g. of product (72.8% yield).

C-1129-4 The above reaction also was carried out on a 0.5 mole scale, using isopropanol as the solvent. In this case the yield of product (b.p. 204-210°C/760 mm.) was only 31.6%.

Purification of $[CF_2{=}CFCH_2CH_2Si(CH_3)_2]_2O$

C-1481-3 About 25 g. of the disiloxane of 99.7% purity was isolated by preparative gas chromatographic techniques for polymerization studies.

Molecular weight (Osmometer), calc. for $C_{12}H_{20}F_6OSi_2$: 350.45; found: 352.

f. Preparation of Bis [2-(2'Chloro-2', 3', 3'-trifluorocyclobutenyl) ethyldimethyl] disiloxane

Preparation of 1-Vinyl-2-Chloro-2, 3, 3-Trifluorocyclobutane

C-1129-29, (C-1134-92) A 1 liter Aminco bomb was charged with 10 ml. dipentene (Hercules No. 122) sealed, and evacuated.

The bomb was cooled in dry-ice and 0.3 lb. (ca. 150 g.) butadiene and 0.6 lb. (ca. 250 g.) chlorotrifluoroethylene were charged. The bomb was then placed in a barricaded rocker and slowly heated to 150° C. A maximum pressure of 350 psig was noted and by the time the bomb has reached 150° C., 1 hour later, the pressure was only 50 psig. The bomb was cooled to room temperature and the volatile products vented through a dry-ice cooled trap (2-5 ml. collected). The liquid material was steam distilled, the organic layer separated, and dried over sodium sulfate. Distillation afforded 200.0 g. of product boiling at 113-116° C., which was identical to that of the material supplied by Park[6]. It is not possible to calculate meaningful yield data on this run as the scale used for weighing the charging cylinders was not accurate.

A second run (C-1129-35) employing an identical charge of reactants under the same conditions gave 163 g. of the vinylcyclobutane, b.p. 113-116° C.

Preparation of 2-(2'-Chloro-2', 3', 3'-trifluorocyclobutyl)ethyldimethylchlorosilane

C-1129-36 In a 500 ml. round-bottom flask fitted with a magnetic stirrer, heating mantle and reflux condenser was added 100 g. (0.59 mole) of the vinyl cyclobutane 29 g. (0.31 mole) chlorodimethylsilane, and 1 ml. of 0.1M H_2PtCl_6. After the solution was stirred at room temperature for 30 minutes, the flask was slowly heated. Shortly after heating was begun a vigorous reaction occurred, causing the condenser to be forcibly ejected with loss of some material. Much of the material was recovered by rinsing the inside and outside of the flask with methylene chloride. Distillation of the methylene chloride solution afforded a fraction boiling at 110-120° C at atmospheric pressure. This was subsequently redistilled under vacuum to produce 50.0 g. of product.boiling at 51° C (5 mm) in 61% yield from chlorodimethylsilane. The vinyl cyclobutane was used in excess as a planned later addition of more chlorodimethylsilane was not possible.

g. Preparation of Tetrafluoroethylene

The following was a typical preparation of tetrafluoroethylene from tetrafluoroethylene dibromide:

C-1129-56 To a stirred, heated mixture of 140 g, zinc in 400 ml. tetrahydrofuran in a 3-necked Morton flask equipped with a pressure-equalizing addition funnel and condenser with gas outlet, was added approximately 1 ml. tetrafluoroethylene dibromide. After about 45 minutes addition was resumed and 520 g. (2.00 moles) tetrafluoroethylene dibromide was added over a period of 3 hours. The tetrafluoroethylene generated was collected in a liquid nitrogen-cooled trap to which approximately 1 ml. d-liminone was added. The tetrafluoroethylene was then transferred in a vacuum system to a 500 ml. Hoke stainless steel cylinder containing approximately 3 ml. d-limonene. The yield was virtually quantitative.

A total of ca. 1 kg. tetrafluoroethylene was prepared by this procedure.

2. Synthesis of Phosphorous and Sulfuryl Isocyanates.

a. Preparation of Phosphorus Triisocyanate

C-1491-23 To a suspension of 115 g. (0.77 mole) of silver cyanate in 150 ml. of benzene was added 45 g. (0.33 mole) of phosphorus trichloride over 0.75 hours. The temperature rose to 60° C. The mixture was then stirred at reflux for 0.5 hours, cooled, and filtered from silver salts. The filtrate was concentrated under reduced pressure and then distilled, without a column, collecting 12 g. of colorless liquid, n_D^{25} 1.5322 b.p. 77-80° C (20 mm.). (Lit[24] b.p. 169° C, n_D^{26} 1.525.) After standing in the refrigerator for a week, the product polymerized to a white solid, m.p. 72-79° C.

b. Attempted preparation of Sulfuryl Isocyanate

C-1491-30 To a stirred suspension of 60 g. (0.4 mole) of silver cyanate in 100 ml. of anhydrous acetonitrile was added 17 g. (0.2 mole) of sulfuryl chloride over 1.5 hours. The temperature rose to 35° C. The mixture was refluxed for 1 hour, cooled and filtered from silver salts. The filtrate was concentrated under reduced pressure and an attempt was made to distill the residue up to 90° C (18 mm.) (bath temperature) without success. A 24 g. solid residue remained which proved to be cyanuric acid by its infrared spectrum.

c. Preparation of Butylphosphonic Dichloride

C-1491-26 To a stirred suspension of 133.4 g. (1.0 mole) of anhydrous aluminum chloride in 137.5 g. (1.0 mole) of phosphorus trichloride was added 139.0 g. of 1-chlorobutane. The aluminum chloride soon dissolved. Later the clear solution became very viscous and stirring was no longer possible. The mixture solidified, and after cutting into lumps, the remainder of the chlorobutane was added. The total addition time was 1.5 hours. After standing 1.0 hour the lumps were crushed, and 150 ml. of dichloromethane added. Practically all of the mixture dissolved. After cooling the mixture in ice, a solution of 50 ml. of concentrated hydrochloric acid in 100 ml. of water was added keeping the temperature at 5° C. A thick white precipitate formed. The mixture was filtered and the filter cake washed with dichloromethane. The combined filtrates were dried and distilled, collecting 66.5 g. (37.8%) of butylphosphonic dichloride, b.p. 55-63° C (0.4 mm), n_D^{25} 1.4680 (Lit.[26] b.p. 89-90° C (14 mm) and n_D^{20} 1.4701 for the 2-butyl derivative)

d. Preparation of Butylphosphonic Diisocyanate

C-1491-21 A mixture of 44 g. (0.25 mole) of butylphosphonic dichloride, 90 g. (0.6 mole) of silver cyanate, and 750 ml. of benzene was stirred at reflux overnight protected from light. After filtering from silver salts, the filtrate was concentrated under reduced pressure and the product distilled through a 17 cm Vigreux column, collecting 14.8 g. (31.3%) of colorless butylphosphonic diisocyanate, b.p. 71-73° C (0.4 mm), n_D^{25} 1.4631. The infrared spectrum shows the presence of the expected bands.

e. Preparation of Phenylphosphonic Diisocyanate

C-1491-33 Phenylphosphonic dichloride 64.5 g. (0.33 mole) (Eastman Kodak) was added to a suspension of 105 g. (0.7 mole) of silver cyanate in 500 ml. of anhydrous acetonitrile over two hours at 28° C. The mixture was stirred at reflux for 1.5 hours, cooled, and filtered from silver salts. The filtrate was distilled without a column to give 28.9 g. (42.1%) of colorless liquid, b.p. 118-120° C (0.5 mm.), n_D^{25} 1.5454 (Lit.[27] b.p. 113-114° (0.75 mm).

f. Preparation of Ethylphosphonic dichloride

C-1491-24 A solution of 419 g. (2.52 moles) of diethyl ethylphosphonate in 450 ml. of concentrated hydrochloric acid was stirred at reflux overnight. Then 50 ml. of liquid was distilled off and another 100 ml. of concentrated hydrochloric acid added. Stirring at reflux was continued for a total of 63 hours. To the somewhat cooled solution was added 300 ml. of benzene and 150 ml.

of toluene and the mixture refluxed overnight with a Dean-Stark trap to remove water. When no more water was collected in the trap, the contents of the flask (two layers) were concentrated under reduced pressure to remove the solvent. The viscous colorless liquid (260 g.) left in the flask was heated to 150° C and 455 g. (2.2 moles) of phosphorus pentachloride added over two hours. Large volumes of hydrogen chloride were evolved. A refluxing liquid (perhaps phosphorus oxychloride) reduced the temperature of the liquid in the flask to 97° C at the end of the addition. The contents of the flask consisted of a colorless liquid floating on a yellow viscous mass. The contents were distilled collecting 43.0 g. of ethylphosphonyl dichloride, b.p. 71-75° C (19 mm), n_D^{25} 1.4626 (Lit.[32] b.p. 51-52° C (6 mm) and n_D^{20} 1.4659). The infrared spectrum indicated that the compound was pure.

Not enough time remained to convert this compound to the diisocyanate.

V. BIBLIOGRAPHY

[1] E. I. DuPont deNemours Company, (a) Fr. Pat. 1,362,548 (1963). (b) Fr. Pat. 1,359,426 (1963).

[2] England, D. C., U. S. Patent 3,133,046 (1964).

[3] Crawford, G. H., Rice, D. E., and Landrum, B. F., J. Polymer Sci., 1(Pt. A), 565 (1963).

[4] Knunyants, I. L. Li Chih-yüan, and Shokina, V. V., Russian Chem. Revs, 32, 461 (1963).

[5] Larson, E. R., Abstracts of Papers, 18K, 148th Meeting, ACS, September, 1964.

[6] Roberts, J. D., and Sharts, C. M., Org. Reactions 12, 1 (1962)

[7] Park, J. D. and Lacher, J. R., WADC Tech. Rept. 56-590, Pt. 1 21-2 (1957); U. S. Army Contr. DA-19-129-QM-1926, 9th Quart. Rept., (1964).

[8] Fordie, E., in Müller, E., Methoden der organischen Chemie (Houben-Weyl), 4th Ed., Vol. V/3, Georg Thieme Verlag, Stuttgart, 437-9 (1962).

[9] Fearn, J. E., and Wall, L. A., SPE (Soc. Plastics Engrs.) Trans., 331 (1963); Straus, S. and Wall, L. A., ibid., 56 (1964).

[10] Park, J. D. and Lacher, J. R. loc. cit. 18-20 (1957).

[11] Tarrant, P. and Lovelace, A. M., J. Am. Chem. Soc. 76, 3466 (1954).

[12] Bloomquist, A. T. and Longone, D. T., J. Am. Chem. Soc., 79 4981 (1957).

[13] Walling, C., and Huyser, E. S., Org. Reactions 13, 91 (1963).

[14] Tarrant, P., and Stump, Jr., E. C., J. Org. Chem. 29, 1198 (1964).

[15] Tarrant, P., Lovelace, A. M., and Lilyquist, M. R., J. Am. Chem. Soc. 77, 2783 (1955).

16 Muramatsu, H. and Tarrant, P., J. Org. Chem., 29, 1796 (1964).

17 Tarrant, P., Sayers, D., Heyes, J., Oliver, W., and Wright, A. C., U. S. Army Contr. DA-19-129-AMC-79(N), Semiann. Rept. 1, 4 (1963).

18 Brace, N. O., U. S. Patent 3,016,407 (1962).

19 Knunyants, I. L., Khrlakyan, S. Ts., Zeifman, Yu., V., and Shokina, V. V., Izvest. Akad. Nauk SSSR, 384 (1964).

20 Twelves, R. R., U. S. Patent 3,076,041 (1963).

21 Petrov, A. D., Mironov, B. F., Ponomarenko, V. A., Chernyshev, E. A., translated by C. N. Turton and T. I. Turton, Synthesis of Organosilicon Monomers, Consultants Bureau, New York, 22ff, 372 (1964).

22 Knunyants, I. L., Ch'ing-yun, Ch'en, and Gambaryan, N. P., Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 647 (1960).

23 Knunyants, I. L., Ch'ing-yun, Ch'en, and Gambaryan, N. P., Zhur. Vsesoyuz Khim. Obschchestva im D. I. Mendeleeva, 5, 112 (1960).

24 Colton, E., and St. Cyr, L., J. Inorg. and Nucl. Chem., 7, 424 (1958).

25 Kosolapoff, G., J. Chem. Soc., 3222 (1954).

26 Geiseler, G., Asinger, F., and Fedtke, M., Chem. Ber., 93, 765 (1960).

27 Popoff, I. C. and King, J. P., Polymer Letters, 1, 247 (1963).

28 Haven, A., J. Am. Chem. Soc., 78, 842 (1956).

29 Graf, R., Chem. Ber., 89, 1071 (1956).

30 Appel, R., and Gerber, H., Chem. Ber., 91, 1200 (1958).

31 Barnhart, W. S., et.al., J. Chem. Eng. Data, 2, 80 (1957).

32 Gerding, H. and Maarson, J., Rec. Trav. Chim., 76, 481 (1957).

TABLE I

MODIFICATION OF VINYLIDENE FLUORIDE/HEXAFLUOROPROPYLENE EMULSION POLYMERIZATION SYSTEM

Exp. No.	Mole % Charge[e]		Na_2HPO_4	p	Temp.	Conv.	Product			
	$CF_3CF=CF_2$	Termonomer	(phr)	(psig)	(°C)	(%)	%F	%Si	%Cl	Description
D871-136[a]	30	-	4	315	35	0	-	-	-	-
D871-143	30	-	4	450	50	17	63.6			Rubber
D871-145	30	-	4	600	70	45	64.7	-	-	Rubber
C1529-19	30		8	560	50	22.5	-	-	-	Rubber
C1529-22	30	-	8	700	70	42.5	-	-	-	Rubber
D871-123[b]	27	3 $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$	4	20	35	1.2	61	-	-	Yellow Powder
D871-148[b]	25	5 $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$	4	630	70	11	66.7[d]	[illegible]	[illegible]	Rubber
C1529-23[c]	25	5 $[CF_2=CFCH_2CH_2SI(CH_3)_2]_2O$	8	500	50	3.5	-	-		Leathery Solid
D871-128[b]	27	3  CF_2CFCl $CH_2CHCH=CH_2$	4	25	35	4	58	-	0.25	White Powder
D871-149[b]	25	5  CF_2CFCl $CH_2CHCH=CH_2$	4	610	70	10	32	-	12.4	Yellow Powder

Polymerization Recipe

Ingredient	Parts by Weight
Monomers	100
Water	200-400
Sodium Perfluorooctanoate	5
Disodium Hydrogen Phosphate	Variable
Potassium Persulfate	4

Notes:

a. Polymerization Time 7 hrs.

b. Termonomer charged to Aminco bomb with aqueous ingredients.

c. Termonomer charged to 75ml. cylinder with $CF_2=CH_2$ and $CF_3CF=CF_2$.

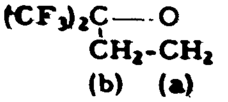
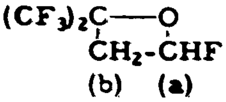
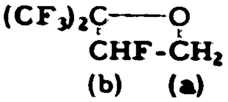
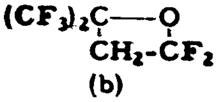
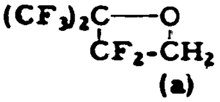
d. Variable: 1.2; 0.14; 0.40 % Si

e. 70 mole % $CH_2=CF_2$ employed throughout.

JAG:ls
11/1/64

TABLE II

PROTON NMR ASSIGNMENTS

 $\begin{array}{l}(CF_3)_2C\text{---}O\\ \quad CH_2\text{-}CH_2\\ \quad (b)\quad (a)\end{array}$	(a)	triplet τ5.31 (J= 8.0 c/s)
	(b)	triplet τ7.06 (J= 8.0 c/s)
 $\begin{array}{l}(CF_3)_2C\text{---}O\\ \quad CH_2\text{-}CHF\\ \quad (b)\quad (a)\end{array}$	(a)	sextuplet τ3.96 (J_{AF} 70 c/s; J_{AB} 3.9 c/s)
	(b)	multiplet τ6.91
 $\begin{array}{l}(CF_3)_2C\text{---}O\\ \quad CHF\text{-}CH_2\\ \quad (b)\quad (a)\end{array}$	(a)	multiplet τ5.11
	(b)	sextuplet τ4.37 (J_{AF} 55 c/s; J_{AB} 6.0 c/s)
 $\begin{array}{l}(CF_3)_2C\text{---}O\\ \quad CH_2\text{-}CF_2\\ \quad (b)\end{array}$	(b)	triplet τ6.59 (J= 7.0 c/s)
 $\begin{array}{l}(CF_3)_2C\text{---}O\\ \quad CF_2\text{-}CH_2\\ \qquad\quad (a)\end{array}$	(a)	triplet τ5.00 (J= 12.2 c/s)

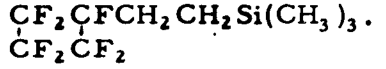
EWC:ls
10/30/64

TABLE III

THERMAL CYCLOADDITION REACTIONS OF TETRAFLUOROETHYLENE WITH FLUORO-OLEFINIC SILANES

Exp. No.	Co-reactants (1:1 mole ratio)	Temp. °C	Time hrs.	Product Composition	Comments
D871-64-B	10.0g. $CF_2=CFCH_2CH_2Si(CH_3)_3$ 5.5g. $CF_2=CF_2$ 0.03g. $(C_4H_9)_3N$	150	17	4.4g. b.p. 116-120°C 0.4g. b.p. 130-149°C	Both fractions almost identical[a]
D871-66	8.86g. $CF_2=CFCH_2CH_2Si(CH_3)_3$ 4.8g. $CF_2=CF_2$ 0.05g. $(C_4H_9)_3N$	200	17	4.93g. b.p. 118-128°C 1.6g. b.p. 130-138°C	Second fraction exhibited less unsaturation than starting material[a]
D871-68	6.78g. $CF_2=CFCH_2CH_2Si(CH_3)_3$[c] 3.7g. $CF_2=CF_2$ 0.04g. $(C_4H_9)_3N$	150	17	4.74g. b.p. 124-136°C	Component I:25%; II[e]:81%[b]
D871-70	4.0g. $CF_2=CFCH_2CH_2Si(CH_3)_3$[d] 2.2g. $CF_2=CF_2$	200	17	3.22 g. b.p. 129-135°C - residue	Component I:19%; II[e]:81%[b] Component II[e]:100%[b]
D871-69	7.5g. $CF=CFSi(CH_3)_3$ 4.8g. $CF_2=CF_2$ 0.04g. Dipentene No. 122[f]	200	17	5.3g. b.p. 70-86°C 0.4g. b.p. 94-98°C	Component I:87%; II[g]:7%[b] Component I:5%; II[g]:87%[b]

a. Determined by infrared spectral analysis after simple distillation
b. Determined by vapor phase chromatography after simple distillation
c. Recovered monomer from D871-66
d. Recovered monomer from D871-68
e. Identified as:



$\underset{CF_2CF_2}{CF_2CFCH_2CH_2Si(CH_3)_3}$. No double bond vibration adsorption in IR spectrum. Anal.: Calc. for $C_9H_{13}F_7Si$: 38.30%C, 4.61%H; found 38.90%C, 4.84%H.

f. Complex mixture of terpenes.
g. Identity undetermined.

JAG:ls
11/1/64

TABLE IV

COPOLYMERIZATION OF $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$ WITH $(CF_2=CFCF_2)_2CFCl$

Exp. No.	Charge $[CF_2=CFCH_2CH_2Si(CH_3)_2]_2O$	Charge $(CF_2=CFCF_2)_2CFCl$	Temp. °C	Time	Comments
C1529-3	5.00g. (0.014 mole)	4.68g. (0.014 mole)	150	52 days	Mixture of low mol. wt. oils (~20% conversion)
D871-140		20g. (0.06 mole)	150	20 hrs.	No reaction
D871-144		18g. (0.054 mole)	200	20 hrs.	~2% conversion of a brittle, amber solid
C1529-5		6.09g. (0.018 mole)	150	52 days	~5% conversion to brown oil
D871-141[1]	14.0g. (0.04 mole)	-	150	20 hrs.	Violent decomposition
C1529-11	4.97g. (0.014 mole)	-	150	52 days	Mixture of low mol. wt. oils (~60% conversion)

[1] Stainless steel reactor employed

JAG:las
11/1/64

TABLE V

CONDENSATION OF PHOSPHOROUS-CONTAINING DIISOCYANATES WITH 2, 2, 3, 3, 4, 4-HEXAFLUOROPENTANEDIOL-1, 5

Exp. No.	C_4H_9-P(O)(NCO)$_2$ charge		HOCH$_2$(CF$_2$)$_3$CH$_2$OH charge		Solvent	Temp. °C	Time hrs.	Product
	grams	millimoles	grams	millimoles				
C1529-33	1.65	8.7	1.82	8.7	acetone	65	2.0	viscous oil
C1529-36	0.90	4.7	1.01	4.7	acetone[2]	65	5.5	viscous oil
C1529-39	1.29	6.8	1.45	6.8	acetone[2]	65	21.0	viscous oil
C1529-40	0.95	5.0	1.07	5.0	none[3]	170-175	1.5	glassy solid
C1529-43	0.83	4.41[1]	1.79	8.49	none[3]	170-180	2.0	horny solid

[1] Plus 0.85g. (4.08 millimoles) of C_6H_5-P(O)(NCO)$_2$

[2] Dry, 0.05% water

[3] Melt

JAG:ls
11/1/64

TABLE VI

COPOLYMERIZATION OF 4-CHLOROPERFLUOROHEPTADIENE-1,6 WITH 2,2,3,3,4,4-HEXAFLUOROPENTANEDIOL-1,5

						Polymer[1]		
Exp. No.	Amt. Diol (g)	Amt. Diene (g.)	KOH (g.)	Solvent Amt. (ml.)	Oil Amt.[2] (g.)	Amt. (g.)	T_g	"T_m"
C1129-64	5.5[3]	8.0[3]	1.5	10 acetone	-	~3	-58[4]	+ 19°(+ 15)[5]
C1129-65	11	16	3.0	50 acetone	11.0	none	-	-
C1129-66	5.5	8.0	1.5	10 acetone	5.7	8.1[6]	-	-
C1129-67	5.5	8.2	1.5	10 acetone	5.5	2.1	-48°[7]	-23°(-30°)
C1129-68	5.5	8.0	1.7	10 acetone	8	3.5	-47°	-24-(-30°)
C1129-69	5.5	8.0	1.5	10 DMF	black tar		-	-
C1129-70	5.5	8.0	1.5	25 H_2O	no reaction observed			-
C1129-71	11	16	3.0	20 acetone	13.4	5.7[8]	-57°	-22°(-30°)
C1129-72[9]	11	16	3.0	20 acetone	14.5	9.3	-	-
C1129-73	11	16	3.0	10 hexane 10 benzene	-	none	-	-
C1481-17[10]	5.5	8.0	1.5	10 acetone	-	12	-	-
C1481-19	5.5	8.0	2 ($NaHCO_3$)	10 acetone	-	none	-	-
C1481-20	5.5	8.0	1.5	5 hexane 5 benzene	-	10.7	-54	+ 14°(2°)

[1] Constants determined with Differential Scanning Calorimeter

[2] There are mechanical losses.

[3] 25 mmole.

[4] Initial run indicated -44°, repeated determinations agree with -58° value.

[5] Figure in parenthesis is smaller endotherm. See discussion.

[6] Lower molecular weight products not extracted from polymer.

[7] Not well defined.

[8] Sample forwarded to Army Natick Laboratories

[9] Reaction conducted at reflux (~60°). Complete in 20 min.

[10] Polymerization time 24 days.

EWC:ls
11/2/64

TABLE VII

DEHALOGENATION OF 4, 6, 7-TRICHLOROPERFLUOROHEPTENE-1 SOLVENT PARAMETERS

Solvent	Yield of 4-Chloroperfluoroheptadiene-1, 6
Dibutoxytetraethylene glycol [1]	43%
Dibutoxytetraethylene glycol [2]	20%
Dibutoxytetraethylene glycol [3]	32%
Dimethoxytetraethylene glycol [4]	24%
Dimethoxytetraethylene glycol/acetone [5]	n/a
Dimethoxytetraethylene glycol [6]	36. 1%
Ethoxydiethylene glycol [6]	9%
Ethoxydiethylene glycol [6]	16%
Tetrahydrofuran [6]	36. 5%
Isopropanol [6]	40. 0%

[1] Park and Lacher, WADC Tech. Rept. 56-590, Pt. 1, p. 22(1957).

[2] Park and Lacher, 9th Quart. Rept. U. S. Army Contr. DA-19-129-QM-1926 (1964).

[3] Park and Lacher, 10th Quart. Rept. U. S. Army Contr. DA-19-129-QM-1926, 7 (1964).

[4] Fearn and Wall SPE Transactions 331 (1963).

[5] Straus and Wall SPE Transactions 56 (1964).

[6] FMC Corp., see Table VIII.

EWC:ls
11/2/64

TABLE VIII

PREPARATION OF 4-CHLOROPERFLUOROHEPTADIENE-1, 6 BY DECHLORINATION OF 4, 6, 7-TRICHLOROPERFLUOROHEPTENE-1

Exp. No.	Source of Heptene	Solvent	Reaction Time [1] (hrs.)	Heptene Charged (g.)	Product b. p. °C	Product n_D^{25}	Product Purity[2]	Yield (g.)	Yield[3] (%)	Heptene Recovered (%)
C1129-5	-	Ethoxy-diethylene glycol	~2.0	159	105-111 (764mm)			13.2	9.0[4]	
C1129-10	-	Ethoxy-diethylene glycol	~2.8	315	108-110 (760mm)			40.6	16.0[4]	
D798-140	-	Tetrahydro-furan (THF)	4.0	25.0	109-122 (761mm)	1.3361	84.3%	8.0	36.4	43.8
D798-141	-	Isopropanol	6.5	25.0	97-112 (761mm)	1.3311	67.5%	11.3	27.6	43.8
D798-146	-	Dimethoxy-tetraethylene glycol	4.0	25.0	101-115 (767mm)	1.3314	64.3%	7.9	36.1	57.3
D798-148	-	Isopropanol	4.0	36.6	102-125 (745mm)	1.3316	82.0%	12.7	40.0	13.6
C1491-3	D798-137B 92.3%pure	THF	5.33	399.5	(1)110-111 (2)111-112	1.3311	93.8% 92.5%	78.8	34.1	33.8
C1491-4	Recovered from above	THF	5.0	135	109-111	1.3305	95.8%	16.9	21.2	31.1
C1491-6	D798-152B 98.7%pure	THF	4.5	599.2	108-111	1.3305	92.5%	112.6	38.7	45.4
C1491-7	Recovered from above	Isopropanol	5.5	276	108-111	1.3328	85.6%	42.4[4]		5.3

[1] Includes addition time.

[2] Determined by VPC.

[3] Based on heptene actually converted, heptadiene yield corrected for impurities.

[4] An additional quantity of low boilers containing perfluoroheptatriene was obtained.

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12/64

TABLE IX

BENZOYL PEROXIDE INITIATED PREPARATION OF $CF_2BrCH_2CH_2Br$

	CF_2Br_2		$CF_2BrCH_2CH_2Br$	
Reference	Charged	Recovered[a]	Produced	Comments
C1129-24 (C1134-70)	910g.	113g. (12%)[b]	- (-%)[c]	5g. Bz_2O_2 used. Bomb heated to 50 °C No reaction Considerable loss is mechanical (spillages)
C1129-26 (C1134-79)	460g.	118g. (26%)	96.6g. (25%)	10g. Bz_2O_2 used
C1129-27 (C1134-84)	577g.	14.8g. (2.6%)	138g. (22%)	15g. Bz_2O_2 used
C1129-28 (C1134-88)	459g.	- (-%)	9.3g. (0.6%)	15g. Bz_2O_2 used Bomb assumed to have leaked.
C1129-31 (C1134-94)	773g.	188g. (24%)	125g. (19%)	15g. Bz_2O_2 used. Some telomers also formed
C1129-32 (C1134-101)	550g.	203g. (37%)	135g. (35%)	15g. Bz_2O_2 used. Some telomers also formed.

a. Recovery of CF_2Br_2 was accompanied by handling losses; these amounts could probably be increased.

b. Amount of CF_2Br_2 recovered, expressed as percent.

c. Yield of $CF_2BrCH_2CH_2Br$ from CF_2Br_2 consumed, expressed as percent.

EWC:ls
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FIGURE 1

Infrared Spectrum of cis-Perfluoroheptatriene-1, 3, 6

(neat, 0.015 mm.)

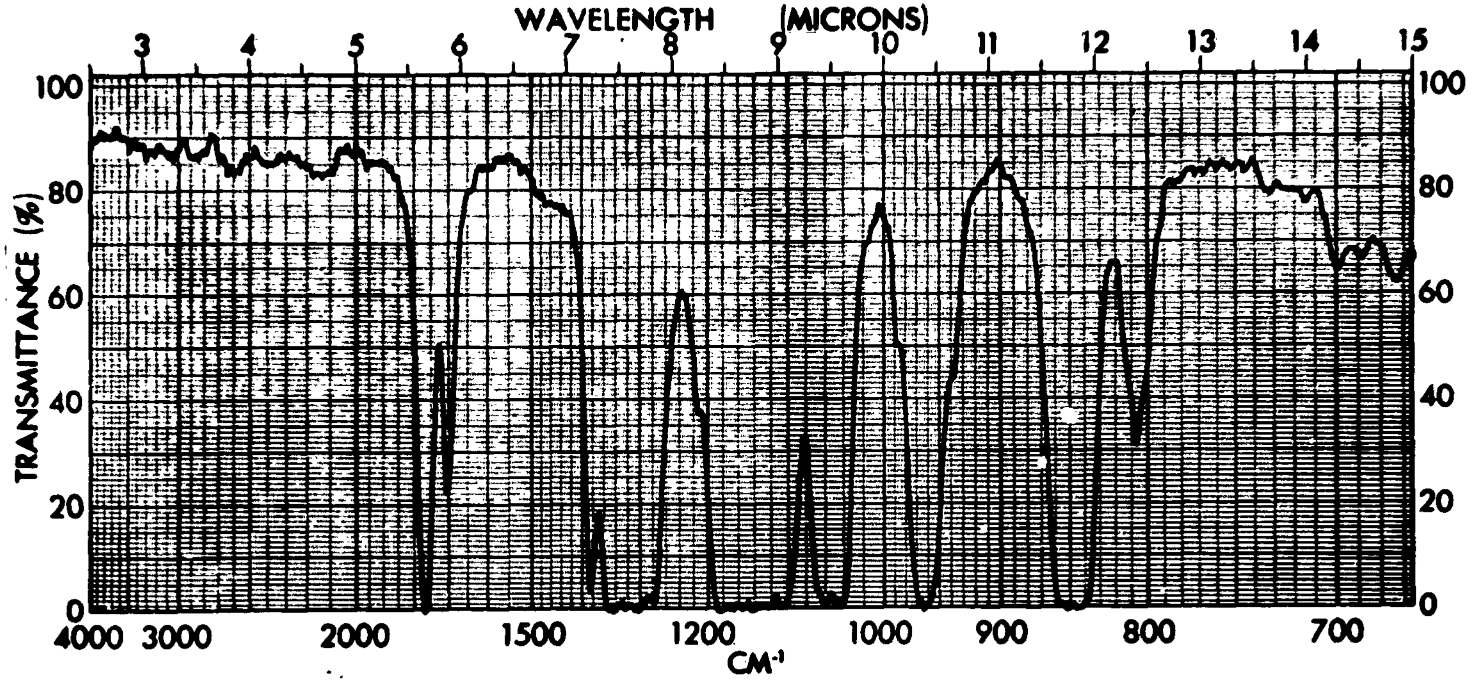


FIGURE 2

Infrared Spectrum of trans-Perfluoroheptatriene-1, 3, 6

(neat, 0.015 mm.)

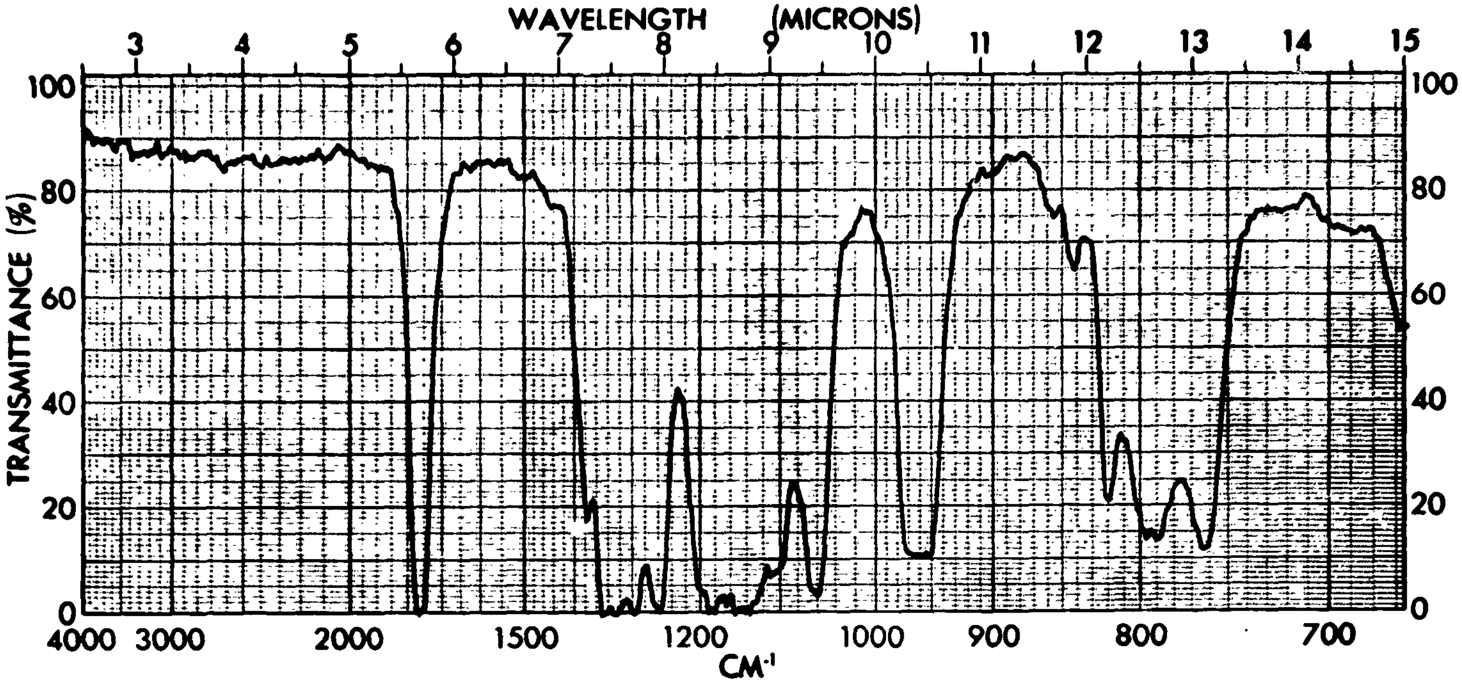


FIGURE 3

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)-2, 2-difluoroöxetane

(neat, 0.015 mm.)

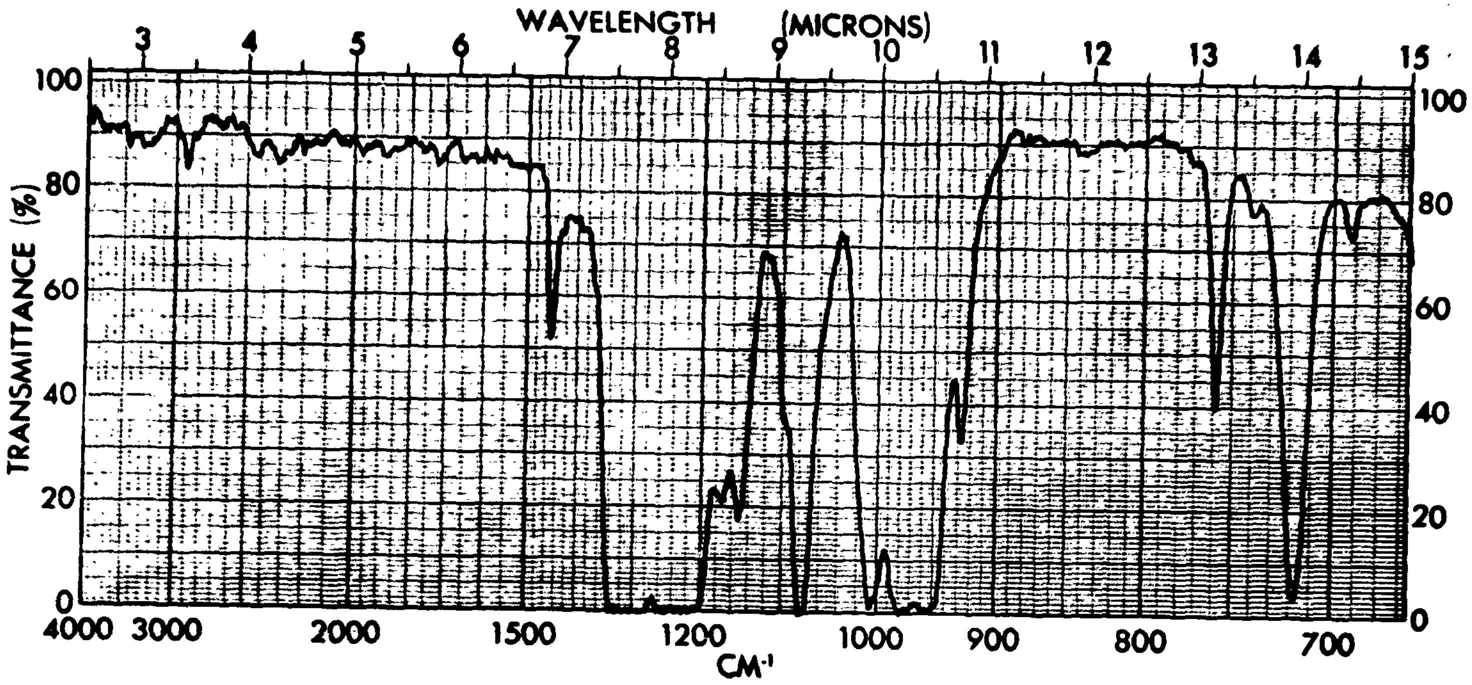


FIGURE 4

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)-3, 3-difluoroöxetane

(neat, 0.015 mm.)

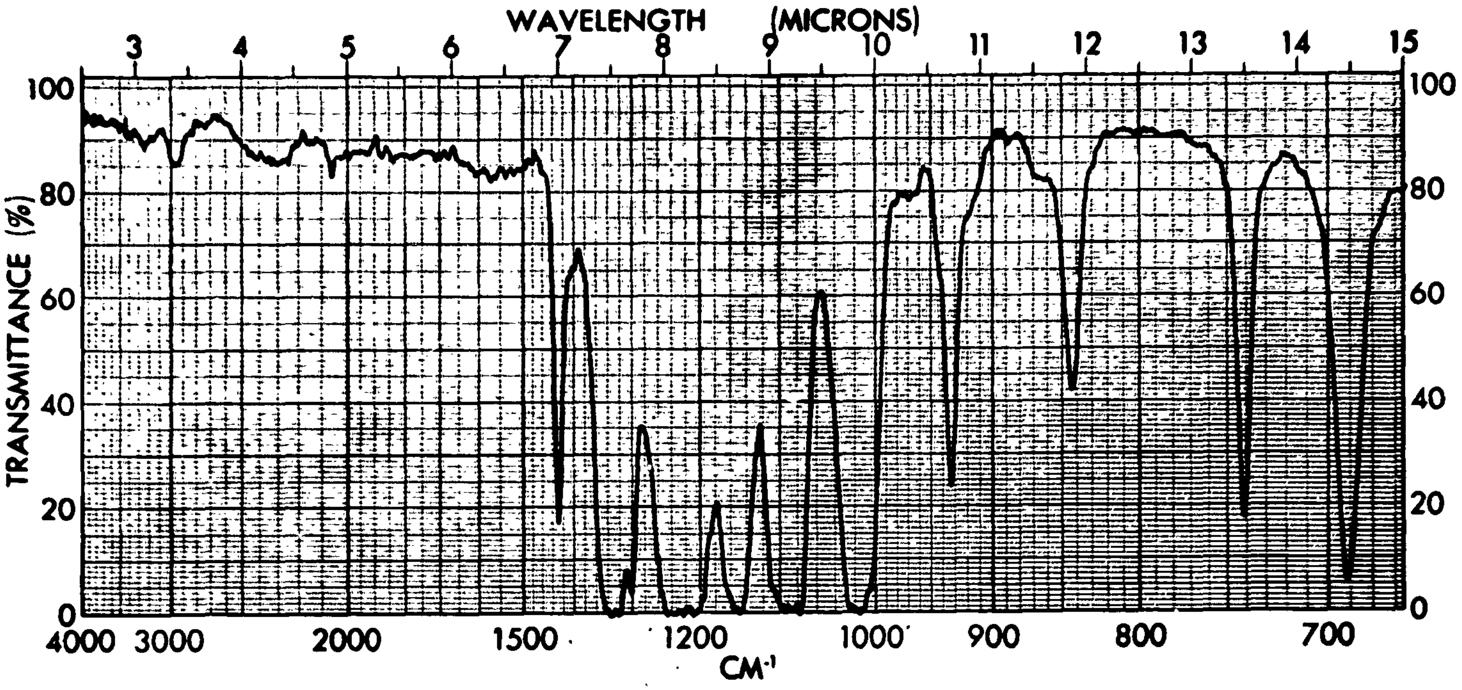


FIGURE 5

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)-2-fluoroöxetane

(neat, 0.015 mm.)

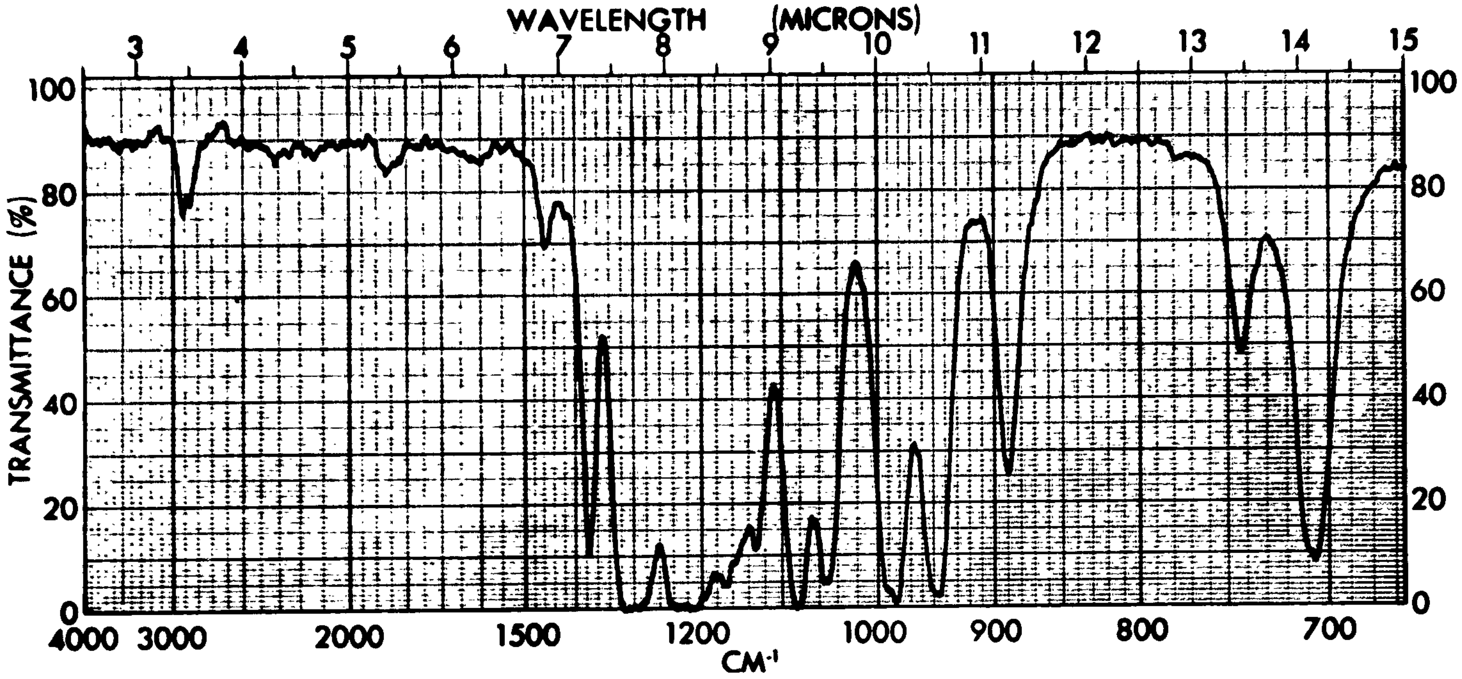


FIGURE 6

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)-3-fluorooxetane

(neat, 0.015 mm.)

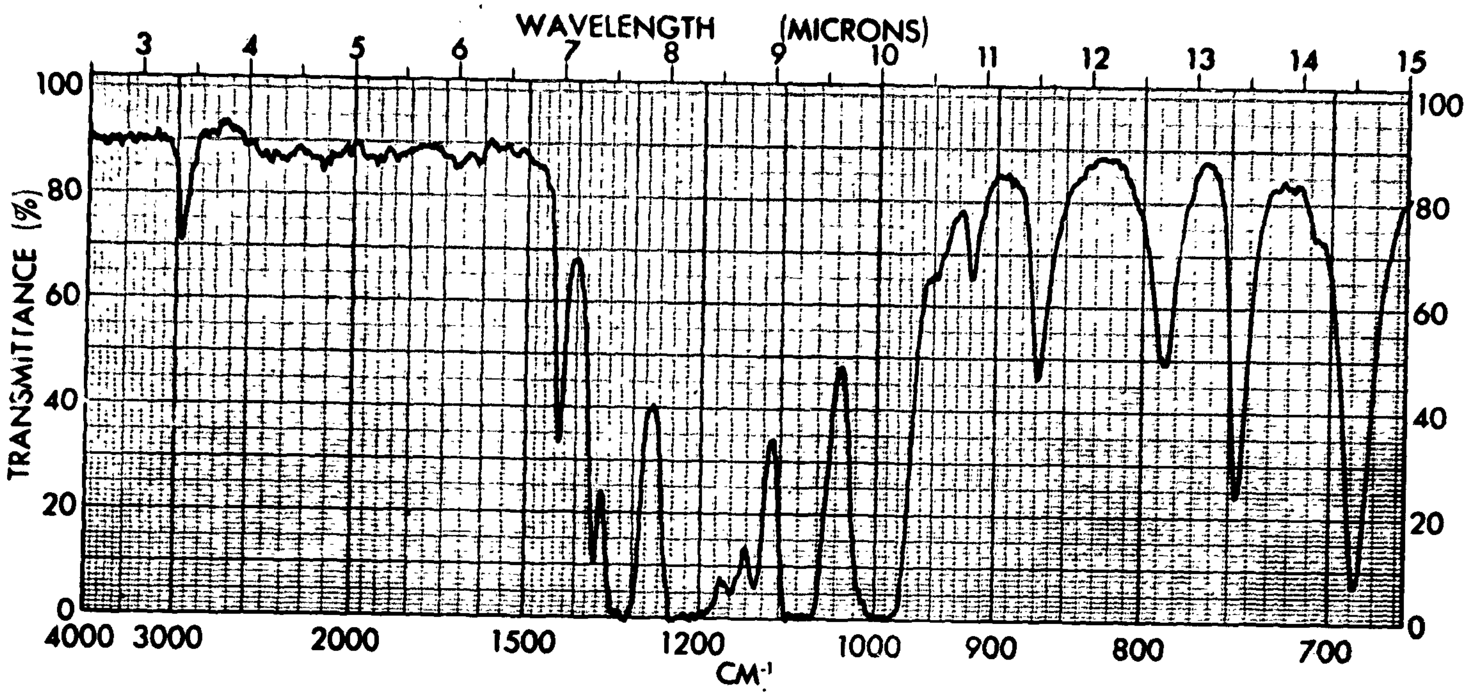


FIGURE 7

Infrared Spectrum of 1, 1-bis(Trifluoromethyl)oxetane

(neat, 0.015 mm.)

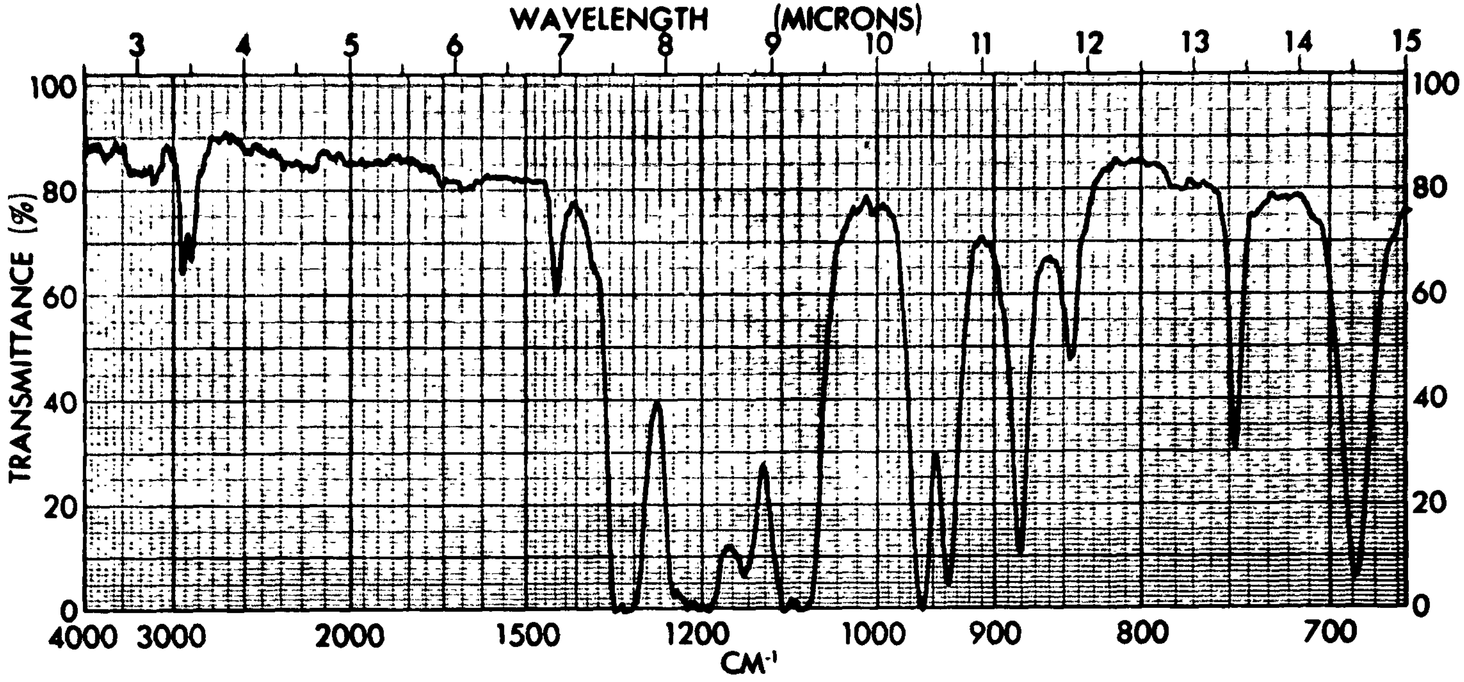
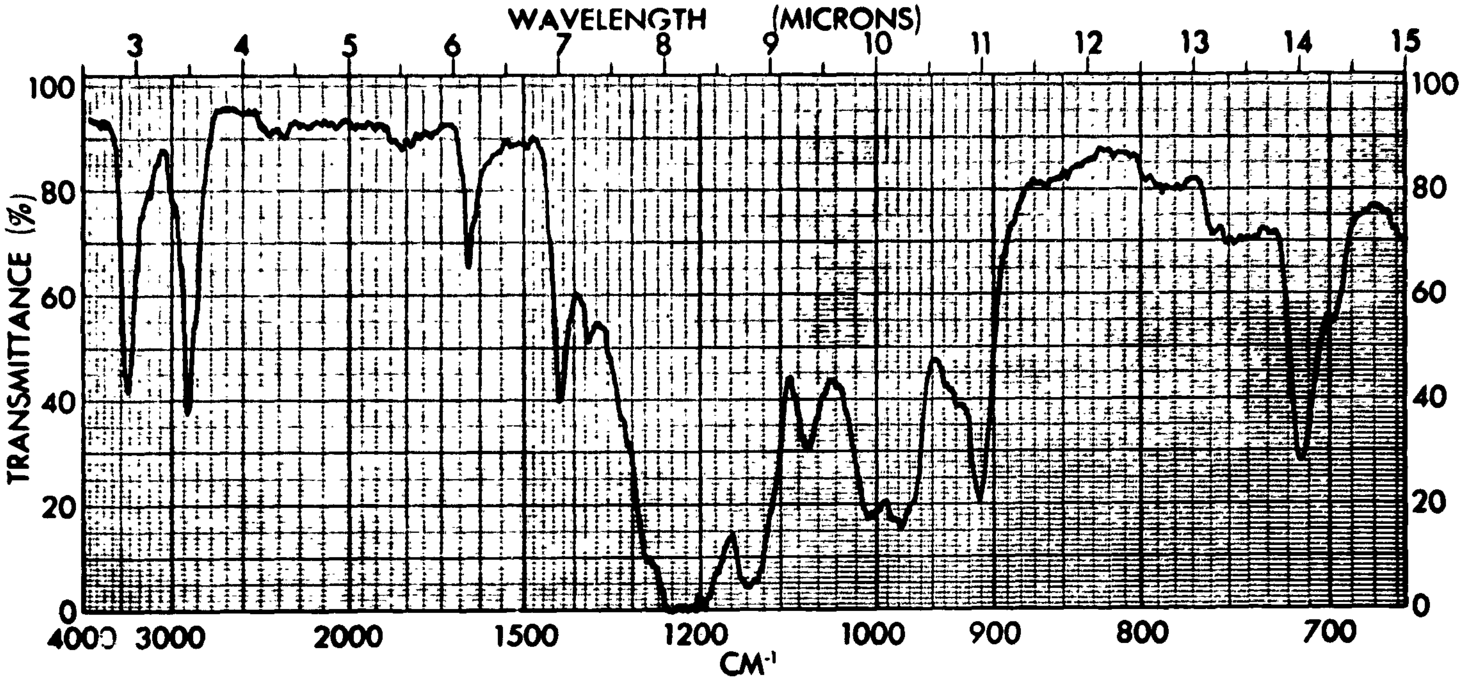


FIGURE 8

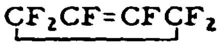
Infrared Spectrum of 1, 1-bis(Trifluoromethyl)nonadiene-3, 7-ol-1

(neat, 0.015 mm.)

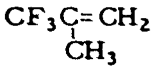
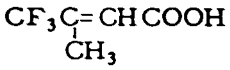


APPENDIX I

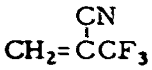
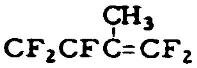
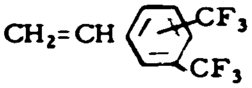
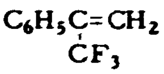
The following is the Monomer List developed during the period 1950-1962 under U. S. Army Quartermaster Corps' sponsorship of contracts with the M. W. Kellogg Company and 3-M.

Monomer No.	Formula
1	$CF_2=CFCl$
2	$CF_2=CH_2$
3	$CH_2=CHCH=CH_2$
4	$CF_2=CFCF=CF_2$
5	$CH_2=CH(CH_3)CH=CH_2$
6	$CH_2=C(CH_3)_2$
7	 $CF_2CF=CFCF_2$
8	$CH_2=CHCl$
9	$CF_2=CCl_2$
10	$CH_2=CHCH_3$
11	 $—CH=CH_2$
12	$CH_2=CCl_2$
13	$CH_2=CClCH=CH_2$
14	$CF_2=CFCF_3$
15	$CF_2=CFCN$
16	$CH_2=CHCN$
17	$CH_2=CHCO_2C_4H_9$ (n)
17A	$CH_2=CHCO_2CH_3$
18	$CF_2=CHCl$
19	$CF_3CCl=CClCF_3$
20	$CF_3C\ \ CCF_3$
21	$CF_2=CFH$
22	$CH_2=CFCl$
23	$CF_3CH=CHCF_3$ (cis)

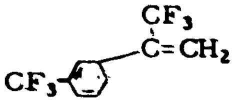
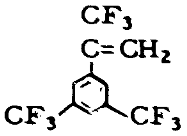
APPENDIX I - Continued

Monomer No.	Formula
24	$CF_2=CF_2$
25	$CF_3CH=CHCF_3$ (trans)
26	$CH_2=CHC_6H_4CH=CH_2$
27	 $CF_3\underset{CH_3}{C}=CH_2$
28	$CH_2=CFCH=CH_2$
29	$(CF_3)_2C=CF_2$
30	$CF_2=CFBr$
31	$CH_2=CH_2$
32	$CF_2=CClCF_3$
33	 $CF_3\underset{CH_3}{C}=CHCOOH$
34	$CH_2=CHCONH_2$
35	$CF_3CH=CH_2$
36	$CH_2=CHBr$
37	$CF_2=CHCH=CH_2$
38	$CCl_2=CClCF_3$
39	$CH_2=CClCF_3$
40	$CH_2=CFH$
41	$CF_2=CHC(CH_3)=CH_2$
42	$CF_2=CHCF_3$
43	$CH_2=CHCH=CHCF_3$
44	$CF_2=C(CH_3)CH=CH_2$
45	$CH_2=CHO_2CCH_3$
45A	$CH_2=CHO_2CCH_2CH_2CH_3$
45B	$CH_2=CHO_2CCH_2Cl$
46	$C_6H_5CH=CHCO_2CH_3$

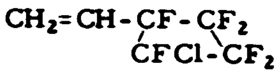
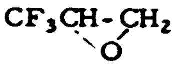
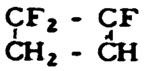
APPENDIX I - Continued

Monomer No.	Formula
47	$CH_2=CH-O-C_2H_5$
48	$CH_2=CH-O-CH_2CH_2Cl$
49	$CH_2=CH-O-CH_2CH(CH_3)_2$
50	$CF_2=C(CH_3)CF=CH_2$
51	$CF_2=CHCF=CH_2$
52	$C_2H_5O_2CCH=CHCO_2C_2H_5$ (trans)
53	$C_2H_5O_2CCH=CHCO_2C_2H_5$ (cis)
54	$CH_2=CH-Si(OC_2H_5)_3$
55	$CF_2=CFC_6H_5$
56	$CF_2=CFCH=CH_2$
57	 $CH_2=\overset{CN}{C}CF_3$
58	$CF_2=CFCH=CF_2$
59	$CH_3(CH_2)_{16}CO_2CH=CH_2$
60	$CF_2Cl(CFClCF_2)_2CF=CF_2$
61	$CF_2ClCF=CFCF_2Cl$
62	 $CF_2CF\overset{CH_3}{C}=CF_2$
63	 3, 4, & 3, 5 isomers
64	 $CH_2=\overset{CF_3}{C}CO_2CH_3$
65	$CF_2=CFCH_2CH=CH_2$
66	$(CN)_2$
67	$CF_3CF=CH_2$
68	$CF_2=CFCH=CFH$
69	 $C_6H_5\underset{CF_3}{C}=CH_2$

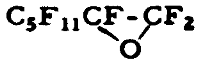
APPENDIX I - Continued

Monomer No.	Formula
70	
71	
72	$CH_2{=}CH{-}O{-}CF_2CF_2H$
73	$Cl(CF_2CFCl)_2CF_2CO_2CH_2CH{=}CH_2$
73A	$Cl(CF_2CFCl)_3CF_2CO_2CH_2CH{=}CH_2$
74	$CH_2{=}C(CF_3)CH{=}CH_2$
75	$CH_2{=}CHCH_2CO_2CF_2(CF_2CFCl)_2CF_2O_2CCH_2CH{=}CH_2$
76	$CF_2{=}CFCF_2CFCl_2$
77	 $CF_2{=}CH\underset{CF_3}{\underset{\mid}{C}}{=}CH_2$
77A	$CF_3CH{=}C(CF_3)CH_3$
78	$CH_2{=}CH{-}O{-}CF_2CHClF$
78A	$CHCl{=}CH{-}O{-}CF_2CHClF$
79	$CF_3CH{=}CClCF_3$
80	$CF_3CF_2CF_2CHO$
81	$C_4F_9{-}N{=}CF_2$
82	$CF_2{=}CFCF_2Cl$
83	
84	
85	$CF_2{=}CFCF_2{-}O{-}CH_2CF_3$
86	$CF_2{=}CClCF{=}CF_2$
87	$CF_2{=}CFCCl{=}CH_2$
88	$CF_2{=}CClCH{=}CF_2$

APPENDIX I - Continued

Monomer No.	Formula
89	$ClCF_2CFClCF_2CO_2CH=CH_2$
90	$CF_2=CFCF_2CFClCF_2Cl$
91	$CF_2=CFCF_2CF_3$
92	$CF_3CH=CHCH=CHCF_3$
93	$CFCl_2CF=CH_2$
94	CF_3CHO
95	 $CF_2=CF\overset{CF_3}{C}=CF_2$
96	 $CF_2=\overset{CF_3}{C}CH=CH_2$
97	$CF_2=CFCF_2CF_2H$
98	$CF_2=CF(CF_2)_4H$
99	$CF_2=CFCF_2CO_2C_2H_5$
100	$CF_2=CFCF_2CF=CF_2$
101	$C_2F_5CH=CH_2$
102	$C_3F_7\,CH=CH_2$
103	$CF_3CH_2CH_2CH=CH_2$
104	$CF_3(CH_2CH_2)_2CH=CH_2$
105	
106	
107	$C_3F_7\,CH_2\text{-}O\text{-}CH=CH_2$
108	$CF_3CF=CFCF_3$
109	
110	$CF_3CH_2\text{-}O\text{-}CH=CH_2$
111	CF_2O

APPENDIX I - Continued

Monomer No.	Formula
112	$CF_3CH_2CH=CH_2$
113	$C_3F_7\,CH_2CH=CH_2$
114	$(CF_3)_2C=CH_2$
115*	$CH_2=CHCF_2-O-CF_3$
116*	$CH_2=CHCF_2-O-C_3F_7$
117*	$CF_2=CHCF-O-CF_3$
118*	$CF_2=CHCF_2-O-C_3F_7$
119*	$CF_2=CFCF_2-O-CF_3$
120*	$CF_2=CFCF_2-O-C_3F_7$
121*	$CH_2=CH-O-CF_2CF_3$
122*	$CF_2=CF-O-CF_3$
123*	$CF_2=CF-O-C_3F_7$
124*	$CF_2=CH-O-CH_2CF_3$
125	$CF_3CF_2CF=CH_2$
126	 $C_5F_{11}\underbrace{CF-CF_2}_{O}$
127	CF_3-NO
128	$CF_2=CFC_6H_4CO_2H$
129	$CFCl=CF-O-CH_3$
130	C_3F_7-NO
131	C_2F_5-NO
132	$C_3F_7-N=CF_2$
133	$C_8F_{17}-NO$

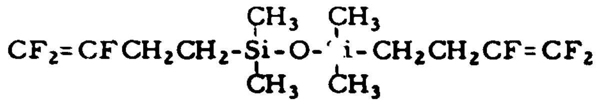
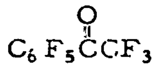
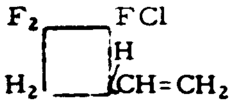
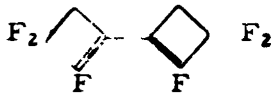
* Monomers 115-124 were requested; however, samples were never received. It is assumed that attempts to prepare these structures were unsuccessful.

APPENDIX I - Continued

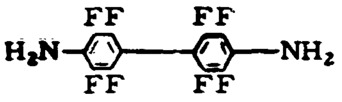
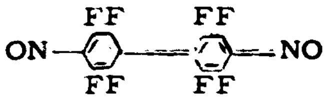
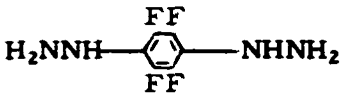
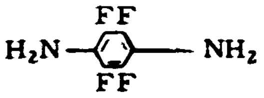
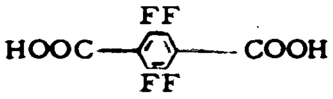
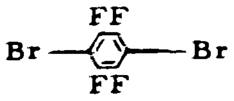
Monomer No.	Formula
134	$CF_2NO_2CFClNO$
135	$CF_2NO_2CCl_2NO$
136	$ON-CF_2CF_2-NO_2$
137	$CF_2ClCFCl-NO$
138	CF_2ClCF_2-NO
139	$CF_3CCl=C(OCH_3)CF_3$
140	$CH_2=C(OCH_2CF_3)CH=CH_2$
141	$C_3F_6(NO)(NO_2)$
142	$CF_2=CFCF_2CO_2H$
143	$CF_3CF_2CF_2COF$
144	Cl_2CS
145	$HCF_2CF_2CF_2CF_2-NO$
146	HCF_2CF_2-NO
147	CH_3CF_2-NO
148P	$(CF_3CFCF_3)_2Hg$
149	CCl_3CCl_2-NO

APPENDIX II

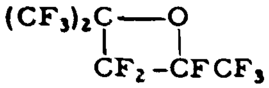
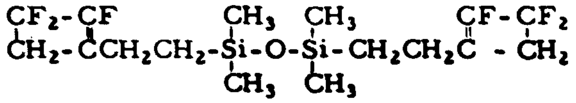
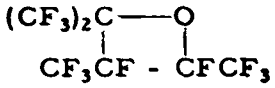
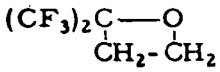
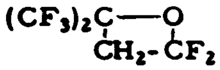
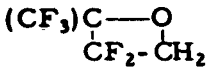
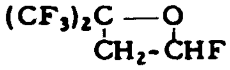
The following is an up to date list of monomer assignments made under the system decided upon by the Army Natick Laboratories and described in the letter to B. F. Landrum from C. B. Griffis, reference AMXRE-CRP, dated 31 January 1964:

Monomer No.	Formula
University of Florida	
200	$CF_2{=}CFCH_2CH_2\text{-}Si(CH_3)_3$
201	$CF_2{=}CF\text{-}Si(CH_3)_3$
202	 $CF_2{=}CFCH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2CH_2CF{=}CF_2$
203	 $C_6F_5\overset{O}{\overset{\|}{C}}CF_3$
204	$EtOSi(CH_3)_2CF{=}CF_2$
205	$CF_2{=}CFCH_2CH_2CF{=}CF_2$
206	$C_6F_5CF{=}CF_2$
207	$CF_2{=}CFCH_2CH{=}CH_2$
University of Colorado	
300	
301	
302	$CF_2{=}CFCF_2CFClCF_2CF{=}CF_2$

APPENDIX II - Continued

Monomer No.	Formula
Peninsular ChemResearch	
400	$F_2C{=}S$
401	$C_6F_5\text{-}NO$
402	$SF_5CH{=}CH_2$
403	$CF_3\text{-}S\text{-}CF{=}CF_2$
404	$(CF_3)_2C{=}S$
405	$CF_3\text{-}N{=}SF_2$
406	$C_6H_5\text{-}NO$
407	$[CF_3CF_2CH_2CH_2\text{-}Si(CH_3)O]_3$
408	$[CF_3CF_2CH_2CH_2\text{-}Si(CH_3)O]_4$
409	$CF_3\text{-}S\text{-}CF(NO)CF_2Cl$
410	
411	
412	
413	
414	
415	

APPENDIX II - Continued

Monomer No.	Formula
FMC Corporation	
500	
501	$CH_2=CHCF_2CF_2CH=CH_2$
502	
503	
504	
505	
506	
507	CF_3-$N=CF_2$
508	HO-$CH_2CF_2CF_2CF_2CH_2$-OH
509	cis-$CF_2=CFCF=CFCF_2CF=CF_2$
510	trans-$CF_2=CFCF=CFCF_2CF=CF_2$
511	$ClOC(CF_2)_3COCl$
512	CF_3COCF_3
513	
514	
515	$P(NCO)_3$
516	$C_4H_9PO(NCO)_2$

APPENDIX II - Continued

Monomer No.	Formula
FMC Corporation (continued)	
517	$C_6H_5PO(NCO)_2$
518	
Thiokol Chemical Corporation	
No assignment received	
U. S. Army Natick Laboratories	
No assignment received	

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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Final Report

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13. ABSTRACT

The synthesis of new fluorinated elastomers servicable at low temperatures is described. Hexafluoroacetone and hydrogen-containing olefins have been found to form both low polymers and hydrogen-containing oxetanes on actinic irradiation. Evidence is presented to show that the intermediate is a biradical. A new elastomer system has been discovered involving the condensation of a polyfluorinated diol with a fluorocarbon diene. This unique fluorinated-polyether has been found to have a very low T_g (-54° C). Evidence has also been found that a polyfluorinated diol will condense with hexafluorobenzene. Polyurethane polymers have been successfully formed by condensation of a polyfluorinated diol with phosphorous-containing diisocyanates. Several new monomers are described. (U)

DD FORM 1 JAN 64 1473

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymerization	8	2				
Condensation reactions	8	2				
Vinyl plastics	1	2				
Fluorinated olefins	1	2				
Isocyanates	1	2				
Elastomers	2	1				
Rubber	4	3				

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