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QUARTERLY REPORT NO. 2

CONTRACT NO. DA 19-129-AMC-152(N)(OI 9116)
WITH
U. S. ARMY NATICK LABORATORIES

Report Period: 1 October 1963 - 31 December 1963

SYNTHESIS AND POLYMERIZATION OF FLUORINATED SULFUR MODIFIED NITROSO RUBBER

BY

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21 January 1964

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FOREWORD

This report was prepared by Peninsular ChemResearch, Inc. under Contract No. DA 19-129-(AMC)-157 (N) (OI 9116) for the U. S. Army Natick Laboratories with Mr. Frank Babers as Project Officer. This is the second Quarterly Report under this contract and covers the period 1 October 1963 through 31 December 1963.

Personnel engaged in this research are Eugene Stump, Project Supervisor, and Calvin Padgett, Research Chemist. Analytical work was performed under the supervision of Van May. Drs. Paul Tarrant and George Butler are acting consultants.

It is estimated that 30% of the work is completed and that 37.9% of the estimated costs have been incurred to date. To the contractor's best knowledge the funds remaining unexpended are sufficient to complete the work called for in the contract.

ABSTRACT

(-- AD-432 900).

Efforts to prepare CF_3SNO and SF_5NO ~~have~~ continued. The new monomer $CF_3SCF{=}CF_2$ ~~has been~~ was prepared and its reactivity with CF_3NO and $CF_2{=}CF_2$ examined. An attempt to homopolymerize $CF_3SCF{=}CF_2$ using cobalt-60 irradiation gave a very low conversion. Ultraviolet irradiation of a mixture of $CF_3SCF{=}CF_2$ and ClNO in the gas phase gives a blue liquid, probably either $CF_3SCFClCF_2NO$ or $CF_3SCF(NO)CF_2Cl$. Attempts to obtain copolymers from both thiocarbonyl fluoride and perfluorothioacetone ~~have~~ were not ~~been~~ successful. The intermediate CF_3SCl ~~has been~~ was prepared by an alternate synthesis involving the gas-phase irradiation of a mixture of CF_3SSCF_3 and chlorine.

TABLE OF CONTENTS

TABLES

FIGURES

I. INTRODUCTION

The research described in this report is part of a continuing program sponsored by the U. S. Army Natick Laboratories and concerned with the development of so-called "nitroso rubber", a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene. A list of references describing prior research was given in the First Quarterly Report.

The primary objective of this contract is to enhance the desirable properties, in particular the low-temperature flexibility, of nitroso rubber by the incorporation of sulfur atoms in a modified polymer structure.

This report describes the synthesis of sulfur-containing monomers and attempts to incorporate them into the nitroso polymer, either as comonomers or as termonomers.

II. DISCUSSION

During this quarter efforts to prepare novel sulfur-containing nitroso compounds and trifluorovinyl thioethers have continued. Several new copolymerizations were attempted, including the systems $F_2C{=}S/CF_3NO$ and $(CF_3)_2C{=}S/CF_3NO$.

A. Synthesis of Sulfur-Containing Nitroso Compounds

The major objective in this area has been the synthesis of two compounds, CF_3SNO and SF_5NO. To date there has been little evidence to indicate that either of these compounds has been formed as a stable end product, suggesting that these systems may be inherently unstable under ordinary conditions.

Our initial report described attempts to prepare these compounds by radical recombination reactions, similar to the synthesis of CF_3NO by irradiation of CF_3I and NO [1]. These investigations have been extended to include the reactions of CF_3SCl with NO and ClNO, and CF_3SSCF_3 with ClNO. In the reaction of CF_3SCl with excess NO a red solid was observed when the reactants were condensed and frozen. This color existed only in the solid phase and could be regenerated by refreezing. This red color was probably not due to nitrosyl chloride since this compound was not detected in the reaction mixture on warming to room temperature. It is possible that CF_3SNO was formed in a solid matrix and is unstable under normal conditions. The few known thionitrites which have been reported [2, 3, 4] (RSNO, where $R{=}CH_3$, C_2H_5,

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(1) R. N Haszeldine, J. Chem. Soc., 1953, 2075.

(2) H. Tasker and H. Jones, J. Chem. Soc., 95, 1917 (1909).

(3) H. Reinbolt, Ber., 59, 1311 (1926).

(4) H. Lecher and W. Siefken, Ber., 59, 1314 and 2594 (1926).

C_6H_5) are described as red, relatively unstable liquids.

Reaction of both CF_3SCl and CF_3SSCF_3 with nitrosyl chloride resulted in products (CF_3Cl, CF_3NO_2) which showed that carbon-sulfur bond cleavage occurs rather easily in the $CF_3S\cdot$ radical to give sulfur and a $CF_3\cdot$ radical.

A new approach was attempted by reacting nitrosyl fluoride and thiocarbonyl

$$F_2C{=}S + FNO \xrightarrow{?} CF_3SNO$$

fluoride but the initial reaction was inconclusive. Infrared analysis of the product mixture indicated the formation of a CF_3S compound, but decomposition occurred before the mixture could be separated.

A similar reaction was carried out in an attempt to synthesize SF_5NO and SF_4ClNO by reaction of SF_4 with nitrosyl fluoride and chloride:

$$SF_4 + FNO \xrightarrow{?} SF_5NO$$

$$SF_4 + ClNO \xrightarrow{?} SF_4ClNO$$

The reactions were carried out in DMF solution by adding the nitrosyl compound to the yellow SF_4. In both cases a green solution resulted, but this may have been due to dissolved nitrogen oxides. Infrared analysis of the volatile products gave no evidence for the formation of any SF_5 compounds other than SF_5Cl. Chlorine was probably introduced either by reaction with Kel-F grease or with the sodium chloride windows of the infrared cell.

A different method for the preparation of SF_5NO was attempted through the use of a recently reported compound containing the novel SF_5 anion. This compound, $CsSF_5$, is reasonably stable and is formed as an intermediate in the reaction of SF_4, CsF and Cl_2 to give SF_5Cl [5]. Attempts to prepare and isolate

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(5) C. W. Tullock, D. D. Coffman, and E. L. Muetterties, paper presented at the Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratories, 4 September 1963 and private communication from Dr. C. W. Tullock, Central Research Department, E. I. duPont deNemours and Co., Wilmington, Del.

is compound in our laboratories have met with some difficulty, partially due to toclave leakage and loss of material when a rupture disc failed. In one case some oduct was obtained as a mixture with unreacted cesium fluoride. This material s reacted with nitrosyl chloride in an attempt to achieve the reaction shown. wever, infrared analysis of the product mixture showed SF_5Cl to be a product

$$\overset{+\ -}{CsSF_5} + \overset{-\ +}{ClNO} \rightarrow \overset{?}{SF_5NO} + CsCl$$

the reaction. This reaction will be examined further using reactants such as O_3 and nitrosyl sulfuric acid as sources of NO^+. Another recently reported mpound containing the SF_5 anion is $(CH_3)_4NSF_5$, formed by reacting $(CH_3)_4NF$ th SF_4.[6]

Another route to SF_5NO which will be investigated is shown below. The st two reactions have been reported[7]. The first three steps might be avoided the unknown acid SF_5COOH could be prepared by a shorter route. In hope of

$$SF_5Cl + CH_2{=}CH_2 \rightarrow SF_5CH_2CH_2Cl$$
$$SF_5CH_2CH_2Cl + KOH \rightarrow SF_5CH{=}CH_2$$
$$SF_5CH{=}CH \xrightarrow{ox.} SF_5COOH$$
$$SF_5COOH \xrightarrow{-H_2O} (SF_5CO)_2O$$
$$(SF_5CO)_2O \xrightarrow{N_2O_3} SF_5COONO$$
$$SF_5COONO \rightarrow SF_5NO + CO_2$$

preparing the acid chloride precursor we reacted sulfur tetrafluoride with

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R. Tunder and B. Siegel, J. Inorg. and Nucl. Chem., 25, 1097 (1963).

J. R. Case, N. H. Ray, and H. L. Roberts, J. Chem. Soc., 1961, 2066.

carbonyl fluoride. The first reaction was carried out undiluted in an autoclave

$$SF_4 + COF_2 \xrightarrow{?} SF_5COF$$

without success. A second reaction in DMF solution showed that carbonyl fluoride reacted with DMF. This reaction will next be attempted using cesium fluoride catalyst in acetonitrile.

Another interesting precursor would be SF_5CF_2Br which might be converted to SF_5CF_2NO by reaction with nitric oxide. We have attempted this synthesis using S_2F_{10} and CF_2Br_2. No reaction occurred when the reactants were heated to 150° or at 110° in the presence of benzoyl peroxide. The sample has been placed in the cobalt-60 source in hope of inducing the free radical reaction.

A similar precursor, $BrCF_2SSCF_2Br$, might be prepared from CF_2Br_2 and sulfur by a reaction similar to that of CF_3I with sulfur to give CF_3SSCF_3[8]. The first attempt resulted in a light red liquid which decomposed during distillation to give bromine and a solid residue. Later runs gave carbon disulfide as the only liquid product. No further efforts have been made to prepare this compound.

The reaction of nitrosyl chloride with trifluoromethyl trifluorovinyl thioether has given a blue compound believed to be the sulfur-containing nitroso adduct. The reaction mixture has not yet been separated, however.

$$CF_3SCF{=}CF_2 + ClNO \xrightarrow[?]{hv} CF_3SCFClCF_2NO \text{ or } CF_3SCF(NO)CF_2Cl$$

B. Synthesis of Trifluorovinyl Thioethers

The new thioether $CF_3SCF{=}CF_2$ has been prepared by the sequence shown.

$$\begin{tikzcd}[column sep=small] CF_3SCl + CF_2{=}CFCl \arrow[r, "hv"] & CF_3SCF_2CFCl_2 + CF_3SCFClCF_2Cl \arrow[d, "Zn"', "Dioxane"] \\ & CF_3SCF{=}CF_2 \end{tikzcd}$$

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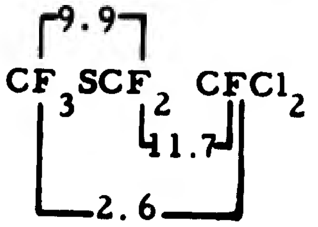
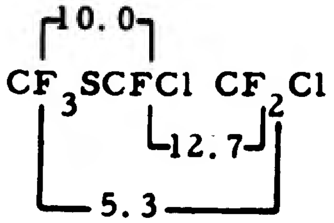
(8) G. A. R. Brandt, H. J. Emeleus and R. N. Haszeldine, J. Chem. Soc., 1952. 2198.

In the first reaction[9] the two adducts are formed in approximately equal quantities, the ratio being easily determined by NMR analysis. Chemical shifts with respect to external CF_3COOH are as follows: (for $CF_3SCF_2CFCl_2$) CF_3, -41.3 ppm.; CF, -6.63 ppm.; CF_2, + 0.29 ppm. (for $CF_3SCFClCF_2Cl$) CF_3, -40.3 ppm.; CF, + 9.61 ppm.; CF_2, -11.9 ppm. The coupling patterns in cycles per second are shown below.



$CF_3SCF_2\ CFCl_2$



$CF_3SCFCl\ CF_2Cl$

The unsaturated thioether was prepared by a dehalogenation of the mixture using powdered zinc in dioxane. No dehalogenation occurred when tetramethylene sulfone (sulfolane) was used as a solvent. Two reactions were carried out in dioxane, giving conversions of about 35 and 72.5% conversion. The reason for the difference in the amount of product in these two dehalogenations is not clear. An infrared spectrum of $CF_3SCF=CF_2$ is shown in Figure 1.

An attempt to prepare the analogous thioether $CH_3SCF=CF_2$ was not successful due to the exceptional resistance of the intermediate $CH_3SCF_2CF_2H$ to dehydrofluorination. This compound was unaffected by powdered KOH at temperatures up to 400°.

C. Polymerization[10]

As mentioned in our First Quarterly Report, one possible route to the incorporation of sulfur in the backbone of the nitroso rubber chain would be the use of $F_2C=S$ or other thiocarbonyl compounds such as perfluorothioacetone as a comonomer

(9) J. F. Harris, Jr., J. Am. Chem. Soc., 84, 3148 (1962).

(10) Polymerizations discussed below are summarized in Tables 1 and 2.

or termonomer. Low temperature bulk polymerizations of $F_2C=S/CF_2=CF_2$ and $F_2C=S/CF_3NO/CF_2=CF_2$ were not successful. During this quarter the former system was examined using cobalt-60[11] as an initiator but again no copolymerization occurred. Perfluorothioacetone was also prepared and attempts were made to obtain copolymers with both CF_3NO and $CF_2=CF_2$ using the low temperature bulk technique. No copolymer was obtained in either case.

Since it has been reported[12] that thiophosgene and tetrafluoroethylene copolymerize in bulk under conditions similar to the nitroso polymerization, we attempted to carry out this reaction to determine the properties of the polymer and to provide information for comparison of $Cl_2C=S$ with $F_2C=S$. However, after 24 hrs. at -38° and 18 days at room temperature there was no evidence of polymer formation.

Recently workers at duPont have been able to homopolymerize $F_2C=S$ and to copolymerize it with olefins using a low temperature free radical system[13]. Free radicals are generated using a trialkylborane/oxygen initiator at temperatures as low as -100°. This technique will be examined to determine its effectiveness in the nitroso polymerization.

In view of the facile polymerization of pentafluoronitrosobenzene with fluoroolefins, described in our last report, we examined the reaction of nitrosobenzene with tetrafluoroethylene in methylene chloride solution. Reaction occurred very readily, resulting in the formation of a black powder. The reaction apparently

(11) All cobalt-60 irradiation reactions were carried out throught the assistance of Dr. R. J. Hanrahan, Department of Chemistry, University of Florida.

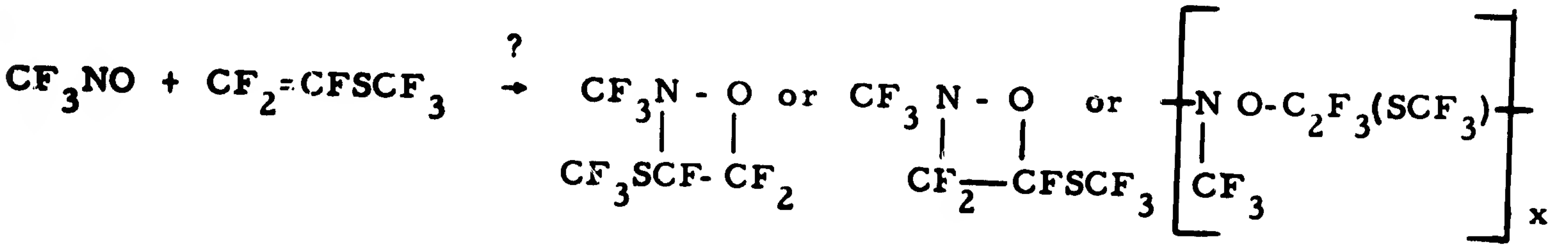
(12) B. F. Landrum, private communication.

(13) C. and E. News, p. 46, 16 December 1963.

does not proceed through the normal mechanism as hydrogen fluoride is formed. The black powder decomposes at 130° but was not characterized further.

Samples of the terpolymer $C_6F_5NO/CF_3NO/CF_2{=}CF_2$ were prepared and submitted to the Natick Laboratories for compounding and testing. The molecular weight of the polymers was so low that the cured samples did not exhibit rubbery properties and were not suitable for further testing. Future work will include attempts to increase the molecular weight of these terpolymers.

An attempt to homopolymerize the new monomer $CF_3SCF{=}CF_2$ by cobalt-60 irradiation resulted in about 5% conversion to what appears to be low molecular weight polymer or cyclized monomer. Reaction of $CF_3SCF{=}CF_2$ with CF_3NO at -38° and under cobalt-60 irradiation produced a small amount of a high boiling liquid. NMR analysis indicates that this is the oxazetidine (I or II), a polymer (III) or a mixture of polymer-oxazetidine. An infrared spectrum of this material is shown in Figure 2.



$$CF_3NO + CF_2{=}CFSCF_3 \xrightarrow{?} \begin{array}{c} CF_3N - O \\ |\qquad| \\ CF_3SCF - CF_2 \end{array} \text{ or } \begin{array}{c} CF_3\,N - O \\ |\qquad| \\ CF_2 - CFSCF_3 \end{array} \text{ or } \left[\begin{array}{l} -N\;O{-}C_2F_3(SCF_3)- \\ \;| \\ CF_3 \end{array} \right]_x$$

I II III

A terpolymerization of $CF_3SCF{=}CF_2/CF_3NO/CF_2{=}CF_2$ resulted in a viscous polymer. A preliminary report of the NMR spectrum of this sample in Freon 113 solution indicated that a small amount of $CF_3SCF{=}CF_2$ was incorporated in the polymer.

A scouting experiment to determine the reactivity of $CF_3N{=}SF_2$ with CF_3NO gave no indication of polymerization. A polymer of trifluoromethyliminosulfur difluoride would be of interest since it would contain both nitrogen and sulfur in the backbone.

It should also be noted that a new solvent has been found for nitroso polymer.

This compound is $CF_3SOCH_2CF_3$, prepared by the reaction of CF_3SCl with CF_3CH_2OH in pyridine[14]. Preliminary observations indicate that it is a better solvent than Freon 113.

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(14) Sam Andreades, U. S. Patent 3, 081, 350 (March 12, 1963).

III. EXPERIMENTAL

A. Synthesis of Sulfur-Containing Nitroso Compounds

1. Attempted Synthesis of CF_3SNO

a. Reaction of Thiocarbonyl Fluoride with Nitrosyl Fluoride

Nitrosyl fluoride (1 g.) was condensed into a Pyrex Fischer-Porter tube containing about 1 g. of impure thiocarbonyl fluoride. The tube was allowed to warm and an infrared spectrum was made of the overgas, which was found to contain SiF_4, COS and N_2O. Absorption between 8 and 9.2 microns and at 13.17 microns indicated a CF_3S group. Other unassigned peaks occurred at 6.15, 6.25 and 6.52 microns. The latter peak is probably due to CS_2 while the first two peaks may be due to NO. The spectrum changed over a period of time, indicating decomposition of the sample at room temperature.

b. Reaction of Trifluoromethanesulfenyl Chloride with Nitric Oxide

Two reactions of CF_3SCl with NO were run. In the first reaction a 1-liter Vycor 7910 flask was charged with CF_3SCl (1.46 g., 10.7 mmoles) and purified NO (0.32 g., 10.7 mmoles). The materials were frozen into the flask as a white solid, allowed to warm to room temperature, and irradiated with ultraviolet light for 16 hours. An infrared spectrum of the product mixture showed NO_2, SO_2 CF_3SCl, CF_3NO, CF_3NO_2, and SiF_4. An attempt was made to separate the mixture by GLC, but unsatisfactory resolution was obtained.

In the second reaction a 1-liter flask was charged with purified NO (0.642 g., 0.021 moles) by freezing it in as a white solid. As soon as the CF_3SCl (1.46 g., 0.011 moles) was condensed in, the solid material became bright red. On warming above the freezing point the color disappeared, but when the sample was solidified again the bright red color returned. Infrared spectra of the gas phase showed only starting materials. The reactants were transferred to a flask containing absolute ethanol and cooled in an attempt to develop the red color in a liquid phase. However no color developed even when the alcohol was cooled to its freezing point. An infrared spectrum still showed CF_3SCl and NO.

c. Reaction of Trifluoromethanesulfenyl Chloride with Nitrosyl Chloride

Two reactions of CF_3SCl with NOCl were run. The following is a description of one reaction.

A magnetic stirring bar and several ml. of Hg were placed in a 1-liter flask which was then evacuated. This flask was charged with CF_3SCl (1.18 g., 0.009 moles) and NOCl (1.71 g., 0.026 moles), immersed in ice-water, and the contents stirred for 3 hours. The volatile products were removed to a trap in liquid air and later separated by a co-distillation. Some of the products were identified by infrared spectra as NO_2, ClNO, SiF_4, CF_3SCl, CF_3Cl, COF_2, and CF_3NO_2. In addition to these products there was a continuous elution of material which gave absorption in the CF region and in the NO_2 region, evidence that sample decomposition was occurring.

d. Reaction of Bis(trifluoromethyl) Disulfide with Nitrosyl Chloride

Three reactions of CF_3SSCF_3 with NOCl were run. The following is a description of one of them.

A 1-liter Vycor 7910 flask was charged with CF_3SSCF_3 (2.16 g., 0.011 moles) and ClNO (0.53 g., 0.011 moles) and placed in sunlight for 4 hours. As soon as the flask was placed in sunlight the brown color of the ClNO began to fade. At the end of 4 hours the flask was filled with a light yellow gas and covered with a thin, white, solid coating. The volatile products were separated by GLC and identified by their infrared spectra as ClNO, CF_3SSCF_3, NO, NO_2, SO_2, CF_3SCl, CF_3Cl, CF_3NO, CF_3NO_2, and an unknown eluted after CF_3SSCF_3.

2. Attempted Synthesis of SF_5NO and SF_4ClNO

a. Reaction of Sulfur Tetrafluoride with Nitrosyl Fluoride

Sulfur Tetrafluoride (5.8 g., 0.054 moles) was condensed into a trap at -78°. Nitrosyl fluoride (5.5 g., 0.112 moles) was condensed into this yellow liquid, resulting in a green solution which was separated by warming to -40° to remove unreacted FNO. The higher boilers were washed free of SF_4 by bubbling through water. Infrared analysis of the products showed the presence of N_2O, SOF_2, NO_2 and SF_5Cl. Chlorine may have been introduced into the system either by Kel-F grease or by reaction with the NaCl windows of the infrared cell.

b. Reaction of $CsSF_5$ with Nitrosyl Chloride

A 300-ml. flask containing a mixture of CsF (~3.8 g., 0.025 moles) and $CsSF_5$ (~6.6 g., .025 moles) was charged with NOCl (1.67 g., 0.025 moles), and the contents stirred. The volatile products were removed to a trap in liquid air and later separated by GLC. They were identified by infrared spectra as ClNO, NO_2, SiF_4, SOF_2, SO_2F_2, SF_4, and SF_5Cl. There was no evidence for the formation of SF_5NO.

c. Reaction of Sulfur Tetrafluoride and Nitrosyl Chloride

A 250-ml. flask was fitted with 2 gas inlets and one outlet vented to a trap in liquid oxygen. Fifty ml. of DMF was placed in the flask, and SF_4 (8.0 g., 0.074 moles) was bubbied into the liquid. This was followed by the addition of ClNO (4.0 g., 0.061 moles) to the mixture, which turned from yellow to light green. Analysis of the product gases caught at -183° showed them to be ClNO, SF_4, NO_2, SO_2F_2, SOF_2, and SiF_4.

3. Addition of Nitrosyl Chloride to Trifluoromethyl Trifluorovinyl Thioether

Two reactions of $CF_3SCF{=}CF_2$ with ClNO have been run. The first was a very small scale run to determine if any reaction would occur. The second reaction was run on a larger scale, and it is described below.

A 1-liter Vycor 7910 flask was charged with $CF_3SCF{=}CF_2$ (3.42 g., 0.019 moles) and ClNO (1.23 g., 0.019 moles) and placed in sunlight for 3 hours. At the end of this time the flask contained a blue liquid and a blue overgas. The overgas was removed and an infrared spectrum of this material showed mostly SiF_4 with some $CF_3SCF{=}CF_2$, ClNO, and NO_2. The dark blue liquid product remained in the reaction flask overnight. It was observed that some solid material had deposited and the blue color had become lighter. An infrared spectrum of the overgas developed by the liquid showed $CF_3SCF{=}CF_2$, a small amount of ClNO, and unknown absorption at 5.3, 6.15-6.25, 10.2, 10.3, 11.28, 11.85, and 12.5 microns. Some of the liquid has been submitted for NMR analysis.

B. Synthesis of Trifluorovinyl Thioethers

1. Preparation of Trifluoromethyl Trifluorovinyl Thioether

Four dehalogenation reactions of $CF_3SCFClCF_2Cl$ have been run. When the reaction was carried out in tetramethylene sulfone no dehalogenation took place. The following is a description of the reaction giving the best conversion.

A 300-ml., 3-neck flask containing dioxane (200 ml.), Zn (15 g.), and a trace of $ZnCl_2$ was fitted with a stirrer, reflux condenser, and addition funnel. A mixture of 56% $CF_3SCFClCF_2Cl$ and 44% $CF_3SCF_2CFCl_2$ (18.9 g. total weight) was placed in the addition funnel. The mixture was added over a 15-minute period after the dioxane was heated to reflux. The condenser was vented to a trap cooled to -183° where the product was caught as a white solid. This material was separated by GLC and 5.5 g., (72.5% conversion) of a pure compound was obtained. Both the infrared spectrum (Figure 1) and nuclear magnetic resonance spectrum of this compound were consistent with the structure $CF_3SCF{=}CF_2$. Molecular weight found, 180 (calcd. 182).

2. Attempted Synthesis of Methyl Trifluorovinyl Thioether

Powdered KOH (3.3 g., 0.57 moles) and $CH_3SCF_2CF_2H$ (4.0 g., 0.27 moles) were placed in an 80-ml. Fischer-Porter tube containing a small Teflon-coated stirring bar. The reactants were heated to 195° with stirring for a total of 20 hours. Infrared analysis indicated that no reaction had occurred. The tube was opened and 1.4 g. of unreacted liquid removed and placed in a 10.5-ml. Fischer-Porter combustion tube with 2 g. of powdered KOH. The reactants were heated at 400°-410° for 1 hour. An infrared spectrum of the product showed only unreacted starting material.

C. Polymerization

1. Preparation of $C_6F_5NO/CF_3NO/CF_2{=}CF_2$ Terpolymer Samples

Terpolymer samples were prepared as described in the First Quarterly Report for submission to the U. S. Army Natick Laboratories. A solution of C_6F_5NO (purified by sublimation) in CH_2Cl_2 was first prepared and placed in a 20-ml. Pyrex ampoule fitted with a Fischer-Porter Teflon needle valve. The solution was degassed and CF_3NO and $CF_2{=}CF_2$ condensed into the ampoule. The samples were shaken for 24 hrs at -39° to -20°. The ampoules were opened and the polymers washed with CH_2Cl_2 and pumped under vacuum for 65 hrs. Amounts and other pertinent observations are given in Table 1.

TABLE 1

Preparation of Terpolymer Samples

No.	C_6F_5NO mmoles	CF_3NO mmoles	$CF_2{=}CF_2$ mmoles	CH_2Cl_2 ml.	g. Polymer	Yield %	Remarks
1		28	28	10	4.03	73.5	$[n]=0.72$
2	1	19	24*	10	3.35	75.0	2, 3, 4 colored light blue-green at end of polymerization, solution turned yellow after 24 hrs. at room temperature, tacky semi-elastomeric gums
3	2	18	24	10	3.40	81.5	
4	4	16	24	10	3.52	82.5	

*- An excess of $CF_2{=}CF_2$ was used so that the actual amount of C_6F_5NO which could be incorporated into the polymer was 2.5, 5.0, and 10.0 mole % in samples 2, 3 and 4, respectively.

TABLE 2

Polymerizations

Monomers	Charge		System	Time hrs.	Temp. °C	Remarks
	g.	moles				
C_6H_5NO	2.0	0.019	Solution in CH_2Cl_2	18	-35	in 10 ml. CH_2Cl_2;
$CF_2=CF_2$	2.0	0.020		96	20	3.07 g. black powder (dec. 130°)
$Cl_2C=S$	1.3	0.011	Bulk	24	-38	no evidence of polymerization
$CF_2=CF_2$	1.2	0.012		432	20	
CF_3NO	0.119	0.0012	Bulk	360	-78	no copolymer
$(CF_3)_2C=S$	0.218	0.0012				
$CF_2=CF_2$	0.100	0.001	Bulk	148	-78	no copolymer
$(CF_3)_2C=S$	0.190	0.001				
$CF_3SCF=CF_2$	0.2		Bulk/Co^{60}	148	Ambient	∿5% conversion by NMR
$CF_3SCF=CF_2$	0.25	0.0014	Bulk	72	-38	no apparent polymerization
CF_3NO	0.14	0.0014				
$CF_3SCF=CF_2$	0.25	0.0014	Cobalt-60	48	Ambient	same sample as above. Solution turned pale blue-green; small amount of high-boilers, possibly polymer
CF_3NO	0.14	0.0014				
$CF_3SCF=CF_2$	0.226	0.0012	Bulk	48	-38	viscous, pale-blue polymer; most of thioether recovered
CF_3NO	0.990	0.010				
$CF_2=CF_2$	0.900	0.009				
CF_3NO	0.119	0.0011	Bulk	20	-38	sample also exposed to Cobalt-60 for 48 hrs; no polymer formed
$CF_3N=SF_2$	0.184	0.0011				
CF_3NO	0.290	0.003	Bulk/Co^{60}	4.5	Ambient	no copolymerization
$F_2C=S$	0.264	0.003				

2. Nitrosobenzene and Tetrafluoroethylene

Nitrosobenzene (2.0 g., 0.019 moles) and methylene chloride (10 ml.) were placed in an 80-ml. Fischer-Porter tube. The green solution was degassed and tetrafluoroethylene (2.0 g., 0.020 moles) condensed into the tube. The tube was placed in a cold bath at -35° for 18 hrs. at which time the mixture contained a tan solid. The bath was allowed to warm slowly with progressive darkening of the solution. At -10° the color was dark brown. After 4 days an infrared spectrum of the overgas showed the presence of $CF_2=CF_2$, CH_2Cl_2 and SiF_4, indicative of the formation of HF. The volatile material was pumped from the tube leaving 3.07 g. of black powder, which decomposes at 130°. The tube was etched during the reaction, further indication of HF formation.

An initial reaction of these two compounds at room temperature resulted in darkening of the solution in 5 minutes with evolution of heat at 10-15 minutes.

3. Thiophosgene and Tetrafluoroethylene

Thiophosgene (1.3 g., 0.011 moles) and tetrafluoroethylene (1.2 g., 0.012 moles) were placed in a 20-ml. ampoule fitted with a Fischer-Porter Teflon needle valve. Thiophosgene was admitted first and degassed, followed by condensation of $CF_2=CF_2$ into the tube. The tube was shaken at -38° for 24 hrs. with no evidence of change. The tube was then allowed to stand at room temperature for 18 days. Again no evidence of polymerization was observed.

4. Perfluorothioacetone and Trifluoronitrosomethane

A 4.5-ml. ampoule was charged with $(CF_3)_2C=S$ (0.0012 moles) and CF_3NO (0.119 g., 0.0012 moles) and placed in a -78° bath for 15 days. A small amount of white solid deposited and the liquid turned a pale green, but no copolymerization occurred.

5. Perfluorothioacetone and Tetrafluoroethylene

A 4.5-ml. ampoule was charged with $(CF_3)_2C=S$ (0.190 g., 0.001 moles) and C_2F_4 (0.100 g., 0.001 moles) and placed in a -78° bath for 1 week. A small amount of solid was deposited and the liquid turned a pale yellow, but no copolymerization occurred.

6. Trifluoromethyl Trifluorovinyl Thioether

A 4.5-ml. ampoule was charged with $CF_3SCF=CF_2$ and placed in a cobalt-60 source for 7 days. No polymerization occurred. A nuclear magnetic resonance spectrum of the product showed only slight reaction (~5%).

7. Trifluoromethyl Trifluorovinyl Thioether and Trifluoronitrosomethane

A 4.5-ml. ampoule was charged with $CF_3SCF=CF_2$ (0.25 g., 0.0014 moles) and CF_3NO (0.14 g., 0.0014 moles) and placed in a -38° bath for 3 days. There was no apparent reaction. The tube was then placed in a cobalt-60 source for 2 days. The color in the tube changed to a pale blue-green. The tube was opened, and the volatiles were transferred to a trap in liquid air; a small amount of clear, high-boiling liquid was left. The volatiles were separated by GLC and identified by infrared spectra as CF_3NO, $CF_3SCF=CF_2$, CF_3NO_2, and SO_2. A nuclear magnetic resonance spectrum was made of the high-boiling liquid product.

8. Trifluoromethyl Trifluorovinyl Thioether, Trifluoronitrosomethane and Tetrafluoroethylene

A 20-ml. ampoule was charged with $CF_3SCF=CF_2$ (0.226 g., 0.0012 moles), CF_3NO (0.990 g., 0.010 moles), and C_2F_4 (0.900 g., 0.009 moles) and placed in a -40° bath for 2 days. A viscous, pale-blue polymer was formed. The volatiles were removed to a trap in liquid air. Calculations from a chromatogram of the volatile material showed it to contain about 0.23 g. of $CF_3SCF=CF_2$. The solution of the polymer in Freon 113 was submitted for NMR analysis.

9. Trifluoronitrosomethane and Trifluoromethyliminosulfur Difluoride

A 4.5-ml. ampoule was charged with $CF_3N=SF_2$ (-.184 g., 0.0011 moles) and CF_3NO (0.119 g., 0.0011 moles) and placed in a bath at -40° for 20 hours. There was no apparent reaction. The ampoule was then placed in a cobalt-60 source for 2 days. There was still no high boiling material present and an infrared spectrum showed no reaction.

10. Trifluoronitrosomethane and Thiocarbonyl Fluoride.

Trifluoronitrosomethane (0.297 g., 0.003 moles) and thiocarbonyl fluoride (0.264 g., 0.003 moles) were condensed into a 2.5 ml. Pyrex ampoule, which was placed in a cobalt-60 source for 4.5 hours. The dose was approximately 2.5×10^{20} e.v. The contents were transferred to another tube leaving only a trace of solid. The volatile material was found to contain CF_3NO, $F_2C{=}S$, COS, CF_3NO_2, COF_2, SiF_4 (trace) and several unidentified compounds.

D. Synthesis of other Monomers and Intermediates

1. Synthesis of Perfluorothioacetone

a. Reaction of Bis(perfluoroisopropyl) Mercury with Sulfur

Two attempts were made to prepared $(CF_3)_2CS$ from $[(CF_3)_2CF]_2Hg$ and sulfur. The first time a water-cooled condenser was use, and it soon plugged. In the second attempt, described below, an air-cooled tube one inch in diameter was used as a condenser.

A 1-liter, 4-neck flask was half filled with melted sulfur and fitted with a condenser, thermometer, stirrer, and addition funnel containing $[(CF_3)_2CF]_2Hg$. The sulfur was heated to its boiling point and the mercury compound slowly added. The condenser was vented through a trap cooled to -78°. Some blue material was caught, but after standing for several days it turned to a white solid and on warming to room temperature to a colorless liquid. Perfluorothioacetone is reported to be a blue liquid which easily dimerizes, and it appears that $(CF_3)_2CS$ was made in this reaction but dimerized during storage.

b. Pyrolysis of 2, 2, 4, 4-Tetrakistrifluoromethyl-1, 3-dithietane

Perfluorothioacetone was prepared by the pyrolysis of 2, 2, 4, 4-tetrakistrifluoromethyl-1, 3-dithietane[15]. An addition funnel containing an undetermined

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(15) A sample of the dithietane was provided by Dr. C. G. Krespan, Central Research Department, E.I. duPont de Nemours and Co., Wilmington, Del.

amount of $(CF_3)_2\underline{CSC(CF_3)_2S}$ was connected to a 12" Vigreaux column heated to 600° C. The column was vented to a trap cooled to -78°. The dithietane was slowly dropped into the heated column as it was being swept with a stream of N_2. The product was trapped as a blue liquid.

2. Synthesis of Bis(perfluoroisopropyl) Mercury [16]

Perfluoropropylene (300 g., 2.0 moles), mercuric fluoride (240 g., 1.01 moles) and hydrofluoric acid (70 g.) were reacted according to a reported procedure [17]. Distillation of the product mixture gave 40 g. of $[(CF_3)_2CF]_2Hg$, b.p. 114°-117°.

3. Synthesis of Sulfur Chloride Pentafluoride

Cesium fluoride (172g., 1.13 moles), SF_4 (108 g., 1.0 moles) and Cl_2 (71 g., 1.0 moles) were reacted according to a reported procedure [5]. The product mixture was washed by passing through two columns each filled with 100 g. $FeSO_4$ in 1-l. of 2N H_2SO_4. A total of 61 g. of SF_5Cl was obtained in a purity of 85-90% as determined by infrared analysis and GLC.

4. Synthesis of Trifluoromethyliminosulfur Difluoride

Sulfur tetrafluoride (70 g., 0.65 moles) and NaSCN (14 g., 0.17 moles) were reacted according to a reported procedure [18]. The products were separated by trap-to-trap distillation in a vacuum line. A portion of the product-rich fraction was subjected to preparative-scale chromatography using a 40' column packed with the ethyl ester of Kel-F Acid 8114 on HMDS-treated Chromosorb to give 2.25 g. of pure $CF_3N{=}SF_2$.

(16) A. 200 g. sample was also received from the U. S. Army Natick Laboratories.

(17) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, J. Org. Chem., 28, 184 (1963).

(18) W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Englehardt, J. Am. Chem. Soc., 82, 551 (1960).

5. Reaction of Disulfur Decafluoride with Dibromodifluoromethane

Disulfur decafluoride[19] (5.34 g., 0.023 moles) and CF_2Br_2 (4.80 g., 0.023 moles) were condensed into an evacuated 80-ml. Fischer-Porter tube and heated to 150° (100 p.s.i. g.) for 1.5 hrs. with no significant changes in the infrared spectrum of the mixture. Benzoyl peroxide (0.2 g.) was added to the solution and the tube was heated at 90°-110° for 1.5 hrs. Infrared analysis again indicated that no reaction had occurred. The solution remained colorless.

6. Reaction of Dibromodifluoromethane with Suflur

Five attempts were made to prepare $BrCF_2SSCF_2Br$ by reacting sulfur with CF_2Br_2. The following is a typical reaction.

A 300-ml. stainless steel autoclave was charged with sulfur (100 g., 3.125 moles) and CF_2Br_2 (35.0 g., 0.167 moles) and heated at 300° for 12 hrs. The only liquid product obtained was approximately 12 g. of CS_2. This material contained dissolved sulfur and a red solid. There was also some undissolved red, solid material left in the autoclave.

7. Reaction of Bis(trifluoromethyl) Disulfide with Chlorine; Alternate Synthesis of CF_3SCl

A 12-liter flask was charged with CF_3SSCF_3 (25.86 g., 0.128 moles) and Cl_2 (18.2 g., 0.256 moles) and irradicated for 2 hrs. with an ultraviolet lamp suspended in an immersion well. Infrared analysis showed that all of the CF_3SSCF_3 had been converted to CF_3SCl (34 g.).

8. Addition of Trifluoromethanesulfenyl Chloride to Chlorotrifluoroethylene

Several additions of CF_3SCl to CF_2CFCl were run. The following is a description of one of these reactions.

A 72-liter flask was charged with $CF_2{=}CFCl$ (35.9 g., 0.308 moles) and CF_3SCl (178 g., 1.31 moles) and irradiated overnight by an ultraviolet lamp suspended in a Vycor immersion well. The low-boiling starting material was

(19) Sample from Dr. James Dale, Monsanto Research Corp., Everett, Mass.

recovered, and the liquid product was distilled through a spinning band column. The following fractions were obtained:

Fraction	b. p. ° C	wt. g.	n_d^{25}	remarks
1	30-38	5		CF_3SSCF_3
2	38-76	6		
3	76-83	14.5	1.3590	
4	above 83	51		

Both the boiling point and refractive index of fraction 3 agree with the literature[20] values given for a mixture of $CF_3SCFClCF_2Cl$ and $CF_3SCF_2CFCl_2$. A nuclear magnetic resonance spectrum of this fraction showed it to contain 54% $CF_3SCF_2CFCl_2$ and 46% $CF_3SCFClCF_2Cl$.

9. Synthesis of $CsSF_5$

Four similar reactions have been attempted between SF_4 and CsF. In three of these no reaction occurred. The following is a description of the reaction which appears to have given some $CsSF_4$.

A 300-ml. stainless steel autoclave was charged with CsF (15.3 g., 0.10 moles) and SF_4 (105 g., 0.97 moles) and heated at 150° for 1 hour, 200° for 1 hour, and 250° for 2 hours. Examination of the overgas of the reaction showed that 5.5 g. of SF_4 had reacted. This should produce 20.8 g. of a mixture of CsF and $CsSF_5$. Actual weight of recovered solid material was 18.5 g.

10. Reaction of Hexafluoroacetone with Nitric Oxide

A 1-liter Vycor 7910 flask was charged with $(CF_3)_2CO$ (1.78 g., 0.017 moles) and NO (0.64 g., 0.021 moles) and placed in sunlight for 4 days. An infrared spectrum of the gas phase showed only starting material. There were also long

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(20) J. F. Harris, Jr., <u>J. Am. Chem. Soc.</u>, <u>84</u>, 3148 (1962)

white crystals present. These volatilized under vacuum to give $(CF_3)_2CO$ and were probably the hydrate.

11. Reaction of Carbonyl Fluoride with Sulfur Tetrafluoride

A 300-ml., stainless steel autoclave was charged with SF_4 (8.0 g., 0.014 moles) and COF_2 (4.40 g., 0.067 moles) and heated at 200° for 6 hours. An infrared spectrum of the product mixture showed that most of the SF_4 had been converted to SOF_2.

A 300-ml., stainless steel autoclave was charged with SF_4 (8.0 g., 0.074 moles), COF_2 (5.9 g., 0.089 moles), and DMF (28.0 g., 0.380 moles) and heated at 200° for 6 hours. Examination of the product overgas by GLC and infrared spectra showed only CO_2 and SOF_2. The autoclave was opened and found to contain only dimethylformamide which had reacted to give a black liquid.

12. Synthesis of 1, 1, 2, 2-Tetrafluoroethyl Methyl Thioether

A 12-liter Pyrex flask was fitted with a Vycor immersion well and inlet valve and evacuated. Methyl mercaptan (9.2 g., 0.192 moles) and tetrafluoroethylene (6.4 g., 0.064 moles) were bled into the flask and irradiated by an Hanovia type SOL lamp for 4 hrs. The contents were then removed and partially purified by passing through traps at -8° and -183°. The contents of the -8° trap were distilled using an 18" spinning band column. A clear, colorless fraction (4.1 g.) was obtained boiling at 65°-68° and identified as $CH_3SCF_2CF_2H$. Conversion was 42%.

IV. CHEMICALS SOURCE

Chemical	Supplier
Nitrosyl fluoride	Ozark-Mahoning
Nitric oxide	Matheson
Nitrosyl chloride	Matheson
Sulfur tetrafluoride	duPont
Cesium fluoride	American Potash and Chemical Corp.
Tetramethylene sulfone	Shell
Potassium hydroxide (powdered)	Hooker
Methyl mercaptan	Eastman
Nitrosobenzene	Aldrich
Thiophosgene	Rapter
Mercuric fluoride	Harshaw
Dibromodifluoromethane	duPont
Chlorotrifluoroethylene	Allied
Hexafluoroacetone	Allied

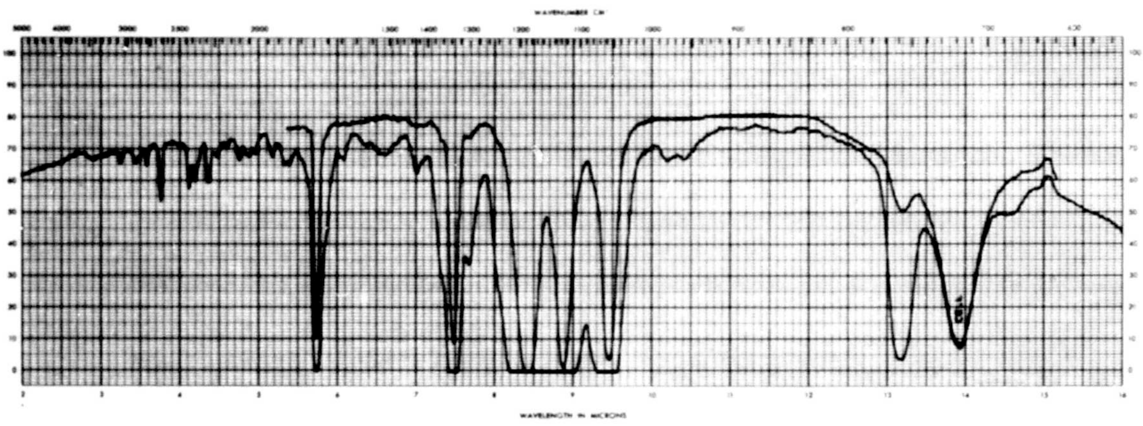

Figure 1. Infrared Spectrum of $CF_3SCF=CF_2$
10 cm. cell, 60 and 4 mm pressure

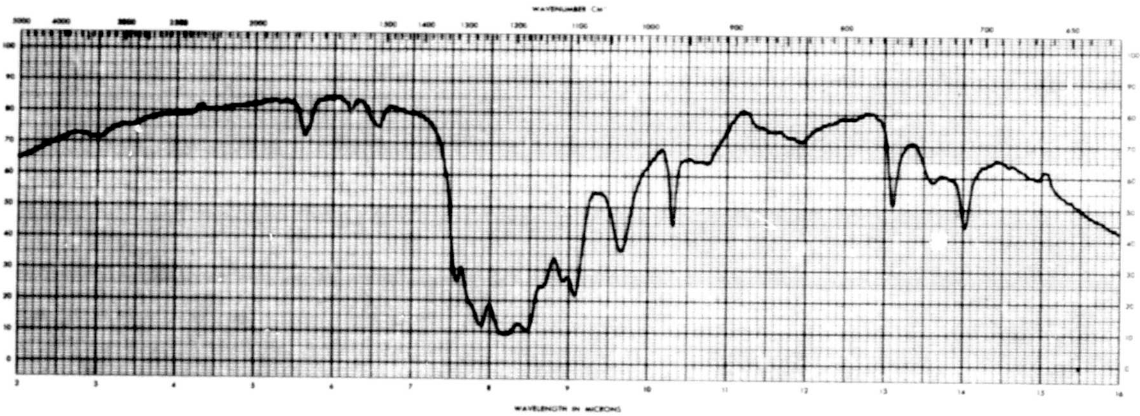

Figure 2. Infrared Spectrum of $CF_3SCF=CF_2/CF_3NO$ High Boilers