

61B 1467

AD 742 486

Rubber Research

The Synthesis of Unsaturated Fluorocarbons

Progress Report

Quarterly Report 11

U. S. Army Contract DA-19-129-QM-1263

QMC Project No. 7-93-15-004

Project Officer: Dr. Juan Montermoso

For the Period Feb. 13, 1961 to May 13, 1961

June 7, 1961

By J. D. Park and J. R. Lacher

University of Colorado ⁴

Boulder, Colorado

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

TECHNICAL LIBRARY
QM RES & ENGR COMMAND
RESEARCH REPORTS

TECHNICAL LIBRARY
U. S. ARMY
NATICK LABORATORIES
NATICK, MASS.

I. Introduction

The purpose of this project is to conduct studies and investigations on fluorinated hydrocarbons with a view toward developing techniques and processes of synthesizing special monomers from which to obtain elastomers which will be chemical and gasoline resistant and will retain their flexibility at extremely low temperatures and thermal stability at high temperatures.

This research is authorized under Contract No. DA-19-129-QM-1263. This is the eleventh quarterly report for the period February 13, 1961 through May 13, 1961.

II. Summary of Current Progress

During this period 1087 g. of pure $\text{C}_2\text{F}_2\text{Cl}-\text{CF}_2\text{NO}$ and 135 g. of $\text{C}_2\text{F}_5\text{NO}$ were packed and shipped to 3M.

The work which appeared to be successful since our last report (No. 10) has fallen into several categories.

1. Adaptation of a successful solvent system for the reaction of $\text{CF}_2=\text{CF}_2$ with NOCl . This method is far superior to the $\text{FeCl}_3-\text{NOCl}$ hot-tube method.

2. Photolysis reactions:

a) Reaction of perfluoroacetic anhydride and NOCl in the presence of actinic light yielded CF_3COONO . Similarly, $\text{C}_2\text{F}_4\text{COONO}$ and $\text{C}_3\text{F}_7\text{COONO}$ were produced from $(\text{C}_2\text{F}_5\text{CO})_2\text{O}$ and $(\text{C}_3\text{F}_7\text{CO})_2\text{O}_x$.

b) The reaction of NOCl and CF_3COOH in the presence of strong ultraviolet radiation yielded $\text{CF}_3-\text{N}=\text{O}$.

- c) The decomposition of C_2F_5COONO to $C_2F_5-N=O$ and CO_2 was carried out in a quantitative manner through the use of ultraviolet radiation.
- d) Continuation of our studies of the reaction of fluoroolefins with NO or $NOCl$ in the presence and/or absence of chlorine. These reactions almost always led to the formation of the nitrosyl adducts of the fluoroolefins.

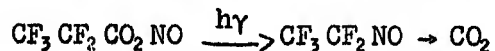
Although a fair solvent system for making CF_2ClCF_2NO was devised which was capable of supplying large quantities of CF_2Cl-CF_2-NO , the emphasis has been shifted to the preparation of perfluoronitroso monomers.

A few attempts were made to make CF_3NO directly from CF_3COOH for lowest raw material costs. Direct passage of $NOCl$ through CF_3CO_2H with and without solvents and peroxides gave very little or not nitroso product. However, photolysis of mixtures of CF_3COOH and $NOCl$ did give CF_3NO (23% yield).

This yield could probably be improved.

Photolysis of $(CF_3CO)_2O$ and $NOCl$ directly gave a 33% yield of CF_3NO with a 48% conversion of the anhydride. Using $NOCl$ both the acid and anhydride suffer yield limitations due to CF_3Cl by-product formation making the maximum yield obtainable only 50%, e.g. $(CF_3CO)_2O + NOCl \xrightarrow{h\nu} CF_3NO + CF_3Cl + CO_2 + CO$.

It is planned to use nitric oxide instead of $NOCl$ to get away from the R_fCl problem. Contrary to Hazeldine's findings, good yields of R_fNO can be had from the silver salts of perfluoro acids. $CF_3CF_2CO_2H$ was converted to CF_3CF_2NO by the following sequence:



The decarboxylation is quite facile by photolysis in a large pyrex bulb using a Hanovia 2000 watt-lamp. At present, thermal decarboxylation is inadequate and dangerous because acyl nitrites especially $\text{CF}_3\text{CF}_2\text{CO}_2\text{NO}$ are prone to detonate. It is planned to make chloride-free CF_3NO also by this method.

Solvent System Vs. Packed Tube Method

Background: As reported in Q.M.C. report No. 10, we continued our efforts to find simpler methods of obtaining higher yields of $\text{CF}_2\text{Cl-CF}_2\text{NO}$ at a faster rate than the previously used packed-tube methods. Accordingly, we have adapted the $\text{NOCl-CF}_2=\text{CF}_2$ reaction to a solvent system and are pleased to report success at last.

Method: The method at present consists in passing an equimolar mixture of $\text{CF}_2=\text{CF}_2$ and NOCl through a solution of a relatively-inert high-boiling solvent such as tetrachloroethane or chlorobenzene containing 10% by weight of anhydrous ferric chloride and 2 1/2 - 3% acetic anhydride. The gases on the exit side are blue (due to $\text{CF}_2\text{Cl-CF}_2\text{NO}$ formation) and are condensed in a cold-trap receiver.

The ferric chloride and acetic anhydride are both needed for the reaction to proceed; without them no significant reaction occurs in the solvent. Apparently the function of the ferric chloride is similar to

that in the packed tube method, it partakes in the reaction by forming a complex with the nitrosyl chloride. The acetic anhydride is used to make the ferric chloride soluble. It was chosen since it also proved of use in the $\text{CF}_2=\text{CFCl}$ reactions with the uranyl nitrate complex $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{N}_2\text{O}_4$. Other oxygenated solvents such as ethanol are too reactive towards nitrosyl chloride. By the use of this solvent-system, the rate of nitroso production can be stepped up about four times over that of the packed tube methods. (see Table I).

III. Discussion

The ferric chloride packed-tube method of making $\text{CF}_2\text{Cl}-\text{CF}_2\text{NO}$ suffered from low conversions of $\text{CF}_2=\text{CF}_2$ thus requiring the handling of large amounts of $\text{CF}_2=\text{CF}_2$ for small yields of nitroso (at best 25 grams $\text{CF}_2\text{ClCF}_2\text{NO}$ per mole (100 g) of $\text{CF}_2=\text{CF}_2$ or about 15%) with repeated repacking and cleaning of the reaction tubes.

The solvent system method is faster, simple to set up, more flexible, and easy to reactivate (after which higher yields are obtained)! Both tetrachloroethane and chlorobenzene are good solvents to use. They are not swept out with the gases and are inexpensive and can be used repeatedly. Dimethylsulfoxide was tried, but decomposed to a white, foul-smelling viscous mass upon passage of the gases and gave no discernable nitroso compounds. Perfluoroacetic acid containing 10 mole percent H_2O_2 (from 90% H_2O_2) gave a sharp exotherm upon introduction of $\text{CF}_2=\text{CF}_2$ and NOCl with no subsequent nitroso formation upon cooling. N,N-dimethylformamide containing 0.5% ditertiarybutylperoxide did give some $\text{CF}_2\text{Cl}-\text{CF}_2\text{NO}$ under the influence of ultraviolet light after introduction of the $\text{CF}_2=\text{CF}_2-\text{NOCl}$

gas mixture but in lower yields than the above solvent system.

After using a freshly prepared solvent system, the initially deep blue condensate picks up a greenish cast with time (NOCl itself coming through) and the yield of nitroso adduct slowly starts to drop as the ferric chloride is used up. By filtering off the spent catalyst (which becomes yellow and gives off NO₂ on water) and adding 10% fresh ferric chloride and 2 1/2% acetic anhydride to the filtrate, the solution is rejuvenated and instantly gives blue nitroso upon introduction of the golden CF₂=CF₂ and NOCl mixture with a corresponding higher conversion of CF₂=CF₂ to the nitrosyl chloride adduct.

Experimental

A. Tube Reactions: The method is essentially the same as reported in previous Q.M.C. reports. A cold trap immersed in liquid nitrogen with the exit end connected to a mercury manometer was added to collect unreacted CF₂=CF₂ coming through the product receiver which was immersed in carbon-ice solution.

1. Using a 50/50 mixture of anhydrous FeCl₃ to crushed glass (43% by weight). It took about 5 hours before first blue condensate came through. As reaction proceeded, FeCl₃ became yellow. Near the end of the reaction the condensate begins to take on greenish hue.

CF₂=CF₂ in . . . 115 gms (1.15 moles)

CF₂=CF₂ caught in liquid N₂ trap 75 gms (0.75 moles)

NOCl passed in 50 gms (0.76 moles)

Weight nitroso condensate 25 gms
Weight held up on column. 56 gms
Time of passage of flow 26 hours
% conversion to $\text{CF}_2\text{Cl-CF}_2\text{-NO}$ 86% (According to
vapor phase chromatography - V.P.C.)

2. Using a column flushed with nitrogen under heat ($\sim 90^\circ$) and then cooled to $45-50^\circ$. Condensate becomes blue within 15 minutes.

$\text{CF}_2=\text{CF}_2$ in 111 gms (1.11 moles)
 $\text{CF}_2=\text{CF}_2$ collected in cold trap. 72 gms (0.72 moles)
Weight NOCl passed through. 57 gms (0.87 moles)
Weight blue condensate. 28 gms
Weight held up on column. 46 gms
Time of flow. 26 hours

Vapor phase chromatography gives 81% conversion to $\text{CF}_2\text{Cl-CF}_2\text{NO}$.

3. Using 4 mesh CaCl_2 as a diluent instead of glass

Weight $\text{CF}_2=\text{CF}_2$ in 103.5 gms (1.03 moles)
Weight $\text{CF}_2=\text{CF}_2$ cold trap 81.5 gms (0.81 moles)
Weight NOCl passed in 43 gms. (0.65 moles)
Weight blue condensate. 24 gms
Weight held up on column. 38 gms
Time of flow of gases 29 hours

V.P.C. gives about 85% nitroso after $\text{CF}_2=\text{CF}_2$

(At best a tube reaction involving 100 gms (1 mole) $\text{CF}_2=\text{CF}_2$
gives 25 gms $\text{CF}_2\text{ClCF}_2\text{NO}$ or 15% of product.)

- B. Solvent System Method: This consists in passing equimolar mixtures
(same rate of bubble flow through mineral oil) of $\text{CF}_2=\text{CF}_2$ and NOCl

through a sintered frit immersed in the solvent system contained in a tube. A reflux condenser is attached to the tube and to a cold trap immersed in carbon-ice bath. At the exit of the product receiver, a tube lead to a mercury manometer so that small pressures (up to 200 mm) can be maintained giving increased solubility of $\text{CF}_2=\text{CF}_2$.

| | | |
|--|--|------------------|
| 1. Weight chlorobenzene | 105.0 gms | } Solvent system |
| Weight FeCl_3 | 10.5 gms | |
| Weight acetic anhydride | 3.0 | |
| Weight $\text{CF}_2=\text{CF}_1$ in: | 27.0 gms (0.27 moles) | |
| Weight NOCl in: | 19.0 gms (0.29 moles) | |
| Weight of blue condensate | 30.5 gms (contains 9 gms $\text{CF}_2=\text{CF}_2$) | |
| Time of flow | 7 1/2 hours | |

V.P.C. shows 75% of adduct

Weight of washed nitroso compound . . 15 gms

2. Reactivated System: The above slurry was filtered and reactivated with fresh FeCl_3 and acetic anhydride.

Weight $\text{CF}_2=\text{CF}_2$ 24 gms (0.24 moles)

Weight NOCl 23 gms (0.23 moles)

Weight nitroso condensate 23 gms

V.P.C. shows about 80% $\text{CF}_2\text{ClCF}_2\text{NO}$

Weight washed and dried nitroso . . . 15 gms

(blue condensate came over immediately as flow was turned on)

3. Tetrachloroethane reactions:

340.0 gms $\text{C}_2\text{H}_2\text{Cl}_4$

34.0 gms FeCl_3

7.1 gms Ac_2O

$\text{CF}_2=\text{CF}_2$ in 66 gms (0.66 moles)

NOCl in 40 gms (0.61 moles)

Weight blue condensate 72 gms

V.P.C. showed 85% after $\text{CF}_2=\text{CF}_2$

(Note - near end it becomes greenish due to some unreacted NOCl coming over.)

4. Reactivated System: The above slurry was filtered and gave yellow solid containing Fe^{xx} and giving NO_2 off with water. It seemed similar to that from the spent packed tubes. The black filtrate was reactivated:

294 gms black liquor

30 gms FeCl_3

65 gms Ac_2O

The blue nitroso product started to come over as the flow was resumed.

Weight $\text{CF}_2=\text{CF}_2$ 60 gms (0.60 moles)

Weight NOCl 39 gms (0.59 moles)

Time of flow 11 1/4 hours

Weight condensate. 70 gms

Weight (washed and dried deep blue nitroso compound). . .45 gms

5. Using chlorobenzene or $\text{CHCl}_2\text{CHCl}_2$ by itself even with ditertiarybutyl peroxide gave no discernable nitroso compound.

6. $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{N}-\text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \begin{array}{c} \text{O} \\ || \end{array}$ with ditertiarybutyl peroxide did give some $\text{CF}_2\text{ClCF}_2\text{NO}$ for a while--about 65% after $\text{CF}_2=\text{CF}_2$ peak by V.P.C.

7. $\overset{\text{O}}{\parallel}$ CH₂SCH₂ became viscous and gave no nitroso compound.

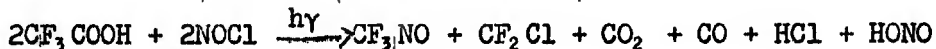
Reaction of CF₂=CF₂ and NOCl under Pressure in Carius Tube

Two runs were made with and without the use of ferric chloride in a sealed tube fitted with a pressure gauge. Into the tube was placed 10.1 grams CF₂=CF₂ (0.10 moles) and 6.5 grams (0.1 moles) of NOCl and in one case 3 grams FeCl₃. The tube was slowly heated to 47°C until constant pressure drop. In neither case was any nitroso formed. The light yellow liquid appeared to be the oxazetidine $\text{CF}_2-\text{CF}_2-\overset{\text{N-O}}{\parallel} \begin{matrix} \text{CF}_2 \\ \text{CF}_2 \end{matrix}$. Under pressure any nitroso intermediate formed goes on to react with CF₂=CF₂ to form the oxazetidine as substantiated by Hazeldine and Andecades (DuPont).

Photolysis Reaction of CF₃COOH and (CF₃CO)₂O with NOCl

A. CF₃COOH

With the hopes of converting trifluoroacetic acid directly to the desired CF₃NO with the lowest raw material costs, CF₃COOH was made to react with NOCl directly in a 7-liter bulb using a Hanovia internal source. The reaction was followed by pressure build up and appeared to follow the following equation.



Into a 7-l bulb was placed 75 grams (0.656 moles) of CF₃COOH. The acid in the bulb was frozen with liquid nitrogen and the bulb was evacuated, then 10 grams of NOCl gas was introduced and the light source turned on. During the course of the reaction the pressure built up from 170 mm to 482 mm. The gases were then drawn off into tubes immersed in liquid nitrogen and another 10 grams of NOCl was added to the unreacted acid in the bulb. This was repeated once more making a total of 30 grams NOCl

Table I

Summary of Data on Packed Tube and Solvent System Reaction of $CF_2=CF_2$ and $NOCl$

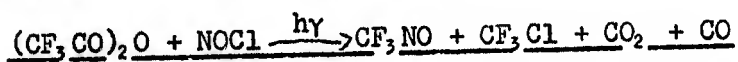
| Experimental Section Number | A-1 A-2 A-3 | | B-1 B-2 B-3 B-4 | | | | | |
|---|--------------|------|-----------------|------|------|--------|------|-----|
| | Packed Tubes | | Solvent System | | | | | |
| Weight of $CF_2=CF_2$ passed into system (Mol wt = 100) | 115 | 111 | 103 | 5 | 27 | 24 | 66 | 60 |
| Weight of $CF_2=CF_2$ recovered | 81 | 76 | 83 | 12 | 12 | 9 | 30 | 23 |
| Weight of $CF_2=CF_2$ consumed | 34 | 35 | 28.5 | 15 | 15 | 15 | 36 | 37 |
| % conversion of $CF_2=CF_2$ | 30 | 31.5 | 20 | 54 | 62.5 | 55 | 55 | 62 |
| Time of gas flow in hours | 36 | 26 | 29 | 7.5 | 6 | 11-1/4 | | |
| Weight of $NOCl$ passed into system (Mol wt = 65.5) | 50 | 57 | 43 | 19 | 15 | 15 | 40 | 39 |
| Weight of washed and dried CF_2ClCF_2NO obtained in gms | 21.5 | 22.6 | 20.5 | 15.1 | 15.0 | 15.0 | 40 | 45 |
| Moles of CF_2ClCF_2NO (Mol wt = 165.5) | .133 | .14 | .124 | .092 | .091 | .091 | .24 | .27 |
| % Yield of CF_2ClCF_2NO $\frac{\text{moles produced}}{\text{moles } CF_2=CF_2 \text{ consumed}} \times 100$ | 40 | 40 | 60.5 | 61 | 60.5 | 60.5 | 66.5 | 73 |
| Moles of CF_2ClCF_2NO per mole $CF_2=CF_2$ passed in | .12 | .126 | .12 | .34 | .38 | .36 | .45 | |
| Rate of CF_2ClCF_2NO production in gms per 24 hours | 14.5 | 20.9 | 17.0 | 48.5 | 60 | 60 | | 96 |

In round figures we can say best tubes gave 25% conversion in 60% yield vs. 60% conversion in 70% yield for reactivated solvent system

(0.467 moles). The recovered acid was 34 grams (0.30 moles), thus giving a 55% conversion. The gases were scrubbed through water and then passed through soda lime to remove the CO_2 . The infrared gave all the peaks of CF_3NO and CF_3Cl . Vapor phase chromatography and the infrared showed the blue gas to be approximately 55% of CF_3NO and 45% CF_3Cl ; thus 8.25 gms (0.0835 moles) of CF_3NO was made representing a 23% yield from CF_3COOH . There is much leeway in the procedure to increase the conversion and yield. But maximum theoretical yield is only 50% due to CF_3Cl byproduct when NOCl is used. Attempts using NO instead of NOCl will be made.

B. $(\text{CF}_3\text{CO})_2\text{O}$

Trifluoroacetic acid was converted to its anhydride $(\text{CF}_3\text{CO})_2\text{O}$ with P_2O_5 . The anhydride was reacted with NOCl in a 22-liter bulb in the system using Hanovia light source.



The large bulb was evacuated and 60 grams (0.286 moles) of perfluoroacetic anhydride and 19.5 grams (0.298 moles) of nitrosyl chloride were introduced. After the ultraviolet light AH-6 was turned on, the pressure increased from 420 mm to 660 mm. The gases were collected in tubes immersed in liquid nitrogen by slowly pumping out the bulb. The blue condensate was then passed through two water scrubbers and finally a soda-lime tower to remove CO_2 and acidic materials. The anhydride recovered was about 31 grams (0.14 moles) representing a 48% conversion. The infrared and V.P.C. chromatograms were identical with the scrubbed gases of this CF_3COOH reaction and found to be about 49% CF_3NO and 51% CF_3Cl . This represents .091 moles CF_3NO thus giving a 32.5% yield. CF_3Cl cannot be physically separated from CF_3NO since their boiling points are too close (-84° vs $-82^\circ/625$ mm). The reaction also suffers the limitation of a 50% theoretical

cooled in a carbon ice bath and the nitrosyl chloride is introduced at the inlet. After the gas has all been added, the flask contents are allowed to warm up to room temperature. An extra few hours contact of the NOCl with the silver salt gives higher conversion to the acyl nitrite. The flask is then warmed slightly in a mineral oil bath and a slowly increasing vacuum is applied on the receiver end to remove the excess NOCl and finally the straw colored $\text{CF}_3\text{CF}_2\text{CO}_2\text{NO}$. The flask is heated to 70°C under 10 mm pressure with stream running through the condenser to remove the last of the acyl nitrate b.p. $110^\circ/625$ mm. The solid remaining in the flask is mainly AgCl which appears to give off some NO (yellowish brown fumes). The condensate in the collecting tube is allowed to warm up to room temperature to remove some of the excess NOCl. The condensate of the three grams were combined and vacuum distilled to give 371 grams (1.93 moles) of $\text{CF}_3\text{CF}_2\text{CO}_2\text{NO}$. The conversion of the silver salt was about 82% with a 90.5% yield.

The transformation of $\text{CF}_3\text{CF}_2\text{CO}_2\text{NO}$ to $\text{CF}_3\text{CF}_2\text{NO}$ was found to be best and safest by employing photolysis methods. At first thermal decomposition was attempted. When a one gram sample seemed to work, it was scaled up to 96 grams. The acyl nitrite was heated at atmospheric pressure and any product was to be collected in a cold trap. The decomposition was very slow and it mainly refluxed. Upon increasing the heat supply, the hot acyl nitrite detonated with a shattering sharp report. The direction of the detonation was downwards and blew the flask to powdered glass and the iron ring supporting the mantle was shattered to pieces. Surprisingly nothing else was damaged, but unfortunately this wasted one fourth of the prepared nitrite. At this point, photodecomposition was looked upon

with great promise. (The acyl nitrite can probably be decomposed safely by passing it through a heated tube under vacuum in the vapor state.)

The photolysis reactions went very smoothly and rapidly in the bulb apparatus described above. The acyl nitrite was photolyzed in light runs in the bulb apparatus. Five runs were made in the 7-1 bulb and three in the 22-1 bulb after it became available. The procedure was to evacuate the bulb and introduce the $\text{CF}_3\text{CF}_2\text{CO}_2\text{NO}$ previously weighed out in a tube which was frozen down and also evacuated. After the acyl nitrite was in the bulb, the Hanovia lamp was turned on. Most of the liquid resided in the well of the bulb which was heated in a mineral oil bath to 50°C to slowly drive the material into the large vapor space. The reaction was followed by increase of pressure (one molecule of liquid giving 2 of gas) and the deepening of the blue color of $\text{CF}_3\text{CF}_2\text{NO}$ in the bulb. The reaction in the 7-1 bulb was fairly rapid and in one case a 25 grams sample went from 20 mm pressure to 725 mm in 4 hours.

After the reaction, the contents of the bulb is slowly evacuated into two tubes immersed in liquid nitrogen. Representative samples of the gas were taken for infrared analysis. The spectragraph showed the strong nitroso absorption at 6.25 microns and CO_2 absorption at 4.3 microns.

The condensate is then washed through two water scrubbers and then a soda-lime tower to remove CO_2 . All the batches were combined and sent to Minnesota Mining and Manufacturing Company in a steel tank.

The unreacted acyl nitrite hydrolyzes in the scrubbers and is recovered as the sodium salt of the acid. In a typical run, 79 grams of acyl nitrite was photolyzed giving $74 \frac{1}{2}$ grams of blue condensate, about 2 grams of a white solid containing NO (perhaps an inorganic polymer), and 2 grams brown

residue. After scrubbing 50 grams of a mixture of CF_3NO and CO_2 (equimolar) is obtained. The wash water shows 0.22 equivalence of acids presumably CF_3COOH and HONO from the hydrolysis of unconverted nitrite and 5 grams of a brownish oil whose composition will be determined. The conversion is therefore about 76% and the yield 85%.

More CF_3NO will be prepared similarly.

Reaction of $\text{CF}_2=\text{CFCl}$ with Nitric Oxide

This reaction has been reported in the previous quarterly report. A rerun was made to determine the weight distribution of products and to obtain more of the unidentified blue compound that was present as ca. 5% of the products in the previous run.

Into a 22 liter flask were passed 52 grams (0.454 moles) of $\text{CF}_2=\text{CFCl}$ and 13.6 grams (0.454 moles) of nitric oxide. The following is a tabulation of the periods of irradiation and the corresponding pressure drops:

| | | |
|--------------|---------|---------------------------|
| 12 hours | 12.2 cm | period of irradiation |
| 82 hours | 17.4 cm | period of non-irradiation |
| 12 1/2 hours | 8.7 cm | period of irradiation |

At the end of this experiment a sample of the crude product was chromatographed and samples of the main peaks were collected and identified by infrared analysis. The major product, $\text{CF}_2\text{Cl-CFClNO}$, was formed in ca. 28% yield and with a conversion of about 74%. Unfortunately, none of the unidentified blue compound formed in the previous run was produced by this run. Other products include $\text{CF}_2\text{Cl-CFCl}_2$ (9% yield) and ca. 38% higher boilers.

Reaction of Tetrafluoroethylene with Nitric Oxide and Chlorine

When 22.7 grams (0.23 moles) of tetrafluoroethylene and 7.0 grams (0.23 moles) of nitric oxide with 8.2 grams (0.115 moles) of chlorine gas

are introduced into the 22 liter flask and irradiated with the 450 watt Hanovia quartz lamp, previously described, a reaction takes place in 2 1/2 hours yielding $\text{CF}_2\text{NO-CF}_2\text{Cl}$ in 81% yield with a 36% conversion.

Reaction of tetrafluoroethylene with Nitrosyl Chloride

When 0.246 moles each of tetrafluoroethylene and nitrosyl chloride are placed in the 22 liter flask and irradiated, a reaction takes place in 6 hours yielding $\text{CF}_2\text{NO-CF}_2\text{Cl}$ in 79% yield with a conversion of 23%.

Attempted Conversion of $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ to $\text{CF}_2\text{Cl-CF}_2\text{NO}$

Into the 22 liter reaction flask were introduced 15.76 grams (0.092 moles) of 97% pure 1,2-dichloro-1,1,2,2-tetrafluoroethane, 6.02 grams (0.092 moles) of nitrosyl chloride and a trace of chlorine gas. The pressure within the flask increased only 7.2 cm Hg during 8 hours of irradiation with 450 watt Hanovia lamp. Chromatography of the crude reaction mixture yielded no blue fractions. Only unreacted starting materials were detected. The visible ultraviolet spectra of $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ shows no absorption from 4000\AA to 2100\AA .

Reaction of CF_3COCl with Nitrosyl Chloride and Chlorine

Trifluoroacetyl chloride was prepared by an exchange reaction between trifluoroacetic acid, previously distilled--b.p. 65-66.5/623 mm Hg, and benzoyl chloride according to the method of Henne, Alm and Smook, J. Am. Chem. Soc., 70, 1948. The infrared spectrum of the product compares favorably with that given in "Fluorine Chemistry," Volume II, by J. H. Simons, 1954, page 485.

Into the 22-liter flask were introduced 31.6 grams (0.225 moles) of trifluoroacetyl chloride, prepared as just described, and 14.6 grams (0.223 moles) of nitrosyl chloride. No chlorine was added until after 6 hours of irradiation. The following is a tabulation of the periods of

irradiation which shows when chlorine was added and when samples were withdrawn for infrared analysis. The infrared spectra of the representative gas samples were taken in a 10 cm gas cell at 30 mm Hg pressure.

| time | pressure change | sample for IR | chlorine added |
|----------|---------------------|---------------|-------------------|
| 0 hours | start | | |
| 4 hours | 11.2 cm Hg increase | x | |
| 6 hours | no pressure change | | 0.002 moles added |
| 13 hours | 5.6 cm Hg increase | x | |
| 19 hours | 2.4 cm Hg increase | x | 0.001 mole added |
| 38 hours | 3.4 cm Hg increase | x | |

The infrared spectra give evidence that CF_3Cl was formed in the reaction. Peaks ascribed to trifluoroacetyl chloride were diminished as the reaction proceeded while peaks ascribed to chlorotrifluoromethane, CF_3Cl , appeared before the chlorine was added and then continued to increase with time of reaction. Peaks at 5.1, 5.2, and 9.74 microns appearing in the reaction mixture were noticeably increased by the addition of chlorine but could not be assigned. The chromatography of each gas sample withdrawn yielded four peaks, shown to be the following: CF_3Cl and air, CF_3COCl , unknown (pink), and $NOCl$. It is postulated that the reaction occurring is the decarbonylation of trifluoroacetyl chloride to yield carbon monoxide, the small pressure increase consistent with the limited occurrence of this reaction.

Attempted Conversion of CF_3Br to CF_3NO

Trifluorobromomethane, 49 grams, 0.329 moles, and nitric oxide, 0.33 moles, were introduced into the 22 liter flask and irradiated with the 450 watt Hanovia lamp for 22 hours. Since a pressure drop of only 1.8 cm Hg occurred within this period of time, a trace of chlorine (0.046 moles) was added, and the gases were irradiated for an additional 94 hours. No

blue material was isolated by chromatography of the crude "product" mixture. The ultraviolet spectra of bromotrifluoromethane shows no absorption from 6000 Å to 2200 Å; an absorption, presumably of the carbon-bromine bond, begins at 2200 Å and continues to increase until it reaches a maximum somewhere below 2000 Å (the limit of our instrument). The 450 watt Hanovia quartz, high-pressure, mercury-vapor lamp (Type L, Ct. No. 679A-36) which we are using is reported to deliver radiations from 13673 Å down to 2224 Å, and only 3.7 watts of its reported 177.0 watt output are at this latter wavelength. It is postulated that a source of radiant energy capable of delivering radiations around 2000 Å is necessary to break the carbon-bromine bond in trifluorobromomethane.

About 450 grams of perfluorobutyric anhydride and 135 grams of perfluoroacetic anhydride were prepared by refluxing the appropriate acids over the anhydride of phosphoric acid.

Perfluoroacetic Anhydride and NOCl

About 70 grams of perfluoroacetic anhydride and 48 grams of nitrosyl chloride were mixed in a 22 liter flask equipped with one 2-way and one 3-way stopcock. The bulb was subjected to a 300 watt incandescent lamp for 24 hours and the materials were distilled.

Results 59 grams anhydride.

3.1 grams perfluoroacetyl nitrite 46% yield

traces of a white solid M.P. 131-135°

Perfluorobutyric Anhydride and NOCl

a) About 332 grams of perfluorobutyric anhydride and 65 grams of nitrosyl chloride were mixed in a 22 liter flask and the bulb was subjected to a 300 watt incandescent lamp for 24 hours.

Distillation results 307 grams anhydride

1.6 grams perfluoronitroso propane

1:1 12% yield

b) About 82 grams of perfluorobutyric anhydride were placed into a glass cylinder filled with a sintered glass frit and a reflux condenser and nitrosyl chloride was passed through at a very slow rate. A Westinghouse sun lamp was positioned approximately 20 inches from the cylinder and irradiation was continued for 24 hours. The solution had turned a light green and an infrared spectrum of a sample revealed carbon dioxide and nitroso peaks. Distillation yielded 69 grams of anhydride; 3.8 grams of perfluoronitroso propane (yield 58%) and less than 2 grams of chloroheptafluoro propane. Small amounts of low boilers believed to be alkyl nitrites were hydrolyzed readily, but no attempt was made to identify them. Control runs were made on small samples of perfluorobutyric anhydride saturated with nitrosyl chloride at room temperature. Four test tubes were exposed to various conditions for 24 hours to determine the effects of radiation on the reaction mixtures. One tube was kept in the dark, one exposed to a 100 watt incandescent lamp, one subjected to a Westinghouse sun lamp and one exposed to an ultraviolet lamp. The results indicate that ultraviolet wave lengths are the most favorable toward producing nitroso compounds from perfluoro anhydrides and nitrosyl chloride. The test tube exposed to ultraviolet light had turned a decided blue and carbon dioxide was detected. The sun lamp and incandescent lamp reactions gave only slight evidence of change while the test tube in the dark gave no sign of a reaction.

c) About 323 grams of perfluorobutyric anhydride were placed into a glass cylinder fitted with a sintered glass frit and a reflux condenser

attached to dry ice and liquid air traps. Nitrosyl chloride was slowly passed through the anhydride while irradiation from an ultraviolet lamp, positioned approximately 12 inches from the cylinder, was continued for 6 days. At the end of this time, the solution had a deep green appearance and some green materials had been trapped in the dry ice receiver. Upon distillation the following compounds were collected and identified by boiling point and infrared spectra.

217 gms anhydride b.p. 101° - 104° /630
11 gms CO_2
49.5 gms $\text{CF}_3\text{CF}_2\text{CF}_2\text{NO}$ b.p. -20° to -15° /630
27 gms $\text{CF}_3\text{CF}_2\text{CF}_2\text{Cl}$ b.p. -6° to -3° /630
2 gms $\text{CF}_3\text{CF}_2\text{CF}_2\text{COCl}$ b.p. 31 - 32° /630
1 gm $\text{CF}_3(\text{CF}_2)_4\text{CF}_3$ b.p. 53 - 55° /630
1.2 gms $\text{CF}_3\text{CF}_2\text{CF}_2\text{NO}_2$ b.p. 18 - 19° /630
8 gms non-distillable oil

Traces of nitrite and $\text{CF}_3\text{CF}_2\text{CF}_2\text{COF}$ were indicated by I.R. analysis.

It might be mentioned that the solution turned a straw color at 100° and blue gases plus CO_2 were evolved. It is evident that a large amount of the perfluorobutyryl nitrite had formed and was decomposing thermally since the head temperature varied erratically during the operation.

d) About 260 grams of perfluorobutyric acid were placed into a glass cylinder fitted with a sintered glass frit and nitrosyl chloride was passed through at a slow rate. Upon irradiation with an ultraviolet lamp and subsequent distillation, 3.5 gms of a gas were collected. The materials were identified by IR analysis and found to be $\text{CF}_3\text{CF}_2\text{CF}_2\text{NO}$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{Cl}$ and CO_2 . The conversions were poor and hence no separation of the components was attempted.

Perfluoroacetic Anhydride and NOCl

About 165 grams of perfluoroacetic anhydride were placed into a glass cylinder fitted with a sintered glass frit and a reflux condenser and nitrosyl chloride was bubbled through slowly. An ultraviolet lamp was positioned approximately 24 inches from the cylinder and irradiation was continued for 5 days. The materials were distilled and the following compounds were obtained.

145 gms anhydride

~3 gms CF_3Cl

< 2 gms CF_3NO

6.2 gms CF_3COONO

4 gms non-distillable oil

CO_2 detected by I.R. analysis