Rubber Research

# The Synthesis of Unsaturated Fluorocarbons

Progress Report

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## 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 fifth quarterly report for the period Aug. 13, 1959 through Nov. 13, 1959.

## II. Summary of Current Progress

Difficulties are still being encountered in the preparation and analyses of the nitroso and dinitroso derivatives of the fluorinated organic compounds. Progress, however, has been made so that relatively pure nitrogen derivatives are now being prepared and the procedures perfected so that duplication of results can be systematically attained.

Satisfactory progress has been made in the synthesis of $CF_2Cl\text{-}CFClNO$, $CF_2Cl\text{-}CFClNO_2$, $CF_3CF(NO)\text{-}CF_2NO$, $CF_3\text{-}NO$, $C_3F_7NO$, and $CF_3COONO$. Other intermediates and compounds were also prepared but not identified. These will be reported later.

## III. Discussion

In line with our plans given in previous progress reports, we are placing greater emphasis on the study of nitroso chemistry(along with nitro chemistry) with particular emphasis on finding new routes

to making $R_f$-NO and other nitroso and dinitroso-containing aliphatic compounds containing fluorine. Some work is also being directed toward the synthesis of fluorine-containing imines and epoxides.

In our study of the addition of nitric oxide (NO) to fluoro-olefins, we are encountering anomalous results. Thus in the reaction of nitric oxide and trifluorochloroethylene, the major product is not the expected dinitroso-adduct, $CF_2(NO)$-$CFCl(NO)$ but rather $CF_2Cl$-$CFCl(NO)$ (31.9%) with $CF_2(NO_2)$-$CFCl_2$, $CF_2(NO_2)$-$CFCl(NO_2)$, $CF_2(NO_2)$-$CFCl(NO)$ and/or $CF_2(NO)$-$CFCl(NO_2)$.

The product $CF_2Cl$-$CFCl(NO)$ can be accounted for if the original adduct $CF_2$-$(NO)$-$CFCl(NO)$ loses NOCl to yield $CF_2$=$CF(NO)$, followed by the subsequent addition of chlorine to yield $CF_2Cl$-$CFCl(NO)$. Further studies will be made on this and other similar compounds.

We have also been successful in isolating the intermediate $CF_3CO_2$-NO from the reaction of $CF_3COOAg$ and NOCl. $CF_3CO_2NO$ upon heating to above 135° yielded $CO_2$ and $CF_3$-NO. However, the same technique applied to $C_3F_7COOAg$ and NOCl was not productive in so far as isolation of $C_3F_7CO_2$-NO was concerned. Study is now in progress with $C_2F_5CO_2Ag$ and NOCl.

Pyrolysis of the reaction product of $(C_3F_7CO_2)_2Cu$ and NOCl did not yield $C_3F_7$-NO. It was hoped that the cupric salt would replace the more expensive silver salt in the pyrolytic process for preparing $R_f$-NO.

The reaction product of perfluorobutyric anhydride and nitrosyl chloride yielded $C_3F_7$-NO (10% conversion) and an additional 10% upon further treatment of the anhydride with NOCl followed by heating to 135°.

This is the first instance whereby, $R_fNO$ has been produced by this method. This procedure is now being applied to trifluoroacetic anhydride.

Amyl nitrite in the presence of zinc chloride as a catalyst reacts with $C_2H_5OCOCHBrCOOEt$ to yield a blue nitroso compound presumed to be EtOCOCBr(NO)COOEt. $CF_3$-CF=$CF_2$ has been successfully reacted with NO to yield $CF_3CF(NO)$-$CF_2(NO)$.

## IV. Experimental

(1) The reaction between $CF_2$=CFCl and nitric oxide was further investigated in order to establish the conditions under which nitroso derivatives could be obtained. In this investigation a catalytic reaction was employed; other methods of bringing about the combination are under study.

160 g. Trifluorochloroethylene (1.4 moles) and nitric oxide in a ratio of two of NO to one of $CF_2$=CFCl were passed (over a period of 15 hours) through a 2.5 ft. 20 mm. pyrex tube packed with anhydrous $FeCl_3$ and heated to 60-75° C. The product which was collected in a dry ice trap was greenish-blue. During the reaction some nitric oxide was escaping from the trap.

The low boiling material in the product was passed through water and through a calcium chloride tube; the part that was a liquid at room temperature was also washed with water and dried over calcium chloride. Both parts (225 grams) were combined and distilled through a 3 ft. low temperature distillation column. The following fractions were obtained:

I 18 grams of $CF_2$=CFCl

II 66 grams (31.9%) of an intensly blue fraction

b.p. 0° C/139 mm.

$n_D^{0°C}$ 1.3489

$d_{0°C}$ 1.5438

Molecular wt. 180

Molar refraction: Calcd. for $CF_2Cl$-$CFClNO$: 25.44
Found: 24.55.

This fraction was 98+% pure as shown by vapor phase chromatography. Its infrared spectrum shows a sharp absorption band between 2.20 and 2.25 microns which is characteristic of the -NO group; there is also another sharp band with two peaks, one at 5.5 and the other at 5.55 microns. The origin of this split peak is not understood at present; this same peak is also present in the reaction products of $CF_2$=$CFCl$ and $CF_2$=$CCl_2$ with NOCl, of $CF_3$-$CF$=$CF_2$ with nitric oxide, and of a gaseous material liberated during the distillation at atmospheric pressure (630 mm) of the compound now under discussion. This liberated gas (above) contains nitrosyl chloride; when washed with water the washings contain nitrite and chloride ions; the rest condenses in dry ice to a blue liquid with a molecular weight of 132.5 corresponding to $CF_2$=$CFNO$. The spectrum of this gas shows the characteristic -NO band together with the split peak described above. Since a very small quantity of this gas was obtained, no other properties were obtained.

Fraction (II) is believed to be $ClCF_2CFClNO$, for upon oxidation with $CrO_3$ in glacial acetic acid it gave a colorless liquid with practically the same physical constants as fraction V, described below, except in that they differ in melting points and in IR

spectra. The physical constants of the oxidation product are as follows:

b.p. 70-71.5/630

$n_d^{25}$ 1.3692

$d_{25}$ 1.6161

Mol. wt. Calcd for $CF_2Cl\text{-}CFClNO_2$: 198
Found 195.7

III 52 grams (25.1%) of a colorless liquid
b.p. 7/139, 41.5/630

$n_d^{25}$ 1.3557

$d_{25}$ 1.5629

mol. wt. 188

This was identified as $CF_2ClCFCl_2$. Its IR spectrum is superimposable on that of $CF_2ClCFCl_2$ from a commercial source.

IV 15 grams (7.25%) of an intensly blue liquid
b.p. 9-13/90 mm which was 98+ % as shown by gas chromatography

$n_d^{25}$ 1.349

$d_{25}$ 1.5494

Mol. wt. Calcd for $CF_2(NO_2)\text{-}CFCl(NO)$: 192

Found: 186

This is suspected to be $CF_2(NO_2)\text{-}CFCl(NO)$; 2 grams of it will be sent to 3M for NMR studies. Infrared spectra show the sharp peak between 6.15 and 6.2 which is characteristic of the -NO and $NO_2$ groups, and also the same split peak at 5.5 and 5.55 microns present in fraction II above; other bands in the spectrum are at 7.4, 7.95, 8.25, 8.5, 8.95, 9.6, 11, 12.25-12.4.

V 35 grams (16.8%) of a colorless liquid

b.p. 71.5/630

$n_d^{25}$ 1.3669

$d_{25}$ 1.6175

Mol. wt. 199
analysis: found C, 12.64%; N, 6.97%; Cl, 34.67%; F, 28.5%
calcd. C, 12.12%; N, 7.07%, Cl, 35.65%; F, 28.8%

NMR data for this compound indicate a $NO_2$ group attached on a $-CF_2-$ function. These data establish the structure of this compound as $O_2NCF_2-CFCl_2$. The oxidation product of fraction II is the other isomer, i.e., $ClCF_2-CFClNO_2$. The latter has a freezing point at about -35 whereas the former does not solidify at dry ice temperatures. The infrared spectra of the two isomers are similar except for a sharp band at 8.9 microns present in $O_2NCF_2-CFCl_2$ and absent in $CF_2Cl-CFClNO_2$, and with some other minor differences. Dehalogenation experiments on these compounds are underway.

VI 15 grams (7.25%) of a colorless liquid
b.p. 92-98/630
Upon second distillation the following properties were obtained:
b.p. 94.5° at 630 mm.

$n_D^{25}$ 1.368

$d_{4°}^{25}$ 1.6404

Molar refraction: Calcd for $CF_2(NO_2)-CFCl(NO_2)$: 27.5
Found: 28.3.

(2) The reaction of nitrosyl chloride with $CF_2=CFCl$ and $CF_2=CCl$ is also under active investigation. Data collected so far indicate that some of the products obtained from these reactions, at least of $CF_2=CFCl$, may be the same as those obtained in the reaction of these olefins with nitric oxide and ferric chloride.

In a typical reaction of this type, 200 grams of $CF_2$=CFCl and an equimolar quantity of NOCl were passed slowly through a 3 ft. 20 mm. pyrex tube packed with coconut shell charcoal. The reaction tube became hot at the point where the two gases met on the charcoal. The product was condensed in a dry ice trap. During the reaction a gas was leaving the dry ice trap; this gas was colorless and became brown in color when it came in contact with air, and smelled like $NO_2$. The product was washed with water and dried with calcium chloride. Upon distillation 110 grams of $CF_2$=CFCl was recovered. Other fractions were:

20 grams of a blue liquid
b.p. 32/630
$n_D^{0°C}$ 1.3455
$d_{0°C}$ 1.5422
Mol. wt. = 185
Molar refraction 24.96

During the distillation of this fraction a green gas was leaving the column. This when passed through $H_2O$ was changed to blue; the water washings gave a heavy precipitate with $AgNO_3$, which did not dissolve in concentrated $HNO_3$. IR spectra of the blue gas show a peak at 6.2 (NO peak) and also a very sharp split peak at 5.5 and 5.55. Its molecular weight was determined to be 138.6 ($CF_2$=CFNO?).

This 32°C boiling fraction is suspected to be the same compound as that obtained in the reaction of this olefin with nitric oxide, but more work must be done for a definite conclusion.

In addition to this a fraction was obtained which was characterized as $CF_2ClCFCl_2$. Several other fractions obtained from this are under

investigation.

(3) Reaction of $CF_3$-$CF$=$CF_2$ with nitric oxide.

$CF_3CF=CF_2$ and nitric oxide in a ratio of 2 of NO to one of olefin were passed through a 3 ft X 20 mm. pyrex tube provided with a heating coil. At first a blue liquid was collected into the receiving dry ice trap, but after about 5 minutes a colorless material was coming out. The tube was heated at several temperatures ranging from room temperature up to 150° C but no blue product was obtained. Of 40 grams of olefin that was passed through the tube 35 g. was recovered unchanged.

A similar experiment with a tube packed with coconut shell carbon gave a reaction. This time a colorless gas was escaping from the trap; this gas did not turn brown upon contact with air, therefore, it was not NO ( it may have been NOF because the reaction tube was badly etched). 40 grams of olefin was used. 20 grams of a green liquid was collected as the product. This was washed with $H_2O$, dried with $CaCl_2$ and distilled. 15 grams of $CF_2=CFCF_3$ was recovered unchanged along with a blue liquid (about 2 grams), b.p. -7 to -5/630.

This gave a molecular weight of 161.2 (calcd. for $C_3F_6NO$: 161) and an IR spectrum showing a C=C band at 5.5 and a -NO band at 6.2. The molecular weight corresponds to $CF_3CF=CFNO$ or $CF_3\overset{NO}{C}=CF_2$.

(4) Reaction of nitric oxide with hexafluoropropene under pressure.

One hundred grams (0.66 mole) of $CF_3CF=CF_2$ was placed in an evacuated autoclave immersed in a dry ice-cellosolve bath. 0.7 mole of nitric oxide was compressed in at dry ice temperature and again let stand overnight at room temperature. At the end of this period

the autoclave was cooled in dry ice and the pressure was relieved by bleeding off the gaseous material into a dry ice trap. A gas which was not condensible at dry ice temperatures came off. This gas did not turn brown upon contact with air, and it did not support combustion; it was insoluble in water (it is suspected to have been nitrogen or perhaps $N_2O$). The autoclave was then brought to room temperature and 60 g. of hexafluoropropene recovered in a dry ice trap. In the autoclave was left 65 grams of a green fuming liquid. The latter was chilled in ice-water and to it ice water was slowly added. A very vigorous reaction occurred accompanied by foaming and evolution of a brown gas. The water solution upon testing showed the presence of fluoride ion. Some product must have been lost during this operation. When the foaming subsided, an intensly blue liquid settled. This was dried over calcium chloride and distilled at atmospheric pressure (630 mm).

Two fractions were collected:

I 14 grams of a blue liquid
b.p. 42/630 mm

$n_d^{25}$ 1.30

$n_d^{0}$ 1.306

$d_{0°C}$ 1.6224

Calcd mol. wt. for $CF_3-\underset{NO}{CF}-\underset{NO}{CF_2}$ = 210; Found: 220

Mol. refraction: Calcd. for $CF_3-CF(NO)-CF_2(NO)$: 24.6

Found: 24.7

II 17 grams of a colorless liquid
b.p. 68.5/630

$n_d^{25}$ 1.322

$d_{25}$ 1.6479

mol. wt = 230

molar refraction 29.3 based on Lorenz-Lorentz

Identification of this equation compound is now in progress. It was noted that during distillation a brown gas was observed leaving the column.

(5) Attempts to nitrosate monohydrogen groups of various compounds with amyl nitrite have not been completed. The following results indicate that further work may be fruitful.

Prepared: Amyl nitrite 400 grams

A. $HCF_2CF_2CF_2Cl$ 20 grams

B. $CF_3CFH-\overset{O}{\overset{\|}{C}}OCH_3$ 50 grams

C. $C_2H_5O\overset{O}{\overset{\|}{C}}-CHBr-\overset{O}{\overset{\|}{C}}OC_2H_5$ 100 grams

These compounds contain monohydrogens where A is fairly inactive, B is activated by the ester group and C is strongly activated by two ester groups.

It was found that neither A nor B yielded a nitrose compound with amyl nitrite using basic or acidic catalysts including the Lewis acids $AlCl_3$, $FeCl_3$, or $ZnCl_2$. However C did yield an intense blue liquid only with the $ZnCl_2$ catalyst. This has not been identified as yet but remains stable in the refrigerator after several months.

Also prepared was trifluoro acetone from the Lithium salt of trifluoro acetic acid plus the methyl grignard. 50 grams.

This will be chlorinated or brominated to yield a mono hydrogenated compound.

(6) Next the cupric salt of perfluoro butyric acid was prepared

(90 grams) in order to attempt an analogous reaction which the silver salt undergoes with NOCl. However, this is a divalent cation which may be responsible for the failure of pyrolysis with NOCl leading to the formation of the corresponding nitroso derivative.

(7) Attempted isolation of liquid intermediate from mixture of NOCl + $CF_3CF_2CF_2COOAg$.

A. The brown fuming liquid was poured out of the reaction flask and the remainder pumped out under vacuum into a dry ice trap.

The liquid reacts moderately with water and vigorously with ether. It may be heated, whereby it yields the $CF_3CF_2CF_2NO + CO_2$. However, in a distillation attempt at 50 mm. and 60° C only a brown gas was evolved and perfluoro butyric anhydride remained, b.p. 103° at 630 mm., $n_D^{25}$ 1.287.

If $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}ONO$ is the right intermediate, the following may have taken place:

$$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}ONO + ONO\overset{O}{\overset{\|}{C}}CF_2CF_2CF_3 \xrightarrow{\Delta} (CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O + N_2O_3 \quad 2NO_2$$

B. The following facts are known:

$$2CF_3CF_2CF_2COOAg \longrightarrow (CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O + Ag_2O$$

$$2CH_3COONa + 2N_2O_4 \rightarrow (RH_3\overset{O}{\overset{\|}{C}})_2O + 2NaNO_3 + N_2O_3$$

Riebsomer "Chem. Rev." 36, 157 (1945)

$$RCOOAg + (CN)Br \rightarrow R\overset{O}{\overset{\|}{C}}OCN + AgBr$$

$$RCOOCN + RCOOAg \rightarrow R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R + AgOCN$$

$$R\overset{O}{\overset{\|}{C}}OCN \rightarrow RCN + CO_2$$ J. Am. Chem. Soc., 79, 4136 (1957)

C. Now if this is correct and the intermediate with NOCl is an acyl nitrite, the anhydride will doubtless be a side product, since it may form in two different ways:

1. $2CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}ONO \longrightarrow (CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O + N_2O_3$

2. $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}ONO + CF_3CF_2CF_2COOAg \longrightarrow (CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O + AgONO$

(8) Acid + NOCl

A. 35 grams $CF_3CF_2CF_2COOH$ + 10 grams NOCl mixed at -30° C. Mixture heated to 135° C and finally to 150° (starting materials recovered).

B. 35 grams of acid + 10 grams NOCl using $ZnCl_2$ catalyst. No nitroso compound evolved.

C. 35 grams + 10 grams NOCl was allowed to set 18 hours and then heated (starting material recovered).

D. 40 grams acid + 12 grams NOCl + 20 grams sym-collidine in the hope that complexing the HCl formed would stabilyze the intermediate

$RCOOH + NOCl \xrightarrow{\text{collidine}} R\overset{O}{\overset{\|}{C}}ONO$ + collidine. HCl

(9) Result - no nitroso on heating to 150° C.

perfluoro butyric anhydride + NOCl (400 grams made)

A. 64 grams anhydride + 47 grams NOCl mixed at -30°C and heated to 150° (starting materials only).

B. 64 grams anhydride + 46 grams NOCl using $ZnCl_2$ catalyst. Heated to 150°, no nitroso compound formed.

C. 60 grams anhydride + 40 grams NOCl allowed to stand for 20 hours. 3.2 grams $CF_3CF_2CF_2NO$ collected after heating to 135°, about 10% conversion.

D. 10 grams more of NOCl added to the reaction flask in (C) and allowed to stand again for 18 hours. 2.3 grams $CF_3CF_2CF_2NO$, about 10% conversion. No $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}Cl$ found on distillation.

E. 35 grams anhydride + 10 grams NOCl allowed to sit overnight at all times in the dark. On heating a trace of nitroso compound formed.

F. 30 grams anhydride + 9 grams NOCl were placed near a 100-watt bulb for 1 1/2 hours. On heating .6 gram nitrose formed about 5% conversion.

(10) 41 grams anhydride + 13 grams NOCl were placed in a double tough pyrex 300 ml. tube (evacuated) affixed with a pressure gauge. U. V. lamp was applied for 2 days at which time the original pressure of 35 lbs. rose to 105 lbs. The tube was bled yielding traces of $CO_2$, NO, NOCl, and a blue gas.

The tube was opened and upon heating to about 140°C, 2.0 grams of $CF_3CF_2CF_2NO$ were obtained, about 10% conversion.

(11) Prepared 200 grams perfluoro acetic anhydride

Perfluoro acetic acid refluxed and distilled over $P_2O_5$ to yield the anhydride.

$CF_3COOH$ B. P. 65°

$(CF_3\overset{O}{\overset{\|}{C}})_2O$ B. P. 35° at 630 mm.

(12) Isolation and Identification of a reactive intermediate believed to be $CF_3-\overset{O}{\overset{\|}{C}}NO$.

112 grams ( .5 mole) $CF_3\overset{O}{\overset{\|}{C}}OAg$ + 52 grams ( .8 mole) NOCl were mixed in a 250 ml. flask at between -40 and -30°C. The mixture was shaken for five minutes and then pumped into a dry ice trap while heating the reaction vessel to 60°C. Evacuation continued for about five hours.

Material collected was then distilled. 30-32 grams of NOCl collected and then reduced pressure was applied. After two hours, equilibrium in the column was obtained and the temperature of the head rose to 60°C at 133 mm. pressure. Refluxing continued while the pot temperature remained steady at 79°-81° and 25 grams of material was collected at 63-64.5°C and 133 mm Hg.

The pure material was a yellow-brown fuming liquid which decomposes in $Et_2O$, Acetone, (turns blue and then colorless), and $H_2O$.

Its physical properties are listed below

B. P. 63-64.5°C at 133 mm. $n_D^{25}$ 1.3770 density 1.5932 at 24°C.

(13) Identification of the above now in progress. Attempts to obtain a similar intermediate upon reacting $C_3F_7COOAg$ and NOCl were unsuccessful. $C_3F_7CO\text{-}COC_3F_7$ was the only product isolated and identified.

## V. Plans for Future Work

Research will be continued to finding new and improving old methods for the preparation of $R_fNO$ and other similar related compounds. Of especial interest at this time is the preaparation of larger amounts of $CF_3CF(NO)\text{-}CF_2(NO_2$, $CF_2{=}CF\text{-}NO$ and $CF_2{=}CF(NO_2)$. A portion of the time will also be devoted to the study of the preparation of fluorinated ethers, imines and epoxides.