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Rubber Research

The Synthesis of Unsaturated Fluorocarbons

Progress Report

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For the Period February 13, 1960 to May 13, 1960

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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 themal stability at high temperatures.

This research is authorized under Contract No. DA-19-129-QM-1263. This is the seventh quarterly report for the period February 13, 1960 through May 13, 1960.

II. Summary of Current Progress

Work is still in progress in attempts to synthesize dinitroso derivatives of fluoroolefins. Various intermediates have been prepared to explore new reactions in attempts to prepare dinitroso derivatives.

Satisfactory progress has been made in the "catalytic" addition of NOCl to fluoroolefins so that data for a pilot stage scale-up is possible. This information has been forwarded to Minnesota Mining and Manufacturing Company for use in developing a pilot plant operation for the fluoroelastomer program under Dr. B. Landrum and Dr. G. Crawford.

Satisfactory progress has been made in the syntheses and proofs of structure of CF_2Cl-CF_2NO, $CF_2(NO_2)-CFCl(NO)$, $CF_2(NO_2)-CFCl_2$, $CF_2(NO_2)-CFCl(NO_2)$, $CF_2Cl-CF_2NO_2$, $CF_2NO-CF_2NO_2$, $CF_2(NO_2)-CF_2NO_2$, $CF_2Cl-CF_2-\underbrace{N-O-CF_2-CF_2}$, CF_2Cl-CF_2ONO.

Preliminary work has been carried out on the addition of NOCl to $CF_2=CCl_2$ and $CF_3CF=CF_2$. These will be reported in detail in the next progress report.

During this period 380g. of relatively pure CF_2Cl-CF_2NO were packaged and shipped to Dr. G. Crawford of the Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

Work has also been in progress for making various other nitroso and dinitroso compounds as well as work on the synthesis of some fluorinated imines for evaluation in the elastomer program.

III. Discussion

In line with our plans given in previous progress reports, we are placing greater emphasis on the study of nitroso chemistry with particular emphasis on finding new routes to making R_fNO and aliphatic fluorinated dinitroso compounds. Some portion of our effort will also be directed toward the sythesis of fluorines containing imines and epoxides.

Our studies on the addition of NO and NOCl on fluoroolefins over ferric chloride leads us to the following conclusions:

1) Maximum yields of CF_2Cl-CX_2NO are obtained when the reaction of the olefin is carried out with NOCl in stoichiometric proportions at high contact times under thermal conditions.

2) Temperature and ratio of reactants play important roles in the distribution of the products formed.

Photochemical reactions between the olefin and NO or NOCl led to products other than the desired nitroso compounds.

EXPERIMENTAL SECTION

Reactions of Fluoroolefins with Nitric Oxide or Nitrosyl Chloride over Ferric Chloride. Construction of the Reactor Tube.

A 3 foot x 20mm pyrex glass tube wound with a heating wire was packed firmly with a 50-50 mixture of powdered anhydrous ferric chloride and 25-75 mesh powdered glass. (The function of powdered glass was to render the packing porous.) Each end of the tube was plugged with glass wool and with a rubber stopper provided with a 5 inch x 8mm glass outlet. This reactor tube was then inserted in a glass jacket. A thermometer was placed between the jacket and the reactor. Plastic tubing was attached to each end of the reactor, one end leading to the product receiver and the other leading to a "T"-tube where the gaseous reactants were premixed. The product receiver was a trap immersed in a dry ice-butylcellosolve bath.

Reaction of $CF_2=CFCl$ with Nitric Oxide and Ferric Chloride at 45°C.

A ferric chloride reactor tube constructed in the manner described above was heated at 100°C and flushed with dry nitrogen for fifteen minutes. The temperature then was lowered to 45°C. and 117 grams (one mole) of $CF_2=CFCl$ by volume were passed through the tube over a period of 24 hours. The ratio and rate of throughput of reactants was roughly measured by means of the two heavy mineral oil bubblers which were mounted between the "T"-tube and the reactant containers. The ratio of the two gases was so adjusted that a very slight excess of olefin was used; that is $2NO < CF_2=CFCl$. The temperature of the tube was maintained at 45°C throughout the reaction period. The product was blue in color and was collected in a trap immersed in a dry-ice butylcellosolve bath. During the course of the reaction a small quantity of a colorless gas that was not condensable at the Dry Ice bath temperature was continuously escaping from the product receiver. As the gaseous reactants were fed in the ferric chloride tube the color of the packing started changing from brownish-black to light brown. This color change traveled slowly along the packing and just before all the olefin was used in the reaction the entire length of the packing had changed its color. At this point the color of the outcoming product also started changing from deep blue to blue-green to green. The crude product (165 grams) was fractionated in a 3-foot low-temperature distillation column which was previously flushed with nitrogen. During the first stages of fractionation a very slow stream of dry nitrogen was passed through the column in order to chase out any dissolved nitric oxide and also to prevent entrace into the system of atmospheric oxygen. The fractionation products were the following:

(a) 12 grams of a fraction bp -30° to +20°/630mm which was green in color and consisted of at least three compounds; namely, the starting olefins $CF_2=CFCl$ (50%), the acid fluoride $ClCF_2COF$, and perhaps the nitrite $ClCF_2CFClONO$. (See below).

(b) 114 grams (71.3%)* of an intensely blue liquid b.p. 31.7°/630mm, 0°/mm n_D^0 1.3455, d_4^0 1.5422, M.W., calcd. for $CF_2ClCFClNO$: 182; found: 180.

Molar refractions calcd. for $ClCF_2CFClNO$, 25.44, obsd. 24.96. No consistent analytical results could be obtained for this compound. Unequevocal proof for its structure and constitution was established by a comparison of its physical constants and its infrared spectrogram with those of the same compound prepared by Professor Tarrant** from $ClCF_2CFClI$ and nitric oxide.

(c) 13 grams (8.12%) of a colorless liquid b.p. 41-42°/630mm, 7°/139mm, n_D^{25} 1.3557, d_4^{25} 1.5629, M.W. Calcd for $CF_2Cl-CFCl_2$: 188, found 188.

The infrared spectrogram of this compound was superimposable on that of $ClCF_2CFCl_2$ which is commercially available; all physical constants of this compound also are in agreement with those of $ClCF_2CFCl_2$.

(d) 3 grams (.87%) of an intensely blue liquid, b.p. 9-13°/90mm, 62°/630mm, which was shown by vapor phase chromatography to be 98% pure, n_D^{25} 1.349, d_4^{25} 1.5494, M.W. Calcd for

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*Unless otherwise stated percentages in yield reported henceforth are based on total weight of the mixture of products obtained minus the unreacted starting material.

**P. Tarrant, University of Florida, personal communication.

$CF_2(NO_2)$-CFClNO: 192; found 188.

Molar refraction calcd for $O_2NCF_2CFClNO$; 25.53; obsd. 26.18.

Consistent analytical results for this compound could not be obtained. Structure proof was based upon oxidation to $O_2NCF_2CFClNO_2$ and upon analysis of its nuclear magnetic resonance spectra which indicated the presence and location of both the -NO and -NO_2 groups.

(e) 12 grams (7.5%) of a colorless liquid, b.p. 70.5-71.5°/630mm, n_D^{25} 1.3669, d_4^{25} 1.6199, M.W. 199.

Molar refraction calcd for $O_2NCF_2CFCl_2$: 26.8; obsd. 27.5

Anal. Calcd for $C_2Cl_2F_3NO_2$: C, 12.12; N, 7.07; Cl, 35.85; F, 28.8

Found: C, 12.44; N, 6.97; Cl, 35.67; F, 28.5

The structure of this compound is assigned as $O_2NCF_2CFCl_2$ on the basis of nuclear magnetic resonance evidence and by the fact that its freezing point and infrared spectra differ from that of $ClCF_2CFClNO_2$ whose structure has been established unequevocally.

(f) 3 grams (1.87%) of a colorless liquid, b.p. 94.5°/630mm, n_D^{25} 1.375, d_4^{25} 1.6704.

Molar refraction calcd. for $O_2NCF_2CFClNO_2$; 27.8, obsd. 28.3

Anal. calcd. for $C_2ClF_3N_2O_4$: C, 11.48; N, 13.39; Cl, 16.98; F, 27.22.

Found: C, 11.69 N, 13.07 Cl, 17.32 F, 27.42

This compound has been prepared recently by Hasseldine who reported the following physical constants; b.p. 98-99°/750mm, n_D^{25} 1.3748, d_4^{25} 1.674.

(g) 6 grams (5%) of higher boiling, non-distillable material.

Reaction of $CF_2=CFCl$ with Nitric Oxide and Ferric Chloride at 80-110°C.

This experiment was carried out exactly in the same way as the preceding one. A freshly packed ferric chloride reactor tube was employed; the temperature of the reactor was maintained between 80° and 110°C. 117 Grams (one mole) of $CF_2=CFCl$ and approximately two moles of nitric oxide were passed through the reactor over a period of 24 hours. The ferric chloride packing in the tube again changed its color as the reaction proceeded. At the higher limit of temperature the light-brown iron complex which developed in the reactor as the gaseous mixture of the starting materials were passed through began to melt. Therefore, it was necessary to keep the temperature lower than 110°C. Under these conditions, the color change in the ferric chloride packing proceeded along the length of the tube at a faster rate than in the previous experiment. During the first 8 to 10 hours of the reaction, the outcoming product was condensing in the receiver to a deep blue liquid. Some gaseous material which was noncondensable at the Dry Ice temperature was escaping from the receiver. At about the end of the tenth hour the entire length of the reactor packing changed its color from brownish-black to light brown. At this point the blue color in the product started fading and developed to green; the evolution of the noncondensable gaseous material increased considerably.

The crude product weighed 155 grams and contained some suspended solid substance. The gaseous material in the product was vaporized into another trap; the remaining liquid was chilled and filtered from the suspended white solid (N_2O_4?). The two parts were then combined and fractionated on a three foot low temperature distillation column.

The following products were obtained:

(a) 15 g CF_2=CFCl b.p. -31/630mm

(b) 14 g (10%) $ClCF_2COF$ b.p. -22.5/630mm. This was identified by its infrared spectra and by conversion to $ClCF_2CO_2C_2H_5$.

(c) 12 g (6.5%) of a blue-green liquid. b.p. 15-25°/630mm. The blue color was due to $ClCF_2CFClNO$ which was a contaminant. Infrared spectra of this sample indicated that the compound could be a nitrite, most likely $ClCF_2CFClONO$. The characteristic absorption bands for the -ONO group were present in the infrared spectrogram. For this compound these bands are at 5.5μ, 5.75μ and 6.2μ. A structure proof is described later.

At this point the liquid in the distillation flask was chilled, washed with ice water (to remove NO_2) and dried over calcium chloride. Fractionation was then continued.

(d) 30 g (21.4%) of $ClCF_2CFClNO$. b.p. 31.7°/630mm.

(e) 25 g. (17.8%) of $ClCF_2CFCl_2$. b.p. 41-42°/630mm.

(f) 6 g (4.3%) of $O_2NCF_2CFClNO$. b.p. 10-12°/90mm.

(g) 31 g. (22.2%) of $O_2NCF_2CFCl_2$. b.p. 70.5-71.5°/630mm.

(h) 3 g. (2.1%) of $O_2NCF_2CFClNO_2$. b.p. 94.5°/630mm.

(i) 19 g. (13.5%) of a higher boiling, nondistillable material.

Reaction of $CF_2=CFCl$ with Ferric Chloride and excess Nitric Oxide at 45°-55°C.

One mole (117 grams) of $CF_2=CFCl$ and nitric oxide in a ratio of slightly more than two molecular proportions of NO to one of olefin were passed through a ferric chloride reactor described on page 3-4 over a period of 24 hours at a temperature of 45 to 55°C. The change in color of the ferric chloride packing was again observed as the reaction proceeded and considerable gaseous material noncondensable at Dry Ice temperatures was lost; part of this gas was unreacted nitric oxide. The product condensing in the Dry-Ice cooled receiver was blue but soon changed to green. At the end of the reaction the collected product weighed 159 grams. The gaseous material in the product was passed through water and a calcium chloride tube and collected in another trap. The liquid portion was chilled, washed with ice water, and dried over calcium chloride. The two combined reactions weighed 144 grams. Thus 15 grams of the product was lost in the wash water. The wash water gave a test for chloride ion as well as for fluoride ion. The 15 grams of product lost in the wash water was a mixture of $ClCF_2COF$ and $ClCF_2CFClONO$

which was converted to the acid $ClCF_2CO_2H$, isolated as the ethyl ester. (See below). Distillation of the product yielded the following:

(a) 8 g. $CF_2=CFCl$ b.p. -31°/630mm

(b) 40 g. (29.5%) $ClCF_2CFClNO$ b.p. 31.7°/630mm.

(c) 38 g. (28%) $ClCF_2CFCl_2$ b.p. 41-42°/630mm.

(d) 4 g. (2.9%) $O_2NCF_2CFClNO$ b.p. 9-13°/90mm.

(e) 45 g. (33%) $O_2NCF_2CFCl_2$ b.p. 71.5°/630mm.

(f) 4 g. (2.9%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm.

(g) 5 g. (3.7%) higher boiling, nondistillable material.

Reaction of $CF_2=CFCl$ with Nitric Oxide over previously reacted (spent) Ferric Chloride.

In this experiment a ferric chloride reactor tube was employed which had been previously used in one of the former experiments until the entire length of the packing had changed its color to light brown.

One mole (117 grams) of $CF_2=CFCl$ and nitric oxide in a ratio of 2NO to slightly more than one olefin were passed through the tube at 45-50°C over a period of 24 hours. The product condensing in the receiver was green in color; a small quantity of a gaseous material noncondensable in the dry ice cooled receiver was continuously escaping from the latter. The crude product collected at the end of the reaction weighed 159 grams. The gaseous components in the product were fractionated through a 3 foot low temperature distillation column. The following were obtained:

(a) 19 g. $CF_2=CFCl$ b.p. -31°/630mm

(b) 17 g. (13.6%) $ClCF_2COF$ b.p. -22.5°/630mm

(c) 13 g. (9.3%) of a light blue liquid b.p. -10 to + 25°/630mm.

This was mainly $ClCF_2-CFClONO$ with some $ClCF_2CFClNO$. At this point the remaining liquid in the distillation flask was chilled, washed with ice water, dried over calcium chloride; then distilled.

(d) 30 g. (21.4%) $ClCF_2CFClNO$ b.p. 31.7°/630mm.

(e) 29 g. (20.8%) $ClCF_2CFCl_2$ b.p. 41-42°/630mm.

(f) 5 g. (3.6%) $O_2NCF_2CFClNO$ b.p. 10-13°/90mm.

(g) 37 g. (26.4%) $O_2NCF_2CFCl_2$ b.p. 71.5°/630mm.

(h) 2.5 g. (1.8%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm.

(i) higher boiling, and nondistillable residue.

Reaction of $CF_2=CFCl$ with Nitric Oxide over Activated Carbon (Coconut Shell).

About 117 grams (one mole) $CF_2=CFCl$ and nitric oxide in a ratio of 2NO:1 $CF_2=CFCl$ were passed over a period of 20 hours at room temperature through a 3 foot x 20mm pyrex glass tube packed tightly with coarse coconut shell carbon. The experimental setup was similar to the ones in which ferric chloride was employed as the reactor packing. During the reaction appreciable quantities of a gas which was not condensable in the dry ice cooled trap was continuously escaping. Much of this gas was unreacted nitric oxide and perhaps some CF_2CFCl and $ClCF_2COF$.

There was a vigorous exothermic reaction on the surface of the carbon packing as the gaseous mixture of the reactants were coming into contact with the former, and the temperature at this spot was about 100°C. The hot spot traveled along the length of the packing as the gaseous mixture was passed through, and when it reached the other end of the packing the reaction practically ceased. During the reaction extensive carbon-fluorine bond cleavage must have occurred because the reactor glass tubing was badly etched. A glass vessel in which the carbon packing was subsequently stored also was badly etched. The blue-green product which weighed 152 grams was washed with water and dried over calcium chloride. 21 grams of this product was lost in the wash water. The latter gave a test for chloride ion and for fluoride ion, and from it the acid $ClCF_2CO_2H$ was isolated in the form of its ethyl ester. (See below).

Distillation of the remaining 131 grams of product gave the following fractions.

(a) 51 g. CF_2=CFCl b.p. -31°/630mm.

(b) 12 g. (15%) $ClCF_2CFClNO$ b.p. 31.7°/630mm.

(c) 14.5 g. (18.1%) $ClCF_2CFCl_2$ b.p. 41-42°/630mm.

(d) 19 g. (23.8%) $O_2NCF_2CFClNO$ b.p. 10-13°/90mm.

(e) 20 g. (25%) O_2NCFCl_2 b.p. 70.5-71.5°/630mm.

(f) 7 g. (8.75%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm.

(g) 7.5 g. (9.35%) residue.

Reaction of CF_2=CFCl with Nitric Oxide over Ferric Fluoride.

This reaction was not investigated extensively.

A 3 foot x 20mm [illegible] tube was packed with a 50-50 mixture of powdered anhydrous ferric fluoride and 25-75 mesh powdered glass. Passage through this medium of nitric oxide and $CF_2=CFCl$ in ratios varying from $1NO:2CF_2=CFCl$ to $2NO:1CF_2=CFCl$ and at temperatures ranging from 22° to 150°C resulted in some reaction but most of the nitric oxide was escaping from the system carrying along some of the unreacted olefin. When a very small quantity of air was premixed with the olefin and nitric oxide a larger percentage of the reactants combined, but still considerable quantities of unreacted material, mostly NO, were escaping from the system. The maximum reaction was obtained at 75-90°C and at a ratio of $4NO:2CF_2=CFCl:2$ air. 117 grams of $CF_2=CFCl$ was processed in this manner. The blue-green product was washed with water, and dried with calcium chloride. The wash water gave a test for both chloride and fluoride ions, and was strongly acidic. Distillation of the product, which weighed 133 grams, after washing, gave the following fractions.:

(a) 59 g. $CF_2=CFCl$

(b) 16 g. (21.6%) of an intermediate cut b.p. 10-45°/630mm.

(c) 34.5 g. (46.6%) $O_2NCF_2CFClNO$ b.p. 10-12/90mm b.p. 62-63°/630mm.

(d) 5 g. (6.76%) of an intermediate cut b.p. 65-80°/630mm.

(e) 3 g. (14%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm.

(f) 12.5 g. (16.9%) higher boiling, nondistillable residue.

Attempted Reaction of $CF_2=CFCl$ with Nitric Oxide and Iodine over Carbon.

A 3 foot x 20 mm pyrex glass tube provided with a heating wire was packed with a mixture of iodine granules and coarse coconut shell carbon in a ratio of 1:1 by volume. The tube was heated at 100-110°C while trifluorochloroethylene and nitric oxide in equimolar proportions were passed through the tube slowly. (The experimental setup for this reaction was the same as described previously.) As the gaseous mixture of the reactants was passed through the tube the latter became blue; the product condensing in the dry ice cooled trap was colorless, however. Subliming iodine carried along with the gaseous mixture started accumulating at the outlet and soon was plugged. The product in the trap contained unreacted $CF_2=CFCl$ and a higher boiling liquid whose constitution was not investigated. (This will be further investigated.)

In another attempt, a 2 foot x 20mm glass tube was packed to one-half its length with iodine and the other one-half with coconut shell carbon. The gaseous mixture of $CF_2=CFCl$ and NO were fed into the tube from the side containing the iodine. No reaction was observable until the tube temperature reached 100-110°C. At this temperature a blue product was formed. This experiment will be investigated further.

Oxidation of $ClCF_2CFClNO$ to $ClCF_2CFClNO_2$.

In a 500 ml. 3-neck flask provided with a stirrer, a dropping funnel and a thermometer were placed 50 g. (0.24 mole) of sodium dichromate, 150 ml of glacial acetic acid, and 50 g. of concentrated sulfuric acid. The mixture was cooled to about 10°C with ice water and while stirring vigorously 56 g (0.38 mole) $ClCF_2CFClNO$ was added dropwise over a period of one-half hour. Stirring was continued for 5 hours at 5-10°C and then for another 2 hours at room temperature. The reaction mixture was then mixed with 600 ml. ice cold water in a separatory funnel. The organic layer which settled in the bottom was drawn off, dried over calcium chloride and distilled. 5 grams of unreacted $ClCF_2CFClNO$ was recovered. The product $ClCF_2CFClNO_2$ weighed 50 grams (90%) b.p. 71-72/630mm, n_D^{25} 1.3692, d_4^{25} 1.6162, m.p. ~ -35°C, M.W. calcd. for $C_2F_3Cl_2NO_2$; 198, found 196.7.

Anal. Calcd. for $C_2F_3Cl_2NO_2$: C, 12.12; N, 7.07; Cl, 35.86; F, 28.78.

Found: C, 11.87; N, 7.23; Cl, 35.58; F, 28.56.

Oxidation of $O_2NCF_2CFClNO$ to $O_2NCF_2CFClNO_2$.

In a 250 ml. 3-neck flask provided with a stirrer, a dropping funnel, and a thermometer were placed 25 g. (0.12 mole) of sodium dichromate, 80 ml. of glacial acetic acid, and 30 g. of concentrated sulfuric acid. The mixture was cooled to about 10°C with ice and while stirring vigorously 38 g. (0.197 mole) $O_2NCF_2CFClNL$ was added slowly over a period of one-half hour. Stirring was continued for 5 hours at 5-10°C and then for another 2 hours at room temp rature. The reaction mixture was then mixed with about 400 ml. cold water in a separatory funnel. The organic layer which settled at the bottom was drawn off, dried over calcium chloride, and distilled. The product, 29 g. (70.5% of theoretical), b.p. 95°/630mm, n_D^{25} 1.3749, d_4^{25} 1.6699, gave an infrared spectrogram which was superimposable on that from the same compound obtained directly from the reaction of CF_2=CFCl with NO over ferric chloride.

Thermal disproportionation of $ClCF_2CFClNO$.

About 25 grams of $ClCF_2CFClNO$ was placed in an evacuated double wall pyrex tube provided with a pressure gauge. The tube was heated in the dark at 100°C for 15 hours. The pressure which developed during heating did not all disappear when the tube was cooled to room temperature. The contents had changed its color from blue to green.

The reaction tube was attached to a Dry Ice cooled trap in which the gaseous products were condensed; a very small quantity of a gas which did not condense at the dry ice temperature was lost. Infrared spectra of the material condensed in the trap showed the presence of the nitrite group -ONO and the presence of the carbonyl group. Gaseous and liquid products were washed with water and dried with calcium chloride. The wash water gave a test for both chloride and fluoride ions. Distillation gave a small fraction, b.p. -10 to 20°/630mm, a very small quantity of starting material $ClCF_2CFClNO$, 11 grams of $O_2NCF_2CFCl_2$, b.p. 70.5-71.5°/630mm, n_D^{25} 1.3668, d_4^{25} 1.62, M.W. calcd. for $CF_2(NO_2)CFCl_2$: 198. Found, 197 (identified also by its infrared spectra) and 2 grams of higher boiling residue.

This change in $ClCF_2CFClNO$ was also effected photochemically.

Attempted dehalogenation of $ClCF_2CFClNO$.

In a 250 ml. 3-neck flask equipped with a stirrer, a dropping funnel, and a reflux condenser were placed 200 ml. of freshly distilled pyridine and 20 g. of zinc dust. The reflux condenser was connected to a trap cooled with a dry ice-butylcellosolve bath. The reaction flask was cooled with ice. 20 grams of $ClCF_2CFClNO$ was added dropwise while stirring vigorously. A very vigorous exothermic reaction ensued immediately but no gaseous material was evolved from the reaction mixture. (The presumed product was expected to be a blue gas with a b.p. around -25°C.) As addition of the starting material to the zinc suspension was continued the reaction mixture became progressively more viscous and at the end stirring was impossible. No product was isolated.

Attempted Dechlorination of $ClCF_2CFClNO_2$.

An attempt to dechlorinate $ClCF_2CFClNO_2$ to $CF_2{=}CFNO_2$ with zinc dust in pyridine following the above procedure resulted in a vigorous reaction, but no distillable product was obtained.

Attempted Dehalogenation of $O_2NCF_2CFCl_2$.

An attempt to dehalogenate $O_2NCF_2CFCl_2$ to $O_2NCF{=}CFCl$ with zinc dust in pyridine, and with zinc dust in dibutoxytetraethylene glycol was unsuccessful. No reaction occurred in either solvent at room temperature. Heating at 72°C (the boiling point of $O_2NCF_2CFCl_2$) for 5 hours resulted in a partial reaction but no material with a boiling point lower than 72°/630mm was obtained. More than 50% of the starting material was recovered from both solvents and zinc. No distillable product was obtained.

Conversion of the mixture of $ClCF_2COF$ and $ClCF_2CFClONO$ to $ClCF_2CO_2C_2H_5$.

In a 250 ml. 3-neck falsk equipped with a stirrer, a fritted bubbler, and a condenser was placed 80 ml. of absolute ethanol. The flask was chilled to about -20°C and while stirring 100 g. of concentrated sulfuric acid was added very slowly. The mixture was then warmed to 0°C and was kept at this temperature during the reaction period. The condenser was attached to a trap cooled by a dry ice-butylcellosolve bath.

20 grams of the green liquid fraction b.p. -20 to +22° collected from the various experiments described above (from the reactions of $CF_2=CFCl$ with nitric oxide and ferric chloride was bubbled through the fritted tubing into the sulfuric acid-ethanol mixture while stirring vigorously. The material that was collected in the dry-ice cooled trap was reprocessed three times through the reaction mixture. About 2-3 g. of a gaseous material which did not react after the third passage through the sulfuric acid ethanol mixture was shown to be $CF_2=CFCl$.

Stirring was continued for one-half hour at room temperature and then at 50° for one hour. Some ethyl ether was produced. The reaction mixture was then mixed with 500 ml. of ice water in a separatory funnel. The organic layer which settled at the bottom was drawn off and dried over magnesium sulfate. Distillation gave 21 grams of $ClCF_2CO_2C_2H_5$ b.p. 91-93°/630mm, n_D^{25} 1.3620, d_4^{25} 1.2512.

Molar refraction calcd for $ClCF_2CO_2C_2H_5$: 25.5, Found 25.2.

The infrared spectrogram of this ester was superimposable on that of the same compound from a commerical source.

Indentification of the acid dissolved in the wash water of the products of the reaction of $CF_2=CFCl$ with NO over $FeCl_3$.

The wash water obtained after washing the product of two runs of the reaction of $CF_2=CFCl$ with nitric oxide and ferric chloride was neutralized with dilute sodium hydroxide solution and evaporated to dryness on a steam bath and then in an oven at 100°C for 8 hours. 40 g. of a white solid was obtained. This solid which consisted of NaCl, NaF, and $ClCF_2CO_2Na$ was suspended in 70 ml. of absolute ethanol and the mixture was cooled to about -20°C. 50 grams of concentrated sulfuric acid was then added slowly while stirring vigorously. The reaction mixture was brought to room temperature and then heated to 50°C for 5 hours while stirring. Some ethyl ether was produced during this period. The flask was brought to room temperature and its contents shaken with 500 ml. ice cold water in a separatory funnel. The organic layer which settled was drawn off and dried over magnesium sulfate. Distillation gave 18 grams of $ClCF_2CO_2C_2H_5$, b.p. 91-93°/630mm, n_D^{25} 1.363, d_4^{25} 1.2512. The infrared spectrogram of this ester was identical to that of the same ester from a commercial source.

Reaction of $CF_2=CFCl$ and Nitric Oxide under pressure.

About 117 g. (one mole) $CF_2=CFCl$ was placed in an evacuated 500cc autoclave which was cooled to -78°C in a Dry Ice-butylcellosolve bath. 2 moles of nitric oxide was then compressed in.

The autoclave was brought to room temperature and was allowed to stand at 22°C for 24 hours. At the end of this period the autoclave was attached to a dry ice cooled trap and the pressure was slowly released. A small quantity of gaseous material condensed to a blue liquid in the trap during this operation; a colorless gas which did not dissolve in water, dilute gas, or dilute acid, and which did not condense at the dry ice temperature was lost through the trap. 160 grams of a blue liquid was collected from the autoclave and the trap. The crude product was washed with water and dried with calcium chloride. The wash water gave a test for both chloride and fluoride ions and was strongly acidic. The product weighed 142 grams after washing. Thus, 18 grams of the product dissolved in water. Distillation of the blue liquid gave the following fractions:

(a) 5 g. $CF_2{=}CFCl$ b.p. -31°/630mm

(b) 5 g. (3.64%) $ClCF_2CFClNO$ b.p. 31.7°/630mm

(c) 6 g. (4.37%) $ClCF_2CFCl_2$ b.p. 41-42°/630mm

(d) 20 g. (14.6%) $O_2NCF_2CFCl_2$ b.p. 70.5-71.5°/630mm

(e) 8.5 g. (6.1%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm

(f) 97.5 g. (71%) higher boiling, nondistillable material.

Attempted Photochemical Reaction of $CF_2{=}CFCl$ with Nitric Oxide.

An evacuated 5 liter flask provided with a 3-way ground glass stopcock was filled with $CF_2{=}CFCl$ and nitric oxide in a ratio of 1 $CF_2{=}CFCl$:2 NO. One end of the stopcock was attached to a manometer. The pressure in the flask was kept at 1200 mm Hg. The flask was irradiated with two ultraviolet lamps. After about one-half hour of irradiation, a blue color developed and liquid started condensing on the walls of the flask. Accumulation of the liquid at the bottom of the vessel was quite slow; the pressure, however, did not seem to be reduced in proportion to the quantity of liquid formed. The stopcock was attached to a trap immersed in liquid air and the volatile contents of the flask were pumped out. After this operation the trap was removed from the liquid air bath and was brought to about 0°C while the volatile material in it was allowed to go back into the flask. Thus, any nitrogen produced during the reaction was removed. More nitric oxide and olefin were added in the flask and the reaction was continued with intermittent withdrawal of the volatile components into a liquid air cooled trap and pumped down. This procedure was continued until 50 grams of a blue product was obtained. The walls of the reaction flask were covered with a thin layer of a white solid which filled the evacuated flask with brown fumes (NO_2?).

Distillation of the product gave no well-defined fraction, the temperature of the distillation flask rose continuously and at 160°C decomposition was evident. Throughout the distillation a green gas was escaping from the column and was condensing in a dry ice cooled trap to a green liquid. This liquid reacted vigorously with water. The resulting water solution gave a test for both chloride and fluoride ions and was strongly acidic. The column and distilling head were covered with a white solid which also reacted with water, and gave off brown fumes (NO_2?).

A colorless fraction b.p. 102-105°/630mm reacted with water and gave off a blue gas. This reaction was not further investigated but will be studied later.

Reaction of CF_2=CFCl with NOCl over $FeCl_3$ at 45°C.

About 125 g. (1.12 moles) of CF_2=CFCl and 66 g. (one mole) of NOCl were passed through a freshly packed ferric chloride reactor over a period of 24 hours at 45°C. The rate of throughput and ratio of the two gases were controlled by two heavy mineral oil bubblers. The ratio of the two reactants was so adjusted that the olefin was always in slight excess over NOCl. The product was condensing in a dry ice cooled trap to a deep blue liquid; practically no gaseous material was escaping from the trap. At the spot where the gaseous mixture of the reactants came in contact with the packing a vigorous exothermic reaction ensued and the temperature of this spot was at about 100°C. This hot spot traveled along the length of the tube concurrently with a color change in the packing which turned from black-brown to light brown. At the end of the reaction the reactor was flushed with a slow stream of nitrogen in order to chase out the last traces of product from the packing. The crude product which weighed 180 grams was washed with water and dried with calcium chloride; 14 grams of the product was absorbed by the water during washing. The wash water gave a test for both chloride and fluoride ions, and from it the acid $ClCF_2CO_2H$ was isolated in the form of its ester. Fractionation of the remaining 166 grams of product yielded the following fractions:

(a) 12 g. $CF_2=CFCl$ b.p. -31°/630mm.

(b) 129.5 g. (78%) $ClCF_2CFClNO$ b.p. 31.7°/630mm

(c) 4.5 g. (2.7%) $ClCF_2CFCl_2$ b.p. 41-42°/630mm

(d) traces of $O_2NCF_2CFClNO$ b.p. 70.5-71.5°/630mm

(e) 12 g. (7.24%) $O_2NCF_2CFCl_2$ b.p. 62-63°/630mm

(f) 1.2 g. (0.72%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm

(g) 5 g. (3%) higher boiling, nondistillable material.

In order to identify the nature of the compounds which were absorbed by water during washing of the crude product, another similar experiment was carried out and the product was directly fractionated without washing. The above results were reproduced; a fraction b.p. -31 to +20°/630mm was collected first. This was a mixture of $CF_2=CFCl$, $ClCF_2COF$, with some $ClCF_2CFClONO$ and traces of $ClCF_2CFClNO$. The olefin and the acid fluoride were separated from this mixture and were characterized. The nitrite was not isolated in a pure state but its presence was indicated by infrared spectra.

Reaction of $CF_2=CFCl$ with NOCl over $FeCl_3$ at 90°C.

About 125 g. (1.12 moles) of $CF_2=CFCl$ and 66 g. (one mole) NOCl were passed through a freshly packed ferric chloride reactor over a period of 24 hours, at about 90°C. The rate of throughput and ratio of the two gases were controlled by means of two heavy mineral oil bubblers. The product condensing in the dry ice cooled receiver was blue-green in color; an appreciable quantity of gaseous material which was not condensable at the dry ice temperature was escaping from the product receiver. At the end of the reaction the reactor tube was flushed with a slow stream of nitrogen in order to remove the last traces of product from the packing. The crude product weighed 175 grams which upon fractionation on a 3 foot distillation column gave the following:

(a) 18 g. $CF_2=CFCl$ b.p. -31°/630mm

(b) 12 g. (7.15%) $ClCF_2COF$ b.p. -22.4°/630mm

(c) 5 g. (3.18%) of a fraction b.p. -5 to +25°/630mm

This was a mixture of $ClCF_2CFClONO$, $ClCF_2CFClNO$, and perhaps some NOCl.

(d) 37 g. (23.6%) $ClCF_2CFClNO$ b.p. 3.17°/630mm

(e) 40 g. (25.5%) $ClCF_2CFCl_2$ b.p. 41-42°/630mm

(f) traces of $O_2NCF_2CFClNO$ b.p. 62-63°/630mm

This compound undergoes decomposition when distilled at atmospheric pressure.

(g) 52.5 g. (33.4%) O_2NCF_2CFCl b.p. 70.5-71.5°/630mm

(h) 2 g (1.27%) $O_2NCF_2CFClNO_2$ b.p. 94.5°/630mm

(i) 7 g. (4.45%) higher boiling, nondistillable material.

(A)Reaction of $CF_2=CFCl$ with excess NOCl over $FeCl_3$ at 45°C.

A freshly packed ferric chloride tube was employed. The reaction was carried out at 45°C. The ratio of reactants was adjusted so that a slight excess of NOCl was used. 117 g. (one mole) of $CF_2=CFCl$ and 75 g. (1.136 moles) of NOCl were reacted over a period of 23 hours. The products obtained upon fractionation of the reaction mixture were the same, with practically the same distribution, as the ones shown in the above experiment carried out at 45°C.

(B)Reaction of $CF_2=CFCl$ with NOCl over Spent $FeCl_3$ at 45°C.

When equimolar quantities of $CF_2=CFCl$ and NOCl were passed at 45°C through a ferric chloride reactor which was previously employed in another similar reaction until the packing had changed its color, the conversion was not quantitative and the yield of $ClCF_2CFClNO$ was again quite low (25%). The yields of the other products were increased: $ClCF_2COF$ (12%); $O_2NCF_2CFClNO$ (5%); $O_2NCF_2CFCl_2$ (35%).

Photochemical Reaction of $CF_2=CFCl$ with NOCl

Exactly 30 g. (0.256 moles) of $CF_2=CFCl$ and 16.8 g. (0.256 moles) of NOCl were placed in an evacuated heavy wall pyrex tube. The tube was sealed and was exposed to an ultraviolet lamp for 2.5 hours. The reaction started in about 15 minutes and was very exothermic. At the end of 2.5 hours the tube was cooled to -75°C. with Dry Ice and was opened. Even at this low temperature some gaseous material escaped from the tube when the seal was broken. The contents were washed with water and dried with calcium chloride. 42 grams of crude product were obtained which on distillation gave 7 g. unreacted $CF_2=CFCl$, b.p. -31°/630mm, 10 g. (28.6%) $ClCF_2CFCl_2$, b.p. 41-42°/630mm, 21 g. (60%) $O_2NCF_2CFCl_2$, b.p. 70.5-72°/630mm, and 4 g. of a higher boiling, nondistillable material.

In another experiment carried out as above and using hexachlorobutadiene as a solvent the same results were obtained.

Reaction of $CF_2=CF_2$ with Nitric Oxide and $FeCl_3$ at 45°C.

A ferric chloride reactor constructed in the manner previously described was heated at 100°C and flushed with dry nitrogen for fifteen minutes. The temperature then was reduced to 45°C. 105 g. (1.05 moles) of $CF_2=CF_2$[*] and nitric oxide in a ratio of approximately $2NO:1\ CF_2=CF_2$ by volume were passed through the tube over a period of 24 hours. The ratio and rate of throughput of reactants was roughly measured by means of two heavy mineral oil bubblers which were mounted between the "T" tube and the reactant containers. A slight excess of $CF_2=CF_2$ was used, i.e., $2NO < CF_2=CF_2$. The product which was collected in a Dry Ice cooled trap was condensing to a deep blue liquid. During the reaction a very small quantity of a noncondensable gas was escaping from the trap. The color change describedin the preceding experiments taking place as the reaction proceeded was observed in this reaction also.

At the end of the reaction the reacotr was flushed with a slow stream of nitrogen in order to chase out the last traces of product in the packing.

The receiver A with the reaction products was attached in series to two Dry Ice-cooled traps, B and C, a wash bottle D (containing a dilute ferrous sulfate solution) and to an evacuated 22-liter flask E. The trap A containing the crude product (154 g.) was removed from the dry ice-cellosolve bath, was wrapped with clean glass wool and was allowed to warm up. The unreacted tetrafluoroethylene along with dissolved nitric oxide were passing through the system of traps and through the $FeSO_4$ solution, and then into the evacuated flask E. During this process the unreacted

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[*] Tetrafluoroethylene was prepared from $BrCF_2CF_2Br$ and zinc dust and was inhibited against polymerization with Terpene "B". (DuPont)

nitric oxide was removed by the $FeSO_4$ solution and thus unreacted $CF_2{=}CF_2$ (14 g.) was recovered. The gaseous products which condensed in the two dry ice cooled traps B, C were combined with the nonvolatile liquid left in the first trap A and fractionated on a 3 foot low temperature distillation column. The following fractions were obtained:

(a) 9 g. (6.42%) of a green liquid b.p. -23 to -10°/630mm.
This fraction consisted of two components; i.e., the acid fluoride $ClCF_2COF$ b.p. -22°/630mm which was later isolated from it, and the nitrite $ClCF_2CF_2ONO$ b.p. -16°/630mm which was present in very small quantities. Evidence for the presence of this nitrite was obtained from its infrared spectra and by chemical means (see below).

(b) 100 g. (71.4%) $ClCF_2CF_2NO$ b.p. -7°/630mm, M.W. 165
No analytical results could be obtained for this compound. Its structure and constitution were established by oxidation to $ClCF_2CF_2NO_2$. The latter was synthesized by a different method. The physical constants, infrared spectra, and analytical results for $ClCF_2CF_2NO_2$ from the two methods were in perfect agreement.

(c) 6 g. (4.28%) $ClCF_2CF_2Cl$ b.p. -1 to 0°/630 mm, M.W. 169.5
This was identified by its infrared spectra.

(d) 6.5 g. (4.64%) $ClCF_2CF_2NO_2$ b.p. 30.8°/630mm, n_D° 1.3236
d_4° 1.5622
The structure of this compound was established by comparison of its physical constants and infrared spectra with

those of $ClCF_2CF_2NO_2$ obtained by oxidation of $ClCF_2CF_2NO$.

(e) 3 g. (2.14%) $O_2NCF_2CF_2NO$ b.p. 19.5-20.5°/630mm, n 1.3354 d 1.5357, M.W. calcd. for $C_2F_2N_4O_3$: 176, found 174.5 No consistent analytical results could be obtained for this compound. Its structure was established by oxidation to $O_2NCF_2CF_2NO_2$.

(f) 3.5 g. (2.5%) $O_2NCF_2CF_2NO_2$ b.p. 52°/630mm n_D^{25} 1.3501 d 1.5962, M.W. calcd for $C_2F_4N_2O_4$: 192, found 190. Literature, n_D^{25} 1.348 d_4^{25} 1.595

Anal. calcd. for $C_2F_4N_2O_4$: C, 25.00; N, 14.59; F, 39.57

Found: C, 25.23; N, 14.27; F, 39.62

(g) 1.5 g. (1.07%) of a colorless liquid b.p. 76°/630mm M.W. calcd. for C_4F_8ClNO: 266, found 268.

Anal. Found: C, 18.11; N, 4.90; Cl, 13.12; F, 56.85

This compound is thought to be the oxazeditine $ClCF_2-CF_2-\underline{N-O-CF_2-C}F_2$ which has a molecular weight of 266 and the following analysis:

C, 18.04; N, 5.26; Cl, 13.34; F, 57.14

(h) 5.5 g. (3.9%) higher boiling, nondistillable material.

Note: The quantities and percentages of fractions (c) to (g) above are estimated values. These values were obtained from a separate fractionation of a mixture containing the above compounds (c) to (g). 58 grams of this mixture was accumulated in two experiments in which CF_2CF_2 was reacted with nitric oxide. In each experiment distillation was discontinued when $ClCF_2CF_2NO$ was removed from the mixture of products; the remaining material was then stored at dry ice temperature until 58 grams of it was accumulated and then fractionated.

Reaction of $CF_2=CF_2$ with Nitric Oxide and Ferric Chloride at 90°C.

In this reaction, the details of the preceding experiment were followed. The reaction temperature was raised to 90°C and a freshly packed ferric chloride reactor was employed.

105 g. (1.05 moles) of $CF_2=CF_2$ was reacted with 2 moles nitric oxide over a period of 24 hours; 153 g. of a blue-green product was obtained which contained the following fractions:

(a) 20 g. $CF_2=CF_2$

(b) 20 g. (15%) of a fraction b.p. -23° to -10°/630mm

This was a mixture of $ClCF_2COF$ b.p. -22°/630mm and of $ClCF_2CF_2NO$ b.p. -16°/630mm in a ratio of 4:1 respectively.

(c) 59.5 g. (44.8%) $ClCF_2CF_2NO$ b.p. -7°/630mm

(d) 12 g. (9.44%) $ClCF_2CF_2Cl$ b.p. -2 to 0°/630mm

At this point distillation was discontinued. The liquid in the distillation flask was chilled, washed with ice water, and dried over calcium chloride. Fractionation was then continued.

(e) 5.5 g. (4.14%) $O_2NCF_2CF_2NO$ b.p. 19.5-20.5°/630mm

(f) 16 g. (12%) $ClCF_2CF_2NO_2$ b.p. 52°/630mm

(g) 5 g. (3.56%) $O_2NCF_2CF_2NO_2$ b.p. 52°/630mm

(h) 10 g. (7.15%) higher boiling, nondistillable material.

Reaction of $CF_2=CF_2$ with excess Nitric Oxide and Ferric Chloride at 45°C.

A freshly packed ferric chloride reactor was used and the reaction carried out at 45°C. The ratio of tetrafluoroethylene to nitric oxide was maintained at about $1CF_2=CF_2$:2.5 NO. During the reaction unreacted nitric oxide was continuously escaping from the system through the open end of the product receiver. Tetraflurosthylene and the low boiling products also must have been carried away by the escaping nitric oxide because the weight of crude product collected at the end of the reaction was much less than the theoretical quantity. The yield of $ClCF_2CF_2NO$ was low (46%) based on total weight of products; 30% based on the quantity of $CF_2=CF_2$ consumed. About the same distribution of products was obtained as in the immediately preceding experiment.

Reaction of $CF_2=CF_2$ with Nitric Oxide over Spent Ferric Chloride at 45°C.

The following reaction which was carried out at 45°C. The ferric chloride reactor employed was one which had been previously used in one of the experiments above; i.e., the reactor packing was spent ferric chloride. 105 g. (1.05 moles) of $CF_2=CF_2$ and 2 moles of nitric oxide were reacted through this reactor over a period of 24 hours. The product condensing in the dry ice cooled trap was blue-green; during the reaction a small quantity of gas which was not condensable at dry ice temperatures was escaping from the system.

Distillation of the product (155 g.) after the unreacted $CF_2=CF_2$ (22 g.) was recovered gave the following fractions:

(a) 35 g. (26.3%) $ClCF_2COF$ b.p. -22 to -20°/630mm

(b) 7 g. (5.26%) $ClCF_2CF_2ONO$ b.p. 16°/630mm

(c) 43.5 g. (32.7%) $ClCF_2CF_2NO$ b.p. -7°/630mm

(d) 10 g. (7.5%) $ClCF_2CF_2Cl$ b.p. -2 to 0°/630mm

At this point distillation was discontinued. The liquid in the distillation flask was chilled, washed with ice cold water, and dried over $CaCl_2$.

(e) 4.5 g. (3.38%) $O_2NCF_2CF_2NO$ b.p. 19-21°/630mm

(f) 19.5 g. (14.66%) $ClCF_2CF_2NO_2$ b.p. 30.8°/630mm

(g) 3 g. (2.26%) $O_2NCF_2CF_2NO_2$ b.p. 52°/630mm

(h) 5 g. (3.76%) higher boiling, nondistillable material.

Conversion of $ClCF_2CF_2ONO$ to $ClCF_2CO_2C_2H_5$.

Fraction (b) obtained in the distillation of the products of the immediately proceding experiment was used in this experiment. In a 100 ml. 3-neck flask provided with a stirrer, a fritted glass tubing and a reflux condenser was placed 15 ml. of 95% ethanol. The flask was chilled to about 0°C and 10 g. concentrated sulfuric acid was dropped in slowly. While stirring and at 0°C. fraction (b) of the preceding experiment was allowed to vaporize into the ethanol-H_2SO_4 solution through the fritted glass tubing. A small quantity of unreacted nitrite escaped from the solution during this process and was collected in a Dry Ice cooled trap which was attached to the reflux condenser; this was reprocessed until all of it had reacted. The reaction mixture was stirred for one hour at 0°C then for one-half hour at 50°C. At the latter temperature some ethyl ether was produced. The reaction mixture was chilled and then mixed in a separatory funnel with 150 ml ice water. The organic layer (4.5 g.) which settled was drawn off and dried with a few granules of calcium chloride. The infrared spectrogram of this compound was superimposable on that of $ClCF_2CO_2C_2H_5$ from a commercial source.

Oxidation of $ClCF_2CF_2NO$ to $ClCF_2CF_2NO_2$

Chromium trioxide, 30 g. (0.33 mole), 100 ml. of glacial acetic acid, and 50 ml. of concentrated sulfuric acid were placed in a 250 ml 3-neck flask provided with a stirrer, a condenser and a fritted glass tubing. The flask was chilled to about 10°C and kept at this temperature during the reaction. While stirring vigorously 50 g. (0.3 mole) $ClCF_2CF_2NO$ was allowed to vaporize into the oxidizing medium. Unreacted starting material escaping from the solution was collected in a dry ice cooled trap which was attached to the reflux condenser; this was reprocessed through the reaction mixture several times until no more of it was absorbed. The flask was then brought to room temperature and stirring was continued for another hour. At the end of this period air was bubbled through the reaction mixture in order to drive off all volatile substances from the solution and lead them into the dry ice cooled trap. The last traces of product were driven off the reaction medium by warming the flask while bubbling air through the solution.

Fractionation of the liquid in the trap gave 29 g. of starting material $ClCF_2CF_2NO$ and 15 g. (65% of theoretical yield) of $ClCF_2CF_2NO_2$ b.p. 10.8°/630mm, n_D^{o} 1.3236, d_4^{o} 1.5632, M.W. 178;

Literature n_D^{20} 1.3145

Anal. Calcd. for $C_2F_3ClNO_2$: C, 13.18; Cl, 19.78; F, 41.75

Found: C, 13.08; Cl, 19.99; F, 41.26

The infrared spectrogram of this nitro compound was superimposable on that of the same compound obtained directly in the reaction of $CF_2 = CF_2$ with nitric oxide.

Oxidation of $O_2NCF_2CF_2NO$ to $O_2NCF_2CF_2NO_2$

About 8.5 g. (0.85 mole) of chromium trioxide, 30 ml. of glacial acetic acid and 10 ml. of concentrated sulfuric acid were placed in a 250 ml. 3-neck flask provided with a stirrer, a reflux condenser, and a dropping funnel. The flask and its contents were chilled to about 10°C and while stirring 15 g. (0.85 mole) $O_2NCF_2CF_2NO$ was added dropwise over a period of 15 minutes. The mixture was stirred at 10°C for one hour, and at room temperature for another hour. At the end of this period the mixture was shaken with 200 ml. ice water in a separatory funnel. The lower layer was drawn off and dried over calcium chloride. Distillation gave traces of starting material $O_2NCF_2CF_2NO$ and 10.2 g. (62.4% of theoretical yield) of $O_2NCF_2CF_2NO_2$ b.p. 52°/630 mm, M.W. 189.7. The infrared spectrogram of this dinitro compound was superimposable on that of the same substance obtained directly from the reaction of $CF_2 = CF_2$ with nitric oxide.

Reaction of $CF_2 = CF_2$ with NOCl and $FeCl_3$ at 45°C.

In this reaction the details of the experimental setup and procedure of the reaction of $CF_2 = CF_2$ and NO as previously outlined were used. 105 g. (0.05 moles) of $CF_2=CF_2$ and 65.5 g. (one mole) of NOCl were passed through a freshly packed ferric chloride reactor over a period of 24 hours and at 45°C. During the reaction traces of a gas which was not condensable at dry ice temperature was escaping from the system through the product receiver. The deep blue crude product (161 g.) was washed with water and dried with calcium chloride. 15 g. of $CF_2=CF_2$ was recovered during this operation. The wash water gave a test for fluoride ion and also for chloride ion, and was strongly acidic. Washing removed 7 grams of product.

Distillation of the remaining 139 g. gave the following fractions:

(a) 110 g. (75%) $ClCF_2CF_2Cl$ b.p. -7°/630mm, M.W. 163

The infrared spectrogram of this compound was superimposable on that of the same substance obtained from the reaction of $CF_2=CF_2$ and nitric oxide.

(b) 6 g. (4.1%) $ClCF_2CF_2Cl$ b.p. -2 to 0°/630mm

(c) 1 g. (0.68%) $O_2NCF_2CF_2NO$ b.p. 19.5-21°/630mm

(d) 8 g. (5.5%) $ClCF_2CF_2NO_2$ b.p. 30.8°/630mm

(e) 1 g. (0.68%) $O_2NCF_2CF_2NO_2$ b.p. 52°/630mm

(f) 2 g. (1.4%) $ClCF_2CF_2\underbrace{N-O-CF_2CF_2}$ b.p. 76°/630mm

(g) 6.5 g. (4.45%) higher boiling, nondistillable material.

<u>Note:</u> The quantities and percentages of fractions (b) to (f) above are estimated values. These values were obtained from a separate fractionation of a mixture containing these compounds (c to f). 50 grams of this mixture was accumulated in two ex-

periments in which $CF_2=CF_2$ was reacted with NOCl. In each experiment distillation was discontinued when $ClCF_2CF_2NO$ was removed from the mixture of products; the remaining material was then stored at dry ice temperature until it was fractionated.