Rubber Research

The Synthesis of Unsaturated Fluorocarbons

Progess Report

~~Quarterly~~ No. 8

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

QMC Project No. 7-93-15-004

For the Period May 13, 1960 to Aug. 13, 1960

August 23, 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 thermal stability at high temperatures.

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

II. Summary of Current Progress

Most of the work in this period has been focused on finding the effects of catalysts, conditions, and procedures for making nitroso-fluorocarbons.

General procedures have involved passing the gases involved through three foot, twenty millimeter glass tubes containing catalysts and powdered pyrex. The products were extensively analysed by vapor phase chromatography and infra-red analysis. The chromatograph used was a Perkin-Elmer Model 154 "Vapor Fractometer" with a silicon oil DC-200 column. The best conditions found for use were at 28°C., 8.0 V., and 7 psi. Helium flow (80 ml/minute). Samples were injected as gases contained in a plastic bag, and liquids of 1 - 2 μl. Yields of products were thus obtained from the chromatograms by combining the analysis of vapor and liquid samples. The retention times in milliliters of helium were used to calibrate and assign peaks to particular compounds in relation to reference compounds. Yields are based on weight of product collected minus the olefin recovered. Coversions are based on amount of olefin reacted.

Substrates Used As Catalysts - In one series of experiments, anhydrous technical $FeCl_3$, CuCl, Columbia Activated Carbon, (6 - 14 mesh), and powdered Pyrex (20 - 40 mesh) were used successively as packing in the tubes. The olefin used in these studies was CF_2CFCl with nitrosyl chloride. The olefin was passed in at a slightly faster rate than the NOCl (approximately 1.1 to 1.0). Temperatures of 45 - 50°C. and room temperature were used successively. Conversions will, of course, vary, depending upon rate of olefin passage through the column.

For producing the NOCl addition product $CF_2ClCFClNO$, ferric chloride catalyst was found best. (55% conversion with 50% nitroso yields) The cuprous chloride gave mainly the nitryl chloride addition product, $CF_2NO_2CFCl_2$, (and/or $CF_2ClCFClNO_2$,) in 75% yield with 10% of the N_2O_4 addition product, but conversion was very low (about 20%). The activated carbon, which was pumped out under 100 C. and vacuum, gave mainly chlorination ($CF_2ClCFCl_2$), 76%, nitrosyl chloride addition ($CF_2ClCFClNO$), 14.6%, with a 34% conversion at 45°C. The powdered glass itself at 50°C. gave the poorest conversions (4%); the yield of NOCl addition product was 30%; the chlorine adduct was 28%, and nitro-nitroso ($CF_2NO_2CFClNO$) was 18%, and 10% of nitrites.

The best results for producing nitroso compounds in high yields and high conversions have been found with the use of N_2O_4 instead of NOCl on $FeCl_3$ catalysts at room temperature. $CF_2ClCFClNO$, for example, was produced in 66% yield with a conversion of 75-85%.

Higher temperatures gave more dinitro and chlorine adduct ($CF_2Cl-CFCl_2$) at the expense of nitroso products.

Further studies were also carried out with various other metal halides, $CoCl_2$, $NiCl_2$, $MnCl_2$ and $CoBr_2$. These were not as efficient as $FeCl_3$. The results are tabulated in the Experimental section of the report.

The reactions of $CF_2=CCl_2$ with nitric oxide and NOCl respectively over ferric chloride have been studied and the following compounds isolated and identified.

$CF_2Cl-CCl_2-NO$, $CF_2Cl-CCl_3$, $C_2F_2Cl_3NO_2$

Photochemical reaction of $CF_2=CCl_2$ and NOCl yielded similar products.

When $CF_2Cl-CCl_2-NO$ was irradiated with ultraviolet light, a change took place with the formation of $CF_2Cl-CCl_3$, $C_2F_2Cl_3NO_2$, and some higher polymeric materials.

The reaction of $CF_3CF=CF_2$ with NO over ferric chloride at 50°C. did not yield any isolable addition product. However, a reaction of $CF_3CF=CF_2$ with NO over activated carbon yielded a compound tentatively identified as either $CF_3-CF=CF(NO)$ or $CF_3-C(NO)=CF_2$.

$CF_3CF=CF_2$ reacted with NO under autogenous pressure to yield $CF_3CF(NO)CF_2NO_2$ and $CF_3CF(NO_2)CF_2(NO_2)$.

Photochemical reaction of $CF_3CF=CF_2$ with NOCl resulted in the isolation and identification of $CF_3CF(NO)CF_2Cl$ and $CF_3CF(NO_2)CF_2Cl$.

In all of the above reactions, reactive compounds which readily hydrolyzed in water were also obtained. These compounds are probably nitrite derivatives since acidic materials were formed as a result of the hydrolysis. These studies will be further pursued.

The preparation of CF_3COONO (intermediate in the production of

CF_3-NO) from $(CF_3CO)_2O$ and NOCl has been verified. In one experiment, a conversion of 32% and a yield of 83% of CF_3COONO were obtained. This method merits closer study and will be pursued accordingly.

The preparation of fluorinated cyclic imines is now in progress. It is too early to predict the outcome of this work.

During the period 200 g. of relatively pure CF_2Cl-CF_2NO were packages and shipped to 3 M.

The next quarters work will be mainly directed towards the preparation of CF_2ClCF_2NO (using four trains) and towards the synthesis of dinitroso derivatives.

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 synthesis of fluorine containing imines and epoxides.

It has been taking longer than anticipated to produce pound quantities of the NOCl adduct of tetrafluoroethylene by gaseous tube reactions. Aside from the slowness of the reaction, setbacks have included polymerization (as mentioned above) upon long storage of impure material containing CF_2CF_2 and nitrites, loss of some pure sealed material due to detonation when being sealed in a glass jacket, losses due to back pressure developed in sintered frits clogging upon washing, and two traps leaking due to CF_2CF_2 pressure build-up when not thoroughly kept iced with CO_2.

However there is currently about 300 grams of washed and dried CF_2Cl-CF_2NO ready for distillation and sealing.

The technique used now to make the NOCl adduct involves placing two jacketed 4' by 25 mm. glass tubes in series. The olefin and NOCl are passed through the first tube with a product collecting cold trap at the end; another NOCl tank and the excess CF_2CF_2 are sent through the second tube with another cold trap at the end to which is connected a third cold trap immersed in liquid nitrogen to trap unreacted olefin (this trap is connected to a mercury seal to prevent oxygen from condensing.) The products are then scrubbed through water using a very coarse frit to prevent clogging. The hydrolysis of the nitrites produces some fluorosilicic acid which clogs ordinary frits. The dried blue nitroso vapors are then distilled through a gas distillation column containing glass helices, and the product accepted with b.pt. range of -3 -0°C. Very pure CF_2ClCF_2NO (b.pt. -2.5°C/630 mm.) upwards of 96% is obtained this way as evidenced by vapor phase chromatography. Fortunately for separation purposes very little Freon-114 (CF_2CF_2Cl) is made in this reaction. The tetrafluoroethylene is produced as needed (which is very often) by the debromination of CF_2BrCF_2Br. It is planned to keep four tubes running continually until all the desired compound is prepared. The ferric chloride-powdered pyrex tubes become spent after about 70-80 grams of product is collected. They become light tan colored (ferrous state) and produce mainly nitrites and 114 when spent.

The use of N_2O_4 in place of NOCl also seems promising for preparing the nitroso compounds of CF_2CF_2. On $FeCl_3$ at 40°C N_2O_4 and CF_2CF_2 gave 48% CF_2ClCF_2NO, 13% CF_2ClCF_2Cl, 24% $CF_2NO_2CF_2NO$, 8% $CF_2NO_2CF_2Cl$, and 7% $CF_2NO_2CF_2NO_2$ (after washing). (No figure for conversion was obtained but it appears high.)

Stability of the Nitroso Compounds

Reaction of ultra-violet light upon the nitroso compounds (discussed below) and the effects of heat as well as prolonged time of contact in catalyst tubes appeared to give lower yields of the more unstable compounds. The nitroso compounds are stable only when kept cold and in the dark. A sample of $CF_2ClCFClNO$ has not undergone any change after two months in a bottle in the refrigerator (as evidenced by infrared and v.p.c.)

After one week of irradiation by ultra violet light, a sample of the nitroso liquid had undergone a complete disproportionation such that only 1.4% was unchanged. The compound apparently split out NOCl to give the most stable products mainly $CF_2Cl\text{-}CFCl_2$ and $CF_2NO_2CFCl_2$ (and/or $CF_2ClCFClNO_2$).

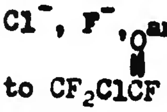
It was also noted that a pure sample of CF_2ClCF_2NO also underwent a complete change when sealed in a tube and left in the daylight. When a sealed tube containing 42 gms. of pure CF_2ClCF_2NO was being sealed in a glass jacket prior to shipment, a detonation occurred due to either heat or intense light near the tip of the seal. It is known (Dr. Stefani) that the nitroso compounds also disproportion with heat. It should also be noted that upon storage in the cold of impure $CF_2Cl\text{-}CF_2NO$ with CF_2CF_2 and acidic nitrites, polymerization sometimes occurred to give a colorless gel.

EXPERIMENTAL

Procedure

The general procedure for most of the tube reactions is the same throughout. The olefin and nitrosating agent were passed through mineral oil bubblers via a T connection to 3' by 20 mm. glass tubing wrapped with nichrome wire. The catalyst and powdered glass were premixed at about 50/50 by volume. The function of the powdered pyrex was to prevent the catalyst from becoming impervious to the gas blow. The products were collected in glass traps immersed in carbon ice-cellosolve coolant; a bubbler was attached to the tube. When $CF_2=CF_2$ was used, another trap in liquid nitrogen was attached to collect the unreacted olefin. The CF_2CF_2 was prepared as needed from CF_2BrCF_2Br and zinc dust.

When using NOCl, a slight excess of olefin was used (about a 1.1/1 ratio. With NO and N_2O_4 the N-oxide was in excess. (The ratio was 1.5 oxide to olefin).

The products were sent through a water tower to remove the hydrolyzable nitrates and unreacted NOCl or other N oxides (NO, N_2O_3 and NO_2 are formed in slight amounts during the reaction.) It was found that regular glass frits clogged extensively during the scrubbing procedure and therefore a very coarse frit was used and found satisfactory. The wash water always contained Cl^-, F^-, and NO_3^-. The nitrites such as $CF_2ClCFClCNO$ decompose to  $CF_2Cl\overset{\overset{O}{\|}}{C}F$ for example which hydrolyzes to the acid and accounts for the F^- and frit clogging.

When $FeCl_3$ was used as packing, it slowly became yellow (ferrous state) as the reaction proceded and had to be replaced usually after about 70 gms of product was collected. The spent catalyst gave much lower yields of nitroso compounds and chlorination as well as nitryl chloride addition predominated. As much as 65 grams of material (mainly Cl_2, and NO_2Cl adduct) was held up on the $FeCl_3$ and activated carbon packings.

Analysis

A Perkin-Elmer Model 154 Vapor Fractometer was used extensively to analyze the products. Considerable time was spent in obtaining a reliable method for the analysis. A silicone oil column (DC-200) was found effective for separating the many components in the products. It was always used at 28°C, 8.0 volts, and 7 psi helium. The actual flow rate was measured by the soap bubble method; a flow rate of about 80 ml/min. was found at 7 psi He if there were no leaks in the column. The flow rate was measured for each different run. The chart speed was 2 minutes per inch. The retention times for each component was therefore measured in ml. of helium. The reference compounds, $CF_2ClCFClNO$, $CF_2ClCFCl_2$, $CFCNO_2CFCl_2$, $CF_2NO_2CFClNO$ and $CF_2NO_2CFClNO_2$ were prepared by distillation of the products and in some cases obtained from Dr. Stefani's crude sample of some. The mole percent of the products was obtained from the areas of the various peaks. The Model 154 has an attenuation up to 256 and therefore after an idea of the relative amounts of the components in the analyzed sample have been obtained on the chromatograms, attenuation settings are charged during the recording so that all peaks will have measurable areas.

To find the overall yields of the products the collected material is separated into liquid and vapor fractions. The vapor fraction (condensed in carbon ice traps) is injected from plastic bags with a gas tight syringe (2 ml.) The liquid fraction is injected with a microliter syringe (1-1.5 μl). The mole percents of the components in the liquid and vapor fractions are then combined to get the overall yields. Conversions of the olefin can also be obtained from the chromatograms or by distilling off the unreacted olefin. The figures should be reliable to ± 5% of the value given. A summary of all the tube reactions is given in the table below. The figures were obtained by the above method. It is felt that this method is more accurate than distillation since there are more losses and some decomposition in the latter and of course better separations are obtained.

Some of the $CF_2=CFCl$ products were subsequently distilled, but after analysis the products from the different reactions were combined to give a large batch for future distillation. Infrared curves have been obtained for all the products on a Beckman IR-5.

In some of the reactions with $CF_2=CFCl$ there has consistently appeared a peak at 135 ml. This might well be the dinitroso $CF_2NOCFClNO$ since it comes off just before $CF_2ClCFClNO$ and this would be expected at that position. As high as 17% was found in the reaction of NO_2 and $CF_2=CFCl$ on $FeCl_3$ at room temperature. It was also noted with $CF_2=CFCl$ that no NO_2Cl addition occurred when $NONO_2$ was apparent and vice-versa.

Disproportionation of $CF_2ClCFClNO$ by Ultra Violet

In order to determine the effect of light upon nitrosofluorocarbons, 9.0 grams of $CF_2ClCFClNO$ b.p. 31°/630 mm. was sealed in a 20 ml. glass tube and irradiated with an ultra violet lamp for one week's duration. The source was distant enough so that no concomitant heat effects were present. During the time of irradiation the originally blue vopors turned brown and the liquid slowly turned from a deep blue to a yellowish brown; a solid was also accumulating. Upon opening, the contents were separated into 7.1 gms liquid phase, 1.2 gms vapor phase, and 0.4 gms of a white solid phase. The liquid and vapor phase were analyzed to give the overall results: Original $CF_2ClCFClNO$, only 1.3% remaining, $CF_2ClCFCl_2$, 54%; $CF_2ClCFClNO_2$ and/or $CF_2NO_2CFCl_2$, 35%; and 2% of $CF_2NO_2CFClNO_2$. When $CF_2ClCFClNO$ was stored in the refrigerator (glass bottle) for two months no change whatsoever accurred.

The results from the tube reactions, , and heat upon nitroso compounds seem to indicate that they are the products of kinetic control and that the stable Cl_2 and NO_2Cl adducts result from equilibrium control (long contact time).

When CF_2CFCl and NOCl were passed together through a vertical tube fitted with an intense ultraviolet source, no reaction was apparent; under these conditons the exposure was probably too brief.

Summary of Reactions Tried in Packed Tubes

	"Catalyst" and Conditions	Nitrosating Agent	% Conversion	Nitrites $CF_2NOCFClNO$ etc.	Yields in Mole Percent				
					$CF_2ClCFClNO$	$CF_2ClCFCl_2$	$CF_2NO_2CFClNO$	$CF_2NO_2CFCl_2$	$CF_2NO_2CFClNO$
Retention at 28°C in ml of He				*135	200-205	370-376	770-780	820-835	1350
	$FeCl_3$ at R.T. (27°C)	NOCl	26		75-80				
Based on washed material	$FeCl_3$ 45-50°	NOCl, + NO	55		51	11	20		5
Using $CF_2 = CFCl$	CuCl at R.T.	NOCl	20		8			75	10
as olefin	Powdered Pyrex 40-60° Mesh 50°C	NOCl	4	10	30	28		18	
	Activated Carbon. No glass	NOCl	34	2	14.6	76	4		3.2
Based on washed material	$FeCl_3$ at R.T.	NO_2	75-85	*17	72	5.4	6.6		17
	$FeCl_3$, 70°	NO_2	high		4.7	47	7.7		32.5
					CF_2ClCF_2NO	CF_2ClCF_2Cl	$CF_2NO_2CF_2NO$	$CF_2ClCF_2NO_2$	$CF_2NO_2CF_2NO_2$
Retention in ml He 28° C					50	81	143	210	390
Using CF_2-CF_2	$FeCl_3$, 50°C	NOCl	50		83	4.8	5.8	0.8	6.0
as olefin	$FeCl_3$, 40°C	NO_2	very high		48	13	24	8	7

* in many of the chromatagrams, there is a peak which would correspond to the position of $CF_2NOCFClNO$ if present.

Studies with other metal halides as substrates

The reactions were run in the gas phase by passing a 1:1 mixture of NOCl and CF_2=CFCl through a 20 X 1000 mm heated tube packed with a 1:1 mixture by volume of 20-40 mesh ground glass and anh. metal halide. The flow rate was regulated to 0.4 mole/day of each gas. The products, collected in a trap cooled in dry ice and acetone, was then washed with water to remove excess NOCl and hydrolizables and then distilled to remove unreacted olefin. The mixture was then quantitively analyzed using a vapor phase chromatograph with a silicone column. Using He as carrier gas, the errors in the calculation due to differences in thermal conductivity of the components should be slight (less than 5%). In all cases the products reported in Table I represent more than 99% of all the peaks recorded.

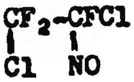
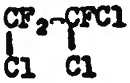
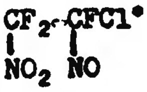
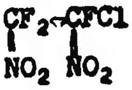
In some cases over 50% of the products were found to be water soluble, yielding an acidic solution which on neutralization and evaporation deposited white needles. In all cases there was little evidence of weight gain or physical change of the metal halide. In no case, was the conversion greater than 50% of total products, although this must be taken lightly in light of inherent difficulties of reproduceabilty in this apparatus.

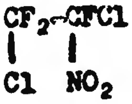
The results so far would tend to indicate that the yield of (I) is directly proportional to the stability of the nitroso complex corresponding to the metal halide used, that is Fe>Co>Ni and I>Br>Cl. It is to be noted that higher temperatures result in lower yields of (I), again in agreement with the observation that the stability of the nitroso complexes decrease with increasing temperature. The lowering of the yields of nitroso adduct is generally accompanied by an increase in hydrolyable material, presumably nitrites. The identification of these acidic materials will be delayed until a more appropriate time. This can be noted both when varying the temperature and when using a different metal halide.

Table I

Metal Halide Temp.

Product, Mole %

		I	II	III	IV
		 $\underset{Cl}{CF_2}-\underset{NO}{CFCl}$	 $\underset{Cl}{CF_2}-\underset{Cl}{CFCl}$	 $\underset{NO_2}{CF_2}-\underset{NO}{CFCl}$*	 $\underset{NO_2}{CF_2}-\underset{NO_2}{CFCl}$
$CoCl_2$	RT	0	0	0	Trace
$CoCl_2$	70°	46	25	28	1.3
$CoCl_2$	100°	4.0	67	28	0.81
$NiCl_2$	70°	14	29	54	3.3
$MnCl_2$	70°	27	70	1.3	1.9
$MnCl_2$	50°	INC.			
$CoBr_2$	70°	INC. but appears to be at least as good as $CoCl_2$			

* There appears the possibility that this may also be  $\underset{Cl}{CF_2}-\underset{NO_2}{CFCl}$ along with III.

Reaction of $CF_2=CCl_2$ with Nitric Oxide and Ferric Chloride at 45°C.

The experimental setup and procedure outlined on pp. were followed in this reaction. In order to maintain a steady flow of $CF_2=CCl_2$ into the system the olefin container was maintained at about 25°C by a water bath. The heavy mineral oil bubbler through which the olefin was introduced into the system was heated to about 50° by means of an electrical heating tape.

140 g. (1.05 moles) of $CF_2=CCl_2$ and 2 moles of nitric oxide were passed through a freshly packed ferric chloride reactor over a period of 24 hours. The reactor temperature was maintained at 45°C throughout the reaction period. At the end of the reaction the reactor was flushed with a slow stream of nitrogen in order to drive the last traces of product into the dry ice cooled product receiver.

The crude product (180 g.) was washed with water and dried over $CaCl_2$. Washing removed 22 grams from the product. The wash water gave a test for both chloride and fluoride ions and was strongly acidic. From this wash water the acid $ClCF_2CO_2H$ was isolated in the form of its ethyl ester.

Distillation of the remaining 158 g. of the blue product gave the following fractions:

(a) 20 g. $CF_2=CCl_2$ b.p. 16°/630mm

(b) 60 g. of an intensely blue liquid b.p. 14-16°/200mm 72.5°/630mm, M.W. 195, n_D^{25} 1.3942, d_4^{25} 1.5898. On the basis of the results of a similar reaction of $CF_2=CFCl$ with nitric oxide, the structure of this compound is assigned as $ClCF_2CCl_2NO$. No consistent analytical results could be obtained for this substance. When this compound is distilled at normal pressures (630mm Hg), it undergoes decomposition.

(c) 31 g. of colorless liquid b.p. 84°/630mm, m.p. 35.5°C. This compound reacted with zinc in ethanol and gave $CF_2=CCl_2$; its structure is $ClCF_2CCl_3$.

Anal. Calcd. for $ClCF_2CCl_3$: C, 11.76; Cl, 69.51; F, 18.72

Found: C, 11.91; Cl, 69.47; F, 18.62

(d) 19 g. of a colorless liquid b.p. 74°/200mm, 110°/630mm, n_D^{25} 1.4178, d_4^{25} 1.6599

Anal. Calcd. for $C_2F_2Cl_3NO_2$: C, 11.16; N, 6.51; Cl, 49.77; F, 17.67

Found: C, 10.88; N, 6.24; Cl, 50.86; F, 17.28

(e) 15 g. higher boiling, nondistillable material

(f) 13 g. of a low boiling green liquid collected in a dry ice cooled trap which was connected to the reflux condenser of the distillation column. The evolution of this substance started as soon as the starting material $CF_2=CCl_2$ was removed from the system and the temperature of the distillation flask reached 80-85° at atmospheric pressure (630mm Hg.). This green material reacted vigorously with water and most of it was absorbed upon washing, leaving behind some $ClCF_2CCl_2NO$.

Distillation of a portion of this green liquid gave the following:

(a) a red-yellow liquid b.p. -12 to -10°/630mm, M.W. 64. This was identified by its infrared spectra to be nitrosyl chloride.

(b) a yellow-grown liquid b.p. -5 to 0°/630mm, M.W. 79. This compound is suspected to be nitryl chloride (NO_2Cl). M.W. calcd. for NO_2Cl: 81.4, found, 79.

(c) a colorless liquid b.p. 16°/630mm which was shown to be $CF_2=CCl_2$.

(d) a blue liquid ($ClCF_2CCl_2NO$) left in the distillation flask which started decomposing when the flask temperature reached 75-80°C.

Reaction of CF_2CCl_2 with NOCl over $FeCl_3$ at 45°C.

140 g. (1.05 moles) CF_2CCl_2 and 66 g. (one mole) of NOCl were passed through a ferric chloride tube (3 ft x 20mm) at 45°C over a period of 24 hours. The details of the preceding experiment were followed in this reaction also. The crude blue product (181 g.) which was collected in a Dry Ice cooled trap was washed with water and dried over clacium chloride. 15 grams of the product dissolved in the wash water during this operation. Distillation yielded the following products:

(a) 14 g. $CF_2=CCl_2$ b.p. 16°/630mm

(b) 67 g. $ClCF_2CCl_2NO$ b.p. 14-16°/200mm

(c) 25 g. $ClCF_2CCl_3$ b.p. 84°/200mm m.p. 34-35.5

(d) 33 g. $C_2F_2Cl_3NO_2$ b.p. 74°/200mm

(e) 11 g. higher boiling, nondistillable material

(f) 13 g. of a low boiling green liquid collected in a dry ice cooled trap, which was attached to the distillation column.

This liquid had the same characteristics as those of fraction (f) in the reaction of $CF_2{=}CCl_2$ with NO.

Photochemical Reaction of $CF_2{=}CCl_2$ with NOCl.

132 g. (one mole) of $CF_2{=}CCl_2$ and 65 g. (one mole) of NOCl were placed in evacuated heavy wall pyrex tube of approximately 300 cc. capacity, which was provided with a pressure gauge. The tube was irradiated with an ultraviolet lamp for about one hour. The reaction started in 15-20 minutes and was extremely exothermic. The color of the contents changed progressively from brown to blue. At the end of one hour the tube was cooled with dry ice and upon opening a small quantity of gas escaped. The crude blue product was washed with water and dried over calcium chloride. The product (169 g.) was distilled at atmospheric pressure (630mm Hg) and gave the following fractions:

(a) 9 g. $CF_2{=}CCl_2$ b.p. 16°/630mm

(b) 14.5 g. $ClCF_2CCl_2NO$ b.p. 71-73°/630mm

(c) 55 g. $ClCF_2CCl_3$ b.p. 84°/630mm m.p. 35.5

(d) 30 g. $C_2F_2Cl_3NO_2$ b.p. 111-113°/630mm

(e) 25 g. higher boiling, nondistillable material

(f) 29 g. of a low boiling green liquid collected in a dry ice cooled trap which was attached to the condenser of the distillation apparatus. Most of this liquid was soluble in water (NOCl, NO_2Cl).

In another similar experiment in which distillation was carried out at reduced pressures, 63 g. of $ClCF_2CCl_2NO$ b.p. 14-16°/200mm was obtained. This compound as well as $C_2F_2Cl_3NO_2$

are thermally unstable and decompose when distilled at normal pressure (630mm Hg).

When the period of irradiation with ultraviolet light is beyond one hour the yield of $ClCF_2CCl_2NO$ is considerably diminished while the yields of $ClCF_2CCl_3$, $C_2F_2Cl_3NO_2$ and of the higher boiling materials are increased.

Note: A violent explosion took place in one of these reactions in which 132 g. of $CF_2{=}CCl_2$ and 66 g. of NOCl were reacted in a 300 cc heavy wall pyrex tube under the influence of two ultraviolet lamps.

Attempted Reaction of $CF_3CF{=}CF_2$ with Nitric Oxide and Ferric Chloride.

Forty g. of $CF_3CF{=}CF_2$ (0.266 mole) and about 0.5 mole of nitric oxide were passed through a ferric chloride reactor over a period of six hours at 50°C. The reaction product which was colorless was collected in a dry ice cooled trap. At the end of the reaction the product was washed with water and dried over calcium chloride. Distillation gave 25 grams of unreacted hexafluoropropene and a very small quantity of a higher boiling liquid which vaporized to a brown gas. This reaction was not investigated further.

ATTEMPTED Reaction of $CF_3CF{=}CF_2$ with Nitric Oxide over Activated Carbon.

Forty g. of $CF_3CF{=}CF_2$ (0.266 mole) and about 0.5 mole of nitric oxide were passed through a 3-ft x 20 mm glass tube packed with coarse activated carbon (cocoanut shell) over a period of six hours. The reaction was carried out at room temperature. At the place where the gaseous mixture came in contact with the carbon packing the tube became very hot; this hot spot traveled along the length of the tube as the reaction proceded. A colorless gas which did not turn brown upon contact with air was continuously escaping from the dry ice cooled product receiver.

During the reaction extensive carbon-fluorine bond cleavage must have occurred because the reactor glass tube was badly etched. A flask in which the carbon packing was subsequently stored was also badly etched.

The product (30 g.) was a green liquid. This was washed with water and dried with calcium chloride. Washing removed 10 grams of a substance and the wash water gave a test for fluoride ion, was strongly acidic, and contained nitrous acid. Distillation of the 20 grams of remaining crude product gave 15 g. of unreacted hexafluoropropene and 4 g. of a blue liquid b.p. -7°/630mm. The infrared spectra of this blue compound show absorption bands characteristic of the carbon-carbon double bond and for the nitroso group. The structure of this compound is tentatively assigned as $CF_3CF=CFNO$ or $CF_3C(NO)=CF_2$. M.W. calcd. for C_3F_4NO: 161, found 161.

Reaction of $CF_3CF=CF_2$ with Nitric Oxide under Pressure.

100 g. of $CF_3CF=CF_2$ (0.666) and 1.2 moles of nitric oxide were placed in an evacuated 500 cc autoclave which was cooled to -75°C in a Dry Ice butylcellosolve bath. The autoclave was allowed to stand at room temperature for 24 hours and at

the end of this period it was chilled again to -75°C. The valve on the autoclave was connected to a Dry Ice cooled trap and the pressure was slowly released. A colorless gas which would not condense at -75° C escaped through the open end of the trap. This gas did not react with air (not NO), was not soluble in water, dilute acid or base, and did not support combustion (probably nitrogen).

The autoclave was then removed from the Dry Ice bath and was allowed to warm up to room temperature. Gaseous material which was vaporizing from the autoclave was collected into the dry ice cooled trap. When no more gaseous products were coming out from the autoclave the latter was chilled with ice and was opened. The contents of both the trap and the autoclave (125 g.) were washed with water and dried with calcium chloride. 15 g. of a water soluble fraction was lost in the wash water during this operation. The wash water was strongly acidic, it contained nitrous acid, and gave a test for fluoride ion.

Distillation of the remaining blue liquid gave the following fractions:

(a) 60 g. unreacted $CF_3CF=CF_2$ b.p. -31°/630mm

(b) 24 g. of a blue liquid b.p. 42°/630mm, n_D^0 1.306, d_D^0 1.6224. No consistent analytical results could be obtained for this compound. Its structure and constitution was established to be $CF_3CF(NO)CF_2NO_2$ by oxidation to $CF_3CF(NO_2)-CF_2NO_2$, and by analysis of its nuclear magnetic resonance spectra which indicated the presence and location of the nitroso and of the nitro groups in the molecule. M.W. calcd. for $C_3F_6N_2O_3$: 226, found, 220.

(c) 17 g. of a colorless liquid b.p. 68.5°/630mm n_D^{25} 1.3220, d_4^{25} 1.6479,

Anal. Calcd. for $CF_3CF(NO_2)CF_2NO_2$: C, 14.88; N, 11.57; F, 47.11

Found: C, 15.15; N, 11.57; F, 47.42

M.W. calcd: 242, found 237.

In another similar experiment the product was fractionated without washing in order to isolate the water soluble fraction mentioned above. From 75 g. of $CF_3CF{=}CF_2$ and one mole nitric oxide, 50 g. unreacted propene was recovered. The products were as follows:

(a) 5 g. of a green liquid b.p. 15-17°/630mm

(b) 7 g. of a green liquid b.p. 27.5°/630mm

(c) 20 g. $CF_3CF(NO)CF_2NO_2$ b.p. 42°/630mm

(d) 12 g. $CF_3CF(NO_2)CF_2NO_2$ b.p. 68.5°/630mm

Fractions (a) and (b) reacted vigorously with water; their infrared spectra show strong absorption bnads which are characteristic for the nitrite group (-ONO) and possibly are isomers.

Oxidation of $CF_3CF(NO)CF_2NO_2$ to $CF_3CF(NO_2)CF_2NO_2$.

Chromium trioxide, 15 g. (0.15 mole), 50 ml. of glacial acetic acid, and 25 ml. of concentrated sulfuric acid were placed in a 250 ml. 3-neck flask equipped with a stirrer, a reflux condenser, and a dropping funnel. The flask was chilled to 5-10°C and was kept at this temperature during the reaction. While stirring vigorously, 33.9 g. (0.15 mole) of $CF_3CF(NO)CF_2NO_2$ was added dropwise over a period of 20 minutes. The reaction mixture was then stirred at 5-10°C for three hours and at room temperature for one-half hour. At the end of this period the reaction mixture was shaken in a separatory funnel with about 400 ml. ice cold water. The organic layer (27 g.) which settled was drawn off and dried over calcium chloride. Distillation gave 5 g. unreacted starting material and 21 g. (67% of theoretical yield) of $CF_3CF(NO_2)CF_2NO_2$, b.p. 68-68.5°/630mm, n_D^{25} 1.3222, d_4^{25} 1.6476, M.W. 239. The infrared spectrogram of this dinitro compound was identical with that obtained from the reaction of $CF_3CF=CF_2$ with nitric oxide described in the preceding experiment.

Photochemical Reaction of $CF_3CF=CF_2$ with NOCl.

Hexafluoropropene, 50 g. (0.333 mole) and nitrosyl chloride, 22 g. (0.333 mole) were placed in an evacuated 22 liter flask. The flask was exposed to sunlight for 8 hours during which a blue green liquid condensed at the bottom and a solid thin white film was deposited on the walls of the flask. At the end of this period the contents of the flask were slowly pumped into a liquid air trap in which it solidified. After about five hours the white solid (N_2O_4) started subliming and filled the evacuated flask with a brown gas which was nitrogen dioxide.

The product collected in the trap was washed with water and dried with calcium chloride. Distillation gave the following fractions:

(a) 25 g. $CF_3CF=CF_2$ b.p. -31°/630mm

(b) 12 g. of a blue liquid, b.p. 20.5°/630mm, n_D^0 1.3003,

d_4^0 1.5729. No consistent analytical results could be obtained for this compound. Its empirical formula is C_3F_6ClNO; this was established by conversion to $C_3F_6ClNO_2$ for which a good analysis was obtained. On the basis of the results of previous experiments its structure is tentatively assigned at $CF_3CF(NO)CF_2Cl$. M.W. calcd. for C_3F_6ClNO: 215.4. found, 212.

(c) 5 g. of a colorless liquid b.p. 30°/630mm, n_D^0 1.3110, d_4^0 1.5977. This compound was shown by its infrared spectra to be $CF_3CFClCF_2Cl$. M.W. calcd. for $C_3F_6Cl_2$: 221, found, 219.

(d) 15 g. of a colorless liquid b.p. 51.5-52°/630mm, n_D^{25} 1.3145; d_4^{25} 1.6313, M.W. 236.

Anal. Calcd. for $C_3F_6ClNO_2$: C, 15.52; N, 6.03; Cl, 15.3;
F, 49.14
Found: C, 15.81; N, 5.82; Cl, 15.11
F, 48.87

Oxidation of C_3F_6ClNO to $C_3F_6ClNO_2$.

9.3 g. (0.093 mole) of chromium trioxide, 50 ml. of glacial acetic acid, and 25 ml. of concentrated sulfuric acid were placed in a 250 ml. 3 neck flask equipped with a stirrer, a reflux condenser and a fritted glass tube. The flask was chilled to 5-10°C and while stirring vigorously 21 g. (0.093 mole) of C_3F_6ClNO (obtained from the reaction of $CF_3CF{=}CF_2$ with NOCl) was allowed to vaporize into the oxidizing medium. After addition of the nitroso compound was completed stirring was continued at 5-10°C for one hour and then at room temperature for one-half hour. At the end of this period the reaction mixture was shaken in a separatory funnel with about 400 ml. ice cold water. The organic layer which settled was drawn off and dried over calcium chloride. Distillation gave about 2 g. of unreacted starting material C_3F_6ClNO b.p. 20-21°/630mm and 13 g. (63.3% of theoretical yield) of a colorless liquid ($C_3F_6ClNO_2$) b.p. 52°/630mm n_D^{25} 1.3142, d_4^{25} 1.6318.

Anal. Calcd. for $C_3F_6ClNO_2$: C, 15.52; N, 6.03; Cl, 15.3; F, 49.14
Found: C, 15.69; N, 5.75; Cl, 15.04; F, 48.89

Examination of the Ferric Chloride packing of the Reactor used in the Reaction of Fluoroolefins with Nitric Oxide.

As was stated repeatedly in several of the preceding experiments the ferric chloride packing of the reactor employed in the reaction of fluoroolefins with nitric oxide changed its color to light brown as the reaction proceeded. A sample of this light brown packing was withdrawn from the reactor and the following observations were made:

(a) The substance reacted with water with evolution of heat and of a brown gas which most likely was nitric oxide. (converted to nitrogen dioxide by atmospheric oxygen)

(b) Its melting point was 85-100°C.

(c) A dilute solution of the sample gave a blue color when mixed with a xolution of potassium ferrocyanide. This indicated the presence of ferric ion.

(d) A dilute solution of the sample gave a blue precipitate and a brown liquid when mixed with a solution of potassium ferricyamide. This indicated the presence of ferrous ion.

A control test for ferrous ion carried out with a sample of the reagent ferric chloride stock was negative.

Studies for the Production of R_fNO from $(R_fCO)_2O$

In an evacuated 7 liter flask equipped with one 2-way stopcock and one 3-way stopcock, 45 gms of $(CF_3\overset{O}{\overset{\|}{C}})_2O$ and 22 gms of NOCl were introduced in the vapor state. The gases were condensed by cooling the flask with dry ice and were then allowed to warm up to room temperature.

A 300 watt incandescant lamp was positioned a few inches from the bulb and irradiation was continued for two days with intermittent shaking. The system was evacuated and the yields of $CF_3\overset{O}{\overset{\|}{C}}ONO$ determined.

Results. 11 gms polymeric material

27 gms $(CF_3\overset{O}{\overset{\|}{C}})_2O$ recovered.

10 gms NOCl recovered

10.1 gms $CF_3\overset{O}{\overset{\|}{C}}ONO$ n_D^{25} 1.3772 b.p. 46°/80 mm

4 gms ($CF_3\overset{O}{\overset{\|}{C}}ONO$-$(CF_3\overset{O}{\overset{\|}{C}})_2O$ mixture) b.p. 42°/38 mm, n_D^{25} 1.360

For CF_3COONO

% conversion based on 45 gms $(CF_3\overset{O}{\overset{\|}{C}})_2O$ is 32%

% yield based on 18 gms $(CF_3\overset{O}{\overset{\|}{C}})_2O$ is 82-85%

Reaction of $(CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O$ and NOCl

175 gms $(CF_3CF_2CF_2\overset{O}{\overset{\|}{C}})_2O$ and 50 gms NOCl were introduced into a 22 liter flask equipped with one 2-way stopcock and one 3-way stopcock. The flask was irradiated with two-300 watt incandescent lamps for 85 hours and then evacuated. Two grams of NO was collected in a liquid air trap and the balance of the product material was collected in a dry ice-cellosolve trap.

Low temperature distillation yielded six grams of a material boiling N-25°C and 37 grams of unreacted NOCl. No pure $CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}ONO$

was obtained, but 36 gms of the $(CF_3CF_2CF_2\overset{O}{C})_2O$-$CF_3CF_2CF_2\overset{O}{C}ONO)$ mixture was collected at 41°C/10 mm. Further distillation resulted in a recovery of 131 grams of $(CF_3CF_2CF_2\overset{O}{C})_2O$ and 10 grams of a yellow residual material. Yields are not obtainable at this time due to the incomplete knowledge on the nature of the constant boiling mixture.

Pyrolysis of $CF_3CF_2CF_2\overset{O}{C}ONO$

A small sample (5 gms) of $CF_3CF_2CF_2\overset{O}{C}ONO$ was introduced into an equalizer funnel and allowed to run very slowly into an attached three foot pyrex tube packed with glass beads. The tube had been placed into an electric furnace and preheated to 200°C. An almost quantitative yield of $CF_3CF_2CF_2NO$ and CO_2 resulted upon pyrolysis except for a minor amount of a green compound. This latter material reacts with water and its hydrolysis product gives an IR spectrum indicative of a carboxylic acid. It is probably a nitrite, but its structure will be confirmed in subsequent experiments.

Pyrolysis of Constant Boiling Mixture $(CF_3CF_2CF_2\overset{O}{C})_2O$-$CF_3CF_2CF_2\overset{O}{C}ONO$

A small sample of the $(CF_3CF_2CF_2\overset{O}{C})_2O$-$CF_3CF_2CF_2\overset{O}{C}ONO$ mixture was pyrolyzed under identical conditions as the previous compound. The products reveal lesser amounts of $CF_3CF_2CF_2NO$, CO_2 but a little less than half of the initial weight is due to $(CF_3CF_2CF_2\overset{O}{C})_2O$. Some charring was noted and no material balance was made.

It is felt that further work is needed to obtain the optimum temperatures, flow rates etc., so that the largest yield of the nitroso compound may be obtained.

Work is being continued on the Ag salts, anhydrides, dihalides, etc., in the attempt to obtain dinitroso compounds.

Historical Background: Three membered cyclic imines have been known for many years. The most commonly known member of the series is ethyleneimine. This compound is useful as a monomer for the preparation of polyethyleneimine. Among the uses of this polymer are the improvement of wet strength and abrasion resistance in paper, and the reduction of swelling tendencies in cotton and rayon. Eltylenimine is usually prepared by the reaction of ethanolamine with sulfuric acid to form the inner salt, followed by reaction with base to form the imine. It was decided to first try this procedure in the synthesis of fluorinated imines.

Summary: Twenty-seven grams of 1-bromo-3,3,4,4,5,5,5-heptafluoro-2-pentanol have been prepared from perfluorobutyric aicd, via the ketone and bromoketone. Yields were very disappointing. This material has been reacted with ammonium hydroxide in an attempt to form the amino alcohol. The product of this reaction has not yet been isolated.

An attempt is now being made to prepare the amino alcohol, 1-amino-3,3,4,4,5,5,5-heptafluoro-2-pentanol, by reduction of perfluorobutyric acid to perfluorobutanal, condensation of the aldehyde with nitromethane to form the nitro alcohol, and reduction of the nitro group to an amino alcohol.

When the amino alcohol is obtained, it will be reacted with sulfuric acid to form the inner salt; the salt will be reacted with base in an attempt to form the imine.

Experimental: Methyl Perfluoro-n-propyl ketone. To a slurry of 2.2 moles lithium perfluorobutyrate in 2 liters anhydrous ether was added 800 ml of a 3 M solution (2.4 moles, 10% excess) of methyl magnesium bromide, the reaction mixture being maintained at ca. 5°C. The mixture was hydrolized with dilute sulfuric acid, and the ether layer combined with ether extractions of the aqueous layer. The ether solution was dried over magnesium sulfate, and the ether distilled. The residue was dried over Drierite, and fractionated in a 20 inch column packed with glass helicies. The fraction with b.p. 51-54°C was collected. This contained 50 g., 0.236 mole, 11% of theory.

<u>1-Bromo-3,3,4,4,5,5,5-heptafluoro-2-pentanone</u>. In 110 ml (200 g., 2.1 moles) concentrated sulfuric acid was mixed 80 g., (0.38 mole) methyl perfluoro-n-propyl ketone, giving a light yellow emulsion. To the rapidly stirred mixture was added 30.2 g., (0.19 mole) bromine over a period of two hours at room temperature. After standing for one day, the layers were separated, and the lighter layer fractionated. The main cut was taken at 106-108°C., giving 68.8 g., 0.237 mole, 63% of theory.

<u>1-Bromo-3,3,4,4,5,5,5-2-pentanol</u> To a slurry of 4.7 g., (0.124 mole) lithium aluminum hydride in 500 ml anhydrous ether was added a solution of 68.8 g., (0.237 mole) 1-bromo-3,3,4,4,5,5,5-heptafluoro-2-pentanone in 100 ml ether. The additon was dropwise over a period of four hours at 0°C. The mixture was stirred at 0° for another 6 hours; then at room temperature for 12 hours. The reaction mixture was then hydrolized with sulfuric acid, the layers separated, and the aqueous layer extracted with ether. The ether layers were combined and dried over magnesium sulfate, then Drierite. The dried solution was then fractionated, the main cut being taken at b.p. 136-137°. This gave 27 g.,

0.092 mole, 39% of theory.

1-Amino-3,3,4,4,5,5,5-heptafluoro-2-pentanol. The previously prepared bromohydrin was stirred with 500 ml (450 g.) ammonium hydroxide solution (equivalent to 126 g. ammonia, 7.4 moles) for one week. At the end of this period, a yellow oil was at the bottom of the flask. The desired amino alcohol is reported in Rausch, et. al. as having b.p. 68-69°, and by McBee as having 68-69°. Thus, the oil may or may not be the desired product.

Perfluorobutanal. To a solution of 300 ml (487 g., 2.28 mole) perfluorobutyric acid in 1700 ml anhydrous ether was added a slurry of 50 g. (1.32 mole) lithium aluminum hydride in 1500 ml ether over a period of two hours at -5°. The mixture was stirred for another hour, then hydrolized with dilute sulfuric acid. The layers were separated, the aqueous layer extracted with ether, and the combined ether fractions fractionated to remove the ether.

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