Colorado U.

Rubber Research

The Synthesis of Unsaturated Fluorocarbons

Progress Report

~~Quarterly~~ No. 6

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

QMC Project No. 7-93-15-004

For the Period November 13, 1959 to February 13, 1960

February 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 sixth quarterly report for the period November 13, 1959 through February 13, 1960.

II. Summary of Current Progress

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

Satisfactory progress has been made in the synthesis of $CF_2Cl-CFClNO$, $CF_2Cl-CFClNO_2$, CF_3-NO, C_3F_7NO, CF_3COONO, and C_2F_5COONO. Other intermediates and compounds were also prepared but not identified. These will be reported later.

The following materials were shipped:

56 g. of $CF_2Cl-CFClNO$ to 3M (Dr. G. Crawford)

15 g. of $CF_2Cl-CFClNO$ to Dr. J. Montermoso

20 g. of CF_2Cl-CF_2NO to 3M (Dr. G. Crawford)

15 g. of CF_2Cl-CF_2NO to Dr. J. Montermoso

Work is now in progress for producing 200 g. of CF_2Cl-CF_2NO to fill a request need.

Work has also been in progress for making various other nitroso and dinitroso compounds as well as work on the synthesis of some oximino ethers as intermediates for the program.

III. Discussion

In line with our plans given in previous progress reports, we are placing greater emphasis on the study of nitroso chemistry (along with nitro chemistry) with particular emphasis on finding new routes to making R_f-NO and other nitroso and dinitroso-containing aliphatic compounds containing fluorine. Some work is also being directed toward the synthesis of fluorine-containing imines and epoxides.

In our study of the addition of nitric oxide (NO) to fluoroolefins, we are continuing to encounter anomalous results. Thus, in the reaction of nitric oxide and trifluorochloroethylene in the presence of $FeCl_3$ the major product is not the expected dinitroso-adduct, $CF_2(NO)-CFCl(NO)$ but rather $CF_2Cl-CFCl(NO)$(63%) with $CF_2(NO_2)-CFCl_2$, $CF_2(NO_2)-CFCl(NO)$ and/or $CF_2(NO)-CFCl(NO_2)$ and some as yet unidentified nitro-nitrite derivatives.

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

The addition of NO to $CF_2=CF_2$ over ferric fluoride yielded a compound believed to be $CF_2(NO_2)CFCl(NO)$. This reaction is being further studied.

The addition of NOCl to $CF_2=CFCl$ over $FeCl_3$ yielded $CF_2Cl-CFClNO$ in 60-65% yields. This adduct was found to be identical with the adduct obtained from $CF_2=CFCl$ and NO over $FeCl_3$ as a catalyst.

We have been successful in increasing the yield of CF_3COONO from $CF_3COO-COCF_3$ and NOCl. On a one pass basis, a 21% conversion to CF_3COONO was obtained with about 67-70% of the anhydride remaining for further reaction with NOCl. It is believed that by this method the yield of CF_3COONO can be raised to over 60-70%. In turn, the CF_3COONO can be efficiently pyrolyzed to CF_3-NO and CO_2.

In addition to the isolation of CF_3COONO, we have been successful in obtaining the intermediate C_2F_5COONO from C_2F_5COOAg and NOCl. As yet, we have not succeeded in isolating C_3F_7COOAg and NOCl.

IV. Experimental

1. Reaction of $CF_2=CFCl$ with NOCl on $FeCl_3$

One hundred and seventy-four grams (1.5 moles) of $CF_2 = CFCl$ and about an equimolar quantity of NOCl were passed slowly over a period of 18 hours through a 3 foot x 20 mm. pyrex tube packed with a 50-50 mixture of anhydrous $FeCl_3$ powder and 20-200 mesh silica (The function of silica gel was to prevent the packing of the iron chloride catalyst; silica gel alone has no effect on the reaction). The reaction tube was heated to 45°C with an electric heating coil. At the point where the two gases met on the packing the temperature was considerably higher (about 100°C). The rate of flow of the two gases was so adjusted so that no gaseous material was escaping from the carbon ice-cellosolve cooled trap in which the product was collected. The product condensed to a blue-green liquid.

In order to obtain the maximum yield of the desired product $CF_2ClCFClNO$, it was necessary to heat the tube to 45°C when no gases were fed in. When the temperature was higher the product was green and considerable gaseous material was escaping through the receiving trap. Variation of the ratio of the two gases also affected the nature of the products; it was necessary to feed in a slight excess of olefin over that of NOCl in order to have the product come out blue. At higher temperatures and with an excess of NOCl the main products of the reaction are $O_2NCF_2CFCl_2$ and $CF_2Cl-CFCl_2$.

The gaseous and liquid products were washed with water and dried with calcium chloride. Fractionation gave the following products:

(a) 25 grams $CF_2=CFCl$

(b) 155 grams (63%) of $CF_2ClCFClNO$

b.p. -2 to 0°C/138 mm. Hg

b.p. 32/630 mm. Hg

(c) 22.5 grams (9.15%) $CF_2ClCFCl_2$

b.p. 42/630 mm. Hg

(d) 11.6 grams (4.7%) $O_2NCF_2CFCl_2$

b.p. 71-72/630 mm. Hg

(e) 37 grams (15%) residue

A small fraction of the product reacted with water during washing. The water solution gave a test for fluoride as well as for the chloride ions. Upon neutralization of this solution and evaporation to dryness a solid extractable with absolute ethanol remained. It is suspected that a nitrite is also formed which is unstable to water. The structure of this compound has not been established yet but it may be $ONCF_2CFClONO$, $O_2NCF_2CFClONO$ or more likely $ClCF_2CFClONO$ which on reaction with water would give $ClCF_2CO_2H$.

2. Attempted Dechlorination of $CF_2ClCFClNO$

Twenty grams of $CF_2ClCFClNO$ was added dropwise to a suspension of 20 grams of zinc dust in 200 ml pyridine while stirring vigorously. A very vigorous exothermic reaction ensued and it was necessary to cool the reaction vessel with ice. When all of the nitroso compound was added, the reaction mixture became very viscous and stirring was impossible. No product was isolated. It is certain that dechlorination occurs during this reaction but if any $CF_2=CF-NO$ is formed it may polymerize under these conditions. In view of the fact that no gaseous material was evolved during this operation and that dechlorination occurred, this reaction merits further study.

3. Reaction of $CF_2=CF_2$ with Nitric Oxide on Ferric Chloride

Eighty grams (0.8 mole) $CF_2 = CF_2$ and nitric oxide in a ratio of one olefin to two nitric oxide were passed through a 3 foot x 20 mm. pyrex tube packed with a 50/50 mixture of anhydrous $FeCl_3$ powder and 25-75 mesh ground glass. The tube was heated at 75°C during the reaction period which was about 12 hours. During the first hour, the product which was collected in a dry-ice-cooled trap was condensing to a blue liquid. As the gases were fed in the color of the packing changed from dark brown-black to light brown and this color change proceeded slowly along the length of the tube. When all the length of the packing in the tube became light brown, the color of the product changed to green. At this point it was observed that by feeding in the gases alternately the blue color in the product returned. During the course of this reaction a small quantity of a non-condensible gas escaped from the dry-ice-cooled trap.

The product collected at the end of the reaction weight 125 grams; this was washed with water and dried with calcium chlorides. During washing, a gas not-condensible in dry ice was collected in a liquid-air trap. This gas was colorless and gave a molecular weight of 83.1. Twenty-two grams of this gas was collected and the material was passed through a solution of aniline in ether giving a product which will be worked up in order to establish whether or not it may be starting material $CF_2 = CF_2$ or some other product.

In addition to the 22 grams of the gas mentioned above 90 grams of a blue liquid (at dry ice temperature) was left after washing. Thus, 13 grams of a substance was lost in the wash solution. The wash solution was strongly acidic and gave a test for fluoride ion but no test for chloride ion. Neutralization and evaporation to dryness gave a white solid extractable with absolute ethanol. In this case also, it is suspected that a nitrite is formed (CF_2ClCF_2ONO) which reacts with water to form CF_2ClCO_2H.

Distillation of the 90 grams material mentioned above gave:

(a) Eighty grams (64% based on total product collected) of a blue liquid b.p. -10 to -5 and with a molecular weight of 158.7. This compound turned out to be CF_2ClCF_2NO for its infrared spectrogram was superimposable with that from the reaction between $CF_2 = CF_2$ and NOCl (see below). Oxidation with CrO_3 in acetic and sulfuric acids gave the known compound $CF_2ClCF_2NO_2$.

(b) Ten grams of higher boiling material which may be the nitro compound.

4. Reaction of $CF_2 = CF_2$ with NOCl on Ferric Chloride

Seventy grams of $CF_2 = CF_2$ and about an equimolar quantity of NOCl were passed through a 3 foot x 20 mm. pyrex tube packed with $FeCl_3$ and ground glass as in .3 above. The tube was heated at 45°C to 55°C during the reaction period which was about 12 hours. The ratio of $CF_2 = CF_2$ to NOCl was so adjusted that the product which was collected in a dry-ice-cooled trap was blue in color and little or no gaseous material escaped from the system. A very slight excess of $CF_2 = CF_2$ was used. This effect was also brought about by introducing the gases alternately with an equal rate of inflow and equal periods of time. The product was worked up in the same manner as in 3 above.

Products obtained:

(a) Nineteen grams of a gas, non-condensible in dry ice; its infrared spectrogram was superimposable on that obtained from $CF_2 = CF_2 + NO + FeCl_3$; molecular weight 83. As stated above, this may be starting material $CF_2 = CF_2$. (The spectrogram of this gas does not show a double bond absorption; however, although all other bands correspond to the spectrum of $CF_2 = CF_2$).

(b) Seventy grams (65%) of a blue liquid b.p. -10 to -5. This was shown to be CF_2ClCF_2NO.

(c) Fifteen grams of a higher boiling colorless liquid.

(d) The wash solution was strongly acidic. Neutralization of this solution with NaOH and evaporation to dryness gave a white solid which was extractable with absolute ethanol and recrystallized from the same solvent. The crystals gave a melting of 305°C. Here again, a nitrite ($CF_2ClCFClONO$) is suspected to have reacted with water.

5. Two Hundred Grams of $CF_2 = CF_2$ was prepared from CF_2BrCF_2Br.

This will be used for the preparation of 200 g. of CF_2ClCF_2NO

requested by 3M.

6. N. M. R. Analysis

N. M. R. Analysis of the nitro-nitroso compound obtained in the reaction of $CF_2 = CFCl$ with NO and $FeCl_3$ indicated that this compound is $O_2NCF_2CFClNO$. The preparation of this compound was included in our last report.

7. The Reaction of $CF_3CF = CF_2$ with nitric oxide under pressure was reinvestigated.

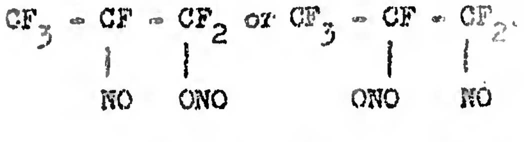
Seventy-five grams of this olefin and one mole of NO were placed in an autoclave for 24 hours at room temperature. 50 grams of $CF_3CF = CF_2$ was recovered along with an undetermined quantity of NO (perhaps mixed with some other very low boiling gas). The other products were the same compounds reported earlier, namely

$CF_3CF(NO_2)CF_2NO_2$ b.p. 68.5/630

$CF_3CF(NO)CF_2NO_2$ or $CF_3CF(NO_2)CF_2NO$

or $CF_3CF(NO)CF_2(NO)$ b.p. 42/630.

Also isolated were two fractions, one boiling at 15-17/630 mm. and another at 27.5/630 mm. Both of these were green liquids and reacted vigorously with H_2O. Possibly these are nitrites having the structures $CF_2 = \underset{ONO}{C} - CF_3$,



$CF_3 - \underset{NO}{\underset{|}{CF}} - \underset{ONO}{\underset{|}{CF_2}}$ or $CF_3 - \underset{ONO}{\underset{|}{CF}} - \underset{NO}{\underset{|}{CF_2}}$.

Another attempt using hexachlorobutadiene as a solvent in the autoclave gave the same results.

8. Reaction of $CF_2 = CFCl$ with NO on FeF_3.

An exploratory experiment was attempted to bring about the reaction of $CF_2 = CFCl$ and nitric oxide on ferric fluoride. A 3 foot x 20 mm. pyrex tube was packed with a 50/50 mixture of powdered FeF_3 and 25-75 mesh ground glass. Passage of the two gases through this medium at various temperatures ranging from room temperature to 100°C resulted in some reaction but most of the nitric oxide was escaping unreacted. When a very small quantity of air was premixed with the olefin and nitric oxide and then passed through the tube a larger percentage of the reactants combined but considerable nitric oxide was still escaping unreacted.

Distillation of the products gave mostly starting material about 70% of total material collected in dry ice trap and three other fractions one of which (b.p. 61.6 - 63.5°C/630) is believed to be $CF_2(NO_2)CFClNO$. A green fraction b.p. 10°C/630 reacted vigorously when mixed with water. The other fraction b.p. 78/630 was colorless. More work in this respect is in progress.

9. Isolation of CF_3COONO

As previously noted by Haszeldine (J. Chem. Soc., 4172 and 2075 (1953)) the pyrolysis of silver perfluoroacetate with nitrosyl chloride gives low yields of CF_3-N=O. However, in our laboratory it was noted that a fuming reactive yellowish-red liquid always accompanied this reaction, and it was hoped that this liquid might perhaps be the key to the low yields. This compound attacked all common solvents. Water, alcohol, ether with evolution of heat, and it was noted that a blue solution resulted when mixing it with acetone. If this were the postulated intermediate CF_3COONO, then it would perhaps be a good nitrosating agent as well as being the pyrolytic precursor of $CF_3-N=O$.

With this in mind, 140 grams of silver perfluoroacetate and excess nitrosyl chloride were mixed in the cold in a round bottom flask. The reaction flask was evacuated for 6 hours at about 2 mm. Hg. and the yellow liquid was collected in a dry-ice-cellosolve-cooled trap along with the excess nitrosyl chloride.

The material was distilled and collected at 45.5-46°C at a pressure of 79 mm. Hg. 45 grams were collected giving a 50% conversion.

Physical Properties are as follows:

(a) B. P. 45.5° at 79 mm. Hg.

(b) n_D^{25} 1.3778

(c) d^{23} 1.5941

An attempted molecular weight using a Regnault bulb and the ideal gas law was not too satisfactory. Due to the high boiling point, a pressure of only 20 mm. could be obtained in the bulb. The experimental value was 136 compared to the calculated value of 143. This may have been fortuitous and is probably not reliable.

However, results of analysis indicates the structure CF_3COONO (perfluoro acetyl nitrite) as being correct.

	%C	%H	%N	%F
Calculated	16.80	0.00	9.79	39.85
Found	17.00	0.04	9.85	39.72

On pyrolysis of the compound with a free flame, the material detonated. Therefore, extreme care should be exercised in handling it. On controlled heating, CF_3-N=O + CO_2 is obtained lending further proof to the assigned structure.

Part of the crude compound was stored in the cold for several weeks and upon distillation a lighter yellow compound resulted B. P. 43°/38 mm., n_D^{25} 1.3609, d^{23} 1.6216.

Analysis	%C	%N	%F	%H
	19.00	6.40	43.63	0.00

This compound may be due to partial decomposition to the anhydride and oxides of nitrogen since these compounds are attacked easily by moisture from the air as well as by light.

10. Isolation of C_2F_5COONO

Attention was turned to the next higher homologue. Thus, 49 grams of silver perfluoropropanoate and 25 grams of nitrosyl chloride were mixed in the cold. The system was evacuated at very low pressures for about 5 hours and a yellowish-green solid collected in the cry-ice-cellosolve-cooled trap. On melting, a yellow-red liquid was obtained.

Fractionation resulted in 12.5 grams (.084 mole) of a yellow-red liquid B. P. 57.5°C at 79 mm. Hg. and thus a conversion of 47% based on 49 grams of salt. Physical properties are as follows:

(a) B. P. 57.5°C at 79 mm. Hg.

(b) $d^{25°}$ 1.6515

(c) $n_D^{25°}$ 1.3570

Results of the analysis lend good evidence for assignment of the structure C_2F_5COONO (perfluoro propanoyl nitrite).

	%C	%H	%N	%F
Calculated	18.66	0.00	7.26	49.22
	18.71	0.00	7.17	49.03

Similar attempts to isolate the next higher homologue from C_3F_7COOAg failed thus far. Thus, on collecting and distilling the reaction mixture from silver perfluorobutyrate and nitrosyl chloride down to 20 mm. Hg. succeeded only in decomposing the yellow liquid to oxides of nitrogen plus the corresponding anhydride. While it is reasonable to assume that this intermediate is more reactive than the corresponding acetyl compound, it is felt that its isolation may still be realized if lower temperatures and pressures are maintained. It should be noted that high yields of nitroso compound results from direct pyrolysis of the initial reaction mixture of the butyric salt while low yields of the nitroso compound from the perfluoro acetic salt are obtained. This is consistent with the observed stabilities of their corresponding intermediates. It was noted also, that the intermediates herein discussed exhibit an unusually high reluctance to wet the surface of their containers.

As was reported previously, perfluorobutyric anhydride plus nitrosyl chloride could be distilled to obtain the nitroso compound $CF_3CF_2CF_2-N=O$. The mixture showed an induction period, sensitive to light and insensitive to ionic catalysts where nitrosonium ions were available. Thus, a free radical mechanism appears to predominate in this system.

11. Reaction of NOCl with $CF_3CO-O-CO\ CF_3$

This experiment gives further evidence as to the relative stabilities of the intermediates formed for these systems.

110 grams of perfluoroacetic anhydride plus 36 grams of nitrosyl chloride were mixed in the cold in a 250 ml. flask to which a reflux condenser cooled to 10°C was attached. The excess nitrosyl chloride was slowly collected into a dry-ice-cellosolve trap and the flask was exposed to diffuse light for about 24 hours.

On distillation, 74 grams of the anhydride was collected and 16 grams of CF_3COONO was obtained at 38.2°C/55 mm. Hg., n_D^{25} 1.3778. On the basis of 110 grams (.524 mole) of anhydride a 21% conversion is obtained. However, it should be noted that 67% of the anhydride is again available for reaction and hence, greater than 60% yields should be achieved in a cyclic process.