Rubber Research.

The Synthesis of Unsaturated Fluorocarbons

Progress Report

Quarterly No. 3 and 4

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

QMC Project No. 7-93-15-004

For the Period Feb. 13, 1959 to Aug. 13, 1959

Sept. 5, 1959

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

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 temperautes.

This research is authorized under Contract No. DA-19-129-QM-1263. This is the third quarterly report for the period Feb. 13, 1959 through May 13, 1959 combined with the fourth quarterly report for the period May 13, 1959 through Aug. 13, 1959.

II. Summary of Current Progress

Due to two things, first, a moving to new quarters in our new chemistry building and secondly, difficulties encountered in the analyses of our nitrogen containing perhalogenated compounds, the desired progress was not attained during these periods. However, in the later stages of our work, we were able to accelerate our program to such a point, that rapid strides were made in the syntheses of various nitroso compounds. Thus, we were able to supply Minnesota Mining and Manufacturing Co., with the following compounds.

18g. of $\begin{matrix} CF_2 \\ | \\ NO \end{matrix} - \begin{matrix} CFCl \\ | \\ NO_2 \end{matrix}$ or $\begin{matrix} CF_2 \\ | \\ NO_2 \end{matrix} - \begin{matrix} CFCl \\ | \\ NO \end{matrix}$ (structure not proven)

20g. of $\begin{matrix} CF_2 \\ | \\ NO \end{matrix} - \begin{matrix} CFCl \\ | \\ NO \end{matrix}$

112 g. of $CF_3 - CFH - CH_2OH$

60 g. of $\begin{matrix} CF_2 & - & CCl_2 \\ | & & | \\ Cl & & NO \end{matrix}$

1 g. of $CF_3 - CF_2 - CF_2 - NO$.

Along with the above materials, the following salts were prepared as intermediates in our study of the following reaction:

$$R_fCOOAg + NOCl \rightarrow R_f-NO + AgCl + CO_2$$

75g. of $CF_3 - CF_2CO_2Ag$

500g. of $CF_3 - CF_2 - CF_2 - CO_2Ag$

30g. of $C_4F_9 - CO_2Ag$

75g. of $C_5F_{11} - CO_2Ag$

90g. of $CF_3(CF_2)_6CO_2Ag$

150g. of $AgCO_2(CF_2)_3CO_2Ag$

200g. of $CF_3 - CF_2 - CF_2 - CO_2Na$

50g. of $CF_2Cl - CFCl - CF_2 - CFCl - CF_2CFClCF_2CO_2Ag$

Other intermediates prepared were

200g. of $CF_3CF = CF_2$

150g. of $CF_2 = CF_2$

200g. of $CF_2 - CF_2 - CF = CF$

175g. of $CF_3CF = CF_2$

All of the above are to be studied with NOCl and NO respectively, to see whether stable adducts could be obtained and kept as such.

III. Discussion

As previously reported in our Progress Report No. 2, we planned to carry out a sequence of steps for the preparation of $CF_3-CFH-CH_2OH$

starting with $CF_3-CF_2CF_2COONa$. These steps have been carried out in good yields and we were able to send 3M about 112g of the alcohol for dehydration to $CF_3-CF=CH_2$.

Also, in line with our plans as given in Progress report, greater emphasis has been given to the study of nitroso chemistry with particular attention to finding new routes to making R_fNO and other nitroso containing aliphatic compounds containing fluorine.

IV. Experimental

The following scheme was used in the preparation of intermediates for the making of $CF_3-CF=CH_2$.

$$CF_3 - CF_2 - CF_2 - COONa \xrightarrow{heat} CF_3CF = CF_2 \xrightarrow[KOH]{CH_3OH}$$

$$CF_3 - CFH - CF_2 - O - CH_3 \xrightarrow{H_2SO_4} CF_3 - CFH - CO_2 - CH_3 \xrightarrow{LiAlH_4}$$

$$CF_3 - CFH - CH_2OH \xrightarrow{-H_2O} CF_3 - CF = CH_2.$$

A. Preparation of $CF_3-CFH-CF_2-O-CH_3$.

The dried sodium salt of perfluorobutyric acid, 1 mole (236g) was pyrolyzed at 180-230°C. The propene (125g.) so generated was passed continuously through two bubblers containing methanol (300 ml.) and potassium hydroxide (7g.). Approximately every two hours, the glass frit on the bubblers became clogged and required cleaning. A dry ice-butyl cellosolve cooled trap was connected at the end of the series to collect any unreacted olefin.

The methanol-fluoro ether mixture was washed with water and distilled to yield one fraction boiling at 44-49° at 635 mm. of Hg. Treatment of this fraction with bromine was carried out to remove

the unsaturated ether, $CF_2=CF-CF_2-O-CH_3$ as the dibromide, $CF_2Br-CFBr-CF_2-O-CH_3$. B. pt. 136° at 760 mm. Hg. Redistillation of the brominated mixture yielded 79.5g (52.6%) of the desired ether, $CF_3-CFH-CF_2-O-CH_3$, b. pt. 47-49° at 635 mm. of Hg.

Several runs were carried out with minor variations. Another run was carried out autogeneous pressure.

A steel autoclave was charged with methanol, 64g., and KOH, 12g. and sealed. It was tested for leaks. When none were found the olefine was introduced into the bomb. Heating at 60°C was begun and maintained for 16 hours.

The bomb was opened and the liquid therein washed with water and distilled. The fraction boiling from 38° - 52° C collected and treated with bromine. Distillation yielded 149 g. (54.5%) of product. B.p. 47-49° at 635 mm.

B. Preparation of $CF_3-CFH-CO_2CH_3$

Method I

A three-neck 500 ml. round bottom flask (not ground glass) was equipped with a mercury sealed-stirrer, stopper and long condensor with a gas take-off to a dry ice trap.

Powdered glass, 15 g., was placed in the flask. To this was added 61 g. (0.3 mol) of the fluoroether and 53 g. of concentrated sulfuric acid. A water bath (40° C) was placed under the flask. The solution began refluxing immediately. The reaction was considered complete when, after 3 hours, refluxing below 70° C had ceased.

The reaction mixture was poured into ice water and the organic layer separated and dried over anhydrous $MgSO_4$. Distillation yielded

24.7 g., B.p. 86° at 630 mm. of the desired product (49.4%). There was no other fraction.

Method II

This was run basically the same as method I. except that the sulfuric acid was added dropwise to the fluoroether. After completion of addition the solution was stirred and heated to 70° C. The reaction was considered complete when there was no refluxing at this temperature.

The reaction mixture was poured into ice water and the organic layer separated and dried over anhydrous Na_2SO_4. This was considered pure enough for further use. Yield of crude product 64.7 g. (61.6%).

C. Preparation of CF_3-CFH-CH_2OH

In a five liter three-neck flask, fitted with a dropping funnel, mechanical stirrer and condenser, was placed 1500 ml. of previously dried anhydrous ether. To this was added 41.8 g. of $LiAlH_4$ and a slurry made and stirred at 0°. In another container was placed 168 g. of CF_3-CFH-CO_2CH_3 (1.0 mole) in 1000 ml. of anhydrous ether. Stirring was started and the solution of the ester (dried over anhydrous magnesium sulfate) was added dropwise at ice-bath temperature at such a rate that reflux was maintained.

After all the ester was added the material was stirred for one-half hour to insure completeness of reaction and then the excess $LiAlH_4$ was decomposed with dilute sulfuric acid (20%) and then water washed. The ether layer was separated and the aqueous layer extracted and the extracts combined with the original ether layer, dried overnight over anhydrous magnesium sulfate and distilled. 112 g. of

alcohol (CF_3CHFCH_2OH) 84% of theory was obtained. B.p. 87-92° at 630 mm.

D. Reaction of Fluoroolefins with Nitric oxide (NO)

1) The following experiments were carried out in attempt to add NO to $CF_2=CFCl$ and $CF_2=CCl_2$ respectively. However, under the following experimental conditions, only low yields of the nitroso derivatives were obtained.

a) Nitric oxide (Matheson) was bubbled slowly through $CF_2=CFCl$ at dry ice temperature. The olefin became intensely blue (visible evidence of nitroso formation)but very little (almost negligible) $CF_2=CFCl$ had reacted over a period of 24 hours. Considerable olefin was carried away with the unreacted escaping NO.

b) Nitric oxide was bubbled through $CF_2=CCl_2$ at 0° for 24 hours. Only distillation, no product was obtained even though the olefin had become intensely blue during the passage of NO. $CF_2=CCl_2$ was then mixed with CS_2 and again treated with NO but without apparent success in so far as an isolable nitroso compound was concerned.

2) Reaction of $CF_2=CFCl$ + NO in an autoclave.

Exactly 116 grams of $CF_2=CFCl$ was placed in an evacuated autoclave at dry ice temperature. Nitric oxide was then compressed in at room temperature until 2 moles had been used. The nitric oxide could not all go in at one time, and it was necessary to wait until what had gone in the autoclave was consume before more was added. During the addition of NO the autoclave was warming up and it

alcohol (CF_3CHFCH_2OH) 84% of theory was obtained. B.p. 87-92° at 630 mm.

D. Reaction of Fluoroolefins with Nitric oxide (NO)

1) The following experiments were carried out in attempt to add NO to $CF_2=CFCl$ and $CF_2=CCl_2$ respectively. However, under the following experimental conditions, only low yields of the nitroso derivatives were obtained.

a) Nitric oxide (Matheson) was bubbled slowly through $CF_2=CFCl$ at dry ice temperature. The olefin became intensely blue (visible evidence of nitroso formation)but very little (almost negligible) $CF_2=CFCl$ had reacted over a period of 24 hours. Considerable olefin was carried away with the unreacted escaping NO.

b) Nitric oxide was bubbled through $CF_2=CCl_2$ at 0° for 24 hours. Only distillation, no product was obtained even though the olefin had become intensely blue during the passage of NO. $CF_2=CCl_2$ was then mixed with CS_2 and again treated with NO but without apparent success in so far as an isolable nitroso compound was concerned.

2) Reaction of $CF_2=CFCl$ + NO in an autoclave.

Exactly 116 grams of $CF_2=CFCl$ was placed in an evacuated autoclave at dry ice temperature. Nitric oxide was then compressed in at room temperature until 2 moles had been used. The nitric oxide could not all go in at one time, and it was necessary to wait until what had gone in the autoclave was consume before more was added. During the addition of NO the autoclave was warming up and it

reached a temperature of about 60°C. The reaction mixture was allowed to stand overnight in the autoclave. No gaseous material was recovered. 160 grams of a blue liquid was obtained. Distillation gave the following distribution of products.

Fraction 1. 5 g. of an intensely blue liquid
b.p. 325-35° at 630 mm Hg.
n_D^{25} 1.3375
d^{25} 1.480
Mol. weight (vapor density method). Calcd for
CF_2-$CFCl$; 176.4
NO NO
Found: 179.3

This compound is new

Fraction 2. 6 g of a light blue liquid
b.p. 41-42° at 630 mm Hg
n_D^{25} 1.3557
d^{25} 1.5418
Mol. weight Calcd. for $C_2F_3ClN_2O_3$, 192.4;
Found 188.1

Probably CF_2Cl-$CFCl_2$

Fraction 3. 20 g. of a colorless liquid
b.p. 70.5° at 630 mm Hg
n_D^{25} 1.3671
d^{25} 1.6176
Mol. weight Calcd. for $C_2F_3Cl_2NO_2$, 198.
Found 198.9

This compound was previously prepared by the Russians (A. Y. Yakubovich et al, Zhur Obshchei Khim 24, 2257 (1954); CA 50, 206 (1956) by the action of NOCl on $CF_2=CFCl$. They reported the following properties

b.p. 77-78° at 760 mm Hg.
n_D^{20} 1.3727
d^{20} 1.6202

Fraction 4. 8.5 g. of a colorless liquid
b.p. 92-98°
n_D^{25}
d^{25}

This compound is probably the dinitro compound, $CF_2(NO_2)-CFCl(NO_2)$, first reported by Haszeldine.

The residue was a viscous brown liquid which was undistillable at a pot temperature of 210° C.

3) Photochemical reaction of $CF_2=CFCl$ + NO

$CF_2=CFCl$ and NO in a ratio of 2 N_9 to 1 $CF_2=CFCl$ were charged in a pressure flask (pyrex) for photochemical reactions. The flask was irradiated with two U.V. lamps. A blue liquid started collecting at the bottom of the flask after about 5 hours. The pressure in the flask was kept at 2 atm. (total) by feeding in the gases. 50 cc of a sky blueliquid was collected and on distillation it gave the following

4.5 grams blue liquid b.p. 54°/630

4.0 grams yellow—green liquid b.p. 102-105.

Since a solid material was collecting on the still head it was decided to wash the latter fraction with H_2O and redistill. When mixed with H_2O a vigorous reaction set in and the organic liquid turned blue. The stopper of the separatory funnel was blown off and everything was lost!

4) Catalytic reaction of $CF_2=CFCl$ + NO

Several experiments were attempted using Lewis acids as catalysts. $AlCl_3$, $FeSO_4$, Al_2O_3, SiO_2, $FeCl_3$, $CuCl_2$, Cu_2Cl_2, and

activated carbon. Of all these only anhydrous $FeCl_3$ gave results. However, it appears that the reaction proceeds satisfactorily only before the catalyst is "poisoned" (?) (perhaps before $FeCl_3$ becomes saturated with nitric oxide).

A 3-foot 20mm pyrex tube wrapped with a heating wire was packed with $FeCl_3$ (anhydrous) and NO and $CF_2=CFCl$ were passed through in a ratio of 2 NO to 1 $CF_2=CFCl$ and at a rate such that very little or no gas escaped from the dry ice cooled traps. The tube was heated at 110-140°C. In the beginning a blue liquid was collecting in the traps but as the reaction proceeded the product became green. 100 ml. of product was collected after 36 hours of continuous operation. The green product was allowed to warm up to room temperature and the gas evaporating from it was passed through a dilute KOH solution and received in another trap. This gas was brownish green before entering the KOH solution but after leaving it condensed to a light yellow liquid. The KOH washing solution gave a heavy white precipitate with $AgNO_3$. This gas gave a mol. weight of 113.3 ($CF_2=CFNO$ mol. wt. = 111)
($CF_2=CFCl$ mol. wt. = 116)

About 10 grams of this was collected. The main part of the product which was a liquid at room temperature was washed with H_2O, dried with $CaCl_2$, and distilled. The following were collected:

3 grams of an intensely blue liquid b.p. 10-32°/630

38 grams of a blue liquid b.p. 32-38°/630

31 grams of a colorless liquid b.p. 71°/630

The blue liquid b.p. 32-38° was then redistilled for fractionation.

However, now no clear-cut fraction could be obtained. During distillation the pot temperature rose steadily while a brown gas was leaving the column and condensing in the dry ice trap to a green liquid. Finally a fraction was collected at 71.5/630 which turned out to be $CF_2ClCFClNO_2$. The green liquid collected in the trap was vaporized and passed through a dilute KOH solution. Practically all of it was taken up except for a little blue liquid that collected in another trap at the other end. It is suspected that during distillation the desired product (CF_2-CFCl) eliminates NOCl which attacks the forming olefin by an addition-oxidation process. The wash solution of KOH gave a heavy white precipitate with $AgNO_3$. In subsequent experiments the compound with b.p. 32.5-35° was isolated and gave the same constants as the one obtained in the autoclave reaction. In addition to this, another light blue compound was isolated with the following constants:

NO NO

b.p. 41/630
n_D^{25} 1.3557
d_{25} 1.5418
Mol. wt. 188.1

This was obtained in about 38% yield when a one foot 20 mm pyrex tube with $FeCl_3$ was used, and distillation carried out under vacuum. This may be CF_2Cl-CCl_2F contaminated with some nitroso compound.

E. Photochemical reaction of fluoroolefins with NO

1) Reaction of $CF_2=CCl_2$ with NO

This reaction was attempted in the sunlight. The reaction is much slower than the corresponding reaction with $CF_2=CFCl$. A

blue-green liquid forms which on distillation loses a brown gas that reacts with H_2O. In view of the fact that heat could decompose some of the product, the reaction was also carried out with U.V. lamps. The product is in the process of purification.

2) Photochemical reaction of $CF_3CF=CF_2$ + NO

This reaction is very slow: No blue gas, or liquid forms. When the gases are mixed in strict absence of O_2 a light brown color appears which then develops to red-brown. Irradiation of the materials with 2 u.v. lamps for one week gave no results, other than the fact that a solid was being deposited on the walls of the flask. Practically all of the starting material ($CF_3CF=CF_2$) was recovered unchanged. This reaction is being studied further.

F. Reaction of Fluoroolefins with NOCl

1) Photochemical reaction of $CF_2=CCl_2$ + NOCl

About 132 grams of $CF_2=CCl_2$ (one mole) and 65 grams NOCl (one mole) were placed in an evacuated pyrex tube provided with a pressure gauge. The mixture was exposed to a U.V. light for one hour during which time the color turned from brown to blue. The reaction mixture was then washed with H_2O and dried. On distillation a blue liquid b.p. 60-80° (13 grams) was collected which on standing in air quickly became colorless. A fraction b.p. 34/630 (45 grams) m.p. 34-35° followed which solidified to colorless waxy crystals. Another 30 grams of a light green liquid was obtained at 108-115°C. A higher boiling residue was left in the pot (20 grams) 50 grams of a low boiling green liquid was also obtained in the dry ice trap connected to the distillation head. This may have been starting

material mixed with NOCl but no tests were carried out on it.

In another run similar to this, the following was isolated

CF_2-CCl_2
Cl NO
b.p. 25-28/100 mm.
n_D^{25} 1.3942
d^{25} 1.554
Mol. wt. 196

In similar reactions of this type Haszeldine [(J. Chem. Soc. 2075 (1953)] and Yakubovich et al., [(Ca. 50, 206 (1956)] were not able to isolate the nitroso compounds.

G. Reaction of R_fCOOAg with NOCl

Both Banus, J. Chem. Soc., (1953) 3755 and Haszeldine, J. Chem. Soc. (1953) 4172 report that the reaction of R_fCOOAg with NOCl gave poor (16% or less) yields of R_fNO and descried the difficulties encountered in their separation. However, preliminary studies by us show that this method may be an excellent way for preparing R_f-NO.

1) The following salts were prepared to study the reaction of R_fCOOAg with NOCl.

a.	$CF_3CF_2CO_2Ag$	75 grams
b.	$CF_3CF_2CF_2CO_2Ag$	500 grams
c.	$CF_3CF_2CF_2CF_2CO_2Ag$	30 grams
d.	$CF_3CF_2CF_2CF_2CF_2CO_2Ag$	75 grams
e.	$CF_3(CF_2)_6CO_2Ag$	90 grams
f.	$AgCO_2CF_2CF_2CF_2CO_2Ag$	150 grams
g.	$CF_3CF_2CF_2CO_2Na$	200 grams
h.	$ClCF_2$-CFCl-CF_2.CFCl-CF_2-CFCl-CF_2-CO_2Ag	50 grams

2) To date, trial runs were made on the following:

a. $CF_3CF_2CF_2CO_2Ag$

b. $CF_3CF_2CF_2CF_2CO_2Ag$

c. $CF_3CF_2CF_2CF_2CF_2CO_2Ag$

d. $AgCO_2CF_2CF_2CF_2CO_2Ag$

e. $CF_3CF_2CF_2CO_2Na$

In all cases, except the sodium salt, a blue compound insoluble in water or 30% NaOH was obtained.

3) Procedure

A slight excess of nitrosyl chloride was added to the cold silver salt, anhydrous conditions being maintained. An instantaneous reaction occurs which results in a yellow-brown liquid being formed which is suspected to be an acyl nitrite R_fCOONO (Sodium salt did not form this liquid). The resulting liquid (in the original flask) was heated with a small flame and invariably the corks were blown out with a loud report. Since the original method yielded so many decomposition products and low yields, it was decided to keep the rate of heating and the input energy to a minimum to avoid explosions and decomposition by hot spots. A mantle was used and upon gradual heating the contents of the flask turned a deep red; at 135-145°C this suddenly turned greenish-blue at which time CO_2 was observed to be eliminated as evidenced by collection in a $Ba(OH)_2$ trap. The crude products, after collection in a dry ice trap, were twice passed through a 30% NaOH solution to eliminate the oxides of nitrogen as well as any excess NOCl present. The resulting gases were sky blue, and after drying through a $CaCl_2$ tube, they were collected in a dry ice trap where it was observed to form a deep purple liquid. Finally the gases were distilled.

4) Results of decomposition of $CF_3CF_2CF_2CO_2Ag$.

a. Equilibrium temperature on distillation of $CF_3CF_2CF_2N=O$ was -18.5°C at 630 mm

b. Theoretical Molecular weight 199

c. Calculated Molecular weight using Ideal Gas Law and the Reguault Method.

(1) 198.8
(2) 195.1

d. Infra Red Spectra shows strong absorption at 6.25m attributed to N=O stretching.

e. Yield 46%

5) Results of decomposition of $CF_3CF_2CF_2CF_2CO_2Ag$.

a. Approximate b.p. 10.5°C at 630mm $CF_3CF_2CF_2CF_2N=O$

b. Theoretical molecular weight 249

c. Calculated molecular weight 245

d. Yield 40% (5 grams collected).

6) Some white solid appears in the purple liquid on standing for 24 hours or longer in the dry ice trap which could possibly be a dimer of R_fNO compound. For example R_fN-O / $O-N-R_f$

On very slight warming the white solid disappeared.

Note: It was observed that no explosions occur unless the pot is heated to dryness at temperatures over 150° for a half hour or longer after vigorous CO_2 evolution has ceased.

H. Reaction of $CF_2=CFCl$ with NO_2

Caution: The following reaction with $CF_2=CFCl$ and NO_2 was attempted and a terrific explosion took place.

$$CF_2=CFCl + 2NO_2 \rightarrow \begin{matrix} CF_2 & - & CFCl \\ | & & | \\ NO_2 & & NO_2 \end{matrix}$$

A steel Parr hydrogention bomb of 500 ml capacity (wall thickness ca. 2 cm.) was cooled for 15 min. in a dry-ice cellosolve bath and then charged with 120 g (1.03 moles) of $CF_2=CFCl$ and then with nitrogen dioxide. Weight loss from the nitrogen dioxide cylinder was 135 g. but the actual charge entering the bomb was much less due to leaks. It was estimated that less than 100 g. (2.18 moles) actually was fed into the bomb. The bomb was then allowed to come to room temperature. About two hours later during this warming up process, the contents of the bomb detonated and the explosive force was such as to actually demolish the bomb. This same reaction is reported to have been carried out by Haszeldine without the dire result encountered by us.

V. Plans for Future Work

Research will be continued to finding new and improving old methods for the preparation of R_fNO and other similarly related compounds. Of especial interest at this time is the preparation of larger amounts of $CF_3-\underset{NO}{CF}-\underset{NO}{CF_2}$ and $CF_2=CF-N=O$ and attention to methods for the preparation of fluorinated tethers, imines, and epoxides.