Colorado U.

# RUBBER RESEARCH

## THE SYNTHESIS OF UNSATURATED FLUOROCARBONS

PROGRESS REPORT
~~QUARTERLY~~ NO. 2

U. S. ARMY CONTRACT DA-19-129-QM-1263
QMC PROJECT NO. 7-93-15-004

For the Period November 13, 1958 - February 13, 1959

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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 second quarterly report for the period November 13, 1958 through February 13, 1959.

# II. SUMMARY OF CURRENT PROGRESS

Due to the fact that most of the time was spent in preparing intermediates, only one sample was sent to Minnesota Minning and Manufacturing Company during this period.

FC-183 $CF_2-CFCl-CH_2-CH_3$ 250 g.

Several pounds of perfluoroadipic acid were also prepared as an intermediate in the making of $CF_2I-CF_2-CF_2I$ for future use in preparing $NO-CF_2-CF_2-CF_2-NO$.

About 500 g of $CF_3-CF = CF_2$ also prepared as an intermediate in the preparation of $CF_3-CH = CF_2$.

# III. DISCUSSION

Previously, as reported in our Progress Report No. 1, we planned to carry out the syntehsis of $CF_3-CH = CF_2$ through the following sequence of steps:

a. $CF_3-CF_2-COOAg + I_2 \rightarrow CF_3-CF_2I + CO_2 + AgI$

b. $CF_3-CF_2I + (CH_2)_2 \rightarrow CF_3-CF_2-CH_2-CH_2I$

c. $CF_3-CF_2-CH_2-CH_2I + Mg \rightarrow CF_3-CF_2-CH_2\overset{CH_2-}{-}MgI$

d. $CF_3-CF_2-CH_2-CH_2MgI \xrightarrow[2.\ H_2O]{1.\ O_2} CF_3-CF_2-CH_2-CH_2OH$

e. $CF_3-CF_2-CH_2-CH_2OH \xrightarrow[2.\ NaOH]{1.\ CrO_3} CF_3-CF_2-CH_2COONa$

f. $CF_3-CF_2-CH_2-COONa \xrightarrow{heat} CF_3-CF = CF_2 + CO_2 + NaF$

Steps a to c inclusive, were carried out with good yields. Difficulty was experienced in obtaining good yields in the oxidation of the alcohol $CF_3-CF_2-CH_2-CH_2OH$ to $CF_3-CF_2-CH_2-COOH$. Since $CF_3-CF_2-COOH$, the acid needed for this sequence of reactions, is practically impossible to obtain (at the present time), we felt it necessary to find other avenues for preparing $CF_3CH = CH_2$.

On this basis, the following sequence of reactions were outlined and studied in which $CF_3-CF_2-CF_2-COOH$ (a readily obtainable acid) was used as the starting material.

a. $CF_3-CF_2-CF_2-COOH \xrightarrow{NaOH} CF_3-CF_2-CF_2-COONa$

b. $CF_3-CF_2-CF_2-COONa \xrightarrow{heat} CF_3-CF = CF_2 + CO_2 + NaF$

c. $CF_3-CF = CF_2 + ROH \rightarrow CF_3-CFH-CF_2-OR$

d. $CF_3-CFH-CF_2-OR + H_2SO_4 \rightarrow CF_3-CFHCOOR$

e. $CF_3-CFH-COOR + LiAlH_4 \rightarrow CF_3-CFH-CH_2OH$

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

Steps a to d inclusive have been carried out successfully in good yields.

Emphasis is still being placed on finding new routes to $R_fNO$ and $NO-R_f-R_f-NO$ type of compounds.

# IV. EXPERIMENTAL

## A. Preparation of COOH-$CF_2$-$CF_2$-$CF_2$-COOH

The method of McBee et al[1] was used in preparing perfluoroadipic acid by the oxidation of $CF_2$-$CF_2$-$CF_2$-CCl = CCl.

A five liter three neck flask was used. It was fitted with agitator, reflux-condenser and a device to add potassium permanganate powder from time to time through a second condenser. Into the 5l flask were placed 500 ml. water and 408.2 grams (1.666 gram moles) of CF2-$CF_2$-$CF_2$-CCl = CCl (Hooker Electrochemical Company). The emulsion was brought to mild reflux with agitation. Then 500 grams (3.16 gram moles) U.S.P. grade potassium permanganate powder was added very gradually over the course of 4.5 hours, while the mixture was kept agitated under mild reflux. The mass was kept under further reflux for another 20 to 24 hours to complete the oxidation.

The brown slurry was then subjected to steam distillation in order to recover the unreacted cyclo-pentene (about 18 grams). The hot distillation residue was filtered and the precipitate of pyrolusite ($MnO_2$) washed with 2 1/2 liters of 90°C water in small portions.

The filtrates from two of the above runs were combined (5.5 to 6 liters). The water from the resulting solution was distilled off in vacuo (capillary to prevent bumping!) until the volume of the concentrated solution was reduced to 667 ml. This distillation residue was brought to 10°C. by outside cooling and 334 ml. conc. sulfuric

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[1] McBee, et al, J. Am. Chem. Soc. 39, 415 (1947).

acid was very slowly added (in hood! HCl escapes!) to free the hexafluoroglutaric acid. A few grams of bisulfite were introduced to reduce small amounts of suspended manganese dioxide. The addition of the sulfuric acid caused much potassium sulfate and white, anhydrous manganese sulfate to precipitate, (while much hydrogen chloride was evolved).

The slurry was well-cooled and well-shaken and extracted with 4 liters of ether. The ether was then distilled off and the residue of crude hexafluoroglutoric acid, a viscous mass, heated under 17 mm. Hg to 100°C. with thermometer in the liquid, in order to remove the water.

The residue crystallized upon standing under cooling. 658 to 716 grams of crude acid were obtained. Yields ranged from 86.2 to 93.8%. The theoretical yield of hexafluoroglutoric acid from the above two combined runs (accounting for pentene recovered) would have been 763.2 grams.

M. P. range 78-88°; B. P. range 134-8°/3mm.

## B. Attempted Preparation of $I(CF_2)_3I$

The di-silver salt of hexafluoroglutaric acid (230 g) was placed in a 2 liter flask along with an excess of iodine. Heating was slowly begun. When the mantle temperature reached 80C., a violent evolution of gas begun and iodine sublimed throughout the apparatus. Very little or no $I(CF_2)_3I$ was obtained.

It is planned to carry out the preparation of $I(CF_2)_3I$ with $COCl(CF_2)_3COCl$ in the following manner.

$$COCl-(CF_2)_3 - COCl + KI - I(CF_2)_3I + 2CO + KCl.$$

A similar procedure for the preparation of $R_FI$ has been shown to be operative by C. G. Krespan.[2]

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[2] C. G. Krespan, J. Org. Chem. 23, 2016 (1958).

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### C. Preparation of $CF_3-CF_2-CF_2-CO_2Na$

The sodium salt of $CF_3-CF_2-CF_2-CO_2H$, (214 g.) was prepared in the usual manner i.e. by treatment of the acid with aqueous sodium hydroxide followed by subsequent evaporation.

### D. Preparation of $CF_3CF = CF_2$

The sodium salt $CF_3-CF_2-CF_2-CO_2Na$ was pyrolyzed (dry distillation) to yield the olefin. B. p. -30°/760 mm.

### E. Preparation of $CF_3-CFH-CF_2-O$ Me or $CF_3-CFH-CF_2-O-Et$[3]

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[3] Knunyants, et. al., C. A. 47, 5787 h (1954)

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The olefin $CF_3$ $CF = CF_2$ (15 g) was heated in a stainless steel auto clave with the alcohol 3 g. and 0.7 g. powdered KOH for 13-14 hours at 60°. This yielded 16.4 g. of product b. p. 44-53°C, which was treated with ice cooling with bromine until reaction ceased and then distilled. Yield 83% pure $CF_3-CFH-CF_2-O-Me$ B. p. 54-55° $n_D^{10}$ 1.429 $d_{10}$ 1.40

Yield of $CF_3-CFH-CF_2-O-Et$ 79.3% B. p. 64-65°C. $n_D^{20}$ 1.2960 $d_{20}$ 1.299

### F. Preparation of $CF_3-CFH-CO_2-Et$

Exactly 6.3 g. $CF_3-CFH-CF_2-O-Et$ and 4 g. conc. $H_2SO_4$ were refluxed for 3 hours at 70° or until reaction ceased. The cooled products were quenched with ice water and the organic layer separated and dried. The dried material was distilled yielding 2.5 g. of desired product (45%) B. p. 99-100° at 630 mm. $n^{25}_{D}$ 1.3240

## G. Preparation of $CF_3-CF_2-CH_2-COOH$

The procedure of Larsen[4] was followed. Into a three neck flask

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[4] Larsen, Ph. D. thesis, University of Colorado (1954)

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equipped with a mechanical stirrer, condenser and dropping funnel were placed 300 ml acetone and 30 g. (0.18 ml) of the fluoroalcohol $CF_3-CF_2-CH_2-CH_2OH$. The mixture was stirred and cooled in an ice salt bath to -5°C. Powdered $CrO_3$ (25 g) was then added portion wise. The solution turned dark. The addition required 1.75 hours and the temperature did not exceed 0°C. conc. sulfuric acid (27 ml) was then added dropwise over a period of 1.5 hours with the temperature kept below 0°C. The misture was then stirred for 0.5 hour at less than 15°C. The bath was removed and the mixture allowed to come to room temperature. After filtration through filter cel the solution was dried over anhydrous $MgSO_4$. The acetone was removed and the residue distilled in vacuo to yield 11.1 g (34%) of product which solidified in the receiver. B. p. 92-94°/61 mm m. p. 60-61.5°

## H. Preparation of $CF_3-CH=CH_2$

To 200 g. KOH in one liter of 95% ethanol was added dropwise and with stirring 436 g. (1.95 moles) of $CF_3-CH_2-CH_2I$. The product, a gas, was collected in a trap cooled in dry-ice cellosolve mixture. 160 g. of product (85%) was obtained.

### I. Attempted preparation of $CF_3-CHCl-CH_2-OH$

a. Into 100 ml. of water with 1 ml. of saturated $FlCl_3$ solution in a 3-neck flask, was bubbled chlorine gas for a period of one hour. Then equal quantities of $CF_3-CH=CH_2$ and $Cl_2$ were passed through the saturated solution. After about 25 g. of $CF_3-CH=CH_2$ had passed through, no volume increase was noted. All of the olefin was recovered unreacted in a dry-ice trap. Apparently, no reaction took place.

b. To 150 g. $CaOCl_2$ and 300 ml. of water in a 3-neck flask was added 200 g. of boric acid. HOCl solution was distilled off until 650 cc of aqueous solution was obtained. This was placed in a steel bomb with 60 g. of $CF_3-CH=CH_2$ and agitated for a period of 24 hours at room temperature. Fifty-two grams of $CF_3-CH=CH_2$ was recovered. No reaction product was obtained upon working up the aqueous reaction mixture.

### J. Reaction of $CF_3-CF_2-CF_2-I$ + NO (attempted prep. of $CF_3-CF_2-CF_2NO$)

A five-liter irradiation flask equipped with a water-cooled Hanovia U. V. lamp was evacuated and charged with 150 g. of mercury and 148 grams (1/2 mole) $CF_3CF_2CF_2I$. To this was added slowly from a tank 1/2 mole NO gas. As soon as the NO entered the flask a brown color appeared which indicated that perhaps the vessel was not free of oxygen ($2\ NO + O_2 \rightarrow 2\ NO_2$) The reaction mixture continued to become darker in color, and the mercury was coated with a dark material;

no blue color, characteristic of $CF_3-CF_2-CF_2-NO$ was evident. After 5 hours of irradiation the pressure dropped to atmospheric press. No product was isolated.

## K. Reaction of $CF_2 = CH_2$ with phenyl hydrazine

About 108 g. (1 mole) $\phi NHNH_2$, 200 ml benzene and 132 g. (1 mole) $CF_2 = CCl_2$ were placed in a steel autoclave and shaken overnight at room temperature. No gases were evolved upon opening the autoclave. The product was a dark brown solid. This was washed with water and taken up with benzene. Evaporation of the solvent gave 80 grams of a yellow-brown solid which upon repeated crystallization did not give a pure compound as indicated by its m. p. This is now being purified chromatographically for characterization.

L. The same reaction as K was effected with $CF_2 = CH_2$. Purification and characterization is now under way.

## M. Reaction of Olefins (fluorinated) with $HONH_2$

This is a reaction which is hoped to lead to a nitroso compound. No pure products isolated as yet; experimental conditions are being worked out.

## V. FUTURE WORK

Research will be continued to find new methods for preparing $R_fNO$ and other similarly related compounds. Attention will also be given to the preparation of fluorinated ethers, imines, epoxides, and other monomers requested from time to time.