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COLORADO U

Rubber Research

The Synthesis of Unsaturated Fluorocarbons

Progress Report

Quarterly No. 9

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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 Snythesizing 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 ninth quarterly report for the period August 13, 1960 through November 13, 1960.

II. Summary of Current Progress

The work in this period is still focused on finding better methods for making nitro- and nitroso- fluorocarbons and at the same time preparing larger quantities of CF_2Cl-CF_2-NO for the low temperature rubber program. The initially desired one pound of CF_2Cl-CF_2-NO has been prepared and forwarded to Dr. George Crawford of 3 M. in several different batches. In addition to the substrates previously reported (quarterly report no. 8), $TiCl_4$ suspended in "Cellite" was also tried. It gave results similar to that obtained with ferric chloride.

As a general "crank" method for producing the nitroso compounds, the gaseous reaction of the olefin with the nitrogen oxides or nitrosyl chloride over ferric chloride seems as good as any yet uncovered. But this method suffers from various serious limitations for large "scale-up". In order to remedy this deficiency, attention was given to the development of a system utilizing a solvent.

Using $CF_2=CFCl$ and passing this olefin along with NOCl through a solution of ferric chloride in tetrachloroethane containing a little acetic anhydride, yields of $CF_2Cl-CFClNO$ as high as 70% were obtained. It is further planned to carry out this type of reaction with $CF_2=CF_2$.

Work is also being pursued in trying out reactions in an effort to obtain dinitroso compounds either by direct synthesis or by reduction of the nitro or dinitro adducts.

The uranyl nitrate complex $(UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4)$ was found to be effective as a nitrating and nitrosating agent when reacted with $CF_2=CFCl$. Both $CF_2NO_2-CFClNO_2$ and $CF_2NO_2-CFClNO$ were isolated and identified.

In one experiment, the reduction of $CF_2Cl-CFClNO_2$ yielded only $CF_2Cl-COOH$.

Work is also being currently carried out on the preparation of fluorinated cyclic imines in order to obtain the latter as a monomer for polymerization studies.

III. Discussion

In line with our plans given in previous progress reports, greater emphasis is still being placed in finding more efficient and effective method for preparing nitroso adducts and compounds. A large part of our efforts are also being placed in the synthesis of a large quantity of CF_2Cl-CF_2-NO for use in the polymer program of 3 M.

Some portion of our effort will still be continued in the field of monomer synthesis (imines and epoxides) and the production of dinitroso compounds.

IV. Experimental

Procedure:

1) Preparation of CF_2ClCF_2NO

For the pound of CF_2ClCF_2NO sent to 3 M the method involved the ferric chloride induced reaction of NOCl and $CF_2=CF_2$ at 40-60°C on jacketed 4' x 25 mm glass tubes packed with anhydrous ferric chloride and crushed glass. The ferric chloride is not merely a catalyst but actively participates in the reaction gradually spending itself in the course of the reaction. It forms a complex with NOCl, which through oxidation and exchange reactions also makes NO_2, N_2O_3, Cl_2, and NO_2Cl available to the olefin. Thus, by the time it spends itself it appears to be a complex of hydrolyzable N_2O_4, partially in the ferrous stage no longer adequate for nitroso production. Although these reactions are sufficient for laboratory size preparations of pure nitroso derivatives by distillation, they suffer drawbacks in large scale production. The neccessity of cleaning, repacking, and preparing $CF_2=CF_2$ for each tube are bottlenecks; the ground glass also has to be washed and dried for reuse. The chemistry involved is complex as previously reported. Aside from the addition products of N_2O_4, Cl_2, N_2O_3, and NO_2Cl side products, there appears to be large amounts of nitrogen evolved during distillation. This most probably comes from the diazonium reaction.

$$R\text{-}CF_2\text{-}NO + NO_2 \rightarrow R\text{-}CF_2N_2NO_3 \rightarrow R\text{-}CF_2ONO_2 + N_2 \xrightarrow{H_2O} RCOOH$$

The yield per reaction tube of pure CF_2ClCF_2NO is in the order of 25 grams. It is planned to continue making the product by this method round the clock until some definitely better methods are scaled up (see below.)

2) Preparation of $CF_2ClCFClNO$ in a solvent system

In order to prepare large quantities of nitroso derivatives it would be desirable to react the olefin directly with nitrosating agent in a solvent system. The olefin used in such preliminary investigations is always $CF_2{=}CFCl$ due to its ready availability and relative lower cost.

A solvent system that worked effectively consisted of tetrachloroethane containing 10% by weight of anhydrous ferric chloride. The ferric chloride was made soluble by the addition of 1% acetic anhydride. Equimolar amounts of NOCl and $CF_2{=}CFCl$ were passed into the solution via a sintered glass frit over a 10 hour period; any gaseous material coming over was collected in CO_2-cooled receivers. During the course of the reaction spent catalyst was being precipitated. The products remaining in the high boiling tetrachloroethane solvent were vacuumed over and combined with that in the cold trap. From the vapor phase chromatogram (see quarterly No. 8) and infrared curve, it was shown that a yield of $CF_2ClCFClNO$ of about 70% was obtained in the vapor collected during reaction. There was only a trace of the chlorination product, $CF_2Cl{-}CFCl_2$.

This technique will now be extended to $CF_2{=}CF_2$. If successful, a large battery of solvent reactions will be set up to make CF_2ClCF_2NO.

Solvents such as pure CCl_4 and Ac_2O failed to give any significant amount of nitroso compound by themselves. For example, NOCl and $CF_2{=}CFCl$ dissolved well in Ac_2O but were essentially recovered upon distillation. That which reacted gave AcCl and AcONO.

3) $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ as nitrating addition agent for unsaturated molecules.

It has been demonstrated that the complex $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ is a potent nitrating agent for aromatic substitution. (Lacher, Ensley, Tenge, and Park, J. Org. Chem., <u>24</u>, 1347, (1959). It therefore, seemed advisable to investigate its potential use as a N_2O_4 addition agent to unsaturated molecules. Specifically, it has been difficult to obtain high yields of N_2O_4 and N_2O_3 addition products of halogenated olefins.

The effectiveness of this uranyl complex exceeded expectations in that quantitative conversion of CF_2=CFCl (the olefin upon which the study was conducted) to nitro compounds resulted from its use. The general procedure used consisted in passing the olefin directly through a sintered glass frit into a 12-15% acetic anhydride solution of $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ maintained at ice temperature; any effluent gases were collected in ice and CO_2 - acetone cooled system. The olefin was passed through until it started to collect in the CO_2 - acetone coolant bath and the rate of input was equal to the rate of effluent gas. As the reaction proceeded the solution became quite green due to the yellow of UO_2^{++} and blue of $CF_2NO_2CFClNO$ (some N_2O_3 addition). After the olefin supply was stopped, the cold acetic anhydride solvent was hydrolyzed with water while still attached to the gas collecting system; a very small amount of CF_2=CFCl (infrared) was evolved. The blue heavy organic layer containing CF_2NO_2-$CFClNO_2$, $CF_2NO_2CFClNO$, and $CF_2NO_2CFCl_2$ was removed. The product distribution was obtained by vapor phase chromatography (see Q. M. C. report No. 8.) From 10.1 g. CF_2CFCl (0.088 moles) and 18.6 g. complex (0.014 moles), 14.7 g. of nitration products were obtained.

Upon a larger scale-up, the same results were obtained with full conversion of the olefin to nitro and nitroso products in the following ratios.

$$\begin{array}{ll} & \text{Ratio} \\ CF_2{=}CFCl + UO_2(NO_3)_2\cdot H_2O\cdot N_2O_4 \rightarrow CF_2NO_2{-}CFClNO_2 & 1 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \left.\begin{array}{l} CF_2NO_2{-}CFClNO \\ CF_2NO_2{-}CFCl_2 \end{array}\right\} & 1.5 \end{array}$$

It is of significance that no NOCl addition ($CF_2ClCFClNO$) occurred whatsoever.

Upon distillation some of the dark blue $CF_2NO_2CFClNO$ disproportioned to the colorless $CF_2NO_2{-}CFCl_2$.

It was further shown that the uranyl complex as a whole is responsible for the addition and not merely the presence of the N_2O_4 associated with it. Under the same conditons as the complex was run, a solution of 0.25 moles of N_2O_4 in acetic anhydride was made, followed by $CF_2{=}CFCl$ passage for ten hours. It was thought that $N_2O_4 + CH_3(CH_3CO)_2O$ giving a 50/50 mixture of $CH_3-\overset{O}{\overset{\|}{C}}-ONO$ and $CH_3-\overset{O}{\overset{\|}{C}}-ONO_2$ might have been responsible for the addition. However, less than 1% nitro addition resulted and all the product was water soluble. The procedure was then repeated making a 0.25 molar CF_2CFCl solution in Ac_2O and then passing in N_2O_4. The same reaction resulted as in the inverse addition and all material was water soluble. The aqueous solution was distilled to give what appears to be some $CF_2NO_2{-}COOH$ (which is to be proven later).

The complex also nitrates $CF_2{=}CFBr$ to form $CF_2NO_2CFBrNO_2$; qualitatively it has also been found that cyclohexene is oxidized to cyclohexanone. Under the conditions for good reaction with "F-113," $CF_2{=}CF_2$ reacted slower and not quantitatively. The dinitro ($CF_2NO_2CF_2NO_2$) and N_2O_3 addition product (CF_2NO_2-CF_2NO) occur but in smaller yields; some unstable N_2O_3 is also formed. With CF_2=CF_2, a higher reaction temperature is needed than with CF_2=CFCl. At atmospheric pressure this means less solubility of CF_2=CF_2 in acetic anhydride and so more of the olefin comes through unreacted; this reaction should be tried at slight pressure to obtain greater solubility with resultant addition of the nitro complex.

At present it seems the complex represents a very safe and easy reagent for general use in both substitution and addition reactions in organic synthesis.

4) Reduction of Nitro Compounds

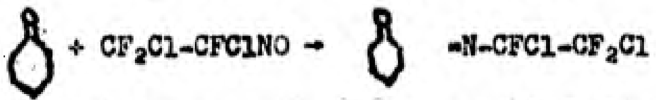
A brief study of reduction of fluoro-nitro-alkanes has been started in hopes of stopping reaction at the nitroso stage. However, attempts in aqueous media have given the corresponding acids.

ex. $CF_2Cl\text{-}CFClNO_2 \xrightarrow[Zn]{NH_4Cl} [CF_2Cl\text{-}CFClNHOH] \rightarrow CF_2Cl\text{-}COOH$

In this reaction the nitro compound was slowly added to an aqueous solution of NH_4Cl containing suspended zinc dust while stirring. There was an exotherm (75°) and all the nitro was reduced. The acid $CF_2ClCOOH$ was worked up as its sodium salt.

The use of anhydrous $SnCl_2$ in a suitable solvent is being investigated and may be promising. $SnCl_2$ dissolves in acetone for example and reduces nitro groups easily. However since the products of reduction boil in the range of usual solvents, cyclohexanone was used.

ex. 0.15 moles of $SnCl_2$ in 100 ml cyclohexanone (dissolved) and 30 grams (0.15 moles) $CF_2ClCFClNO_2$. There was an exotherm, but nothing came over from the cold trap. Flask contents was a purple tar; vacuum distillation gave some cyclohexanone. Trace ingredients in the distillate will be looked for by vapor phase chromatography. Cyclohexanone was a bad choice for solvent due to the probable following reaction:



The choice of a solvent in which $SnCl_2$ dissolves and which does not contain any active hydrogen may be a critical factor.

5) Attempted Reactions to Obtain Dinitroso Compounds

Ninety grams of CF_2Br-CF_2Br and 100 grams of NO were introduced into a 22 liter flask and irradiated with an ultra-violet lamp for two days. Starting materials were recovered.

The experiment was repeated with 150 grams of Mercury to eliminate NO_2 formed. Irradiation again yielded only starting materials.

Fifty grams of CF_2Br-CF_2Br, 45 grams of NO and 100 grams Hg were introduced into a 7 liter pyrex flask and irradiated with an ultra-violet lamp for ten days. Starting materials were recovered.

A special 7 liter flask fitted with a quartz insert was then used with the CF_2Br-CF_2Br plus NO mixture in hopes that the shorter wavelengths of the UV would effect reaction. Only starting materials were recovered.

Fifty grams of the di-silver salt of perfluoroglutaric acid was treated with 30 grams of NOCl. Upon heating, a blue liquid was collected in a dry ice trap. Distillation led to decomposition with the formation of five grams of perfluoroglutaric anhydride and polymer materials.

Forty grams of CF_2I-CF_2I and 30 grams of NO and 50 grams of Hg were introduced into a 7 liter flask and irradiated with an ultra-violet lamp for two hours. Intense blue materials were collected and the IR spectra revealed extremely strong absorption of nitroso peak. M.W. found, 161.2.

6) The Preparation of Fluorinated, Cyclic Imines

187 grams of 3,3,4,4,5,5,5-heptafluoro-1-nitro-2-pentanol have been prepared from perfluorobutyric acid, via reduction of the acid to the aldehyde, followed by condensation with nitromethane. The nitro alcohol is currently being reduced in small quantities by hydrogenation with palladium on charcoal to 3,3,4,4,5,5,5-heptafluoro-1-amino-2-pentanol.

Plans for Future Work: The amino alcohol will be reacted with concentrated sulfuric acid to form the inner salt; the salt will then be reacted with base in an attempt to form the imine. If the preceding is unsuccessful, the following paths will be tried:

1. Gabriel reaction: Conversion of the amino alcohol to to the 2-bromo amine, followed by reaction with base to give the imine.
2. Reaction of an oxime with Grignard reagent to give the imine.
3. Conversion of the 2-bromo amine to the brosylate, which may then cyclicize to the imine.
4. Reaction of an olefin with phenyl azide, which upon heating may give the imine.

Experimental: Perfluorobutanal. To a solution of 300 ml (487 g, 2.28 moles) perfluorobutyric acid in 1700 ml anhydrous ether was added a slurry of 50 g (1.32 moles) lithium aluminum hydride in

1500 ml ether, over a period of two hours at -5°C. The mixture was stirred for another hour, then hyrolized with dilute sulfuric acid. The layers were separated, the aqueous layer extracted with ether, and the combined ether fractions fractionated to remove ether, to 85°. The hydrate was dehydrated by addition of of the residue to a mixture of 50 g phosphorus pentoxide in 200 ml concentrated sulfuric acid, the low boiling aldehyde being collected in a trap cooled in Dry Ice/acetone while the pot temperature aas raised to 95°. The aldehyde was fractionated and the fraction with b.p. 24.5-25.0°C. collected. Yield was 198 g (1.0 mole; 44% of theory.)

3,3,4,4,5,5,5-Heptafluoro-1-nitro-2-pentanol. To 198 g (1.0 mole) perfluorobutanal was added 18 g (1.0 mole) water, to form the hydrate. To the hydrate was added 2.1 g potassium carbonate and 70 g (1.17 mole) nitromethane. The mixture was heated with stirring for 3 hours at 50-60°C. The reaction mixture was extracted thrice with water to remove potassium carbonate, and the aqueous washings combined and extracted thrice with ether. The etherial extract was combined with the non-aqueous portion of the reaction mixutre, and fractionated through a 20 in. glass helicies column, the fraction with b.p. 63-70°C. at 1-2 mm Hg being collected. Yield of this material was 187 g (0.72 moles; 72% of theory) n_D^{20} 1.3518

3,3,4,4,5,5,5-Heptafluoro-1-amino-2-pentanol. To a 1 pint bottle was added 2.6 g (0.01 mole) of the nitro alcohol, 20 ml absolute ethanol, and ca. 10 mg palladium on charcoal. The apparatus was pressurized with hydrogen to 34.5 psig. After 2 hours, a pressure drop of only 0.2 psig was indicated. Another 10 mg of catalyst was added, and the apparatus again pressurized to 34.7 psig.

After four more hours, the indicated pressure was 32.5 psig. Total pressure drop; 2.4 psig; calculated drop for reduction of 0.01 mole; 2.4 psig. To insure complete reduction, the reaction was continued for another 60 hours. The infra-red spectrum of the ethanol solution indicated complete disappearance of the peak at 1565 cm^{-1}, characteristic of a nitro group. The reaction is now being gradually scaled up for reasons of safety. To date, 13 g have been reduced in one run, and the quantity will nextbe increased to the maximum of 26 g (0.1 mole).

Bibliography:

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