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II. Summary of Current Progress

Since the last report (No. 9) was submitted, we have shipped over 1087 g. of $\text{CF}_2\text{Cl}-\text{CF}_2\text{NO}$ to 3M for evaluation in their program.

Work is still progressing in finding better operating conditions for the preparation of $\text{CF}_2\text{Cl}-\text{CF}_2\text{NO}$ by means of ferric chloride and nitrosyl chloride.

About 20 g. of pure $\text{CF}_2\text{H}-\text{CF}=\text{CF}_2$ was also prepared and forwarded to Dr. George Crawford of 3M.

The production of $\text{CF}_2\text{Cl}-\text{CF}_2-\text{NO}$ was on a routine procedure but was stopped for several weeks due to Christmas vacation and the unavailability of $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ resulting from the temporary shut down in Dupont's tetrafluoroethylene facilities. After Dupont came on stream again we were able to go on "stream" also and are now making more $\text{CF}_2\text{Cl}-\text{CF}_2\text{NO}$. The product will be continued to be shipped in batches as it is made.

The open flow solvent system procedure which was shown to be effective in making the nitrosyl chloride adduct of $\text{CF}_2=\text{CFCl}$ was applied to $\text{CF}_2=\text{CF}_2$. Unfortunately no nitroso adducts were formed with $\text{CF}_2=\text{CF}_2$ under these conditions. It has been our experience that C_2F_4 reactions require more heat than $\text{CF}_2=\text{CFCl}$ and at atmospheric pressure this results in less solubility and therefore little or no reaction results. It is planned to try a solvent system reaction of $\text{CF}_2=\text{CF}_2$ and NOCl under autogenous pressure at 50°C . It is hoped eventually to get this free radical reaction going well in a two liter Parr apparatus for quick large-scale nitroso production.

Several attempts at nitrochlorination of fluorinated olefins ($\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CF}_2$ and $\text{CF}_3\text{CF}=\text{CFCF}_3$) at -70° in absolute methanol have been attempted. However, no nitroso compounds were formed at all (only sweet smelling

colorless low boiling materials containing no nitroso functions were obtained). Under the same conditions completely methylated olefins were found to give quantitative yields of NOCl adduct (1). The failure of fluorinated olefins to react is simply due to the fact that the addition of NOCl is a free radical reaction. In the case of hydrocarbon olefins, the methanol system makes NO^+ available to olefins that are prone to electrophilic attack. Cyclohexene was also tried under these conditions and did react to give some blue (nitroso) compounds and colorless (probably oxime) material which will be identified at some later date.

The uranyl nitrate complex $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{N}_2\text{O}_4$ (see QMC report No. 9) was tried with propylene gas. Much blue N_2O_3 was given off. The products which do not contain nitroso groups will also be worked on later.

The tetrafluoroethylene - uranyl nitrate complex reaction will be tried under autogenous pressure at 50° heat with a view towards obtaining results similar to the $\text{C}_2\text{F}_3\text{Cl}$ - uranyl nitrate complex reaction at room temperature and atmospheric pressure (QMC report No. 9).

Perfluorocyclobutene is being made from the dimer of $\text{CF}_2=\text{CFCl}$ for the purpose of subsequent nitroschlorination.

III. Discussion

At present the ferric chloride packed tube method of making the nitrosyl chloride adduct of tetrafluoroethylene still appears to be the best for routine production despite previously reported drawbacks. Several undergraduates have been trained in the various aspects of its production to keep the "mill rolling." Unfortunately Christmas vacation and finals intervened just after they were trained so that they were not available this past month. They will be available several hours a week evenings etc.

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so that a constant stream of $\text{CF}_2\text{ClCF}_2\text{NO}$ will be made. The main drawback in making the nitroso adduct is the need for continual production of $\text{CF}_2=\text{CF}_2$ from the dibromide. The $\text{CF}_2\text{BrCF}_2\text{Br}$ needs are anticipated at least one month in advance. However due to a temporary shut down in Dupont's facilities, we were without this needed starting material for several weeks (mainly during the above time interval).

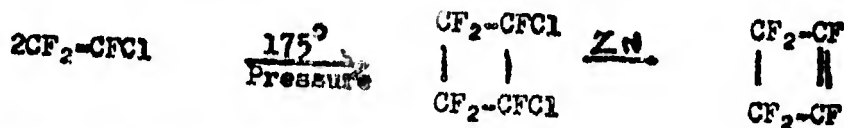
Two stainless steel tanks were ordered to facilitate the $\text{CF}_2=\text{CF}_2$ supply. Since this gas boils below carbon ice-acetone temperature, it has to be transferred into tanks capable of being immersed in liquid nitrogen without crystallization. Only a stainless steel tank has been adequate for this use. Then the $\text{CF}_2=\text{CF}_2$ had to be transferred to regular cast iron tanks immersed in carbon ice solution to make the stainless steel tank available for more $\text{CF}_2=\text{CF}_2$. It is therefore evident that this was a bottleneck in nitroso production.

It was reported by Gless and Brois⁴ in their new synthesis of a aziridene that completely methylated olefins undergo quantitative nitroschlorination in absolute methanol at -70°C . Consequently this procedure was tried here with fluorinated olefins, but failed to give any nitroso products. This further points out that nitroschlorination of fluorinated olefins proceed only by free radical reaction. In methanol solvent at -70°C nitrosyl cation (NO^+) is made available to the dissolved olefins by electrophilic attack. A completely methylated olefin has a very electron rich double bond and therefore undergoes reaction whereas fluorinated olefins are electron deficient and are not attacked by NO^+ . Cyclohexene did react under these conditions to give a light blue material (containing some nitroso). It would be expected to rearrange to an oxime due to its alpha hydrogen.

The solvent system of ferric chloride dissolved in tetrachloroethane

with the aid of acetic anhydride failed to give CF_2ClCF_2NO with $CF_2=CF_2$ and $NOCl$. This system was reported (QMC report No. 9) to give the $NOCl$ adduct of C_2F_3Cl . This may well be due to lower solubility of $CF_2=CF_2$ in the solvent compared to $CF_2=CFC1$ and the need of more heat for the reaction ($50^\circ C$ versus room temp. for $CF_2=CFC1$) This reaction will be studied in a closed system at $50^\circ C$. (autogenous pressure). A two liter Parr apparatus is available and it is hoped to eventually make CF_2ClCF_2NO in it in large scale when the right conditions can be found. The above mentioned causes may also be the main factor in the poor yields obtained in the uranyl nitrate complex ($UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$) reaction with $CF_2=CF_2$ compared with $CF_2=CFC1$. This reaction will also be investigated under autogenous pressure conditions. The reaction of propylene and the uranyl nitrate complex gave large amounts of blue condensate in the cold trap, but this was found to be N_2O_3 . If the interest warrants, the other products will be identified.

Perfluorocyclobutene is being made by the dimerization of $CF_2=CFC1$ for subsequent nitroschlorination study.



We have been successful in carrying out the reaction of $CF_2Cl-CFC1$ with NO in the presence of actinic light (and in absence of mercury) 60% of the converted material was identified as $CF_2Cl-CFC1NO$.

Following this lead, we have been able to react $CF_2=CFC1$ and $CF_2=CCl_2$ respectively with NO in the presence of actinic light to obtain high conversions of $CF_2ClCFC1NO$ and CF_2ClCCl_2NO .

One attempted reaction of perfluorocyclobutene with NO in the presence

of actinic light was unsuccessful in producing a nitroso compound. However, the addition of a small amount of chlorine to the above resulted in the production of a blue compound (presumably a nitroso compound). This product is now being investigated.

We also believe that the dinitroso compound $\text{CF}_2(\text{NO})-\text{CF}_2(\text{NO})$ has been prepared from the corresponding $\text{CF}_2\text{I}-\text{CF}_2\text{I}$. The IR spectra revealed a strong absorption at 6.2μ and the mol. wt. found was 161.2 as compared to 160 (theory for $\text{CF}_2(\text{NO})-\text{CF}_2(\text{NO})$).

Work is still being carried out to prepare fluorinated cyclic imines.

IV. Experimental

1. Preparation of $\text{CF}_2\text{ClCF}_2\text{NO}$. (See page 3 QMC quarterly No. 9)
2. Attempted Nitroschlorination of Fluorinated Olefins in Methanol at -70°C .

a. $\text{CF}_2=\text{CFCl}$

Into a 500 ml two necked flask was placed 200 ml of absolute methanol. The flask was equipped with a magnetic stirrer, carbon ice-acetone cooling bath, gas inlet tube, and reflux condenser to which was attached a collecting receiver immersed in carbon ice-acetone. After the flask contents were cooled to -71°C , 0.10 moles, 11.6 grams $\text{CF}_2=\text{CFCl}$ (previously condensed and weighed) was passed into the cold methanol via the inlet tube. Subsequently 0.11 moles, 7.2 grams of red nitrosyl chloride liquid (contained in a cold tube) was passed in. Instead of the contents of the flask becoming blue as expected, the material remained colorless.

The reactants in the flask were stirred for one and one half hours at -71°C . After this time, the cooling bath was removed and the contents were allowed to warm up to room temperature. Calcium chloride drying

towers were attached on the inlet and exit side of the cold receiving tube. Some colorless vapors had condensed by this time. Into a self equalizing dropping funnel was placed 200 ml iced water and this was added to the flask to drive out dissolved low boiling materials into the collection receiver.

The colorless material received in the collecting unit was shown by infrared to contain some unreacted olefin and other material (somewhat sweet smelling). This latter material showed the presence of H (C-H stretching peak at 3.4μ), nitrite groupings (split peaks at 5.95 and 6.15μ) and C-Cl stretching. These peaks were identical to those obtained when $\text{CF}_2=\text{CF}_2$ was used as the olefin and leads us to suspect that only a reaction of NOCl and methanol occurred.

The molecule weight after the unreacted olefin was stripped off was 93. This would correspond to CH_2ClONO (if possible) taking into consideration the absorptions. Since the solution was colorless, some reaction of NOCl and methanol must have occurred. Of course a better identification would be needed to state the composition of this material. The above formula sounds wild to me.

b. $\text{CF}_2=\text{CF}_2$

This was tried under similar conditions to above with just about the same results and absorptions.

c. $\text{CF}_3\text{CF}=\text{CFCF}_3$

Into the above set up was placed 0.05 moles (10.0 grams) or liquid $\text{CF}_3\text{CF}=\text{CFCF}_3$ and 4.1 grams (0.06 moles) NOCl . No nitroso compounds were formed. No product was isolated.

d. Cyclohexene

Similarly 8.2 grams (0.10 moles) of cyclohexene and 6.5 grams

(0.10 moles) NOCl were reacted in the methanol system. The contents of the flask turned a light blue (some nitroso formation). After adding water, a small amount of a white solid was suspended in the aqueous methanol solution (probably oxime). Products were not identified.

3. Attempted Reaction of $CF_2=CF_2$ and NOCl in a Solvent System

A solution of 325 grams tetrachloroethane, 50 grams acetic anhydride, and 20 grams of anhydrous ferric chloride was made. The acetic anhydride was used to make the ferric chloride soluble. The set up was the same as reported in QMC quarterly No. 9. Over a 15 hour period, 20 grams, 0.2 moles, and an equimolar amount of NOCl were passed through. No nitroso compounds were collected; only a small amount of pale yellow material (perhaps $CF_2=CF_2$) was received. The difficulties involved were due to low solubility of $CF_2=CF_2$ and inability to heat a system which would further drive out $CF_2=CF_2$ before reaction could occur. This reaction will be repeated in a Carius tube and a Parr apparatus.

4. Reaction of Propylene and Uranyl Nitrate Complex $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$

Under the conditions reported in Q. 3 No. 9, propylene gas was passed through the system containing a 15% acetic anhydride solution of $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ over a 20 hour period. Blue condensate was found in the cold receiver which was subsequently found to be N_2O_3 .

The uranyl nitrate complex reaction with $CF_2=CF_2$ will be tried in a Carius tube and Parr apparatus.

1. Closs and Brois, JACS 82, 6068 (1960)

5. 2,2,4,4,5,5,5-Heptafluoro-1-amino-2-pentanol hydrochloride

In a pint hydrogenation bottle was placed a solution of 13.0 g (0.05 mole) nitro alcohol in 50 ml ethanol. Ca. 0.1 g palladium on charcoal was added, and the apparatus flushed with hydrogen and evacuated three times. After shaking for 24 hours, a pressure drop of 8.2 psig was indicated (calc. for 0.05 mole is 12.0 psig drop.) To the bottle was added ca. 50 mg more catalyst, the bottle evacuated and flushed three times, and finally repressured to 38.5 psig. After another 20 hrs., a pressure drop of 5.0 psig was indicated. The reaction mixture was filtered to remove catalyst, and an IR taken of the filtrate. A peak was still evident at 1565 cm^{-1} , indicating incomplete reduction after 44 hours and a pressure drop of 13.2 psig. More catalyst was added, and hydrogenation continued for another four days, during which there was a pressure drop of 15.6 psig. The reaction mixture was filtered, and to the filtrate was added 15 ml (0.18 mole) and concentrated hydrochloric acid. The solvent was then removed under the reduced pressure of the aspirator, with gentle heating on a steam bath. After five hours, a greenish solid, ca. 10 g, was obtained. This was recrystallized from ethanol-ethyl acetate to yield the following crops:

Crop	Yield (grams)	m.p. (Fisher-Johns)
1	2.5	136-138
2	2.4	123-125
3	0.5	

The remaining filtrate was allowed to stand; evaporation of the solvent left a dark brown residue.

In the hydrogenation bottle was placed 30.0 g (0.116 mole) nitro alcohol and 200 ml absolute ethanol, along with a pinch of platinum dioxide. After one hour, a pressure drop of only 0.3 psig was indicated. Ca 1 g of catalyst was added and the bottle repressured to 38.0 psig. After 114 hours, a pressure drop of 16.2 psig was indicated. The bottle was repressured, and after another 78 hours, a pressure drop of 10.4 psig was indicated. After filtration of the reaction mixture to remove catalyst, an IR of the filtrate showed a very strong peak at 1565 cm^{-1} , indicating little or no reduction of the nitro group. The filtrate was returned to the hydrogenation bottle, and ca 0.1 g of palladium on charcoal added, along with 8 drops of concentrated hydrochloric acid to activate the catalyst. After a total elapsed time of 22 hours, a pressure drop of 19.7 psig was indicated. The reaction mixture was filtered to remove catalyst; an IR of the filtrate indicated complete reduction of the nitro group.

In the hydrogenation bottle was placed 31.0 g (0.119 mole) of nitro alcohol, 200 ml absolute ethanol, and ca. 1 g Raney nickel (W-2). After a total reaction time of 29.5 hours, a total pressure drop of 35.6 psig was indicated. (Calc. for complete reduction; 28.6 psig.)

The reaction mixtures from three reductions (92.0 g, 0.354 mole nitro alcohol) were combined. To the solution was added 90 ml (1.08 moles) concentrated hydrochloric acid, and the resulting solution evaporated on the steam bath under aspirator vacuum to a wet, yellow semi-solid. This material was recrystallized from ethanol-ethyl acetate, crops being taken as follows:

Crop	Yield (grams)
1	13
2	8
3	17
4	8
5	11

Total material obtained was 57 g (0.214 mole). A sixth crop of brown material was obtained, but this was not added to the previous crops.

6. 3,3,4,4,5,5,5-Heptafluoro-1-amino-2-pentanol

A solution of 50 g (0.188 mole) of the amine hydrochloride in 250 ml water was mixed with a solution of 25 g (0.236 mole) sodium carbonate in 250 ml water, resulting in the immediate formation of a gelatinous precipitate. The precipitate was filtered with suction, washed twice with water, and air dried for three hours, giving 37 g (0.162 mole; 86% yield) of the free amine; some crystals gave m.p. 45-50°C., while others gave 67-70°.

7. Perfluoropropylethylenimine

To 22.9 g (0.1 mole) of the amino alcohol was added a solution of 5.6 ml (10.2 g; 0.1 mole) concentrated sulfuric acid in 30 ml water. It was necessary to heat the mixture to boiling in order to achieve solution. The solution was heated to a pot temperature of 230°C. under partial aspirator vacuum until white fumes began to appear in the receiver. Throughout the distillation, severe difficulty was encountered due to frothing, necessitating an air bleed into the top of the distilling flask, and very gentle heating of the oil bath and careful regulation of the vacuum. The

flask was cooled, and 25.7 g of a brown-gray powder easily removed. This material, assumed to be the inner sulfate salt (0.083 mole) was placed in a flask with 250 g of 40% sodium hydroxide solution (2.5 moles), and the mixture distilled with a head temperature of 93.5-93.8° until a pot temperature of 160° was reached, once again severe frothing being experienced. Ca. 250 ml of distillate was collected; only one yellow phase was evident. The distillate was saturated with potassium hydroxide in an ice-water bath, causing the separation of a brown solid. The distillate was extracted three times with 33 ml portions of ether, the extract then being dried over potassium hydroxide. The ethereal solution was fractionated through a ten inch glass helices column, with head temperature of 30.5°, and pot temperature of 30.5-76.0°, until only a few drops remained in the pot. The pot residue was distilled in a side-arm test tube, two cuts being taken; b.p. 30-45° and b.p. 45-70°. The second cut, with a strong amine-like odor, will be submitted for elemental analysis after purification by vapor phase chromatography.

Discussion

It was found that for the reduction of the nitro alcohol, palladium on charcoal activated with hydrochloric acid, or Raney nickel are satisfactory catalysts, the latter being preferable. Platinum dioxide is ineffective; the pressure drop during the long reaction period with this catalyst was probably due mostly to leakage from the apparatus.

Yields were lower than expected in the preparation of the amino alcohol. The yield of amino alcohol could probably be increased by diluting the reaction mixture from the reduction with water, as decomposition during the concentration of the hydrochloride mother liquors

was suspected.

The insolubility of the amino alcohol in the 25% sulfuric acid solution is rather surprising. The amino alcohol will be further checked to ascertain that it is in fact the amino alcohol.

The yield of material thought to be the inner sulfate salt was as expected, but the very small amount of material isolated from the distillate after addition of 40% sodium hydroxide solution is rather surprising. Considerable formation of the vinyl amine was expected, but this should probably bpil around 70°, as should the imine. The intermediates from the amino alcohol on should be more fully characterized, if this route is to be further pursued.

Bibliography:

1. Cook, Pierce, McBee, JACS 76, 83 (1954)
2. Wenker, JACS 57, 2328 (1935)
3. Cairnes, JACS 63, 871 (1941)
4. Elderfield, Heterocyclic Compounds, Vol. I, New York, Wiley (1950)
5. Gless and Brois, JACS 82, 6068 (1960)

6. Reaction of CF₂Cl-CFClI with Nitric Oxide

After 4 to 6 hours of irradiation in the 7 liter reaction chamber previously described, the gaseous contents of the flask were transferred to two dry-ice/dutylcellosolve cooled traps connected in series with a vacuum pump. The products were then passed through water and a drying tube packed with calcium chloride and indicating drierite, collected and chromatographed. By assuming that the area under each peak is proportional to the weight percent of each component, one arrives at the following product distribution: CF₂Cl-CFCINO

(60%), $\text{CF}_2\text{Cl}-\text{CFCl}_2$ (26%), $\text{CF}_2\text{NO}_2-\text{CFCl}_2$ (9%), and two unidentified components (5%). The identification of these products was based upon their infrared spectra which have been reported by A. Stefani, Ph. D. Thesis, University of Colorado, 1960.

9. Reaction of CF_2-CFCl with Nitric Oxide

In a typical reaction 25 cm of the olefin and 30 cm of nitric oxide were introduced into the 7 liter reaction chamber previously described. After 2 hours of irradiation the pressure reached a minimum (after dropping 13 cm) at which time the contents were transferred to appropriately cooled traps. After washing the product with water and drying as previously described, a small sample of the product mixture was chromatographed. There were 16% of low boilers, including unreacted olefin and nitric oxide, ca. 5% of an unidentified blue compound showing the nitroso absorption in its infra-red spectrum but other absorption characteristics which differ from that shown by $\text{CF}_2\text{Cl}-\text{CFClNO}$, 63% of the blue $\text{CF}_2\text{Cl}-\text{CFClNO}$, 13% of $\text{CF}_2\text{Cl}-\text{CFCl}_2$ and 3% of higher boilers.

10. Reaction of CF_2-CCl_2 with Nitric Oxide

After 4 hours of irradiation the pressure reached a minimum, and the gaseous contents of the flask were bluish in color. These were treated in the usual way, and a small sample was chromatographed. An extremely complex chromatogram showed 8 peaks of very low boilers (approx. 50%), $\text{CF}_2\text{Cl}-\text{CCl}_2\text{NO}$ (ca. 40%) and 12 additional peaks of higher boilers. Identification of the blue $\text{CF}_2\text{Cl}-\text{CCl}_2\text{NO}$ was based upon the infrared spectrum reported by A. Stefani, Ph. D. Thesis, University of Colorado, 1960, p. 154. The yield of $\text{CF}_2\text{Cl}-\text{CCl}_2\text{NO}$ based upon moles of CF_2-CCl_2 was ca. 25%.

11. Reaction of $\text{CFCl}=\text{CFCl}$ with Nitric Oxide

This olefin was prepared by the dechlorination of $\text{CFCl}_2-\text{CFCl}_2$ in 77% yield in 99% purity, as shown by its chromatogram. The olefin and nitric oxide were introduced into the 7 liter reaction chamber and irradiated. After an initial rise in pressure the minimum was reached in 6 hours, during which time a blue liquid began to collect in the bottom of the flask. This liquid became more blue-green as the reaction progressed. The low boiling products were transferred to cooled traps, washed, dried and chromatographed. Products identified by their infrared spectra were $\text{CFCl}=\text{CFCl}$ (starting material) and $\text{CFCl}_2-\text{CFCl}_2$. A blue compound, presumably $\text{CFCl}_2-\text{CFClNO}$, showing infrared absorption at 6.25 microns and boiling just lower than $\text{CFCl}_2-\text{CFCl}_2$, was isolated. A higher boiling yellow viscous liquid was also formed from this reaction.

12. Attempted reaction of perfluorocyclobutene with Nitric Oxide

Into the 7 liter reaction chamber previously described were introduced 23.3 g (0.144 moles) of perfluorocyclobutene (40 cm Hg) and nitric oxide (40 cm Hg). After 5 1/2 hours of irradiation, the pressure dropped only 2.6 cm Hg and a clear colorless solid (?) was observed to have coated the quartz insert. No blue color was observed within the flask.

13. Reaction of Perfluorocyclobutene with Chlorine and Nitric Oxide

Following the apparent failure of the nitric oxide to react with the olefin, 8.0 cm of chlorine gas was added to the reaction chamber. After only 10 minutes of irradiation, blue-green drops began to form on the insert and the pressure began to fall. An additional 12 cm of chlorine was added so that there were 1 cm of

nitric oxide and 1/2 cm of chlorine present for each cm of olefin. Over a period of 9 hours the pressure dropped 52 cm to a minimum. From this reaction only 22.4 grams of crude product were recovered. After washing and drying the mixture, it was chromatographed. The chromatogram showed only 8 peaks, 4 of which are major: starting material (21%), an unidentified, colorless organic material (38%), a blue compound presumed to be the NOCl adduct (13%), and impure trans-1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane (28%)--the chlorine adduct.

14. Reaction of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene with nitric oxide

The reactants were introduced into the 7 liter reaction chamber and irradiated. The pressure reached a minimum after 33 hours, during which time a blue-green liquid collected in the bottom of the flask. After extensive pumping on the chamber, a blue liquid was at last transferred to traps, leaving a green high boiled in the flask. Unfortunately, chromatography of the blue liquid failed to separate any blue components. Only unreacted olefin and the dichloro adduct were isolated and identified by their infrared spectra. Nine other peaks appeared on the graph.