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Rubber Research

The Synthesis of Unsaturated Fluorocarbons

Progress Report

Quarterly Report 12

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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 twelfth quarterly report for the period May 13, 1961 through August 13, 1961.

II. Summary of Current Progress

During this period 1200 g. of pure CF_3COONO and 200 g. of C_3F_7COONO were prepared as intermediates for the preparation of the corresponding nitroso compounds.

Olefins containing a vinylic chlorine such as 1-chloro-1,2,2-trifluoroethene, 1,1-dichloro-2,2-difluoroethene, and 1,2-dichloro-1,2-difluoroethene were irradiated in the presence of a 1:1 molar ratio of nitric oxide. Blue compounds, gaseous at room temperature, were subsequently identified as the nitrosyl chloride adducts: 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane in 28% yield and ca. 14% conversion from 1-chloro-1,2,2-trifluoroethene, 1,1,2-trichloro-2,2-difluoro-2-nitrosoethane in 40% yield and 30% conversion from 1,1-dichloro-2,2-difluoroethene, and 1,1,2-trichloro-1,2-difluoro-2-nitrosoethane from 1,2-dichloro-1,2-difluoroethene. In addition to the nitrosyl chloride adduct, each olefin produced some of the dichloro-, the nitrochloro-, and in one case the dinitro-adduct. For example, 1,1,2-trichloro-1,2,2-trifluoroethane (9%), 1,1-dichloro-1,2,2-trifluoro-1,2-dinitroethane were obtained from the reaction of 1-chloro-1,2,2-trifluoroethene and nitric oxide. A mechanism was postulated to account for the formation of these products.

Perfluorinated olefins, such as perfluorocyclobutene, were found to be unreactive towards nitric oxide when irradiated if nitrogen dioxide were carefully excluded from the reaction flask. The addition of chlorine, it was found, initiated the reaction of perfluoroölefins with nitric oxide. Tetrafluoroethylene and hexafluorocyclobutene with stoichiometric quantities of nitric oxide and chlorine, upon irradiation, yielded the nitrosyl chloride, dichloro-, and nitrochloro- adducts. The nitrosyl chloride adduct, 1-chloro-1,2,3,3,4,4-hexafluoro-2-nitrosocyclobutane, was formed in 13% yield. The tetrafluoroethylene adduct, 1-chloro-1,1,2,2-tetrafluoro-2-nitrosoethane, was formed in 81% yield with a conversion of 36%. Slightly less favorable results were obtained when a 1:1 molar ratio of tetrafluoroethylene and nitrosyl chloride was employed.

Photolysis methods were unsuccessful in the attempted preparation of 1-chloro-1,1,2,2-tetrafluoro-2-nitrosoethane from 1,2-dichloro-1,1,2,2-tetrafluoroethane. No trifluoronitrosomethane was obtained from the reaction of trifluoroiodomethane and nitric oxide or from trifluoroacetyl chloride and nitrosyl chloride.

Study of the reaction of CF_3COOH and C_3F_7COOH and their anhydrides with NO and NOCl are being continued.

EXPERIMENTAL

Experimental Procedure

A 6.7 or a 22 liter pyrex flask with a three-way stopcock and a standard taper 60/55 female ground glass joint was fitted with a water-cooled quartz immersion well (Hanovia Cat. No. 19434). An ultraviolet light source, a 450 watt Hanovia quartz, high pressure, mercury-vapor lamp (Type L, Cat. No. 679A-36) rested within this well during the periods of irradiation and delivered 177 watts of light energy over the range 1367 Å to 2224Å. Hanovia ballast no. 8354-1 was used with this lamp.

After the bulb had been evacuated and checked for leaks, a weighed amount of oxygen-free olefin was transferred into the flask from a trap through plastic tubing and the three-way stopcock. The pressure within the flask at this point and during the subsequent reaction was followed by reading an open-end manometer connected by plastic tubing to the three-way stopcock. When a mole to mole ratio of olefin to nitric oxide was desired, enough nitric oxide was introduced into the flask to equal the partial pressure exerted by the gaseous olefin. After the reactants were within the bulb, the initial pressure was read, and the lamp was turned on. In most cases the reaction flask was irradiated only until the pressure within the flask had reached a minimum. At this point the irradiation was discontinued, since nitroso compounds of the type being made have been reported to decompose photochemically. The gases and liquids in the flask were transferred to two liquid nitrogen-cooled traps. The product was warmed slowly and was passed through a scrubber and then a water bubbler fitted with a fritted glass inlet to remove chlorine, oxides of nitrogen, and any nitrites present. From here the gases were passed through a drying tube, packed with calcium chloride and sodium sulfate, and condensed at the end of the system.

The major components of the product were separated by vapor phase chromatography and then identified. Whenever possible, the infrared spectra of the products were compared with those of known compounds. In the case of new compounds, it was necessary to carry out the reaction several times to obtain several milliliters of the relatively pure nitroso compound. When this had been further purified by vapor phase rechromatography, physical properties such as the molecular weight, refractive index, and density were determined.

The percent yields and percent conversions reported were calculated from the chromatographic curve obtained when a representative sample of the unwashed product was analyzed. The percent yield of each major component was calculated by assuming that the area under each peak was proportional to the weight percent. After the amount of unreacted starting material had been subtracted from the total sample, the percent conversions were calculated from the remainder. When the identification of a minor component was desired, a product formed with less than a ten percent conversion, the reaction was repeated several times in order to collect enough for distillation.

Reaction of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane with nitric oxide.

When 0.1 mole of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane and 0.11 mole of nitric oxide were irradiated in the seven liter flask for six hours, iodine crystals were deposited upon the inside surfaces of the flask, and the gaseous contents had turned blue. The contents of the flask were transferred to two liquid nitrogen-cooled traps, passed through water and a drying tube packed with calcium sulfate and calcium chloride, and recondensed. A chromatogram of the mixture yielded the following product distribution, excluding unreacted starting material: 1,2-dichloro

-1,1,2-trifluoro-2-nitrosoethane (60%), 1,1,2-trichloro-1,2,2-trifluoroethane (26%), 1,1-dichloro-1,2,2-trifluoro-2-nitroethane (9%), and two unidentified minor products (ca. 5%).

Reaction of 1-chloro-1,2,2-trifluoroethene with nitric oxide.

Into a twenty-two liter flask were passed 52 g. (0.45 mole) of 1-chloro-1,2,2-trifluoroethene and 13.6 g- (0.45 mole) of nitric oxide. The following is a tabulation of the periods of irradiation and the corresponding pressure drops:

time	pressure change	illumination
12 hours	12.2 cm. decrease	lamp on
82 hours	17.4 cm. decrease	lamp off
12 1/2 hours	8.7 cm. decrease	lamp on

At the end of 106 1/2 hours a sample of the product was withdrawn from the reaction flask and chromatographed. Samples of the main components were collected and identified by comparing their infrared spectra with those previously reported by us. The major product, 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane was formed in ca. 28% yield with a conversion of about 14%. Other products formed included 1,1,2-trichloro-1,2,2-trifluoroethane (9% yield), 1,1-dichloro-1,2,2-trifluoro-2-nitroethane, and 1-chloro-1,2,2-trifluoro-1,2-dinitroethane in undetermined amounts.

Samples of the latter two compounds were obtained from the distillation of a large batch of product collected from several runs. Brief contact of the former compound, 1,1-dichloro-1,2,2-trifluoro-2-nitroethane, with the skin lasting several days. The effect of contact of the vapors of this compound with the skin was not known. The latter compound, 1-chloro-1,2,2-trifluoro-1,2-dinitroethane, caused an immediate reddening of the area of contacted skin which healed like a burn after several days, but no paralysis resulted.

Reaction of 1,1-dichloro-2,2-difluoroethene with nitric oxide.

Into the seven liter flask were placed 10.9 grams (0.082 mole) of 1,1-dichloro-2,2-difluoroethene which gave a pressure of 20.4 cm. Accordingly, 20.4 cm. of nitric oxide was also introduced. In five hours of irradiation the pressure dropped 7.2 cm. The 450 watt Hanovia lamp was turned off and in 17 1/2 hours the pressure rose 20.6 cm. The contents of the flask were transferred to two liquid nitrogen-cooled traps. The traps were then allowed to warm up to dry ice-butyl cellosolve temperature (-80°C) and the noncondensable gases were allowed to go back into the flask.

The product was poured as a liquid into a cold vial. From this vial a sample was withdrawn by syringe and injected into the vapor phase chromatograph for analysis. The chromatograph column showed an increase in weight of 11.5 mg. when this sample, estimated to weigh 75 mg., was passed through it. Assuming that the material retained in the column was not a nitroso but a higher boiling nitro derivitive, the yield of 1,1,2-trichloro-2,2-difluoro-2-nitrosoethane was ca. 40% and the conversion ca. 30%.

The reaction of 1,2-dichloro-1,2-difluoroethene with nitric oxide.

Into the twenty-two liter reaction flask were introduced 41.4 g. (0.311 mole) of 1,2-dichloro-1,2-difluoroethene and a 1:1 molar ratio of nitric oxide. After 30 1/2 hours of irradiation with the Hanovia ultraviolet light, the pressure dropped 24.6 cm., and there was present in the bulb a bluegreen liquid and a pale blue gas. The product was condensed in traps at carbon dioxide-butyl cellosolve temperatures from which a sample was transferred to a small vial and chromatographed. Unreacted starting olefin was recovered, 70%.

The blue compound, believed to be 1,1,2-trichloro-1,2-difluoro-2-nitrosoethane was formed in 24% yield with a 7% conversion; the colorless 1,1,2,2-tetrachloro-1,2-difluoroethane was formed in 10% yield. The higher boiling compounds were not identified, but the infrared spectrum of one of them showed an absorption at 6.20 microns, evidence that it may be a nitro derivative. Physical properties were determined for the blue nitroso compound: Mol. wt. (calcd) 198.39, found 191.7; $d_4^{0^\circ C} = 1.50$; b.p. = 79.0-79.5°C/633 mm. (micro boiling-point).

Anal. Calcd. for $C_2F_2Cl_3NO$: Cl, 53.50.
Found: Cl, 53.13

Attempted reaction of perfluorocyclobutene with nitric oxide.

Into the seven liter reaction flask were introduced 23.3 g. (0.144 mole) of perfluorocyclobutene and 0.145 mole of nitric oxide. After 5 1/2 hours of irradiation the pressure within the flask dropped only 2.6 cm. and a clear colorless solid which fumed in the presence of water was observed to have coated the quartz insert. No blue color was detected within the flask.

Reaction of perfluorocyclobutene with chlorine and nitric oxide.

Following the apparent failure of the attempted reaction of nitric oxide alone with perfluorocyclobutene, 0.072 mole of chlorine was introduced into the flask. The ratio of olefin to nitric oxide to chlorine was 1 : 1 : 0.5. After only ten minutes of irradiation, bluegreen drops began to form on the insert and the pressure within the flask began to decrease. Over a period of nine hours the pressure dropped fifty-two cm. and reached a minimum. The contents of the flask were transferred to two liquid nitrogen-cooled traps, passed through water and a tower packed with calcium sulfate and calcium chloride, and recondensed. A chromatogram of the product showed the presence of unreacted perfluorocyclobutene, a blue compound presumed to be the nitrosyl chloride adduct (13% yield), impure trans-1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane (28% yield) and four higher boiling components, three of which have shown infrared absorptions at 6.20-6.25 microns, indicating the presence of the nitro or nitroso group.

This reaction was repeated four times in order to collect material for a distillation. In each case the pressure reached a minimum in ca. nine hours, but the pressure drops observed were not so great as previously observed, being ca. 38 cm. From the distillation at 630 mm. a blue fraction, b.p. 52-54°C., was collected. Chromatography of the blue fraction yielded a purified nitroso compound with the following physical properties: $n_D^{4} = 1.336$, $n_D^{20} = 1.334$, $d_4^{0.5} = 1.679$, MR_D(found)= 27.79, MR_D (calcd.) = 28.01.

Anal. Calcd. for C_4F_6ClNO: N, 6.16;
Cl, 15.60.
Found: N,6.36; Cl, 15.90.

Reaction of tetrafluoroethylene with nitric oxide and chlorine.

When 22.7 grams (0.23 mole) of tetrafluoroethylene and 7.0 grams (0.23 mole) of nitric oxide with 8.2 grams (0.115 mole) of chlorine gas were introduced into the twenty-two liter flask and irradiated, the pressure reached a minimum in 2 1/2 hours. The blue-green gaseous product was chromatographed and it was found that the major product, 1-chloro-1,1,2,2-tetrafluoro-2-nitrosoethane, was formed in 81% yield with a conversion of 36%. Three other minor products were indicated by the chromatogram, one of which was identified from its infrared spectrum as being 1-chloro-1,1,2,2-tetrafluoro-2-nitroethane.

Reaction of tetrafluoroethylene with nitrosyl chloride.

When 0.246 mole each of tetrafluoroethylene and nitrosyl chloride were placed in the twenty-two liter flask and irradiated, a pressure decrease of 6.2 cm. was observed in the first three hours. During the next three hours of irradiation, the pressure increased 6.2 cm., and during the next twelve hours the product was allowed to remain in the bulb without being irradiated, and the pressure increased another 8.3 cm. Either an air leak or the decomposition of the product was thought to be responsible for this increase of pressure. A sample of the product was condensed in a liquid nitrogen-cooled trap and vaporized into a thin plastic glove from the trap eighteen hours after the reaction was begun. A gaseous sample was withdrawn from the glove by syringe and chromatographed. Based on this chromatogram, the major product, 1-chloro-1,1,2,2-tetrafluoro-2-nitrosoethane, was formed in 79% yield with a conversion of 23%.

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

When 16.3 g. (0.084 mole) of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, prepared by the method of Cohen, b.p. 60.0-60.5/625 mm., and 0.084 mole of nitric oxide were irradiated in the seven liter flask, the pressure dropped 10.6 cm. in thirty-three hours. A blue-green liquid had collected in the bottom of the flask and was transferred after extensive pumping to dry-ice cooled traps, leaving a green high boiling liquid in the flask. Chromatography of the blue liquid failed to distinguish any blue component; only unreacted olefin and the known dichloro adduct, 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane, were isolated and identified by their infrared spectra. Nine other components were present as shown by the chromatogram.

Attempted conversion of 1,2-dichloro-1,1,2,2-tetrafluoroethane to 1-chloro-1,1,2,2-tetrafluoro-2-nitrosoethane.

Into the twenty-two liter flask 15.76 g. (0.092 mole) of 27. pure 1,2-dichloro-1,1,2,2-tetrafluoroethane, 6.02 g. (0.092 mole) of nitrosylchloride and a trace of chlorine gas were introduced. After eight hours of irradiation the pressure within the flask had increased 7.2 cm. The two major peaks in the chromatogram of a sample of this reaction mixture were shown by their infrared spectra to be unreacted starting compounds. No blue product was detected. The ultraviolet and visible spectrum of the starting compound, 1,2-dichloro-1,1,2,2-tetra-fluoroethane, showed no absorption from 6000Å to 2100Å.

Reaction of trifluoroacetyl chloride and nitrosyl chloride and chlorine.

Trifluoroacetyl chloride was prepared by an exchange reaction between trifluoroacetic acid, previously distilled, b.p. 65-66.5/623 mm., and benzoylchloride.

Into the twenty-two liter flask were introduced 31.6 grams (0.225 mole) of trifluoracetyl chloride, prepared as just described, and 14.6 grams (0.223 mole) of nitrosyl chloride. After four hours of irradiation the pressure increased 11.2 cm. and remained constant during the next two hours. At this time samples were withdrawn for infrared and chromatographic analysis. Peaks ascribeable to trifluoroacetyl chloride, nitrosyl chloride, and chlorotrifluoromethane were present. Nitrosotrifluoromethane was not detected in the mixture, neither by infrared analysis nor by vapor phase chromatography.

Chlorine, 0.002 mole, was added for the first time at this point, and the pressure increased 8.0 cm. during the next thirteen hours of irradiation. Then an additional 0.001 mole of chlorine was added and the pressure rose only 3:4 cm. more after nineteen hours of irradiation. Peaks ascribed to trifluoroacetyl chloride and nitrosyl chloride were diminished as the reaction proceeded, while peaks ascribed to chlorotrifluoromethane continued to increase with the time of irradiation. Peaks at 5.1, 5.2, and 9.74 microns appeared in the spectrum taken at the end of six hours and were noticeable increased by the addition of chlorine but could not be assigned. It was postulated that the reaction that occurred was the decarbonylation of trifluoroacetyl chloride to yield carbon monoxide and chlorotrifluoromethane. The small pressure increase observed after the chlorine was added to the reaction, 11.4 cm. in thirty-two hours, would be consistent with the limited occurance of this reaction.

<u>Attempted conversion of bromotrifluoromethane trifluoronitrosomethane.</u>

Bromotrifluoromethane, 49 g. 0.329 mole, and nitric oxide, 0.33 mole, were introduced into the twenty-two liter flask and irradiated with the 450 watt Hanovia lamp for twenty-two hours. Since a pressure drop of only 1.8 cm. occurred within this period of time, a trace of chlorine (0.046 mole) was added, and the gases were irradiated for an additional ninety-four hours. Since the pressure did not vary more than 0.5 cm. during this time, the irradiation was discontinued. No blue material was isolated by chromatography of the crude product. The visible and ultraviolet spectra of bromotrifluoromethane showed no absorption from 6000 Å to 2200 Å. An absorption, presumeably of the carbon-bromine bond, began at 2200 Å and continued to increase until it reached a maximum somewhere below 2000 Å (the limit of our instrument).

Reactions of Trifluoroacetic Anhydride with Nitrosyl Chloride.

A. About 70 g. (0.33 moles) of trifluoroacetic anhydride and 48 g. (0.75 moles) of nitrosyl chloride were frozen in carbon-ice in a 22-liter flask equipped with one 2-way and one 3-way stopcock. The system was evacuated and then the bulb was subjected to a 300 watt incandescent lamp for two days. The materials were slowly evacuated into a series of carbon-ice and liquid air cooled traps until nothing but 2 g. of a white solid were left in the bulb. Distillation of the combined materials yielded 59 g. of trifluoroacetic anhydride; b.p. 34-35°C./630 mm., which represents a 15% conversion. The remaining materials were distilled under a partial vacuum and 3.1 g. of a yellow liquid was collected; b.p. 46-48° C./75 mm., n_D^{24} 1.378. An infrared spectrogram of this compound was identical with that of a pure sample of trifluoroacetyl nitrite and, therefore, represents a yield of 46%.

B. A 22-liter bulb was evacuated and 60 g. (0.29) of perfluoroacetic anhydride and 19.5 g. (0.30 moles) of nitrosyl chloride were introduced. After the ultraviolet light AH-6 was turned on, the pressure increased from 420 to 660 mm. The gases were collected in tubes immersed in liquid nitrogen by slowly pumping out the bulb. The blue condensate was then passed through two water scrubbers and finally a soda-lime tower to remove carbon dioxide and acidic materials. The anhydride recovered was approximately 31 g. (0.14 moles), b.p. 35-36° C./630mm., representing a 48% conversion. The infrared spectrum and vapor phase chromatograms revealed a 1:1 mixture of trifluoronitrosomethane and trifluorochloromethane. Thus, 0.091 moles of trifluoronitrosomethane was present, which represents a 32.5% yield. In addition, traces of trifluoroacetyl fluoride and carbonyl fluoride were detected spectroscopically in the unwashed product.

C. About 145 g. (0.69 moles) of trifluoracetic anhydride were placed into a glass cylinder fitted with a sintered glass frit and a reflux condenser, and nitrosyl chloride was bubbled through at a slow rate. The system was connected in series to carbon-ice and liquid air cooled traps to collect gaseous products which evolve during the course of the reaction. An ultraviolet lamp was positioned approximately 24 inches from the cylinder and irradiation of the liquid was continued for 5 days. Gas and liquid products were collected and purified separately using distillation and vapor phase chromatography techniques. Infrared analysis was employed on all fractions and the spectra were compared to the spectra of known compounds where applicable. Thus, it was observed that a 1:1 mixture of trifluoronitrosomethane and trifluorochloromethane were present in the reaction mixture. The anhydride recovered was 85.6 g., b.p. 34-36 C./630 mm., representing a 41% conversion. Also, 0.103 moles of trifluoronitrosomethane was present, which represents a 36% yield. Vacuum distillation resulted in the collection of 1.3 g. of trifluoroacetyl nitrite; b.p. 47-48°C./80 mm, n_D^{24} 1.377, and 4 g. of a non-distillable residue. In addition, traces of trifluoroacetyl fluoride and carbonyl fluoride were detected spectroscopically in the crude product.

Reaction of Pentafluoropropionic Anhydride with Nitrosyl Chloride

About 31 g. (0.10 moles) of pentafluoropropionic anhydride and 12 g. (0.18 moles) of nitrosyl chloride were frozen in carbon-ice in a 7-liter bulb equipped with one 2-way and one 3-way stopcock. The system was evacuated and then subjected to a 300 watt incandescent lamp for 2 days. The materials were slowly evacuated into a series of carbon-ice and liquid air cooled traps until nothing but a small amount of a white solid was left in the bulb. 25.4 g. of pentafluoropropionic anhydride were recovered; b.p. 65-66°C./630 mm., which represents an 18% conversion. The remaining materials were distilled under a partial vacuum and 1.5 g. of a yellow liquid was obtained. It was collected at 58-59°C./80 mm. from a micro distillation apparatus and had a refractive index and infrared spectrum identical to that of a pure sample of pentafluoropropionyl nitrite. Thus, a 42% yield of the nitrite was observed. However, some had decomposed since the presence of pentafluoronitrosoethane was noted in one of the spectrograms.

Reactions of Heptafluorobutyric Anhydride with Nitrosyl Chloride

A. About 332 g. (0.80 moles) of heptafluorobutyric anhydride and 65 g. (1 mole) of nitrosyl chloride were frozen in carbon-ice in a 22-liter flask equipped with 2 stopcocks. Air was evacuated from the system and then the bulb was subjected to a 300 watt incandescent lamp for 12 hours. The materials were slowly evacuated into a liquid air cooled trap and were then distilled. The solution in the distilling flask was a straw color and, at approximately 100°, blue gases began to evolve. It was evident that heptafluorobutyryl nitrite had formed in the reaction and was decomposing thermally since the head temperature began to vary erratically. The gases were collected in a carbon-ice cooled trap and, at the end of 3 hours, evolution of the gases ceased. Distillation was continued to yield 307 g. (0.75 moles) of heptafluorobutyric anhydrice b.p. 101-103°C./630 mm., representing a 7% conversion. Infrared analysis of the blue condensate collected in the carbon-ice cooled trap revealed that only heptafluoronitroso-propane and carbon dioxide were present. After scrubbing the mixture to eliminate carbon dioxide, 9.8 g. of heptafluoronitrosopropane, representing a 50% yield, was obtained. Gaseous materials from the original reaction mixture were found to contain heptafluorochloropropane but additional work was not attempted.

B. About 41 g. (0.10 moles) of heptafluorobutyric anhydride were placed into a 300 ml. double tough pyrex tube affixed with a pressure gauge. The anhydride was frozen in carbon-ice and the tube was evacuated. Nitrosyl chloride was then introduced until the pressure gauge indicated 35 lbs. An ultraviolet lamp was positioned a few inches away from the sustem and irradiation was continued for 2 days, at which time the pressure had increased to 105 lbs. The contents of the tube were bled into a carbon-ice cooled trap and a slow evacuation was performed using a vacuum pump. Intrared analysis of the crude product revealed absorption peaks ascribed to carbon dioxide and nitrosyl chloride as well as a peak at 6.25 microns. The latter is indicative of the nitrogenoxygen stretching frequency assigned to perfluoronitroso compounds. Increased pressure appeared to have decreased the conversions of perfluorobutyric anhydride to the 1-nitrosoheptafluoropropane and therefore no further work was done on this reaction.

C. About 82 g. (0.20 moles) of heptafluorobutyric anhydride were placed into a glass cylinder fitted with a sintered glass frit and a reflux condenser, and nitrosyl chloride was passed through at a very slow rate. A Westinghouse sun lamp was positioned approximately 20 inches from the cylinder and irradiation was continued for 24 hours. The solution had turned a light green during this period and an infrared spectrogram of a sample revealed carbon dioxide and nitroso peaks at 4.3 and 6.25 microns, respectively. Distillation of the combined materials resulted in a recovery of 69 g. (0.17 moles) of perfluorobutyric anhydride; b.p. 100-102°C./630 mm., which represents a 15% conversion. In addition, 2.9 g. (48% of theory) of heptafluoronitrosopropane, b.p. -18 to -16°C./630 mm., and 1.8 g. of heptafluorochloropropane, b.p. -7 to -4.5°C./630 mm., were collected. Small amounts of low boilers believed to be alkyl nitrites were hydrolyzed readily, but no attempt was made to identify them.

D. About 325 g. (0.79 moles) of heptafluorobutyric anhydride were placed into a glass tube fitted with a sintered glass frit and a reflux condenser attached in series to carbon-ice and liquid air cooled traps. Nitrosyl chloride was slowly passed through the anhydride while irradiation from an ultraviolet lamp, positioned approximately twelve inches from the tube, was continued for six days. At the end of this time, the solution had developed a deep green color while some of the product had been trapped in the carbon-ice receiver revealed traces of carbon dioxide.

At this point, the green solution was poured into a 500 ml. flask which was fitted with a thermometer well and connected to a distillation apparatus equipped with a carbon-ice and liquid air cooled traps. At approximately 100°C., the solution turned a straw color and blue gases mixed with carbon dioxide were evolved. After 13 hours, the solution had turned colorless and evolution of the gases had ceased. Combination of the materials from the carbon-ice and liquid air cooled traps, and subsequent distillation, yielded the following products which were identified by their boiling points and infrared spectrograms:

(1) 11.5 g. of carbon dioxide containing approximately a 5% impurity which was identified as nitrous oxide.

(2) Traces of heptafluorobutyryl fluoride and pentafluoropropionyl fluoride.

(3) 217 g. of heptafluorobutyric anhydride, b.p. 101-104°C./630 mm., representing a 32.8% conversion.

(4) 49.5 g. (48.1%)* of 1-nitrosoheptafluoropropane, b.p. -20 to -15°C./630 mm., M. W. 198.1.

(5) 27 g. (25.6%) of 1-chloroheptafluoropropane, b.p. -6 to -3°C./630 mm.

(6) 1.2 g. of 1-nitroheptafluoropropane, b.p. 18-19°C./630 mm.

(7) 2 g. of heptafluorobutyryl chloride, b.p. 31-32°C./630 mm.

(8) 0.7 g. of perfluorohexane, b.p. 53-55°C./630 mm.

(9) 8 g. of a non-distillable residue.

Reaction of Trifluoroacetic Anhydride with Nitric Oxide

Into a previously evacuated 7-liter bulb equipped with a quartz insert and an attached manometer, 42 g. (0.20 moles) of trifluoroacetic anhydride and 540 mm. of nitric oxide were introduced. The Hanovia lamp was used to irradiate the materials and it was continued for fourteen hours. The lamp was turned off and it was noted that the pressure had decreased from 580 mm. to 475 mm. Representative samples of the gaseous materials for infrared analysis indicated a

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*Percentages in yield reported are based on total weight of the mixture of products obtained minus the untreacted starting material. In addition, yields of perfluoroaklyl compounds are based on a 2:1 ratio, with respect to all anhydrides.

significant amount of carbonyl fluoride with trace amounts of trifluoroacetyl fluoride and hexafluoroethane present in the reaction mixture. The bulb was slowly evacuated into two liquid air cooled receivers and the materials were combined and distilled. 17.7 g. of a blue solid were collected in a liquid air cooled trap attached to the distilling apparatus and an infrared spectrogram revealed a mixture of trifluoronitrosomethane and carbon dioxide. Upon washing the material through a dilute solution of barium hydroxide, 13.7 g. of trifluoronitrosomethane were collected. In addition, 13 g. of trifluoroacetic anhydride, 2 g. of a dark residue and 6 g. of an undetermined white solid were collected from the reaction. The conversion of trifluoroacetic anhydride was therefore 69% with a 52% yield of trifluoronitrosomethane.

Reaction of Heptafluorobutyric Anhydride with Nitric Oxide

About 101 g. (0.246 moles) of heptafluorobutyric anhydride were placed into a glass tube fitted with a sintered glass frit and a reflux condenser attached in series to carbon-ice cellosolve and liquid air cooled traps. Nitric oxide was slowly passed through the anhydride while irradiation from an ultraviolet lamp, poisitioned approximately 8 inches from the tube, was continued for 5 days. At the end of this time, the solution had developed a deep green color, and the liquid level had decreased about 50%. A very thin coating of a white solid had formed on the walls of the tube which was found to fume in air and react with water. Gaseous materials were combined and representative samples were taken for infrared analysis. The spectrograms revealed the presence of carbon dioxide, 1-nitrosoheptafluoropropane, heptafluoropropionyl fluoride and strong absorptions indicative of nitrites. The materials were scrubbed in water and subsequently distilled to yield 17.5 g. (0.09 moles) of pure 1-nitrosoheptafluoropropane. The wash water contained heptafluorobutyric acid which probably was formed from the hydrolysis of the acid fluorides and nitrites present in the reaction mixture. Higher boilers from the cold traps and the liquid from the reaction tube were combined and distilled to yield 52 g. (0.127 moles) of heptafluorobutyric anhydride, b.p. 100-103°C./630 mm., and 5 g. of a non-distillable residue. In addition, traces of a blue gas were collected in an attached carbon-ice cooled trap. This was identified as 1-nitrosoheptafluoropropane and carbon dioxide by an infrared spectrogram. The conversion of heptafluorobutyric anhydride was therefore 48.4% with a total of 28.6 g. (0.143 moles) of 1-nitrosoheptafluoropropane collected. Thus, a 60.4% yield of the nitroso compound was effected.

Reaction of Perfluorosuccinic Anhydride with Nitric Oxide

About 25 g. (0.15 moles) of perfluorosuccinic anhydride were placed into a 7-liter bulb equipped with a quartz insert. The material was frozen in carbon-ice and the system evacuated. 520 mm. of nitric oxide were introduced and the reaction mixture was then irradiated with a Hanovia mercury vapor lamp. The reaction was followed by the increase in pressure as indicated by an attached manometer. After six hours, the pressure had increased from 520 mm. to 645 mm. and the lamp was turned off. The bulb was slowly evacuated into carbon-ice and liquid air cooled traps. Infrared analysis of the products indicated that the major components were carbonyl fluoride, tetrafluoroethylene and carbon dioxide. The expected nitrogen-oxygen stretching frequencies were observed but only insignificant amounts seemed to be present. A dinitroso compound may have formed but, under the conditions of ultraviolet radiation, was undoubtedly degraded to carbonyl fluoride.

Reaction of Trifluoroacetic Acid with Nitrosyl Chloride

About 75 g. (0.656 moles) of trifluoroacetic acid were placed into a 7-liter bulb equipped with a quartz insert. The acid was frozen with liquid nitrogen and the bulb was evacuated. 10 g. of nitrosyl chloride were introduced and irradiation of the mixture with a 450 watt Hanovia lamp was initiated. During the course of the reaction the pressure built up from 170 mm. to 482 mm. The gases were then drawn off into traps immersed in liquid nitrogen and another 10 g. of nitrosyl chloride was added to the unreacted acid in the bulb. This was repeated once more making a total of 30 g. of nitrosyl chloride. 34 g. of unreacted acid were recovered, therefore, a 55% conversion was effected. The gases were scrubbed through water and then passed through soda lime to remove the carbon dioxide. A gas chromatogram revealed a 1:1 mixture of trifluoronitrosomethane and trifluorochloromethane which were identified by infrared analysis. Thus, 8.25 g. of trifluoronitrosomethane, representing a 23% yield, were made from trifluoroacetic acid.

Reaction of Heptafluorobutyric Acid with Nitrosyl Chloride

About 260 g. (1.2 moles) of heptafluorobutyric acid were placed into a glass cylinder fitted with a sintered glass frit, and nitrosyl chloride was passed through at a slow rate. Irradiation of the materials with an ultraviolet lamp for 24 hours and subsequent distillation yielded 3.5 g. of gaseous material. Infrared analysis indicated the presence of 1-nitrosoheptafluoropropane, 1-chloroheptafluoropropane and carbon dioxide. Vapor phase chromatography revealed a mixture containing 55% 1-nitrosoheptafluoropropane and 40% 1-chloroheptafluoropropane. Since the conversions were poor, no additional work was attempted on this reaction.

Attempted Reactions of 1,2-Dibromotetrafluoroethane with Nitric Oxide

A. 90 g. of 1,2-dibromotetrafluoroethane, obtained commercially from E. I. du Pont de Nemours and Company, Inc., were frozen in a 22-liter bulb and the system was then evacuated. 420 mm. of nitric oxide were introduced and the materials were allowed to warm up to room temperature. An ultraviolet lamp was positioned a few inches from the bulb and irradiation was continued for two days. The contents were slowly evacuated into carbon-ice and liquid air cooled traps but only starting materials were recovered.

B. 45 g. of mercury and 80 g. of 1,2-dibromotetrafluoroethane were frozen in a special 7-liter flask fitted with a quartz insert. The system was evacuated and 475 mm. of nitric oxide were introduced. The Hanovia mercury vapor lamp was placed into the quartz insert and irradiation was continued for 36 hours. The contents of the bulb were slowly evacuated into carbon-ice and liquid air cooled traps but a distillation resulted in a quantitative yield of 1,2-dibromotetrafluoroethane; b.p. 41-42°C./630 mm.

Preparation of 1,2-Diiodotetrafluoroethane

Tetrafluoroethylene was prepared by the debromination of 1,2-dibromotetrafluoroethane with zinc-dust in ethanol. A 500 ml. stainless steel Parr bomb was charged with 200 g. (0.79 moles) of iodine and one ml. of "Terpene-B" inhibitor. The bomb was cooled in carbon-ice and 20 g. (0.20 moles) of tetrafluoroethylene were introduced.

The reaction mixture was heated at 145° for 24 hours. After cooling to room temperature, volatile products were bled from the bomb and the addition of tetrafluoroethylene and subsequent heating were repeated three times more. 275 g. of crude 1,2-diiodotetrafluoroethane were obtained. Since distillation at atmospheric pressure does not afford a clean separation from the iodine in the mixture, pure product was collected under reduced pressure. Thus, 254 g. of 1,2-diiodotetrafluoroethane were obtained; b.p. 51-52°C./98 mm., n_D^{25} 1.489.

Attempted Reaction of Tetrafluoroethylene with Nitric Oxide

Into a previously evacuated 7-liter bulb equipped with a quartz insert and an attached manometer, 200 mm. of tetrafluoroethylene and 300 mm. of nitric oxide were introduced. The Hanovia lamp was placed into the quartz insert and turned on. After ten hours, the pressure had decreased from 500 mm. to 387 mm. and irradiation was then discontinued. The gaseous materials were slowly evacuated into two liquid air cooled receivers and representative samples were taken for intrared analysis. The spectrograms revealed no peaks which could be ascribed to a nitroso compound but nitrites and carbonyl fluoride were indicated. Study of the reaction was then discontinued.

Reaction of 1,2-Diiodotetrafluoroethane with Nitric Oxide

33.0 g. (0.09 moles) of 1,2-diiodotetrafluoroethane were placed into a 7-liter bulb equipped with a quartz insert. The material was frozen in carbon-ice and then the system was evacuated. 600 mm. of nitric oxide were introduced, as measured by an attached manometer, and the bulb was allowed to warm up to room temperature. Since a pressure decrease was expected, the reaction was followed with the manometer. A Hanovia mercury vapor lamp was placed into the quartz insert and then turned on. The pressure decreased from 600 mm. to 442 mm. in twenty-four hours and irradiation was then discontinued. The flask had a deep red appearance due to nitrogen dioxide and iodine vapors and it was noted that iodine had collected on the water-cooled quartz insert. The contents were slowly evacuated into carbon-ice and liquid air cooled traps and representative samples of the lowest boilers were taken for infrared analysis. It was found that the major products were carbonyl fluoride and tetrafluoroethylene with only a trace of a compound exhibiting a typical nitrogen-oxygen stretching frequency at 6.25 microns. In addition, 21 g. of 1,2-diiodotetrafluoroethane and a small amount of polymeric material were recovered.

Preparation of 1,2-Dinitrosotetrafluoroethane

51.0 g. (0.143 moles) of 1,2-diiodotetrafluoroethane and 30 g. of mercury were placed into a 7-liter bulb equipped with a quartz insert. The material was frozen in carbon-ice and then the system was evacuated. 588 mm. of nitric oxide were introduced and the bulb was allowed to warm up to room temperature. Since a pressure decrease was expected, the reaction was followed with an attached manometer. A Hanovia mercury vapor lamp was placed into the quartz insert and then turned on. Thre pressure decreased from 588 mm. to 408 mm. in thirteen hours and irradiation was then discontinued. The bulb had a green-blue appearance and the mercury had reacted with the iodine and nitrogen dioxide formed in the reaction. The materials were slowly evacuated into carbon-ice and liquid air cooled traps and the lowest boilers were then combined. A sample was taken for infrared analysis and an unusually strong nitrogen-oxygen stretching frequency at 6.2-6.3 microns was observed. Only traces of carbonyl fluoride and tetrafluoroethylene were apparent in this experimental run. The materials were washed twice with water and then distilled to give the following:

(1) 5.5 g. of a deep blue liquid, b.p. -15 to -13°C./630 mm. The infrared spectrogram indicated a strong N-O absorption at 6.2-6.3 microns.

(2) 1.5 g. of deep blue liquid, b.p. 18-19 C./630 mm. Molecular weight 175.4, calcd. for 1-nitroso,2-nitrotetrafluoroethane; 176.0.

(3) 31.1 g. of 1,2-diiodotetrafluoroethane, b.p. 56-56.5°C./20 mm.

(4) 2 g. of an undetermined polymeric material.

The conversion of 1,2-diiodotetrafluoroethane was 39.8% with a 60.7% yield of 1,2-dinitrosotetrafluoroethane.

Reaction of Heptafluorobutyryl Chloride with Nitrosyl Chloride

About 10 g. of heptafluorobutyryl chloride and 8 g. of nitrosyl chloride were introduced into a previously evacuated 7-liter bulb equipped with a quar . insert. The system was frozen in carbon-ice and then irradiated with a Hanovia lamp for six hours. Gas samples were taken periodically for infrared analysis. Peaks ascribed to the acid chloride diminished over a period of time while those ascribed to 1-nitrosoheptafluoropropane and 1-chloroheptafluoropropane increased. By and large, the main product was 1-chloroheptafluoropropane and, therefore, work was discontinued on this reaction.

Reaction of Heptafluorobutyryl Chloride with Nitric Oxide

About 8.5 g. of heptafluorobutyryl whloride were placed into a 7-liter bulb equipped with a quartz insert. The material was frozen in carbon-ice and then evacuated. 500 mm. of nitric oxide were introduced and the resulting mixture was allowed to warm up to room temperature. Irradiation of the contents of the bulb was continued for 4.5 hours by means of a Hanovia mercury vapor lamp. Representative samples from the bulb were taken for infrared analysis and the major products were found to be 1-nitrosoheptafluoropropane and 1-chloroheptafluoropropane with traces of heptafluorobutyryl fluoride and pentafluoropropionyl fluoride. A gas chromatogram indicated an approximately equimolar ratio of the two major products of the reaction. However, no attempt was made to isolate the materials.