boiling several minutes to remove dissolved air was added through the condenser, and the resulting green solution was maintained at reflux in the dark under a nitrogen atmosphere for 5 hr. The solvent was removed by distillation at room temperature using a water aspirator to yield a brown solid which was shown by its infrared spectrum (potassium bromide disc) to be 73% IX contaminated by unknown decomposition products but not by the isomeric nitroso compound X. An experiment under the same conditions starting with X gave the similar result that no isomerization to IX was detected, although some decomposition occurred.

Isomerizations in refluxing tetrachloroethane. A 50-ml. round bottom flask containing 50 mg. of IX was fitted with a reflux condenser and the assembly was flushed with nitrogen. Twenty-five milliliters of dry 1,1,2,2-tetrachloroethane which had been boiling several minutes to remove dissolved air was added through the condenser. The flask was immediately placed in a preheated mantle so that the boiling of the solvent was not appreciably interrupted, and the reaction mixture was maintained at reflux in the dark under a nitrogen atmosphere for 1.0 min. The flask was then quickly plunged in an ice bath and cooled to room temperature during about 30 sec. The solvent was evaporated at room temperature using an oil pump to leave a brown solid residue which was shown by its infrared spectrum (potassium bromide disc) to be a mixture of IX (56%), X (19%), and unknown decomposition products (25%). The above procedure was followed for a series of eight isomerization runs starting from X as well as IX for reaction times of 1, 5, 10, and 20 min. The data are given in Table II.

A set of three runs was carried out as described above with varying amounts of IX in 25 ml. of tetrachloroethane for a reaction time of 3.5 min. The amounts of starting material and the product compositions for the three cases were: 20 mg., 49% IX, 51% X; 40 mg., 51% IX, 49% X; 60 mg. 54% IX, 46% X.

BRYN MAWR, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Fluorinated C-Nitroso Compounds. The Action of Nitric Oxide on Some Fluoroolefins. I

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Nitric oxide reacts with tetrafluoroethylene, trifluorochloroethylene, and hexafluoropropene to yield nitroso compounds, nitro compounds, and other substances most of which have been isolated and characterized. These reactions exhibit characteristics of free radical processes which apparently are set in operation by nitrogen dioxide.

It is the purpose of this series of papers.(of which the present one is the first of the series) to report the results of a systematic study of reactions of fluorine-containing olefins with nitric oxide, nitrosyl halides, and other nitrogen-containing compounds, for use as possible intermediates in polymerization studies.

In the reaction of nitric oxide with unsaturated organic compounds, Bloomfield and Jeffrey[5] first reported that nitrogen was one of the byproducts of the reaction and Brown concluded that pure nitric oxide (NO) had no effect on the organic substrate, and that nitrogen dioxide (NO_2) was required for the initiation of the reaction. From these observations together with other known chemical characteristics of nitric oxide, Brown[6] offered an explanation for the appearance of nitro- and nitro-nitroso compounds in his products. Brown's argument was centered on the known reaction of the NO group in RNO with nitric oxide which results in a diazonium nitrate, $R{=}N_2NO_3$. The latter decomposes to nitrogen, R· and NO_3·, and in the presence of more nitric oxide the reaction proceeds to give nitrogen dioxide with the overall effect of a disproportionation of nitric oxide to nitrogen and nitrogen dioxide.

The most recent report on the action of nitric oxide on an unsaturated compound is that of Haszeldine[7] which appeared in print while the present series of investigations were in progress. Haszeldine studied the reaction of tetrafluoroethylene with nitric oxide and obtained a mixture of products, one of which was 1,1,2,2-tetrafluoro-1-nitro-2-nitrosoethane.

In our work we studied the reactions of trifluorochloroethylene, hexafluoropropene and tetrafluoroethylene with nitric oxide in the gas phase at atmospheric or superatmospheric conditions.

Trifluorochloroethylene with two molar proportions of nitric oxide in a pressure vessel underwent an exothermic reaction in which practically all of the nitric oxide and the olefin were consumed. The products isolated were a clear nondistillable material which constituted the main bulk of the reaction mixture, water soluble materials, and the following five pure compounds: $ClCF_2CFClNO$, (I), $ClCF_2CFCl_2$ (II), O_2NCF_2-

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[4] Address; Minnesota Mining and Manufacturing Company, St. Paul, Minn.

[5] G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

[6] J. F. Brown, *J. Am. Chem. Soc.*, **79**, 2480 (1957).

[7] R. N. Haszeldine, *Proc. Chem. Soc.*, **368**, Nov. 1959.

$CFClNO$ (III), $O_2NCF_2CFCl_2$ (IV), $O_2NCF_2CFClNO_2$ (V).

The nature of the polymeric material as well as the water-soluble fraction was not investigated. The water solution, however, gave tests for both fluoride and chloride ions. The structure and constitution of I was established by oxidation to $ClCF_2CFClNO_2$ (VI) for which a good analysis was obtained, and by comparing its infrared spectra and physical constants with those of the same compound prepared from $CF_2Cl—CFClI$ and nitric oxide.[8] The structures of the isomeric compounds IV and VI were determined by chemical means and from their NMR spectra. The structure and constitution of III were determined by oxidation to V which is a known compound[9] and from its NMR spectra. The products of this reaction are those which would be formed if the reaction of trifluorochloroethylene was carried out respectively with nitrosyl chloride, chlorine, nitrogen oxide (N_2O_3), nitryl chloride (NO_2Cl) and dinitrogen tetroxide (N_2O_4). Evidently Brown's proposal[6] of the disproportionation of nitric oxide to nitrogen and nitrogen dioxide is also applicable in this case.

The following reaction path is tentatively proposed. Nitrogen dioxide which is shown as the initiator of the free radical process is thought either to be present as an impurity in commercial nitric oxide or is formed from the latter and traces of oxygen in the reacting system. Once the reaction proceeds reaction (4) generates more of it.

$$CF_2{=}CFCl + NO_2 \longrightarrow O_2NCF_2CFCl\cdot \tag{1}$$

$$O_2NCF_2CFCl\cdot + NO \longrightarrow O_2NCF_2CFClNO \tag{2}$$

$$O_2NCF_2CFClNO + 2NO \longrightarrow O_2NCF_2CFClN_2NO_3 \tag{3}$$

$$O_2NCF_2CFClN_2NO_3 + NO \longrightarrow O_2NCF_2CFCl\cdot + N_2 + 2NO_2 \tag{4}$$

$$O_2NCF_2CFCl\cdot + NO_2 \longrightarrow O_2NCF_2CFClNO_2 \text{ and/or } O_2NCF_2CFClONO \tag{5}$$

$$O_2NCF_2CFClONO \longrightarrow O_2NCF_2CFClO\cdot + NO \tag{6}$$

$$O_2NCF_2CFClO\cdot \longrightarrow O_2NCF_2COF + Cl\cdot \tag{7}$$

$$Cl + NO \text{ (or } NO_2) \longrightarrow NOCl \text{ (or } NO_2Cl) \tag{8}$$

$$CF_2{=}CFCl + Cl\cdot \longrightarrow ClCF_2CFCl\cdot \tag{9}$$

$$ClCF_2CFCl\cdot + NO \longrightarrow ClCF_2CFClNO \tag{10}$$

$$O_2NCF_2CFCl\cdot + NOCl \text{ (or } NO_2Cl) \longrightarrow O_2NCF_2CFCl_2 \tag{11}$$

$$ClCF_2CFCl\cdot + NOCl \text{ (or } NO_2Cl) \longrightarrow ClCF_2CFCl \tag{12}$$

$$XCF_2CFCl\cdot + nCF_2{=}CFCl \longrightarrow X(CF_2CFCl—)_n \tag{13}$$

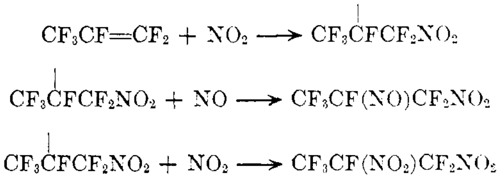
$$X = NO_2 \text{ or } Cl$$

This reaction path is explicitly written as a free radical process because the products obtained here and also the products of other similar reactions in which blue nitroso derivatives were obtained in high yields (to be reported in a later paper) cannot be consistently explained by an ionic process. Relevant to this argument are the experiments of Knunyants and Fokin[10] and of Shechter and Ley,[11] who worked with nitrogen sesquioxide and various olefins, and who also have argued for free radical processes.

The fact that in this and in similar experiments no compounds of the type $ONCF_2CX_2NO$, $ONCF_2CX_2NO_2$ (X = halogen) have been obtained is of significance and leads to the conclusion that nitric oxide, at least under the conditions of these experiments, is not capable of initiating free radical chains; it only terminates them.

The products isolated are accounted for by reactions 2, 5, 10, 11, and 12. The acid fluoride of reaction 7 and the nitrite of reaction 5, both of which would react with water to form nitrodifluoroacetic acid, may well account for the acidity of the wash water and for the positive tests for fluoride and chloride ions. Indeed analogous compounds have been isolated in other similar reactions during the course of these investigations.

The products of hexafluoropropene and nitric oxide either in a pressure vessel or in a flask at normal pressures and in the dark were mainly 2-nitroso-3-nitro-1,1,1,2,3,3-hexafluoropropene (VII) and 2,3-dinitro-1,1,1,2,3,3-hexafluoropropene (VIII) together with two other low boiling water-soluble compounds. No polymeric material was obtained in this case. It is thought that the products of this reaction were formed by a process analogous to the one written above for trifluorochloroethylene and nitric oxide.

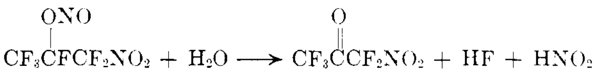


$$CF_3CF{=}CF_2 + NO_2 \longrightarrow CF_3\overset{|}{C}FCF_2NO_2$$

$$CF_3\overset{|}{C}FCF_2NO_2 + NO \longrightarrow CF_3CF(NO)CF_2NO_2$$

$$CF_3\overset{|}{C}FCF_2NO_2 + NO_2 \longrightarrow CF_3CF(NO_2)CF_2NO_2$$

The location of the NO and NO_2 groups on VII were established by NMR spectra. The two water soluble products were not studied in detail but on the basis of their infrared spectra they are suspected to be the nitro-acetone $CF_3\overset{\overset{O}{\|}}{C}CF_2NO_2$ and the nitrite $CF_3\overset{\overset{ONO}{|}}{C}FCF_2NO_2$. The latter upon reaction with water would give the same nitroacetone, hydrogen fluoride and nitrous acid:



$$CF_3\overset{\overset{ONO}{|}}{C}FCF_2NO_2 + H_2O \longrightarrow CF_3\overset{\overset{O}{\|}}{C}CF_2NO_2 + HF + HNO_2$$

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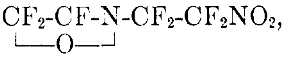
[8] P. Tarrant, University of Florida, personal communication.

[9] A. M. Lovelace, D. A. Rausch, W. Postelnek, *Aliphatic Fluorine Compounds*, Reinhold, N. Y., 1958.

[10] I. L. Knunyants and A. V. Fokin, *Nitration of Fluoroolefins With Nitrogen Dioxide;* paper read at a session of the Division of Chemical Sciences of The Academy of Sciences of the U. S. S. R., October 30, 1957; *Chem. Abstr.*, **51**, 9472 (1957).

[11] H. Shechter and D. E. Ley, *Chem. & Ind.*, 535 (1955).

Tetrafluoroethylene and nitric oxide will react under a variety of conditions of temperature and pressure to produce addition products. In these studies, $ONCF_2CF_2NO_2$, $O_2NCF_2CF_2NO_2$, $O_2NCF_2CF_2ONO$, and $CF_2\text{-}CF\text{-}N\text{-}CF_2\text{-}CF_2NO_2$, were isolated and identified. Conditions favoring formation of $ONCF_2\text{-}CF_2NO_2$ were achieved by using equal molar quantities of NO and C_2F_4 in a pyrex flask. Yields of 80–90% (based on C_2F_4 consumed) were obtained. NMR spectrum supports the structure $ONCF_2\text{-}CF_2NO_2$.



$$\underbrace{CF_2\text{-}CF\text{-}N}_{O}\text{-}CF_2\text{-}CF_2NO_2$$

The infrared spectra of these and other nitro and nitroso derivatives of fluoroolefins will be discussed in later papers.

NMR spectra. The NMR spectrum[12] of CF_2Cl—$CFClNO$ at 25% solution in trichlorofluoromethane showed two strong absorptions in the ratio of 1:2 at 73.8 ϕ (C—F) and at 96.5 ϕ ($-CF_2-$). The former is a triplet and the latter a double triplet. Coupling constants are $J_F - {}_F{}^1 = 8.1$ cps. and $J_N - {}_F{}^1 = 11.2$ cps.

The spectrum for CF_3—$CF(NO)$—$CF_2(NO_2)$ shows strong absorption at 73.8 ϕ (CF_3-), 91.0 ϕ ($-CF_2\text{-}NO_2$), and at 167.5 ϕ ($-CF\text{-}NO$).

EXPERIMENTAL

Trifluorochloroethylene and nitric oxide under pressure. About 117 g. (1 mole) trifluorochloroethylene was transferred to an evacuated 750 ml. autoclave which was cooled to −78°. Two moles of nitric oxide was then added and the autoclave brought to room temperature and allowed to stand at about 22° for 24 hr.

About 160 g. of a blue liquid was collected from the autoclave in a Dry Ice cooled trap. The crude product was washed with water and dried with calcium chloride. Eighteen grams of product dissolved in the water during this operation. The wash solution gave tests for both chloride and fluoride ions and was strongly acidic. Distillation of the blue mixture yielded the following: (a) 5 g. of trifluorochloroethylene b.p. −31°/630 mm. (b) 5 g. of 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane, b.p. 3.17°/630 mm. n_D^0 1.3455, d_4^0 1.5422. Mol. wt., Calcd. 181.8. Found 180. No consistent analytical results could be obtained for this compound. Proof for its structure was based upon a comparison of its infrared spectra with that of the same compound prepared by Tarrant[8] from 1,2-dichloro-1,1,2-trifluoro-2-iodoethane and nitric oxide and by oxidation to 1,2-dichloro-1,1,2-trifluoro-2-nitroethane for which a good analysis was obtained.

(c) 6 g. of 1,2,2-trichloro-1,1,2-trifluoroethane, b.p. 41–42°/630 mm. n_D^{25} 1,3557, d_4^{25} 1.5629, Mol. wt., Calcd. 187. Found 180; identified by its infrared spectra and physical constants. (d) 4 g. of 1-nitro-1,1,2-trifluoro-2-chloro-2-nitrosoethane b.p. 62°/630 mm. 10–12/90. n_D^{25} 1.349, d_4^{25} 1.5494. Mol. wt. Calcd. 182. Found 186. No consistent analytical results for this blue compound could be obtained. Structure proof was based upon oxidation to 1,2-dinitro-1,1,2-trifluoro-2-chloroethane (which is a known compound) and on the basis of its NMR spectra which indicated the location of both the $-NO$ and $-NO_2$ groups.

(e) 20 g. of 1,1,2-trifluoro-2-dichloro-1-nitroethane b.p. 70.5–71.5°/630 mm. m.p. less than −78°, n_D^{25} 1.3669, d_4^{25} 1.6199. Mol. wt., Calcd. 189. Found 199.

Anal. Calcd. for $C_2Cl_2F_3NO_2$: C, 12.12; N, 7.07; Cl, 35.86; F, 28.78. Found: C, 12.44; N, 6.97; Cl, 35.67; F, 28.5.

The structure of this compound is assigned as such on the basis of NMR evidence.

(f) 8.5 g. of 1,2-dinitro-1,1,2-trifluoro-2-chloroethane, b.p. 94.5°/630 mm., n_D^{25} 1.375, d_4^{25} 1.6704. Lit.[10] b.p. 98–99°/750 mm., n_D^{25} 1.3748, d_4^{25} 1.674. (g) about 65 g. of a nondistillable material.

Hexafluoropropene and nitric oxide under pressure. One hundred grams of hexafluoropropene (0.666 mole) and 1.2 moles nitric oxide were combined and worked up exactly as in the preceding experiment. A colorless gas which did not condense at Dry Ice temperatures and which did not react with oxygenated acids or base was produced in this reaction. In this reaction the quantity of this inert gas which is suspected to be nitrogen was considerable. Washing of the reaction mixture removed 15 g. of a water-soluble fraction. Distillation of the dried mixture gave 60 g. of unchanged hexafluoropropene, b.p. −31°/630 mm. and two other fractions:

(a) 24 g. of a blue liquid, b.p. 42°/630 mm., n_D^0 1.306, d_4^0 1.6224. This blue compound was assigned the structure $CF_3\text{-}CF(NO)CF_2NO_2$ on the basis of NMR data. Mol. wt., Calcd. 226; Found 220. No consistent analytical results could be obtained. Oxidation gave 2,3-dinitro-1,1,1,2,3,3-hexafluoropropane.

(b) 17 g. of 2,3-dinitro-1,1,1,2,3,3-hexafluoropropene, b.p. 68.5°/630 mm. n_D^{25} 1.3220, d_4^{25} 1.6479, Mol. wt. 237. Lit.[11] b.p. 76°/760 mm., n_D^{20} 1.3141.

Anal. Calcd. for $C_3F_6N_2O_4$: C, 14.88; N, 11.57; F, 47.11. Found: C, 15.05; N, 11.57; F, 47.42 and 47.36.

In another experiment the product was fractionated without washing in order to isolate the water soluble fraction. From 75 g. of hexafluoropropene and 1 mole of nitric oxide, two green liquids were isolated; one boiling at 15–17°/630 mm. and the other at 27.5°/630 mm. The latter reacted vigorously with water. Identification of these products is still in progress.

Hexafluoropropene and nitric oxide in a flask. An evacuated 22-l. flask was charged with 50 g. (0.33 mole) of hexafluoropropene and 18 g. (0.6 mole) of nitric oxide. The flask was kept in the dark for 1 month. As time passed the contents changed from colorless to blue, and a thin white solid film started depositing on the walls of the flask; finally the gaseous mixture became blue-green. At the end of 1 month, the content of the flask was withdrawn into a liquid air trap with a pump. The crude reaction mixture was washed with water and dried with calcium chloride. Distillation yielded three fractions of which the first was 27 g. of unchanged hexafluoropropene, and the other two were, (a) 12 g. of 2-nitroso-2-nitro-1,1,1,3,3,3-hexafluoropropane; (b) 10 g. of 2,3-dinitro-1,1,1,2,3,3-hexafluoropropane.

Oxidation of 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane to 1,2-dichloro-1,1,2-trifluoro-2-nitroethane. In a 500-ml. three-neck flask provided with a stirrer, a dropping funnel, and a thermometer were placed 50 g. (0.24 mole) sodium dichromate, 150 ml. of glacial acetic acid, and 50 g. of concd. sulfuric acid. The mixture was cooled to about 10° with ice and while stirring vigorously 56 g. (0.38 mole) of cold 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane was added dropwise during 0.5 hr. Stirring was continued for 5 hr. at 5–10°. The reaction mixture was then mixed with 600 ml. of ice cold water in a separatory funnel. The organic layer which settled was drawn off, dried over calcium chloride and distilled. Five grams of unchanged 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane was recovered. The product 1,2-dichloro-1,1,2-trifluoro-2-nitroethane weighed 50 g., b.p. 71–72°/630 mm., n_D^{25} 1.3692, d_4^{25} 1.6162, m.p. ∼ −35°. Mol. wt., Calcd. 198; Found 197.

Anal. Calcd. for $C_2F_3Cl_2NO_2$: C, 12.12; N, 7.07; Cl, 35.86; F, 28.78. Found: C, 11.87; N. 7.23; Cl, 35.58; F, 28.56.

Oxidation of 1,1,2-trifluoro-2-chloro-1-nitro-2-nitrosoethane. In a 250-ml. three-neck flask set up as in the preceding experiment were placed 25 g. (0.12 mole) of sodium dichromate, 80 m . of glacial acetic acid, and 30 g. of concd. sulfuric acid. The mixture was cooled to about 10° with ice and while stir-

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(12) G. Filipovitch and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

ring 38 g. (0.197 mole) of 1,1,2-trifluoro-2-chloro-1-nitro-2-nitrosoethane was added slowly during 0.5 hr. The reaction mixture was worked up as above. The product, 29 g., b.p. 95°/630 mm., n_D^{25} 1.3749, d_4^{25} 1.6699, gave an infrared spectrogram which was identical with that of 1,1,2-trifluoro-1-chloro-1,2-dinitroethane which was obtained directly from the reaction of trifluorochloroethylene with nitric oxide (see above).

Oxidation of 2-nitro-2-nitroso-1,1,1,2,3,3-hexafluoropropane. Thirty-four grams (0.15 mole) of 2,3-dinitro-1,1,1,2,3,3-hexafluoropropane was oxidized as in the preceding experiments with 15 g. (0.15 mole) of chromium trioxide in 50 ml. of glacial acidic acid and 25 ml. of concd. sulfuric acid. The product, 27 g., was worked up similarly and gave 5 g. of unchanged starting material, and 21 g. of 2,3-dinitro-1,1,1,2,-3,3-hexafluoropropane, b.p. 68–68.5°/630 mm., n_D^{25} 1.3222, d_4^{25} 1.6476. Mol. wt., Calcd. 242; found 240. The infrared spectrogram of this compound was identical with that of 2,3-dinitro-1,1,1,2,3,3-hexafluoropropane described above.

Chemical distinction between 1,2-dichloro-1,1,2-trifluoroethane and 1-nitro-1,1,2-trifluoro-2,2-dichloroethane. 1,2-Dichloro-1,1,2-trifluoro-2-nitroethane reacted vigorously at room temperature with zinc dust in either anhydrous pyridine or in dibutoxy tetraethylene glycol. 1-Nitro-1,1,2-trifluoro-2,2-dichloroethane did not react with zinc dust in either solvent at room temperature or at 50°. A partial reaction was brought about at 75–80° for 5 hr., but 60% of the starting material was recovered unchanged.

Tetrafluoroethylene and nitric oxide. Equivalent quantities of nitric oxide and tetrafluoroethylene were charged into an evacuated 12.5-l. glass vessel to 1 atm. pressure, (0.25 mole each). After 16 hr. at 20°, the pressure dropped to 0.5 atm. The flask was then repressured to 1 atm. with nitric oxide. After an additional 16 hr., the pressure dropped to 0.7 atm. The blue product was fractionated in a screen-saddle packed column. To the pot residue was added 10 cc. of water for hydrolysis of the remaining impurities. Deep-blue liquid, 21 g., accounting for 60 wt. % of the starting materials was obtained, b.p. 24.5–25.5°. The infrared spectrum showed an absorption of 6.17 μ (contrasted to 6.25 μ for R_fNO).

Anal. Calcd. for C_2ClF_4NO: C, 13.2; F, 41.0; N, 14.6. Found: C, 13.6; F, 41.2, N, 14.9. Mol. wt. (Dumas), Calcd. 179; found 176. NMR spectrum supports the structure $ONCF_2CF_2NO_2$.

The following condition favoring the formation of $ONCF_2CF_2NO_2$ was used. Equimolar quantities of nitric oxide and tetrafluoroethylene are charged into a 50-l. Pyrex vessel. After 16–24 hr. the pressure dropped to 0.5 to 0.6 atm. The contents of the vessel were sent through water scrubber, dried and collected in a Dry Ice trap, and the uncondensed material returned to the reactor. The reactor was then re-pressured with nitric oxide and the cycle repeated. Yields of 80–90% (based on tetrafluoroethylene consumed) were obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Fluorinated C-Nitroso Compounds. II.[1] The Reaction of Nitric Oxide with Some Fluoroolefins in the Presence of Ferric Chloride

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Received October 3, 1960

The fluorinated olefins tetrafluoroethylene, trifluorochloroethylene and 1,1-difluoro-2,2-dichloroethylene react with nitric oxide in the presence of anhydrous ferric chloride to give good yields of the nitrosoethanes $ClCF_2CF_2NO$, $ClCF_2CFClNO$, and $ClCF_2CCl_2NO$, respectively. Along with these compounds, which constitute the major part of the reaction mixture, are formed nitro-nitroso, nitro, and fully halogenated derivatives all of which have been isolated and characterized. Ferric chloride participates in the reaction by making chlorine available to the reacting system, and the ferric ion is reduced to the ferrous state.

The success of Haszeldine,[3] and of Banus[4] in preparing trifluoronitrosomethane and heptafluoronitrosopropane from the corresponding normal perfluoroalkyl iodides and nitric oxide, and also Brown's[5] extension of an earlier study[6] of the reaction of nitric oxide with unsaturated organic compounds demonstrated clearly the latent capacity of nitric oxide to behave as a free radical. This capacity of nitric oxide was known since Hinshelwood's[7] first kinetic studies with it, but was not exploited in organic reactions for the preparation of nitroso compounds until trifluoronitrosomethane and heptafluoronitrosopropane were synthesized.

From the results of our earlier studies reported in the first paper of this series it became evident that formation of nitroso compounds as major products in the interaction of nitric oxide with fluorinated olefins could not be effected in a static system under the conditions employed in these studies. The reaction was therefore adapted to a flow system in which the reactants, nitric oxide and fluoroolefin, were passed through a Pyrex tube packed with various finely divided solid surfaces which were expected to promote or catalyze the reaction.

As Lewis acids of trivalent cations in the solid state are known to absorb nitric oxide reversibly, it was thought that with some of these acids, a temperature could be found at which nitric oxide and

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[1] Paper I in this series, *J. Org. Chem.*, **26**, 3316 (1961).

[2] Present address, State University College of Forestry, Baker Hall, Syracuse 10, N. Y.

[3] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).

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[5] J. F. Brown, *J. Am. Chem. Soc.*, **79**, 2480 (1957).

[6] G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

[7] J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc.*, **159**, 32 (1937).