**584.** *Perfluoroalkyl Derivatives of Nitrogen. Part X.[1] The Reaction of Nitric Oxide with Tetrafluoroethylene, and Formation of a Nitroso-polymer.**

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Tetrafluoroethylene reacts with nitric oxide, under very mild conditions, to give tetrafluoro-1-nitro-2-nitrosoethane ($NO_2 \cdot CF_2 \cdot CF_2 \cdot NO$) (68%) and a number of other products. Evidence for initiation of the chain reaction by dinitrogen tetroxide is presented, and physical and chemical properties of the nitronitroso-compound are discussed. The nitronitroso-compound readily reacts with more tetrafluoroethylene to give the oxazetidine

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot \overline{N \cdot O \cdot CF_2 \cdot CF_2}$$
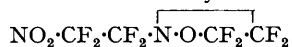
and the 1 : 1 copolymer $[\cdot N(CF_2 \cdot CF_2 \cdot NO_2) \cdot O \cdot CF_2 \cdot CF_2 \cdot]_n$, which may also be prepared directly in good yield by the reaction of tetrafluoroethylene with nitric oxide under a variety of conditions.

THE reactions of dinitrogen tetroxide and of dinitrogen trioxide with olefins have received considerable attention. Nitrosonitrates, nitronitrates, nitronitrites, dinitrites, and dinitro-compounds have been reported as products of reactions involving dinitrogen tetroxide, whilst dinitrogen trioxide reacts with olefins to give nitronitroso-adducts and a number of by-products.[2] Reactions between fluoro-olefins and dinitrogen tetroxide are known to give mainly dinitro-compounds,[3,4] but nitronitrites and their decomposition products are often formed.[5] Comparatively little is known concerning the reactions of nitric oxide with olefins: it has been stated that nitric oxide does not attack unsubstituted alkenes,[6] and this statement has been confirmed recently by Brown, who found no reaction to occur between isobutene and " scrupulously purified nitric oxide " in the liquid phase.[7] The method of purification of the nitric oxide used was not described. Isobutene reacts readily with nitric oxide containing traces of dinitrogen tetroxide, and gives a complex mixture containing a dimer of 2-methyl-1-nitro-2-nitrosopropane $[(NO_2 \cdot CH_2 \cdot CMe_2 \cdot NO)_2]$ and unstable compounds which dissociate into 2-methyl-1-nitropropene on distillation.[7] The reactions of nitric oxide with cyclohexene [8] and with styrene [9] have also been described.

The reaction between nitric oxide and tetrafluoroethylene has now been investigated; it provides a convenient route to a new member of the interesting series of fluoroalkyl nitroso-compounds.

The Compound $NO_2 \cdot CF_2 \cdot CF_2 \cdot NO$.—When a mixture of tetrafluoroethylene (1 mol.) and nitric oxide (2 mol.), at a total pressure of about one atmosphere, was set aside in the dark at room temperature, a deep brown colour developed. This colour slowly gave way to green and finally, after 48 hours, to deep blue. The products of this reaction, separated by fractional distillation, chemical methods, and gas–liquid chromatography, were (yields based on tetrafluoroethylene converted): tetrafluoro-1-nitro-2-nitrosoethane (I) (68%), tetrafluoro-1,2-dinitroethane (II) (15%), perfluoro-2-(2-nitrotetrafluoroethyl)-1,2-oxa-zetidine (III) (5%), a mixture of water-soluble compounds (*ca.* 10%) believed to contain

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* Preliminary publication, *Proc. Chem. Soc.*, 1959, 367.

[1] Part IX, Barr, Haszeldine, and Willis, *J.*, 1961, 1351.
[2] Riebsomer, *Chem. Rev.*, 1945, **36**, 196.
[3] Coffman, Raasch, Rigby, Barrick, and Hanford, *J. Org. Chem.*, 1949, **14**, 747.
[4] Haszeldine, *J.*, 1953, 2075.
[5] Knunyants and Fokin, *Doklady Akad. Nauk S.S.S.R.*, 1956, **111**, 1035.
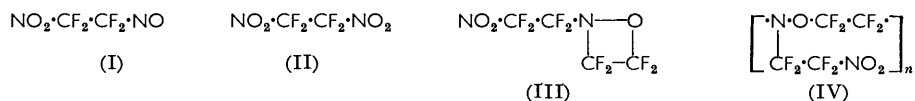[6] Sidgwick, " The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1949, p. 213.
[7] Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 2480.
[8] Bloomfield and Jeffrey, *J.*, 1944, 120.
[9] Benson, U.S.P. 2,656,395/1955.

tetrafluoro-2-nitroethyl nitrite ($NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot NO$) and, on the basis of infrared spectroscopy and molecular-weight measurements, difluoronitroacetyl fluoride ($NO_2 \cdot CF_2 \cdot COF$), and nitrogen (34% on initial nitric oxide). Some tetrafluoroethylene (34%) remained, and traces of nitric oxide, carbonyl fluoride, carbon dioxide, silicon tetrafluoride, and polymer (IV) were also found.

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot NO \qquad NO_2 \cdot CF_2 \cdot CF_2 \cdot NO_2 \qquad NO_2 \cdot CF_2 \cdot CF_2 \cdot N{-\!\!-}O$$

(I) (II) (III) (IV)

Slightly higher temperatures (up to 30°) increase the rate of the reaction, but have no significant effect on the composition of the products.

In attempts to increase the yield of the main product (I) by increasing the conversion of tetrafluoroethylene, the olefin was allowed to react with three molecular proportions of nitric oxide. Despite an almost quantitative conversion of the tetrafluoroethylene, the yield of nitroso-compound (I) was reduced to 45% and the yields of dinitro-compound (II), oxidative breakdown products, and polymeric material were increased. As shown later, this decrease in yield can be attributed to the further reaction of the nitroso-compound with the excess of nitric oxide. When an 8 : 1 molar ratio of nitric oxide to tetrafluoroethylene was used, there was extensive degradation, no nitroso-compound was formed, and only a low yield of the dinitro-compound was isolated. An experiment with stoicheiometric proportions of dinitrogen tetroxide and nitric oxide (dinitrogen trioxide) also gave a decreased yield of nitronitroso-compound (44%), although the reaction time was reduced.
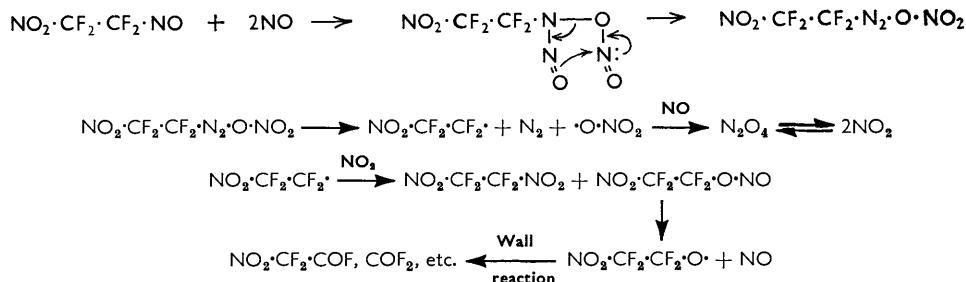
Tetrafluoro-1-nitro-2-nitrosoethane exhibits the brilliant blue colour characteristic of monomeric nitroso-cómpounds. Its infrared spectrum (vapour) contains a prominent band at 6·18 μ, attributed to the presence of nitro- and nitroso-groups in the same molecule [cf. $CF_3 \cdot NO$, 6·25 μ; $CF_3 \cdot NO_2$, 6·13 and 6·17 μ (doublet) [10]]. The ultraviolet spectrum (vapour) clearly shows the presence of nitroso- and nitro-chromophores by bands at 681 and 282 mμ respectively [cf. $CF_3 \cdot NO$, $\lambda_{max.}$ 683 mμ; $CF_3 \cdot NO_2$, $\lambda_{max.}$ 279 mμ [10]]. Additional evidence for structure (I) is provided by the nuclear magnetic resonance spectrum, which shows two separate triplets, attributed to the two $\cdot CF_2 \cdot$ groups in different environments.

Tetrafluoro-1-nitro-2-nitrosoethane closely resembles the perfluoroalkyl nitroso-compounds in its chemical properties, and the presence of the chemically inert nitro-group has little effect on the characteristic properties of the nitroso-group. Like trifluoronitroso-methane,[10] the nitronitroso-compound is stable in contact with mercury, Pyrex, air, and oxygen, when stored in the dark at room temperature. The vapour decomposes very slowly in daylight to give tetrafluoro-1,2-dinitroethane, dinitrogen tetroxide, oxidative breakdown products, and unidentified polymeric material. Irradiation with ultraviolet light greatly accelerates this decomposition, and in a single experiment no indication was obtained of the formation of a dimer [$(NO_2 \cdot CF_2 \cdot CF_2)_2 N \cdot O \cdot NO$] similar to that produced by irradiation of trifluoronitrosomethane. Although it can be distilled at atmospheric pressure without decomposition (b. p. 24·2°), breakdown of the nitronitroso-compound occurs at 90°, and tetrafluoro-1,2-dinitroethane is then formed in 48% yield. Smooth oxidation to the dinitro-compound occurs when the nitronitroso-compound is heated with oxygen at 80°.

Dinitrogen tetroxide reacts only slowly with tetrafluoro-1-nitro-2-nitrosoethane: 91% of the nitronitroso-compound was recovered after 24 hours at room temperature with dinitrogen tetroxide in the vapour phase, whilst 86% was recovered after 12 hours in the liquid phase. Nitric oxide, however, reacts rapidly with the nitronitroso-compound in the liquid phase, and an excess of nitric oxide effects complete decomposition in the vapour phase in 24 hours, giving tetrafluoro-1,2-dinitroethane in approximately 50% yield,

[10] Jander and Haszeldine, *J.*, 1954, 912.

together with dinitrogen tetroxide and nitrogen. The reaction with nitric oxide may be explained by assuming the formation of a diazonium nitrate intermediate, which rapidly decomposes:

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot NO \ + \ 2NO \ \longrightarrow \ NO_2 \cdot CF_2 \cdot CF_2 \cdot N \underset{\substack{N \diagup N: \\ O \quad O}}{\overset{O}{\vert \diagdown \vert}} \ \longrightarrow \ NO_2 \cdot CF_2 \cdot CF_2 \cdot N_2 \cdot O \cdot NO_2$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot N_2 \cdot O \cdot NO_2 \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot + N_2 + \cdot O \cdot NO_2 \xrightarrow{NO} N_2O_4 \rightleftharpoons 2NO_2$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot \xrightarrow{NO_2} NO_2 \cdot CF_2 \cdot CF_2 \cdot NO_2 + NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot NO$$

$$NO_2 \cdot CF_2 \cdot COF, \ COF_2, \ etc. \ \underset{\text{reaction}}{\overset{\text{Wall}}{\longleftarrow}} \ NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot + NO$$

The 50% yield of the compound $(CF_2 \cdot NO_2)_2$ suggests that in the overall reaction

$$2NO_2 \cdot CF_2 \cdot CF_2 \cdot NO + 6NO \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot NO_2 + 2N_2 + 2NO_2 + [NO_2 \cdot CF_2 \cdot COF + \text{Breakdown products}]$$
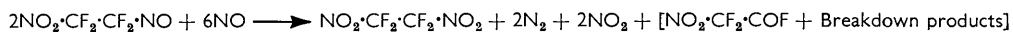
approximately half of the $NO_2 \cdot CF_2 \cdot CF_2 \cdot$ radicals, under these particular conditions, decompose on the walls of the vessel or form nitrite.
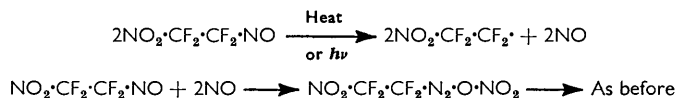
The formation of diazonium nitrates from aromatic nitroso-compounds and nitric oxide is well established,[11] and a homolytic decomposition, giving rise to a fluoroalkyl radical and a nitrate radical, is preferred to a heterolytic process, favoured by Brown during his discussion of the reaction between isobutene and nitric oxide.[7] Heterolytic decomposition, namely,

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot N:N \cdot O \cdot NO_2 \longrightarrow NO_3^- + NO_2 \cdot CF_2 \cdot CF_2 \cdot \overset{+}{N} \equiv N \longrightarrow NO_2 \cdot CF_2 \cdot \overset{+}{C}F_2 + N_2$$

seems unlikely in the gas phase, although it may occur on the wall of the vessel, and subsequent production of dinitrogen tetroxide would require the unlikely reaction between a neutral nitric oxide radical and a negative nitrate ion.

Studies of the reaction between tetrafluoroethylene and dinitrogen tetroxide support the postulated formation of the dinitro-compound and the nitronitrite from the tetrafluoro-2-nitroethyl radical.[5] Decomposition of tetrafluoro-2-nitroethyl nitrite by loss of nitric oxide is expected to lead to some difluoronitroacetyl fluoride, but neither this compound nor the nitrite itself was detected during the present work, since the experimental procedure involved washing the products with water or aqueous alkali during purification of the dinitro-compound.

The thermal and photochemical transformations of tetrafluoro-1-nitro-2-nitrosoethane into the dinitro-compound probably proceed by similar paths after initial fission of the C–NO bond:

$$2NO_2 \cdot CF_2 \cdot CF_2 \cdot NO \xrightarrow[\text{or } h\nu]{\text{Heat}} 2NO_2 \cdot CF_2 \cdot CF_2 \cdot + 2NO$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot NO + 2NO \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot N_2 \cdot O \cdot NO_2 \longrightarrow \text{As before}$$

The fact that the yield of the compound $(CF_2 \cdot NO_2)_2$ is 48% in the thermal decomposition reaction, thus accounting for all the oxygen present in the original nitronitroso-compound, shows that one molecule of the nitronitroso-compound is oxidised to the dinitro-compound at the expense of a second molecule of the nitronitroso-compound; the nitroso-group of this second molecule acts (i) as oxygen supplier, and (ii) as the source of molecular nitrogen according to the overall equation:

$$2NO_2 \cdot CF_2 \cdot CF_2 \cdot NO \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot NO_2 + \tfrac{1}{2}N_2 + \text{Decompn. products}$$

[11] Bamberger, *Ber.*, 1897, **30**, 506; 1918, **51**, 634; Wieland, *Annalen*, 1921, **424**, 79; Westheimer, Segel, and Schram, *J. Amer. Chem. Soc.*, 1947, **69**, 776.

The residual $NO_2 \cdot CF_2 \cdot CF_2 \cdot$ radical thus decomposes by reaction with the wall of the vessel to give silicon tetrafluoride and gaining oxygen from the silica or silicate to yield the acyl fluoride and other breakdown products observed. Formation of the acyl fluoride $NO_2 \cdot CF_2 \cdot COF$ *via* the nitrite $NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot NO$ thus cannot occur to any great extent under these conditions, since the oxygen of the acyl fluoride would then arise from oxygen originally present as C–NO in the original nitronitroso-compound, and the yield of the dinitro-compound would not then be as high as 48%. This in turn indicates that under these conditions the radical combination of $NO_2 \cdot CF_2 \cdot CF_2 \cdot$ with NO_2 must yield mainly the dinitro-compound and not the nitronitrite.

Irradiation of tetrafluoro-1-nitro-2-nitrosoethane in the presence of chlorine gives the known [4] 1-chlorotetrafluoro-2-nitroethane $(NO_2 \cdot CF_2 \cdot CF_2Cl)$ (81%) and tetrafluoro-1,2-dinitroethane (10%). Since the dinitro-compound does not react with chlorine, dinitrogen tetroxide, or nitric oxide under the conditions used during the experiments described above, the reactions taking place with the nitronitroso-compound must involve the nitroso-function, and the products obtained provide clear evidence for the structure of tetrafluoro-1-nitro-2-nitrosoethane, and for the possibility of homolysis of the C–NO bond of the nitronitroso-compound.

Tetrafluoro-1-nitro-2-nitrosoethane is slowly attacked by water and by dilute sulphuric acid at room temperature, but is recovered in 90% yield after 4 weeks in contact with these reagents. The aqueous phases give positive tests for nitrite and for fluoride ions. Dilute aqueous alkali rapidly destroys the nitroso-compound, without the evolution of volatile products. The resulting aqueous solution contains only simple inorganic ions, and attempts to isolate organic compounds fail. Since tetrafluoro-1,2-dinitroethane is stable under these conditions, degradation of the nitronitroso-compound must occur through attack at the nitroso-group.

Polymer and Oxazetidine Formation.—Tetrafluoro-1-nitro-2-nitrosoethane, like the perfluoroalkyl nitroso-compounds,[1,12] reacts readily with tetrafluoroethylene, at pressures of the order of 0·5—10 atm., to give the oxazetidine (III) and the related 1 : 1 copolymer (IV). The proportions and yields of these two products depend markedly on the reaction conditions. At —78°, no reaction occurs between the nitronitroso-compound and tetrafluoroethylene, but the two compounds react smoothly in the liquid phase at room temperature to give high yields (95—97%) of the polymer and small amounts of the oxazetidine. Although equimolar quantities of nitroso-compound and olefin are involved in the reaction, a slight excess of tetrafluoroethylene is required to remove final traces of the blue nitroso-compound dissolved in the polymer.

Polymer formation is favoured at higher pressures and lower temperatures than oxazetidine formation, and the polymer is always formed if a liquid phase is present during the reaction. Reactions carried out entirely in the gas phase at lower pressures lead to exclusive formation of the oxazetidine. In reactions at room temperature with an initial partial pressure of the nitroso-compound of more than about 10 cm., the oxazetidine produced (b. p. 78°) condenses on the wall of the vessel, and polymer formation occurs in solution in the oxazetidine.

The reaction between the nitroso-compound and tetrafluoroethylene is faster at higher temperatures (50—100°) and the proportion of oxazetidine produced increases, but the polymer is still formed in the presence of liquid nitroso-compound. Some decomposition of the nitroso-compound occurs if the reaction is carried out at 100°, and tetrafluoro-1,2-dinitroethane is formed in low yield.

The presence of glass wool in the reaction vessel has no significant effect on the rate of the gas-phase reactions and causes no change in the reaction products. This suggests that oxazetidine formation does not occur on a surface and is not ionic in nature. The difference in reaction rate and in the products formed in either the liquid or the gas phase appears to
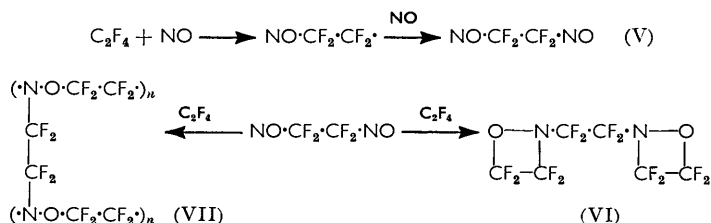
[12] Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

be due to a concentration effect, and not to a difference in the mechanism of formation of the oxazetidine and copolymer. The reactions of trifluoronitrosomethane with olefins have been discussed previously,[1] and a free-radical mechanism has been proposed for both oxazetidine and copolymer formation: the reaction between tetrafluoro-1-nitro-2-nitroso-ethane and tetrafluoroethylene appears to proceed similarly.

Conditions may be chosen for synthesis of the oxazetidine or the copolymer directly from nitric oxide and tetrafluoroethylene, without isolation of the nitronitroso-compound. Thus, an 83% yield of the oxazetidine is obtained when nitric oxide and an excess of tetra-fluoroethylene at *ca.* 10 atm. are heated at 90°; at 100° and *ca.* 40 atm., the yield of oxazetidine is 75%. The reaction does not proceed smoothly at 100° and one atm., and extensive breakdown occurs. The polymer may be obtained in 60—72% yield by the reaction of nitric oxide with tetrafluoroethylene under pressure at room temperature, either alone or in carbon tetrachloride as solvent.

Perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine is a colourless stable liquid, unaffected by hot concentrated sulphuric acid and irradiation in the presence of chlorine, but slowly attacked by aqueous alkali. Its infrared spectrum (vapour) shows prominent bands at 6·16 and 7·05 μ, respectively, indicating the presence of nitro- and oxazetidine groups.[10,12] The ultraviolet spectrum (vapour) shows a band at 281 mμ, again confirming the presence of the nitro-chromophore.

The polymer (IV), formed in the presence of liquid nitronitroso-compound, is a sticky, transparent, viscous fluid, which can be pulled into fine threads. Polymer formed on the walls of the reaction vessel, probably after initial condensation of the oxazetidine has occurred, is loosened by acetone, but is insoluble in this and other common solvents. It is considerably more elastomeric and translucent, but less sticky, than the sample described above, and cannot be pulled into threads. Both samples of the polymer are unaffected by hot concentrated sulphuric acid, but are slowly attacked by aqueous alkali; these treatments appear to have little effect on the viscosity or transparency of the polymer. Like the polymers formed from perfluoroalkyl nitroso-compounds and fluoro-olefins,[1] the polymer thus ranges from a viscous oil to a tough elastomer, insoluble in common solvents and having good low-temperature characteristics.

Interpretation of the Reaction between Nitric Oxide and Tetrafluoroethylene.—The only nitroso-compound produced during the reaction of nitric oxide with tetrafluoroethylene is tetrafluoro-1-nitro-2-nitrosoethane. No tetrafluoro-1,2-dinitrosoethane (V), which would be expected to result from a direct addition, was detected among the products of any of the experiments described above. Examination of the products formed during the early stages of the reaction also led to the isolation of only the nitronitroso-compound. The formation of pentafluoronitrosoethane during the reaction of nitrosyl fluoride with tetrafluoroethylene has been demonstrated previously by conversion into the oxazetidine

$\overline{N(C_2F_5)\cdot O\cdot CF_2}\cdot CF_2$ and the 1 : 1 copolymer $[\cdot N(C_2F_5)\cdot O\cdot CF_2\cdot CF_2\cdot]_n$ by carrying out the reaction in the presence of an excess of tetrafluoroethylene.[13] Experiments designed to trap the dinitroso-compound (V) as dioxazetidine (VI) and copolymer (VII) in a similar manner gave only the oxazetidine (III) and copolymer (IV) derived from the nitronitroso-compound.
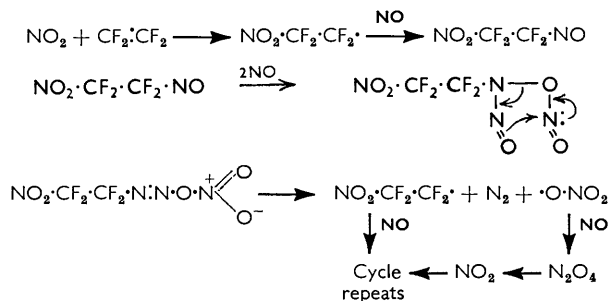
$$C_2F_4 + NO \longrightarrow NO\cdot CF_2\cdot CF_2\cdot \xrightarrow{\ NO\ } NO\cdot CF_2\cdot CF_2\cdot NO \quad (V)$$

(VII) ← C_2F_4 ← NO·CF₂·CF₂·NO → C_2F_4 → (VI)

[13] Barr and Haszeldine, *J.*, 1960, 1151.

The absence of tetrafluoro-1,2-dinitrosoethane and derived compounds suggests that direct attack of nitric oxide on tetrafluoroethylene does not take place, or that, if it does occur initially, the dinitroso-compound is rapidly converted (*e.g.*, by further reaction with nitric oxide) into the nitronitroso-compound. This deduction is in agreement with the previous work on alkenes, cited above. The preferred alternative for initiation of the main reaction involves attack by a more reactive nitrogen dioxide radical, to produce the intermediate (VIII) which readily reacts by radical combination with nitric oxide present in excess:

$$C_2F_4 + NO_2 \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot \xrightarrow{\text{NO}} NO_2 \cdot CF_2 \cdot CF_2 \cdot NO$$
$$\text{(VIII)}$$
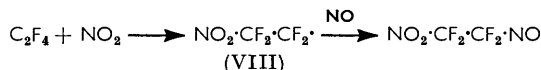
The nitrogen dioxide required initially could be generated by further reaction of nitric oxide with a nitroso-group of the dinitroso-compound (V), if this were formed as an intermediate in the early stages of the reaction. It seems more probable, however, that a trace of nitrogen dioxide is always present in nitric oxide and cannot be removed by fractionation, since nitric oxide decomposes very slowly to give nitrogen dioxide and nitrogen, a process which is accelerated by heat and pressure.[14] Furthermore, it is probably impossible, with the vacuum-techniques employed in the present work, to remove all trace of oxygen from the gas phase and from the walls of reaction vessels, and this must lead to the presence of traces of nitrogen dioxide. An experiment with nitric oxide, which had been shaken with mercury for four days to remove nitrogen dioxide, did not give definite results, since the reaction time was not lengthened sufficiently to justify the belief that reaction would not be initiated by absolutely pure nitric oxide. However, the presence of an excess of nitric oxide does not increase the reaction rate, again suggesting that initiation of the reaction by nitric oxide is not important, whereas the deliberate addition of a trace of dinitrogen tetroxide to the reaction mixture reduces the reaction time to one-half of that when carefully purified nitric oxide is used, and there is no detectable difference in the products.
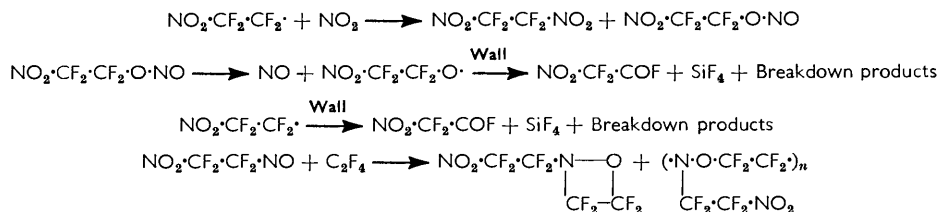
This evidence, therefore, is in favour of initiation of the reaction by nitrogen dioxide, present in traces in the nitric oxide used. The deep brown colour which develops during the early stages of the reaction, and may be destroyed with mercury, shows that the reaction itself generates nitrogen dioxide. This is readily accounted for by the reaction of tetrafluoro-1-nitro-2-nitrosoethane with the excess of nitric oxide, shown above to lead to the generation of two nitrogen dioxide radicals and a molecule of nitrogen for each molecule of the nitroso-compound. Decomposition of the nitronitroso-compound formed initially, therefore, leads to extensive chain branching:

$$NO_2 + CF_2 \colon CF_2 \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot \xrightarrow{\text{NO}} NO_2 \cdot CF_2 \cdot CF_2 \cdot NO$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot NO \xrightarrow{\text{2NO}} NO_2 \cdot CF_2 \cdot CF_2 \cdot N$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot N \colon N \cdot O \cdot N \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot + N_2 + \cdot O \cdot NO_2$$

In the early stages of the reaction, the $NO_2 \cdot CF_2 \cdot CF_2 \cdot$ radical thus acts as a carrier for the conversion of nitric oxide into dinitrogen tetroxide and nitrogen. The concentration of the nitronitroso-compound increases and the nitric oxide concentration decreases as reaction proceeds. Towards the end of the reaction, the concentration of nitrogen dioxide

[14] Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1928, p. 419.

becomes comparable with that of nitric oxide, and other processes, leading to chain termination and the production of by-products, then begin to play an important part.

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot + NO_2 \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot NO_2 + NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot NO$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot NO \xrightarrow{\text{Wall}} NO + NO_2 \cdot CF_2 \cdot CF_2 \cdot O \cdot \xrightarrow{\text{Wall}} NO_2 \cdot CF_3 \cdot COF + SiF_4 + \text{Breakdown products}$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot \xrightarrow{\text{Wall}} NO_2 \cdot CF_2 \cdot COF + SiF_4 + \text{Breakdown products}$$

$$NO_2 \cdot CF_2 \cdot CF_2 \cdot NO + C_2F_4 \longrightarrow NO_2 \cdot CF_2 \cdot CF_2 \cdot \overset{\displaystyle |}{N}\!\!-\!\!-\!\!\overset{\displaystyle |}{O} + (\cdot N \cdot O \cdot CF_2 \cdot CF_2 \cdot)_n$$
$$\underset{CF_2-CF_2}{} \quad \underset{CF_2 \cdot CF_2 \cdot NO_2}{}$$

More recently, Crawford [15] has accepted the mechanism put forward in our preliminary publication, and has confirmed the results there described, though without acknowledgement. The reaction of nitric oxide with other fluoro-olefins has been shown [16] to follow the general pattern established for the nitric oxide–tetrafluoroethylene reaction.

Hitherto, fluoroalkyl nitroso-compounds have been available in good yield only from the relatively expensive fluoroalkyl iodides; their preparation from the reaction of nitric oxide with a fluoro-olefin now provides a convenient route.

Experimental

Gas–liquid chromatography was carried out with a Perkin–Elmer no. 154B instrument, calibrated with known mixtures of pure components when possible. Analytical columns (2 m. long × 4 mm. internal diameter) were packed with 33% by wt. of dinonyl phthalate on Celite, except where otherwise stated; the carrier gas was nitrogen and the column temperature was 10° above the mean b. p. of the mixture under investigation. Preparative-scale columns are described in the text.

Nitric Oxide.—This was prepared by the controlled addition of 50% v/v aqueous sulphuric acid to aqueous potassium nitrite and potassium iodide. The product was washed with 30% aqueous sodium hydroxide and dried with concentrated sulphuric acid. Final purification was effected by shaking the gas with mercury for 24 hr., to give nitric oxide (Found: M, 30. Calc. for NO: M, 30) as a colourless gas condensing to a purple-blue liquid.

Reaction of Nitric Oxide with Tetrafluoroethylene at Pressures of One Atmosphere or Below.— (a) *Preparation of tetrafluoro-1-nitro-2-nitrosoethane.* Nitric oxide (18·75 g., 0·625 mole) and tetrafluoroethylene (31·25 g., 0·3125 mole), expanded into a 21-l. Pyrex flask, were kept at room temperature, in darkness, for 48 hr. After 6 hr. the gas phase began to turn brown; this colour increased in intensity throughout the following 6 hr. period, and then slowly gave way to green and finally to deep blue. An excess of oxygen was added, and the contents of the flask were shaken with mercury (100 ml.) for 6 hr., transferred to an apparatus for the manipulation of volatile compounds at low pressure, and distilled *in vacuo* to yield fractions condensing at $-196°$ and at $-78°$. The former (10·91 g.; M, 98) was shown by infrared spectroscopy to consist mainly of tetrafluoroethylene, containing traces of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride; it was washed with aqueous 10% sodium hydroxide and dried by distillation *in vacuo*, to give pure tetrafluoroethylene (10·82 g., 34%) (Found: M, 99. Calc. for C_2F_4: M, 100). The $-78°$ fraction (36·0 g.) was washed with water, dried (P_4O_{10}), and distilled at atmospheric pressure, to give *tetrafluoro-1-nitro-2-nitrosoethane* (24·5 g., 68% on tetrafluoroethylene consumed) (Found: C, 13·6; N, 15·7%; M, 176. $C_2F_4N_2O_3$ requires C, 13·6; N, 15·9%; M, 176), as a deep blue liquid, b. p. 24—25°. A fraction, b. p. 53—60°, was separated into two components by gas–liquid chromatography, on a column (3 m. × 2 cm. internal diameter) packed with 33% by wt. of dinonyl phthalate on Celite, and gave tetrafluoro-1,2-dinitroethane (5·85 g., 15% on tetrafluoroethylene consumed) (Found: C, 12·5; N, 14·5%; M, 190. Calc. for $C_2F_4N_2O_4$: C, 12·5; N, 14·6%; M, 192) and *perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine* (2·80 g., 5% on tetrafluoroethylene consumed) (Found: M, 275. $C_4F_8N_2O_3$ requires M, 276), identified by infrared spectroscopy.

(b) *Examination of the water-soluble products.* Nitric oxide (18·75 g., 0·625 mole) and tetrafluoroethylene (31·25 g., 0·3125 mole) were allowed to react for 48 hr. under conditions

[15] Crawford, *J. Polymer Sci.*, 1960, **45**, 259.
[16] Park, Stefani, Crawford, and Lacher, *J. Org. Chem.*, 1961, **26**, 3316.

identical with those described above. Non-condensable gas was adsorbed on active charcoal at $-196°$ and found to be nitrogen ($3\cdot001$ g., 34%) (Found: M, 29. Calc. for N_2: M, 28) and not oxygen (M, 32), since some nitric oxide remained unchanged. Attempts to fractionate the condensable products *in vacuo* were only partially successful, since residual nitric oxide appeared to react with the liquid nitronitroso-compound during the distillation. An excess of oxygen was admitted to the fraction condensing at $-196°$, and the fraction was again distilled *in vacuo*, to give dinitrogen tetroxide and tetrafluoroethylene. The quantity of unconsumed nitric oxide was calculated, by the difference in volumes obtained, to be 1—2% of the initial reactant.

Higher-boiling products from this experiment were fractionated at atmospheric pressure. A fraction boiling below 24° was shown by infrared spectroscopy to contain tetrafluoro-1-nitro-2-nitrosoethane and an acyl fluoride (strong band at $5\cdot25$ μ), and was kept at room temperature with an excess of tetrafluoroethylene for 24 hr. The resulting volatile products were distilled *in vacuo* and yielded tetrafluoroethylene and perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine, identified by their molecular weights and by infrared spectroscopy, and a fraction ($2\cdot82$ g., 10% on tetrafluoroethylene originally consumed) condensing at $-78°$, which was shown to consist of two components by gas–liquid chromatography (column of 33% by wt. of squalane on Celite). Preparative-scale chromatography on squalane (column, 3 m. $\times$ 1 cm.) similarly gave two fractions; one consisted only of traces of carbon dioxide and carbonyl fluoride: the other, larger, fraction gave an infrared spectrum which was consistent with that expected for difluoronitroacetyl fluoride, but analytical figures were in only approximate agreement with this deduction (Found: C, $18\cdot3$; N, $9\cdot3$%; M, 145. Calc. for $C_2F_3NO_3$: C, $16\cdot8$; N, $9\cdot8$%; M, 143). This substance was rapidly destroyed by water, which then gave an acid reaction and positive tests for fluoride and nitrite ions. It is believed that the second component of the mixture submitted to chromatographic separation was originally tetrafluoro-2-nitroethyl nitrite, and that this unstable compound decomposed during its passage through the instrument.

(c) *With a 3 : 1 ratio of nitric oxide to tetrafluoroethylene.* Nitric oxide ($3\cdot00$ g., 100 mmole) and tetrafluoroethylene ($3\cdot48$ g., $34\cdot8$ mmole) were kept in a 3-l. flask, in darkness, for 48 hr. The green colour which developed after 12 hr. was still evident after 48 hr. and the sides of the flask were coated with off-white solid, which evolved dinitrogen tetroxide on admission of air and could not be satisfactorily extracted with solvents. The products were shaken with mercury (50 ml.) for 1 hr.; the blue nitroso-compound then became clearly visible. Unconsumed nitric oxide was destroyed by the admission of an excess of oxygen, and the products were again shaken with mercury, then distilled *in vacuo* to yield tetrafluoroethylene ($0\cdot23$ g., 5%) (Found: M, 98) containing traces of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride, and a fraction condensing at $-78°$. The latter was washed with water, dried, and distilled *in vacuo*, to give tetrafluoro-1-nitro-2-nitrosoethane ($2\cdot58$ g., 42%; 45% on tetrafluoroethylene consumed) (Found: M, 175. Calc. for $C_2F_4N_2O_3$: M, 176) and tetrafluoro-1,2-dinitroethane ($1\cdot48$ g., 22%; 23% on tetrafluoroethylene consumed) (Found: M, 193. Calc. for $C_2F_4N_2O_4$: M, 192), identified by infrared spectroscopy.

(d) *With an 8 : 1 ratio of nitric oxide to tetrafluoroethylene.* Nitric oxide ($3\cdot28$ g., 107 mmole) and tetrafluoroethylene ($1\cdot34$ g., $13\cdot4$ mmole) were kept in a 3-l. flask for 48 hr. A brown colour, which began to appear after 6 hr., increased to a maximum intensity in 12 hr. and then remained unchanged throughout the remaining period. The product was washed with 10% aqueous sodium hydroxide, dried (P_4O_{10}), and distilled, to yield tetrafluoro-1,2-dinitroethane ($0\cdot48$ g., 18%), identified by its molecular weight and by gas–liquid chromatography.

(e) *With an excess of tetrafluoroethylene at 100°.* Nitric oxide ($0\cdot90$ g., 30 mmole) and tetrafluoroethylene ($12\cdot05$ g., 120 mmole) were heated at 100° in a 3-l. flask for 7 days. The gas phase remained colourless throughout the reaction. Nitrogen ($0\cdot18$ g., 40%) was rejected, and distillation of the condensable products *in vacuo* yielded tetrafluoroethylene, a considerable quantity of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride, and a liquid ($3\cdot10$ g.) which contained the oxazetidine, the dinitro-compound, and an acyl fluoride.

Reaction of Nitric Oxide with Tetrafluoroethylene in the Presence of Dinitrogen Tetroxide.—
(a) *Catalytic amount.* Nitric oxide ($0\cdot152$ g., $5\cdot0$ mmole), tetrafluoroethylene ($0\cdot25$ g., $2\cdot5$ mmole), and dinitrogen tetroxide ($0\cdot002$ g., $0\cdot02$ mmole) were kept in darkness in a 200-ml. sealed tube. After 24 hr. the gas phase was deep blue, and the yields of the products, which were isolated by distillation *in vacuo* and reaction with water as previously described, were identical (±2%) with those from a parallel control experiment from which dinitrogen tetroxide

was omitted. The gas phase in the latter experiment was brown-green after 24 hr. and became blue only after a further 24 hr., whereafter the reaction was terminated.

(b) *Theoretical amount for dinitrogen trioxide formation.* Nitric oxide (1·50 g., 50 mmole), tetrafluoroethylene (5·00 g., 50 mmole), and dinitrogen tetroxide (2·30 g., 25 mmole) were kept in a 3-l. flask for 48 hr. The initial brown colour changed to green during 24 hr., and after 48 hr. the mixture was green-blue, the blue of the nitroso-compound remaining masked by the nitrogen dioxide. Nitric oxide and dinitrogen tetroxide were removed by the admission of oxygen and shaking with mercury. The condensable products were separated by distillation *in vacuo* and washing with water, and gave tetrafluoro-1-nitro-2-nitrosoethane (3·84 g., 44%), tetrafluoro-1,2-dinitroethane (2·35 g., 24%), and tetrafluoroethylene (0·28 g., 7%) containing traces of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride. The products were identified by molecular-weight measurements and infrared spectroscopy, and the nitronitroso- and the dinitro-compound were each shown to consist of one component by gas–liquid chromatography. Perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine was not detected among the products of this reaction.

Reaction of Nitric Oxide with Tetrafluoroethylene at Elevated Pressure.*—(a) *With a* 1 : 1 *ratio of reactants.* Nitric oxide (1·41 g., 47 mmole) and tetrafluoroethylene (4·70 g., 47 mmole) were kept at room temperature in a 350-ml. tube for 24 hr. (initial pressure *ca.* 6·5 atm.) Volatile products, including nitrogen (7·1 mmole), were pumped away from the brown residue, which was washed from the tube with acetone, and identified as a 1 : 1 *copolymer* of tetrafluoro-1-nitro-2-nitrosoethane and tetrafluoroethylene (2·70 g., 76%) [Found: C, 17·3; N, 10·0. $(C_4F_8N_2O_3)_n$ requires C, 17·4; N, 10·2%]. The volatile products were distilled *in vacuo* and yielded a pale green liquid, condensing at −78°, and tetrafluoroethylene (2·12 g., 45%). The former was washed with 2N-aqueous sodium hydroxide, dried (P_4O_{10}), and separated by preparative-scale chromatography (dinonyl phthalate column; 3 m. × 2 cm.), to give perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine (0·39 g., 11%) and tetrafluoro-1,2-dinitroethane (0·21 g., 4%), identified by their molecular weights and chromatographic retention times.

(b) *With a* 2 : 1 *ratio of nitric oxide to tetrafluoroethylene.* Nitric oxide (2·56 g., 85 mmole) and tetrafluoroethylene (4·30 g., 43 mmole) were sealed into a 480-ml. tube, and kept for 24 hr. (initial pressure *ca.* 6·5 atm.). Volatile products were separated by distillation *in vacuo*, washing with water, and preparative-scale chromatography, and identified by molecular-weight measurements and infrared spectroscopy as perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine (0·65 g., 12%), tetrafluoro-1,2-dinitroethane (0·51 g., 7%), tetrafluoro-1-nitro-2-nitrosoethane (0·36 g., 5%), tetrafluoroethylene (0·56 g., 13%), and nitrogen (6·7 mmole). The residue was the 1 : 1 copolymer (3·62 g., 72%) [Found: C, 17·3; N, 10·1. Calc. for $(C_4F_8N_2O_3)_n$: C, 17·4; N, 10·2%].

(c) *With an excess of tetrafluoroethylene.* Nitric oxide (0·857 g., 28·6 mmole) and tetrafluoroethylene (14·28 g., 143 mmole) under conditions identical to those of (b), gave nitrogen (3·6 mmole), tetrafluoroethylene (12·05 g.), and the oxazetidine (0·55 g., 18%). A thick brown oil was identified as the 1 : 1 copolymer (1·56 g., 50%) [Found: C, 17·4; N, 10·0. Calc. for $(C_4F_8N_2O_3)_n$: C, 17·4; N, 10·2%].

(d) *With an excess of tetrafluoroethylene at* 90°. Nitric oxide (0·857 g., 28·6 mmole) and tetrafluoroethylene (14·28 g., 143 mmole) were heated at 90° in a 480-ml. tube for 6 hr. (initial pressure *ca.* 11 atm.). Nitrogen (4·5 mmole) was produced, and a trace of brown polymer remained in the tube and was not examined. The volatile products were distilled *in vacuo* and gave tetrafluoroethylene (12·2 g.) containing traces of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride, and a fraction condensing at −45°. The latter was purified by gas–liquid chromatography and gave the oxazetidine (2·38 g., 83%) (Found: M, 274. Calc. for $C_4F_8N_2O_3$: M, 276); a very minor component of this fraction had a retention time identical with that of tetrafluoro-1,2-dinitroethane.

(e) *With an excess of tetrafluoroethylene at* 100°. Nitric oxide (0·666 g., 22 mmole) and tetrafluoroethylene (11·16 g., 112 mmole) were heated at 100° in a 100-ml. autoclave for 12 hr. (initial pressure *ca.* 41 atm.). Nitrogen (4·5 mmole) and a trace of polymer were produced, and tetrafluoroethylene (9·51 g.) was recovered. The main product condensed *in vacuo* at −45°: it was washed with water (2 ml.), dried (P_4O_{10}), and purified by gas–liquid chromatography to give the oxazetidine (1·70 g., 75%) (Found: M, 275. Calc. for $C_4F_8N_2O_3$: M, 276).

Reaction of Nitric Oxide with Tetrafluoroethylene in Carbon Tetrachloride Solution.*—Nitric

* Percentage yields throughout these sections are based on tetrafluoroethylene consumed.

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oxide (0·15 g., 5 mmole), tetrafluoroethylene (1·50 g., 15 mmole), and carbon tetrachloride (4·66 g.) were kept in a 50-ml. tube for 24 hr. The volatile products were nitrogen (0·7 mmole), tetrafluoroethylene (1·22 g., 81%), and carbon tetrachloride (4·72 g.) containing traces of the dinitro-compound and the oxazetidine. The residue was a clear colourless polymer (0·28 g., 72%) [Found: C, 17·9; N, 9·0. Calc. for $(C_4F_8N_2O_3)_n$: C, 17·4; N, 10·2%].

Properties of Tetrafluoro-1-nitro-2-nitrosoethane.—The vapour pressure of this intensely blue liquid, measured over the range $-40°$ to $+20°$, is represented by the equation $\log_{10} p$ (mm.) = $7·933 - 1503/T$, whence the b. p. is calculated to be 24·2°, the latent heat of vaporisation is 6880 cal./mole, and Trouton's constant is 23·1. The ultraviolet absorption spectrum of the vapour shows maxima at 282·5 (ε 54) and 681 mμ (ε 18) and minima at 244 (ε 22) and 420—440 mμ (ε <0·1).

Reactions of Tetrafluoro-1-nitro-2-nitrosoethane.—(a) *Effect of light.* (i) The vapour of tetrafluoro-1-nitro-2-nitrosoethane (1·54 g.), in a Pyrex vessel, was exposed to daylight for 2 months. The brown products were distilled *in vacuo*, and the colourless liquid condensing at $-78°$ was washed with water (5 ml.) and dried (P_4O_{10}) to yield tetrafluoro-1,2-dinitroethane (0·58 g., 35%) (Found: *M*, 191. Calc. for $C_2F_4N_2O_4$: *M*, 192).

(ii) The vapour of tetrafluoro-1-nitro-2-nitrosoethane (2·75 g.), in silica, was exposed to ultraviolet light (250-w Hanovia lamp) for 24 hr. The products were washed with aqueous 2N-sodium hydroxide (20 ml.) and dried (P_4O_{10}), to give tetrafluoro-1,2-dinitroethane (0·85 g., 28%), shown to be pure by gas–liquid chromatography and identified by its retention time and molecular weight.

(b) *Effect of heat.* Tetrafluoro-1-nitro-2-nitrosoethane (7·98 g.) was heated in a 50-ml. tube at 90° for 5 days. Nitrogen (4·5 mmole)was produced, and distillation of the volatile products *in vacuo* gave a mixture of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride (*ca.* 0·5 g.), and a pale blue liquid condensing at $-78°$. The latter was washed with 2N-aqueous sodium hydroxide (10 ml.); the colourless organic phase was dried (P_4O_{10}), and yielded tetrafluoro-1,2-dinitroethane (4·2 g., 48%) (Found: C, 12·4; N, 14·5%; *M*, 191. Calc. for $C_2F_4N_2O_4$: C, 12·5; N, 14·5%; *M*, 192). An unidentified solid of low density, formed on the walls of the reaction tube, evolved dinitrogen tetroxide in air.

(c) *Reaction with oxygen.* (i) Tetrafluoro-1-nitro-2-nitrosoethane (1·5 g.) was recovered quantitatively after being mixed with oxygen (0·48 g.) at a total pressure of 8 atm. for 12 hr.

(ii) Tetrafluoro-1-nitro-2-nitrosoethane (1·5 g., 8·5 mmole) and oxygen (0·48 g., 15 mmole) were heated at 80° in a 50-ml. tube for 12 hr. The brown liquid products were shaken with mercury to yield colourless tetrafluoro-1,2-dinitroethane (1·43 g., 88%), identified by its molecular weight and by infrared spectroscopy.

(d) *Stability towards dinitrogen tetroxide.* (i) In the gas phase. The nitroso-compound (0·44 g., 2·5 mmole) and dinitrogen tetroxide (0·46 g., 5 mmole) were expanded into a 150-ml. flask and kept for 24 hr. Mercury (20 ml.) was added, and the flask was shaken until the gas phase was deep blue. Distillation *in vacuo* gave the nitroso-compound (0·40 g., 91%) and traces of volatile breakdown products.

(ii) In the liquid phase. The nitroso-compound (0·36 g., 2 mmole) and dinitrogen tetroxide (0·28 g., 3 mmole) were kept in a 10-ml. tube for 12 hr., and the volatile material was then expanded into a 100-ml. flask and shaken with mercury for a few minutes until the gas phase became blue. Distillation *in vacuo* yielded the nitroso-compound (0·31 g., 86%) and traces of volatile breakdown products.

(e) *Reaction with nitric oxide.* The nitroso-compound (1·10 g., 6·3 mmole) was expanded into a 1-l. flask and nitric oxide (1·57 g., 52 mmole) was admitted. The blue gas rapidly became green and then brown, and an off-white solid was formed on the walls of the flask. After 24 hr., nitrogen (0·31 g.) was pumped off, and the condensable products were distilled *in vacuo* and gave nitric oxide (0·13 g., 7%), traces of volatile breakdown products, condensing at $-196°$, and a green liquid (1·84 g.), condensing at $-78°$. The liquid was shaken with mercury (20 ml.) to remove dinitrogen tetroxide (*ca.* 1·2 g.), washed with 2N-aqueous sodium hydroxide (10 ml.), and dried (P_4O_{10}), to give tetrafluoro-1,2-dinitroethane (0·51 g., 42%), identified by its molecular weight and by gas–liquid chromatography. The solid remaining in the reaction vessel was not identified. A second experiment, with the nitroso-compound (0·625 g., 3·6 mmole) and nitric oxide (1·98 g., 66 mmole), under conditions identical with those described above, gave nitrogen (0·43 g.), low-boiling breakdown products (traces), nitric oxide (0·20 g.), dinitrogen tetroxide (0·81 g.), and tetrafluoro-1,2-dinitroethane (0·36 g., 53%).

(f) *Reaction with chlorine.* The nitroso-compound (1·13 g., 6·4 mmole) and chlorine (1·2 g., 17 mmole), in a 150-ml. Pyrex tube, were irradiated with a 250-w Hanovia ultraviolet lamp for 48 hr. Distillation *in vacuo* gave a very pale blue liquid, condensing at −78°, which was washed with 2N-aqueous sodium hydroxide (5 ml.) and dried (P_4O_{10}). Preparative-scale gas–liquid chromatography (dinonyl phthalate column; 3 m. × 2 cm.) gave 1-chlorotetrafluoro-2-nitro-ethane (0·96 g., 81%) (Found: C, 13·3; N, 7·7%; *M*, 180. Calc. for $C_2ClF_4NO_2$: C, 13·3; N, 7·7%; *M*, 181·5) and tetrafluoro-1,2-dinitroethane (0·12 g., 10%) (Found: *M*, 190. Calc. for $C_2F_4N_2O_4$: *M*, 192), identified by their infrared spectra and chromatographic retention times.

(g) *Hydrolysis.* (i) With water. Tetrafluoro-1-nitro-2-nitrosoethane (1·85 g.) and water (10 ml.) were kept in a sealed tube for 14 days. The organic phase was dried by distillation *in vacuo* and identified as unchanged nitroso-compound (1·70 g., 92%) by its molecular weight. The aqueous phase gave positive tests for fluoride and nitrite ions.

(ii) With sulphuric acid. The nitroso-compound (2·18 g.) was kept in contact with 2N-aqueous sulphuric acid (10 ml.) for 14 days. The organic phase was distilled *in vacuo*, and gave the nitroso-compound (2·06 g., 94%), identified by its molecular weight. The aqueous phase gave a positive test for nitrite ions.

(iii) With alkali. The blue colour of the nitroso-compound (0·5 g.) was rapidly destroyed by 2N-aqueous sodium hydroxide (20 ml.) at room temperature, with generation of heat but without evolution of volatile products. The aqueous solution, which gave positive tests for nitrite and fluoride ions, was acidified with dilute sulphuric acid and extracted with light petroleum (b. p. 30—40°; 3 × 5 ml.). The extracts were dried ($MgSO_4$) and evaporated, but no residue remained.

In a separate experiment, the nitroso-compound (0·637 g.) was condensed on to 4N-aqueous sodium hydroxide (20 ml.), and the mixture was allowed to warm to room temperature. When all the blue colour had disappeared, the excess of alkali was titrated against N-hydrochloric acid (to phenolphthalein). The nitroso-compound was thus shown to require 6 equivalents of alkali for its complete destruction.

Reaction of Tetrafluoro-1-nitro-2-nitrosoethane with Tetrafluoroethylene to Give mainly Copolymer.—(a) *Excess of nitroso-compound at* ca. 4 atm. Tetrafluoro-1-nitro-2-nitrosoethane (1·34 g., 7·6 mmole) and tetrafluoroethylene (0·067 g., 0·67 mmole) were kept in a 5-ml. tube for 24 hr. Distillation of the volatile products *in vacuo* gave unchanged nitroso-compound (1·23 g.); a 1 : 1 copolymer (0·175 g., 95% on tetrafluoroethylene) [Found: C, 17·6; N, 10·1. Calc. for $(C_4F_8N_2O_3)_n$: C, 17·4; N, 10·2%], coloured blue by dissolved nitroso-compound, remained in the reaction tube.

(b) *Large excess of tetrafluoroethylene at* ca. 6 atm. The nitroso-compound (0·47 g., 2·7 mmole) and tetrafluoroethylene (1·10 g., 11 mmole), kept in a 50-ml. tube for 24 hr., gave tetrafluoroethylene (0·827 g.) and a clear, colourless, 1 : 1 copolymer (0·72 g., 98% on nitroso-compound) (Found: C, 17·5; N, 10·2%).

(c) *Small excess of tetrafluoroethylene.* (i) At ca. 3 atm. The nitroso-compound (4·22 g., 24 mmole) and tetrafluoroethylene (2·80 g., 28 mmole) were kept in a 350-ml. tube for 24 hr. Traces of blue nitroso-compound remained unconsumed, and the tube was heated at 50° for 30 min.; a clear colourless liquid was then present. Volatile products were distilled *in vacuo* and gave perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine (0·53 g., 8%) (Found: C, 17·4; N, 10·1%; *M*, 275. Calc. for $C_4F_8N_2O_3$: C, 17·4; N, 10·2%; *M*, 276), condensing at −45°, and tetrafluoroethylene (0·38 g., 14%) (Found: *M*, 100. Calc. for C_2F_4: *M*, 100). A colourless, very viscous, fluid was washed from the reaction tube with acetone and identified as a 1 : 1 copolymer (5·95 g., 90%) (Found: C, 17·4; N, 10·2%).

(ii) At ca. 1 atm. The nitroso-compound (12·65 g., 72 mmole) and tetrafluoroethylene (7·54 g., 75 mmole) were kept in a 3-l. flask for 2 weeks. The walls became coated with liquid after the first 2 hr., but a trace of the blue nitroso-compound remained throughout the experiment. The volatile products were distilled *in vacuo* and gave tetrafluoroethylene (0·49 g.), tetrafluoro-1-nitro-2-nitrosoethane (0·25 g., 2%), and perfluoro-2-(tetrafluoro-2-nitro-ethyl)-1,2-oxazetidine (3·65 g., 18%), identified by their molecular weights and chromato-graphic retention times. A colourless semi-solid was washed from the reaction flask with acetone and identified as 1 : 1 copolymer (15·60 g., 79%) Found: C, 17·3; N, 10·1%).

(d) *Effect of temperature.* The nitroso-compound (7·88 g., 45 mmole) and tetrafluoro-ethylene (4·46 g., 44·6 mmole) were sealed into a 400-ml. tube and heated rapidly to 100° (initial pressure ca. 7 atm.). After 2 hr., traces of nitrogen were pumped off, and the volatile products

were distilled *in vacuo*, to give tetrafluoroethylene (0·44 g., 10%) and a fraction condensing at −45° (5·35 g.). The latter was separated by preparative-scale chromatography (dinonyl phthalate column; 3 m. × 2 cm.) into the oxazetidine (4·95 g., 40%) (Found: C, 17·3; N, 10·1%; *M*, 275. Calc. for $C_4F_8N_2O_3$: C, 17·4; N, 10·2%; *M*, 276) and tetrafluoro-1,2-dinitroethane (0·43 g., 5%) (Found: C, 12·5; N, 14·5%; *M*, 192. Calc. for $C_2F_4N_2O_4$: C, 12·5; N, 14·6%; *M*, 192). The clear, colourless, viscous fluid formed in the reaction was washed from the tube with acetone, and identified as a 1 : 1 copolymer (6·03 g., 49%) (Found: C, 17·5; N, 10·1%).

Reaction of Tetrafluoro-1-nitro-2-nitrosoethane with Tetrafluoroethylene to give Oxazetidine.— (a) *Effect of partial pressure of nitroso-compound.* The nitroso-compound (1·12 g., 6·4 mmole) and tetrafluoroethylene (4·32 g., 43 mmole) were kept in a 1-l. flask for 10 days (initial pressure *ca.* 1·2 atm.). The colourless gaseous products were distilled *in vacuo* and gave tetrafluoro-ethylene (3·68 g.) and perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine (1·50 g., 85%), identified by their molecular weights. 1 : 1 Copolymer (0·24 g., 14%) was washed from the flask with acetone.

In a second experiment, the nitroso-compound (0·58 g., 3·3 mmole) and tetrafluoroethylene (4·07 g., 41 mmole) were kept in a 1-l. flask for 14 days (initial pressure *ca.* 1·1 atm.), and gave only tetrafluoroethylene (3·74 g.) and the oxazetidine (0·90 g., 99%).

(b) *Effect of surface.* The nitroso-compound (0·265 g., 1·5 mmole) and tetrafluoroethylene (1·65 g., 16·5 mmole) were kept in a 500-ml. flask, packed with glass wool, for 2 weeks. The products, separated and identified as before, were tetrafluoroethylene (1·52 g.) and the oxazetidine (0·395 g., 95%).

Stability of Tetrafluoro-1,2-dinitroethane.—Tetrafluoro-1,2-dinitroethane was kept in contact with two-molar excesses of dinitrogen tetroxide and of nitric oxide for 48 hr.; it was recovered in 96% and 98% yield, respectively.

Tetrafluoro-1,2-dinitroethane (0·58 g., 3 mmole) and chlorine (1·5 g., 21 mmole), in a 180-ml. Pyrex tube, were irradiated with a 250-w Hanovia ultraviolet lamp for 48 hr. Distillation *in vacuo* then gave the dinitro-compound (0·56 g., 97%), shown to be pure by gas–liquid chromatography, and chlorine (1·45 g., 96%).

Properties of Perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine.—The vapour pressure of this compound, measured over the range 0—70°, is represented by the equation $\log_{10} p$ (mm.) = 7·494 − 1620/T, whence the b. p. is calculated to be 78°, the latent heat of vaporisation is 7400 cal./mole, and Trouton's constant is 21·1. The ultraviolet absorption spectrum of the vapour shows a maximum at 281 mμ (ε 40) and a minimum at 244·5 mμ (ε 15).

Stability of Perfluoro-2-(tetrafluoro-2-nitroethyl)-1,2-oxazetidine.—(a) *Towards alkali.* The oxazetidine (0·156 g.) and 30% aqueous sodium hydroxide (1 ml.) were heated at 100° in a 5-ml. tube for 3 days. The organic layer was dried (P_4O_{10}) and distilled, to give unchanged oxazetidine (0·13 g., 83%), identified by its molecular weight and shown to be pure by gas–liquid chromatography. The aqueous phase gave positive tests for nitrite and fluoride ions.

(b) *Towards sulphuric acid.* The oxazetidine was recovered in 98% yield after being heated with concentrated sulphuric acid at 100° for 3 days. On dilution, the sulphuric acid gave a negative test for nitrite ion.

(c) *Towards chlorine.* The oxazetidine (0·42 g., 1·5 mmole) and chlorine (1·12 g., 16 mmole), in a 150-ml. Pyrex tube, were irradiated by a 250-w Hanovia ultraviolet lamp for 48 hr. Distillation *in vacuo* gave unchanged oxazetidine (0·41 g., 98%) and chlorine (1·11 g., 99%).

Stability of the Copolymer.—(a) *Towards alkali.* The 1 : 1 copolymer of tetrafluoro-1-nitro-2-nitrosoethane and tetrafluoroethylene (0·423 g.) and 30% aqueous sodium hydroxide (2 ml.) were heated at 100° for 3 days. Most of the copolymer (0·402 g., 95%) was recovered, but the aqueous phase gave positive tests for fluoride and nitrite ions.

(b) *Towards concentrated sulphuric acid.* The copolymer (0·518 g.) and concentrated sulphuric acid (2 ml.) were heated at 100° for 3 days. The copolymer (0·510 g., 98%) was recovered, and the sulphuric acid, on dilution, gave a negative test for nitrite ion.