235. *Perfluoroalkyl Derivatives of Nitrogen. Part VII.* Reaction of Nitrosyl Halides with Tetrafluoroethylene.*

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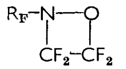
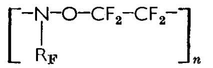
Nitrosyl chloride or fluoride reacts with a fluoro-olefin such as tetrafluoroethylene to give an oxazetidine $\overline{N(CF_2{\cdot}CF_2X){\cdot}O{\cdot}CF_2{\cdot}CF_2}$, where X = Cl or F, and a 1 : 1 copolymer $[N(CF_2{\cdot}CF_2X){\cdot}O{\cdot}CF_2{\cdot}CF_2]_n$, derived from the nitroso-compound $CF_2X{\cdot}CF_2{\cdot}NO$ and the olefin.

A PERFLUOROALKYLNITROSO-COMPOUND R_FNO reacts with a fluoro-olefin such as tetrafluoroethylene to give an oxazetidine (I) and a 1 : 1 copolymer (II) with the –N–O–C–C– repeating unit in the main chain.[1] The polymer can be an oil, a wax, or an elastomer depending upon the conditions chosen and the nature of the olefin. The oxazetidine predominates in reactions carried out at higher temperatures (*ca.* 100°), and the polymer at lower temperatures (*ca.* 0°).

(I) 

 (II)

$$\left[\begin{array}{l}-\mathrm{N}-\mathrm{O}-\mathrm{CF_2}-\mathrm{CF_2}-\\ \ \ |\\ \ \mathrm{R_F}\end{array}\right]_n$$

The possible extension of this novel reaction to purely inorganic nitroso-compounds was examined some years ago and is now reported. If the NO group of a nitrosyl halide NOX shows a resemblance to $C{:}C$, as does the NO group in R_FNO, oxazetidines (III) and

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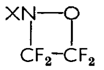
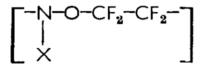
* Part VI, Haszeldine and Mattinson, *J.*, 1957, 1741.

[1] Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

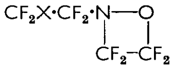
polymers (IV) might result when the nitrosyl halide is allowed to react with tetrafluoroethylene. These initial products would contain the >NCl or >NF bond, so that subsequent reactions involving, for example, addition across the C:C bond of another olefin molecule might occur to give oxazetidines (V) or polymers (VI). Such products would also arise if the initial reaction of the nitrosyl halide involved addition in the sense $^+NO\ F^-$ across the double bond of the olefin to give the nitrosoalkane $CF_2X{\cdot}CF_2{\cdot}NO$; the reaction of this with tetrafluoroethylene to give (V) or (VI) would follow the course already noted for R_FNO with this olefin.



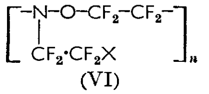
(III)



(IV)

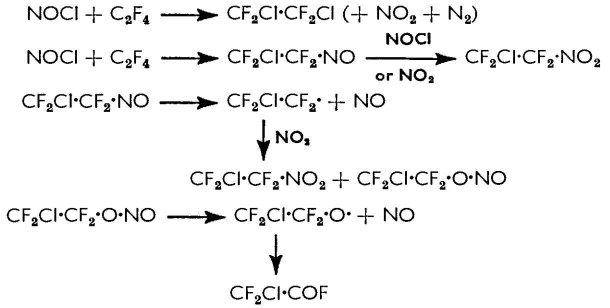


(V)



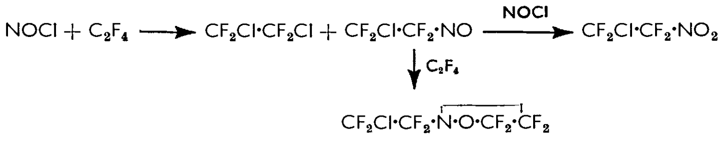
(VI)

When approximately equimolar amounts of nitrosyl chloride and tetrafluoroethylene were allowed to react at room temperature, the only products isolated were 1-chlorotetrafluoro-2-nitroethane (62% yield based on C_2F_4), 1,2-dichlorotetrafluoroethane (36% yield), and chlorodifluoroacetyl fluoride (2% yield), *i.e.*:



The nitroso-compound $CF_2Cl{\cdot}CF_2{\cdot}NO$ was not isolated, but its rapid subsequent oxidation to the nitro-compound $CF_2Cl{\cdot}CF_2{\cdot}NO_2$ by liquid nitrosyl chloride, or by the oxides of nitrogen produced during the reaction yielding the dichloride $CF_2Cl{\cdot}CF_2Cl$, would be in accord with the known properties of perfluoroalkyl nitroso-compounds.[1,2] Formation of the acyl fluoride $CF_2Cl{\cdot}COF$ by the above scheme is consistent with known reactions of perfluoroalkyl and perfluoroalkoxy-radicals.[3]

Reaction of nitrosyl chloride with an excess of tetrafluoroethylene at 100° should favour oxazetidine formation, and indeed the identified products were (V; X = Cl) (58% yield based on C_2F_4), 1,2-dichlorotetrafluoroethane (7% yield), 1-chlorotetrafluoro-2-nitroethane (4% yield), and 1-chlorotetrafluoro-2-nitrosoethane (3% yield), *i.e.*:



The isolation of the compound $CF_2Cl{\cdot}CF_2{\cdot}NO$, with the characteristic intense blue colour of compounds containing the $-CF_2{\cdot}NO$ group, strongly suggests that it, rather than (III; X = Cl), is the intermediate in the formation of the oxazetidine. The higher reaction temperature clearly favours the further reaction of the alkyl nitroso-compound with tetrafluoroethylene over the oxidation of the alkyl nitroso-compound.

Reaction at room temperature with a molar excess of tetrafluoroethylene gave a low yield of the polymer (VI; X = Cl), although the competing reaction of oxidation of the

[2] Haszeldine, *J.*, 1953, 2075.

[3] Francis and Haszeldine, *J.*, 1955, 2151; Haszeldine and Nyman, *J.*, 1959, 387, 420, 1084.

nitrosoalkane still predominated; use of a larger excess of the olefin would doubtless increase the polymer yield substantially.

Nitrosyl chloride thus reacts with tetrafluoroethylene by initial cleavage of the $>$N–Cl bond rather than by addition to the –N=O double bond.

The oxazetidine and the polymer were prepared as reference materials by the following sequence:

$$C_2F_4 \xrightarrow{ICl} CF_2Cl{\cdot}CF_2I \xrightarrow{h\nu,\ NO} CF_2Cl{\cdot}CF_2{\cdot}NO \qquad CF_2Cl{\cdot}CF_2{\cdot}NO \xrightarrow{C_2F_4} (V;\ X = Cl) \text{ or } (VI;\ X = Cl)$$

The yield of oxazetidine was greater at higher temperature, and that of the polymer greater at lower temperature.

The N–F bond appears to be less reactive than the N–Cl bond [*e.g.*, cf. $(CF_3)_2NF$ and $(CF_3)_2NCl$], so the possibility of isolating the compound (III; X = F) by interaction of nitrosyl fluoride and tetrafluoroethylene was probably greater than that of isolating (III; X = Cl) from the nitrosyl chloride reaction. Nitrosyl fluoride is reactive towards moisture, glass, etc., and the reaction with tetrafluoroethylene (mole ratio 1 : 2) was therefore carried out at —100° or —78°. The products were the oxazetidine (V; X = F), the polymer (VI; X = F), the dinitro-compound $CF_2(NO_2){\cdot}CF_2{\cdot}NO_2$, pentafluoronitrosoethane, pentafluoronitroethane, and difluoronitroacetyl fluoride. These indicate that pentafluoronitrosoethane is the predominant initial product rather than (III; X = F) or (IV; X = F). The acyl fluoride $CF_2(NO_2){\cdot}COF$ is a known product of the reaction of dinitrogen tetroxide with tetrafluoroethylene.[4]

Both oxazetidine and polymer were identical with the products obtained as follows:

$$C_2F_5{\cdot}CO_2Ag \xrightarrow{I_2} C_2F_5I \xrightarrow{h\nu,NO} C_2F_5{\cdot}NO \qquad C_2F_5{\cdot}NO \xrightarrow{C_2F_4} (V;\ X = F) + (VI;\ X = F)$$

The reaction of a nitrosyl halide with a fluoro-olefin thus provides a route to oxazetidines and polymers similar to, or identical with, the products hitherto obtained only by initial synthesis of a perfluoroalkyl nitroso-compound from the corresponding perfluoroalkyl iodide.

EXPERIMENTAL

Compounds were purified, stored, transferred, etc., by means of an apparatus for the manipulation of volatile materials *in vacuo*. Molecular weights were determined by Regnault's method.

Reaction of Pentafluoronitrosoethane with Tetrafluoroethylene.—Pentafluoronitrosoethane [1,2] (0·24 g., 1·6 mmoles) and tetrafluoroethylene (0·18 g., 1·8 mmoles) reacted in a sealed 15 ml. Pyrex tube at 85° (20 hr.) to give *perfluoro-2-ethyl-1,2-oxazetidine* (V; X = F) (0·36 g., 1·45 mmoles, 90% based on $C_2F_5{\cdot}NO$) as a colourless liquid (Found: C, 19·5; N, 5·8%; *M*, 250. C_4ONF_9 requires C, 19·2; N, 5·6%; *M*, 249), b. p. 26·0° (isoteniscope), and tetrafluoroethylene (0·02 g., 0·2 mmole); the *polymer* (VI; X = F) (0·04 g., 10%) remained in the reaction tube as a clear viscous oil (Found: C, 19·3; N, 5·7. C_4ONF_9 requires C, 19·2; N, 5·6%), which on trituration with ether formed a colourless, translucent elastomeric gum. Reaction of the nitroso-compound with tetrafluoroethylene at room temperature gave the polymer in 65% yield.

Reaction of 1-Chlorotetrafluoro-2-nitrosoethane with Tetrafluoroethylene.—The iodide, $CF_2Cl{\cdot}CF_2I$, was prepared by reaction of iodine monochloride (6·10 g., 37·5 mmoles) with tetrafluoroethylene (3·95 g., 39·5 mmoles) at room temperature (65 hr.) in a Pyrex tube.[3] Treatment of the products with mercury followed by fractionation *in vacuo* gave 1-chlorotetrafluoro-2-iodoethane (7·43 g., 28·3 mmoles, 75%), b. p. 56·5°. This compound (7·43 g., 28·3 mmoles), nitric oxide (5·0 g., 160 mmoles), and mercury (400 ml.) were shaken and irradiated in the 20 l. apparatus described earlier for 6 hr. The excess of nitric oxide was removed by admission of oxygen and then shaking with mercury, and the products were distilled to give unchanged chlorotetrafluoroiodoethane (0·85 g., 3·3 mmoles, 12%) and 1-chlorotetrafluoro-2-nitrosoethane (2·81 g., 17·0 mmoles; 68% yield based on iodo-compound used) (Found: C, 14·4; N, 8·2%; *M*, 165. Calc. for C_2ONF_4Cl: C, 14·5; N, 8·5; *M*, 165·5%), b. p. —5° (cf. lit.,[2] b. p. —2°).

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[4] Unpublished results.

The nitroso-compound (1·01 g., 6·1 mmoles) and tetrafluoroethylene (0·66 g., 6·6 mmoles) were kept in a sealed 200 ml. Pyrex tube at 100° for 6 hr. Removal of the volatile products from the clear colourless viscous *polymer* (VI; X = Cl) (Found: C, 17·9; N, 5·3. C_4ONF_8Cl requires C, 18·1; N, 5·3%) remaining in the tube, and fractionation, gave unchanged 1-chlorotetrafluoro-2-nitrosoethane (0·132 g., 0·80 mmole), unchanged tetrafluoroethylene (0·130 g., 1·30 mmoles), and 2-(2-*chlorotetrafluoroethyl*)*tetrafluoro*-1,2-*oxazetidine* (V; X = Cl) (1·07 g., 3·8 mmoles, 72% based on $CF_2Cl{\cdot}CF_2{\cdot}NO$ used) (Found: C, 18·0; N, 5·0%; *M*, 265·5. C_4ONF_8Cl requires C, 18·1; N, 5·3%; *M*, 265·5), b. p. 57° (isoteniscope). The yield of the polymer increased to 58% when a similar reaction was carried out at 25°.

Nitrosyl Halides.—Nitrosyl chloride was a commercial sample, redistilled before use to analytical purity. Nitrosyl fluoride was prepared by interaction of fluorine and nitric oxide. Fluorine (6·5 g./hr.) was passed into one limb of a copper T-piece whilst nitric oxide and nitrogen (1 : 3), previously dried by passage through concentrated sulphuric acid and phosphoric anhydride, were passed slowly through the other arm so as to maintain a slight excess of fluorine in the reaction zone. The mixed gases then moved through a silica tube (30 cm. long) and thence into a 25 ml. Pyrex trap cooled at −80°. This trap was fitted with a break-seal and contained potassium fluoride (1 g., heated to 600°, then cooled) to remove traces of hydrogen fluoride. A trap cooled at −110° protected the contents of the −80° trap from moisture, etc. The whole apparatus was dried extremely carefully before the experiment began. Nitrosyl fluoride collected steadily in the −80° trap. It was transferred to an all-glass vacuum-apparatus *via* the break-seal after being kept at −183° and evacuated to remove nitrogen and any dissolved fluorine. The number of transfers of nitrosyl fluoride was kept to a minimum since it readily attacks glass; grease must be avoided.

Reaction of Nitrosyl Chloride with Tetrafluoroethylene.—(a) *At room temperature.* Nitrosyl chloride (2·12 g., 32·2 mmoles) and tetrafluoroethylene (3·60 g., 36·0 mmoles) were kept in a sealed 200 ml. Pyrex tube in the dark at room temperature for 9 weeks. After removal of a non-condensable gas (nitrogen), distillation of the colourless products gave (i) unchanged tetrafluoroethylene (1·20 g., 12·0 mmoles, 37%) (Found: *M*, 99. Calc. for C_2F_4: *M*, 100), (ii) 1-chlorotetrafluoro-2-nitroethane (2·70 g., 14·9 mmoles, 62% based on C_2F_4 used) (Found: *M*, 182. Calc. for $C_2O_2NF_4Cl$: *M*, 181·5), (iii) 1,2-dichlorotetrafluoroethane (1·50 g., 8·8 mmoles, 36% based on C_2F_4 used) (Found: *M*, 170. Calc. for $C_2F_4Cl_2$: *M*, 171), and (iv) chlorodifluoroacetyl fluoride (0·070 g., 0·53 mmole, 2% based on C_2F_4 used) (Found: *M*, 135. Calc. for C_2OF_3Cl: *M*, 132). These products were identified by comparison of physical properties and infrared spectra with those of known compounds prepared by unambiguous routes.

(b) *At room temperature with an excess of tetrafluoroethylene.* Nitrosyl chloride (1·78 g., 27·2 mmoles) and tetrafluoroethylene (5·3 g., 53·0 mmoles) were kept in a sealed 200 ml. Pyrex tube in the dark at room temperature for 3 weeks. Removal of the colourless volatile products left a viscous colourless polymer (VI; X = Cl) (0·1 g.) (Found: C, 18·2; N, 5·8. Calc. for C_4ONF_8Cl: C, 18·1; N, 5·3%). The infrared absorption spectrum of the oil showed the absence of –NO, $-NO_2$, $-N{:}N^{+}(O^{-})-$, etc., groups, and its identity with the polymer prepared from 1-chloro-2-nitrosotetrafluoroethane and tetrafluoroethylene.

(c) *At* 100° *with an excess of tetrafluoroethylene.* Nitrosyl chloride (0·65 g., 10·0 mmoles) and tetrafluoroethylene (1·5 g., 15·0 mmoles) in a sealed 200 ml. Pyrex tube heated at 100° (15 hr.) gave a blue gas phase and liquid products. After removal of nitrogen produced in the reaction, distillation gave 2-(2-chlorotetrafluoroethyl)tetrafluoro-1,2-oxazetidine, (V; X = Cl) (1·14 g., 4·3 mmoles, 58% based on C_2F_4) (Found: *M*, 260. Calc. for C_4NOF_8Cl: *M*, 265·5), 1,2-dichlorotetrafluoroethane (0·19 g., 1·1 mmoles, 7% based on C_2F_4), 1-chlorotetrafluoro-2-nitroethane (0·11 g., 0·6 mmole; 4% based on C_2F_4), and 1-chlorotetrafluoro-2-nitrosoethane (0·08 g., 0·5 mmole, 3% based on C_2F_4). Other products include silicon tetrafluoride, carbonyl fluoride, the acyl fluoride $CF_2(NO_2){\cdot}COF$, and an unidentified nitro-compound possibly (V; X = NO_2). The compounds were separated by trap-to-trap distillation, followed by washing with aqueous alkali, etc., to remove the minor impurities; they were identified by their physical properties, and by comparison of their infrared spectra with those of known compounds synthesised by unambiguous methods.

Reaction of Nitrosyl Fluoride with Tetrafluoroethylene.—Pure nitrosyl fluoride (0·4 g., 7 mmoles) was transferred rapidly by means of thoroughly-dried, all-glass, vacuum-apparatus to a sealed-on 200 ml. Pyrex tube. Tetrafluoroethylene (1·50 g., 15·0 mmoles) was then introduced through a break-seal and condensed into the Pyrex tube, which was then sealed and placed in a bath at $-100°$. The tube was allowed to warm to room temperature during 36 hr.; a small amount of yellow liquid could then be observed, and after a total of 5 days the liquid had deepened in colour and gelatinous material was present. The volatile products were removed and shaken with mercury, then fractionated to give perfluoro-2-ethyl-1,2-oxazetidine (0·13 g., 13%), tetrafluoro-1,2-dinitroethane (0·12 g., 7%), pentafluoronitroethane (0·007 g., 1%), pentafluoronitrosoethane (0·007 g., 1%), and difluoronitroacetyl fluoride (0·24 g., 17%). Yields are based on tetrafluoroethylene. Separation and identification was achieved by initial trap-to-trap distillation followed by spectroscopic examination, then removal of the acyl fluoride, silicon tetrafluoride, etc., by treatment with aqueous alkali, before final infrared spectroscopic examination and comparison of properties with those of known specimens.

A small amount of the polymer (VI; X = F) (0·11 g.) (Found: C, 19·2; N, 5·4. Calc. for C_4ONF_9: C, 19·2; N, 5·6%) remained in the reaction tube. It was analysed after being shaken successively with ether, water, ethanol, and ether to remove small amounts of inorganic and organic impurities; the polymer is a colourless almost transparent elastomer.

A second experiment in which the reactants were kept at $-78°$ for 10 hr., $-45°$ for 12 hr., 0° for 3 hr., and 20° for 24 hr. gave a 22% yield of the oxazetidine and a 27% yield of the elastomeric polymer based on tetrafluoroethylene.

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