663. *Perfluoroalkyl Derivatives of Nitrogen. Part III.* Heptafluoronitrosopropane, Perfluoro-2-*n*-propyl-1 : 2-oxazetidine, Perfluoro(methylene-*n*-propylamine), and Related Compounds.*

By D. A. Barr and R. N. Haszeldine.

The preparation and physical and spectroscopic properties of pure heptafluoronitrosopropane are described. This compound reacts with aqueous base to give trifluoroacetic and pentafluoropropionic acid, with oxygen to give heptafluoronitropropane, with active carbon to give perfluoro-1 : 1′-azoxypropane, and with tetrafluoroethylene to give perfluoro-2-*n*-propyl-1 : 2-oxazetidine and a polymer $[\cdot N(C_3F_7)\cdot O\cdot CF_2\cdot CF_2\cdot]_n$. Pyrolysis of the oxazetidine or of the polymer gives, quantitatively, equimolar amounts of perfluoro(methylene-*n*-propylamine), $C_3F_7\cdot N{:}CF_2$, and carbonyl fluoride; the pyrolyses are considered to involve elimination of carbonyl fluoride from a perfluoroalkoxy-radical, and other examples of this general reaction are cited. Mechanisms for the formation of the oxazetidine and the polymer and for the reaction of perfluoro(methylene-*n*-propylamine) with water are considered. Controlled hydrolysis of the compounds $C_3F_7\cdot N{:}CF_2$ and $CF_3\cdot N{:}CF_2$ yields the *iso*cyanates $C_3F_7\cdot NCO$ and $CF_3\cdot NCO$.

The first general method for the preparation of perfluoronitrosoalkanes[1] involved the free-radical reaction of a perfluoroiodoalkane with nitric oxide in presence of mercury. The development of more convenient experimental techniques for this type of reaction[2] has made the nitroso-compounds readily available, and heptafluoroiodopropane has now given heptafluoronitrosopropane in excellent yield (75—80%). The latter product is more readily purified and, in particular, only very small amounts of pentafluoronitrosoethane and trifluoronitrosomethane are produced by degradation of the fluorocarbon chain. Improved physical properties are reported for heptafluoronitrosopropane.

Banus[3] confirmed the synthesis of heptafluoronitrosopropane, but reported that it decomposed spontaneously at room temperature, faster in the gas phase. Since this last

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* Part II, *J.*, 1955, 2532. Part I, *J.*, 1955, 1881, where references to earlier related work are given.

[1] Haszeldine, *Nature*, 1951, **168**, 1028; *J.*, 1953, 2075.

[2] Barr and Haszeldine, *J.*, 1955, 1881; Haszeldine and Mattinson, *Chem. and Ind.*, 1956, 81; Haszeldine and Jander, *J.*, 1954, 696.

[3] Banus, *J.*, 1953, 3755.

report was at variance with our original observations, the stability of heptafluoronitrosopropane has been re-examined carefully. Our original observations have been fully confirmed and heptafluoronitrosopropane is not unstable. It undergoes no reaction on storage in Pyrex apparatus or on contact with mercury, whereas moist soda-glass surfaces, bases, or light rapidly cause decomposition. Trifluoronitrosomethane, which was also reported to be unstable,[3] is similarly stable [1,2] provided that these precautions are taken. Light converts trifluoronitrosomethane into the orange dimer $(CF_3)_2N\cdot O\cdot NO$.[2]

The vapour-pressure equation, determined for a highly purified sample, leads to a value of 22·6 for Trouton's constant for heptafluoronitrosopropane. Heptafluoronitrosopropane is thus not strongly associated, as was concluded [3] from an apparent Trouton's constant of 28. Analytically and spectroscopically pure perfluoronitrosoalkanes show normal Trouton's constants, *e.g.*, $CF_3\cdot NO$ 21·9,[4] $C_2F_5\cdot NO$ 22·0, $C_3F_7\cdot NO$ 22·6, as do all the other perfluoroalkyl derivatives of nitrogen so far investigated, and there is as yet no legitimate evidence for marked association of liquid or vapour.

Perfluoroalkoxy-radicals.—Some breakdown of the perfluoroalkyl chain occurs during the preparation of heptafluoronitrosopropane. Over-irradiation increases the breakdown, and pentafluoronitrosoethane and trifluoronitrosomethane are then formed in 4 and 2% yield respectively. Perfluoro-*n*-hexane (27%) is also a product, and heptafluoronitropropane, pentafluoronitroethane, and trifluoronitromethane can be detected spectroscopically. These products support the free-radical mechanism proposed for the reaction [1] and also the idea that perfluoroalkoxy-radicals break down by loss of carbonyl fluoride to give a perfluoroalkyl radical containing one fewer carbon atom.[5,6] The formation of a perfluoroalkoxy-radical during the reaction of a perfluoroiodoalkane with nitric oxide very probably occurs by reaction of the perfluoroalkyl radical with nitrogen dioxide, which is present under non-optimum conditions, to give a perfluoroalkyl nitrite; this decomposes by O–N fission to give nitric oxide and a perfluoroalkoxy-radical which then loses carbonyl fluoride to give a perfluoroalkyl radical of shorter chain length :

$$C_3F_7I \xrightarrow{h\nu} C_3F_7\cdot + I\cdot \xrightarrow{Hg} HgI_2$$

(i) Formation of nitroso-compound :

$$C_3F_7\cdot + NO \longrightarrow C_3F_7\cdot NO$$

(ii) Dimerisation :

$$2C_3F_7\cdot \longrightarrow C_6F_{14}$$

(iii) Formation of nitro-compounds :

$$C_3F_7\cdot + NO_2 \longrightarrow C_3F_7\cdot NO_2$$

(iv) Formation of nitrite :

$$C_3F_7\cdot + NO_2 \longrightarrow C_3F_7\cdot O\cdot NO$$

(v) Chain degradation *via* alkoxy-radical :

$$C_3F_7\cdot O\cdot NO \xrightarrow{h\nu} C_3F_7\cdot O\cdot + NO$$

$$C_3F_7\cdot O\cdot \longrightarrow C_2F_5\cdot + COF_2$$

$$C_2F_5\cdot + NO \longrightarrow C_2F_5\cdot NO$$

$$C_2F_5\cdot \xrightarrow{NO_2} C_2F_5\cdot O\cdot NO \xrightarrow{h\nu} C_2F_5\cdot O\cdot \longrightarrow CF_3\cdot + COF_2 \xrightarrow{NO} CF_3\cdot NO$$

$$CF_3\cdot \xrightarrow{NO_2} CF_3\cdot O\cdot NO \xrightarrow{h\nu} CF_3\cdot O\cdot \xrightarrow{SiO_2} COF_2 + SiF_4$$

The dual rôle of mercury—removal of iodine to prevent radical recombination, and removal of dinitrogen tetroxide to prevent decomposition of the fluorocarbon chain—was emphasised earlier.[1,2]

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

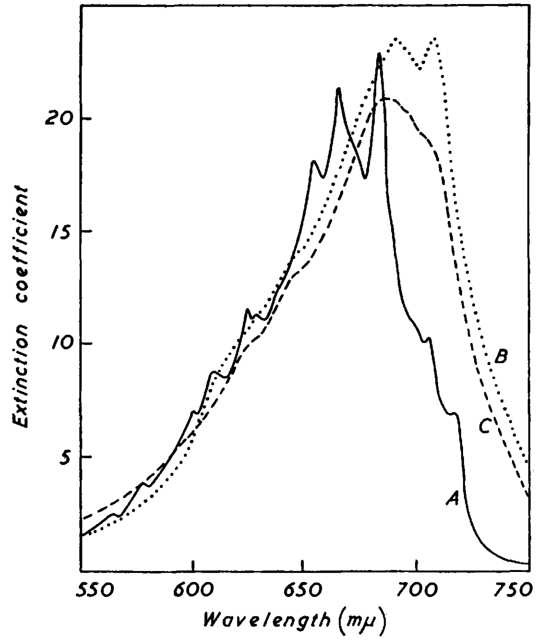
[5] Francis and Haszeldine, *J.*, 1955, 2151.

[6] Barr, Francis, and Haszeldine, *Nature*, 1956, **177**, 185.

The above scheme is supported by the photochemical reaction of heptafluoroiodopropane with dinitrogen tetroxide, which by reactions (iii), (iv), and (v) above yields heptafluoronitropropane (38%), pentafluoronitroethane (7%), and trifluoronitromethane (17%), and small amounts of trifluoronitrosomethane, as well as the main breakdown products carbonyl fluoride and silicon tetrafluoride :

$$CF_3{\cdot}[CF_2]_n{\cdot} \xrightarrow{NO_2} CF_3{\cdot}[CF_2]_n{\cdot}NO_2 + CF_3{\cdot}[CF_2]_{n-1}{\cdot}NO_2 + CF_3{\cdot}[CF_2]_{n-2}{\cdot}NO_2 + \ldots \text{ etc.}$$

It was earlier shown [4] that trifluoroiodomethane reacts with dinitrogen tetroxide to give trifluoronitromethane. The photochemical reaction of a perfluoroalkyl iodide with dinitrogen tetroxide is the simplest and quickest way of preparing the nitro-compounds on a small scale. The ready loss of carbonyl fluoride from a perfluoroalkoxy-radical parallels the decomposition of alkoxy-radicals into alkyl radicals and formaldehyde.[7]



Ultraviolet spectra of perfluoronitrosoalkanes.
A, $CF_3{\cdot}NO$. *B*, $C_2F_5{\cdot}NO$. *C*, $C_3F_7{\cdot}NO$.
(*All as vapour.*)

The ultraviolet spectrum of trifluoronitrosomethane shows appreciable fine structure in its long-wavelength band which has two main peaks at 665 and 683 mμ (see Figure and ref. 4 where comparison with other *C*-nitroso-compounds is made). Pentafluoronitrosoethane has a spectrum essentially similar in shape to that of trifluoronitrosomethane but with the two main peaks in the long-wavelength band shifted to the red by 20—25 mμ (692, 708 mμ) and with less fine structure (see Fig. and Table). Loss of fine structure is almost complete with heptafluoronitrosopropane which shows only a single broad peak (686 mμ) with several inflections (see Figure and Table).

The infrared spectrum of pentafluoronitrosoethane (D.M.S.*) shows the strong C–F stretching absorptions centred on 8·10 μ and the stretching vibration of the nitroso-group is clearly at 6·24 μ (cf. 6·25 μ in $CF_3{\cdot}NO$, ref. 4). The corresponding bands in heptafluoronitrosopropane (D.M.S.) are at 7·93, 8·07, and 6·23 μ. These N⁚O stretching vibrations should be compared with those of other *C*-, *O*-, and *N*-nitroso-compounds.[4, 6, 9]

Application of the method developed later for the oxidation of trifluoronitrosomethane

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* Spectra thus marked have been offered for the D.M.S. scheme to Messrs. Butterworths, 88 Kingsway, London, W.C., to whom application should be made.

[7] See, for example, Adler, Pratt, and Gray, *Chem. and Ind.*, 1955, 1517.

to trifluoronitromethane, namely, heating with oxygen, now enables heptafluoronitropropane[1] to be prepared in 75—80% yield. The last compound, which has a Trouton's constant of 22·8, has an ultraviolet spectrum very similar to that of trifluoronitromethane and alkyl and halogenoalkyl nitro-compounds.[4,9,10] Its infrared spectrum (D.M.S.) shows the asymmetric stretching vibration at 6·16 μ and the symmetric stretching vibration at 7·79 μ or possibly at 8·09 μ [cf. $CF_3\cdot NO_2$ 6·13, 6·17 μ (doublet) and 7·64, 7·78, 7·87 μ (triplet), and see refs. 4 and 10 for a discussion of the spectra of such compounds]. Pentafluoronitrosoethane is similarly oxidised to pentafluoronitroethane in good yield; the asymmetric stretching vibration of the nitro-compound is at 6·15 μ, and the symmetric stretching vibration is at 7·85 or 8·05 μ.

Ultraviolet spectra (vapour).

	$\lambda_{max.}$ (mμ)	ε	$\lambda_{min.}$ (mμ)	ε	$\lambda_{infl.}$ (mμ)	ε
(a) *C-Nitroso-compounds*						
$C_2F_5\cdot NO$	708	23·4	702	2·22	647	14·2
	692	23·6	—	—	625	11·4
$C_3F_7\cdot NO$	686	22·0	—	—	705	19·3
	—	—	—	—	695	20·5
	—	—	—	—	645	13·3
	—	—	—	—	612	7·7
(b) *C-Nitro-compounds*						
$CF_3\cdot NO_2$ [a]	279	11·0	239	2·0	—	—
$C_2F_5\cdot NO_2$	281	28·5	239	8·0	—	—
$C_3F_7\cdot NO_2$	282	36·0	236	3·8	—	—
(c) *Azoxy-compounds*						
$CF_3\cdot{}^+N{:}N\cdot CF_3$ [b]	303	7·4	280	6·0	—	—
O^-	211	8000	—	—	—	—
$C_3F_7\cdot{}^+N{:}N\cdot C_3F_7$	305	17·0	285	14·6	—	—
O^-	220	2740	—	—	—	—

[a] Taken from ref. 4. [b] Taken from ref. 8 where ε was printed as 17·4 instead of 7·4; the diagram in ref. 8 is correct.

Heptafluoronitrosopropane is decolorised when heated with active carbon at 150° and yields perfluoro-1 : 1′-azoxypropane, b. p. 94·5°, and heptafluoronitropropane :

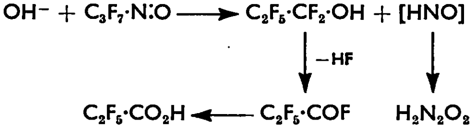
$$3C_3F_7\cdot NO \longrightarrow C_3F_7\cdot{}^+N(O^-){:}N\cdot C_3F_7 + C_3F_7\cdot NO_2$$

The ultraviolet spectrum of perfluoroazoxypropane shows the characteristic weak long-wavelength and powerful short-wavelength maxima of azoxy-compounds. The asymmetric stretching vibration of the azoxy-group,[8] which electronically resembles a *C*-nitro-group, is well-defined in perfluoroazoxypropane (D.M.S.) at 6·39 μ (cf. 6·37 μ in hexafluoroazoxymethane). The symmetric stretching vibration is probably at 8·08 μ, but this assignment is less certain.

The reaction of heptafluoronitrosopropane with 10% aqueous base is interesting, since it yields pentafluoropropionic and trifluoroacetic acid as main products as well as fluoride, nitrite, and carbonate :

$$C_3F_7\cdot NO \xrightarrow[H_2O]{OH^-} C_2F_5\cdot CO_2H + CF_3\cdot CO_2H$$

Nucleophilic attack on the α-carbon atom of heptafluoronitrosopropane, possibly with formation of hyponitrous acid, readily explains the formation of pentafluoropropionic acid :



$$\begin{tikzcd}
OH^- + C_3F_7\cdot N{:}O \arrow[r] & C_2F_5\cdot CF_2\cdot OH \arrow[d, "-HF"] & + [HNO] \arrow[d] \\
C_2F_5\cdot CO_2H & C_2F_5\cdot COF \arrow[l] & H_2N_2O_2
\end{tikzcd}$$

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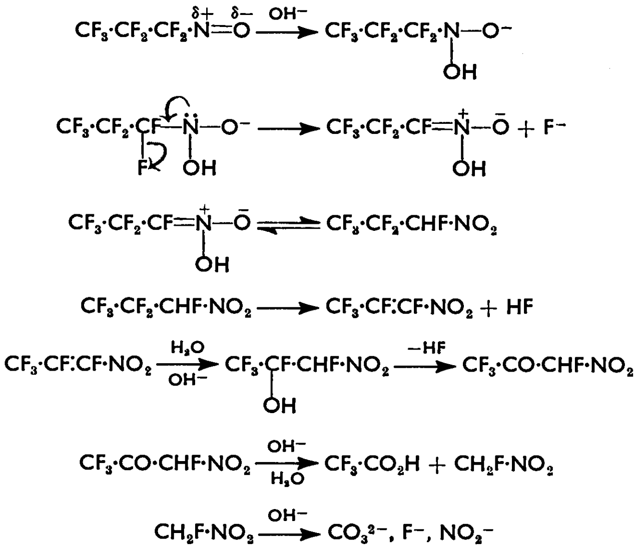
[8] Jander and Haszeldine, *J.*, 1954, 919.

[9] Haszeldine and Jander, *J.*, 1954, 691; Haszeldine and Mattinson, *J.*, 1955, 4172; *Chem. and Ind.*, 1955, 81; Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

[10] Haszeldine, *J.*, 1953, 2525.

The following reaction scheme is suggested to explain the partial breakdown of the perfluoroalkyl group, which is normally extremely resistant to attack:



$$\mathrm{CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}\overset{\delta+}{N}{=}\overset{\delta-}{O}} \xrightarrow{\mathrm{OH^-}} \mathrm{CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}\underset{OH}{N}{-}O^-}$$

$$\mathrm{CF_3{\cdot}CF_2{\cdot}\underset{F}{C}F{-}\underset{OH}{N}{-}O^-} \longrightarrow \mathrm{CF_3{\cdot}CF_2{\cdot}CF{=}\underset{OH}{\overset{+}{N}}{-}\bar{O}} + \mathrm{F^-}$$

$$\mathrm{CF_3{\cdot}CF_2{\cdot}CF{=}\underset{OH}{\overset{+}{N}}{-}\bar{O}} \rightleftharpoons \mathrm{CF_3{\cdot}CF_2{\cdot}CHF{\cdot}NO_2}$$

$$\mathrm{CF_3{\cdot}CF_2{\cdot}CHF{\cdot}NO_2} \longrightarrow \mathrm{CF_3{\cdot}CF{:}CF{\cdot}NO_2} + \mathrm{HF}$$

$$\mathrm{CF_3{\cdot}CF{:}CF{\cdot}NO_2} \xrightarrow[\mathrm{OH^-}]{\mathrm{H_2O}} \mathrm{CF_3{\cdot}\underset{OH}{C}F{\cdot}CHF{\cdot}NO_2} \xrightarrow{-\mathrm{HF}} \mathrm{CF_3{\cdot}CO{\cdot}CHF{\cdot}NO_2}$$

$$\mathrm{CF_3{\cdot}CO{\cdot}CHF{\cdot}NO_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-}} \mathrm{CF_3{\cdot}CO_2H} + \mathrm{CH_2F{\cdot}NO_2}$$

$$\mathrm{CH_2F{\cdot}NO_2} \xrightarrow{\mathrm{OH^-}} \mathrm{CO_3^{2-}},\ \mathrm{F^-},\ \mathrm{NO_2^-}$$

In this scheme nucleophilic attack on the nitrogen of the nitroso-group is followed by fluoride elimination in a manner similar to that postulated earlier for olefin formation from fluorocarbanions.[11] Rearrangement into hexafluoronitropropane is followed by elimination of hydrogen fluoride and base-catalysed hydration of the resultant olefin to give the fluoronitro-ketone. In an alkaline medium this ketone would undergo hydrolytic cleavage to trifluoroacetic acid (cf. $CF_3{\cdot}CO{\cdot}CF_3 \longrightarrow CF_3{\cdot}CO_2H$; $C_3F_7{\cdot}CO{\cdot}C_3F_7 \longrightarrow C_3F_7{\cdot}CO_2H$). Reaction schemes which involve formation of $C_3F_7^-$ or $C_2F_5^-$ are not likely, since such ions would yield C_3HF_7 or C_2HF_5, which are stable to base, as well as fluoro-olefins such as C_3F_6 and C_2F_4 by fluoride elimination, and such compounds were not detected. Aldehydes such as $C_2F_5{\cdot}CHO$ are similarly improbable intermediates, since they are known to be cleaved to formic acid and the corresponding hydrofluorocarbon (C_2HF_5) in an alkaline medium.

In marked contrast, heptafluoronitropropane is unchanged by prolonged contact with aqueous base at 120°. This suggests that initiation of the hydrolysis of heptafluoronitrosopropane is at the reactive nitroso-group and not at the α-carbon atom, and that the intermediate $C_2F_5{\cdot}CF_2{\cdot}N(OH){\cdot}O^-$ then decomposes either by nucleophilic attack on the α-carbon atom to give pentafluoropropionic acid as above, or by fluoride elimination with breakdown of the chain. The marked inertness of heptafluoronitropropane to aqueous alkali made re-investigation of the stability of trifluoronitromethane necessary, since the last compound was earlier considered to be stable to cold aqueous alkali[4] but slowly decomposed by prolonged contact.[8] Trifluoronitromethane is, in fact, stable to aqueous base at temperatures up to 100° and is thus very similar to heptafluoronitropropane.

Heptafluoronitrosopropane reacts in the dark with tetrafluoroethylene to give almost quantitatively a colourless liquid (b. p. 50·5°) and an involatile, clear, colourless, viscous oil. This reaction thus parallels that between trifluoronitrosomethane and tetrafluoroethylene.[2] Both products have empirical formula C_5NOF_{11}, *i.e.*, contain a 1 : 1 ratio of $C_3F_7{\cdot}NO$ to C_2F_4, and are unaffected by water or aqueous acid or alkali. Their infrared spectra fail to show the presence of groups such as N:O, NO_2, $N{:}^{+}N{\cdot}(O^-)$, O·NO, $O{\cdot}NO_2$, C:C, C:N, or N:N. The liquid, which has a molecular weight of 299, is perfluoro-2-*n*-propyl-1 : 2-oxazetidine (I), and proof of structure is afforded by its pyrolysis at 550° at

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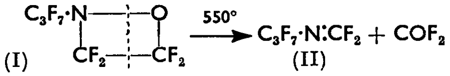
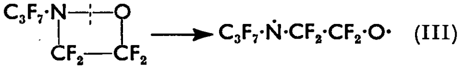
[11] Haszeldine, *Nature*, 1951, **168**, 1028; *J.*, 1952, 4259; *J.*, 1954, 4026 *et seq.*

low pressure in absence of air to yield twice the original volume of gas, shown to consist of equimolar amounts of carbonyl fluoride and perfluoro(methylene-*n*-propylamine) (II):



The infrared spectrum (D.M.S.) of the oxazetidine (I) is very similar to that of perfluoro-2-methyl-1 : 2-oxazetidine [2] with C–F stretching absorptions centred on 8·0 μ and with a sharp band at 7·06 μ (cf. 7·05 μ in $CF_3\cdot\overline{N\cdot O\cdot CF_2\cdot CF_2}$) which is possibly characteristic of this ring system. The structure of the perfluoro(methylenepropylamine) (II) follows from the method of preparation, from its infrared spectrum (D.M.S.), and from its hydrolysis described below.

It seems very probable that pyrolysis of the oxazetidine (I) occurs by initial fission of the N–O bond to give the diradical (III) which is also a perfluoroalkoxy-radical. As pointed out earlier (see also ref. 5), a perfluoroalkoxy-radical readily eliminates COF_2:



$$C_3F_7\cdot\dot{N}\cdot CF_2\cdot CF_2\cdot O\cdot \longrightarrow COF_2 + C_3F_7\cdot\dot{N}\cdot CF_2\cdot \longrightarrow C_3F_7\cdot N{:}CF_2$$

Formation of perfluoro(methylenepropylamine) is thus readily visualised.

The infrared spectrum of the compound (II) shows the strong C:N stretching vibration at 5·51 μ with other strong bands at 9·85, 10·75, and 13·37 μ (cf. 5·53, 9·95, and 13·8 μ for $CF_3\cdot N{:}CF_2$, ref. 2).

It has recently been claimed [12] that pyrolysis of perfluoro-*tert.*-amines yields azomethines, *i.e.*, perfluoro(alkylenealkylamines), and one of the compounds reported was perfluoro-(methylene-*n*-propylamine), obtained by pyrolysis of perfluoro-*tert.*-propylamine at 660—670°. It is unlikely that the material obtained by this route was in fact perfluoro(methylene-*n*-propylamine), since the b. p. reported (12·3°) for the unanalysed material is much lower than that which we observe (25·6°) for an analytically pure sample. The pyrolysis of a tertiary perfluoroamine, which has to be carried out under very stringent conditions in the presence of metal fluorides as catalysts, and must involve concurrent formation of fluorocarbons such as CF_4, C_2F_4, C_2F_6, C_3F_8, C_3F_6, C_4F_{10}, C_4F_8, etc., is unlikely to give good yields of perfluoro(methylenealkylamines), $CF_3\cdot[CF_2]_n\cdot N{:}CF_2$, to the exclusion of all other perfluoro(alkylenealkylamines) such as $CF_3\cdot[CF_2]_n\cdot CF_2\cdot N{:}CF\cdot[CF_2]_n\cdot CF_3$. Degradation from either end of a perfluoro(alkylenealkylamine) molecule is feasible:

$$CF_3\cdot[CF_2]_n\cdot CF_2\cdot N{:}CF\cdot[CF_2]_n\cdot CF_3 \longrightarrow CF_3\cdot[CF_2]_x\cdot CF_2\cdot N{:}CF\cdot[CF_2]_n\cdot CF_3$$
$$\text{or}\quad CF_3\cdot[CF_2]_n\cdot CF_2\cdot N{:}CF\cdot[CF_2]_x\cdot CF_3$$

where $x < n$.

Products such as $CF_3\cdot N{:}CF_2$, $C_2F_5\cdot N{:}CF_2$, $C_2F_5\cdot N{:}CF\cdot CF_3$, $CF_3\cdot N{:}CF\cdot CF_2\cdot CF_3$, $C_3F_7\cdot N{:}CF\cdot C_2F_5$, $C_3F_7\cdot N{:}CF\cdot CF_3$, $C_2F_5\cdot N{:}CF\cdot C_2F_5$, are thus to be expected when an amine such as $(C_3F_7)_3N$ is pyrolysed, and we therefore suggest that the product of b. p. 12·3° reported by Pearlson and Hals is either a mixture or the isomeric perfluoro(propylidenemethylamine) (IV):

$$(C_3F_7)_3N \longrightarrow C_2F_5\cdot CF{:}N\cdot CF_3 \quad \text{(IV)}$$

The last compound, like perfluoro(methylene-*n*-propylamine) (II) (see below), would give pentafluoropropionic acid when treated with an excess of aqueous base:

$$\text{cf.}\quad CF_3\cdot CF_2\cdot CF_2\cdot N{:}CF_2 + 4H_2O \longrightarrow C_2F_5\cdot CO_2H + NH_4F + CO_2 + 3HF$$

$$\text{and}\quad C_2F_5\cdot CF{:}N\cdot CF_3 \xrightarrow[OH^-]{H_2O} C_2F_5\cdot CF(OH)\cdot NH\cdot CF_3 \longrightarrow C_2F_5\cdot CO\cdot NH\cdot CF_3 + HF$$

$$C_2F_5\cdot CO\cdot NH\cdot CF_3 \xrightarrow[H_2O]{OH^-} C_2F_5\cdot CO_2H + CO_2 + NH_4F + 2HF$$

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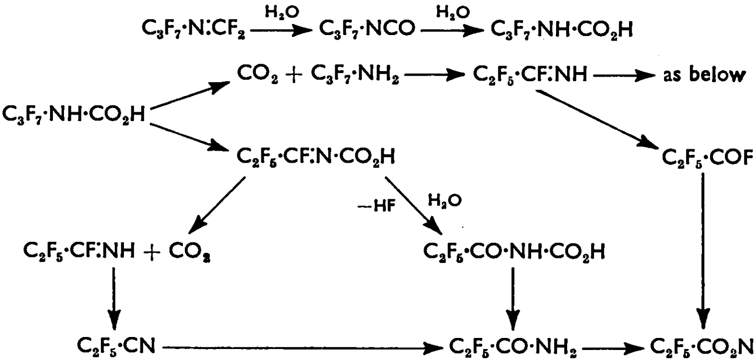
[12] Pearlson and Hals, U.S.P. 2,643,267; *Chem. Abs.*, 1954, **48**, 6461.

That the pyrolysis product of perfluoro-2-*n*-propyl-1 : 2-oxazetidine is actually perfluoro-(methylene-*n*-propylamine) is shown by its reactions. When treated with an *excess* of water it is hydrolysed to, initially, carbon dioxide and pentafluoropropionitrile; the last compound can be identified by means of its infrared spectrum.[13] The nitrile is further hydrolysed to give pentafluoropropionamide and a smaller amount of ammonium pentafluoropropionate. Reaction of perfluoro(methylene-*n*-propylamine) with only a ***limited amount*** of water gave unchanged starting material and an almost quantitative yield of heptafluoro-*n*-propyl *iso*cyanate (b. p. 24·5°), spectroscopically identical with the material prepared from heptafluorobutyryl chloride as described in Part IV of this series (following paper). Heptafluoropropyl *iso*cyanate and pentafluoropropionitrile can also be isolated when perfluoro(methylene-*n*-propylamine) is treated with an excess of water, provided that the reaction time is short. The isolation of heptafluoropropyl *iso*cyanate clearly proves that a heptafluoropropyl group is present in perfluoro(methylene-*n*-propylamine) and that the material is not admixed with other perfluoro(alkylenealkylamines) such as $C_2F_5\cdot CF{:}N\cdot CF_3$ or $CF_3\cdot CF{:}N\cdot C_2F_5$. The difluoromethylene fluorine atoms are clearly very reactive :

$$C_3F_7\cdot N{:}CF_2 + H_2O \longrightarrow C_3F_7\cdot NCO + 2HF$$

The following reaction scheme is thus suggested for the hydrolysis of perfluoro(methylene-*n*-propylamine) with an *excess* of water :



Heptafluoropropyl *iso*cyanate is also formed when perfluoro(methylenepropylamine) is heated in glass at 160°, again revealing the reactivity of the difluoromethylene fluorine atoms :

$$C_3F_7\cdot N{:}CF_2 \xrightarrow{SiO_2} C_3F_7\cdot NCO + SiF_4$$

Perfluoro(methylenemethylamine) was shown to react [2] with a deficit of water to give unchanged starting material, silicon tetrafluoride, carbonyl fluoride, and an unknown volatile product showing infrared absorption at 4·4 μ (doublet); cyanogen fluoride and trifluoromethyl *iso*cyanate were considered to be possibilities. That the unknown product is actually trifluoromethyl *iso*cyanate produced by the reaction

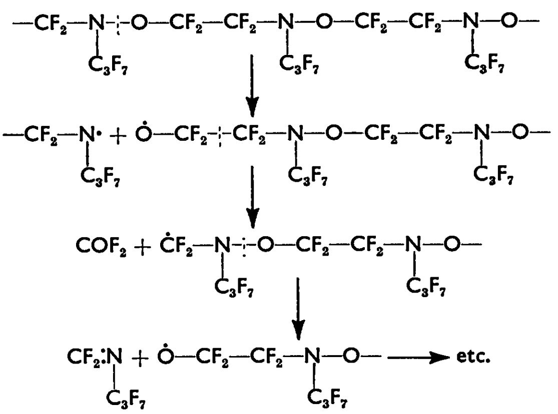
$$CF_3\cdot N{:}CF_2 + H_2O \longrightarrow CF_3\cdot N{:}C{:}O + 2HF$$

has now been shown by comparison of its infrared spectrum with that of a known specimen, whose synthesis will be described in Part IV. A reaction scheme for the hydrolysis of perfluoro(methylenemethylamine) involving trifluoromethyl *iso*cyanate is clearly now to be preferred over that involving initial C=N fission proposed earlier.[2] Trifluoromethyl *iso*cyanate is also produced when perfluoro(methylenemethylamine) is heated in silica, and there is thus a complete parallel between the reactions of $CF_3\cdot N{:}CF_2$ and $C_3F_7\cdot N{:}CF_2$.

The Polymer.—The clear, colourless, viscous oil obtained concurrently with perfluoro-2-*n*-propyl-1 : 2-oxazetidine is formed by copolymerisation of heptafluoronitrosopropane and

[13] See Haszeldine and Leedham, *J.*, 1953, 1548, for derivatives of pentafluoropropionic acid.

tetrafluoroethylene in a 1 : 1 ratio to give the polymer (V). Its infrared spectrum (D.M.S.) is similar to that of the oil obtained from trifluoronitrosomethane and tetrafluoroethylene, with C–F absorption at 8·10 and 8·80 μ and strong bands at 13·57 and 10·83 μ (cf. 13·45 and 10·93 μ, ref. 2). Proof of structure is given by pyrolysis of the oil to equimolar amounts of perfluoro(methylene-*n*-propylamine) and carbonyl fluoride quantitatively. This reaction probably proceeds by N–O fission followed by elimination of carbonyl fluoride from the resultant perfluoroalkoxy-radicals :

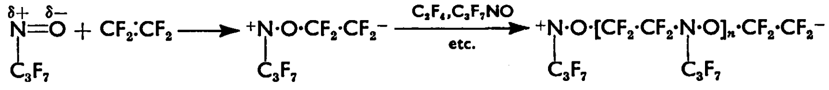


(V)

$$-CF_2-\underset{C_3F_7}{N}-O-CF_2-CF_2-\underset{C_3F_7}{N}-O-CF_2-CF_2-\underset{C_3F_7}{N}-O- \quad \text{(V)}$$
$$\downarrow$$
$$-CF_2-\underset{C_3F_7}{N}\cdot + \dot{O}-CF_2-CF_2-\underset{C_3F_7}{N}-O-CF_2-CF_2-\underset{C_3F_7}{N}-O-$$
$$\downarrow$$
$$COF_2 + \dot{C}F_2-\underset{C_3F_7}{N}-O-CF_2-CF_2-\underset{C_3F_7}{N}-O-$$
$$\downarrow$$
$$CF_2{:}\underset{C_3F_7}{N} + \dot{O}-CF_2-CF_2-\underset{C_3F_7}{N}-O- \longrightarrow \text{etc.}$$

Reaction of heptafluoronitrosopropane with tetrafluoroethylene followed by pyrolysis of both the oxazetidine and the polymer produced thus gives perfluoro(methylene-*n*-propylamine) almost quantitatively.

Mechanism of Polymerisation.—The copolymerisation of a nitroso-compound and an olefin was noted for the first time with trifluoronitrosomethane and tetrafluoroethylene, and produces a novel copolymer.[14] Application of the ionic mechanism suggested for this copolymerisation [2, 14] to the heptafluoronitrosopropane–tetrafluoroethylene case gives :



$$\underset{C_3F_7}{\overset{\delta+}{N}}{=}\overset{\delta-}{O} + CF_2{:}CF_2 \longrightarrow {}^{+}\underset{C_3F_7}{N}{\cdot}O{\cdot}CF_2{\cdot}CF_2^{-} \xrightarrow[\text{etc.}]{C_2F_4,\,C_3F_7NO} {}^{+}\underset{C_3F_7}{N}{\cdot}O{\cdot}[CF_2{\cdot}CF_2{\cdot}\underset{C_3F_7}{N}{\cdot}O]_n{\cdot}CF_2{\cdot}CF_2^{-}$$

In support of such an ionic mechanism are : (*a*) The fact that the polymer : oxazetidine ratio varies markedly with reaction temperature; at 70° the ratio is 0·2 : 1, and at 20° is 5 : 1, with reaction essentially complete at both temperatures. A low temperature would favour a liquid-phase reaction and hence polymerisation to a polymer of high molecular weight; it is significant that the polymer formed at 70° is appreciably more mobile and has a lower molecular weight that than formed at 20°. (*b*) The formation of the oxazetidine from the intermediate $C_3F_7{\cdot}{}^{+}N{\cdot}O{\cdot}CF_2{\cdot}CF_2^{-}$ is readily visualised. (*c*) The formation of a 1 : 1 copolymer is as expected. Fluoro-olefins are known to be readily attacked by nucleophilic reagents (RO^-, R_2N^-, RS^-, etc.), and attack of the $-CF_2{\cdot}CF_2{\cdot}N(C_3F_7){\cdot}O^-$ ion on tetrafluoroethylene should occur readily.

Further investigation of the influence of catalysts on the polymerisation has shown that a free-radical mechanism for the reaction must also be considered. A large increase in the surface area of the system produced by filling the reaction tube with glass wool caused no significant change either in rate or in the product ratio; this suggests that the reaction is not a heterogeneous surface reaction, or catalysed by glass. Exposure to ultraviolet radiation for a short period, or the addition of *tert.*-butyl peroxide to the reaction mixture, leads to a slightly increased rate of reaction, and the polymer : oxazetidine ratio is doubled. By contrast, reaction in the presence of quinol approximately halves the overall rate of

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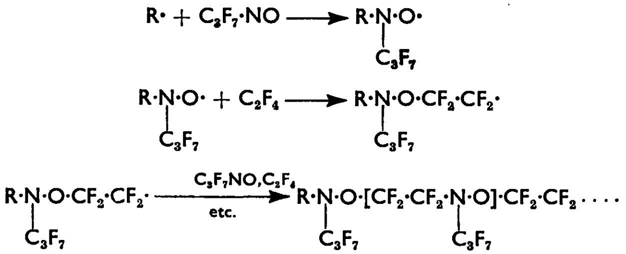
[14] Barr and Haszeldine, *Nature*, 1955, **175**, 991.

reaction and decreases the polymer : oxazetidine ratio eight-fold. All these observations suggest a free-radical reaction in the gas phase, *e.g.* :



$$R\cdot + C_3F_7\cdot NO \longrightarrow R\cdot\underset{C_3F_7}{N}\cdot O\cdot$$

$$R\cdot\underset{C_3F_7}{N}\cdot O\cdot + C_2F_4 \longrightarrow R\cdot\underset{C_3F_7}{N}\cdot O\cdot CF_2\cdot CF_2\cdot$$

$$R\cdot\underset{C_3F_7}{N}\cdot O\cdot CF_2\cdot CF_2\cdot \xrightarrow[\text{etc.}]{C_3F_7NO,C_2F_4} R\cdot\underset{C_3F_7}{N}\cdot O\cdot[CF_2\cdot CF_2\cdot\underset{C_3F_7}{N}\cdot O]\cdot CF_2\cdot CF_2\cdot\cdots$$

where R is an initiating free radical, possibly derived from heptafluoronitrosopropane :

$$C_3F_7\cdot NO \longrightarrow C_3F_7\cdot + NO$$

Since the molecular weight of the polymer is high, R would have but little influence on the overall polymer composition.

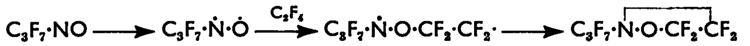
In favour of the free-radical mechanism is the effect of light, peroxide, and quinol and the absence of effect of surface area on the gas-phase reaction. The nitroso-group of a perfluoronitrosoalkane is known to be susceptible to free-radical attack which occurs at the nitrogen atom,[15] *e.g.* :

$$CF_3\cdot NO \longrightarrow CF_3\cdot + NO$$

$$CF_3\cdot + CF_3\cdot N{:}O \longrightarrow (CF_3)_2N\cdot O\cdot \xrightarrow{NO} (CF_3)_2N\cdot O\cdot NO$$

A free-radical mechanism does not involve the continual increase in charge separation as growth of polymer proceeds which is necessary in the ionic mechanism. It is also particularly suitable for the trifluoronitrosomethane–tetrafluoroethylene reaction;[2] here the reactants are in the gas phase, and increased surface area has negligible effect on reaction rate or product ratio.

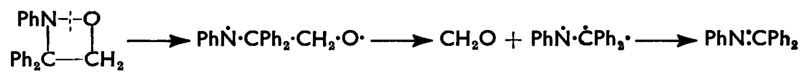
The new evidence thus suggests a free-radical mechanism, but kinetic studies are clearly merited to enable full distinction between the mechanisms to be made. Initial attempts, involving use of solvents of differing dielectric constants, have proved unsuccessful, since reaction with the solvent also occurs. The main features against a radical mechanism are : (*a*) The marked specificity of the copolymerisation, which is strictly 1 : 1; this is unusual for a radical reaction. (*b*) The difficulty of explaining the formation of the oxazetidine without recourse to diradicals, *e.g.* :



$$C_3F_7\cdot NO \longrightarrow C_3F_7\cdot\dot{N}\cdot\dot{O} \xrightarrow{C_2F_4} C_3F_7\cdot\dot{N}\cdot O\cdot CF_2\cdot CF_2\cdot \longrightarrow C_3F_7\cdot N\cdot O\cdot CF_2\cdot CF_2$$

(*c*) The fact that reaction occurs readily even at −40° and gives a higher yield of polymer at the lower temperatures. Despite these points, the evidence at present available favours the radical mechanism for the formation of oxazetidine or polymer, or both.

Pyrolytic Decomposition of Other Oxazetidines.—The products obtained by pyrolysis of the oxazetidines prepared many years ago[16] from nitrosobenzene and 1 : 1-diphenylethylene diethyl methylenemalonate, or diphenylketen are somewhat unexpected at first sight. The idea of intermediate formation of an alkoxy-radical by initial N–O fission of the type postulated for the fluoro-oxazetidines makes the formation of these products somewhat easier to understand. Thus the oxazetidine (VI) would give an alkoxy-radical which could readily lose formaldehyde :

(VI) 

$$\longrightarrow Ph\dot{N}\cdot CPh_2\cdot CH_2\cdot O\cdot \longrightarrow CH_2O + Ph\dot{N}\cdot\dot{C}Ph_2\cdot \longrightarrow PhN{:}CPh_2$$

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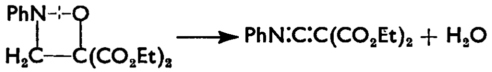
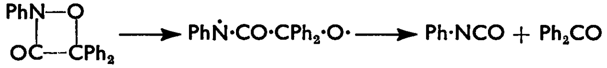
[15] Haszeldine and Mattinson, *Chem. and Ind.*, 1956, 81.

[16] Ingold and Weaver, *J.*, 1924, **125**, 1456; Staudinger and Jelagin, *Ber.*, 1911, **44**, 365.

whereas the oxazetidine (VII) would give an alkoxy-radical which could not lose formaldehyde; it apparently decomposes by loss of water :

(VII) 

The oxazetidine (VIII) would yield an alkoxy-radical which could lose neither formaldehyde nor water, and in this case C–CO bond fission apparently occurs :

(VIII) 

Experimental

Reactions were carried out in sealed tubes unless otherwise stated.

Preparation of Heptafluoronitrosopropane.—The apparatus and technique were similar to those described in Part I (*loc. cit.*).* In a typical experiment heptafluoroiodopropane (35·3 g., 0·119 mole), nitric oxide (12·0 g., 0·40 mole), and mercury (400 ml.) were introduced into the 20 l. flask which was then shaken for 20—25 hr. whilst irradiated with an internal 12″ Hanovia ultraviolet lamp. The course of the reaction is followed by the development of the intense blue colour.

Oxygen was then admitted to the flask until the pressure reached atmospheric, and the flask was set aside for 1 hr. to complete the oxidation of the unused nitric oxide. The volatile contents of the flask were slowly pumped (2 hr.) through three traps in series cooled by liquid oxygen. The condensable products were then fractionated *in vacuo*, to give unchanged heptafluoroiodopropane (57%) and heptafluoronitrosopropane (7·8 g., 76%). No difficulty is experienced in obtaining spectroscopically and analytically pure heptafluoronitrosopropane by this method provided that care is taken to exclude moisture, air, etc., to use clean apparatus, and to avoid over-irradiation.

The effects of over-irradiation are shown by the results of an earlier experiment in which heptafluoroiodopropane (2·43 g., 8·2 mmole), nitric oxide (0·51 g., 17 mmole), and mercury (75 ml.) were mechanically shaken in a 1 l. silica flask exposed to an external ultraviolet lamp (24 hr.). The products of six such experiments were combined and fractionated, to give heptafluoroiodopropane (traces only), heptafluoronitrosopropane (4·7 g., 23·6 mmole; 48%), perfluoro-*n*-hexane (2·25 g., 6·7 mmole; 27%), pentafluoronitrosoethane (2 mmole; 4%), trifluoronitrosomethane (1 mmole; 2%), heptafluoronitropropane, pentafluoronitroethane, trifluoronitromethane, carbon dioxide, and carbonyl fluoride. These products were identified by means of their molecular weight, vapour pressure, and infrared spectra.

Properties of Heptafluoronitrosopropane.—Heptafluoronitrosopropane is a blue gas which condenses to a purple liquid. The vapour pressure of a highly purified sample (Found : C, 18·1; N, 7·1%; *M*, 199. Calc. for C_3ONF_7 : C, 18·1; N, 7·1%; *M*, 199), determined over the range $-46°$ to $-23°$, is represented by the equation $\log_{10} p(\text{mm.}) = 7{\cdot}825 - 1303/T$, whence the b. p. is calculated to be $-9{\cdot}7°$, the latent heat of vaporisation is 5960 cals./mole, and Trouton's constant is 22·6. The compound as prepared originally [1] had b. p. $-12°$. Banus [3] reported $-14{\cdot}5°$ but the high value of the Trouton constant (28) reported by this author reveals substantial impurity.

Heptafluoronitrosopropane shows maximum absorption in the ultraviolet only near 700 mμ (see Table) and its extinction coefficient is < 1 between 300 and 500 mμ. Heptafluoroiodopropane can be detected when present in trace amounts as impurity by the peak which appears at 270 mμ. Heptafluoronitrosopropane, like trifluoronitrosomethane,[2,4] has no maximum between 220 and 550 mμ.

Pentafluoronitrosoethane.—Pentafluoroiodoethane (2·46 g., 10·0 mmole), nitric oxide (0·90 g., 30 mmole), and mercury (100 ml.) were shaken in a 2 l. silica flask irradiated by an external Hanovia S250 ultraviolet lamp (20 hr.). The products were treated with oxygen to remove unused nitric oxide, then freed from the excess of oxygen by slow pumping through traps cooled with liquid oxygen. The condensable products were distilled *in vacuo*, to give pentafluoronitrosoethane (1·27 g., 8·5 mmole), trifluoronitrosomethane (0·015 g., 0·15 mmole), pentafluoroiodoethane (0·054 g., 0·22 mmole), and small amounts of carbon dioxide, carbonyl fluoride, and

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* [*Note added*, 15.3.56.] An overriding advantage of this method of preparation of perfluoronitrosoalkanes is that relatively large amounts of the pure nitroso-compound can be obtained in a short time without the use of large silica apparatus and without the repeated filling of small silica tubes.

silicon tetrafluoride. The yield of pentafluoronitrosoethane is 87% calculated on the iodo-compound used (98%).

Properties of pentafluoronitrosoethane. The vapour pressure of a highly pure specimen of this blue gas (Found: C, 15·9; N, 9·6%; *M*, 150. Calc. for C_2ONF_5: C, 16·1; N, 9·4%; *M*, 149), determined over the range −80° to −46°, is represented by the equation $\log_{10} p(\text{mm.}) = 7{\cdot}690 - 1094/T$, whence the b. p. is calculated as −45·7°, the latent heat of vaporisation is 5005 cals./mole, and Trouton's constant is 22·0. Haszeldine[1] gives b. p. −42°. The compound shows maximum absorption in the ultraviolet near 700 mμ, and no maximum between 220 and 550 mμ; its extinction coefficient is <1 between 300 and 500 mμ.

Heptafluoronitropropane and Pentafluoronitroethane.—In a typical experiment heptafluoronitrosopropane (1·49 g., 7·5 mmole) and oxygen (10 mmole) were heated in a 400 ml. Pyrex tube in absence of light at 70° (4 days); the gas was then green. The products condensable by liquid oxygen were shaken with mercury in a Carius tube to remove dinitrogen tetroxide, then distilled *in vacuo* to give heptafluoronitropropane (0·82 g., 78%) (Found: C, 16·9; N, 6·7%; *M*, 216. Calc. for $C_3O_2NF_7$: C, 16·8; N, 6·5%; *M*, 215), heptafluoronitrosopropane (0·52 g., 35%), and carbon dioxide. The vapour pressure equation of the nitro-compound, determined over the range −26° to 23°, is $\log_{10} p(\text{mm.}) = 7{\cdot}865 - 1491/T$, whence the calculated b. p. is 26·0°, the latent heat of vaporisation is 6820 cals./mole, and Trouton's constant is 22·8. Haszeldine[1] gives b. p. 26°.

Pentafluoronitrosoethane was similarly converted into pentafluoronitroethane[1] in good yield.

Photochemical Reaction of Heptafluoroiodopropane with Dinitrogen Tetroxide.—The iodo-compound (0·500 g., 1·7 mmole) and dinitrogen tetroxide (0·370 g., 8·0 mmole) in a 50 ml. sealed tube were exposed to ultraviolet light (24 hr.). The excess of dinitrogen tetroxide was removed by treatment with mercury, and fractionation of the volatile products *in vacuo* gave heptafluoronitropropane (0·138 g., 38%), pentafluoronitroethane (0·018 g., 7%), trifluoronitromethane (0·033 g., 17%), carbonyl fluoride, carbon dioxide, and silicon tetrafluoride. The products were identified by infrared spectroscopic examination. Small amounts of trifluoronitrosomethane were detected spectroscopically in the most volatile fraction which was blue.

*Perfluoro-*1 : 1′*-azoxypropane.*—Heptafluoronitrosopropane (2·5 g., 12·5 mmole) and active carbon (5 g.; activated by heating at 150° *in vacuo* for 2 hr.) were sealed in a 200 ml. tube in absence of air, then heated at 70° in the dark (5 days). The contents of two such tubes were combined and fractionated, to give heptafluoronitropropane (identified spectroscopically) and *perfluoro-*1 : 1′*-azoxypropane* (1·3 g., 3·4 mmole; 27% based on heptafluoronitrosopropane). The last product was dried over calcium oxide (0·2 g.), then fractionated *in vacuo*, to give the pure compound, b. p. 94·5° (isoteniscope) (Found: C, 19·0; N, 7·1%; *M*, 378. $C_6ON_2F_{14}$ requires C, 18·9; N, 7·3%; *M*, 382).

Hydrolyses.—(a) *Heptafluoronitrosopropane.* The nitroso-compound (0·99 g., 0·5 mmole) and 10% aqueous sodium hydroxide (5 ml.), sealed in a 50 ml. Pyrex tube in absence of air and shaken mechanically at room temperature in the dark until the blue colour disappeared (12 hr.), gave a solution which contained nitrite, fluoride, and carbonate ions. Neutralisation of the aqueous solution by nitric acid was followed by treatment with 20-vol. hydrogen peroxide (0·5 ml.) and silver nitrate (1 g.). Extraction by moist ether of the solid obtained by evaporation of the aqueous solution to dryness gave silver pentafluoropropionate (0·051 g., 0·22 mmole; 44%) and silver trifluoroacetate (0·034 g., 0·14 mmole; 28%), identified and analysed spectroscopically. A control experiment showed that 80% of a perfluoro-acid was recovered as silver salt by this procedure, and if corrected by this factor the above yields become 55 and 35% respectively.

(b) *Heptafluoronitropropane.* The nitro-compound (0·077 g., 0·37 mmole) and 20% aqueous sodium hydroxide (5 ml.) were sealed in a 20 ml. Pyrex tube in absence of air and heated at 120° for 30 hr. The tube was attacked and a gelatinous precipitate of silicate was apparent. Fractionation of the volatile products gave unchanged heptafluoronitropropane (0·076 g., 0·355 mmole; 99%) (Found: *M*, 212. Calc. for $C_3O_2NF_7$: *M*, 215).

(c) *Trifluoronitromethane.* The nitro-compound (0·101 g., 0·88 mmole) and 10% aqueous sodium hydroxide (1 ml.) failed to react at 70° (20 hr.), and trifluoronitromethane (0·100 g., 99%) (Found: *M*, 115. Calc. for CO_2NF_3: *M*, 115) was recovered.

Reaction of Heptafluoronitrosopropane with Tetrafluoroethylene.—In a typical experiment, heptafluoronitrosopropane (1·99 g., 10 mmole) and tetrafluoroethylene (1·05 g., 10·5 mmole) were sealed in a 250 ml. Pyrex tube in absence of air and heated at 80° in absence of light until the gas was nearly colourless (4 days). The volatile products were fractionated *in vacuo*, to give unchanged reactants (5%) and *perfluoro-*2-n-*propyl-*1 : 2*-oxazetidine* (1·80 g., 6·0 mmole;

63%), b. p. 50·5° (isoteniscope) (Found : C, 20·2; N, 4·7%; *M*, 302. C_5ONF_{11} requires C, 20·0; N, 4·7%; *M*, 299). The reaction vessel also contained an involatile colourless viscous oil which was a 1 : 1 *copolymer* of heptafluoronitrosopropane and tetrafluoroethylene [Found : C, 20·0; N, 5·0%. $(C_5ONF_{11})_n$ requires C, 20·0; N, 4·7%].

Effect of Conditions on the Heptafluoronitrosopropane–Tetrafluoroethylene Reaction.—(a) *Temperature.* Heptafluoronitrosopropane (0·495 g., 2·49 mmole) and tetrafluoroethylene (0·260 g., 2·6 mmole), sealed in a 40 ml. Pyrex tube in absence of air and kept in the dark at 20° (4 days), gave unchanged reactants (10%), perfluoro-2-propyl-1 : 2-oxazetidine (0·105 g., 0·35 mmole; 15%), and the colourless viscous polymer (0·5 g., 75%).

A parallel reaction carried out at 70° (24 hr.) gave unchanged reactants (10%), perfluoro-2-propyl-1 : 2-oxazetidine (75%), and the polymer (15%). The polymer was noticeably less viscous than that obtained by experiments at lower temperatures.

(b) *Catalysts.* In a series of experiments carried out under controlled conditions, heptafluoronitrosopropane (0·615 g., 3·1 mmole) and tetrafluoroethylene (0·310 g., 3·1 mmole) were sealed in a 50 ml. Pyrex tube containing the catalyst under investigation. The tube was warmed rapidly to room temperature, and placed in an oven at 30° for 24 hr. Both reactants were thus in the vapour phase. Reaction was then stopped by cooling in liquid oxygen, and the volatile products were fractionated rapidly *in vacuo*. Unchanged reactants and the oxazetidine were identified by their b. p. and molecular weight. The weight of polymer produced was obtained by weighing the reaction tube, then removing the polymer by pyrolysis, after which the tube was reweighed.

Results, which are reproducible to 2%, are given in the annexed Table.

	Control	Glass wool [1]	U.V. light [2]	$Bu^t_2O_2$ [3]	Quinol [3]
Reaction (%) after 24 hr.	52	50	56	62	26
Yield of oxazetidine based on reactants used	37	38	25	25	83
Ratio, polymer/oxazetidine	1·7	1·6	3·0	3·0	0·2

[1] Reaction tube packed with Pyrex glass wool. [2] Pyrex reaction tube exposed to radiation from a Hanovia ultraviolet lamp for 10 min. [3] 7% by weight of total reactants.

Pyrolysis of the Heptafluoronitrosopropane–Tetrafluoroethylene Copolymer.—The polymer (0·350 g.) in a silica tube was heated in absence of air at 450—500° at 10^{-3} mm., the technique described earlier[2] being used, and the pyrolysate was condensed in a trap cooled by liquid oxygen. Fractionation of the products gave unchanged polymer, carbonyl fluoride (0·046 g., 0·7 mmole) (Found : *M*, 66. Calc. for COF_2 : *M*, 66), and *perfluoro(methylene-*n*-propylamine)* (1·63 g., 0·7 mmole) (Found : C, 20·7; N, 5·8%; *M*, 234. C_4NF_9 requires C, 20·6; N, 6·0%; *M*, 233). The conversion was 60%, *i.e.*, essentially quantitative after allowance for the recovered polymer. The vapour pressure of perfluoro(methylene-n-propylamine), determined over the range −23° and 18°, is given by the equation $\log_{10} p$(mm.) = 7·827 − 1478/*T*, whence the b. p. is calculated as 25·6°, the latent heat of vaporisation is 6760 cals./mole and Trouton's constant is 22·5.

*Pyrolysis of Perfluoro-*2-n-*propyl-*1 : 2-*oxazetidine.*—The oxazetidine (0·33 g., 1·1 mmole) was passed at 5 mm. pressure and in absence of air through a silica tube of 15 mm. internal diameter, heated at 550—600° over a length of 30 cm. (15 min.). There was no reaction at 450°. The products were fractionated *in vacuo*, to give carbonyl fluoride (0·074 g., 1·12 mmole) (Found : *M*, 67. Calc. for COF_2 : *M*, 66) and perfluoro(methylene-*n*-propylamine) (0·245 g., 1·05 mmole; 96%). The infrared spectrum of the last compound was identical with that of the compound obtained by pyrolysis of the polymer.

*Reactions of Perfluoro(methylene-*n*-propylamine).*—(a) *With an excess of water.* The compound (0·10 g., 0·44 mmole) and water (0·5 g., 28 mmole), sealed in a 5 ml. Pyrex tube in absence of air, reacted with effervescence as the tube warmed to room temperature and two liquid phases could be seen. After 5 min. the tube suddenly became warm and crystals appeared; there was apparently no further change on storage. Fractionation of the volatile products gave carbon dioxide (0·13 mmole) and pentafluoropropionitrile (0·20 mmole, 45%), both identified by means of their infrared spectra. The crystalline material was spectroscopically identified as pentafluoropropionamide (*ca.* 0·12 mmole, 27%), contaminated by ammonium pentafluoropropionate (*ca.* 0·03 mmole, 7%).

In a second experiment, perfluoro(methylenepropylamine) (0·47 mmole) and water (28 mmole), sealed in a 5 ml. tube in absence of air, reacted as above to give two liquid phases. The volatile products were at once fractionated, to give unchanged perfluoro(methylenepropylamine) (0·19 mmole, 41%), heptafluoropropyl *iso*cyanate (0·05 mmole, 17%), carbon dioxide (0·11 mmole), and pentafluoropropionitrile (0·11 mmole, 40%).

(b) *With a deficit of water.* Perfluoro(methylenepropylamine) (0·091 g., 0·39 mmole) was sealed in absence of air in a 5 ml. tube which was attached by rubber tubing to a 3 l. flask which was then evacuated. Water (0·029 g., 1·6 mmole) was introduced into the flask, and in this volume was all in the vapour phase. The tip of the tube containing the perfluoro(methylenepropylamine) was then broken so that this compound entered the reaction flask and mixed rapidly with water vapour. After 32 hr. the contents of the flask were fractionated *in vacuo*, to give water, perfluoro(methylenepropylamine) (0·052 g., 0·22 mmole), and heptafluoropropyl *iso*cyanate (0·034 g., 0·16 mmole); the products were identified and analysed by means of their molecular weight and infrared spectra. The yield of heptafluoropropyl *iso*cyanate calculated on the basis of perfluoro(methylenepropylamine) used (44%) is quantitative within the experimental error. The preparation and infrared spectrum of heptafluoropropyl *iso*cyanate are discussed in the following paper.

(c) *With glass.* Perfluoro(methylenepropylamine) (0·072 g., 0·31 mmole) and powdered Pyrex glass (0·2 g.) were heated at 160° in a 5 ml. Pyrex tube in absence of air or moisture (27 hr.), to give unchanged perfluoro(methylenepropylamine), silicon tetrafluoride, and heptafluoropropyl *iso*cyanate (*ca.* 20%), all identified by means of their infrared spectra.

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