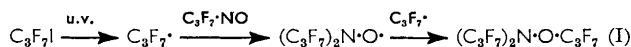**1326.** *Perfluoroalkyl Derivatives of Nitrogen. Part XIX.*[1] *Synthesis, Pyrolysis, and Nuclear Magnetic Resonance Evidence for Restricted Inversion at the Nitrogen Atom of Trisheptafluoro-n-propylhydroxylamine*
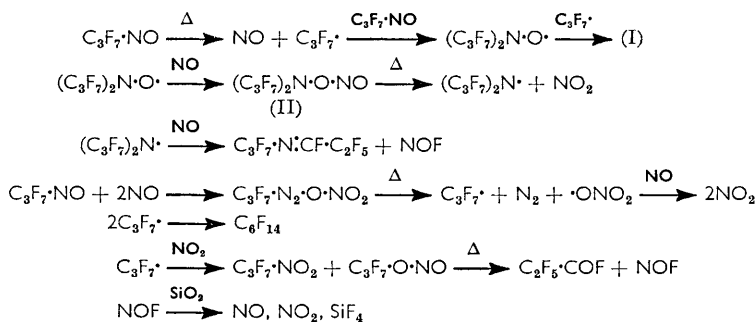
By R. E. BANKS, M. G. BARLOW, R. N. HASZELDINE, and M. K. McCREATH

The ^{19}F n.m.r. spectrum at room temperature of trisheptafluoro-n-propylhydroxylamine, obtained in high yield from heptafluoro-1-nitroso-propane by photochemical reaction with heptafluoro-1-iodopropane or by pyrolysis, is explained in terms of restricted inversion at the nitrogen atom. The products arising by pyrolysis of trisheptafluoro-n-propylhydroxylamine are identified and discussed.

TRISHEPTAFLUORO-n-PROPYLHYDROXYLAMINE (I), a colourless liquid, b. p. $128°/770$ mm., is obtained in 82% yield by photolysis of heptafluoro-1-iodopropane in the presence of heptafluoro-1-nitrosopropane (cf. the preparation of tristrifluoromethylhyroxylamine [2]):

$$C_3F_7I \xrightarrow{\text{u.v.}} C_3F_7 \cdot \xrightarrow{C_3F_7 \cdot NO} (C_3F_7)_2N \cdot O \cdot \xrightarrow{C_3F_7 \cdot} (C_3F_7)_2N \cdot O \cdot C_3F_7 \quad (I)$$

Compound (I) is also formed (88% yield based on 91% conversion) when heptafluoro-1-nitrosopropane is pyrolysed in platinum at $250°/7$—9 mm.; this, and the minor products observed, could arise as follows:

$$C_3F_7 \cdot NO \xrightarrow{\Delta} NO + C_3F_7 \cdot \xrightarrow{C_3F_7 \cdot NO} (C_3F_7)_2N \cdot O \cdot \xrightarrow{C_3F_7 \cdot} (I)$$

$$(C_3F_7)_2N \cdot O \cdot \xrightarrow{NO} (C_3F_7)_2N \cdot O \cdot NO \xrightarrow{\Delta} (C_3F_7)_2N \cdot + NO_2$$
$$\text{(II)}$$

$$(C_3F_7)_2N \cdot \xrightarrow{NO} C_3F_7 \cdot N \ddot{:} CF \cdot C_2F_5 + NOF$$

$$C_3F_7 \cdot NO + 2NO \longrightarrow C_3F_7 \cdot N_2 \cdot O \cdot NO_2 \xrightarrow{\Delta} C_3F_7 \cdot + N_2 + \cdot ONO_2 \xrightarrow{NO} 2NO_2$$

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

$$C_3F_7 \cdot \xrightarrow{NO_2} C_3F_7 \cdot NO_2 + C_3F_7 \cdot O \cdot NO \xrightarrow{\Delta} C_2F_5 \cdot COF + NOF$$

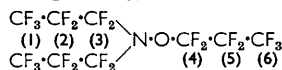$$NOF \xrightarrow{SiO_2} NO, NO_2, SiF_4$$

[1] Part XVIII, R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J.*, 1965, 6149.
[2] A. H. Dinwoodie and R. N. Haszeldine, *J.*, 1965, 1681.

Thermal degradation of *O*-nitrosobisheptafluoro-n-propylhydroxylamine (II) *via* $(C_3F_7)_2N$–O fission is suggested by analogy with the mode of breakdown of its homologue $(CF_3)_2N\cdot O\cdot NO$;[2] perfluoronitrosoalkanes react with nitric oxide to yield nitrogen dioxide, possibly *via* a diazonium nitrate intermediate;[3] perfluoroalkyl radicals are known to react with nitrogen dioxide to yield perfluoronitroalkanes and perfluoroalkyl nitrites;[4] and the last readily decompose to nitrosyl fluoride and a carbonyl compound.[5]

Spectroscopic Properties of Trisheptafluoro-n-propylhydroxylamine.—The mass spectrum of trisheptafluoro-n-propylhydroxylamine, which is characterised by the occurrence of a series of peaks corresponding to $C_nF_{2n}NO^+$ ions (where $n = 2$—6), shows a very weak parent ion (relative abundance 0·04%). The base peak is due to CF_3^+ at *m/e* 69, and is only slightly more intense than that due to the $C_3F_7^+$ ion; a peak due to $C_2F_5^+$ is also prominent. Two metastable peaks at mass numbers 324 and 126 are assigned to the processes $C_7F_{16}NO^+(418) \longrightarrow C_6F_{14}NO^+(368) + CF_2(50)$ and $C_4F_8NO^+(230) \longrightarrow C_3F_7^+(169) + CFNO(61)$.

The ^{19}F n.m.r. spectrum of trisheptafluoro-n-propylhydroxylamine at room temperature shows five absorption regions (i—v) that exhibit certain unusual features. Absorption region (i) is an unsymmetrical quintet (relative intensities = $2:4:3:2:1$; total integrated intensity 9·0) and is ascribed to two overlapping triplets, the one at lower field (81·9 ϕ^*;[6] 10·1 c./sec. splitting) being assigned to the fluorine nuclei of type (1) and that at higher field (82·2 ϕ^*; 6·1 c./sec. splitting) to the fluorine nuclei of type (6), which are

$$\begin{array}{c} CF_3\cdot CF_2\cdot CF_2 \\ (1)\ (2)\ (3) \\ CF_3\cdot CF_2\cdot CF_2 \end{array}\!\!\!\!\!\diagdown\!\!\!\diagup N\cdot O\cdot CF_2\cdot CF_2\cdot CF_3 \quad\begin{array}{c} \\ (4)\ (5)\ (6) \\ \ \end{array}$$

coupled to the fluorines of type (3) and (4), respectively. Absorption region (ii) (88·8 ϕ^*; intensity 2·0) is either a broad octet (relative intensities $1·0:2·2:4·4:6·6:6·6:4·6:2·5:1·0$; splitting *ca.* 8·0 c./sec.) or, possibly, a decet with very weak outer members; it is assigned to the fluorine nuclei of type (4), although this structure is not readily explained. Absorption region (iii), centred at 96·0 ϕ^* (intensity 4·0), appears as an AB quartet ($\sigma_A - \sigma_B = 4·31$ p.p.m.; $J_{AB} = 230$ c./sec.) with very broad individual bands (widths at half height: low field doublet *ca.* 56 c./sec; high field doublet *ca.* 48 c./sec.); this is assigned to the fluorine nuclei of type (3), the non-equivalence of the fluorines within each CF_2 group being ascribed to the asymmetry of substitution at the nitrogen atom. Absorption region (iv) (125·0 ϕ^*; intensity 4·0), a broadened heptet (relative intensities $1·0:3·7:7·0:8·0:5·9:3·3:1·1$; splitting 8·6 c./sec.), is assigned to the fluorine nuclei of type (2), and is tentatively analysed as being basically an AB quartet; each component of this quartet is split into a $1:4:6:4:1$ quintet with two inner components 17 c./sec. apart and two outer components that are only just discernible above the background. Region (v) (129·1 ϕ^*; intensity 2·0) appears as a broadened singlet (width at half height 5·7 c./sec.) that shows evidence of unresolved fine structure and is assigned to the fluorine nuclei of type (5).

The splitting into two triplets of absorption region (i) is probably due to coupling to the fluorines of types (3) and (4), since coupling of a CF_3 group to the adjacent CF_2 group in a heptafluoro-n-propyl group is small.[7] The fluorines of a CF_2 group removed by one or more bonds from a centre of molecular asymmetry, in this case the nitrogen with its lone-pair and the substituents n-C_3F_7 and n-$C_3F_7\cdot O$, may show magnetic non-equivalence. The origin of this type of non-equivalence has been discussed by many workers.[8] The broadness of the components of absorption region (iii) may be due to one or more of the following

[3] D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J.*, 1961, 1351; J. M. Birchall, A. J. Bloom, R. N. Haszeldine, and C. J. Willis, *J.*, 1962, 3021.
[4] I. L. Knunyants and A. V. Fokin, *Doklady Akad. Nauk S.S.S.R.*, 1956, **111**, 1035; 1957, **112**, 67.
[5] S. Andreades, *J. Org. Chem.*, 1962, **27**, 4157.
[6] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, 1959, **63**, 761.
[7] L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, 1961, **35**, 1243.
[8] E. I. Snyder, *J. Amer. Chem. Soc.*, 1963, **85**, 2624; G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 2628, and refs. therein.

causes: (*a*) coupling to the fluorine nuclei of the CF_3 group (type 1); (*b*) coupling of the fluorines (type 3) of one CF_2 group across the nitrogen atom to the other corresponding CF_2 group is not negligible, and gives rise to further unresolved lines, *i.e.*, to an AA'BB' type spectrum rather than to a superposition of two AB quartets; (*c*) appreciable coupling to the fluorine nuclei of type (4) (in tristrifluoromethylhydroxylamine an F–F coupling of 5·2 c./sec. is observed[2]); (*d*) the fluorine of one CF_2 group (type 3), although expected to be only weakly coupled to those (type 2) of the adjacent CF_2 group,[7] may be appreciably coupled to those of the corresponding CF_2 group in the other side-chain; (*e*) inversion at the nitrogen is occurring at an intermediate rate (see below); and (*f*) incomplete collapse by intermediate quadrupole relaxation of coupling to ^{14}N.

In the absence of inversion at the nitrogen atom, the configuration $C_2F_5 \cdot CF_2 \cdot N(OC_3F_7) \cdot CF_2 \cdot C_2F_5$ can exist in nine staggered interconvertible rotamer conformations about the two C–N bonds: three with effectively C_s symmetry, and three mirror-image pairs of C_1 symmetry. These conformations (I—IX) are shown in the annexed Figure; the fluorine nuclei of the CF_2 groups are labelled F_A–F_D, the C_2F_5 groups are denoted by P for clarity, and the O refers to the n-$C_3F_7 \cdot O$ substituent. The populations of (I—IX) and the chemical shifts of the individual fluorine nuclei are listed in Table 1. Averaging of the effective chemical shifts (δ_A to δ_D) of the four fluorine nuclei of the two CF_2 groups over conformations (I—IX) leads to the conclusions (i) that

$$\delta_A = \delta_D = p_1\delta_{1A} + p_2\delta_{2A} + p_3\delta_{3A} + p_4(\delta_{4A} + \delta_{4D}) + p_5(\delta_{5A} + \delta_{5D}) + p_6(\delta_{6A} + \delta_{6D})$$
$$\delta_B = \delta_C = p_1\delta_{1B} + p_2\delta_{2B} + p_3\delta_{3B} + p_4(\delta_{4B} + \delta_{4C}) + p_5(\delta_{5B} + \delta_{5C}) + p_6(\delta_{6B} + \delta_{6C})$$

and (ii) that their spectrum will be of the AA'BB' type, even if rotation is rapid, and even if the conformations are all equally populated (*i.e.*, $p_1 = p_2 = \ldots = p_6$).

Inversion at the nitrogen allows access to a further nine conformations (X—XVIII), each of which corresponds to one of the above conformations (I—IX) with the positions of F_A and F_B and of F_C and F_D interchanged. When both inversion and rotation are rapid,
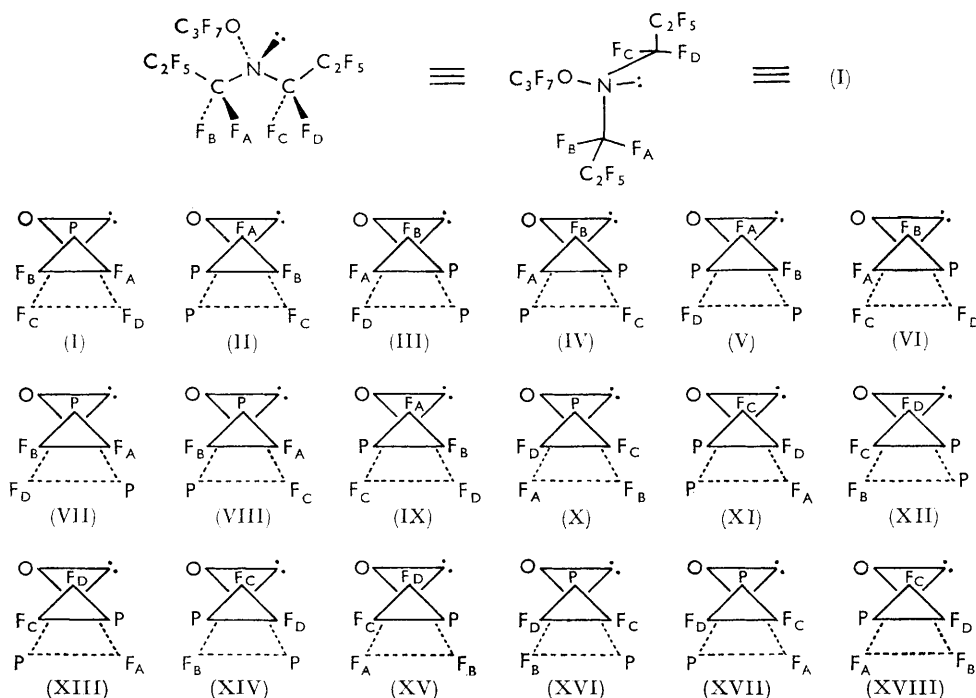
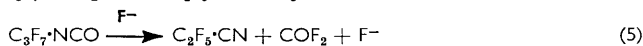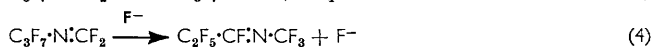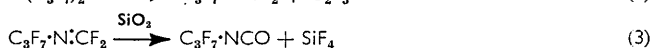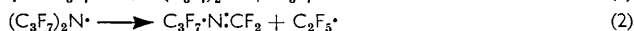Rotamer conformations of trisheptafluoro-n-propylhydroxylamine

TABLE 1

| Conformation	Symmetry	Population	Chemical shifts			
			F_A	F_B	F_C	F_D
I	C_s	p_1	δ_{1A}	δ_{1B}	δ_{1B}	δ_{1A}
II	C_s	p_2	δ_{2A}	δ_{2B}	δ_{2B}	δ_{2A}
III	C_s	p_3	δ_{3A}	δ_{3B}	δ_{3B}	δ_{3A}
IV	C_1	p_4	δ_{4A}	δ_{4B}	δ_{4C}	δ_{4D}
V	C_1	p_4	δ_{4D}	δ_{4C}	δ_{4B}	δ_{4A}
VI	C_1	p_5	δ_{5A}	δ_{5B}	δ_{5C}	δ_{5D}
VII	C_1	p_5	δ_{5D}	δ_{5C}	δ_{5B}	δ_{5A}
VIII	C_1	p_6	δ_{6A}	δ_{6B}	δ_{6C}	δ_{6D}
IX	C_1	p_6	δ_{6D}	δ_{6C}	δ_{6B}	δ_{6A}
X	C_s	p_1	δ_{1B}	δ_{1A}	δ_{1A}	δ_{1B}
XI	C_s	p_2	δ_{2B}	δ_{2A}	δ_{2A}	δ_{2B}
XII	C_s	p_3	δ_{3B}	δ_{3A}	δ_{3A}	δ_{3B}
XIII	C_1	p_4	δ_{4C}	δ_{4D}	δ_{4A}	δ_{4B}
XIV	C_1	p_4	δ_{4B}	δ_{4A}	δ_{4D}	δ_{4C}
XV	C_1	p_5	δ_{5C}	δ_{5D}	δ_{5A}	δ_{5B}
XVI	C_1	p_5	δ_{5B}	δ_{5A}	δ_{5D}	δ_{5C}
XVII	C_1	p_6	δ_{6C}	δ_{6D}	δ_{6A}	δ_{6B}
XVIII	C_1	p_6	δ_{6B}	δ_{6A}	δ_{6D}	δ_{6C}

the effective chemical shifts are averaged over all eighteen conformations (I—XVIII), leading to $\delta_A = \delta_B = \delta_C = \delta_D$ and the equivalence of the four fluorine nuclei. That this is not so at room temperature indicates that inversion is restricted: trisheptafluoro-n-propylhydroxylamine appears to be the first reported example of an open-chain nitrogen compound showing this effect.

It has been reported very recently that the iodophosphine $(n-C_3F_7)_2PI$ shows magnetic non-equivalence of the fluorine nuclei of the CF_2 group α to the phosphorus, although the corresponding chloro- and fluoro-phosphines do not.[9] Restricted inversion at a nitrogen atom has been detected by n.m.r. spectroscopy for N-ethylethyleneimine at room temperature,[10] and for N-ethylalleneimine [10] and certain polyfluoro-oxazetidines [11] at low temperatures.

*Pyrolysis of Trisheptafluoro-*n-*propylhydroxylamine.*—The hydroxylamine is decomposed to the extent of only 8% when heated at 260° for 24 hr. in a Pyrex ampoule, but at 310° during 6 hr. it undergoes 70% decomposition to give perfluoro-n-butane (100%), perfluoro-(n-propylidenemethylamine) (55%), heptafluoro-n-propyl isocyanate (10%), pentafluoro-propionitrile (35%), pentafluoropropionyl fluoride (7%), carbonyl fluoride (24%), carbon dioxide, and silicon tetrafluoride; yields in parentheses are based on the following suggested reaction scheme:

$$(C_3F_7)_2N\text{-}\dot{\cdot}\text{-}O\cdot C_3F_7 \xrightarrow{\Delta} (C_3F_7)_2N\cdot + C_3F_7\cdot O\cdot \tag{1}$$

$$(C_3F_7)_2N\cdot \longrightarrow C_3F_7\cdot N\dot{\cdot}CF_2 + C_2F_5\cdot \tag{2}$$

$$C_3F_7\cdot N\dot{\cdot}CF_2 \xrightarrow{SiO_2} C_3F_7\cdot NCO + SiF_4 \tag{3}$$

$$C_3F_7\cdot N\dot{\cdot}CF_2 \xrightarrow{F^-} C_2F_5\cdot CF\dot{\cdot}N\cdot CF_3 + F^- \tag{4}$$

$$C_3F_7\cdot NCO \xrightarrow{F^-} C_2F_5\cdot CN + COF_2 + F^- \tag{5}$$

$$C_3F_7\cdot O\cdot \longrightarrow C_2F_5\cdot + COF_2 \tag{6}$$

$$2C_2F_5\cdot \longrightarrow n\text{-}C_4F_{10} \tag{7}$$

$$COF_2 \xrightarrow{SiO_2} CO_2 + SiF_4 \tag{8}$$
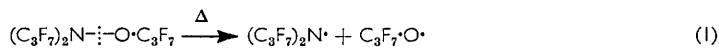
Neither perfluoro-(N-fluorodi-n-propylamine) nor perfluoro(propylidene-n-propylamine) was detected among the products, so disproportionation of the $(C_3F_7)_2N\cdot$ radicals:

$$2(C_3F_7)_2N\cdot \longrightarrow (C_3F_7)_2NF + C_3F_7\cdot N\dot{\cdot}CF\cdot C_2F_5$$
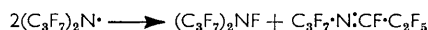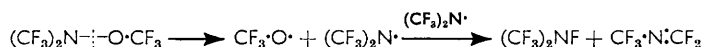
[9] J. F. Dixon, *J.*, 1965, 777.
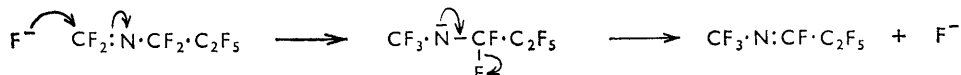[10] A. J. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 5126; 1958, **80**, 5203.
[11] S. Andreades, *J. Org. Chem.*, 1962, **27**, 4163; J. Lee and K. G. Orrell, to be published.

formed in (1) did not occur. This is in contrast to the thermal decomposition of tristri-fluoromethylhydroxylamine at 775° under flow conditions in silica: [2]

$$(CF_3)_2N\text{-}\!|\text{-}O\cdot CF_3 \longrightarrow CF_3\cdot O\cdot + (CF_3)_2N\cdot \xrightarrow{\text{(CF}_3)_2N\cdot} (CF_3)_2NF + CF_3\cdot N\!:\!CF_2$$

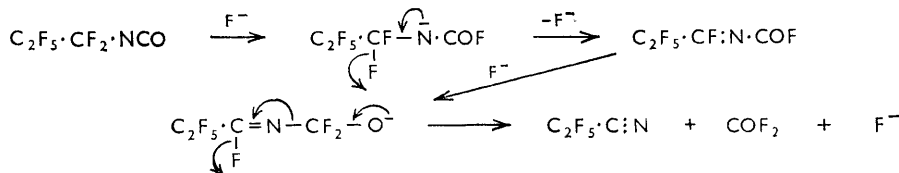but in this case stabilisation by C–C cleavage [cf. step (2)] cannot occur.

No perfluoro(methylene-n-propylamine) [formed in (2), isomerised in (4) by sources of fluoride ion formed by etching of the reaction vessel] was detected; in a separate experiment, this amine was converted by reaction with anhydrous potassium fluoride in Pyrex into a mixture of perfluoro-(n-propylidenemethylamine) (55% yield), pentafluoropropionitrile (29%), pentafluoropropionyl fluoride (3%), heptafluoro-n-propyl isocyanate (0·5%), carbon dioxide, and silicon tetrafluoride. Fluoride ion-catalysed isomerisation of a compound of the type $R_F CF_2\cdot N\!:\!CF_2$ to $R_F\cdot CF\!:\!N\cdot CF_3$ (R_F = perfluoroalkyl):

$$F^-\ \overset{\frown}{CF_2}\!:\!N\cdot CF_2\cdot C_2F_5 \longrightarrow CF_3\cdot \overset{\frown}{N}\!\!-\!\!CF\cdot C_2F_5 \longrightarrow CF_3\cdot N\!:\!CF\cdot C_2F_5\ +\ F^-$$

does not appear to have been effected deliberately previously, although it has been postulated to account for the formation of perfluoro-(n-butylidenemethylamine) and not perfluoro-(methylene-n-butylamine) by pyrolysis of undecafluoropiperidine over iron–ferric fluoride mixtures [12] and by pyrolysis of tris(nonafluoro-n-butylamine) in a carbon tube packed with metal fluorides.[13] Isomerisation of perfluoro-α-olefins in the presence of metal fluorides has been studied, e.g.,[14]

$$CF_3\cdot [CF_2]_4\cdot CF\!:\!CF_2 \xrightarrow{\text{KF, 250°}} CF_3\cdot [CF_2]_3\cdot CF\!:\!CF\cdot CF_3\ (99\%)$$
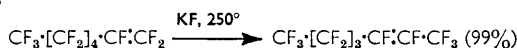
Conversion of heptafluoro-n-propyl isocyanate [formed in (3)] into pentafluoropropio-nitrile [in (5)] by fluoride ion possibly follows the pathway:

$$C_2F_5\cdot CF_2\cdot NCO \xrightarrow{F^-} C_2F_5\cdot CF\!\!-\!\!N\cdot COF \xrightarrow{-F^-} C_2F_5\cdot CF\!:\!N\cdot COF$$

$$C_2F_5\cdot C\!=\!N\!-\!CF_2\!-\!O^- \longrightarrow C_2F_5\cdot C\!:\!N\ +\ COF_2\ +\ F^-$$

EXPERIMENTAL

Products were separated by trap-to-trap fractional condensation *in vacuo* or by precise distillation, and were identified by molecular-weight determination (Regnault's method), infrared spectroscopy (Perkin-Elmer spectrometer model 21 with sodium chloride optics), nuclear magnetic resonance spectroscopy (A.E.I. RS2 spectrometer operating at 60 Mc./sec.), mass spectrometry (A.E.I. MS/2H instrument), and gas–liquid chromatography (Perkin-Elmer " Vapor Fraktometer," model 116). Molar % compositions of mixtures were calculated from gas-chromatographic peak areas by triangulation, and columns used (mainly packed with 30% Kel-F No. 1 oil–Celite) were calibrated with known mixtures.

Heptafluoro-1-nitrosopropane was prepared by pyrolysis of heptafluoro-n-butyryl nitrite,[15] heptafluoro-1-iodopropane by pyrolysis of a mixture of iodine and silver heptafluoro-n-butyrate,[16] and perfluoro(methylene-n-propylamine) by pyrolysis of perfluoro-(2-n-propyl-1,2-oxazetidine).[17]

Preparation of Trisheptafluoro-n-propylhydroxylamine.—(a) *By pyrolysis of heptafluoro-1-nitrosopropane.* Heptafluoro-1-nitrosopropane (7·25 g., 36·4 mmoles) was passed at 7—9 mm.

[12] R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J.*, 1962, 3407; W. M. Cheng, Ph.D. Thesis, Manchester, 1963.

[13] W. H. Pearlson and L. J. Hals, U.S.P. 2,643,267/1953; a personal communication from Dr. F. W. Hoffman is gratefully acknowledged.

[14] H. H. Gibbs, U.S.P. 3,000,979/1961.

[15] R. E. Banks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 1961, 64; R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, publication in preparation.

[16] R. N. Haszeldine, *J.*, 1951, 584.

[17] D. A. Barr and R. N. Haszeldine, *J.*, 1955, 1881; 1956, 3416.

pressure through a 100×0.9 cm. platinum tube heated to $250°$ over 55 cm. of its length during 80 min. The product was collected in a series of traps cooled to -45, -95, -131, and $-196°$, severally, so as to avoid condensing together nitric oxide and unchanged nitroso-compound, which interact very rapidly in the liquid phase;[3] the material which condensed at $-131°$ (mainly $C_3F_7 \cdot NO$) was then recycled (three times). The final product consisted of unchanged nitroso-compound (3·1 mmoles; 8·5% recovery) and *trisheptafluoro-n-propylhydroxylamine* (5·25 g., 9·78 mmoles; 88% based on $C_3F_7 \cdot NO$ consumed), nitric oxide (20·0 mmoles; 60%), nitrogen dioxide (0·2 mmole; 0·5%), pentafluoropropionyl fluoride (0·4 mmole; 1%), heptafluoro-1-nitropropane (2·2 mmoles; 7%), perfluoro-n-hexane (0·3 mmole; 2%), and perfluoro-propylidene-n-propylamine (0·25 mmole; 1·5%), that was spectroscopically (infrared) and chromatographically identical with an authentic sample,[18] together with traces of the compounds CO_2, COF_2, N_2O, SiF_4 (from attack on the glass traps used), and unidentified products containing $C\ddot{:}N$ or NCO (absorption at $4·35~\mu$) and $N\ddot{:}CF_2$ or $N \cdot O \cdot NO$ (absorption at $5·51~\mu$) groups. Chromatographically-pure trisheptafluoro-n-propylhydroxylamine (Found: C, 20·7; N, 2·8. $C_9F_{21}NO$ requires C, 20·1; N, 2·6%), b. p. (Siwoloboff) $128°/770$ mm., n_D^{20} 1·275, d_4^{20} 1·786, was readily obtained by distillation of the contents of the $-95°$ trap in a semimicro Vigreux still at atmospheric pressure.

(b) *By irradiation of heptafluoro-1-nitrosopropane with heptafluoro-1-iodopropane.* A mixture of heptafluoro-1-nitrosopropane (2·09 g., 10·5 mmoles) and heptafluoro-1-idodopropane (6·22 g., 21·0 mmoles) was divided into four equal portions, each of which was sealed in a 300-ml. silica tube (calculated initial pressure *ca.* 0·5 atm.) containing mercury (2 ml.). The tubes were then irradiated with ultraviolet light from a 500w Hanovia mercury vapour lamp placed 15 cm. away, and shaken occasionally. After 1 hr., the blue colour of the nitroso-compound had almost disappeared and the product consisted of unchanged heptafluoro-1-nitrosopropane (0·3 mmole; 3% recovery) and heptafluoro-1-iodopropane (2·5 mmoles; 12% recovery), together with (% yields based on $C_3F_7 \cdot NO$ consumed) trisheptafluoro-n-propylhydroxylamine (4·48 g., 8·34 mmoles; 82%), heptafluoro-1-nitropropane (0·1 mmole; 1%), pentafluoropro-pionyl fluoride (0·1 mmole; 1%) perfluoro-n-hexane (0·05 mmole; 1%), the compounds CO_2, COF, N_2O, SiF_4 (total 1·7 mmoles), and traces of unidentified compounds.

TABLE 2

Mass-spectral data for trisheptafluoro-n-propylhydroxylamine

m/e	Ion	Rel. intensity * (%)	m/e	Ion	Rel. intensity (%)
30	NO	1·95	126	C_3F_4N	0·13
31	CF	6·82	130	C_2F_4NO	0·62
47	CFO	1·38	131	C_3F_5	0·76
50	CF_2	2·22	145	C_3F_5N	0·35
64	CF_2N	0·17	150	C_3F_6	0·59
66	CF_2O	0·27	164	C_3F_6N	2·11
69	CF_3	100·0	169	C_3F_7	98·9
76	C_2F_2N	0·50	180	C_3F_6NO	0·15
78	C_2F_2O	0·15	214	C_4F_8N	3·64
81	C_2F_3	0·44	230	C_4F_8NO	3·59
85	CF_3O	0·63	264	$C_5F_{10}N$	0·21
93	C_3F_3	0·23	280	$C_5F_{10}NO$	0·11
95	C_2F_3N	0·44	314	$C_6F_{12}N$	0·48
97	C_2F_3O	0·24	330	$C_6F_{12}NO$	2·29
100	C_2F_4	6·09	368	$C_6F_{14}NO$	0·24
114	C_2F_4N	5·08	418	$C_7F_{16}NO$	0·76
119	C_2F_5	33·87	537	$C_9F_{21}NO$	0·04

* All the ions listed except the parent ion are of relative intensity $>0·10\%$. Two metastable peaks at $m/e = 324$ and 126 were observed.

The mass-spectrum of trisheptafluoro-n-propylhydroxylamine is described in Table 2; the infrared spectrum of its vapour shows no strong bands at wavelengths shorter than $7·41~\mu$, and, by analogy with tristrifluoromethylhydroxylamine,[2] the following assignments are suggested: C–F stretch at 7·41, 7·48, 7·94, 7·99, 8·26, 8·70, 8·83; N–O stretch at 9·11; C–N stretch at 10·25; $\overset{C}{\underset{C}{>}}N$ and $\overset{C}{\underset{C}{>}}C$ bending at 10·92, 11·04, 11·98, 12·41 (all weak); and C–F deformation at 13·26, 13·57, and $14·27~\mu$.

[18] R. E. Banks, W. T. Flowers, and R. N. Haszeldine, unpublished results.

Pyrolysis of Trisheptafluoro-n-propylhydroxylamine.—Trisheptafluoro-n-propylhydroxylamine (0·952 g., 1·77 mmoles), sealed in a 30-ml. Pyrex ampoule and heated at 310° for 6 hr., gave unchanged hydroxylamine (0·284 g., 0·53 mmole; 30% recovery), pentafluoropropionitrile (0·44 mmole; 35% based on hydroxylamine consumed), pentafluoropropionyl fluoride (0·09 mmole; 7%), perfluoro-n-butane (1·24 mmole; 100%), heptafluoro-n-propyl isocyanate (0·13 mmole; 10%), perfluoro(n-propylidenemethylamine) (0·68 mmole; 55%), carbonyl fluoride (0·30 mmole; 24%), carbon dioxide (1·90 mmole), and silicon tetrafluoride (0·75 mmole). Remaining in the etched reaction tube was a white, crystalline, water-soluble residue (*ca.* 0·025 g.), which gave positive tests for the ions Na^+, F^-, and SiF_6^{2-}.

In similar experiments at 235°/24 hr., 260°/3 hr., 260°/24 hr., and 295°/15 hr., trisheptafluoro-n-propylhydroxylamine suffered 0·5, 2, 8, and 44% decomposition, severally. When the oxazetidine $CF_3\cdot\overline{N\cdot O\cdot CF_2\cdot CF_2}$ or the copolymer $[-N(CF_3)\cdot O\cdot CF_2\cdot CF_2-]_n$ from reaction of trifluoronitrosomethane with tetrafluoroethylene [17] were heated at 260°/24 hr. under similar conditions, they suffered 34 and 89% decomposition, respectively.

Rearrangement of Perfluoro(methylene-n-propylamine) in the Presence of Potassium Fluoride.— Perfluoro(methylene-n-propylamine) (0·890 g., 3·82 mmoles) and anhydrous potassium fluoride (0·10 g., 1·7 mmoles), sealed in a 50-ml. Pyrex ampoule and heated at 290° for 13 hr., gave perfluoro(n-propylidenemethylamine) (2·08 mmoles; 55% yield) (Found: C, 21·0; N, 6·2%; *M*, 231. Calc. for C_4F_9N: C, 20·8; N, 6·0%; *M*, 233), spectroscopically (infrared) identical with an authentic sample,[19] pentafluoropropionyl fluoride (0·12 mmole; 3%), pentafluoropropionitrile (1·10 mmole; 29%), heptafluoro-n-propyl isocyanate (0·02 mmole; 1%), and carbon dioxide and silicon tetrafluoride (total 2·11 mmoles).

THE CHEMISTRY DEPARTMENT, FACULTY OF TECHNOLOGY,
        UNIVERSITY OF MANCHESTER.   [*Received, May 13th*, 1965.]

[19] R. N. Haszeldine and A. E. Tipping, unpublished results.