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-nitrosopropane 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]):

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

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:

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

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

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

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

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

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

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

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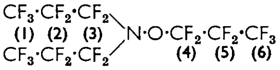
[1] Part XVIII, R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J.*, 1965, 6149.

[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 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 ($\sigma_A - \sigma_B = 4{\cdot}31$ 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).



$$\begin{array}{l} \underset{(1)}{CF_3}\cdot\underset{(2)}{CF_2}\cdot\underset{(3)}{CF_2} \searrow \\ \qquad\qquad\qquad N\cdot O\cdot\underset{(4)}{CF_2}\cdot\underset{(5)}{CF_2}\cdot\underset{(6)}{CF_3} \\ CF_3\cdot CF_2\cdot CF_2 \nearrow \end{array}$$

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

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[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.

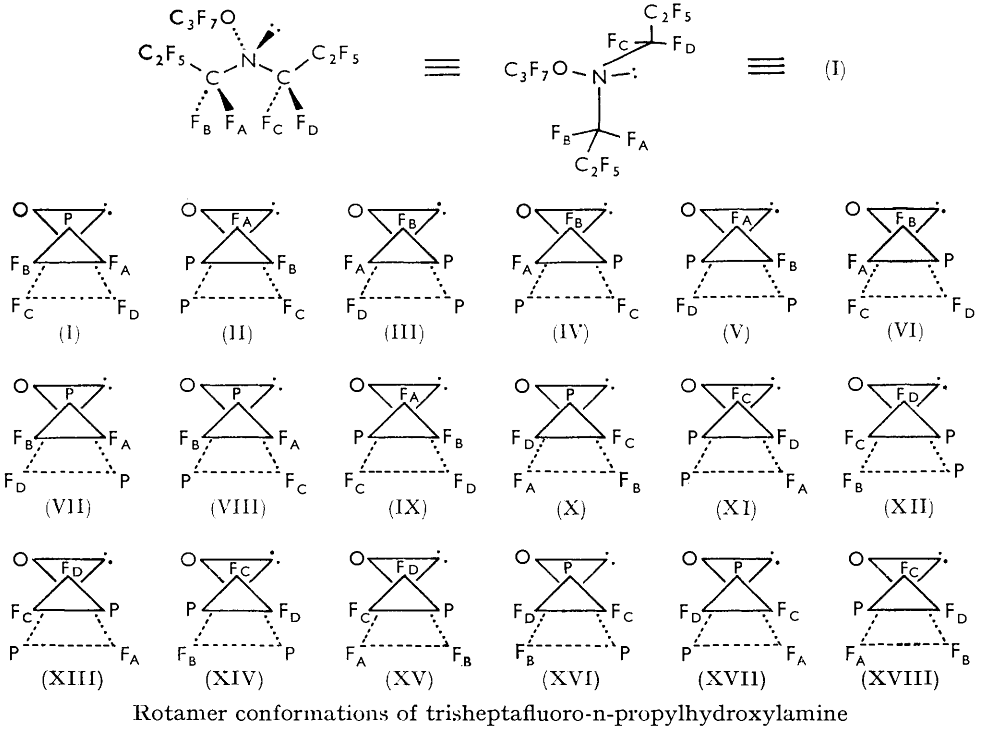
causes: (*a*) coupling to the fluorine nuclei of the CF_3 group (type 1); (*b*) coupling of the fluorines (type 3) of one CF_2 group across the nitrogen atom to the other corresponding CF_2 group is not negligible, and gives rise to further unresolved lines, *i.e.*, to an AA'BB' type spectrum rather 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 $(n\text{-}C_3F_7)_2PI$ 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%), pentafluoropropionitrile (35%), pentafluoropropionyl fluoride (7%), carbonyl fluoride (24%), carbon dioxide, and silicon tetrafluoride; yields in parentheses are based on the following suggested reaction scheme:

$$(C_3F_7)_2N\!-\!\vdots\!-\!O{\cdot}C_3F_7 \xrightarrow{\Delta} (C_3F_7)_2N{\cdot} + C_3F_7{\cdot}O{\cdot} \qquad (1)$$

$$(C_3F_7)_2N{\cdot} \longrightarrow C_3F_7{\cdot}N{:}CF_2 + C_2F_5{\cdot} \qquad (2)$$

$$C_3F_7{\cdot}N{:}CF_2 \xrightarrow{SiO_2} C_3F_7{\cdot}NCO + SiF_4 \qquad (3)$$

$$C_3F_7{\cdot}N{:}CF_2 \xrightarrow{F^-} C_2F_5{\cdot}CF{:}N{\cdot}CF_3 + F^- \qquad (4)$$

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

$$C_3F_7{\cdot}O{\cdot} \longrightarrow C_2F_5{\cdot} + COF_2 \qquad (6)$$

$$2C_2F_5{\cdot} \longrightarrow n\text{-}C_4F_{10} \qquad (7)$$

$$COF_2 \xrightarrow{SiO_2} CO_2 + SiF_4 \qquad (8)$$

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:

$$2(C_3F_7)_2N{\cdot} \longrightarrow (C_3F_7)_2NF + C_3F_7{\cdot}N{:}CF{\cdot}C_2F_5$$

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[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.

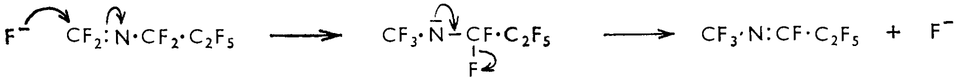
[11] S. Andreades, *J. Org. Chem.*, 1962, **27**, 4163; J. Lee and K. G. Orrell, to be published.

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

$$(CF_3)_2N\text{-}\vdots\text{-}O\cdot CF_3 \longrightarrow CF_3\cdot O\cdot + (CF_3)_2N\cdot \xrightarrow{(CF_3)_2N\cdot} (CF_3)_2NF + CF_3\cdot N{:}CF_2$$

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

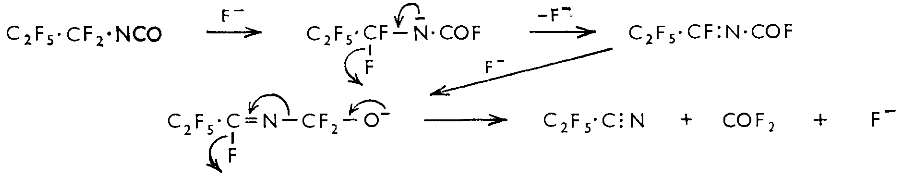
No perfluoro(methylene-n-propylamine) [formed in (2), isomerised in (4) by sources of fluoride ion formed by etching of the reaction vessel] was detected; in a separate experiment, this amine was converted by reaction with anhydrous potassium fluoride in Pyrex into a mixture of perfluoro-(n-propylidenemethylamine) (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 $R_FCF_2\cdot N{:}CF_2$ to $R_F\cdot CF{:}N\cdot CF_3$ (R_F = perfluoroalkyl):



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]

$$CF_3\cdot[CF_2]_4\cdot CF{:}CF_2 \xrightarrow{\text{KF, }250^\circ} CF_3\cdot[CF_2]_3\cdot CF{:}CF\cdot CF_3\ (99\%)$$

Conversion of heptafluoro-n-propyl isocyanate [formed in (3)] into pentafluoropropionitrile [in (5)] by fluoride ion possibly follows the pathway:



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 perfluoropropylidene-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 $C{\vdots}N$ or NCO (absorption at 4·35 μ) and $N{:}CF_2$ or $N{\cdot}O{\cdot}NO$ (absorption at 5·51 μ) 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%), pentafluoropropionyl 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 μ, 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; $\genfrac{}{}{0pt}{}{C}{C}\!>\!N$ and $\genfrac{}{}{0pt}{}{C}{C}\!>\!C$ bending at 10·92, 11·04, 11·98, 12·41 (all weak); and C–F deformation at 13·26, 13·57, and 14·27 μ.

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[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 $CF_3\cdot\overline{N\cdot O\cdot CF_2\cdot C}F_2$ 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).

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