22. *Perfluoro*-tert.-*amines.*

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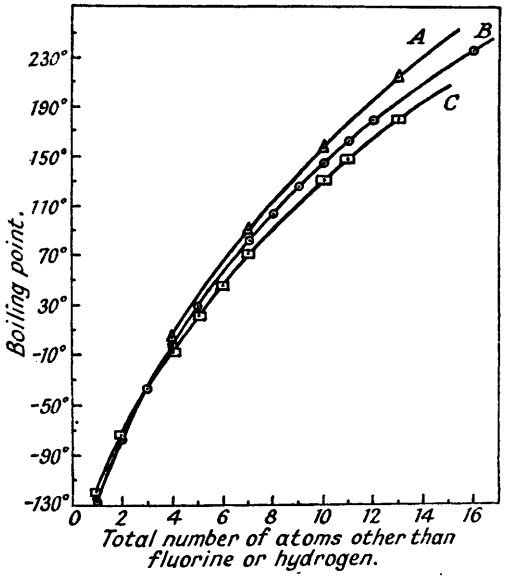
The passage of tertiary amines over cobalt trifluoride gives the corresponding perfluoro-*tert.*-amines in small yield. The physical properties of these compounds are compared with those of fluorocarbons of similar volatility.

The interaction of nitrogen-containing organic compounds and fluorine on the surface of gold-plated copper turnings, or the passage of such compounds over heated cobalt trifluoride has been shown to yield the corresponding perfluoro-compounds (Haszeldine, *J.*, 1950, 1966). A series of perfluoro-*tert.*-amines whose properties are very similar to fluorocarbons of comparable boiling point has now been prepared.



A : Tertiary amines, $C_nH_{2n+3}N$. *B : Fluorocarbons*,* $C_{n+1}F_{2n+4}$. *C : Perfluoro*-tert.-*amines*, $C_nF_{2n+3}N$.

* The boiling-point data for the fluorocarbons are from Haszeldine and Smith (*J.*, in the press).

The fluorination of the tertiary amines was accompanied by extensive decomposition and possibly by rearrangement, and the low yields of the perfluoro-*tert.*-amines are attributed in part to non-volatile hydrofluoride formation. The product from trimethylamine contained only small amounts of perfluorotrimethylamine and somewhat larger amounts of perfluorodimethylamine, perfluoromethylamine, and higher-boiling, completely fluorinated compounds, some of which may be cyclic. The products from the higher tertiary amines were complex, and only the material corresponding to the perfluoro-*tert.*-amine was therefore isolated.

The seven perfluoro-compounds prepared were: $N(CF_3)_3$, $N(CF_3)_2(C_2F_5)$, $N(CF_3)(C_2F_5)_2$, $N(C_3F_7)_3$, $N(C_3F_7)_2(iso\text{-}C_4F_9)$, and $N(C_4F_9)_3$. The boiling points of these compounds lie on a smooth curve, and NF_3, b. p. −120°, $NF(CF_3)_2$, b. p. −37° (Haszeldine, *loc. cit.*; Emeléus and Thompson, *J.*, 1949, 3080), and $NF_2{\cdot}CF_3$, b. p. −75° (Haszeldine, *loc. cit.*), lie on a con-

tinuation of this curve as shown in the diagram. The boiling points of the parent tertiary amines are also recorded and are seen to lie substantially above those of the fluorinated compounds. A comparison of the boiling points of the fluorocarbons and the perfluoro-*tert.*-amines reveals that the latter, $C_nF_{2n+3}N$, have a volatility similar to the fluorocarbons, $C_{n+1}F_{2n+4}$, derived from the *n*-paraffins. Hence, replacement of a carbon atom in a fluorocarbon by nitrogen, although it gives a compound containing one less fluorine atom, has little effect on the boiling point. This effect was noted earlier (Haszeldine, *loc. cit.*) with perfluoropiperidine and perfluoro*cyclo*hexylamine, and would indicate that the compound, m. p. 94—95°, originally believed to be perfluorodimethylpiperidine (Haszeldine, *J.*, 1950, 1638), was incompletely fluorinated and contained one hydrogen atom, since the perfluoro-compound would be expected to boil in the region 90—100°.

Carbon tetrafluoride and hexafluoroethane have boiling points slightly below nitrogen trifluoride and perfluoromethylamine; the boiling points of octafluoropropane and perfluorodimethylamine are almost identical, and above this point the two curves gradually diverge with increase in molecular weight, but even when $n = 9$ (perfluorodecane) the difference in boiling point in the two series is only 15°. The boiling points of perfluoropiperidine and perfluoro*cyclo*hexylamine lie between the two curves.

The refractive indices (n_D) and densities (g./c.c.), both at 25°, of the perfluoro-*tert.*-amines are also similar to those of the fluorocarbons; *e.g.*, C_7F_{16}, *n* 1·267, *d* 1·741, and $N(C_2F_5)_3$, *n* 1·262, *d* 1·736; $C_{10}F_{22}$, *n* 1·279, *d* 1·816, and $N(C_3F_7)_3$, *n* 1·279, *d* 1·822; $C_{11}F_{24}$, *n* 1·286, *d* 1·857, and $N(C_3F_7)_2(iso\text{-}C_4F_9)$, *n* 1·283(5), *d* 1·84(1). The values of n_D^{25} and d_4^{25} for $C_{10}F_{22}$ and $C_{11}F_{24}$ are extrapolated from the data of Haszeldine and Smith (*J.*, in the press), since these fluorocarbons, unlike the nitrogen-containing compounds, are solids. The atomic refraction of fluorine, derived on the assumption that the atomic refraction of nitrogen is the same as in tertiary amines, is 1·21 (see table), a value similar to that derived from the fluorocarbons (Haszeldine and Smith, *loc. cit.*).

Chemically, the perfluoro-*tert.*-amines are inert like the fluorocarbons and show no basic character; like perfluoro*cyclo*hexylamine and perfluoropiperidine, they resemble nitrogen trifluoride.

Experimental.

Apparatus.—The cobalt fluoride apparatus and the technique employed were as described by Haszeldine (*loc. cit.*). A nitrogen stream of 10 l./hr. and a reaction temperature (not necessarily the best) of 250—350° were used, depending upon the b. p. of the compound under examination. Trimethyl-, triethyl-, tripropyl-, and tributyl-amine were studied in most detail, only small quantities of the other *tert.*-amines being available.

Fluorination of Trimethylamine.—Trimethylamine (5 ml./hr.) was passed over cobalt trifluoride kept at 250°. From a total of 100 g. of tertiary amine there were isolated : (*a*) perfluoromethylamine (1·6 g.) (Found : *M*, 119. Calc. for CNF_5 : *M*, 121), b. p. *ca.* −75° (Haszeldine, *loc. cit.*, reports b. p. −75°); (*b*) perfluorodimethylamine (4·1 g.) (Found : *M*, 170. Calc. for C_2NF_7 : *M*, 171), b. p. −38° to −35° (Emeléus and Thompson, *loc. cit.*, report b. p. −37·0°); (*c*) *perfluorotrimethylamine* (2·2 g.; 6%) (Found : C, 16·3; N, 5·9; F, 76·8%; *M*, 220. C_3NF_9 requires C, 16·3; N, 6·3; F, 77·4%; *M*, 221), b. p. −6° to −7°; (*d*) unidentified and possibly cyclic compounds with b. p.'s between 0° and 70°, one of which, b. p. 54—56° (cf. C_6F_{14}, b. p. 58°) may be *perfluorotetramethylhydrazine*, $(CF_3)_2N{\cdot}N(CF_3)_2$ (Found : N, 9·0%; *M*, 298. $C_4N_2F_{12}$ requires N, 9·2%; *M*, 304). The yields of the compounds given here are lower than the true yields because of the exhaustive fractionation required to separate them from partly fluorinated and degradation products.

Fluorination of Ethyldimethylamine.—A total of 52 g. of this amine, added at 4 ml./hr., was fluorinated at a temperature of 250°. *Perfluoroethyldimethylamine* (1·3 g.) (Found : C, 17·7; N, 5·5; F, 76·7%; *M*, 268. C_4NF_{11} requires C, 17·7; N, 5·2; F, 77·1%; *M*, 271), b. p. 20—22°, was isolated by fractionation of the product with b. p. >0°. In this and subsequent experiments, no attempt was made to separate the other, complex, reaction products.

Fluorination of Diethylmethylamine.—The amine (37 g.), passed over cobalt trifluoride at 3·5 ml./hr. at 260°, gave *perfluorodiethylmethylamine* (1·1 g.) (Found : C, 18·5; N, 4·3; F, 76·4%; *M*, 322. C_5NF_{13} requires C, 18·7; N, 4·35; F, 76·95%; *M*, 321), b. p. 45·5—46·5°.

Fluorination of Triethylamine.—Triethylamine (210 g.) was added at 5 ml./hr. to the reaction vessel heated initially to 270° and kept at this temperature throughout the reaction. *Perfluorotriethylamine* (6·3 g.), b. p. 69·8—71·0°, was isolated by fractional distillation (Found : C, 19·2; N, 3·5; F, 76·3%; *M*, 368. C_6NF_{15} requires C, 19·4; N, 3·8; F, 76·8%; *M*, 371). The vapour pressure, determined over the range 12—70°, is given by the equation $\log_{10} p = 7{\cdot}936 - 1736{\cdot}0/T$, whence the b. p. is calculated as 70·3°, the latent heat of vaporisation as 7940 cals./mole, and Trouton's constant as 23·1. Also determined were n_D^{15} 1·270, n_D^{25} 1·262, and d_4^{25} 1·736.

Fluorination of Tripropylamine.—Tripropylamine (196 g. at 5 ml./hr.) was passed over cobalt trifluoride at 300°, and yielded *perfluorotripropylamine* (7·1 g.) (Found : C, 20·6; N, 2·95; F, 76·1%; *M*, 515, 519. C_9NF_{21} requires C, 20·7; N, 2·8; F, 76·6%; *M*, 521), b.p. 129·5—130·5°, $n_D^{14.5}$ 1·284, n_D^{25} 1·279, d_4^{25} 1·822. The vapour-pressure equation, calculated from only six points measured in the

range 60—130°, is given by $\log_{10} p = 8{\cdot}143 - 2121{\cdot}0/T$, whence the calculated b. p. is 129·9° ±0·15°, the latent heat of vaporisation is 9710 cals./mole, and Trouton's constant is 24·1.

Fluorination of iso*Butyldipropylamine.*—The passage of 28·5 g. of this amine over cobalt trifluoride at 320°, followed by recycling at 300°, gave *perfluoro*iso*butyldipropylamine* (0·5 g.) (Found : C, 20·6; N, 2·6; F, 75·8. $C_{10}NF_{23}$ requires C, 21·0; N, 2·4; F, 76·5%), b. p. 146—148°, n_D^{25} 1·283(5); d_4^{25} 1·84(1).

Fluorination of Tributylamine.—Tributylamine (175 g. at 4 ml./hr.) was treated with cobalt trifluoride at 350° and gave *perfluorotributylamine* (5·8 g.) [Found : C, 21·2; N, 2·1; F, 76·0%; *M* (ebullioscopic), 663, 668. $C_{12}NF_{27}$ requires C, 21·45; N, 2·1; F, 76·45%; *M*, 671], b. p. 179·1—179·5°, n_D^{25} 1·291, n_D^{14} 1·296, d_4^{25} 1·873.

Chemical Properties of the Perfluoro-tert.-*amines.*—These compounds resemble nitrogen trifluoride and the fluorocarbons. They are stable, unreactive, and show no basic properties.

Physical Properties of the Perfluoro-tert.-*amines.*—The molecular refractions of these amines, calculated by the Lorentz–Lorenz expression from the data recorded above, are shown below :

Compound.	$N(C_2F_5)_3$.	$N(C_3F_7)_3$.	$N(C_3F_7)_2$(*iso*-C_4F_9).	$N(C_4F_9)_3$.
$[M]_D$	35·28	49·95	55·03	65·09
Atomic refraction (fluorine)	1·20	1·21	1·22	1·23

In the calculation of the atomic refraction of fluorine, the atomic refraction of nitrogen was taken as 2·74, the value derived by Vogel (" Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 898) for tertiary amines, and the atomic refraction of carbon as 2·418.

The molecular refractions of perfluoropiperidine and perfluoro*cyclo*hexylamine are 28·45 and 33·31 and the atomic refraction (fluorine) is 1·24 and 1·23(5). These values for the atomic refraction of fluorine are in agreement with those derived earlier for fluorocarbons.

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