Nitroxide Chemistry. Part 13.[1] Reaction of *NN*-Bis(trifluoromethyl)-amino-oxyl with Hexafluoroisopropylideneimine and Related Compounds

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The initial product from reaction of the oxyl $(CF_3)_2N-O^{\cdot}$ with hexafluoroisopropylideneimine is the substituted imine $(CF_3)_2C=N-O-N(CF_3)_2$ (isolated in 81% yield) which, *via* further oxyl attack at carbon, gives the compounds $(CF_3)_2CO$, $(CF_3)_2N-NO$, $(CF_3)_2N-O-N(CF_3)_2$, and $(CF_3)_2N-O-C(CF_3)_2\overset{+}{N}(\overset{-}{O})=N-C(CF_3)_2-O-N(CF_3)_2$. Oxyl attack on hexafluoroacetone oxime affords as major products $(CF_3)_2CO$, $(CF_3)_2NH$, and $(CF_3)_2N-O-NO$. The oxyl reacts with hexafluoroacetone anil to yield a hexaoxyl adduct, with hexafluoroacetone hydrazone to afford the diazoalkane $(CF_3)_2CN_2$ (100%), and with hexafluoroacetone azine to give the bis-1 : 4-adduct $(CF_3)_2N-O-C-(CF_3)_2-N=N-C(CF_3)_2-O-N(CF_3)_2$ (100%). Thus, initial radical attack of the oxyl invariably takes place at carbon in the series of imines studied.

RADICAL addition to imine derivatives of type $R^1R^2C\colon NR^3$ has received little attention. Trifluoroacetonitrile reacts with trifluoromethyl radicals [generated from u.v. irradiation of $(CF_3)_2CO$] to give the substituted imine

(6) (1.5% on oxyl), *NN*-bis(trifluoromethyl)hydroxylamine (7) (47% on oxyl), and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (8) (5% on oxyl). The major products (4) and (7) could arise by two distinct reactions

$$CF_3-C\colon N \xrightarrow{\text{CF}^{\cdot}} (CF_3)_2C\colon N^{\cdot} \longrightarrow (CF_3)_2C\colon N-N\colon C(CF_3)_2$$

$$(CF_3)_3C-N(CF_3)-N(CF_3)-C(CF_3)_3 \longrightarrow (CF_3)_3C-N=N-CF_3 + C(CF_3)_4 \qquad (E1)$$

$(CF_3)_2C\colon N\cdot CF_3$ (25%), the amine $(CF_3)_3C-N(CF_3)_2$ (*ca.* 1%), and the azo-compound $(CF_3)_3C-N=N-CF_3$ (2.5%), postulated as being formed *via* $CF_3^{\cdot}$ radical attack on the intermediate azine (1) [equation (E1)].[2] Reference was made [2] to the unpublished results of the reaction of fluorosulphate radicals with the azine (1) to give the 1,4-adduct $FSO_2\cdot O\cdot C(CF_3)_2\cdot N\colon N\cdot C(CF_3)_2\cdot O\cdot SO_2F$.[3] In contrast the thermal reaction of trimethylsilane with the azine (1) gives products consistent with initial silyl radical attack at nitrogen [equation (E2)].[4]

[equations (E3) and (E4)], which present evidence does not differentiate.

The amine $(CF_3)_2NH$ is presumably formed by abstraction of hydrogen [*e.g.* from imine (3a)] by the $(CF_3)_2N^{\cdot}$ radical arising by the known homolytic N–O bond fission in compound (8), while the remaining products can originate from secondary reactions of the initial product (4) Thus treatment of the imine (4) with the oxyl (2) (1 : 2 molar ratio) at 60 °C gave unchanged (2) (15% recovered), hexafluoroacetone (70%

$$(1) \xrightarrow{\text{Me}_3\text{Si}^{\cdot}} (CF_3)_2C-N(SiMe_3)-N=C(CF_3)_2 \xrightarrow{\text{HSiMe}_3} (CF_3)_2CH-N(SiMe_3)-N=C(CF_3)_2$$

$$(CF_3)_2CH-NH-N=C(CF_3)_2 + 2(CF_3)_2C=N-SiMe_3 \qquad (E2)$$

Prolonged photolysis of a mixture of tris(trifluoromethyl)-hydroxylamine and perfluoro-2-azapropene gives a complex mixture of products containing the 1 : 1 adducts $(CF_3)_2N-CF_2-N(CF_3)-O-CF_3$ (10%) and $(CF_3)_2N-N(CF_3)-CF_2-O-CF_3$ (4%).[5] The reactions of *NN*-bis(trifluoromethyl)amino-oxyl (2) with *N*-substituted hexafluoroisopropylideneimines $(CF_3)_2C=NR$ (3a—d; R = H, OH, Ph, and NH$_2$) and (1) have now been investigated.

RESULTS AND DISCUSSION

$(CF_3)_2C\colon NH$.—Treatment of the imine (3a) with the oxyl (2) (1 : 2 molar ratio) at room temperature gave the substituted imine (4) (81% on imine, 40% on oxyl), the azoxy-compound (5) (11% on imine, 5% on oxyl), *NN*-bis(trifluoromethyl)amine (1% on oxyl), hexafluoroacetone (4% on imine), *N*-nitrosobis(trifluoromethyl)amine

on imine), (5) (30% on imine, 18% on oxyl), (6) (41% on oxyl), and (8) (41% on oxyl). The formation of these products may be visualised as in Scheme 1.

$$(CF_3)_2C=NH + (CF_3)_2N-O^{\cdot} \longrightarrow (CF_3)_2N-OH +$$
$$\text{(3a)} \qquad\qquad \text{(2)} \qquad\qquad\qquad\qquad \text{(7)}$$

$$(CF_3)_2C=N^{\cdot} \xrightarrow{\text{(2)}} (CF_3)_2C=N-O-N(CF_3)_2 \quad (E3)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(4)}$$

$$\text{(3a)} + 2\text{(2)} \longrightarrow (CF_3)_2N-O-C(CF_3)_2-NH-O-N(CF_3)_2$$
$$\longrightarrow \text{(4)} + \text{(7)} \quad (E4)$$

The ratio of products formed indicates that the intermediate radical (9) reacts further with the oxyl (2) [route (a)] to give the adduct (10) (70%) and dimerises [route (b)] to give compound (11) (30%); decomposition
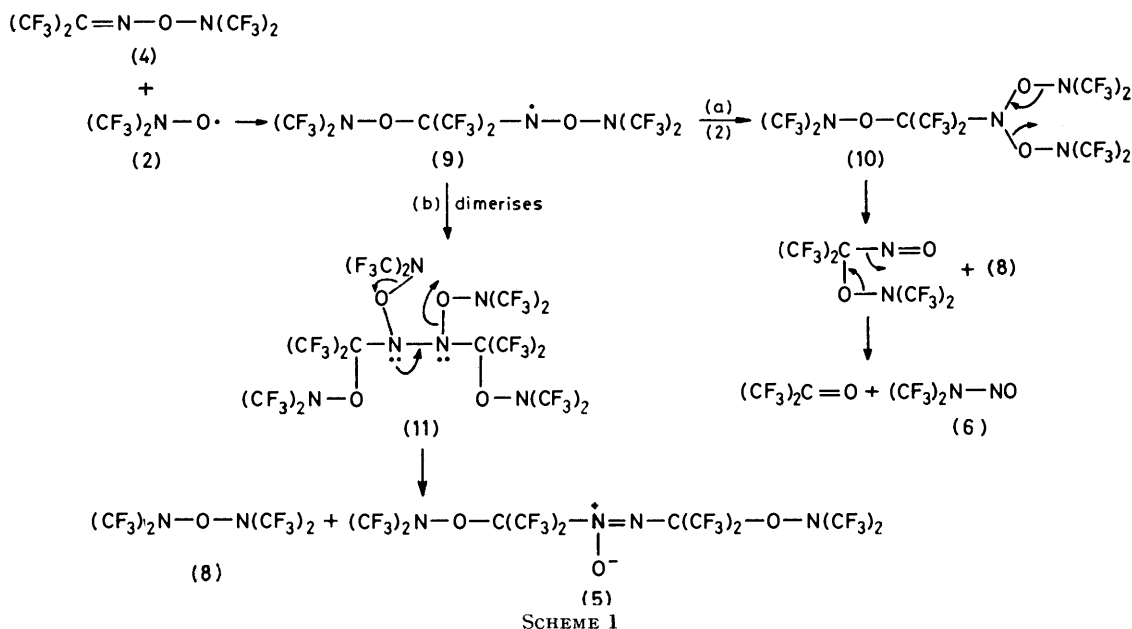
of compounds (10) and (11) then affords the observed products.

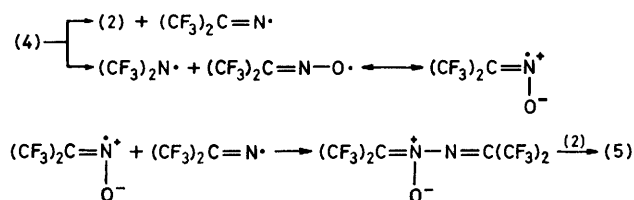An alternative, but less likely, route to compound (5) is shown in Scheme 2.

Although compound (4) undergoes reaction with olefins to form 1 : 1 adducts derived from the two alternative

high-boiling material prior to distillation showed a band in its i.r. spectrum at 6.0 μm (C=N str.) and [19]F n.m.r. resonances at δ -7.0 [$(CF_3)_2C$] and -8.8, -9.0, -9.6, and -10.4 [all $(CF_3)_2N-O$] (ratio 2 : 2 : 1 : 1) and on this limited evidence the hexaoxyl adduct is tentatively assigned structure (15); the [19]F n.m.r. spectrum of an

$$(CF_3)_2C=N-O-N(CF_3)_2$$
$$(4)$$
$$+$$

$(CF_3)_2N-O\cdot$ $\longrightarrow$ $(CF_3)_2N-O-C(CF_3)_2-\overset{\cdot}{N}-O-N(CF_3)_2$ $\xrightarrow{(a)}{(2)}$ $(CF_3)_2N-O-C(CF_3)_2-N\overset{O-N(CF_3)_2}{\underset{O-N(CF_3)_2}{}}$

(2) (9) (10)

(b) | dimerises

$(CF_3)_2C\overset{N=O}{\underset{O-N(CF_3)_2}{}}$ + (8)

$(F_3C)_2N$
$(CF_3)_2C-\overset{}{N}-\overset{}{N}-C(CF_3)_2$
$(CF_3)_2N-O$ $O-N(CF_3)_2$
(11)

$(CF_3)_2C=O$ + $(CF_3)_2N-NO$
(6)

$(CF_3)_2N-O-N(CF_3)_2$ + $(CF_3)_2N-O-C(CF_3)_2-\overset{\cdot}{N}=N-C(CF_3)_2-O-N(CF_3)_2$

(8) O^-
                                                                          (5)

SCHEME 1

modes of N–O bond fission, such reaction does not take place below 100 °C.[6]

($(CF_3)_2C=N-OH$.—Oxyl (2) reacted readily with hexafluoroacetone oxime (3b) (ca. 2 : 1 molar ratio) at room temperature to afford hexafluoroacetone (82% on oxime), hexafluoroacetone monohydrate (16% on oxime), NN-bis(trifluoromethyl)amine (45% on oxyl), O-

(4) ——[$\to$ (2) + $(CF_3)_2C=N\cdot$
            $\to (CF_3)_2N\cdot$ + $(CF_3)_2C=N-O\cdot$ $\longleftrightarrow$ $(CF_3)_2C=\overset{\cdot}{\underset{O^-}{N}}$

$(CF_3)_2C=\overset{\cdot}{\underset{O^-}{N}}$ + $(CF_3)_2C=N\cdot$ $\longrightarrow$ $(CF_3)_2C=\overset{}{\underset{O^-}{N}}-N=C(CF_3)_2$ $\xrightarrow{(2)}$ (5)

SCHEME 2

nitrosobis(trifluoromethyl)hydroxylamine (12) (46% on oxyl), and (7) (3% on oxyl). These products can be accounted for by decomposition of either the intermediate radical (13) or the 2 : 1 adduct (14) via a six-centre transition state as shown in Scheme 3. The hydroxylamine (7) is formed in only low yield and this indicates that hydrogen abstraction from the oxime by the oxyl (2) is a less favoured reaction.

($(CF_3)_2C=NPh$.—Treatment of hexafluoroacetone anil (3c) with the oxyl (2) (ca. 1 : 3 molar ratio) at -10 °C (28d) gave only high-boiling material from which unchanged anil (56% recovered) was recovered by distillation, leaving a charred residue. The anil and the oxyl had thus reacted approximately in the ratio 1 : 6. The

alternative adduct (16) would be expected to show separate absorptions for the non-equivalent CF_3-C groups [cf. $(CF_3)_2C=NPh$ δ -7.0 and -14.7 p.p.m.]. A possible route to (15) is shown in equation (E5).

$(CF_3)_2C=N-NH_2$.—Reaction of the oxyl (2) with hexafluoroacetone hydrazone (3d) (2 : 1 molar ratio) at 25 °C gave the hydroxylamine (7) and diazoalkane (17) in quantitative yield [equation (E6)]; the amino-compounds $(CF_3)_2C(NH_2)_2$ and $(CF_3)_2C(NH_2)-N_3$ are simil-

$(CF_3)_2C=N-OH$ + (2) $\to$ $(CF_3)_2C\overset{O}{\underset{N}{}}N(CF_3)_2$ $\longrightarrow$ $(CF_3)_2NH$
$(3b)$ (13) +
                                                                       $(CF_3)_2CO$ + NO

NO + (2) $\longrightarrow$ $(CF_3)_2N-O-NO$
(12)

(13) + (2) $\longrightarrow$ $(CF_3)_2C\overset{O}{\underset{(CF_3)_2N-O-N}{}}N(CF_3)_2$ $\longrightarrow$ (12) + $(CF_3)_2NH$
                                                                             +
(14) $(CF_3)_2CO$

SCHEME 3
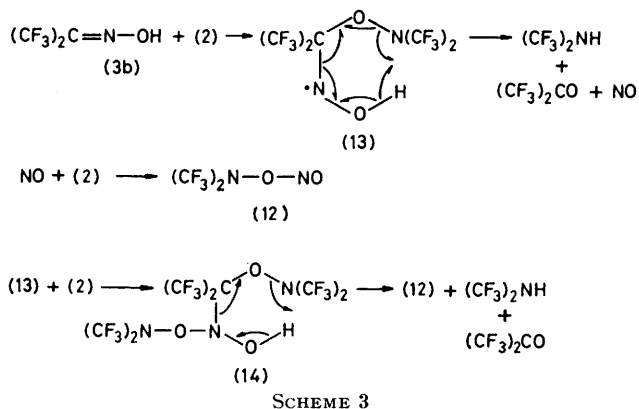
arly oxidised quantitatively by the oxyl (2) to afford the diazirine $(CF_3)_2C-N=N$.[6] Other reported oxidations of the hydrazone (3d) generally result in lower yields of diazoalkane (17), e.g. (3d) + $Pb(OAc)_4-PhCN\longrightarrow(17)$ (77%).[7]

The hydrazone (3d) has been prepared previously by the following routes: (*i*) (3a) + $NH_2NH_2 \xrightarrow{0\,^{\circ}C}$ $(CF_3)_2C\text{-}(NH_2)NHNH_2 \xrightarrow[distil]{P_4O_8}$ (3d) (68%);[8] (*ii*) $(CF_3)_2C(NH_2)\text{-}N_3$ $\xrightarrow{350\,^{\circ}C}$ (3d) (60%) + $(CF_3)_2\overline{C\text{-}NH\text{-}NH}$ (11%);[8] and (*iii*) (3c) + $NH_2NH_2 \xrightarrow{EtOH}$ $[(CF_3)_2C(NHPh)\text{-}NH\cdot NH_2]$ (18) $\xrightarrow[+P_4O_8, 100\,^{\circ}C]{Et_2O\ solution}$ 90 : 10 (3d): Et_2O azeotrope (50%).[9] In the present work preparation (*iii*) was successfully modified. Treatment of the anil (3c) with hydrazine hydrate afforded the adduct (18) (100%), and a mixture of the

with air or moisture. The oxyl (2) was prepared by oxidation of NN-bis(trifluoromethyl)hydroxylamine with silver(I) oxide [11] and was stored at room temperature in a blackened Pyrex bulb fitted with a Springham's greaseless stopcock (Viton diaphragm). Reactions were carried out *in vacuo* in Pyrex ampoules (*ca.* 300 cm³) fitted with PTFE needle valves, and were terminated when the purple colour of the oxyl had disappeared. Products were separated by fractional condensation *in vacuo* or by distillation (0.5 m spinning-band column) and were examined by molecular-weight determination (Regnault's method), i.r. spectroscopy (Perkin-Elmer model 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer

$$(CF_3)_2CR\text{-}N\!=\!\overline{C\text{-}[CHR]_4\text{-}CHR} \qquad (CF_3)_2C\!=\!N\text{-}\overline{CR\text{-}[CHR]_4\text{-}CHR} \quad [\text{where } R = O\text{-}N(CF_3)_2]$$
$$\text{(15)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(16)}$$

$$(CF_3)_2C\!=\!NPh \xrightarrow{(2)} (CF_3)_2N\text{-}O\text{-}C(CF_3)_2\text{-}\overset{\bullet}{N}Ph \longleftrightarrow (CF_3)_2N\text{-}O\text{-}C(CF_3)_2\text{-}N\!=\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\cdot \longleftrightarrow etc.$$
$$\text{(3c)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow(2)$$

$$(CF_3)_2N\text{-}O\text{-}C(CF_3)_2\text{-}N\!=\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!\overset{H}{\underset{O\text{-}N(CF_3)_2}{}} \xrightarrow{(2)} \text{(15)} \qquad \text{(E5)}$$
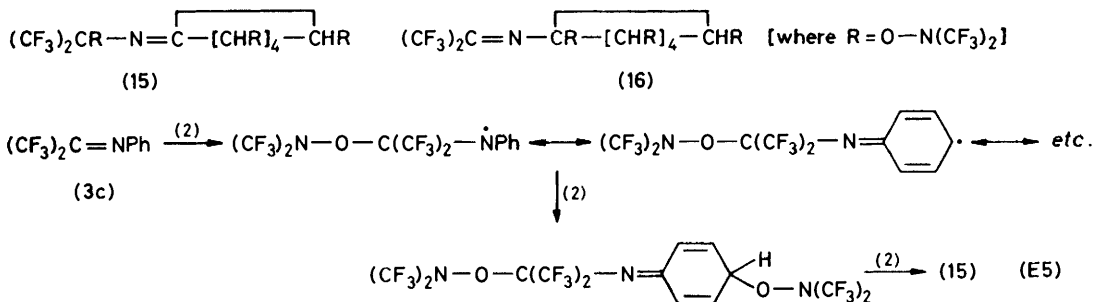
dried adduct and phosphorus pentaoxide, heated at 100 °C, gave pure hydrazone (3d) 94%).

Adduct (18) is a useful precursor to mixed azines; treatment of the adduct with an excess of acetone followed by distillation from phosphorus pentaoxide gave the azine $(CF_3)_2C\!=\!N\text{-}N\!=\!CMe_2$ (91%), prepared

$$(CF_3)_2C\!=\!N\text{-}NH_2 + (CF_3)_2NO^{\bullet} \longrightarrow (CF_3)_2NOH +$$
$$\text{(3d)}$$
$$(CF_3)_2C\!=\!N\text{-}\overset{\bullet}{N}H \longleftrightarrow (CF_3)_2\overset{\bullet}{C}\text{-}N\!=\!NH$$
$$\downarrow(2)$$
$$(CF_3)_2CN_2 + (7) \qquad \text{(E6)}$$
$$\text{(17)}$$
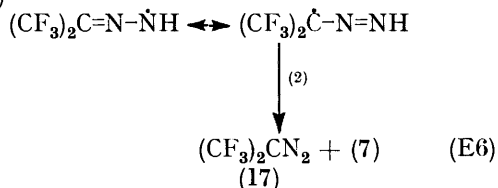
previously in much lower yield (50%), by reaction of the hydrazone (3d) with acetone in the presence of phosphorus pentaoxide.[10]

$(CF_3)_2C\!=\!N\text{-}N\!=\!C(CF_3)_2$.—Treatment of the azine (1) with the oxyl (2) (1 : 2 molar ratio) at room temperature gave the bis-1 : 4-adduct (19) (100%) [equation (E7)] analogous to the fluorosulphate radical product. Radicals of type $RO^{\bullet}$ [R = SO_2F or $(CF_3)_2N$] attack carbon,

$$(1) + 2 (2) \longrightarrow$$
$$(CF_3)_2N\text{-}O\text{-}C(CF_3)_2\text{-}N\!=\!N\text{-}C(CF_3)_2\text{-}O\text{-}N(CF_3)_2 \quad \text{(E7)}$$
$$\text{(19)}$$
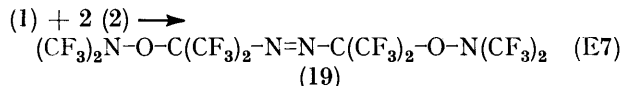
in contrast with silyl radical which attack at nitrogen, presumably because silicon forms a much stronger bond with nitrogen than with carbon. The adduct (19) is a useful source of $(CF_3)_2N^{\bullet}$ radicals.[6]

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum apparatus to avoid contact

R10 or Varian HA100 spectrometer operating at 56.46 and 94.1 MHz, respectively, with external trifluoracetic acid as reference), mass spectrometry (AEI MS 902 instrument), and g.l.c. [4 m methylsilicone gum (OVI) (30%) on Celite]. Boiling points were determined by Siwoloboff's method.

The reactant imine derivatives were prepared by literature methods, *i.e.* $(CF_3)_2C\!=\!NH$,[8] $(CF_3)_2C\!=\!N\text{-}N\!=\!C(CF_3)_2$,[12] $(CF_3)_2C\!=\!NPh$,[13] and $(CF_3)_2C\!=\!NOH$.[14]

Reactions of NN-Bis(trifluoromethyl)amino-oxyl.—(a) *With hexafluoroisopropylideneimine.* A mixture of the oxyl (10.1 g, 60.0 mmol) and the imine (4.84 g, 29.3 mmol) maintained for 11 d at room temperature, gave (*i*) a mixture (0.43 g, 2.6 mmol) which was shown by i.r. and n.m.r. spectroscopy to consist of NN-bis(trifluoromethyl)amine (0.09 g, 0.6 mmol, 1% on oxyl), hexafluoroacetone (0.18 g, 1.1 mmol, 4% on imine), and N-nitrosobis(trifluoromethyl)-amine (6) (0.16 g, 0.9 mmol, 1.5% on oxyl); (*ii*) a higher boiling volatile fraction (13.38 g); and (*iii*) a colourless liquid residue (1.07 g) which was identified as azoxy[per-fluoro(1,1,3-trimethyl-2-aza-2-oxobutane)] (5) (1.07 g, 1.6 mmol, 5% on oxyl, 11% on imine) (Found: C, 17.8; F, 66.8. $C_{10}F_{24}N_4O_3$ requires C, 17.6; F, 67.1%), b.p. 133—134 °C; i.r., $\lambda_{max.}$ 6.36s [N=$\overset{+}{N}(\overset{-}{O})$ str]μm; δ_F −6.8 [6F, $(CF_3)_2CN$], −8.0 [6F, $(CF_3)_2\overset{+}{C}\overset{-}{N}(O)$], −9.9 [6F, $(CF_3)_2NOCN$], and −10.2 [6F, $(CF_3)_2NOC\overset{+}{N}(\overset{-}{O})$]. The higher boiling volatile fraction was fractionated to afford NN-bis(trifluoromethyl)hydroxylamine (7) (4.80 g, 28.4 mmol, 47% on oxyl), b.p. 32 °C (lit.,[15] 32.5 °C), perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (8) (0.47 g, 1.47 mmol, 5% on oxyl), b.p. 49–51 °C (lit.,[16] 48.5 ± 0.5 °C), and *perfluoro-(2,5-dimethyl-4-oxa-3,5-diazahex-2-ene)* (4) (7.88 g, 23.7 mmol, 39.5% on oxyl, 81% on imine) (Found: C, 18.5; N, 8.5; F, 68.3%; *M*, 330. $C_5F_{12}N_2O$ requires C, 18.1; N, 8.4; F, 68.7%; *M*, 332), b.p. 55 °C; i.r., $\lambda_{max.}$ 6.0s (C=N str.) μm; δ_F −11.4 [3F, q, CF_3C (*syn*), *J* 6.8 Hz] and −8.2 [9F, overlapping s and q, $(CF_3)_2N$ and CF_3C (*anti*)].

(b) *With perfluoro(2,5-dimethyl-4-oxa-3,5-diazahex-2-ene).*

—A mixture of the oxyl (3.40 g, 20.2 mmol) and the imine (3.36 g, 10.1 mmol), heated at 60 °C (60 h), gave (i) a mixture (2.87 g, 17.1 mmol) of unchanged oxyl (0.50 g, 3.0 mmol, 15% recovered), hexafluoroacetone (1.18 g, 7.1 mmol, 70% on imine), and N-nitrosobis(trifluoromethyl)amine (6) (1.29 g, 7.1 mmol, 41% on oxyl) as shown by i.r. and ^{19}F n.m.r. spectroscopy, (ii) perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (8) (2.75 g, 8.6 mmol, 41% on oxyl), and (iii) the azoxy-compound (5) (1.05 g, 1.5 mmol, 18% on oxyl), 30% on imine).

(c) *With hexafluoroacetone oxime.* A mixture of the oxyl (3.48 g, 20.7 mmol) and the oxime (1.74 g, 9.6 mmol), maintained at room temperature (17 h), gave (i) a mixture (2.73 g, 17.2 mmol) of hexafluoroacetone (1.31 g, 7.9 mmol, 82% on oxime) and NN-bis(trifluoromethyl)amine (1.42 g, 9.3 mmol, 45% on oxyl) as shown by i.r. and ^{19}F n.m.r. spectroscopy, (ii) an orange gas identified as O-nitrosobis(trifluoromethyl)-hydroxylamine (12) (1.90 g, 9.6 mmol, 46% on oxyl) (Found: M, 198. Calc. for $C_2F_6N_2O_2$: M, 198) by a comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample prepared by the reaction of oxyl (2) with nitric oxide, (iii) NN-bis(trifluoromethyl)hydroxylamine (7) (0.10 g, 0.6 mmol, 3% on oxyl), and (iv) a hygroscopic white solid identified as hexafluoroacetone monohydrate (0.28 g, 1.5 mmol, 16% on oxime) by a comparison of its i.r. and ^{1}H and ^{19}F n.m.r. spectra with those of an authentic sample.

(d) *With hexafluoroacetone anil.* A mixture of the oxyl (15.77 g, 93.8 mmol) and the anil (8.64 g, 35.8 mmol), maintained at −10 °C (28 d), gave only a high-boiling liquid which on spinning-band distillation afforded unchanged anil (4.87 g, 20.2 mmol, 56% recovered), b.p. 133 °C, and a semi-charred viscous residue (ca. 19 g). The original high-boiling liquid and the residue both showed i.r. absorptions at $\lambda_{max.}$ 3.5w (C–H str) and 6.0m (C=N str) μm and ^{19}F n.m.r. signals at δ −7.0 [6F, $(CF_3)_2$C], −8.8 [12F, 2 × $(CF_3)_2$NO], −9.0 [12F, 2 × $(CF_3)_2$NO], −9.6 [6F, $(CF_3)_2$NO], and −10.4 [6F, $(CF_3)_2$NO].

(e) *With hexafluoroacetone hydrazone.* A mixture of the oxyl (4.45 g, 26.5 mmol) and the hydrazone (2.39 g, 13.3 mmol), maintained at 25 °C (24 h), gave NN-bis(trifluoromethyl)hydroxylamine (7) (4.47 g, 26.5 mmol, 100%) and a yellow gas identified as perfluorodiazoisopropane (17) (2.38 g, 13.3 mmol, 100%), b.p. 12 °C (lit.,[7] 12 °C), by a comparison of its i.r. and ^{19}F n.m.r. spectra with those reported.[7]

(f) *With hexafluoroacetone azine.* A mixture of the oxyl (5.68 g, 33.8 mmol) and the azine (5.42 g, 16.9 mmol), maintained at 25 °C (3 d), gave a yellow liquid identified as perfluoro(1,4,4,7,7,9-hexamethyl-3,8-dioxa-2,5,6,9-tetra-aza-dec-5-ene) (19) (11.10 g, 16.9 mmol, 100%) (Found: C, 18.2; N, 8.5; F, 68.8 $C_{10}F_{24}N_2O_2$ requires C, 18.1; N, 8.4; F, 68.7%); δ_F −5.07 [6F, s, $(CF_3)_2$C] and −9.58 [6F, s, $(CF_3)_2$NO].

Reaction of Hexafluoroacetone Anil with Hydrazine Hydrate.—A mixture of the anil (9.93 g, 41.2 mmol) and hydrazine hydrate (2.47 g, 49.4 mmol) was shaken in a tightly stoppered flask (ca. 50 cm³) until the yellow colour of the anil had disappeared (ca. 5 min). The reaction was exothermic and on cooling the flask a white crystalline

solid was obtained which was filtered off, washed with cold water (3 × 05 cm³), and dried in vacuo (CaCl$_2$, 12 h) to give (1-anilino-2,2,2-trifluoro-1-trifluoromethyl)ethylhydrazine (18) (11.25 g, 41.2 mmol, 100%) (Found: C, 39.6; H, 3.1; N, 15.3; F, 41.8%; M^+, 273. $C_9H_9F_6N_3$ requires C, 39.6; H, 3.3; N, 15.4; F, 41.7%; M, 273), m.p. 69—70 °C; n.m.r. (25% solution in CDCl$_3$); ^{1}H τ 2.87 (5 H, m, Ph), 5.74 (1 H, br s, NH), 5.82 (1 H, br s, NH), and 6.68 (2 H, br s, NH$_2$); ^{19}F, δ −2.5 (s).

Reactions of (1-Anilino-2,2,2-trifluoro-1-trifluoromethyl)-ethylhydrazine.—(a) *Thermolysis in the presence of phosphorus pentaoxide.* The adduct (3.07 g, 11.24 mmol) was treated with phosphorus pentaoxide (5 g) in vacuo and the mixture was shaken and then heated at 100 °C (1 h) to give hexafluoroacetone hydrazone (1.90 g, 10.58 mmol, 94%) (Found: C, 20.3; H, 1.2; N, 15.5; F, 63.3%; M, 179; M^+, 180. Calc. for $C_3H_2F_6N_2$: C, 20.1; H, 1.1; N, 15.6; F, 63.3%; M, 180), b.p. 95 °C (lit.,[8] 95—96 °C).

(b) *With acetone.* The adduct (10.41 g, 38.1 mmol) was dissolved in acetone (50.0 g, 0.865 mol) and the resultant solution was treated with phosphorus pentaoxide (25 g). After the initial exothermic reaction had subsided the mixture was heated under reflux (until the i.r. spectrum of a sample showed an absence of a band due to N–H str, ca. 1 h) and the volatile material (56.2 g) was then condensed in vacuo and distilled to give unchanged acetone (47.7 g, 0.825 mol, 95% recovered) and a bright yellow liquid identified as 1,1,1-trifluoro-5-methyl-2-trifluoromethyl-3,4-diaza-hexa-2,4-diene (7.62 g, 34.7 mmol, 91%), b.p. 98—100 °C (lit.,[10] 100—103 °C), the i.r. and n.m.r. spectra of which were identical to those reported.[10]

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