Bis(trifluoromethyl) Nitroxide: a Novel Synthesis and Some Reactions

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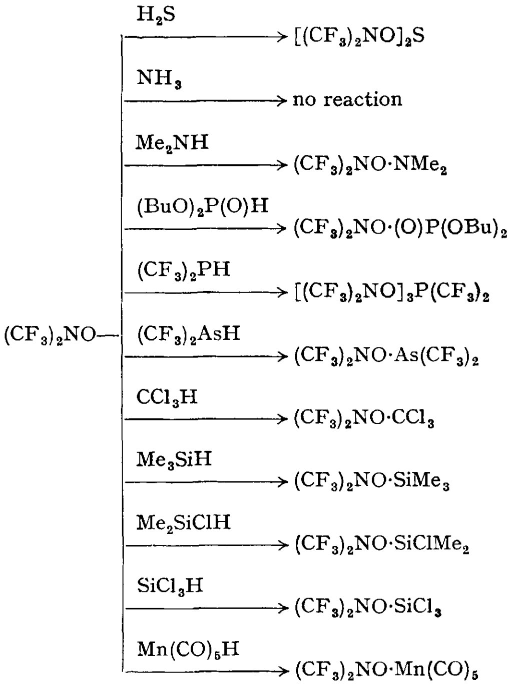
BIS(TRIFLUOROMETHYL) NITROXIDE, a stable purple gas, has been prepared by the oxidation of bis(trifluoromethyl)hydroxylamine with argentous oxide, fluorine,[1] potassium permanganate,[2] or sodium fluoride,[3] and by electrochemical fluorination.[4] We now report that a 100% conversion of bis(trifluoromethyl)hydroxylamine into the radical can be achieved readily by its reaction with argentic oxide,

$$2(CF_3)_2NOH + 2AgO \longrightarrow 2(CF_3)_2NO + H_2O + Ag_2O$$

In a typical experiment, bis(trifluoromethyl)-hydroxylamine, prepared by treating trifluoronitrosomethane with ammonia (1 : 1·5 molar ratio), was sealed in an ampoule containing a two-fold excess of argentic oxide. A purple gas soon developed and the reaction was virtually over in about six hours at room temperature. Grey argentous oxide was formed, and the liquids, on fractionation, gave water and bis(trifluoromethyl) nitroxide in quantitative yield.

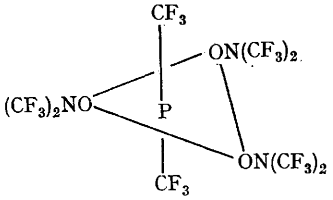
Bis(trifluoromethyl) nitroxide (I) reacts with benzene and toluene to give 1,2,4-tris(hexafluorodimethylamino-oxy)benzene[2] and $PhCH_2ON(CF_3)_2$[3] respectively. Its reactions with substituted fluoro-olefins gave only 2 : 1 adducts. These reactions therefore indicate that the nitroxide (I) is both an excellent hydrogen abstractor and a free-radical scavenger. We now report that these dual properties of the radical can be utilised to advantage in the syntheses of bis(trifluoromethyl) nitroxide derivatives of a number of inorganic elements.



All the reactions occurred readily at room temperature, and the other main product was bis(trifluoromethyl)hydroxylamine.

The radical (I) did not react with ammonia even at elevated temperatures. However, with dimethylamine, the product $(CF_3)_2NOMe_2$, which was first synthesized by El-Nigumi by radical exchange reactions between tris(dimethylamino)-phosphine and bis(trifluoromethyl) nitroxide,[5] was formed if the reaction ampoule was allowed to warm up overnight from −65°. At room temperature, especially if set aside for about a day, a heavy intractable oil was formed.

Reaction with bis(trifluoromethyl)phosphine gave a colourless liquid which, on the basis of its elemental analyses and molecular weight, could be formulated as $(CF_3)_2P[ON(CF_3)_2]_3$. This was confirmed by its mass spectrum which gave a molecular ion at 673, as well as by its ^{19}F n.m.r. spectrum which gave $\Phi_{CF_3P} = 61{\cdot}2$, $\Phi_{(CF_3)_2NO} = 85{\cdot}5$ p.p.m., and $J_{CP-P} = 119$ c./sec. There was no coupling between the fluorine in $(CF_3)_2NO$ and the central phosphorus. The spectral information suggests the conformation,



Reaction with bis(trifluoromethyl)arsine, prepared by the reduction of bis(trifluoromethyl)iodoarsine with hydrogen iodide in the presence of mercury, gave only the trivalent derivative, $(CF_3)_2NO{\cdot}As(CF_3)_2$. Its ^{19}F n.m.r. spectrum gave $\Phi(CF_3As) = 63{\cdot}0$, and $\Phi(CF_3)_2NO = 76{\cdot}4$ p.p.m. An appreciable long-range F_{CN}–F_{CAs} coupling (1·4 c./sec.) was observed, whereupon each peak was split into a 1 : 6 : 15 : 20 : 15 : 6 : 1 septet. This is interesting since the fluorine atoms are separated by five atoms. Arsenic itself reacted with the nitroxide to give the trivalent derivative, $[(CF_3)_2NO]_3As$, a white crystalline solid, m.p. 29·5°, which can be transferred readily under vacuum. It reacted with hydrogen chloride to give arsenic trichloride and three mol. of bis(trifluoromethyl)-hydroxylamine. Antimony gave no reaction under similar conditions.

Bis(trifluoromethyl)nitroxytrimethylsilane, $(CF_3)_2NO{\cdot}SiMe_3$, which was first prepared by the reaction of trimethylchlorosilane with the sodium salt of bis(trifluoromethyl)amine, can also be prepared by the reactions of the radical with either trimethylsilane or bis(trimethylsilyl)-mercury.

The author thanks Peterhouse, Cambridge, and the Royal Commission for the Exhibition of 1851 for Research Fellowships.

(*Received, July* 30*th*, 1968; *Com.* 1039.)

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