Synthesis of Bistrifluoromethylnitroxy-compounds

By R. E. BANKS, R. N. HASZELDINE, and D. L. HYDE

(Chemistry Department, University of Manchester Institute of Science and Technology, Manchester 1)

HITHERTO bistrifluoromethyl nitroxide has been the only general reagent available for the introduction of the $(CF_3)_2N{\cdot}O{\cdot}$ group into compounds,[1] and its use has been exemplified in cases where the substrate is a free radical, contains an atom or group capable of undergoing radical abstraction, or has an unsaturated group which will partake in a radical-addition reaction, *e.g.*,

$$(CF_3)_2N{\cdot}O{\cdot} + NO \xrightarrow{20^\circ} (CF_3)_2N{\cdot}O{\cdot}NO$$

$$(CF_3)_2N{\cdot}O{\cdot} + PhCHR_2 \xrightarrow{20^\circ}$$

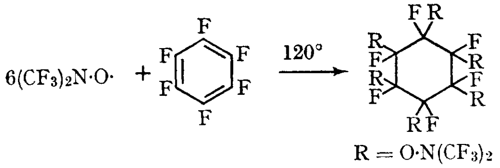
$$(CF_3)_2N{\cdot}OH + Ph\dot{C}R_2 \xrightarrow{(CF_3)_2N{\cdot}O{\cdot}}$$

$$PhCR_2{\cdot}O{\cdot}N(CF_3)_2$$

(where R = H or Me)

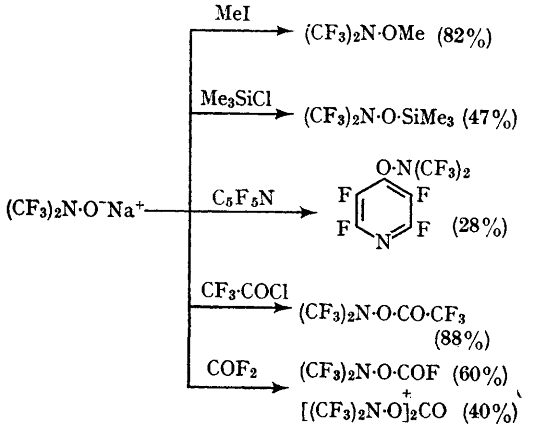
$$2(CF_3)_2N{\cdot}O{\cdot} + CH_2{:}CH_2 \xrightarrow{20^\circ}$$

$$(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$$



Preparation of the sodium salt of bistrifluoromethylhydroxylamine, $(CF_3)_2N{\cdot}O^-Na^+$, the usefulness of which arises from its nucleophilic reactivity, has now provided an alternative, and in some cases exclusive, reagent for the introduction of the $(CF_3)_2N{\cdot}O{\cdot}$ group into organic or inorganic molecules. Syntheses effected so far are shown below; all the reactions were carried out in tetrahydrofuran at room temperature, and the identities of the products were established by elemental analysis and spectroscopic methods (i.r., n.m.r., and mass).

The solutions of sodium bistrifluoromethyl nitroxide used in the above reactions were prepared by treatment of a solution of bistrifluoromethylhydroxylamine[2] in tetrahydrofuran with an equimolar amount of powdered sodium hydroxide in the presence of Linde molecular sieve type 4A at 0—20°. Evaporation of a solution thus obtained yields a white solid which is difficult to free from tetrahydrofuran, and which reacts rapidly with water, giving bistrifluoromethylhydroxylamine and sodium hydroxide. The salt, contaminated with sodium fluoride, can also be obtained by passing gaseous bistrifluoromethylhydroxylamine over sodium wire at 20°/50 mm.; this method is inconvenient, and on one occasion its use led to a violent explosion.



Bistrifluoromethylnitroxy-compounds are useful as intermediates in the synthesis of other fluoro-compounds. Thus, pyrolysis of the compound $(CF_3)_2N{\cdot}O{\cdot}CO{\cdot}CF_3$ in a platinum-lined autoclave at 220° yields tristrifluoromethylamine (33%), tristrifluoromethylhydroxylamine (50%), carbon dioxide, and carbon monoxide.

(*Received, March 6th,* 1967; *Com.* 212.)

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[1] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.* (*C*), 1966, 901; R. E. Banks, R. N. Haszeldine, P. M. Lloyd, G. Shaw, and M. J. Stevenson, unpublished results.

[2] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1957, 1741.