

Preparation of Mercury(II) Bis(trifluoromethyl)nitroxide

By H. J. EMELÉUS* and P. M. SPAZIANTE

(University Chemical Laboratory, Lensfield Road, Cambridge)

THE stable bistrifluoromethylnitroxide radical, $(\text{CF}_3)_2\text{NO}\cdot$, first prepared by Blackley and Reinhard,¹ is known to react with lead to form the salt-like compound $\text{Pb}[\text{ON}(\text{CF}_3)_2]_2$ and with tin to form a mixture of tin(II) oxide and $\text{Sn}[\text{ON}(\text{CF}_3)_2]_2$.² The sodium derivative $\text{NaON}(\text{CF}_3)_2$ has also been made from the hydroxylamine, $(\text{CF}_3)_2\text{NOH}$, and used as a reagent in various syntheses.³ We have now found that the radical reacts at room temperature with mercury to give a white solid, identified by analysis as mercury(II) bis(trifluoromethyl)nitroxide, $\text{Hg}[(\text{CF}_3)_2\text{NO}]_2$. Reaction occurs either with the gaseous radical or when excess of the liquid radical is shaken with mercury in a sealed tube. By recovering and weighing unchanged radical the conversion has been shown to be quantitative. The mercurial separates from the liquid-phase reaction as long colourless needles, the form of which suggests that they may be built up of long chains of four-co-ordinated mercury atoms linked through oxygen by double $(\text{CF}_3)_2\text{NO}$ bridges. The structure is being investigated.

Attempts to sublime the mercurial in vacuum at 100° resulted in its complete decomposition and

bis(trifluoromethyl)nitroxide radical was recovered quantitatively without the formation of dimer. The decomposition resembles that of mercury(II) oxide at a higher temperature. The mercurial reacted quantitatively with hydrogen iodide to form bis(trifluoromethyl)hydroxylamine, $(\text{CF}_3)_2\text{NOH}$, and mercuric iodide. Bromine gave mercuric bromide together with radical, recovery of which was quantitative. No evidence was obtained in this and other experiments that the radical will combine with chlorine, bromine, or iodine.

The mercurial appears to be a useful preparative reagent and to resemble bis(trifluoromethylthio)mercury rather than bis(trifluoromethyl)mercury. Thus it reacts with acetyl chloride to form $(\text{CF}_3)_2\text{NOCOMe}\dagger$ and mercuric chloride. With bis(trifluoromethyl)iodophosphine the products were $(\text{CF}_3)_2\text{NOP}(\text{CF}_3)_2$ and a second compound, which was probably a phosphorus(V) derivative. Reactions with other halides have been observed and will be reported.

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† Prepared by another route; private communication by J. M. Shreeve.

¹ W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, 1965, **87**, 802.

² S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Doklady Akad. Nauk, S.S.S.R.*, 1965, **160**, 1319.

³ R. E. Banks, R. N. Haszeldine, and D. L. Hyde, *Chem. Comm.*, 1967, 413.