

Received March 29, 1988, accepted July 9, 1988

REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH GERMANE

H.G. ANG and F.K. LEE

Chemistry Department, National University of Singapore, Lower Kent Ridge, Singapore 0511 (Singapore)

SUMMARY

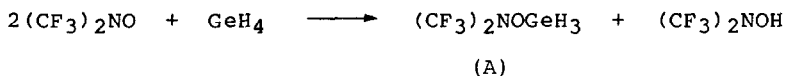
Bis(trifluoromethyl)nitroxyl reacts with germane to give bis(trifluoromethyl)nitroso-germane. This latter is unstable at room temperature, and is converted to di-[bis(trifluoromethyl)-germanium, germane and hydrogen. The new bis(trifluoromethyl)-nitroxyl derivatives are confirmed by their elemental analyses, infrared spectra and their reactions with hydrogen chloride.

INTRODUCTION

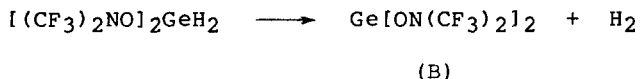
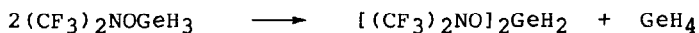
Bis(trifluoromethyl)nitroxyl has been found to be a good hydrogen abstractor as well as a radical scavenger [1,2]. This has been used to advantage as a synthetic route to obtain derivatives containing the nitroxyl group. In this paper, we report the reactions of the nitroxyl radical with germane and the properties of the derivatives.

DISCUSSION

The reactions of bis(trifluoromethyl)nitroxyl and germane at -70 C proceed according to the equation:

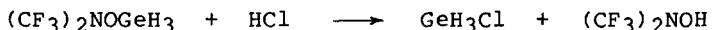


Bis(trifluoromethyl)nitroso-germane (A), a colourless gas, is unstable at room temperature. On standing for three hours, it undergoes disproportionation followed by reductive elimination to give the divalent germanium derivative, $\text{Ge}[\text{ON}(\text{CF}_3)_2]_2$ (B), germane and hydrogen, according to the equations:



Compound (B) is a stable yellow solid whose ^{19}F nmr gives a single resonance at 34.4 ppm downfield w.r.t. CF_3COOH .

Compound A reacts with excess hydrogen chloride to give a stoichiometric amount of the corresponding chlorogermane and bis(trifluoromethyl)hydroxylamine, as shown below:



The reactions with compound B at room temperature, on the other hand, give only one mole of bis(trifluoromethyl)hydroxylamine. The yellow residue, which is hygroscopic and contains chlorine and the nitroxyl group is most probably $(\text{CF}_3)_2\text{NOGeCl}$.

The infrared spectra of compounds A and B (Table 1) are consistent with formulation as $(\text{CF}_3)_2\text{NOGeH}_3$ and $[(\text{CF}_3)_2\text{NO}]_2\text{Ge}$ respectively.

TABLE 1
IR Spectra of R_2Ge and $RGeH_3$ ($R = (CF_3)_2NO$)

R_2Ge	$RGeH_3$	Assignment
	2154 (vs,s)	Ge-H str
1617 (s,s)		Ge-O str
	1397 (m)	
1312 (s,s)	1311 (vs,s)	
1264 (s,s)	1274 (vs,s)	C-F str
1214 (s,s)	1232 (vs,s)	
1069 (s,s)	1039 (s,s)	N-O str
973 (s,s)	971 (s,s)	C-N str
	807 (m)	Ge-H str
815 (vs,b)	785 (m)	Ge-O str
	712 (s,s)	C-F def

EXPERIMENTAL

Reaction with Germane

0.1110 g (1.45 mmole) of germane and 0.4872 g (2.90 mmole) of bis(trifluoromethyl)nitroxyl were reacted in an evacuated sealed pyrex tube. On warming to room temperature, a colourless liquid was obtained. Later, an orange-brown solid appeared. Vacuum fractionation gave (a) bis(trifluoromethyl)hydroxylamine (0.4590 g, 2.715 mmole), identified by its i.r. spectrum (b) unreacted germane (0.0547 g, 0.072 mmole), and (c) a colourless liquid (A). Its molecular weight determined by Regnault's method gives 238. $(CF_3)_2NOGeH_3$ requires 244.

On standing at room temperature for three hours, compound (A) was converted to a yellow solid whose elemental analysis gave C, 12.12% and N, 7.21 %. $[(CF_3)_2NO]_2Ge$ requires C, 11.76% and N, 6.8%. Germane and a non-condensable gas which was assumed to be hydrogen were also formed.

Reaction of Compound A with anhydrous HCl

0.2050 g (0.830 mmole) of Compound A and 0.1212 g (3.30 mmole) of anhydrous HCl were reacted in an evacuated sealed tube. On warming to room temperature, a colourless liquid was obtained. Vacuum fractionation gave (a) bis(trifluoromethyl)hydroxylamine (0.1263 g, 0.747 mmole) and (b) a colourless vapour identified as GeH_3Cl by its infrared spectrum with the following peaks: 2109 s, 1035 s, 840 (doublet) m [3]. Its molecular weight determined by Regnault's method gives 110. GeH_3Cl requires 111.

Reaction of Compound B with anhydrous HCl

0.0522 g (0.128 mmole) of Compound B and 0.0175 (0.480 mmole) of anhydrous HCl were reacted in an evacuated sealed tube. A colourless liquid was formed on warming to room temperature. Vacuum fractionation yields bis(trifluoromethyl)hydroxylamine (0.0213 g, 0.126 mmole) and unreacted HCl. A yellow residue in the reaction tube is hygroscopic. It dissolves in 10% nitric acid and gives a positive test for chloride. Its IR spectrum shows the presence of bis(trifluoromethyl)nitroxyl group.

ACKNOWLEDGEMENT

We thank the National University of Singapore for a research grant. One of us (LFK) thanks the University for a Research Scholarship.

REFERENCES

- 1 H.G. Ang, Chem. Commun. (1968) 1320.
- 2 H.G. Ang and Y.C. Syn, Adv. Inorg. Radiochem., 1974, Vol. 16.
- 3 D.E. Freeman, K.H. Rhee and M.K. Wilson, J. Chem. Phys., 39 (1963) 2908.