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REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH GERMANE

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SUMMARY

Bis(trifluoromethyl)nitroxyl reacts with germane to give bis(trifluoromethyl)nitroxy-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.

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DISCUSSION

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

$$2(CF_3)_2NO + GeH_4 \longrightarrow (CF_3)_2NOGeH_3 + (CF_3)_2NOH$$

(A)

Bis(trifluoromethyl)nitroxy-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, $Ge[ON(CF_3)_2]_2$ (B), germane and hydrogen, according to the equations:

$$2(CF_3)_2NOGeH_3 \longrightarrow [(CF_3)_2NO]_2GeH_2 + GeH_4$$

$$[(CF_3)_2NO]_2GeH_2 \longrightarrow Ge[ON(CF_3)_2]_2 + H_2$$

(B)

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:

$$(CF_3)_2NOGeH_3 + HCl \longrightarrow GeH_3Cl + (CF_3)_2NOH$$

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 $(CF_3)_2NOGeCl$.

The infrared spectra of compounds A and B (Table 1) are consistent with formulation as $(CF_3)_2NOGeH_3$ and $[(CF_3)_2NO]_2Ge$ 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.

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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.