[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHN CARROLL UNIVERSITY]

DIBUTOXYISOTHIOCYANOSILANE AND THE SILICON-HYDROGEN BOND

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Received November 12, 1951

Several aryl, alkyl, and alkoxy isocyanates and isothiocyanates have been prepared by reacting the corresponding chlorosilanes with the isocyanate or isothiocyanate of lead or silver. This method, however, has been shown to be unsuitable for the preparation of isocyanates or isothiocyanates containing a silicon-hydrogen bond (1). It was believed that thiocyanogen would be satisfactory for this purpose.

Thiocyanogen was reacted with tri-*n*-butoxysilane to give di-*n*-butoxyisothiocyanosilane, leaving the silicon-hydrogen bond intact. When an attempt was made to analyze for the isothiocyanate group (2), it was found that silver thiocyanate was not precipitated as expected, but that the silver ion had been reduced, apparently by the hydrogen of the silicon-hydrogen bond. To substantiate this contention, the work of Forbes and Anderson (1) was repeated, and it was found that when trichlorosilane reacts with silver isocyanate an appreciable amount of elemental silver is precipitated, the reaction apparently taking the following course:

$$\text{(a)} \quad 2SiHCl_3 + 8AgNCO \rightarrow 2Si(NCO)_4[+Si(CNO)_4] + 6AgCl + 2Ag + H_2$$

EXPERIMENTAL

Preparation of di-n-butoxyisothiocyanosilane. Tri-*n*-butoxysilane was prepared from *n*-butanol and trichlorosilane by the method of Havill, Joffe, and Post (3). Thiocyanogen was prepared by the action of bromine on lead thiocyanate (4).

Tri-*n*-butoxysilane (30 g., 0.12 mole) was added to 50 ml. of dry benzene in a three-necked flask fitted with a stirrer, reflux condenser, and dropping-funnel. The flask was cooled in an ice-bath and a freshly prepared benzene solution containing approximately 0.2 mole of thiocyanogen was added with stirring. The reaction mixture was stirred for three hours, at the end of which time the greenish-yellow solution was decanted and fractionated. The yield of pure di-*n*-butoxyisothiocyanosilane was 10.4 g. (44%); b.p. 98–99°/6 mm.

Anal. Calc'd for $(C_4H_9O)_2SiH(NCS)$: C, 46.3; H, 8.12; Si, 12.0; Mol. wt., 233.
Found: C, 46.1; H, 8.14; Si, 11.9; Mol. wt., 235.

Reaction of trichlorosilane with silver isocyanate. The reactants were used in the same proportion as was done by Forbes and Anderson (1). After the reaction was completed, the reaction mixture was shielded from light and allowed to stand for two days. After filtration the residue was extracted with large volumes of benzene to remove slightly soluble isocyanates, and then treated with concentrated ammonium hydroxide to extract any silver salts. The ammonium hydroxide extractions were continued until there was no longer any silver in the filtrate.

The black residue was then washed with water and heated with dilute nitric acid. After filtering the acid solution, silver chloride was precipitated by the addition of hydrochloric acid. There was obtained 11.74 g. of silver chloride, representing 8.83 g. of elemental silver.

This indicates that 20.4% of the silver introduced as silver isocyanate was regained as metallic silver. Equation (a) indicates a theoretical reduction of 25%.

SUMMARY

1. Tri-*n*-butoxysilane reacts with thiocyanogen to form di-*n*-butoxyisothiocyanosilane, showing that the *n*-butoxy group is displaced in preference to the hydrogen.

2. When a solution of silver nitrate is added to the isothiocyanosilane, the silver ion is reduced, apparently by the silane hydrogen.

3. The reaction of trichlorosilane with silver isocyanate has been repeated, and it was shown that metallic silver is a product of the reaction. An equation for the reaction has been proposed.

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REFERENCES

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