Summary

Cobalt and sulfur are entrained to various degrees when iron is separated by means of phosphate, ammonia and ammonium salts, and zinc oxide. A single phosphate separation leaves practically no cobalt or sulfur in the precipitate. Separation of iron with ammonia and ammonium salts gives almost complete recovery of sulfur in one precipitation, but cobalt is very strongly entrained and a large number of re-precipitations are necessary to liberate this element completely from ferric hydroxide in ammoniacal solution. Separation of iron with zinc oxide if the filtration is performed hot yields most of the cobalt and sulfur in one precipitation, though the recovery is not satisfactory and for exact analyses a second precipitation is necessary. If filtration is done in the cold the retention of cobalt is slightly increased and the entrainment of sulfur is very markedly increased.

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NOTES

The Reaction between Triethylsilane and Methyllithium

BY HENRY GILMAN AND SAMUEL P. MASSIE, JR.

In connection with studies concerned with the preparation of lithium triethylsilicide, $(C_2H_5)_3SiLi$, an examination was made of the reaction of triethylsilane with methyllithium. The course of reaction is apparently best expressed as

$$(C_2H_5)_3SiH + CH_3Li \longrightarrow (C_2H_5)_3Si(CH_3) + LiH$$

An examination is being made of some other related hydrides, particularly those of germanium and tin.

Kraus and Nelson[1] in a comprehensive study of reactions in liquid ammonia and in liquid ethylamine presented convincing evidence for the preparation of lithium triethylsilicide by an indirect procedure. They showed that triphenylgermanyltriethylsilane was cleaved by lithium in liquid ethylamine to give lithium triphenylgermanide and lithium triethylsilicide.

$$(C_6H_5)_3Ge\text{-}Si(C_2H_5)_3 + 2Li \longrightarrow (C_6H_5)_3GeLi + (C_2H_5)_3SiLi$$

The salts could not be separated and identified as such, but their formation was demonstrated by reaction of the mixture of salts with ammonium bromide to give triphenylgermane and triethylsilane; and by reaction with ethyl bromide to give ethyltriphenylgermanium and tetraethylsilicon.

Experimental

First, silicochloroform was prepared[1] from dry, finely powdered ferrosilicon[2] by heating in a stream of hydrogen chloride for ten and one-half hours at 270–295°. Then, in accordance with the procedure of Kraus and Nelson,[1] the triethylsilane was formed by interaction of silicochloroform and ethylmagnesium bromide.

In a flask provided with a mercury-sealed stirrer, a dropping funnel, a condenser, and an outlet tube connecting with a Dry Ice trap and a gas-collecting bulb, was placed 0.064 mole of methyllithium[3] in 80 cc. of ether subsequent to sweeping out with dry nitrogen. On the slow addition, with stirring, of 7.7 g. (0.066 mole) of triethylsilane there was only a slight reflux. As the reaction proceeded the mixture increased in cloudiness, and after three and one-half hours Color Test I[4] was positive. However, the color test was negative after stirring an additional ten hours at room temperature and then refluxing for twelve and one-half hours. No gas was evolved. When stirring was stopped, a white solid settled out leaving a yellow supernatant liquid. The weight of solid obtained after filtration under nitrogen was 0.7 g. Analysis of the solid by treating an aliquot with water and measuring the hydrogen evolved, and then by titrating the aqueous hydrolysate with standard acid showed the solid to be composed of lithium hydride and a basic material which was largely lithium hydroxide. In a typical analysis 0.0108 g. of the solid gave on hydrolysis 9.63 cc. of hydrogen which corresponds to a 42% yield of lithium hydride. The total amount of lithium hydroxide as determined by titration of the hydrolysate was 0.000779 mole. The calculated quantity of lithium hydroxide on the basis of a 42% yield of lithium hydride, with the remainder of the solid being lithium hydroxide, is 0.000737 mole.

From the ether filtrate was obtained by distillation, 4.5 g. (54%) of triethylmethylsilicon; b. p., 119–123°; d^{20}_{20} 0.7420.

Anal.[5] Calcd. for $C_7H_{18}Si$: Si, 21.54. Found: Si, 21.56 and 21.66.

The yields of triethylmethylsilicon from two other reactions starting with 0.066 mole of triethylsilane were 3.0 g. (35%) and 3.3 g. (38%), respectively.

Triphenylsilane reacts with RLi compounds in the manner described for triethylsilane and methyllithium. However, under corresponding conditions there appears to be no reaction wih some Grignard reagents (studies by Horace Melvin).

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(1) Kraus and Nelson, THIS JOURNAL, **56**, 200 (1934).

(2) Furnished in part by Keokuk-Electro Metals Co., Keokuk, Iowa.

(3) Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933). See, also, Gilman, Zoellner, Selby and Boatner, *Rec. trav. chim.*, **54**, 584 (1935).

(4) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(5) The analysis for silicon was by the Parr bomb fusion procedure. See, Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 802 (1941); Schumb, Ackermann, and Saffer, *ibid.*, **60**, 2488 (1938); and Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1**, (No. 4) 21 (1936) [*C. A.*, **31**, 655 (1937)].