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PRELIMINARY COMMUNICATION

REACTIONS OF DIMETHYL SULFOXIDE WITH ORGANOSILICON HYDRIDES

VALERIE J. KUCK* and ROBERT W. WRIGHT
Owens–Illinois, Inc., Toledo, Ohio (U.S.A.)

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Dimethyl sulfoxide is known as an oxidizing agent for a wide variety of organic and inorganic compounds. A recent review[1] surveys the literature through May, 1966 on reactions in which dimethyl sulfoxide functions as the oxidizing agent. Organic sulfoxides have also been investigated as ligands in coordination compounds with Lewis acids. Issleib and Tzschach[2] studied the reactions of diphenyl sulfoxide with silicon halides. They found that depending upon the halide, silica or chlorosiloxanes were formed in addition to diphenyl sulfides and halogenated diphenyl sulfides. Lappert and Smith[3] investigated addition compounds of sulfoxides with boron, silicon, and tin halides. They reported that dimethyl sulfoxide reacts with silicon tetrachloride in an inert solvent to give chloromethyl methyl sulfide, and a quantitative yield of silica according to the following equation:

$$2(CH_3)_2SO + SiCl_4 \rightarrow 2CH_3SCH_2Cl + SiO_2 + 2HCl$$

More recently, sulfoxide complexes of Group IV organometallic compounds were investigated by Langer and Blut[4]. A number of stable organotin and lead halide complexes were prepared, but the organosilicon and germanium halides were said to undergo hydrolysis or solvolysis in dimethyl sulfoxide with formation of less well-defined oxide or hydroxide complexes.

We now report that reactions of the type indicated above are not limited to the silicon halides, but that they also occur with organosilicon hydrides, giving a new method for the preparation of siloxanes.

In a preliminary study, we have found that diphenyl methylsilane reacts at ambient temperatures with dimethyl sulfoxide solutions containing trace amounts of zinc chloride (dried in a stream of hydrogen chloride at 200°) to give the expected disiloxane in greater than 90% yield according to the stoichiometry:

$$2Ph_2MeSiH + Me_2SO \xrightarrow{ZnCl_2} (Ph_2MeSi)_2O + H_2 + Me_2S$$

In the absence of a Lewis acid, no reaction is observed even at elevated temperatures.

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*Present address: Bell Telephone Laboratories, Murray Hill, New Jersey (U.S.A.)

Dimethyl sulfide and hydrogen were identified by mass spectroscopy. The molar ratio of the silane starting material to the hydrogen produced is 1.89:1.

In order to gain some understanding of the reaction mechanism, perdeuterated dimethyl sulfoxide, $(D_3C)_2SO$, was employed as the reactant and solvent. The gases, volatile below –78°, were collected and, by mass spectroscopy, found to be a mixture of H_2 and HD in a H_2:HD ratio of 27:1. From this result, one is led to conclude that little α-hydrogen abstraction, or elimination from the sulfoxide has taken place. Consequently, the mechanism must differ from that reported earlier for the silicon halide reactions[3].

Other Lewis acids were investigated as catalysts for the reaction. Acids of moderate strength, *i.e.*, cadmium chloride, titanium tetrachloride, and di(n-butyl)tin dichloride, are satisfactory catalysts. Other Lewis acids, such as, ferric chloride, cupric bromide, chromic chloride, and aluminum chloride were inactive as catalysts. The latter may form very stable addition compounds with dimethyl sulfoxide which are not expected to participate in further reaction.

EXPERIMENTAL

The appropriate silane was dissolved in DMSO which had been previously dried over molecular sieves. After the addition of the catalyst, the reactants were maintained at 105° under a dry nitrogen atmosphere for approximately four hours. With diphenyl methyl silane, the disiloxane was extracted from the reaction medium with petroleum ether (65–70° cut). The petroleum ether solution was separated from the reaction medium, evaporated to dryness under vacuum, and the residue recrystallized in methanol to give a product identified by infrared analysis as the expected disiloxane, $(Ph_2MeSi)_2O$ (92% yield, m.p. 47–48°, b.p. 422°; reported[5] m.p. 50°, b.p. 418°). The hydrogen was collected in a gas cell and identified by mass spectroscopy. A quantitative estimate of the hydrogen produced was obtained by a water displacement method. Dimethyl silane was trapped in a liquid nitrogen trap and identified by infrared and gas chromatography analyses.

Melting points were obtained both from a Fisher–Johns instrument and on a DuPont 900 Differential Thermal Analyser. Boiling points were measured on the latter instrument.

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