

Preliminary communication

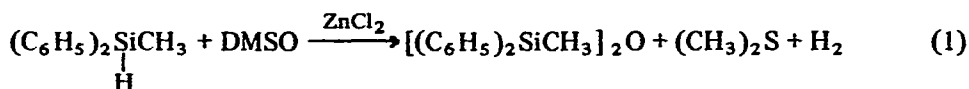
An unexpected reaction involving triphenylgermylsodium and dimethylsodium in dimethyl sulfoxide

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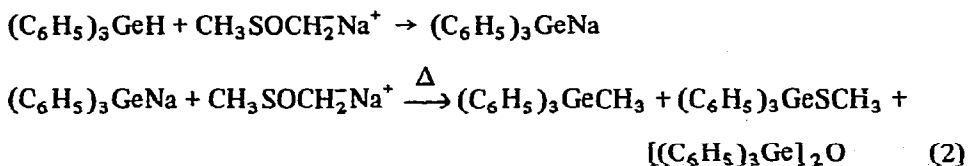
Reactions of organometallic hydrides and alkali metal derivatives of Group IV with dimethylsulfoxide (DMSO) or its conjugated base have not been extensively studied. Dimethylsodium(I) in DMSO converts methyl-diphenylsilane(II) to a mixture of the corresponding silanol and disiloxane at room temperature¹, and diphenylsilane is converted to octaphenylcyclotetrasiloxane under the same conditions. We have observed that the analogous reaction of I and triphenylsilane gives triphenylsilanol. Also, II reacts with DMSO at room temperature in the presence of Lewis acids, such as zinc(II) chloride, to give the corresponding disiloxane according to Eq. 1². Triphenylgermane (III) has been reported to undergo an acid-base



reaction with dimethylpotassium in DMSO at room temperature³.

In connection with some other work, we wanted to generate triphenylgermylsodium (IV) from I and III in DMSO, remove the DMSO by vacuum distillation, and use IV in a further reaction in a different solvent. However, when this experiment was performed, we isolated the unexpected products methyltriphenylgermane (V) and thiomethyltriphenylgermane (VI).

Subsequent experiments revealed that when III was heated with dimethylsodium or -potassium in DMSO at 85–90°, typically for a period of 4 h, V, VI, and small amounts of hexaphenyldigermoxane VII were also formed (Eq. 2):



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The above products were not formed in the absence of base, and use of 0.10 equivalents of I did not lead to detectable quantities of V and VI. The relative amounts of V and VI formed in these reactions are dependent on the concentration of I. When I and III are reacted in equimolar quantities at 85–90° for 4 h and the mixture subsequently hydrolyzed, the ratio III/V/VI is ca. 1.5/1.0/1.0, as determined by NMR. Use of a 3/1 ratio of I to III under the same conditions gave a 2.1/1.0 ratio of V to VI; no recovered III was found in this experiment. Yields of V up to 50% may be isolated.

A number of reactions in the literature show at least a formal analogy to that discussed above. Both aromatic hydrocarbons^{4–6} and conjugated dienes⁶ are methylated by DMSO in the presence of base under experimental conditions comparable to ours. The reaction of I with benzophenone^{7,8} leads to a variety of products among which 1,1-diphenyl-2-thiomethylethylene was identified. It has been suggested⁹ that alkali metals react with DMSO to give methanesulfenate and the methyl derivative of the metal. It is known that I undergoes a decomposition under prolonged heating at temperatures above 80°,^{10,11} and the volatile products of this decomposition have been identified as methyl-substituted butadienes and dimethyl sulfide¹¹.

Although the mechanistic aspects of the reaction under discussion are still under investigation, it seems probable that IV reacts with the as yet unidentified intermediates formed in the thermal decomposition of I to give V, VI, and VII. It also seems reasonable to assume that these intermediates are involved in the methylation of aromatic hydrocarbons and dienes discussed above. However, another mechanistic pathway, involving addition of I and subsequent elimination of methanesulfenate ion, has also been proposed^{4–8} for these reactions.

Initial identification of V and VI was based on a comparison of their infrared and proton NMR spectra (60 MHz) with those reported. The IR spectrum of V was in excellent agreement with that reported¹² and its NMR spectrum in CCl₄ exhibited a Ge–CH₃ resonance at δ 0.85. Compound VI exhibited an S–CH₃ resonance in its NMR spectrum at 113 Hz downfield from tetramethylsilane (lit.¹³ 114.8 Hz) and Ge–S stretching in the IR at ca. 395 cm⁻¹. In thiomethyltrimethylgermane¹⁴, Ge–S stretching is assigned at 385 cm⁻¹ and ν_{as} and ν_s for Ge–S–C are given as 404 and 400 cm⁻¹, respectively¹⁵.

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