

A New Route to Iodomethyl-substituted Methylpolysilanes¹⁾

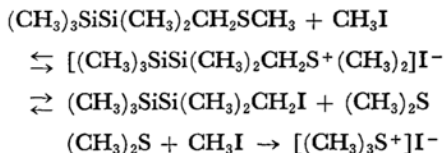
Hideki SAKURAI, Mitsuo KIRA and Makoto KUMADA

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

(Received April 17, 1968)

In a previous communication,²⁾ we have described a new method of preparing methylthiomethyl-substituted silanes using a novel methylthiomethyl Grignard reagent. We wish to report the reaction of these methylthiomethylsilanes with methyl iodide leading to iodomethyl-substituted silanes.

(Methylthiomethyl)pentamethyldisilane (I) gave an expected sulfonium salt, $(\text{Me}_2\text{S}^+\text{CH}_2\text{Si}_2\text{Me}_5)\text{I}^-$, mp 98.5°C, when I was treated with methyl iodide in ether solution at room temperature. However, when I was refluxed in benzene with an excess amount of methyl iodide, (iodomethyl)-pentamethyl disilane, bp 79.5–80.0°C/17 mmHg, was obtained in 73.3% yield together with trimethylsulfonium iodide.



1) Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, Apr., 1968; Preprint, III, p. 1942.

2) H. Sakurai, M. Kira and M. Kumada, *Chem. Commun.*, **1967**, 889.

Many procedures for preparing carbon-functional silanes such as halogenations or other reactions with electrophiles³⁾ cannot be extended generally to higher polysilanes because of extensive silicon-silicon bond cleavage. Alternatively, nucleophilic substitutions on a silicon atom would be a preferred route to the carbon-functional organopolysilanes.⁴⁾ Therefore, the present procedure, methylthiomethylation of chlorosilanes followed by conversion to iodomethylsilanes, may be of value to open a new route to the iodomethyl-substituted silanes.

As another example was prepared 1,2-bis(iodomethyl)tetramethyldisilane, bp 113–116°C/8 mmHg, n_D^{20} 1.5820, d_4^{20} 1.7097. This compound has been once reported⁵⁾ but later disclosed to be a mixture of 1,2- and 1,1-bis(iodomethyl)tetramethyldisilane.⁶⁾

Satisfactory analyses and NMR spectra were obtained for these compounds.

3) C. Eaborn, "Organosilicon Chemistry," Butterworths, London (1960), p. 377.

4) H. Sakurai, H. Yamamori and M. Kumada, *J. Org. Chem.*, **33**, 1527 (1968).

5) M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 411 (1964).

6) M. Kumada and M. Ishikawa, unpublished results.