A New Route to Iodomethyl-substituted Methylpolysilanes[1]

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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, $(Me_2S^+CH_2Si_2Me_5)\,I^-$, 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.

$$(CH_3)_3SiSi(CH_3)_2CH_2SCH_3 + CH_3I$$

$$\leftrightarrows [(CH_3)_3SiSi(CH_3)_2CH_2S^+(CH_3)_2]I^-$$

$$\rightleftarrows (CH_3)_3SiSi(CH_3)_2CH_2I + (CH_3)_2S$$

$$(CH_3)_2S + CH_3I \rightarrow [(CH_3)_3S^+]I^-$$

Many procedures for preparing carbon-functional silanes such as halogenations or other reactions with electrophiles[3] 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 reported[5] 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.

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

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[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[6] M. Kumada and M. Ishikawa, unpublished results.