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Preliminary communication

Silyl anions
III*. A facile synthesis of hexaalkyldisilanes from trialkylchlorosilanes

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During a study of trialkylsilyl anions[1,2], we have discovered a very convenient method of preparing hexaalkyldisilanes from chlorosilanes.

In a typical experiment, 33g (0.22 mole) of triethylchlorosilane was added to a dark blue mixture of lithium chips (1.39 g, 0.20 mole) and hexamethylphosphoramide (HMPA, 36 g, 0.20 mole) in diethyl ether (100 ml). After being stirred for 3 h, the mixture was worked up to give 17 g (0.074 mole) of pure hexaethyldisilane (74% yield based on Li). Hexaethyldisiloxane was only the detectable by-product.

$$2R_3SiCl + 2Li \xrightarrow[\text{ether}]{2(Me_2N)_3PO} (R_3Si)_2 + 2LiCl$$

Other examples are listed in Table 1. It is essential to use HMPA in an equimolar ratio to the chlorosilane. Use of excess HMPA (as solvent) resulted in extensive oxidation to give hexaalkyldisiloxanes[3], and use of less than one equimolar amount of HMPA leads to poorer results. Thus, when half of the equivalent ratio of HMPA to trimethylchlorosilane was used, the yield of hexamethyldisilane was only 36%. However, when another half equivalent of HMPA was added to the mixture the yield was increased to 76%. Use of a solvent such as ether or THF is advantageous, since without the ether solvent the yield of hexamethyldisilane was decreased to 45%. Similar results were obtained with sodium, and the form of the metals, whether small pieces or sand, did not affect the results. HMPA can be recovered after the reaction.

The reaction has several advantages as a general method of preparation of hexaalkyldisilanes compared with earlier methods[4,5], *e.g.*: (i) inexpensive sodium metal and diethyl ether can be used, (ii) the reaction does not require vigorous stirring nor any special technique, (iii) the reaction proceeds smoothly to give satisfactory yield under mild conditions involving only a relatively short time at room temperature.

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*For part II, see ref. 2.

TABLE 1

HEXAALKYLDISILANES FROM R_3SiCl AND ALKALI METALS

R	Metal[a]	HMPA to R_3SiCl ratio	Solvent	Reaction time	R_3SiSiR_3 (%)[f]
Me	Li	1	Et_2O	6 h	74[b]
Me	Li	1	Et_2O	1 day	76[b]
Me	Li	0.5	THF	1 day	36[c]
Me	Li	1	THF	2 days[e]	76[c]
Me	Li	1	none	1 day	45
Me	Na-sand	1	Et_2O	1 day	80
Me	Na-pieces	1	THF	1 day	65
Me	Na-sand	1	THF	2 days	67
Me	Na-sand	1	none	6 h	49[d]
Me	Na-sand	1	none	1 day	49[d]
Et	Li	1	THF	1 day	80

[a] An equivalent amount to chlorosilane was used. [b,c,d] The same run, respectively. [e] 0.5 equivalent of HMPA was added after 1 day, see text. [f] Determined by GLC analysis.

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