Preparation of Decamethyltetrasilane by Coupling of Pentamethylchlorodisilane with Lithium

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In a previous paper,(1) we have described the preparation of (chloromethyl)pentamethyldisilane by coupling of chlorobromomethane and pentamethylchlorodisilane with lithium metal in tetrahydrofuran (THF). However, the yield was not reasonably good and among other products, a considerable amount of decamethyltetrasilane was obtained. This fact indicating the coupling of pentamethylchlorodisilane to decamethyltetrasilane seemed interesting to us, since usually trialkylchlorosilanes do not undergo the coupling easily in this reaction condition. Shackelford *et al.*(2) reported that triethylbromosilane did not afford hexaethyldisilane by the coupling with lithium metal in THF. Preparation of hexamethyldisilane by the coupling of trimethylchlorosilane requires usually drastic conditions.(3)

On the other hand, coupling reactions of halosilanes having at least one phenyl group on silicon are known to proceed quite smoothly.(3)

We are now reporting a facile coupling of pentamethylchlorodisilane with lithium metal in THF to give decamethyltetrasilane. Pentamethylchlorodisilane is by no means a *trialkylchlorosilane* but it is interesting to compare the present results with those of chloromonosilanes.

Pentamethylchlorodisilane underwent the coupling reaction very smoothly with lithium in THF to give decamethyltetrasilane in good yield (~84%).

$$2(CH_3)_3SiSi(CH_3)_2Cl + 2Li \xrightarrow{\text{THF}} CH_3[Si(CH_3)_2]_4CH_3 + 2LiCl$$

Coupling of pentamethylchlorodisilane with sodium-potassium alloy was reported to give tetrasilane in 27%(4) or in 50% yield(5), previously.

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

(2) J. M. Shackelford, H. Deschmertzing, C. H. Henther and H. Podall, *ibid.*, **28**, 1700 (1963).

(3) H. Gilman, W. H. Atwell and F. K. Cartledge, *Adv. Organometal. Chem.*, **4**, 1 (1966).

(4) G. R. Wilson and A. G. Smith, *J. Org. Chem.*, **26**, 557 (1961).

(5) M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963).

The yield of the present reaction is therefore exceptionally high compared with these results. Accordingly, it provides a preferable route to decamethyltetrasilane.

Observations of such a smooth reaction prompted us to attempt isolating a possible intermediate of the reaction, pentamethyldisilanyllithium. Stolberg[6] has reported that the cleavage of decamethyltetrasilane by sodium-potassium alloy followed by coupling with trimethylchlorosilane gave a complicated mixture containing several lower homologs of methylpolysilanes. The result has been interpreted in terms of an intermediate pentamethyldisilanyl anion which would be stabilized by the charge distiribution over two silicon atoms.

$$(CH_3)_3Si\text{–}\overset{\ominus}{Si}(CH_3)_2 \longleftrightarrow (CH_3)_3\overset{\ominus}{Si}\text{=}Si(CH_3)_2$$

However, even in the presence of an excess amount of lithium metal, pentamethylchlorodisilane afforded no stable solution of pentamethyldisilanyllithium; quenching of the solution with trimethylchlorosilane gave only a trace amount of octamethyltrisilane. Therefore, it is concluded that pentamethyldisilanyllithium could be produced at first but it reacts very rapidly with pentamethylchlorodisilane. Cleavage of decamethyltetrasilane with lithium in THF is a very slow process contrary to cases of phenyl-substituted disilanes.[7]

$$(CH_3)_3SiSi(CH_3)_2Cl + 2Li \rightarrow (CH_3)_3SiSi(CH_3)_2Li + LiCl$$

$$(CH_3)_3SiSi(CH_3)_2Li + (CH_3)_3SiSi(CH_3)_2Cl \rightarrow CH_3[Si(CH_3)_2]_4CH_3$$

$$(CH_3)_3SiSi(CH_3)_2Li + (CH_3)_3SiCl \rightarrow CH_3[Si(CH_3)_2]_3CH_3$$

Experimental

Materials. Pentamethylchlorodisilane was prepared from hexamethyldisilane by the procedure described before.[8] Trimethylchlorosilane, generously supplied by the Tokyo Shibaura Electric Co. Ltd., was distilled before use. Tetrahydrofuran was distilled from a stock solution containing lithium aluminum hydride.

Coupling of Pentamethylchlorodisilane with Lithium Metal. To a fine powdered lithium metal (2.5 g, 0.36 g atom) in 100 m*l* of THF, was added with stirring 15 g (0.090 mol) of pentamethylchlorodisilane dissolved in 20 m*l* of THF. The reaction mixture was heated to keep a gentle reflux during the addition. After addition was complete, the mixture was stirred and refluxed for 8 hr. After hydrolysis and work-up, 9.6 g (0.037 mol, 82% yield) of decamethyltetrasilane was obtained as a colorless liquid (homogeneous on vpc). Physical constants, IR spectra and retention times on vpc agreed with those of the authentic sample.[5]

An Attempt to Isolate Pentamethyldisilanyllithium. By the essentially same procedure, 17 g (0.1 mol) of pentamethylchlorodisilane in 100 m*l* of THF was allowed to react with 1.4 g (0.2 g atom) of lithium powder placed in 100 m*l* of THF. A grey solution was obtained but a considerable amount of lithium was remained unreacted. After filtering through an L-shaped sidearm packed with glass wool into a dropping funnel, this solution was added to 22 g (0.2 mol) of trimethylchlorosilane quickly. No appreciable heat evolution was observed. After refluxing 6 hr and standing overnight, solvent and then products were removed from the mixture under reduced pressure. Gas-chromatographic examination of the products showed existence of octamethyltrisilane only in a very small amount. Redistillation of the products gave 11 g (0.042 mol 84% yield) of decamethyltetrasilane, bp 109°C (16 mmHg), $n_D^{20}=1.4893$, $d_4^{20}=0.8126$, $MR_D=92.41$ (calcd 92.43).

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[6] U. G. Stolberg, *Z. Naturforsch.*, **18b**, 765 (1963).

[7] H. Sakurai, *Yukigosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem. Japan)*, **25**, 555 (1967).

[8] H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Letters*, **1966**, 5493.