

Medium-ring Cyclosilanes from the Reaction of Dimethyldichlorosilane with Lithium

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Summary The reaction of Me_2SiCl_2 and Li in tetrahydrofuran at or below 0°C produces the new cyclosilanes $(\text{Me}_2\text{Si})_8$ and $(\text{Me}_2\text{Si})_9$, as well as the known compounds, $(\text{Me}_2\text{Si})_5$, $(\text{Me}_2\text{Si})_6$, and $(\text{Me}_2\text{Si})_7$.

mixture of white crystalline solids which could be separated by g.l.c. or (best) by high pressure liquid chromatography on octadecylsilane-coated silica, using methanol as a solvent. Yields are given in the Table.

In a recent communication Laguerre, Dunogues, and Calas¹ reported a high-yield synthesis of dodecamethylcyclohexasilane $(\text{Me}_2\text{Si})_6$ from reaction of Me_2SiCl_2 and lithium metal at 0°C in tetrahydrofuran (THF). We find that $(\text{Me}_2\text{Si})_6$ is indeed formed in good yield in this reaction provided excess of lithium metal is present. The results are, however, quite different when exactly 1 equiv. (or a slight deficiency) of lithium is used. In these cases the products include significant amounts of $(\text{Me}_2\text{Si})_5$, $(\text{Me}_2\text{Si})_7$, $(\text{Me}_2\text{Si})_8$, and $(\text{Me}_2\text{Si})_9$, as well as $(\text{Me}_2\text{Si})_6$, and dimethylsilylene polymer.

In a typical reaction 25.8 g of Me_2SiCl_2 dissolved in 50 ml of THF was added dropwise to 2.78 g (1.00 equiv.) of lithium granules in 600 ml of THF at 0°C , during 1 h, under N_2 . The mixture was stirred for an additional 23 h at 0°C and 250 ml of hexane was then added. The precipitate was filtered off, washed with another 300 ml of hexane and then water, dried, concentrated, and passed through a short alumina column. Evaporation gave a

TABLE. Yields of cyclosilanes from reaction of Me_2SiCl_2 and lithium

Compound	%	^1H n.m.r., δ^a
$(\text{Me}_2\text{Si})_5$	4.9	0.135
$(\text{Me}_2\text{Si})_6$	16.7	0.131
$(\text{Me}_2\text{Si})_7$	7.2	0.127
$(\text{Me}_2\text{Si})_8$	15.8	0.144
$(\text{Me}_2\text{Si})_9$	3.3	0.163
polymer	45.5	—

^a In CCl_4 .

The cyclosilane $(\text{Me}_2\text{Si})_7$ is obtained in 1% yield in the usual synthesis of $(\text{Me}_2\text{Si})_6$ from Me_2SiCl_2 and Na-K alloy,² $(\text{Me}_2\text{Si})_8$ has been detected in trace amounts but never obtained pure,³ and $(\text{Me}_2\text{Si})_9$ is entirely new. These compounds were identified by high resolution mass spectroscopy. Like the other permethylcyclopolysilanes, $(\text{Me}_2\text{Si})_8$ and $(\text{Me}_2\text{Si})_9$ are easily soluble in organic solvents and give sharp singlets in their ^1H n.m.r. spectra (room temperature).

The reaction reported here makes these interesting medium-ring cyclosilanes easily available for further study.

Stirring with excess of lithium in THF converts the seven-, eight-, and nine-membered rings, as well as most of the polymer, into $(\text{Me}_2\text{Si})_6$, accounting for the results published by Laguerre *et al.*¹ The rings which are larger than $(\text{Me}_2\text{Si})_6$ are evidently kinetic products, but why they are formed in such large quantity in this reaction is not

clear, nor is it yet known why the amount of $(\text{Me}_2\text{Si})_8$ invariably exceeds that of both $(\text{Me}_2\text{Si})_7$ and $(\text{Me}_2\text{Si})_9$. The soluble fraction from our reactions includes traces of still larger cyclosilane rings; these have also been found in other syntheses, and will be reported elsewhere.⁴

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¹ M. Laguerre, J. Dunogues, and R. Calas, *J.C.S. Chem. Comm.*, 1978, 272.

² R. West, L. Brough, and W. Wojnowski, *Inorg. Synth.*, 1979, **19**, in the press; cf. U. Graf zu Stolberg, *Angew. Chem.*, 1963, **75**, 206.

³ E. Carberry and R. West, *J. Amer. Chem. Soc.*, 1969, **91**, 5440, 5446.

⁴ R. West, abstracts of papers, Fifth International Symposium on Organosilicon Chemistry, Karlsruhe, Germany, August 1978.