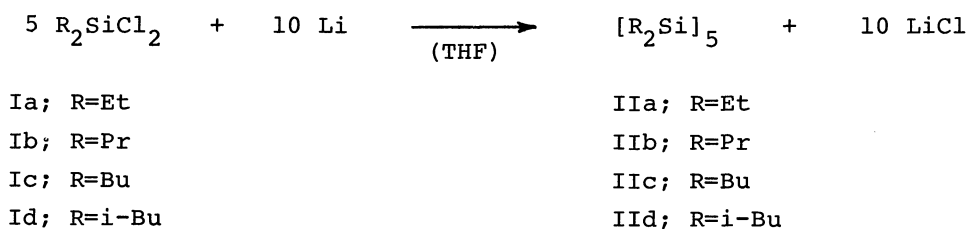


PREPARATION OF PERALKYLCYCLOPENTASILANES, $[R_2Si]_5$ ¹⁾

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Peralkylcyclopentasilanes $[R_2Si]_5$ (where R=Et, Pr, Bu and i-Bu) were prepared by the reactions of corresponding dialkyldichlorosilanes (R_2SiCl_2) with lithium.

The chemistry of cyclopolysilanes is a subject of current interest.²⁾ A six-membered cyclopolysilane, dodecamethylcyclohexasilane,³⁾ and a four-membered one, tetramethyltetra-t-butylcyclotetrasilane,⁴⁾ have been prepared by the reactions of dimethyl- and methyl-t-butyl-dichlorosilane with lithium, respectively. However, workable methods for preparation of peralkylcyclopentasilanes from the chlorosilane-Li system are not available, although Husk et al. reported that the reaction of di-i-butyldichlorosilane with Na-K alloy-biphenyl gave the corresponding cyclopentasilane in only ca. 0.3% yield.⁵⁾ We have now found that the reactions of diethyl-, dipropyl- and dibutyl-dichlorosilane (I)⁶⁾ with lithium gave five-membered ring systems (cyclopentasilanes) in reasonable yields.



Typically,³⁾ to a cold mixture of Li (0.83g) and THF (ice-water bath) was added, under N_2 , a solution of dipropyldichlorosilane (9.3 g) in THF over 40 min with stirring. The mixture was stirred for 2.5 h at 0 °C and for 41 h at room temperature and then cyclohexane was added (50 ml). Work-up gave colorless fine crystals of IIb, mp 178-180 °C (from EtOH), 3.9 g (68%) (Table 1).

The present reaction provides a direct synthetic method for five-membered peralkylcyclopolysilane derivatives,⁷⁾ although indirect synthesis of permethylated

Table 1 Reactions of dialkyldichlorosilanes with lithium^a

Reactants		Reaction time		Product and yield (%) ^b		
R ₂ SiCl ₂	Li	0°	r.t.			
R	(mmol)	(g. atom)	(h)	(h)		[mp] (°C) or c (bp °C/mm)
Et	0.05	0.12	3.5	; 43	(Et ₂ Si) ₅ (IIa)	72 (49) [60-70] (170-172/0.4)
Pr	"	"	2.5	; 41	(Pr ₂ Si) ₅ (IIb)	.. (68) [178-180] ^d
Bu	0.04	0.096	3.5	; 98	(Bu ₂ Si) ₅ (IIc)	67 (56) (180-182/0.14)
<i>i</i> -Bu ^e	0.05	0.12	2.5	; 25	(<i>i</i> -Bu ₂ Si) ₅ (II d)	10 [>300] ^{d, f}

^aIn THF (80 ml). ^bGLC yield using an external standard, *n*-alkane; isolated yield is given in parenthesis. ^cSatisfactory elemental analyses and IR and PMR spectra were obtained for all compounds. ^dFrom EtOH; in a sealed capillary. ^eSee ref. 8. ^fLiterature (ref. 5) mp 178-180 °C: see also ref. 9.

cyclopentasilane can be achieved by photolysis of dodecamethylcyclohexasilane.¹⁰⁾ It is also worthwhile to note that the UV spectra of the cyclopolysilanes, IIa-d, are quite similar each other and close to that of [Me₂Si]₅, but significantly different from that of [Me₂Si]₆,¹¹⁾ and that the cyclopentasilanes obtained in the present work might be expected to serve as versatile precursors for various dialkylsilylenes [R₂Si:].

References and notes

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- 7) Five-membered perphenylcyclopolysilane, decaphenylcyclopentasilane: see H. Gilman and G. L. Schwebke, J. Am. Chem. Soc., 86, 2693 (1964).
- 8) In this reaction, octa-*t*-butylcyclotetrasilane, mp 219-222 °C (sealed capillary) (from EtOH), was also obtained in 36% yield (GLC).
- 9) Other major discrepancies in the physical properties of this compound between our work and that of Husk et al. are as follows: IR (cm⁻¹) 1258w, 1212m [lit., 1255w, 1250s]; UV (c-C₆H₁₂) (nm) λ_{max} 260(sh) (ε ca.2000) [lit., 254.4 (ε 5900)]; PMR (CCl₄) (δ) 0.99(CH₃, d, J=6.3 Hz), 0.60-1.31(CH₂, broad), 1.82(CH, multiplet center) [lit., 1.97(CH₃, d, J=5 Hz), 0.77(CH₂, d), 1.64(CH, multiplet center)]. Husk et al. also gave two boiling points for this compound: bp 250 °C/4 mm in the text and 250 °C/0.4 mm in the experimental.
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