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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.

$$5\ R_2SiCl_2 + 10\ Li \xrightarrow[(THF)]{} [R_2Si]_5 + 10\ LiCl$$

Ia; R=Et
Ib; R=Pr
Ic; R=Bu
Id; R=i-Bu

IIa; R=Et
IIb; R=Pr
IIc; R=Bu
IId; R=i-Bu

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				
R_2SiCl_2		Li	0° ; r.t.		Product and yield (%)[b]		
R	(mmol)	(g.atom)	(h)	(h)			[mp] (°C) or c (bp °C/mm)
Et	0.05	0.12	3.5	; 43	$(Et_2Si)_5$(IIa)	72(49)	[60-70] (170-172/0.4)
Pr	"	"	2.5	; 41	$(Pr_2Si)_5$(IIb)	..(68)	[178-180][d]
Bu	0.04	0.096	3.5	; 98	$(Bu_2Si)_5$(IIc)	67(56)	(180-182/0.14)
i-Bu[e]	0.05	0.12	2.5	; 25	$(i\text{-}Bu_2Si)_5$(IId)	10	[>300][d,f]

[a]In THF (80 ml). [b]GLC yield using an external standard, n-alkane; isolated yield is given in parenthesis. [c]Satisfactory elemental analyses and IR and PMR spectra were obtained for all compounds. [d]From EtOH; in a sealed capillary. [e]See ref. 8. [f]Literature (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 $[Me_2Si]_5$, but significantly different from that of $[Me_2Si]_6$,[11] and that the cyclopentasilanes obtained in the present work might be expected to serve as versatile precursors for various dialkylsilylenes $[R_2Si:]$.

References and notes

1) This paper was presented at the 41st Annual Meeting of the Japan Chemical Society, March 31-April 4, 1980 (Osaka); Abstracts II, p. 807, No. 1029.
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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-C_6H_{12})(nm) λ_{max} 260(sh)(ε ca.2000)[lit., 254.4 (ε 5900)]; PMR (CCl_4)(δ) 0.99(CH_3, d, J=6.3 Hz), 0.60-1.31(CH_2, broad), 1.82(CH, multiplet center)[lit., 1.97(CH_3, d, J=5 Hz), 0.77(CH_2, 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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