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AN ALTERNATIVE ROUTE TO PERALKYLCYCLOPOLYSILANES: THE REACTION OF 1,2-DICHLOROTETRAALKYLDISILANES WITH LITHIUM

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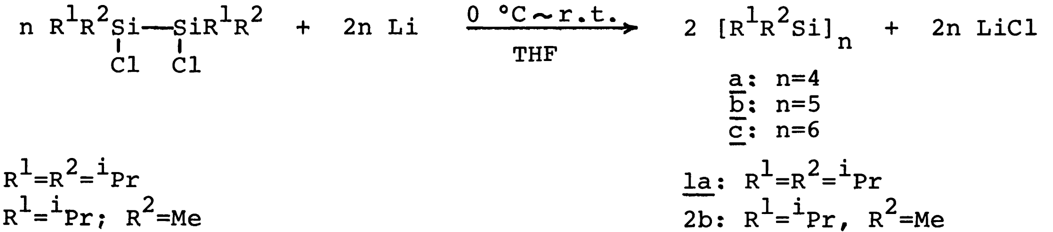
The reaction of 1,2-dichlorotetraalkyldisilanes, $Cl(R^1R^2Si)_2Cl$ ($R^1=R^2={}^iPr$; R^1, $R^2={}^iPr$, Me; R^1, $R^2=Me_3SiCH_2$, Me; R^1, $R^2={}^tBuCH_2$, Me; R^1, $R^2={}^tBu$, Me), with an excess amount of lithium in tetrahydrofuran gave the corresponding peralkylcyclopolysilanes, $[R^1R^2Si]_n$ (n=4-5), under mild conditions.

The chemistry of peralkylcyclopolysilanes is an intriguing subject of current interest because of their versatile physical and chemical properties. Various peralkylcyclopolysilanes,[1,2] including the first example of peralkylcyclotrisilane, hexaneopentylcyclotrisilane,[3] are usually prepared via the lithium-mediated coupling of $R^1R^2SiCl_2$. However, there are no synthetic studies of peralkylcyclopolysilanes starting from dichlorodisilanes bearing alkyl groups other than methyl groups, although the reaction of $Cl(Me_2Si)_2Cl$ with Na/K alloy in THF (reflux; 3 d) has been reported to give a permethylcyclopolysilane, $[Me_2Si]_6$, in rather low yield (30%).[4] We now wish to report on an alternative route to peralkylcyclopolysilanes, $[R^1R^2Si]_n$ where n=4-5; $R^1=R^2$ and $R^1 \neq R^2$, through the reaction of 1,2-dichlorodisilanes, $Cl(R^1R^2Si)_2Cl$, with lithium as reducing agent (Eq. 1). The present reaction was found to proceed readily to afford the expected cyclopolysilanes in fair to good yields under mild conditions.



$$n\ \underset{Cl}{R^1R^2Si}-\underset{Cl}{SiR^1R^2} + 2n\ Li \xrightarrow[THF]{0\ ^\circ C \sim r.t.} 2\ [R^1R^2Si]_n + 2n\ LiCl \quad (1)$$

a: n=4
b: n=5
c: n=6

1: $R^1=R^2={}^iPr$	1a: $R^1=R^2={}^iPr$
2: $R^1={}^iPr$; $R^2=Me$	2b: $R^1={}^iPr$, $R^2=Me$
3: $R^1=Me_3SiCH_2$; $R^2=Me$	3b: $R^1=Me_3SiCH_2$; $R^2=Me$
4: $R^1={}^tBuCH_2$; $R^2=Me$	4a: $R^1={}^tBuCH_2$; $R^2=Me$
5: $R^1={}^tBu$; $R^2=Me$	5a: $R^1={}^tBu$; $R^2=Me$

Table 1. Reaction of 1,2-dichlorotetraalkyldisilanes (1-5)[a] with Li in THF.[b]

Run	Dichlorodisilane	(mmol)	Reaction time 0 °C (h)	r.t. (h)	Product[c] and yield/%[d]
1	1	1.0	1	0	$[{}^{i}Pr_2Si]_4$ (1a)[e] 63
2	2	4.1	0	2	$[{}^{i}PrMeSi]_5$ (2b)[f,h] 30
3	3	3.0	0	1	$[(Me_3SiCH_2)MeSi]_5$ (3b)[g,h] 38
4	4	1.7	0	2	$[({}^{t}BuCH_2)MeSi]_4$ (4a)[g,h] 10
5	5	7.1	0	7	$[{}^{t}BuMeSi]_4$ (5a)[e,g,h] 27(24)

[a] Prepared as shown in Ref. 7. [b] Li: 10-20% excess amount relative to the dichlorodisilane used; THF: 3-10 ml. [c] Compounds, 2b, 3b, and 4a, were fully characterized in the usual manner (NMR, IR, and MS, as well as elemental analysis) (Ref. 8). [d] GLC yield; isolated yield in parenthesis (recrystallized from EtOH). [e] Known compound; isolated by a preparative GLC and identified in the usual manner (1a: Ref. 1b; 5a: Refs. 1c, 2g, and 9). [f] Liquid. [g] Viscous liquid. [h] Mixture of geometrical isomers.

Typically, a mixture of lithium (6.0 mg-atom) and THF (2 ml) was stirred, under Argon, with a solution of $Cl[(Me_3SiCH_2)MeSi]_2Cl$ (3) (3.0 mmol) in THF (5 ml) for 1 h at room temperature. The resulting mixture, on work-up, gave a light-orange liquid. GLC analysis for the mixture showed that the major product was $[(Me_3SiCH_2)MeSi]_5$ (3b) (viscous liquid), 38% yield (GLC), which was isolated by a preparative GLC.

The reactions using dichlorodisilanes, 1-5, gave rise to four- and five-membered rings in 10-63% yields (Table 1). It is of interest to note that the reactions of 2 and 3 gave primarily the corresponding pentamers (2b and 3b) rather than the tetramers (2a[10] and 3a[11]) while other dichlorodisilanes gave tetramers (1a, 4a, and 5a) as major products. Previous papers[1,5,6] have shown that a series of cyclopolysilanes gives the major product with thermodynamically the most stable ring via rapid equilibrium when excess lithium is employed. Thus, cyclopolysilanes listed in Table 1 represent ones with the most stable ring size among their homologues and comparison of bulkiness of the substituents[12] with the ring size indicates that the bulkier the substituents is, the smaller the ring size is (Table 2).

This reaction may provide a novel and sometimes convenient method for the preparation of various cyclopolysilanes starting from the other 1,2-dichlorodisilane

Table 2. Relationship between $\Sigma Es(Si)$ values[a)] for two substituents on silicon and ring size in cyclopolysilanes, $[R^1R^2Si]_n$.

Compound	Substituents R^1	R^2	$\Sigma Es(Si)$	n
6c[b)]	Me	Me	0.00	6
2b	^{i}Pr	Me	-0.556	5
3b	Me_3SiCH_2	Me	..	5
4a	$^tBuCH_2$	Me	..	4
1a	^{i}Pr	^{i}Pr	-1.112	4
5a	^{t}Bu	Me	-1.46	4

a) Ref. 12. b) Ref. 13.

derivatives which are readily accessible in large amounts.[7,14)]

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7) 1: $PhSiCl_3 \xrightarrow{^iPrLi} Ph^iPr_2SiCl \xrightarrow{Li} Ph(^iPr_2Si)_2Ph \xrightarrow[AlCl_3\ cat.]{HCl}$
$Cl(^iPr_2Si)_2Cl$ (1) (overall yield, 46%)
bp 169 °C/70 mmHg

2: $Me(Cl_2Si)_2Me$ (Ref. 15) $\xrightarrow{^iPrLi}$ $Cl(^iPrMeSi)_2Cl$ (2) (63%)
bp 92-94 °C/9 mmHg

3: $Me(Cl_2Si)_2Me$ $\xrightarrow{Me_3SiCH_2MgCl}$ $Cl[(Me_3SiCH_2)MeSi]_2Cl$ (3) (54%)
bp 100-104 °C/5 mmHg

4: $Me(Cl_2Si)_2Me$ $\xrightarrow{^tBuCH_2Li}$ $Cl[(^tBuCH_2)MeSi]_2Cl$ (4) (82%)
bp 135-137 °C/16 mmHg

5: $Me(Cl_2Si)_2Me$ $\xrightarrow{^tBuLi}$ $Cl(^tBuMeSi)_2Cl$ (5) (53%)
bp 98 °C/3 mmHg

All the dichlorodisilanes were fully characterized in the usual manner.

8) 2b: ^1H NMR (CCl_4) δ 0.11-0.24((, $Si\underline{Me}$, 15H), 1.06(s), 1.12(s) (^iPr, 35H); MS (10 eV) m/e 430 [M^+]; IR (liquid film) 2940, 2860(CH), 1241(SiMe) cm^{-1}.

3b: ^1H NMR (CCl_4) δ -0.17(s, $C\underline{H}_2$, 10H), 0.04(s, $C\text{-}Si\underline{Me}_3$, 45H), 0.22(s, $Si\underline{Me}$, 15H); MS (10 eV) m/e 650 [M^+]; IR (liquid film) 2955, 2900(CH), 1247(SiMe) cm^{-1}.

4a: ^1H NMR (CCl_4) δ 0.06-0.33(m, $Si\underline{Me}$, 13H), 1.00(broad s), 1.08(s) ($C\underline{H}_2\text{-}C\underline{Me}_3$, 44H); MS (10 eV) m/e 456 [M^+]; IR (liquid film) 2950, 2960(CH), 1245, 1230(Si-Me) cm^{-1}.

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10) Monitored by GLC technique and the corresponding oxygen-containing five-membered, $[^iPrMeSi]_4O$ (2a') and six-membered compound, $[^iPrMeSi]_4O_2$ (2a") were detected, by GC-MS technique, as minor compounds in the reaction mixture.

11) Identified by GC-MS technique and the corresponding oxygen-containing five-membered compound, $[(Me_3SiCH_2)MeSi]_4O$ (3a') was also detected.

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13) A reaction of $Cl(Me_2Si)_2Cl$ with lithium under similar conditions (see Table 1) afforded $[Me_2Si]_6$ (6c) (30%).

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