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Preliminary communication

PREPARATION AND PROPERTIES OF PERISOPROPYLCYCLOTETRASILANE, $[(Me_2CH)_2Si]_4$

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Summary

Octaisopropylcyclotetrasilane has been prepared in high yield. This cyclotetrasilane was found to undergo ready ring-opening reactions with various reagents, but displacement of the isopropyl group from silicon was not observed.

Although the chemistry of four-membered peralkylcyclopolysilane is of current research interest*, only tetramethyltetra-t-butylcyclotetrasilane, $[SiMeBu^t]_4$, has been studied in detail [1]**. In our continuing work on peralkylcyclopolysilanes [2], we have found that octaisopropylcyclotetrasilane. $[SiPr^i_2]_4$, can be readily prepared in larger quantities, by the reaction of diisopropyldichlorosilane with lithium (eq. 1), and that this cyclotetrasilane behaves somewhat differently from $[SiMeBu^t]_4$ [1].

$$4\ Pr^i_2SiCl_2 + 8\ Li \rightarrow [SiPr^i_2]_4 + 8\ LiCl \qquad (1)$$

To a cold mixture of Li (3.76 g; 0.54 g.-atom) and tetrahydrofuran (THF) (400 ml; dried over Na wire) (ice-water bath) was added, under nitrogen, a solution of diisopropyldichlorosilane (46.4 g; 0.25 mol)*** in THF (100 ml) over 3 h with stirring. The mixture was stirred for 2 h at 0°C and then cyclohexane (300 ml) was added. After filtration, the resulting solution was concentrated, treated with water and then extracted with cyclohexane. Evaporation of the extracts afforded a crystalline solid. Recrystallization from ethanol gave fine colorless needles of octaisopropylcyclotetrasilane, m.p.

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*$[SiMe_2]_4$ [6], $[SiEt_2]_4$ [7] and $[SiBu^i_2]_4$ [ref. 2, Table 1, footnote *e*].

**There have been many reports on octaphenylcyclotetrasilane, $[SiPh_2]_4$.

***This compound was readily prepared in good yield from the reaction of H_2SiCl_2 with Pr^iMgBr giving $Pr^i_2SiH_2$ [see also ref. 3] which was chlorinated with CCl_4 in the presence of $PdCl_2$ catalyst [4].

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317—321°C (sealed capillary), 21.2 g (74% based on the dichlorosilane used).

In order to investigate its chemical properties, the cyclotetrasilane was treated with various reagents. Typically, a mixture containing $[SiPr^i_2]_4$ (1.37 g; 3.0 mmol), $AlCl_3$ (0.41 g; 3.0 mmol) and CH_3COCl (11.0 g; 90 mmol) in CCl_4 (15 ml) was stirred at room temperature for 70 h. After addition of acetone (0.6 ml) and then n-pentane (30 ml), the resulting mixture was filtered and concentrated to give a pale yellow liquid. GLC analysis showed that this liquid contained α,ω-dichloro-octaisopropyltetrasilane in 93% yield. A pure sample of the product, isolated by preparative GLC [0.4 × 30 cm stainless-steel column; Silicone SE-30 10% on Celite 545-AW (60/80 mesh); column temp. 220°C; He carrier), was obtained as a colorless, viscous liquid. The structure was established by the analytical and spectral data as follows: Analysis, Found: C, 54.96; H, 10.38. Calcd. for $C_{28}H_{54}Si_4Cl_2$: C, 54.60; H, 10.69%; NMR (CCl_4, TMS) (δ, ppm) 1.33, 1.25, 1.13 (three peaks, C—CH_3) and 0.67—1.83 (m, CH); IR (neat liquid, sandwich) (cm^{-1}) 2980(sh), 2955s, 2875s, 1464vs, 1380m, 1364m, 1285w, 1232m, 1152w, 1065s, 1022m, 1003(sh), 994s, 964w, 909m, 875vs, 800w and 710w; MS m/e 491, 493 ($M^+ - Cl$).

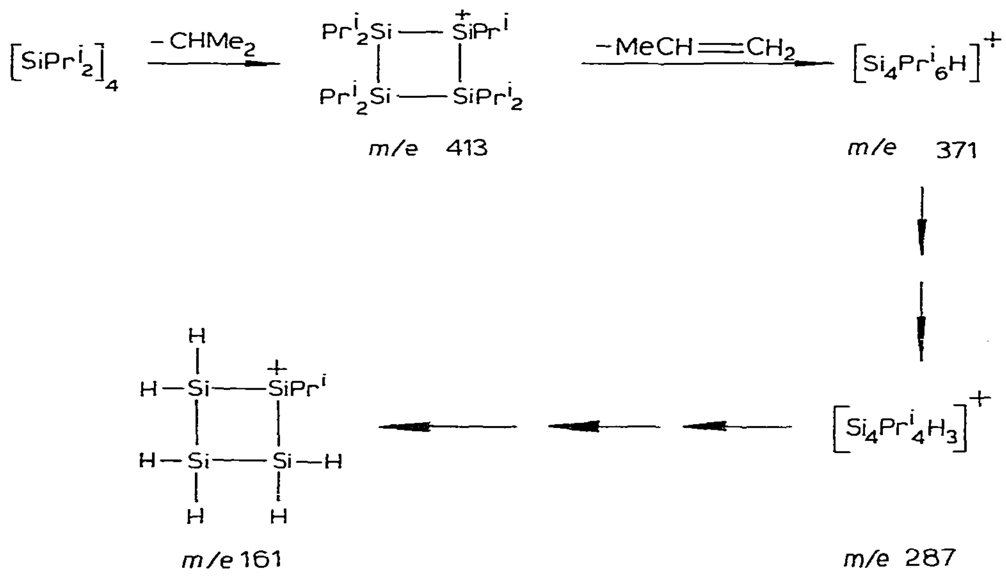
The results for other reactions listed in Table 1 show that the cyclotetrasilane is prone to ring-opening reactions to give linear products (Runs 1—4). However, neither attempted displacement of the propyl substituent(s) (Runs 2, 6 and 8) nor skeletal rearrangement [5] (Runs 2 and 7) was successful. No displacement from silicon occurred in $[SiPr^i_2]_4$, in contrast to the case of $[SiMeBu^t]_4$ [1]. This might be attributable in part to the bulkiness of the isopropyl substituents.

TABLE 1

REACTIONS OF $[SiPr^i_2]_4$ (I) WITH VARIOUS REAGENTS

Run	Reactants (mmol)		Solvent	(ml)	Conditions		Product [a] and yield (%) [b]	
					Temp. (°C);	Time (h)		
1	I	1.0	C_6H_6	10	r.t.	16	$H(SiPr^i_2)_4Cl$	94
	HCl (gas)	bubbling						
2	I	1.0	C_6H_6	10	r.t.		$H(SiPr^i_2)_4Cl$	trace
	$AlCl_3$	2.2						
3	I	3.0	A: CCl_4	15	r.t.	70	$Cl(SiPr^i_2)_4Cl$	93
	$AlCl_3$	3.0						
	CH_3COCl	90	B: C_6H_{12}	10	r.t.	50	$Cl(SiPr^i_2)_4Cl$	71
4	I	1.0	C_6H_6	3	r.t.	0.23	$I(SiPr^i_2)_4I$	95 [c]
	I_2	1.0						
5 [d]	I	1.0	C_6H_6	2	r.t.	20	cyclo-$Si_4Pr^i_8O$	13
	I_2	1.0						
	H_2O	10						
6	I	1.0						
	$HSiCl_3$	4.0	$C_6H_4Me_2$	3	130	48	N.R. [e]	
	H_2PtCl_6 [f]	0.001						
7	I	1.0	$C_6H_4Me_2$	5	130	30	N.R. [e]	
	$AlCl_3$	0.13						
8	I	0.75	C_6H_{12}	5	80	80	N.R. [e]	
	H_2SO_4 (conc.)	0.25						

[a] Satisfactory elemental analyses and IR and NMR spectra were obtained for all compounds. [b] GLC yield based on the cyclosilane used. [c] Uncorrected yield. [d] After the reaction of I with I_2, the resulting mixture was treated with water. [e] No reaction occurred. [f] Used as Speier catalyst.



SCHEME 1

Interestingly, the mass spectrum of the cyclotetrasilane shows that the dominant mode of the decomposition on electron impact appears to be loss of C_3H_7 ($M^+ - 43$) followed by successive loss of propylene, forming Si—H bonds (Scheme 1). Thus, the four-membered ring was stable during the electron impacts and this is in sharp contrast to the chemical reactions.

The UV spectrum of the cyclotetrasilane revealed no sharp absorption band, but only a weak shoulder at 290 nm (ϵ, ca. 100; c-C_6H_{12}). This behavior was very similar to that observed for a steroisomeric mixture of $[SiMeBut]_4$ prepared by the reaction of $ButMeSiCl_2$ with lithium in THF.

Finally, it should be noted that octaisopropylcyclotetrasilane may be a useful starting material for the synthesis of the other derivatives because of its facile accessibility, and is a versatile model compound for the study of various physico-chemical properties.

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