ORGANOMETALLICS

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Organometallics, **1984**, 3 (1), 141-147• DOI: 10.1021/om00079a025 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Synthesis and Some Spectral Properties of Peralkylcyclopolysilanes, $[\mathrm{R^1R^2Si}]_n$ (n = 4–7)

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Received August 2, 1983

The reaction of various dialkyldichlorosilanes, $\mathrm{R^1R^2SiCl_2}$ ($\mathrm{R^1 = R^2}$ = Et, Pr, *i*-Pr, Bu, *i*-Bu, *sec*-Bu; $\mathrm{R^1}$, $\mathrm{R^2}$ = Pr, Me; *i*-Bu, Me; *t*-Bu, Pr; *t*-Bu, Me), with an excess of lithium in tetrahydrofuran gave the corresponding peralkylcyclopolysilanes, $[\mathrm{R^1R^2Si}]_n$ (n = 4–7), in reasonable to good yields. The reaction using the dialkyldichlorosilanes bearing bulky substituents was found to afford smaller ring compounds, mainly four-membered ones, while the dialkyldichlorosilanes with less hindered silicons gave rise to larger ring cyclopolysilanes, mainly five- to seven-membered ones. Ultraviolet and mass spectral properties of these peralkylcyclopolysilanes were investigated.

Introduction

The chemistry of peralkylated cyclopolysilanes is a subject of current interest because of the unique physical and chemical properties of such compounds. Although a number of publications are available on the chemistry of permethylcyclopolysilanes,[1] synthetic studies of peralkylcyclopolysilanes bearing alkyl groups other than methyl are so far limited to rings such as $(i\text{-}\mathrm{Bu_2Si})_5$,[2] $[t\text{-}\mathrm{BuMeSi})_{4-5}$,[3] $[\mathrm{Et_2Si}]_{5-8}$,[4] $t\text{-}\mathrm{BuMeSi(Me_2Si)}_{4-5}$,[5] $t\text{-}\mathrm{Bu_2Si(Me_2Si)}_{4-5}$,[5] $[(\mathrm{CH_2})_4\mathrm{Si}]_{5-12}$,[6] $[(\mathrm{CH_2})_5\mathrm{Si}]_{5-6}$,[6] and $[(t\text{-}\mathrm{BuCH_2})_2\mathrm{Si}]_3$.[7] Recently, we reported in a preliminary communication that peralkylcyclopentasilanes $[\mathrm{R_2Si}]_5$, where R = Et, Pr, Bu, and *i*-Bu, can be prepared by the reactions of dialkyldichlorosilanes ($\mathrm{R_2SiCl_2}$) with lithium.[8] A very satisfactory synthesis of a cyclotetrasilane, $[i\text{-}\mathrm{Pr_2Si}]_4$, via a similar reaction was also published.[9]

This paper deals with a full account of the preparation of a series of peralkylcyclopolysilanes from various dialkyldichlorosilanes by the lithium-mediated reductive coupling and also with some spectral properties (UV and MS) of the cyclopolysilanes.

Results and Discussion

Reductive Coupling of Dialkyldichlorosilanes. Reductive coupling of dialkyldichlorosilanes **1–10** with 20% excess of lithium in tetrahydrofuran (THF) at 0 °C to room temperature gave the corresponding peralkylcyclopolysilanes $[\mathrm{R^1R^2Si}]_n$, where n = 4, 5, and 6, in 26–74% yields (eq 1). The reactions of **2**, **5**, and **7** gave,

$$\underset{\mathbf{1\text{–}10}}{n\mathrm{R^1R^2SiCl_2}} + 2n\mathrm{Li} \xrightarrow[\mathrm{THF}]{0\ ^\circ\mathrm{C\text{–}room\ temp.}} \underset{\substack{\mathbf{3a,5a\text{–}7a,10a}\\ \mathbf{1b,2b,4b,8b}\\ \mathbf{7c}}}{[\mathrm{R^1R^2Si}]_n} + 2n\mathrm{LiCl} \tag{1}$$

a, n = 4; **b**, n = 5; **c**, n = 6

1, $\mathrm{R^1 = R^2}$ = Et; **2**, $\mathrm{R^1 = R^2}$ = Pr; **3**, $\mathrm{R^1 = R^2}$ =
i-Pr; **4**, $\mathrm{R^1 = R^2}$ = Bu; **5**, $\mathrm{R^1 = R^2}$ = *i*-Bu; **6**, $\mathrm{R^1 = R^2}$ =
sec-Bu; **7**, $\mathrm{R^1}$ = Pr, $\mathrm{R^2}$ = Me; **8**, $\mathrm{R^1}$ = *i*-Bu, $\mathrm{R^2}$ =
Me; **9**, $\mathrm{R^1}$ = *t*-Bu, $\mathrm{R^2}$ = Pr; **10**, $\mathrm{R^1}$ = *t*-Bu, $\mathrm{R^2}$ = Me

besides the main products, the higher homologues, **2d** (n = 7), **5b** (n = 5), and **7b** (n = 5), respectively, in low yields (9–11%). Also, GLC analysis for the reaction mixture obtained from **1** showed that **1b** was accompanied by small amounts (less than 5%) of the presumed two larger rings, $[\mathrm{Et_2Si}]_6$, **1c**, and $[\mathrm{Et_2Si}]_7$, **1d**.[4] Cyclopolysilanes derived from the mixed dialkyldichlorosilanes **7–10** were obtained as mixtures of geometrical isomers (Experimental Section). Table I summarizes the results which show that the coupling reactions are quite rapid so that the starting dichlorosilanes were completely consumed within a few hours. Further, the yields and compositions of the products did not change substantially even after a prolonged period of time. From these observations, it is obvious that each reaction gives the respective thermodynamic product mixture (vide infra).

These cyclopolysilanes that are indefinitely air-stable were identified in the usual manner (IR, NMR, UV, and MS as well as elemental analysis). Isotopic pattern coefficients for parent ion clusters showed good agreement with calculated values, confirming the ring size of the cyclopolysilanes to be as indicated (see Table V). In melting point determinations, all the solid samples were found to undergo phase transitions and melted over broad temperature ranges. Similar behavior of cyclic polysilanes has been observed by West and co-workers.[10]

Finally, it should be noted that physical properties (melting point, NMR, and IR) of $[i\text{-}\mathrm{Bu_2Si}]_5$ reported in 1971 by Husk et al.[2] are quite different from those of our compound, **5b**. Although the discrepancies cannot readily be explained, we feel that our compound is more fully characterized.

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Table I. Reaction of Dialkyldichlorosilanes with Lithium in THF

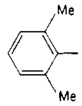
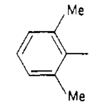
run	reactants: $R^1R^2SiCl_2$ R^1	R^1	mol	Li, mol	reactn time, h: 0 °C	room temp	product [yield,[a] %]	mp,[b,n] °C	bp, °C (mmHg)
1	Et	Et	0.05[c]	0.12[d]	3.5	43[e]	$[Et_2Si]_5$[f] (**1b**) [49 (72)]	120–200[g]	170–172 (0.4)
2	Pr	Pr	0.05[c]	0.12[d]	2.5	41[e]	$[Pr_2Si]_5$ (**2b**) (36) $[Pr_2Si]_7$ (**2d**) (9)	210–220 332–414[h] 414–430	
3	*i*-Pr	*i*-Pr	0.25[g]	0.54[i]	2.0	1	[*i*-$Pr_2Si]_4$ (**3a**) [74]	340–424[h] 424–429	
4	Bu	Bu	0.04[c]	0.096[d]	3.5	98[e]	$[Bu_2Si]_5$ (**4b**) (67)		180–182 (0.14)
5	*i*-Bu	*i*-Bu	0.05[c]	0.12[d]	2.5	25[e]	[*i*-$Bu_2Si]_4$[g] (**5a**) (36) [*i*-$Bu_2Si]_5$[g] (**5b**) (10)	240–260[h] 260–278 334–450[h] 450–468	
6	*sec*-Bu	*sec*-Bu	0.034[c]	0.084[d]	2.0	1	[*sec*-$Bu_2Si]_4$[g] (**6a**) (61)	300–418[h] 418–426	
7	Pr	Me	0.10[j]	0.24[k]	2.0	18[e]	$[PrMeSi]_5$ (**7b**) (10) $[PrMeSi]_6$ (**7c**) (34)		liquid[l,m] liquid[l,m]
8	*i*-Bu	Me	0.05[c]	0.12[d]	2.5	1	[*i*-$BuMeSi]_5$ (**8b**) [56]		188–190 (1.2)
9	*t*-Bu	Pr	0.04[c]	0.096[d]	2.0	3	[*t*-$BuPrSi]_4$ (**9a**) [35]	285–384[h] 384–395	
10	*t*-Bu	Me	0.039[c]	0.098[d]	2.0	0.5	[*t*-$BuMeSi]_4$ (**10a**) [26]	255–270	

[a] Based on the dichlorosilane used; isolated yield; GLC yield in parentheses. [b] In a sealed capillary and by microscopic determination. [c] THF, 20 mL. [d] THF, 60 mL. [e] Reaction essentially was completed within several hours. [f] Glassy solid. [g] Separated by GLC and then recrystallized from EtOH. [h] Colorless clear glassy solid between the temperatures. [i] THF, 400 mL. [j] THF, 40 mL. [k] THF, 120 mL. [l] Separated by GLC. [m] Boiling point was not determined. [n] Previously reported melting points (ref 8 and 9) are incorrect.

Ring Sizes of Cyclopolysilanes and Alkyl Substituents on Silicon. Previous results suggest that the ring size of cyclopolysilanes to be produced depends primarily on the steric bulk of substituents on silicon and also on the reaction conditions employed.[8,9] Thus, West and co-workers[4] reported that condensation of Et_2SiCl_2 with Li produces a series of $[Et_2Si]_n$, where $n = 5–8$. Then it has been shown that, although $[Me_2Si]_6$ is the most stable oligomer in the $[Me_2Si]_n$ series,[11] the thermodynamically favored product in the $[Et_2Si]_n$ series is the five-membered ring compound.[4] Since the equilibrium is reached rapidly when excess lithium is used (and we used excess lithium in all our experiments), the cyclopolysilanes listed in eq 1 are the thermodynamically favored products.

Quite recently, Cartledge proposed a new series of steric parameters for various alkyl groups attached to silicon, Es(Si) values.[12] Comparison of the ring size of the most favored product in the $[R^1R^2Si]_n$ series with the sum of the Es(Si) values for R^1 and R^2 substituents is shown in Table II. It is seen from Table II that qualitatively the increase in the sum of the Es(Si) values resulted in the decrease in the ring size. This observation led us to an expectation that smaller ring compounds such as cyclotrisilanes can be produced if alkyl groups of appropriate steric bulk are introduced onto silicon. Accordingly, we conducted the condensation of *t*-Bu_2SiCl_2 with lithium, but the products were found to be straight-chain compounds such as H-*t*-Bu_2SiSi-*t*-Bu_2H, **11**,[13] rather than the expected cyclotrisilane. However, we have recently succeeded in the synthesis of the first peralkylcyclotrisilane, [(*t*-$BuCH_2)_2Si]_3$, **12**, using dineopentyldichlorosilane as the starting material.[7] This result parallels the first successful synthesis of a perarylcyclotrisilane, hexakis(2,6-dimethylphenyl)cyclotrisilane, **13**, by Masamune and co-workers.[14] The preparation and properties of hexaneopentylcyclotrisilane are described elsewhere.[7]

Table II. Relationship between Sum of the Es(Si) Values[a] for Two Substituents on Silicon and Ring Size in Various Cyclopolysilanes, $[R^1R^2Si]_n$

compd	subst: R^1	R^2	ΣEs(Si)	*n*[b]	ref
B	Me	Me	0.00	6	11
7c	Pr	Me	−0.216	6	*c*
1b	Et	Et	−0.298	5	4, *c*
8b	*i*-Bu	Me	−0.405	5	*c*
2b	Pr	Pr	−0.432	5	*c*
4b	Bu	Bu	−0.450	5	*c*
5a	*i*-Bu	*i*-Bu	−0.810	4	*c*
3a	*i*-Pr	*i*-Pr	−1.112	4	*c*
10a	*t*-Bu	Me	−1.46	4	3, *c*
9a	*t*-Bu	Pr	−1.676	4	*c*
6a	*sec*-Bu	*sec*-Bu		4	*c*
12	*t*-$BuCH_2$	*t*-$BuCH_2$		3	7 (our work)
13				3	14

[a] See ref 12. [b] Thermodynamically controlled product as main product.

Electronic Spectra. It is generally recognized that the electronic properties of cyclopolysilanes are associated with the delocalized σ-bonding framework in the ring systems and the energy transitions of the bondng electrons can be observed in UV absorptions arising from either σ(Si–Si)–σ* or σ(Si–Si)–π* excitations.[1a,3,15] Thus, it is of great interest to compare the UV absorption spectra of the peralkylcyclopolysilanes of different ring size. The UV spectra of these cyclopolysilanes are shown in Figure 1a–c, and their absorption maxima are summarized in Table III. Thus, as seen in Table III, the lowest energy transitions for $[R^1R^2Si]_7$, $[R^1R^2Si]_6$, $[R^1R^2Si]_5$, and $[R^1R^2Si]_4$ occur in the 240–245, 250–260, 260–280, and 290–301 nm regions with varying extinction coefficients, respectively. Previously,

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Table III. UV Spectra for Peralkylcyclopolysilanes, $[R^1R^2Si]_n$

$[R^1R^2Si]_n$			absorptn max[a]	
R^1	R^2	n	λ_{max}, nm (ϵ)	ref
Me	Me	7	242 (5000), 219 (10000)[b]	16
Pr	Pr	7	242 (6200)	c
Me	Me	6	258 sh (1100), 240 sh (5400), 232 (5900)[b]	16
Me	Me	6	257 sh (1300), 233 (5800)	c
Pr	Me	6	257 sh (2800), 232 (7700)	c
Me	Me	5	275 (700), 264 (800)[b]	16
Et	Et	5	265 sh (1400)	c
Pr	Pr	5	260 (1300)	c
Bu	Bu	5	262 (1300)	c
i-Bu	*i*-Bu	5	260 sh (2300)	c
i-Pr	*i*-Pr	4	290 sh (200)	c
i-Bu	*i*-Bu	4	290 sh (200)	c
sec-Bu	*sec*-Bu	4	290 sh (200)	c
t-Bu	Me	4	300 (290), 255 sh (3200), 245 (3400)[b,d]	3
t-Bu	Me	4	301 (190), 262 sh (1900), 247 sh (2080)[e]	c

[a] In cyclohexane. [b] In 2,2,4-trimethylpentane. [c] This work. [d] Compound *10aa*. [e] A mixture of **10aa**/**10ab**/**10ac**/**10ad** = 13:73:12:2 (see Experimental Section).

Table IV. Visible Spectra of CT Complexes between Some Peralkylcyclopolysilanes and Tetracyanoethylene[a]

complex	λ_{max}, nm	color	ref
$[n\text{-}Bu_2Si]_5$/TCNE	590, 440 sh	blue-green	b
$[n\text{-}Pr_2Si]_5$/TCNE	550 sh	red-purple	b
$[t\text{-}BuMeSi]_4$/TCNE	510, 460 sh, 395 sh	red-purple	3, b
$[i\text{-}Pr_2Si]_4$/TCNE	510	red-purple	b
$[Me_2Si]_6$/TCNE	507	red-purple	17, b

[a] In CH_2Cl_2. [b] This work.

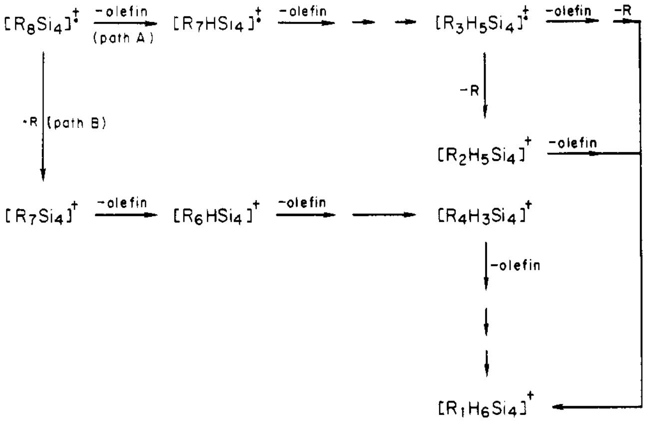
West and co-workers pointed out that decreasing the ring size in permethylcyclopolysilanes destabilizes the σ(Si–Si) bonding levels and shifts the absorptions to longer wavelengths.[3a] The bathochromic shifts with decreasing ring size for the peralkylcyclopolysilanes reported here is in keeping with the trend in the permethylcyclopolysilanes.[16] Moreover, the long wavelength absorption for hexaneopentylcyclotrisilane is shifted to 310 nm, and it is of considerable interest to note that a transient peralkyldisilene, tetraneopentyldisilene, the smallest ring in a sense, exhibits the absorption at 400 nm.[7] These results imply that the interpretation by West et al. holds well in the small ring polysilanes.

Table V. Isotopic Pattern Coefficient for Molecular Ions via Electron-Impact Decompositions of Peralkylcyclopolysilanes[a]

compd	isotopic coeff of mol ions, found (calcd)		
	M^+	$[M + 1]^+$	$[M + 2]^+$
$[Pr_2Si]_7$ (**2d**)	100 (100)	80 (83)	59 (56)
$[PrMeSi]_6$ (**7c**)	100 (100)	55 (57)	34 (36)
$[Me_2Si]_6$ (**B**)	100 (100)	44 (44)	28 (29)
$[Et_2Si]_5$ (**1b**)	100 (100)	49 (48)	29 (27)
$[Pr_2Si]_5$ (**2b**)	100 (100)	56 (59)	31 (32)
$[PrMeSi]_5$ (**7b**)	100 (100)	40 (48)	26 (27)
$[i\text{-}BuMeSi]_5$ (**8b**)	100 (100)	53 (53)	33 (30)
$[Bu_2Si]_5$ (**4b**)	100 (100)	70 (70)	41 (40)
$[i\text{-}Bu_2Si]_5$ (**5b**)	100 (100)	78 (70)	44 (40)
$[i\text{-}Pr_2Si]_4$ (**3a**)	100 (100)	50 (47)	25 (24)
$[i\text{-}Bu_2Si]_4$ (**5a**)	100 (100)	51 (56)	35 (28)
$[t\text{-}BuMeSi]_4$ (**10a**)	100 (100)	43 (43)	22 (22)
$[t\text{-}BuPrSi]_4$ (**9a**)	100 (100)	41 (52)	(26)

[a] IP = 10–20 or 70 eV.

Scheme I. Electron-Impact Fragmentation of Peralkylcyclotetrasilanes



path A: $(i\text{-}Bu_2Si)_4$

path B: $(i\text{-}Pr_2Si)_4$, $(t\text{-}BuPrSi)_4$, $(sec\text{-}Bu_2Si)_4$

It is also known that compounds with Si–Si bonds form CT complexes with the acceptor tetracyanoethylene (TCNE), even though these silanes lack either π bonds or a lone electron pair.[17,18] In fact, the long wavelength CT bands of cyclopolysilanes, $[Me_2Si]_6$ and $[t\text{-}BuMeSi]_4$, were found by West et al. to occur at 507[17] and 510 nm,[3a] respectively. In the present study, we observed visible CT absorptions for the TCNE complexes of some selected cyclopolysilanes in CH_2Cl_2 solution (Figure 2). The colors and wavelength maxima for the CT-complexes are listed in Table IV. Of particular interest are the lowest energy CT bands for cyclopentasilanes, $[n\text{-}Bu_2Si]_5$ and $[n\text{-}Pr_2Si]_5$, which occur at 590 and 550 nm, respectively. The former is the longest wavelength CT band ever observed in any cyclic or linear alkylpolysilane and might reflect the lowest value for the ionization potential for any silicon framework.[17,18] However, this expectation may or may not be the case, since there is no theoretical reason to expect a linear relationship[19] between ionization potentials for a wide range of polysilanes and their CT frequencies with common acceptor species.

Mass Spectra. Gilman and co-workers[20] determined the mass spectra of $[Me_2Si]_n$, where n = 5–7, and more recently Brough and West[16b] studied those of a number of $[Me_2Si]_n$ compounds, where $n \geq 8$. The latter investigators noted that good agreement is found between the calculated isotope ratios for the parent clusters and those observed and that in all of the rings the parent peaks are quite intense. These two features are found in our case also (Table V). In addition, our four- and five-membered rings were found to undergo two types of fragmentation: (1) initial loss of an olefin derived from the alkyl substituent leaving an Si–H bond followed by successive elimination of the olefin and loss of an alkyl substituent (path A); (2) initial loss of an alkyl substituent followed by successive loss of an olefin (path B). Schemes I and

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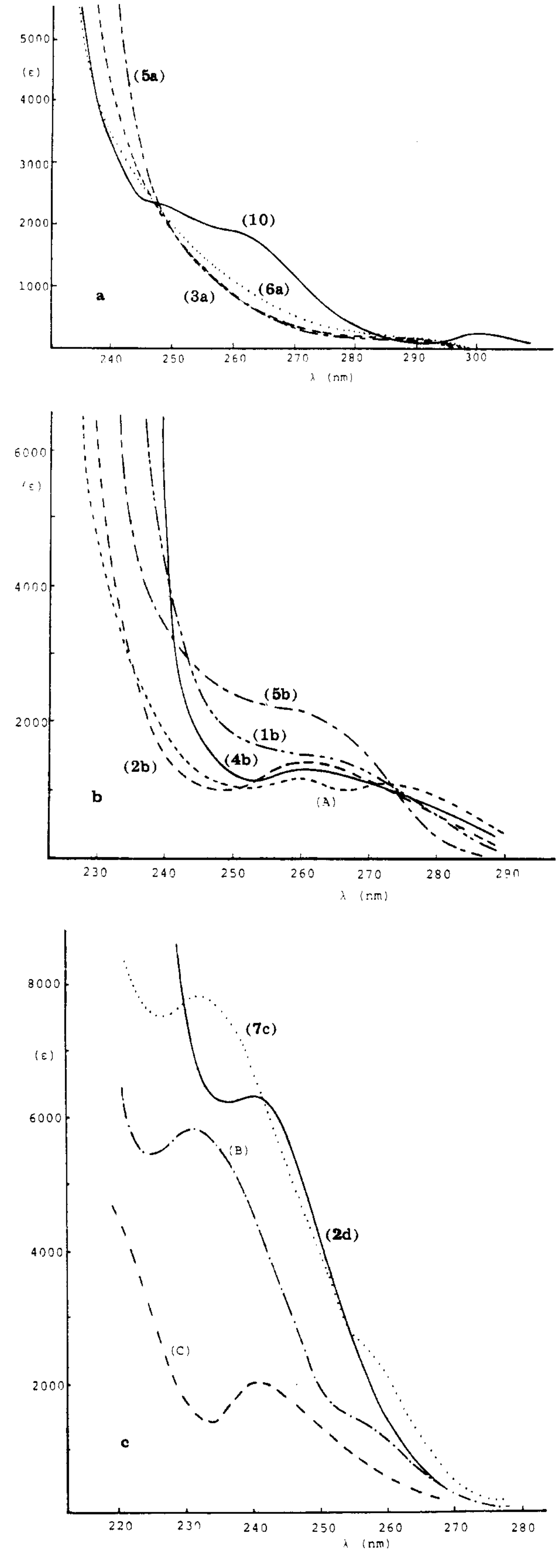


Figure 1. (a) UV absorption spectra for peralkylcyclotetrasilanes: ---, [i-$Pr_2Si]_4$ (**3a**); ‒‒‒, [i-$Bu_2Si]_4$ (**5a**); ···, [sec-$Bu_2Si]_4$ (**6a**); —, [t-$BuMeSi]_4$ (**10a**) (see Experimental Section). (b) UV absorption spectra for peralkylcyclopentasilanes: --- $[Me_2Si]_5$ (A); -----, $[Et_2Si]_5$ (**1b**); ‒‒‒, $[Pr_2Si]_5$ (**2b**); —, $[Bu_2Si]_5$ (**4b**); -‒-, [i-$Bu_2Si]_5$ (**5b**); A, see ref 16. (c) UV absorption spectra for peralkylcyclohexa- and peralkylcycloheptasilanes: ···, $[PrMeSi]_6$ (**7c**); -‒-, $[Me_2Si]_6$ (B); —, $[Pr_2Si]_7$ (**2d**); ‒‒‒, $[Me_2Si]_7$ (C); **B** and **C**, see ref 16.

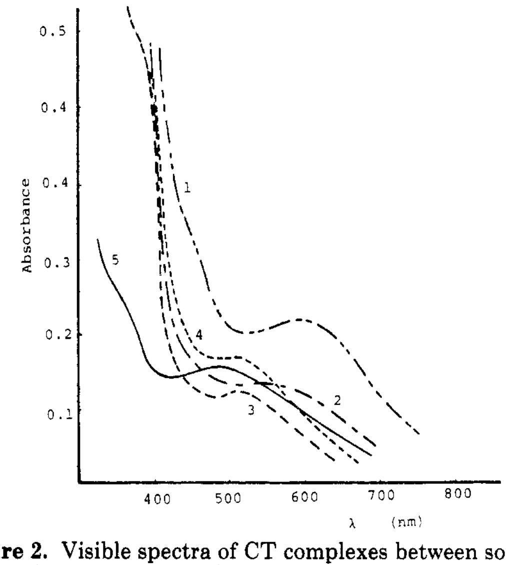


Figure 2. Visible spectra of CT complexes between some peralkylcyclopolysilanes and tetracyanoethylene: -----, [n-$Bu_2Si]_5$/TCNE (1); -‒-, [n-$Pr_2Si]_5$/TCNE (2); ‒‒‒, [t-$BuMeSi]_4$/TCNE (3); ---, [i-$Pr_2Si]_4$/TCNE (4); —, $[Me_2Si]_6$/TCNE (5) (see ref 17).

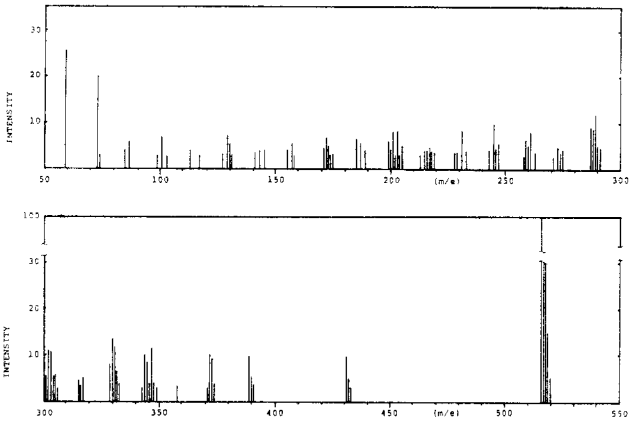


Figure 3. Mass spectrum of hexamethylhexapropylcyclohexasilane, [n-$PrMeSi]_6$ (**7c**) (15 eV).

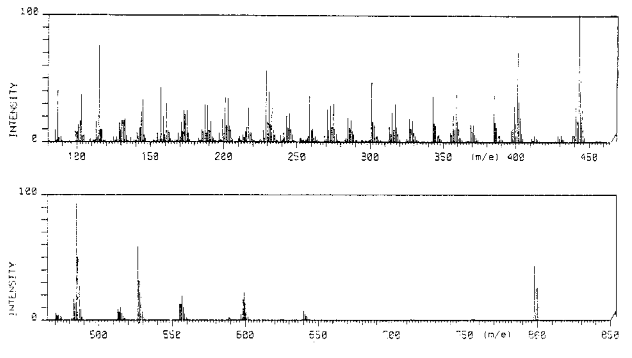
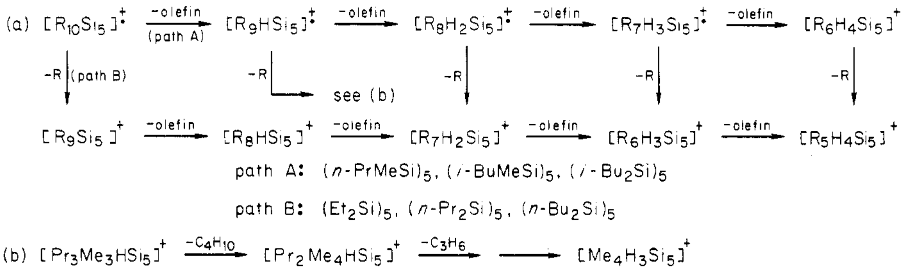


Figure 4. Mass spectrum of tetradecapropylcycloheptasilane, [n-$Pr_2Si]_7$ (**2d**) (70 eV).

II show the main electron-impact fragmentation patterns of cyclotetrasilanes and cyclopentasilanes, respectively. It should be noted that in the decomposition of cyclopentasilanes bearing a methyl group on silicon the methyl groups remain intact until all alkyl groups other than methyl are eliminated. It is also worth noting that the four- and five-membered charged ions apparently are stable enough to keep the original Si_n unit during the electron impact. On the other hand, the decompositions of six- and seven-membered rings are much more complicated and cannot readily be explained (see Figure 3 and 4).

Scheme II. Electron-Impact Fragmentation of Peralkylcyclopentasilanes



Experimental Section

All boiling and melting points are uncorrected. All the reactions were carried out by using a dry flask under an atmosphere of inert gas (N_2 or Ar). IR spectra were recorded by using neat liquid films and KBr disks with Hitachi EPI G-3 and JASCO A-102 spectrometers. ^{1}H NMR spectra were recorded at 60 MHz using a Varian EM-360A and A-60D spectrometers in CCl_4 with Me_4Si as an internal standard. For some compounds, high-resolution NMR spectra (^{1}H NMR at 400 MHz; ^{13}C at 100.40 MHz) were recorded by using a JEOL JNM FX-400 FT spectrometer in $CDCl_3$ (Me_4Si internal standard). Mass spectral analyses were conducted by using JEOL JMS-07 and JMS-D300 spectrometers (IP = 10–20 or 70 eV). UV spectra were obtained by using a Hitachi 200-100 spectrometer. GLC analyses for alkylchlorosilanes were performed by using an Ohkura Model 802 instrument equipped with a 2 m × 4 mm Teflon column packed with SF-96 (20%) on Celite 545-AW (60–80 mesh) (column temperature 80–200 °C) (He carrier) and for peralkylcyclopolysilanes were performed with 0.3 and 1 m × 4 mm stainless-steel columns packed with SE-30 (10%) on Celite 545-AW (60–80 mesh) (column temperature 150–300 °C). Thermal conductivity correction using an external standard (*n*-alkanes selected from C_{20}–C_{30} hydrocarbons) has been made for the GLC yields of peralkylcyclopolysilanes.

Materials. Tetrahydrofuran was dried over sodium wire. Lithium was cut into small pieces. Speier catalyst was prepared by dissolving chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 1.0 g) in *i*-PrOH (20 mL) (ca. 9.65 × 10^{-8} mol/L). *sec*- and *tert*-butyllithium solutions were titrated with a standard *sec*-BuOH solution in xylene with *o*-phenanthroline as indicator.[21] Palladium chloride and other materials were commercially available.

Preparation of Dialkyldichlorosilanes. Dialkyldichlorosilanes used were prepared from dichlorosilane (H_2SiCl_2), trichlorosilane ($HSiCl_3$), and methyldichlorosilane ($MeHSiCl_2$) by the methods shown (eq 2–7).[22,23]

$$\mathrm{H_2SiCl_2} \xrightarrow[\mathrm{H_2PtCl_6}]{\mathrm{RCH{=}CH_2}} \underset{77\%}{\mathrm{Et_2SiCl_2}},\ \underset{91\%}{\mathrm{Pr_2SiCl_2}},\ \underset{90\%}{\mathrm{Bu_2SiCl_2}} \qquad (2)$$

$$\mathrm{R = H, Me, Et}$$

$$\mathrm{H_2SiCl_2} \xrightarrow[\mathrm{(Ph_3P)_3RhCl}]{\mathrm{CH_2{=}CMe_2}} \underset{83\%}{i\text{-}\mathrm{BuSiHCl_2}} \xrightarrow[\mathrm{H_2PtCl_6}]{\mathrm{CH_2{=}CMe_2}} \underset{95\%}{i\text{-}\mathrm{Bu_2SiCl_2}} \qquad (3)$$

$$\mathrm{H_2SiCl_2} \xrightarrow{\mathrm{RM}} \mathrm{R_2SiH_2} \xrightarrow[\mathrm{PdCl_2}]{\mathrm{CCl_4}} \underset{76\%}{i\text{-}\mathrm{Pr_2SiCl_2}},\ \underset{88\%}{sec\text{-}\mathrm{Bu_2SiCl_2}},\ \underset{86\%}{t\text{-}\mathrm{Bu_2SiCl_2}} \qquad (4)$$

$$\mathrm{RM} = i\text{-}\mathrm{PrMgBr},\ sec\text{-}\mathrm{BuLi},\ t\text{-}\mathrm{BuLi}$$

$$\mathrm{HSiCl_3} \xrightarrow[\mathrm{H_2PtCl_6}]{\mathrm{CH_2{=}CHMe}} \underset{83\%}{\mathrm{PrSiCl_3}} \xrightarrow{t\text{-}\mathrm{BuLi}} \underset{70\%}{t\text{-}\mathrm{BuPrSiCl_2}} \qquad (5)$$

$$\mathrm{MeHSiCl_2} \xrightarrow[\mathrm{H_2PtCl_6}]{\mathrm{CH_2{=}CMe_2}} \underset{81\%}{i\text{-}\mathrm{BuMeSiCl_2}} \qquad (6)$$

$$\mathrm{MeHSiCl_2} \xrightarrow{t\text{-}\mathrm{BuLi}} \underset{74\%}{t\text{-}\mathrm{BuMeSiHCl}} \xrightarrow[\mathrm{PdCl_2}]{\mathrm{CCl_4}} \underset{62\%}{t\text{-}\mathrm{BuMeSiCl_2}} \qquad (7)$$

Preparation of Peralkylcyclopolysilanes. The progress of the reactions of dialkyldichlorosilanes with lithium was monitored by GLC analysis. When dichlorosilanes were completely consumed, cyclohexane was added to the colored reaction mixtures that were then worked up to give the product mixtures. The products were isolated by crystallization, by distillation, or by preparative GLC. Solid products were purified by recrystallization from ethanol. Some of the product yields were determined by means of GLC. The procedure used for octaisopropylcyclotetrasilane will be described as a typical example of the method employed for all peralkylcyclopolysilanes. The reaction conditions and the results are summarized in Table I.

[*i*-Pr$_2$Si]$_4$ (3a). To a cold mixture of lithium (3.76 g, 0.54 mol) and THF (400 mL) (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 (dark brown color) was stirred for 2 h at 0 °C, and then cyclohexane (300 mL) was added (light yellow color). After filtration, the resulting solution was concentrated, treated with water, and then extracted with cyclohexane. Evaporation of the extracts afforded a solid product that was recrystallized from EtOH to give fine colorless needles of compound **3a**, 21.2 g (74%), based on the dichlorosilane used. In the melting point determination of this compound using a metal-block heating apparatus equipped with a microscope, the fine needles of the sample changed at 340 °C to form a clear glassy solid that remained unchanged at 340–424 °C and then liquified at 424–429 °C in a sealed capillary. The pertinent spectral (UV, NMR, IR and MS) and analytical data for compound **3a** were as follows: UV (c-C_6H_{12}) (λ_{max}, nm (ϵ)) 290 sh (<200); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 1.296 (d, CH_3, 48 H) and 1.428 (sept, CH, 8 H) ($J_{a,b}$ = 7.080 Hz); ^{13}C NMR (100.40 MHz, $CDCl_3$, δ) 22.866 (CH_3, 8 C) and 15.070 (CH, 4 C); IR (KBr, cm^{-1}) 2960 s, 2935 s, 2910 s, 2880 s, 1455 s, 1445 s, 1380 s, 1355 s, 1285 w, 1222 m, 1150 m, 1070 s, 1008 s, 983 s, 962 w, 913 s, 877 s, 720 w, 629 s, 600 w, 590 w, 569 m, 516 m, 473 m, 430 s; MS (15 eV), *m/e* (relative intensity) 456 [M$^+$] (80), 413 (61), 373 (10), 371 (37), 329 (17), 287 (11); MS (70 eV) *m/e* (relative intensity) 456 [M$^+$] (64), 413 (57), 371 (80), 329 (100), 287 (87), 255 (22), 245 (59), 213 (27), 203 (41), 171 (32), 161 (40), 81 (64), 73 (67), 59 (100). Anal. Calcd for $C_{24}H_{56}Si_4$; C, 63.07; H, 12.35. Found: C, 62.54; H, 12.36.

[Et$_2$Si]$_5$ (1b): bp 170–172 °C (0.4 mmHg); mp 120–200 °C; UV (c-C_6H_{12}) (λ_{max}, nm (ϵ)) 265 sh (1400); NMR (δ) 0.38–1.72 (m); IR (liquid film, cm^{-1}) 2950 s, 2910 s, 2900 s, 2870 s, 2805 s, 2720 s, 1460 m, 1418 m, 1373 m, 1230 w, 1008 w, 970 w, 718 sh, 708 s, 698 s, 665 sh, 615 m; MS (15 eV), *m/e* (relative intensity) 430 [M$^+$] (100), 401 (15), 373 (9), 345 (6), 317 (5), 314 (18), 313 (9), 287 (24), 286 (50), 285 (32), 257 (21), 229 (10), 227 (4), 201 (6), 115 (10), 87 (7). Anal. Calcd for $C_{20}H_{50}Si_5$: C, 55.73; H, 11.69. Found: C, 55.27; H, 11.70.

[*n*-Pr$_2$Si]$_5$ (2b): mp 210–220 °C; UV (c-C_6H_{12}) (λ_{max}, nm (ϵ)) 260 (1400); NMR (δ) 0.42–1.72 (m); IR (KBr, cm^{-1}) 2950 s, 2925 s, 2870 s, 1453 s, 1410 m, 1370 m, 1325 m, 1210 w, 1190 w, 1062 w, 997 m, 890 w, 808 sh, 789 s, 767 m, 720 m, 714 sh, 698 m, 660 m; MS (15 eV), *m/e* (relative intensity) 570 [M$^+$] (100), 527 (15), 485 (45), 443 (14), 401 (17), 370 (75), 328 (44), 286 (9), 228 (6), 157 (11). Anal. Calcd for $C_{30}H_{70}Si_5$: C, 63.07; H, 12.35. Found: C, 62.94; H, 12.40.

[*n*-Pr$_2$Si]$_7$ (2d): glassy solid at 332–414 °C; mp 414–430 °C; UV (c-C_6H_{12}) (λ_{max}, nm (ϵ)) 242 (6300); NMR (δ) 0.43–1.80 (m); IR (KBr, cm^{-1}) 2950 s, 2924 s, 2856 s, 1458 sh, 1454 s, 1410 s, 1372

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s, 1323 s, 1215 m, 1190 m, 1060 s, 1035 m, 995 m, 990 sh, 896 m, 814 sh, 788 s, 768 s, 712 s, 688 s, 664 s, 653 sh; MS (70 eV) (relative intensity), *m/e* 798 [M$^+$] (44), 755 (2), 713 (1), 640 (8), 599 (23), 598 (16), 557 (20), 555 (14), 527 (58), 515 (10), 514 (7), 513 (8), 485 (93), 484 (15), 483 (17), 473 (7), 471 (6), 443 (100), 441 (29), 401 (70), 399 (30), 385 (37), 359 (37), 357 (20), 343 (37), 317 (30), 315 (24), 301 (47), 275 (30), 273 (29), 271 (25), 259 (36), 254 (22), 243 (21), 233 (27), 231 (40), 229 (55), 217 (27), 203 (35), 189 (28), 187 (29), 161 (30), 157 (42), 145 (33), 115 (75), 103 (37), 87 (40). Anal. Calcd for $C_{42}H_{98}Si_7$; C, 63.07; H, 12.35. Found: C, 63.00; H, 12.42.

[*n*-Bu$_2$Si]$_5$ (4b): bp 180–182 °C (0.14 mmHg); UV (c-C_6H_{12}) (λ_{max}, nm (ϵ)) 260 (1300); NMR (δ) 0.38–2.55 (m); IR (liquid film, cm^{-1}) 2960 s, 2925 s, 2870 s, 2850 s, 1460 s, 1413 m, 1375 s, 1340 m, 1290 m, 1270 w, 1195 sh, 1175 s, 1080 s, 1050 w, 1025 m, 1000 m, 962 s, 886 s, 872 s, 780 m, 751 w, 724 s, 694 s, 665 s; MS (70 eV), *m/e* (relative intensity) 710 [M$^+$] (98), 653 (3), 597 (7), 541 (15), 485 (19), 454 (22), 429 (15), 398 (38), 373 (14), 342 (27), 317 (18), 287 (21), 286 (18), 285 (13), 261 (21), 231 (32), 230 (20), 229 (25), 205 (20), 175 (45), 173 (42), 143 (52), 101 (28), 87 (49), 85 (42), 59 (100). Anal. Calcd for $C_{40}H_{90}Si_5$: C, 67.52; H, 12.75. Found: C, 67.36; H, 12.89.

[*i*-Bu$_2$Si)$_4$ (5a): glassy solid at 240–260 °C; mp 260–278 °C; UV (λ_{max}, nm (ϵ)) 290 sh (200); NMR (β) 0.27–1.37 (m, CH_2), 1.02 (d, *J* = 6.0 Hz, Me, 64 H), 1.37–2.27 (m, CH, 8 H); IR (KBr, cm^{-1}) 2950 s, 2925 s, 2885 s, 2870 s, 1458 s, 1378 m, 1362 s, 1324 m, 1213 m, 1162 s, 1087 s, 1035 s, 1025 sh, 958 sh, 946 m, 827 s, 750 s, 714 s, 702 s, 650 w; MS (10 eV), *m/e* (relative intensity) 568 [M$^+$] (2), 456 (2), 400 (6), 344 (9), 315 (7), 288 (7), 259 (6), 228 (9), 173 (9), 172 (5), 149 (6), 97 (5), 85 (7), 71 (8), 56 (100), 55 (9). Anal. Calcd for $C_{32}H_{72}Si_4$: C, 67.52; H, 12.75. Found: C, 66.93; H, 12.69.

[*i*-Bu$_2$Si]$_5$ (5b): glassy solid at 334–450 °C; mp 450–468 °C; UV (λ_{max}, nm (ϵ)) 260 sh (2100); NMR (δ) 0.79 (a peak of CH_2 doublet; another peak is overlapped with CH_3 doublet), 0.99 (d, *J* = 6.4 Hz, C-Me, 80 H), 1.47–2.22 (m, CH 10 H); IR (KBr, cm^{-1}) 2950 s, 2925 s, 2895 s, 2870 s, 1460 s, 1400 m, 1379 s, 1364 s, 1328 w, 1315 m, 1220 m, 1160 s, 1085 s, 1034 s, 955 sh, 915 w, 828 m, 764 s, 750 s, 710 s, 685 w, 648 w; MS (70 eV), *m/e* (relative intensity) 710 [M$^+$] (19), 654 (1), 598 (3), 542 (7), 541 (3), 486 (9), 485 (8), 455 (5), 454 (3), 429 (14), 399 (28), 398 (27), 373 (20), 343 (56), 342 (60), 317 (20), 315 (11), 287 (52), 286 (46), 261 (23), 259 (12), 231 (38), 230 (23), 215 (25), 205 (30), 199 (50), 187 (44), 175 (45), 159 (34), 143 (100), 115 (26), 101 (23), 87 (29), 85 (36), 73 (15), 59 (75), 56 (15). Anal. Calcd for $C_{40}H_{90}Si_5$: C, 67.52; H, 12.75. Found: C, 67.25; H, 12.82.

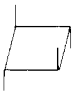
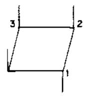
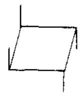
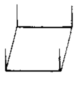
The above melting point, IR, and NMR data are quite different from those reported by Husk et al.,[2] and our **5b** was found to be a crystalline compound. In contrast to this, Husk et al. reported that this is a liquid compound that boils at 250 °C (4 mmHg) in the text and 250 °C (0.4 mmHg) in the experiment.[2]

[*sec*-Bu$_2$Si]$_4$ (6a): glassy solid at 300–418 °C; mp 418–426 °C; UV (λ_{max}, nm (ϵ)) 290 sh (200); NMR (δ) 0.68–2.50 (m); IR (KBr, cm^{-1}) 2975 s, 2950 s, 2900 s, 2860 s, 2850 sh, 2720 w, 1458 s, 1375 s, 1365 s, 1327 m, 1300 w, 1260 w, 1210 sh, 1205 m, 1140 m, 1092 s, 1033 s, 1000 s, 960 s, 840 s, 770 s, 665 s; MS (15 eV), *m/e* (relative intensity) 568 [M$^+$] (25), 511 (3), 455 (27), 399 (100), 343 (98), 287 (81), 231 (24), 229 (14), 175 (8), 56 (17). Anal. Calcd for $C_{32}H_{72}Si_4$: C, 67.52; H, 12.75. Found: C, 67.89; H, 12.99.

[*n*-PrMeSi]$_5$ (7b): liquid; NMR (δ) 0.15 (s, SiMe, 15 H), 0.43–1.73 (m, *n*-Pr, 35 H); IR (liquid film, cm^{-1}) 2950 s, 2920 s, 2900 s, 2865 s, 2795 m, 1725 vw, 1460 s, 1455 sh, 1410 s, 1373 m, 1328 m, 1258 sh, 1245 s (SiMe), 1210 w, 1193 m, 1060 s, 1028 w, 995 s, 890 m, 872 w, 810 w, 765 s, 715 s, 665 m; MS (15 eV), *m/e* (relative intensity) 430 [M$^+$] (100), 388 (6), 345 (8), 303 (11), 286 (21), 261 (12), 258 (13), 244 (24), 219 (18), 217 (14), 216 (21), 203 (10), 202 (11), 188 (9), 175 (13), 174 (11), 172 (14), 160 (10), 130 (19), 129 (11), 103 (12), 101 (17), 87 (19), 73 (33), 59 (34). Anal. Calcd for $C_{20}H_{50}Si_5$: C, 55.73; H, 11.69. Found: C, 54.67; H, 11.41.

[*n*-PrMeSi]$_6$ (7c): liquid; UV (λ_{max}, nm (ϵ)) 235 (7800), 255 sh (2400); NMR (δ) 0.15 (s, SiMe, 18 H), 0.43–1.73 (m, *n*-Pr, 42 H); IR (liquid film, cm^{-1}) 2960 s, 2930 s, 2895 s, 2870 s, 2800 w, 1460 s, 1452 s, 1410 s, 1373 m, 1328 m, 1260 sh, 1245 s (SiMe), 1212 w, 1190 w, 1062 s, 1030 w, 1000 s, 890 m, 875 sh, 810 s, 765 s, 713 s, 664 m; MS (15 eV), *m/e* (relative intensity) 516 [M$^+$] (100), 431 (9), 389 (10), 373 (9), 372 (10), 347 (11), 344 (10), 331 (12), 330 (13), 305 (6), 303 (12), 302 (12), 289 (12), 73 (20), 59 (26). Anal. Calcd for $C_{24}H_{60}Si_6$: C, 55.73; H, 11.69. Found: C, 55.57; H, 11.69.

Table VI

	 **10aa**	 **10ab**			 **10ac**	 **10ad**
		1	2	3		
$SiCH_3$	0.463	0.485	0.334	0.231	0.352	0.217
ref 3b[a]	0.490	0.553	0.414	0.327	0.441	0.334
CCH_3	1.033	1.029	1.078	1.185	1.078	1.159
ref 3b[a]	1.096	1.104	1.145	1.255	1.152	1.237

[a] In benzene-d_6.

[*i*-BuMeSe]$_2$ (8b): bp 188–190 °C (1.2 mmHg); NMR (δ) 0.18 (s, SiMe, 15 H), 0.75 (d, *J* = 7.0 Hz, CH_2, 10 H), 0.98 (d, *J* = 6.5 Hz, CH-*Me*, 30 H), 1.73 (octet, *J* = 6.5–7.0 Hz, CH, 5 H); IR (liquid film, cm^{-1}) 2950 s, 2925 sh, 2890 s, 1865 s, 1460 s, 1444 sh, 1401 sh, 1368 m, 1360 s, 1320 m, 1242 s (SiMe), 1208 m, 1160 s, 1090 s, 1035 s, 948 w, 830 w, 808 sh, 778 s, 715 s, 668 m; MS (20 eV), *m/e* (relative intensity) 500 [M$^+$] (40), 441 (1), 388 (10), 332 (24), 331 (12), 276 (34), 275 (43), 272 (45), 258 (18), 233 (16), 230 (37), 216 (100), 202 (23), 188 (14), 174 (55), 160 (31), 59 (12), 56 (26). Anal. Calcd for $C_{25}H_{60}Si_5$: C, 59.91; H, 12.06. Found: C, 59.81; H, 11.62.

[*t*-Bu-*n*-PrSi]$_4$ (9a): glassy solid at 285–384 °C; mp 384–395 °C; NMR (δ) 0.98 (s), 1.13 (s, C-Me), 1.18 (s, C-Me), 1.25 (s), 0.30–2.20 (broad peaks); IR (KBr, cm^{-1}) 2960 s, 2940 s, 2890 s, 2860 s, 1462 s, 1452 s, 1410 w, 1386 w, 1372 w, 1360 w, 1320 w, 1260 s, 1218 w, 1185 m, 1095 s, 1060 s, 1010 s, 932 w, 895 w, 860 w, 812 s, 800 s, 660 s; MS (20 eV), *m/e* (relative intensity) 512 [M$^+$] (very weak), 455 (6), 399 (19), 357 (15), 343 (10), 315 (11), 301 (15), 273 (13), 259 (21), 245 (7), 231 (16), 227 (11), 217 (22), 203 (10), 201 (11), 199 (11), 189 (12), 187 (14), 185 (22), 175 (19), 173 (15), 171 (16), 161 (9), 159 (14), 129 (27), 101 (48), 87 (40), 85 (22), 73 (100), 59 (60), 57 (24), 56 (15). Anal. Calcd for $C_{28}H_{64}Si_4$: C, 65.54; H, 12.57. Found: C, 64.86; H, 12.52.

[*t*-BuMeSi]$_4$ (10a): mp 255–270 °C after one recrystallization from EtOH; UV (λ_{max}, nm (ϵ)) 247 sh (2080), 262 sh (1800), 301 (190); NMR (δ) 0.22 (s), 0.33 (s), 0.47 (s, SiMe, 12 H), 1.02 (s), 1.07 (s), 1.19 (s, C-Me, 36 H); IR (KBr, cm^{-1}) 2950 s, 2930 s, 2880 s, 2850 s, 1468 s, 1455 s, 1410 m, 1365 m, 1358 s, 1260 m, 1242 s (SiMe), 1188 s, 1100 m, 1005 s, 962 w, 935 w, 930 w, 814 s, 806 w, 770 s, 755 s, 745 sh, 670 s; MS (15 eV), *m/e* (relative intensity) 400 [M$^+$] (100), 344 (67), 343 (18), 288 (15), 287 (25), 286 (15), 245 (11), 231 (15), 227 15), 213 (23), 73 (31), 56 (32).

The isomeric distribution of this sample, which was determined by a high-resolution NMR spectrum (400 MHz), was found to be a **10aa**/**10ab**/**10ac**/**10ad** (13:73:12:2) mixture (see also ref 3b). The proton chemical shifts at 400 MHz for the mixture are shown in Table VI.

Analytical Experiment for the Formation of Perisobutylcyclopolysilanes 5a and 5b vs. Reaction Time in the Reductive Coupling Reaction of *i*-Bu$_2$SiCl$_2$. In a 30-mL three-necked flask, previously flushed with Ar, sealed with a serum cap and fitted with a condenser, were placed lithium cut (0.097 g, 12 mmol), *n*-octacosane (0.0591 g, as the internal standard), and THF (8 mL). The solution was stirred magnetically at room temperature under Ar, and *i*-Bu_2SiCl_2 (1.0665 g, 5 mmol) in THF (2 mL) was added through the serum cap with a hypodermic syringe. At suitable time intervals, small aliquots of the solution were extracted through the serum cap by means of a syringe and analyzed by GLC. The yields of [*i*-Bu_2Si]$_4$ and [*i*-Bu_2Si]$_5$ after a 4-h reaction period were 50 and 15% and also after a 25-h period were 47 and 13%, respectively.

At the end of the 54-h period of time, the resulting solution was worked up to give a concentrated product mixture from which the two cyclopolysilanes **5a** and **5b** were isolated by the preparative GLC and identified in the usual manner (see the previous section and the preparative reaction in Table I).

Attempted Reactions of *t*-Bu$_2$SiCl$_2$ with Lithium. Several reactions were attempted by using lithium (or sodium) in the presence (or absence) of biphenyl as an electron-transfer agent. All the reactions substantially gave similar results in which no cyclic products such as cyclotetra- and cyclotrisilane could not be obtained. The following example is representative.

A mixture of t-Bu_2SiCl_2 (1.1 g, 5 mmol), lithium (0.14 g, 20 mmol) and biphenyl (0.25 mmol, 5 mol % relative to the dichlorosilane used) in THF (10 mL) was stirred for 4 h and then refluxed for 3 h under Ar. The resulting wine red solution was worked up to give a viscous light yellow liquid. GLC analysis for the liquid showed that it was a mixture containing many products from which three products were isolated by a preparative GLC. The first eluted product was identified by the usual manner to be tetra-*tert*-butyldisilane, [H-t-Bu_2SiSi-t-Bu_2H]:[13,24] IR (neat, cm^{-1}) 2070 (SiH); NMr (δ) 1.03 (s), 1.17 (s, t-Bu, 36 H), 3.58 (s, SiH, 2 H); MW 286 (M^+ by MS). The other higher molecular weight products were found by IR and NMR to contain both SiH and *tert*-butyl groups, respectively, but the structures remain unclear.

Acknowledgment. We are grateful to the Toshiba Silicone Industry Co. Ltd. and the Shin-etsu Chemical Industry Co. Ltd. for a gift of chlorosilanes and also are grateful to Mr. M. Yanagisawa and Ms. K. Hiraizumi of the National Chemical Laboratory for Industry for measurements of the high-resolution NMR (^1H and ^{13}C) spectra.

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Reactions of $(CO)_5MnSi(CH_3)_3$ and CO with Aldehydes and Cyclic Ethers. Syntheses of Functionalized Pentacarbonylmanganese Acyls and Homologated Organic Compounds

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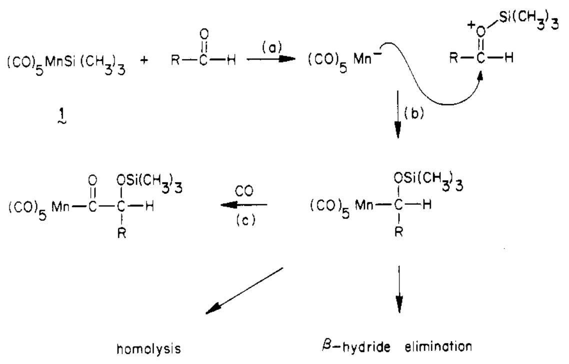
Received July 26, 1983

Reactions of $(CO)_5MnSi(CH_3)_3$ (**1**) and CO with aldehydes RCHO and cyclic ethers $\overline{OCH_2(CH_2)_nCH_2}$ (n = 0–2) give manganese acyls $(CO)_5MnCOCH(R)OSi(CH_3)_3$ and $(CO)_5MnCOCH_2(CH_2)_nCH_2OSi(CH_3)_3$ (n = 0, **6**; n = 1, **9**; n = 2, **10**) in 26–72% and 54–87% yields, respectively. Experiments conducted in the absence of CO show that these transformations proceed via labile alkyl intermediates $(CO)_5MnCH(R)$-$OSi(CH_3)_3$ and $(CO)_5MnCH_2(CH_2)_nCH_2OSi(CH_3)_3$. Reactions of propylene oxide and cyclohexene oxide with **1** and CO give the manganese acyls expected from S_N2 ring opening. When the reaction of **1** with aldehydes is conducted in the presence of $(CO)_5MnH$ under careful conditions, homologated aldehydes $(CH_3)_3SiOCHRCHO$ form in 55–78% yields. Reaction of **1** and $(CO)_5MnH$ with oxetane gives $(CH_3)_3$-$SiOCH_2CH_2CH_2CHO$ (**13**, 38%) and $(CH_3)_3SiO\overline{CHCH_2CH_2CH_2O}$ (**14**, 59%). Reaction of **9** and **10** with $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2^-$ yields γ-butyrolactone (84–95%) and δ-valerolactone (60–85%), respectively. The mechanisms of these transformations, and their utility in organic and organometallic synthesis, are discussed.

Introduction

For some time, we have been engaged in the development of new stoichiometric reactions of transition-metal trialkylsilanes[2] which are of potential use in organic and organometallic synthesis.[3-8] Many of these reactions employ oxygen-containing organic substrates. The subsequent formation of a strong silicon–oxygen bond (106–127 kcal/mol)[9] provides a driving force for the formation of a weak[10] metal–carbon bond. The organometallic product may be isolable or trappable or may readily convert to organic and inorganic products.

Scheme I. Proposed Mechanism for the Formation of Manganese Acyls $(CO)_5MnCOCH(R)OSi(CH_3)_3$ from Aldehydes, 1, and CO



In this paper, we give a full account of our investigation of the reactions of $(CO)_5MnSi(CH_3)_3$ (**1**)[11] with aldehydes

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