THE ETHYLMETHYLCYCLOSILANES *

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(Received February 28th, 1984)

Summary

Reaction of ethylmethyldichlorosilane with alkali metals yields per(ethylmethyl)cyclosilanes, $(EtMeSi)_n$. Rings with $n = 4$ to 8 have been isolated and characterized; those with $n = 4$ to 6 were reduced chemically or electrolytically to electron-delocalized anion-radicals.

Introduction

Alkylcyclopolysilanes are of interest because of their properties arising from electron delocalization in the Si–Si σ framework [1]. The permethylcyclopolysilanes $(SiMe_2)_n$ have been most extensively studied, and their unusual properties, including UV absorption, formation of charge transfer complexes [2], and reduction to delocalized radical anions [3] have been reported. Preparations for the $(Me_2Si)_n$ rings, where $n = 4$ to 35, have been described [4–7]. More recently, the perethylcyclopolysilanes, $(Et_2Si)_n$, where $n = 4$ to 8, have been synthesized and characterized [8]. The larger bulk of the ethyl substituents leads to some important differences between the two series of cyclosilanes.

The related per(ethylmethyl)cyclopolysilanes have now been examined; they exhibit properties generally falling between those of the diethyl and dimethyl cyclosilanes, although not in a predictable fashion. In this paper, the synthesis of the new polysilanes $(EtMeSi)_n$, where $n = 4$ to 8 [9], will be reported. The rings were isolated as unresolved mixtures of stereoisomers and were characterized spectroscopically. The photolysis of the $(EtMeSi)_n$ cyclosilanes and the electron spin resonance of $(EtMeSi)_4$, $(EtMeSi)_5$, and $(EtMeSi)_6$ anion-radicals will also be described.

Results and discussion

Synthesis

The per(ethylmethyl)cyclopolysilanes are made by reaction of ethylmethyldichlorosilane with alkali metals (eq. 1). These reactions produce mixtures of cyclic products whose composition depends upon the choice of conditions; typical results are given in Table 1.

$$EtMeSiCl_2 + M \rightarrow (EtMeSi)_n + MCl \tag{1}$$

Reactions of dialkyldichlorosilanes using excess alkali metal are known to cause ring to ring redistribution of the polysilanes, leading to an equilibrium mixture of the various rings. For instance, condensation of Me_2SiCl_2 with sodium-potassium (Na/K) alloy forms $(Me_2Si)_6$ (90%) as the thermodynamically favored oligomer, along with smaller amounts of $(Me_2Si)_5$ (9%) and $(Me_2Si)_7$ (1%) [4,11]. Reactions of potassium and Et_2SiCl_2 produce mainly $(Et_2Si)_5$; the equilibrium composition in this series is about 96% $(Et_2Si)_5$, 2% $(Et_2Si)_4$, and 2% $(Et_2Si)_6$ [8,12]. By contrast, when $EtMeSiCl_2$ is reacted with 2.4 equiv of potassium in refluxing THF, a mixture of $(EtMeSi)_5$ (5, 68%) and $(EtMeSi)_6$ (6, 25%), along with traces of $(EtMeSi)_7$ (7), is obtained. These results show that the cyclic pentamer 5 is the most stable ring, and that the relative stability of the cyclohexasilane 6 is slightly higher than in the $(Et_2Si)_n$ series.

Nonequilibrium condensations of $EtMeSiCl_2$ led to somewhat different results. The reaction of 2.0 equiv of Li with $EtMeSiCl_2$ at 0°C in THF gave 5 (23%) and $(EtMeSi)_8$ (8, 13%) as the major components, along with slightly lower yields of 6 (8%) and 7 (7%). Medium-ring compounds 7 and 8 are evidently kinetic products in this reaction. By comparison, the analogous condensation of Me_2SiCl_2 and Li at 0°C gave $(Me_2Si)_6$ and $(Me_2Si)_8$ as the main cyclic products [6], and in condensations of Et_2SiCl_2 and Li the seven- and five-membered rings were favored [8]. The reasons leading to the high and selective yields of medium-rings in these reactions are not known; possibly they result from sterically-dependent reactions occurring at the Li surface.

Analysis by HPLC showed that very large cyclics $(EtMeSi)_n$, up to $n = 42$ in condensations using Li, and up to $n = 21$ in those using potassium, were formed in the nonequilibrium reactions of $EtMeSiCl_2$. Rings from 5 to ca. 35 for the $(Me_2Si)_n$ [7] and the $[(CH_2)_4Si]_n$ series [14] have previously been observed. Because the liquid

TABLE 1

PRODUCTS FROM THE REACTIONS OF $EtMeSiCl_2$

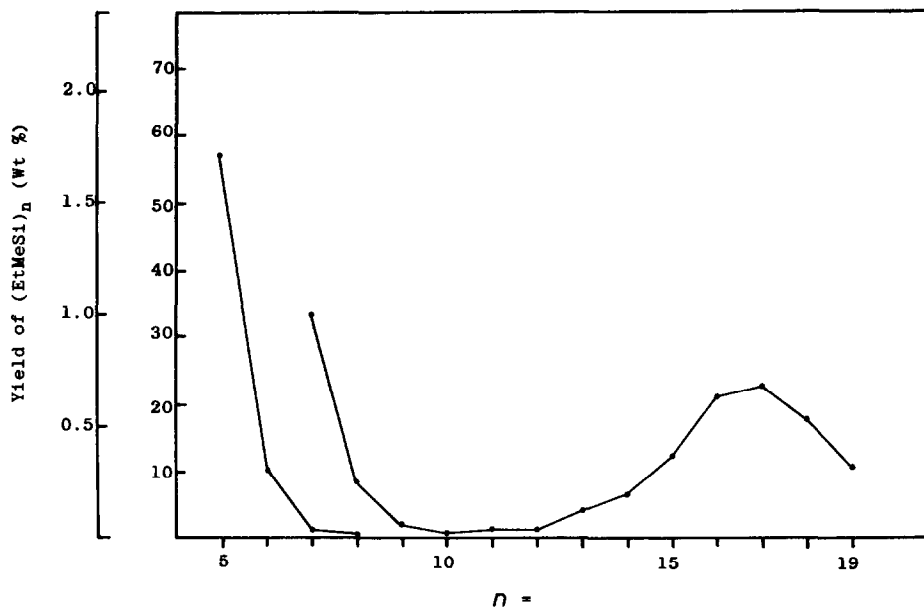| Conditions for $EtMeSiCl_2 + M$	Yields (wt.%), $(EtMeSi)_n$, $n =$				
	4	5	6	7	8
2.0 equiv Li, 0°C, THF	0	23	8	7	13
10% excess Li, 0°C, THF	0	35	44	5	6
2.0 equiv K, 65°C, THF	0	57	10	1	trace
10% excess K, 65°C, THF	0	68	25	1	0
10% excess Na, 110°C, toluene	19	17	4	0	0

Fig. 1. Estimated wt.% yields of the (EtMeSi)$_n$ cyclics, $n = 5$–19, from the reaction of EtMeSiCl$_2$ and potassium.

chromatograph used a UV detector operating at 254 nm, the molar absorptivity of each ring at 254 nm (ε_{254}) would be required in order to accurately determine the yield from HPLC peak areas. The UV spectra for (EtMeSi)$_n$ rings larger than $n = 8$
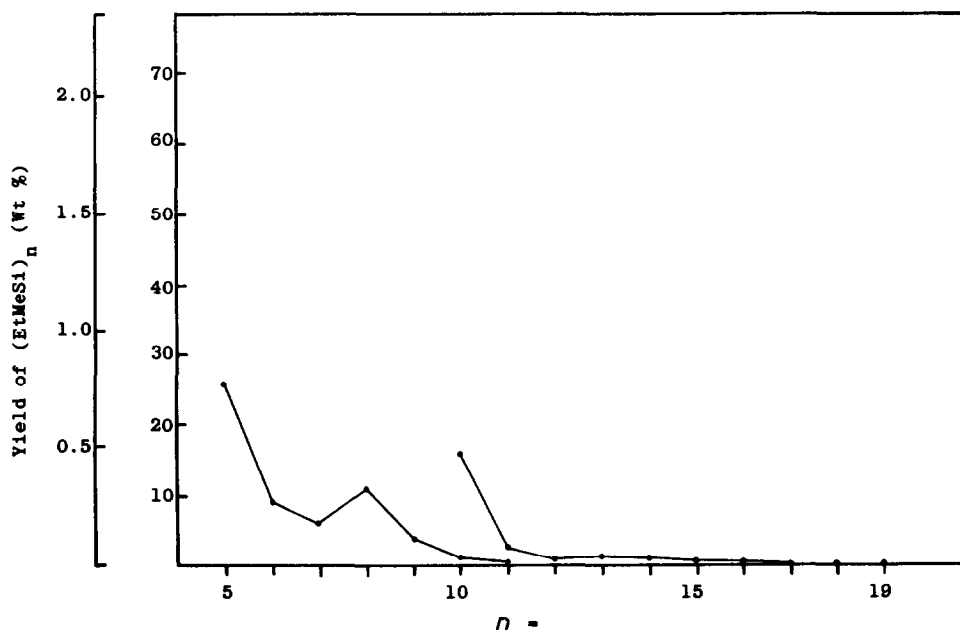

Fig. 2. Estimated wt.% yields of the (EtMeSi)$_n$ cyclics, $n = 5$–19, from the reaction of EtMeSiCl$_2$ and Li.

are not known, but crude estimates of the yields were calculated based on known ε_{254} values of the $(Me_2Si)_n$ rings, $n = 9$ to 19 [15]; plots of the weight % yields of $(EtMeSi)_n$, $n = 5$ to 19, obtained in this fashion are shown in Figs. 1 and 2. Interestingly, although the yields of the rings obtained from the Li reaction gradually decline as the size of the ring increases, in the potassium reaction the yields increase beyond $(EtMeSi)_{12}$, to a maximum of ~ 0.7 wt.% at about $n = 17$. A similar trend is observed in the yields of ring closure reactions leading to carbocyclic rings [15], and in both cases the increasing yields may result because the increasing entropy requirement (decreasing probability of ring closure) as the ring size increases is more then compensated by a decrease in strain energy of the ring.

Although the reaction of $EtMeSiCl_2$ and 2.2 equiv of Li in THF was expected to form the equilibrium mixture of **5** and **6**, the product instead contained **6** as its major component. It is not clear why the yields of **6** should be larger than those of **5** in this case, since the yields from the reaction of $EtMeSiCl_2$ with only 2.0 equiv of Li suggest that **6** is not a highly favored kinetic product in these reactions. Studies of the analogous condensation of Et_2SiCl_2 with excess Li show that a kinetic mixture of $(Et_2Si)_n$ rings, for $n = 5$ to 8, is produced initially; rings larger than $n = 5$ then undergo slow rearrangement to thermodynamically favored $(Et_2Si)_5$. Incomplete equilibration is observed even after prolonged reaction times, demonstrating that Li is a less effective equilibration agent than potassium. In the reaction of $EtMeSiCl_2$ with excess Li, we speculate that redistribution of the first-formed, kinetically-produced rings or polymer takes place, which initially produces **6** as the main rearrangement product. Subsequent conversion of **6** to **5** may then be slow [16].

Low yields of per(ethylmethyl)cyclopolysilanes may also be obtained from the reaction of $EtMeSiCl_2$ and sodium in refluxing toluene. The products are **4** (19%), **5** (17%), **6** (4%), along with a large amount of polymer. By comparison, reactions of sodium and Me_2SiCl_2 in toluene give quantitative yields of polymer, while those using Et_2SiCl_2 also yield the cyclic tetramer and the cyclic pentamer [8], although in the latter condensation the yield of $(Et_2Si)_4$ is considerably higher than the yield of **4** observed here. Minor products arising from oxidation of **4**, cyclo-$(EtMeSi)_4O$, and from cleavage of **4** by HCl [17], $H(EtMeSi)_4Cl$, are also obtained.

General properties

Each of the per(ethylmethyl)cyclosilanes **5–8** was readily obtained by preparative HPLC. Cyclosilanes **7** and **8** are highly crystalline, while **5** and **6** form crystals which are greasy in appearance, even after repeated purification. The strained cyclotetrasilane **4** is obtained as a colorless oil by preparative GLC. Cyclosilane **4** is moderately oxygen-sensitive, but fails to undergo spontaneous polymerization as observed for $(Me_2Si)_4$ [5] and so may be stored indefinitely in the absence of air.

Spectroscopy

The NMR data for cyclosilanes **4–8** are given in Table 2, and are listed in greater detail in the Experimental section. The ^1H NMR in each case shows one or more singlets at about 0.3 ppm, assigned to the methyl groups attached at silicon (α-methyl); overlapping quartets and triplets assignable to the methylene and methyl (β-methyl) of the ethyl group are found at lower field. Multiple, broadened lines are observed in the ^{13}C NMR of the ethylmethylcyclopolysilanes. They fall into sets between -5 and -7 ppm, 5 and 7 ppm, and 10 and 11 ppm for the α-methyl,

TABLE 2

NMR DATA FOR THE PER(ETHYLMETHYL)CYCLOPOLYSILANES

(EtMeSi)$_n$, n =	^{1}H NMR ^{a}		^{13}C NMR ^{a}	
	Si–Me	Si–Et	Si–Me	Si–Et
4	0.31 ^{c}	0.90 ^{b,c}	−7.45 ^{c}	5.6 ^{c}
		1.12		10.79
5	0.27	0.82	−7.9 ^{c}	5.1 ^{c}
		1.13		10.6 ^{c}
6	0.30	0.96	−7.1 ^{c}	6.10
		1.13		10.39
7	0.32	0.97	−6.5 ^{c}	6.51
		1.12		10.32
8	0.36	0.75–1.25(m)	−5.63	6.96
				10.38

^{a} In benzene-d_6 relative to TMS as the internal standard. ^{b} Contains overlapping upfield quartet (2H) and downfield triplet (3H), $J \sim 6$ Hz, except as noted. ^{c} Average value.

methylene, and β-methyl resonances, respectively. The mean values of the ^{1}H and ^{13}C chemical shifts, averaged among the different values in each set, resemble the shifts observed for the methyl and ethyl substituents in the corresponding (Me$_2$Si)$_n$ and (Et$_2$Si)$_n$ compounds. The ^{29}Si NMR was determined only for 5. Its spectrum contained seven lines, falling from −35.87 and −36.62 ppm; the average, −36.3 ppm, lies almost exactly midway between the ^{29}Si chemical shift of (Et$_2$Si)$_5$ (−30.4 ppm) [8] and that of (Me$_2$Si)$_5$ (−42.1 ppm) [18].

All known cyclopolysilanes are fluxional on the NMR timescale, giving resonances averaged by rapid interconversions among the conformers [1]. Hence, the multiple lines observed in the NMR spectra of the per(ethylmethyl)cyclopolysilanes undoubtedly arise from the existence of geometrical isomers for each ring. The information provided by NMR spectroscopy was insufficient to identify the stereo-
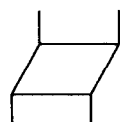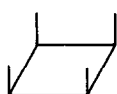
SCHEME 1
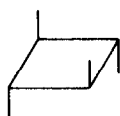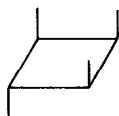
(4a , 1)   (4b , 1/2/1)


(4c , 1)   (4d , 1)

isomers present in **4-8** [19]. The four possible geometrical isomers of **4** and the number of expected α-methyl (or methylene) resonances are shown diagramatically in Scheme 1. The ^{13}C and ^1H NMR of **4** show four α-methyl signals of roughly equal intensity, suggesting that all four isomers **4a-4d** are present in significant amounts [20]. Similarly, the four stereoisomers of **5** leads to ten possible α-methyl signals, of which eight are observed by ^{13}C NMR, requiring that at least three of the four possible isomers must be present. The NMR spectra of the remaining per(ethylmethyl) compounds indicate that complex mixtures of stereoisomers are present in these rings as well.

The ultraviolet absorption maxima for the per(ethylmethyl)cyclopolysilanes are given in Table 3. Such absorptions are thought to result from electronic transitions in the Si–Si σ framework; not unexpectedly, similar UV spectra are observed for cyclopolysilanes of the same ring size. The small differences observed between the per(ethylmethyl)cyclosilanes and other per(alkyl)cyclosilanes (including $(Me_2Si)_n$ [7], $(Et_2Si)_n$ [8], and $[(CH_2)_4Si]_n$ [14]) probably result from small conformational differences arising from the somewhat different steric effects of the substituents. Low energy absorption such as is seen for **4** at 298 nm is characteristic of cyclic tetrasilanes; similar long wavelength bands are observed for $(Et_2Si)_4$ (304 nm) [8] and $(t\text{-}BuMeSi)_4$ (300 nm) [21].

Photolysis

Irradiation of degassed isooctane solutions of the per(ethylmethyl)cyclopolysilanes at 254 nm leads to concurrent elimination of ethylmethylsilylene and contraction to the next smaller ring (eq. 2). Similar behaviour is well-known for other alkyl

$$(EtMeSi)_n \xrightarrow{h\nu} (EtMeSi)_{n-1} + EtMeSi \qquad (2)$$
$$n = 8,7,6 \text{ and } 5$$
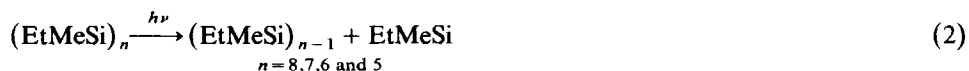
cyclosilanes [5,8,14]. Photolysis of **5** gave high yields of tetrasilane **4** after 1.0 h; continued irradiation (5.8 h) formed the linear trisilane, $H(EtMeSi)_3H$, as the major volatile product. The trisilane evidently arises from photolysis of **4**, which leads to ejection of EtMeSi and formation of the 1,3-diradical (either directly or via unstable trimethyltriethylcyclotrisilane, which could subsequently open to the diradical); abstraction of hydrogen from the solvent then gives $H(EtMeSi)_3H$. By comparison, $(Et_2Si)_4$ also forms a linear trisilane upon photolysis [8], while irradiation of $(Me_2Si)_4$ results mainly in ring opening to the 1,4-diradical, $H(Me_2Si)_4H$ [5].

TABLE 3

ULTRAVIOLET SPECTRAL DATA FOR $(EtMeSi)_n$, $n = 4-8$

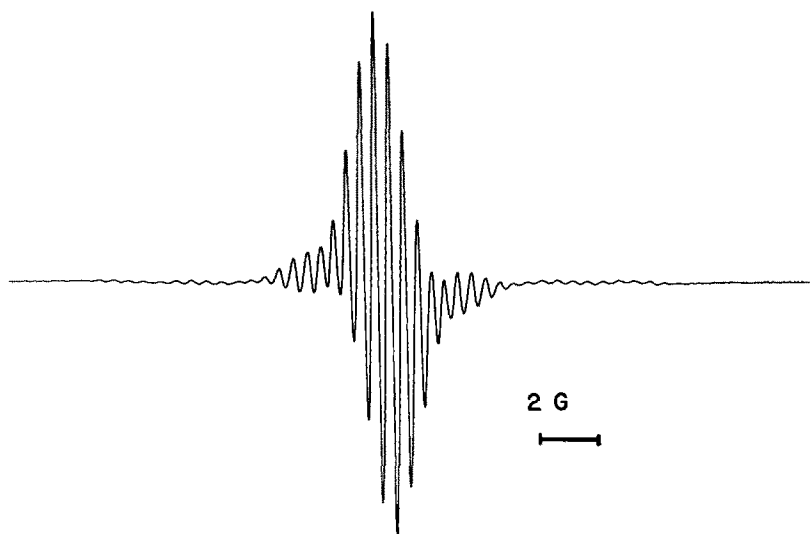| n	$\lambda_{max}(\epsilon)$ [a] (nm)
4	298 (350), 250sh (1600), 229sh (11000), 211sh (17000)
5	268 [b] (790), 228sh (8100), 212sh (23000)
6	260sh (1200), 239 (5200)
7	245 (4000), 223sh (8000)
8	248sh (8200), 238 (14000), 217sh (15000)

[a] In isooctane. [b] Probable doublet.

Fig. 3. ESR spectrum of (EtMeSi)$_5^-$ at $-85°C$ in THF, from reduction with Na/K alloy.

Large scale photolysis of a mixture of the cyclosilanes **5–8** produced a mixture containing mostly **4** and **5** after 30 h irradiation, showing that larger rings also undergo ring-contraction upon photolysis. This reaction provided a useful route to tetrasilane **4**, which is not readily obtained by other methods. The presence of [EtMeSi] as a reactive intermediate in the photolysis of **5** was confirmed by trapping with Et$_3$SiH; high yields of the insertion product, Et$_3$SiEtMeSiH, were formed.

Electron Spin Resonance spectra of anion-radicals

Reduction of the (Me$_2$Si)$_n$ compounds, where $n = 4$, 5 and 6, to anion-radicals observable by ESR has been previously reported [1a,3]. The ESR coupling patterns in each of these compounds is consistent with the delocalization of unpaired electron density throughout the molecule. The perethylcyclopolysilanes (Et$_2$Si)$_4$ and (Et$_2$Si)$_5$

TABLE 4

ESR PARAMETERS FOR SELECTED CYCLOPOLYSILANE ANION-RADICALS

Compound	Color	g	a^1_H (G)	a_{13C} (G)	a_{29Si} (G)	Ref.
(EtMeSi)$_4$	blue	2.0037	0.59	17.0,22.5	–	this work
(EtMeSi)$_5$	blue	2.0033	0.50	13.1,18.4	5.9 [a]	this work
(EtMeSi)$_6$	yellow	2.0030	0.49	8 [a], 15.7	–	this work
(Me$_2$Si)$_4$	blue	2.0037	0.67	21.0	–	22
(Me$_2$Si)$_5$	blue	2.0032	0.53	16.0	6.1	3
(Me$_2$Si)$_6$	yellow	2.0028	0.49	14.6	–	3
(Et$_2$Si)$_4$	blue	2.0037	< 0.01	1.9,18.4	4.7	22
(Et$_2$Si)$_5$	blue	2.0034	< 0.01	2.5,14.1	4.5	22
(EtMeSi)$_6$	–	–	0.60	14.5,18.9	6.2	10

[a] Partially resolved coupling.

have been similarly reduced [1b,22]. A surprising difference between the dimethyl and diethyl anion-radicals is that the proton hyperfine splitting is very small in the perethyl compounds; the reason for this behavior is not known. The analogous per(ethylmethyl)cyclosilane anion-radicals produce ESR patterns which show coupling only to the hydrogens of the α-methyl groups.

Generation of the anion-radical of **5** was carried out by both electrolytic and chemical (using Na/K alloy) reduction. The radical species **5**⁻ had the blue color characteristic of other cyclopentasilane radical-anions, and produced a symmetrical ESR spectrum (Fig. 3 and Table 4). The hyperfine splitting of 0.50 G was assigned to proton coupling and is similar in magnitude to the analogous coupling in $(Me_2Si)_5$⁻. Partially resolved satellites (which replicate the pattern of the central line) arising from the ^{29}Si coupling were also observed; the splitting constant is about 5.9 G, like that of $(Me_2Si)_5$⁻, but somewhat larger than the splitting in $(Et_2Si)_5$⁻. Two much smaller satellites of equal intensity were visible (at 13.1 and 18.4 G), most clearly at high gain, which probably result from ^{13}C coupling by the α-carbons [23]. The ^{13}C splitting for the β-carbons is expected to be small, and is apparently buried within the spectrum. The observed g-value of 2.0033 lies exactly between the g-values of 2.0032 for $(Me_2Si)_5$⁻ and 2.0034 for $(Et_2Si)_5$⁻. These values match, with some exceptions [24], those previously reported by Nefedov, et al. to be due to **6**⁻ [10], showing their assignment of the radical species as a cyclic hexamer to be in error.

The interpretation of the ESR spectrum is complicated by the presence of the various geometrical isomers in unreduced **5**. The well-resolved splitting pattern and the observation of only a single pair of ^{13}C satellites suggests that the signal arises from preferential reduction of a single isomer or from reduction of several isomers which do not exhibit greatly different ESR spectra. Analysis of the intensities of the lines in the central portion of the spectrum show them to correspond very nearly to a 16-line pattern [25], as might be expected if only the coupling between the 15 hydrogens of the α-methyl groups and the unpaired electron density was resolved.
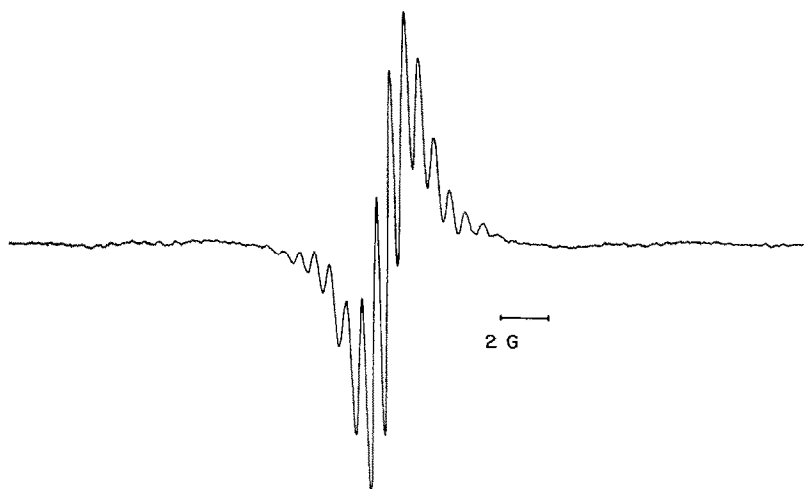

Fig. 4. ESR spectrum of (EtMeSi)₄⁻ at −85°C in THF, from reduction with Na/K alloy.

Cyclotetrasilane **4** was reduced in THF using Na/K alloy. Despite the presence of stereoisomers in the unreduced sample, blue anion-radicals **4**⁻ gave a well resolved, symmetrical ESR signal (Fig. 4), with proton hyperfine splitting of 0.59 G, somewhat larger than the corresponding coupling in **5**. The ^{13}C satellites (17.0, 22.5 G) also show larger splitting than in **5**⁻. The increased magnitude of the coupling is expected on the basis of a higher spin density at each silicon atom in **4**⁻. Neither ^{29}Si or β-carbon satellites are observed, and are evidently concealed within the spectrum. The observed g-value of 2.0037 is identical to that of $(Me_2Si)_4$ [1a]. Analysis of the line intensities shows a pattern due to an even number of hydrogens present, probably resulting from equal splitting by each of the 12 α-methyl protons [26]. The intensities deviate somewhat from the calculated values, perhaps because of poor resolution as well as overlap with signals from the ^{29}Si satellites.

The anion-radical of **6** could also be obtained, albeit with greater difficulty, by electrolysis of **6** in 3/1 (v/v) 2-methyltetrahydrofuran/1,2-dimethoxyethane. Cyclohexasilane radical-anions are rather uncommon, and only $(Me_2Si)_6$ [3] and a few substituted permethylcyclohexasilanes [27] have previously been reduced. Other hexameric cyclosilanes, including $(Et_2Si)_6$, $[(CH_2)_5Si]_6$, and $[(CH_2)_4Si]_6$, do not give observable radical species upon reduction [22]. Radical **6**⁻ was observed to have the yellow color typical for cyclohexasilane anion-radicals, and exhibited a g-value, 2.0030, and a ^{13}C coupling constant, 15.7 G, different from those of both **4**⁻ and **5**⁻. A partially resolved satellite, also assigned to ^{13}C coupling was observed to have a splitting constant of about 8 G. The lower magnitudes of the ^{13}C splitting constants,
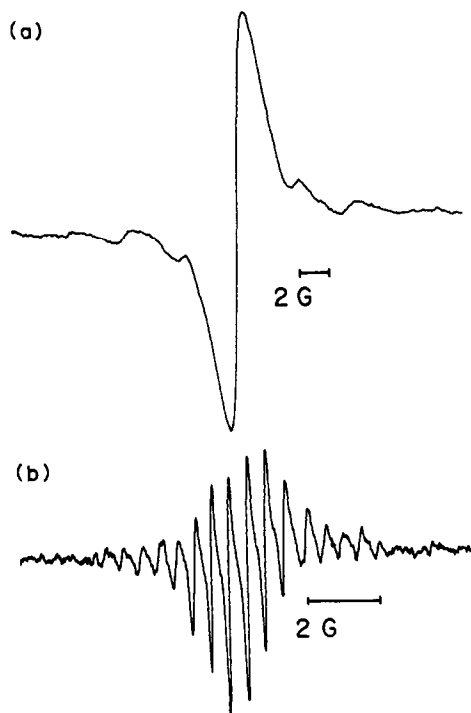
(a)

2 G

(b)

2 G

Fig. 5. ESR spectra of $(EtMeSi)_6$⁻ reduced electrolytically in 3/1 MeTHF/DME (a) −110°C; (b) −80°C.

compared to **5**ᵗ, are consistent with the decrease in the spin densities at silicon on expansion to the six-membered ring in **6**ᵗ. Although only a broad line was detected at $-120\,°C$, the spectrum was resolved somewhat at higher temperatures ($-80\,°C$), and proton hyperfine splitting of 0.49 G was observed (Fig. 5). Noticeable asymmetry was detected at the higher temperatures, which may arise from overlap of a weak signal due to **5**ᵗ, a probable decomposition product of the reduction, with that of **6**ᵗ.

Experimental

Methods

Ethylmethyldichlorosilane was obtained from Petrarch Systems, Inc. and was distilled before use. Toluene was refluxed over sodium for 12–24 h and then distilled. Tetrahydrofuran (THF) was predried over KOH and distilled from lithium aluminum hydride. Sodium-potassium alloy (Na/K, 78% potassium by weight) was supplied by Callery Chemical Co. Reactions were carried out under an atmosphere of dry nitrogen or argon using oven-dried glassware. Moisture- and oxygen-sensitive compounds were handled using syringe and Schlenk techniques. Yields were determined by analytical GLC using $C_{18}H_{38}$ as an internal standard, and were corrected for the different responses of the cyclosilanes and the standard on the detector. Analyses were completed by Galbraith Laboratories, Knoxville, Tenn.

GLC analyses on an analytical scale were done on a Hewlett-Packard 5720A gas chromatograph equipped with a flame-ionization detector using either a $2.5' \times 1/8''$ Dexsil column (5% on Chromosorb W) or $6' \times 1/8''$ SE-30 column (20% on Chromosorb W). Separations on a preparative scale was carried out with a Varian Model 90-P gas chromatograph equipped with a thermal conductivity detector and using a $6' \times 3/8''$ SE-30 column (20% on Chromosorb W). HPLC analyses and separations were completed on a Whatman M-9 ODS-2 reverse phase semipreparative column with a mobile phase of MeOH/THF using a Waters Associates 6000 LC pump and an Altex Model 153 UV detector.

Spectroscopy

All NMR spectra were obtained using benzene-d_6 as a solvent and TMS as an internal standard. ¹H NMR were determined using a JEOL MH-100, and ¹³C NMR were run on either a JEOL FX-60 or a JEOL FX-200, operating at 15.04 and 50.10 MHz, respectively. ²⁹Si NMR were collected on the JEOL FX-200 (39.60 MHz) using the INEPT method with Δ 25.7 msec and τ 38.5 msec [28].

IR spectra were recorded with a Perkin–Elmer 457 spectrometer using NaCl liquid IR cells and either $CHCl_3$ or CS_2 as solvents. Ultraviolet spectra were obtained on a Cary 118 spectrophotometer using spectrograde isooctane. Mass spectra were run at 70 eV on a Kratos MS902C mass spectrometer. ESR spectra were obtained on a Varian E-15 spectrometer with 100 KHz field modulation and equipped with a Varian V-4343 temperature controller; g-values were determined relative to a pitch sample using a Hewlett-Packard 2454L frequency counter to measure the microwave frequency.

Synthesis

Synthesis and work-up procedures have been previously described for the pre-

paration of $(Et_2Si)_n$, $n = 4$–8, from Et_2SiCl_2 [8] and identical procedures were followed in this study. All additions of $EtMeSiCl_2$ were carried out dropwise over ca. 2–2.5 h.

Reaction of EtMeSiCl$_2$ and lithium

The condensation of $EtMeSiCl_2$ (4.3 g, 30 mmol) and Li wire (0.42 g, 60 mmol) in 70 ml THF at 0°C produced a colorless solution, which upon work-up gave 0.2 g insoluble polymer (9%) and 1.8 g of a white oil containing the cyclosilanes. The yields were 26% **5**, 9% **6**, 6% **7**, and 11% **8** (GLC analysis). The product was also found to contain large $(EtMeSi)_n$ rings, as shown by HPLC, and a slightly soluble material, presumably low molecular weight polymer. A second attempt under identical conditions yielded 23% **5**, 8% **6**, 7% **7**, and 13% **8**. From these mixtures, ethylmethylcyclosilanes **5–8** were isolated pure by HPLC.

For **5**: m.p. 64–67°C; Anal. Found: C, 49.94; H, 11.17. $C_{15}H_{40}Si_5$ calcd.: C, 49.92; H, 11.17%. Mass spectrum, exact mass: calcd. 360.1965, meas. 360.1975, dev. 2.8 ppm. ^{13}C NMR (50.10 MHz), δ (relative intensity): 10.61(4.5), 10.59(4.5), 10.55(7.9), 5.34(2.5), 5.24(3.4), 5.21(3.2), 5.17(3.3), 5.12(2.9), 5.02(3.2), 4.91(1.3), $-7.54(1.8)$, $-7.63(2.8)$, $-7.77(2.6)$, $-7.81(3.0)$, $-7.86(1.9)$, $-7.95(1.9)$, $-8.13(2.1)$, $-8.29(1.0)$. ^{29}Si NMR, δ (relative intensity): $-35.87(1.2)$, $-35.95(2.2)$, $-36.20(2.0)$, $-36.29(5.6)$, $-36.44(3.4)$, $-36.51(3.6)$, $-36.62(1.0)$.

For **6**: m.p. preshrinkage 155–160°C, cloudy melt 162–164°C, clear melt 164–165°C. Anal. Found: C, 49.98; H, 11.28. $C_{18}H_{48}Si_6$ calcd.: C, 49.92; H, 11.17%. Mass spectrum, exact mass: calcd. 432.2358, meas. 432.2371, dev. 3.0 ppm. ^{13}C NMR (15.04 MHz), δ (relative intensity): 10.38(6.7), 6.10(5.6), $-6.79(1.3)$, $-6.96(1.3)$, $-7.34(1.0)$.

For **7**: m.p. preshrinkage 172–184°C, melts 184–186°C. Anal. Found: C, 49.82; H, 11.13. $C_{21}H_{56}Si_7$ calcd.: C, 49.92; H, 11.17%. Mass spectrum, exact mass: calcd. 504.2751, meas. 504.2749, dev. 0.4 ppm. ^{13}C NMR (15.04 MHz), δ (relative intensity): 10.32(5.5), 6.51(5.6), $-6.35(3.1)$, $-6.62(1.0)$.

For **8**: m.p. preshrinkage 180–184°C, cloudy melt 187–192°C, clear melt 192–195°C. Anal. Found: C, 49.78; H, 11.17. $C_{24}H_{64}Si_8$ calcd.: C, 49.92; H, 11.17%. Mass spectrum, exact mass: calcd. 576.3144, meas. 576.3163, dev. 3.3 ppm. ^{13}C NMR (15.04 MHz), δ (relative intensity): 10.38(3.3), 6.96(3.6), $-5.63(1.0)$.

The IR spectra of the ethylmethylcyclosilanes were similar and showed only the expected C–H, C–C and Si–C bands. Each of these polysilanes gave similar mass spectra, illustrated for **5** below:

Selected m/e (relative intensity): 362(19.2), $M + 2$; 361(38.3), $M + 1$; 360(100.0), M^+; 331(1.0), $M - C_2H_5$; 303(16.9), $M - C_2H_5 - C_2H_4$; 275(7.7), $Et_4Me_3Si_4H_2$; 217(1.7), $Et_2Me_3Si_3H$; 145(1.0), $Et_2Me_2Si_2H$; 101(5.7), Et_2MeSi; 87(7.5), $EtMe_2Si$; 73(26.1), $EtMeSiH$; 59(35.2), $EtSiH_2$.

The reaction of $EtMeSiCl_2$ (30 mmol) using 2.2 equiv Li (66 mmol) in 70 ml THF at 0°C formed a deep green solution. Work-up after 15 h stiring gave 2.1 g of a colorless oil, containing the cyclics in yields of 35% **5**, 44% **6**, 5% **7**, and 6% **8**. A second trial also led to high yields of the cyclosilanes, in which **6** was again the major component.

Reaction of EtMeSiCl$_2$ with potassium

When $EtMeSiCl_2$ (30 mmol) is reacted with 2.4 equiv of potassium (2.8 g, 72

mmol) in 70 ml refluxing THF, a deep blue-green solution resulted; after 16 h, quenching and work-up produced 2.1 g of oily product. Analysis by GLC showed 68% **5**, 25% **6** and 1% **7** were present. A similar reaction of $EtMeSiCl_2$ (30 mmol) and 2.0 equiv of potassium (60 mmol) in 70 ml refluxing THF formed a blue (not blue-green) solution and gave 57% **5**, 10% **6**, and traces of **7** after 14 h reaction. Small amounts of partially soluble, polymeric-like material was also seen. Experiments in which the reaction between $EtMeSiCl_2$ and excess potassium was followed by GLC showed that **5** and **6** both form in the initial stages of the reaction, then increase gradually in yield. No **4**, and only traces of **7**, were seen.

Analogous attempts to condense $EtMeSiCl_2$ using 2.2 equiv. Na/K yielded 25% **5**, 8% **6**, and traces of **7** and **8** as the only cyclic products.

Reaction of $EtMeSiCl_2$ with sodium

A condensation of $EtMeSiCl_2$ (50 mmol) using sodium spheres (2.53 g, 110 mmol) in 150 ml refluxing under carefully oxygen-free conditions produced a deep purple solution; 19% **4**, 17% **5**, and 4% **6** were obtained after 48 h. In addition to insoluble (1.4 g, 39%) and partly soluble polymers, two derivatives of **4**, cyclo-$(EtMeSi)_4O$ (1%) and $H(EtMeSi)_4Cl$ (2%), were present. Cyclotetrasilane **4** could be isolated by preparative GLC following work-up of the product, but was more conveniently obtained from photolysis mixtures (vide infra). Exposure of aliquots from the reaction to air led to further conversion of **4** to cyclo-$(EtMeSi)_4O$ and $H(EtMeSi)_4Cl$; they were subsequently purified by preparative GLC and identified by their mass spectra.

For cyclo-$(EtMeSi)_4O$: Mass spectrum selected m/e (relative intensity): 306(13.2), $M+2$; 305(25.9), $M+1$; 304 (100), M^+; 275(64.7), $M-C_2H_5$; 247(18.7), $M-C_2H_5-C_2H_4$; 203 (10.1), $Et_2Me_2Si_3O$; 145(10.3), $Et_2Si_2Me_2H$; 101(13.1), Et_2MeSi; 87(21.6), $EtMe_2Si$; 73(40.6), $EtMeSiH$; 59(64.2), $EtSiH_2$. Exact mass: calcd. 304.1521, meas. 304.1530, dev. 3.0 ppm.

For $H(EtMeSi)_4Cl$: Mass spectrum, selected m/e (relative intensity): 326(0.7); 324(1.6); M^+, 295(3.7), $M-C_2H_5$; 267(1.5), $M-C_2H_5-C_2H_4$; 253(69.4),; 251(100), cyclo-$(EtMeSi)_3Cl$; 223(38.9), m/e 251-C_2H_4; 217(11.9), $Et_3Me_3Si_3H$; 195(18.8), m/e 251 $-C_2H_4-C_2H_4$; 144(61.5), $C_6H_{16}Si_2$; 101(21.1); 87(34.2); 73(42.4); 59(82.7). Exact mass: calcd. 324.1339, meas. 324.1347, dev. 2.5 ppm.

Photolysis of $(EtMeSi)_n$

Photolyses were carried out in degassed solutions of spectrograde isooctane in quartz tubes; the solutions were irradiated at 254 nm using a Rayonet photochemical reactor. When a solution of 20 mg (0.06 mmol) **5** in 2 ml isooctane was photolyzed, 58% **4** and 35% **5** (GLC analysis) were present after 1.0 h. Continued photolysis led first to the disappearance of **5**, and then to slow reaction of **4**. After 5.8 h, the solution contained 44% of a new product, shown by its mass spectrum to be $H(EtMeSi)_3H$, as well as 6% **4**, 6% cyclo-$(EtMeSi)_4O$, and numerous minor products. A white precipitate, possibly poly(ethylmethylsilylene) polymer, was also observed.

For $H(EtMeSi)_3H$: Mass spectrum, selected m/e (relative intensity); 218(4.4), M^+; 145(21.1), $Et_2Me_2Si_2H$; 144(61.7), $C_6H_{16}Si_2$; 117(25.5), $EtMe_2Si_2H_2$; 101(6.2); 87(5.5); 73(34.5); 57(100). Exact mass: calcd. 218.1335, meas. 218.1328, dev. 3.2 ppm.

When 1.2 g of a mixture consisting of 39% **5**, 46% **6**, 7% **7**, and 8% **8** was photolyzed in 20 ml isooctane for 30 h, a mixture of 36% **4**, 47% **5**, and 6% **6** (weight %, as estimated by GLC) was obtained, in addition to polymer. From such mixtures, **4**, a colorless oil, was isolated by preparative GLC: Mass spectrum, selected m/e (relative intensity): 290 (5.7), $M + 2$; 289(26.7), $M + 1$; 288(100), M^+; 275(7.2), $M - CH_3$; 259(2.2), $M - C_2H_5$; 247(16.0), $M - C_2H_5 - CH_2$; 217(3.8); 145(10.0); 101(25.3); 87(22.8); 73(69.6); 59 (87.5). Exact mass: calcd. 288.1572, meas. 288.1582, dev. 3.5 ppm. ^{13}C NMR (50.10 MHz) δ (relative intensity): 10.79(3.5), 5.71(2.3), 5.63(2.2), 5.49(1.5), $-7.31(1.2)$, $-7.44(1.0)$, $-7.45(1.5)$, $-7.58(1.6)$. ^1H NMR: δ 1.12(5, J 6 Hz, 3H); 0.75–1.05(m, 2H); four overlapping resonances in the Si-methyl region are present, showing a total integration of 3H; the δ (relative intensity) values are: 0.36 (1.6), 0.35(2.2), 0.31(1.0), 0.26(1.1).

A trapping experiment using 33 mg (0.09 mmol) **5**, 116 mg (1.0 mmol) Et_3SiH, and 3 ml isooctane resulted in 23% **5** and 46% **4** after 1.5 h; the trapping adduct, $Et_3SiSiEtMeH$, was obtained in 93% yield. No polymer was observed. The disilane was identifed from its mass spectrum following isolation by GLC: Mass spectrum, selected m/e (relative intensity): 188(7.2), M^+; 159(3.2), $M - C_2H_5$; 131(11.1), $M - C_2H_5 - C_2H_4$; 115(72.5), Et_3Si; 87(100), Et_2SiH; 73(35.5), $EtMeSiH$; 59(71.3), $EtSiH_2$. Exact mass: calcd. 188.1410, meas. 188.1417, dev. 3.7 ppm.

Electron Spin Resonance

Solvents used for ESR studies were purified THF, 2-methyltetrahydrofuran (MeTHF), both stored over lithium aluminum hydride, and 1,2-dimethoxyethane (DME), which was stored over sodium benzophenone ketyl. Samples were prepared on a vacuum line. Chemical reductions were carried out in sample cells consisting of a 3 mm Pyrex tube and an attached sidearm into which a small drop of Na/K alloy was added. After adding the cyclosilane, THF was distilled into the cell, the solution was degassed, and the tube sealed under vacuum. The anion-radicals were generated by cooling the solution and allowing it to contact the alloy; the tube was then placed in the ESR cavity. Electrolytic reductions were carried out in a cell equipped with a 3 mm soft glass tube and platinum wire electrodes [29]. The sample and supporting electrolyte (tetra-n-butylammoniumperchlorate) were added and the solvent (THF or 3/1 (v/v) MeTHF/DME) was then distilled into the cell. After degassing, the cell was placed under argon, inserted into the ESR cavity, and cooled to the desired temperature. Electrolysis was attempted using the lowest voltage that gave an acceptable current (0.2–0.5 μA).

Cyclopolysilanes **4** and **5** were reduced chemically in THF to blue anion-radicals. Radical **4**⁻ was generated at $-95\,°C$ in a toluene slush bath, while **5**⁻ was reduced at $-77\,°C$ using an isopropanol bath. In each case, the temperature of the ESR cavity was set initially at $-95\,°C$, then increased slowly to obtain the best resolved spectrum. For both **4**⁻ and **5**⁻, this occurred at about $-85\,°C$. Further temperature increases up to $-45\,°C$ caused only minor changes in the spectra, and signals for both anion-radicals were observed to fade above $-45\,°C$. Cyclopentasilane **5** was also reduced electrolytically and gave a spectrum identical to that from chemical reduction.

Although attempts to reduce **6** electrolytically in THF (-85 to $-95\,°C$) led only to signals assigned to **5**⁻, electrolytic reduction of **6** was possible in 3/1 MeTHF/glyme. The starting temperature was $-130\,°C$, which was then slowly

increased. Signals for yellow radical-anion **6**⁻ were first observed at $-120\,°C$, and splitting assigned to coupling by the protons was best resolved at $-80\,°C$. At $-70\,°C$, the signal assigned to **6**⁻ became noticeably weaker, and all radical signals faded completely at still higher temperatures. No other temperature dependence was seen.

Acknowledgement

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9 $(EtMeSi)_6$ has been previously reported [10]; however, no details of its synthesis or proof of its structure were given, and so there is some question whether the product obtained was in fact the cyclohexasilane.

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12 The preferred ring size in cyclopolysilanes depends upon the steric bulk of the substituents; if larger substituents than ethyl are present, even smaller rings are favored. For example, $(t\text{-}BuMeSi)_4$ is the thermodynamically most stable cyclosilane in the $(t\text{-}BuMeSi)_n$ series [13].

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16 An analogous process is known whereby $(Me_2Si)_5$ is formed initially in higher yields than $(Me_2Si)_6$ in the redistribution reaction of $Ph_3SiSiMe_2SiPh_3$ and Ph_3SiLi, but where the equilibrium mixture of $(Me_2Si)_n$ rings is brought about by continued stirring in the presence of the silyllithium compound. See M. Kumada, J. Organomet. Chem., 100(1975)127.

17 This tetrasilane evidently arises from hydrolysis of unreacted Si–Cl bonds, which produces HCl; the HCl then reacts with **4** to yield the ring-opened product $H(EtMeSi)_4Cl$. A similar reaction of $(Et_2Si)_4$ with HCl is known [8].

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19 The geometrical isomers of related cyclosilanes $(t\text{-}BuMeSi)_4$ and $(t\text{-}BuMeSi)_5$ have previously been identified [13]. The results from these studies demonstrate that the composition of the isomeric mixture is dependent upon the synthetic method by which the cyclosilanes are obtained. In this study, only samples of **5–8** isolated from the reaction of $EtMeSiCl_2$ and Li, and samples of **4** isolated by photolysis of **5**, were examined.

20 The smaller signals for **4b** are not observed, but may be concealed under the other lines in the spectrum.

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23 The observed intensity of each of the ^{13}C satellites is about 1%, considerably less than the calculated value of 2.8%. The ^{29}Si satellite intensity (8%) is also smaller than the predicted value (11.7%). The reason for such reduced intensities is not apparent, but has been previously observed for $(Et_2Si)_5$. The anion-radicals of 4 and 6 also show unexpectedly small ^{13}C intensities of ca. 1%.

24 We located the centers of the ^{13}C and ^{29}Si satellites somewhat differently than in ref. 10, and hence obtained slightly different values for the coupling constants. The reported value of 0.6 G for the proton hyperfine splitting is possibly in error; examination of the published spectrum established a somewhat smaller value of ca. 0.52 G.

25 Observed intensities for the ten centermost lines of 5^-: 0.083, 0.15, 0.39, 0.73, 1.00, 1.00, 0.73, 0.38, 0.15, 0.082; calcd. for $n = 15$: 0.071, 0.21, 0.47, 0.78, 1.00, 1.00, 0.78, 0.47, 0.21, 0.071.

26 Observed intensities for the 11 centermost lines of 4^-: 0.056, 0.071, 0.14, 0.37, 0.79, 1.00, 0.74, 0.33, 0.14, 0.081, 0.056; calcd. for $n = 12$: 0.013, 0.071, 0.24, 0.54, 0.86, 1.00, 0.86, 0.54, 0.24, 0.071, 0.013.

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