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CYCLIZATION OF TERMINAL ETHOXYSILYL-SUBSTITUTED PROPOXY- AND BUTOXYTRIMETHYLSILANES

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Several new (ω-ethoxysilylalkoxy)trimethylsilanes of the type $(C_2H_5O)_n(CH_3)_{3-n}Si(CH_2)_mOSi$.$(CH_3)_3$ ($n = 1—3$; $m = 3, 4$) were synthesized. These compounds are unstable and undergo acid-base catalyzed decomposition to trimethylethoxysilane and 1-oxa-2-silacycloalkanes of the type $(C_2H_5O)_n(CH_3)_{2-n}Si(CH_2)_mO$ ($n = 0—2$; $m = 3,4$) already at room temperature. Relative rate constants of this decomposition were determined and its mechanism is discussed.

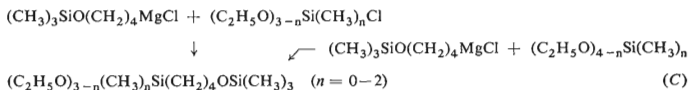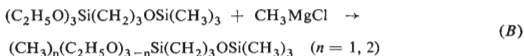Intramolecular interaction of silicon with oxygen in the ground state of the compounds R_3Si. .$(CH_2)_nO—$ ($n > 1$) has so far attracted only little attention. The reason may be difficulty in obtaining model compounds with such properties of the silicon and oxygen which would enable to observe such an interaction. A possible formation of a $(p \rightarrow d)_\sigma$ coordination bond between the oxygen and the silicon in the ketones $R_3SiCH_2COCH_3$ has been considered by Musker and coworkers[1,2], and, based on the data reported by Fessenden[3], the interaction of this type can also be expected to occur in the esters R_3SiCH_2COOR'. Measurements of dissociation constants of the acids $R_3Si(CH_2)_3COOH$ (ref.[4]) and $(CH_3)_3Si(CH_2)_nCOOH$ (ref.[5]) revealed that such coordination does not take place in these compounds, analogously to the alcohols $(CH_3)_3Si(CH_2)_nOH$ (ref.[6]) and their O-trimethylsilyl-substituted derivatives $(CH_3)_3Si(CH_2)_nOSi(CH_3)_3$ (ref.[7]) ($n > 1$). The compounds in which the silicon acts as stronger electron acceptor and the oxygen as stronger electron donor are unstable. It is the low stability of these compounds which in a number of cases can be explained in terms of the coordination interaction $O \rightarrow Si$. So for example Russian[8] and German[9,10] authors reported thermal decomposition of terminal alkoxysilyl-substituted propoxysilanes and Bailey[11] described thermal decomposition of bis(trimethylsilyl)-methyl(hydroxypropyl)silane. In these and other cases[10,12—14] the formation of cyclic products can be explained by assuming that already weak coordination of the oxygen to the silicon may stabilize transition state of the reaction which proceeds *via* nucleophilic attack at the silicon. That is why it is assumed in four-centre states of thermal rearrangements of acids[15], ketones[16] and ethers[17]. The stabilization of a five-centre transition state by $(p \rightarrow d)_\sigma$ interaction has been suggested by Rijkens and coworkers[18] to be the reason for anomalous reactivity of ethyl (3-triethyl-silyl)propionate in base-catalyzed hydrolysis. According to Brook[19], this interaction might exist even in the three-centre transition state of rearrangement of silylmethanols to methoxysilanes. It is surprising, however, that this rearrangement has not been observed with the alcohols $R_3Si(CH_2)_nOH$ ($n = 2, 3$)[20] (ref.), the structure of which creates by far the more favourable
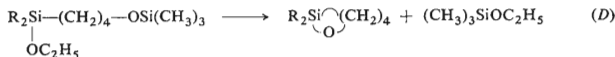
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steric conditions for the transition state of this type. The coordination $O \rightarrow Si$ in these compounds has not yet been established, despite of the attempt by Mironov and Pogonkina[32].

In a previous work[6] we studied the possibility of the interaction between the silicon and the oxygen in the compounds $(CH_3)_3Si(CH_2)_nOH$ $(n > 2)$. In this case the interaction was found not to be significant. The reason may be insufficient electron-donor power of the oxygen and especially a relatively low electron-acceptor ability of the silicon. For that reason in the present work we have studied intramolecular interaction of the type $O \rightarrow Si$ in the compounds in which the acceptive ability of the silicon is enhanced by its substitution by ethoxy groups: $(C_2H_5O)_n(CH_3)_{3-n}Si(CH_2)_mOSi.$ $.(CH_3)_3$ $(n = 1-3; m = 3, 4)$.

The compounds were synthesized by the following routes:

$$(CH_3)_3SiOCH_2CH{=}CH_2 + (C_2H_5O)_3SiH \rightarrow (C_2H_5O)_3Si(CH_2)_3OSi(CH_3)_3 \quad (A)$$

$$(C_2H_5O)_3Si(CH_2)_3OSi(CH_3)_3 + CH_3MgCl \rightarrow$$
$$\rightarrow (CH_3)_n(C_2H_5O)_{3-n}Si(CH_2)_3OSi(CH_3)_3 \quad (n = 1, 2) \qquad\qquad (B)$$

$$(CH_3)_3SiO(CH_2)_4MgCl + (C_2H_5O)_{3-n}Si(CH_3)_nCl$$
$$\downarrow \qquad\qquad \swarrow (CH_3)_3SiO(CH_2)_4MgCl + (C_2H_5O)_{4-n}Si(CH_3)_n$$
$$(C_2H_5O)_{3-n}(CH_3)_nSi(CH_2)_4OSi(CH_3)_3 \quad (n = 0-2) \qquad\qquad (C)$$

In reactions of 4-trimethylsiloxybutylmagnesium chloride with ethoxychlorosilanes or ethoxysilanes, in addition to 4-trimethylsiloxybutyl(ethoxy)silane, approximately equimolar amounts of 1-oxa-2-silacyclohexane and trimethylethoxysilane were always formed. The formation of these by-products can be explained by decomposition reaction (D).

$$R_2Si{-}(CH_2)_4{-}OSi(CH_3)_3 \longrightarrow R_2Si{\frown}(CH_2)_4 + (CH_3)_3SiOC_2H_5 \qquad (D)$$
$$\underset{OC_2H_5}{\mid} \qquad\qquad\qquad O$$

We have found that the compounds $(C_2H_5O)_n(CH_3)_{3-n}Si(CH_2)_mOSi(CH_3)_3$ $(n = 1-3; m = 3, 4)$ decompose to trimethylethoxysilane and the compounds $(C_2H_5O)_n(CH_3)_{2-n}.$ $.Si(CH_2)_mO$ $(n = 0-2; m = 3, 4)$ already on their storing in glass vessels and that this decomposition is catalysed by hydrogen chloride or sodium ethanolate. A similar decomposition has so far been observed to occur only at elevated temperatures[8]. Relative reactivities of the cyclization were determined by the method of competition reactions.

EXPERIMENTAL

Reaction of chlorosilanes with alcohols. Light petroleum and stoichiometric amount of chlorosilane and pyridine were placed in a round-bottom reaction flask, then stoichiometric amount of an alcohol was added with efficient stirring, and the mixture was refluxed for 5 h. The liquid portion was filtered and the salts formed were extracted with light petroleum for 10—20 h. The filtrate and the extract were combined and rectified. This general procedure was modified only

in three cases. In preparation of allyltrimethylsilane, allyl alcohol was added dropwise to trimethylchlorosilane with stirring and the hydrogen chloride evolved was boiled off by spontaneous heating the reaction mixture. After the reaction mixture had refluxed for 5 h, sodium was added until disappearance of the exothermic reaction. In preparation of triethoxysilane, ethanol was added to benzene solution of trichlorosilane at 0°C and the mixture was allowed to stand at this temperature for 2 h. In preparation of (4-chlorobutoxy)trimethylsilane, ammonia was introduced to equimolar mixture of 4-chlorobutan-1-ol and trimethylchlorosilane in benzene at 0°C so long as ammonium chloride precipitated. Reaction conditions and physical constants of the compounds prepared are recorded in Table I.

Triethoxy(3-trimethylsiloxypropyl)silane was obtained[8] in 58% yield by chloroplatinic acid-catalysed addition of triethoxysilane to allyloxytrimethylsilane as fraction boiling 118°C/10 Torr (n_D^{20} 1·4109, d_4^{20} 0·9153; ref.[8] n_D^{20} 1·411, d_4^{20} 0·918). For $C_{12}H_{30}OSi_2$ (294·6) calculated: 48·93% C, 10·27% H, 19·07% Si; found: 48·76% C, 10·24% H, 18·84% Si.

4-Chlorobutanol was prepared[30] by cleavage of tetrahydrofuran with gaseous hydrogen chloride in 50% yield, b.p. 62—66°C/6 Torr.

Reaction of organomagnesium reagents with ethoxysilanes and ethoxy(chloro)silanes. A solution of an ethoxysilane or an ethoxy(chloro)silane in ether (tetrahydrofuran) was placed in a reaction

TABLE I

Reaction Conditions and Physical Constants of Alkoxysilanes

Product	Starting compound	Yield, %	B.p., °C/Torr found	Ref.
$(CH_3)_3SiOCH_2CH=CH_2$	$(CH_3)_3SiCl$	40	100 100—100·2	21
$(C_2H_5O)_3SiH$	$SiHCl_3$	65	128—31 132—5	22
$(CH_3)_3SiO(CH_2)_4Cl$	$(CH_3)_3SiCl$	55	78—9/22 81/24	23
$(C_2H_5O)_4Si$	$SiCl_4$	50	165 166·1	24
$(C_2H_5O)_3SiCH_3$	CH_3SiCl_3	55	142 144·5	25
$(C_2H_5O)_2Si(CH_3)_2$	$(CH_3)_2SiCl_2$	63	114 114	26
$(C_2H_5O)_3SiCl$	$SiCl_4$	60	156—8 156·5	27
$(C_2H_5O)_2CH_3SiCl$	CH_3SiCl_3	64	125—6 125·6—7·5	28
$C_2H_5O(CH_3)_2SiCl$	$(CH_3)_2SiCl_2$	63	95—6 94—5	2

flask and stoichiometric amount of an organomagnesium reagent was added with stirring. The reaction mixture was refluxed with stirring for 5—10 h and then it was allowed to stand overnight. The combined filtrate and extract were rectified. Reactions of 4-trimethylsiloxybutylmagnesium chloride with ethoxysilanes or ethoxy(chloro)silanes (Table II) gave besides 4-trimethylsiloxybutyl(ethoxy)silane also nearly equimolar amounts of 1-oxa-2-silacyclohexane and trimethylethoxysilane. Reaction products, their physical constants and reaction conditions are presented in Tables II and III.

TABLE II

Reactions of Organomagnesium Reagents with Ethoxysilanes and Ethoxy(chloro)silanes

Starting compounds mol	Products	Amount mol	Yield[b] %
$(C_2H_5O)_3SiCl + 0.68\ II^a$	$(C_2H_5O)_3Si(CH_2)_4OSi(CH_3)_3$	0.02	3
	$(C_2H_5O)_2Si(CH_2)_4O$	0.12	18
	$(CH_3)_3SiOC_2H_5$	0.14	21
$(C_2H_5)_2CH_3SiCl + 0.85\ II$	$(C_2H_5O)_2CH_3Si(CH_2)_4OSi(CH_3)_3$	0.33	39
	$C_2H_5OCH_3Si(CH_2)_4O$	0.06	7
	$(CH_3)_3SiOC_2H_5$	0.07	8
$(C_2H_5O)(CH_3)_2SiCl + 1.41\ II$	—	—	—
	$(CH_3)_2Si(CH_2)_4O$	0.54	38
	$(CH_3)_3SiOC_2H_5$	0.45	32
$(C_2H_5O)_4Si + 0.50\ II$	$(C_2H_5O)_3Si(CH_2)_4OSi(CH_3)_3$	0.14	28 (64)
	$(C_2H_5O)_2Si(CH_2)_4O$	0.06	12 (27)
	$(CH_3)_3SiOC_2H_5$	0.07	14 (32)
$CH_3Si(OC_2H_5)_3 + 0.50\ II$	$CH_3(C_2H_5O)_2Si(CH_2)_4OSi(CH_3)_3$	0.15	30 (54)
	$C_2H_5OCH_3Si(CH_2)_4O$	0.04	8 (14)
	$(CH_3)_3SiOC_2H_5$	0.05	10 (18)
$(CH_3)_2Si(OC_2H_5)_2 + 0.50\ II$	$C_2H_5O(CH_3)_2Si(CH_2)_4OSi(CH_3)_3$	0.06	12 (25)
	$(CH_3)_2Si(CH_2)_4O$	0.02	4 (8)
	$(CH_3)_3SiOC_2H_5$	0.03	6 (13)
$0.43(C_2H_5)O)_3Si(CH_2)_3OSi(CH_3)_3$ $+ 0.86\ CH_3MgCl$	$(C_2H_5O)_2CH_3Si(CH_2)_3OSi(CH_3)_3$	0.038	9
	$C_2H_5O(CH_3)_2Si(CH_2)_3OSi(CH_3)_3$	0.085	20

^{a} $(CH_3)_3SiO(CH_2)_4MgCl$ (II). ^{b} The yield given in parenthesis is calculated with respect to the amount of the reacted ethoxysilane.

Spectral measurements. IR spectra of the compounds were recorded with a double-beam Zeiss, Model UR 20, spectrophotometer in the $400-850$ cm^{-1} (KBr prism), $650-1700$ cm^{-1} (NaCl prism), and $1600-4000$ cm^{-1} (LiF prism) regions. Frequency calibration was carried out in the conventional way[33]. Dilute solutions (5%) of the compounds in pure CCl_4 or CS_2 were used. The liquid-phase spectra were also recorded. The spectra of the compounds containing methyl groups on silicon show absorption maxima for this arrangement at $800-860$ cm^{-1}, 1250 to 1260 cm^{-1}, $1410-1420$ cm^{-1}, 2920 cm^{-1}, and 2960 cm^{-1}. Absorption bands arising from

TABLE III

Physical Constants of Compounds Obtained by Reaction of Organomagnesium Reagents with Ethoxysilanes and Ethoxy(chloro)silanes

Compound	B.p., °C/Torr found/lit.	n_D^{20} found/lit.	d_4^{20} found[a]
$(C_2H_5O)_3Si(CH_2)_4OSi(CH_3)_3$[b]	175/88 —	—	—
$(C_2H_5O)_2CH_3Si(CH_2)_4OSi(CH_3)_3$[c]	103/5 —	1·4168	0·8859
$C_2H_5O(CH_3)_2Si(CH_2)_4OSi(CH_3)_3$[d]	95/8 —	—	—
$(C_2H_5O)_2CH_3Si(CH_2)_3OSi(CH_3)_3$[e]	117/25 —	1·4145	—
$C_2H_5O(CH_3)_2Si(CH_2)_3OSi(CH_3)_3$[f]	108/32 —	1·4157	—
$(C_2H_5O)_2Si(CH_2)_4O$[g]	187·5 —	1·4283	1·0207
$C_2H_5O(CH_3)Si(CH_2)_4O$[h]	41/5 —	1·4289	0·9472
$(CH_3)_2Si(CH_2)_4O$[i,j]	84/196 123—126	1·4282 1·4275	0·8810

[a] d_4^{24}; [b] for $C_{13}H_{32}O_4Si_2$ (308·6) found: 50·59% C, 10·48% H, 18·20 %Si; m.w. 299; calculated: 50·43% C, 10·48% H, 17·95% Si; [c] for $C_{12}H_{30}O_3Si_2$ (278·6) found: 51·96% C, 10·95% H, 19·71% Si, m.w. 281; calculated: 51·74% C, 10·86% H, 20·17% Si; [d] for $C_{11}H_{28}O_2Si_2$ (248·5) found: 52·90% C, 11·31% H, 22·88% Si; calculated: 53·17% C, 11·36% H, 22·61% Si; [e] for $C_{11}H_{28}O_3Si_2$ (264·5) found: 49·75% C, 10·60% H, 10·05% Si; m.w. 258; calculated: 49·95% C, 10·67% H, 21·24% Si; [f] for $C_{10}H_{26}O_2Si_2$ (234·5) found: 51·71% C, 11·12% H, 23·66% Si; calculated: 51·22% C, 11·18% H, 23·96% Si; [g] for $C_8H_{18}O_3Si$ found: 50·69% C, 9·70% H, 14·58% Si; calculated: 50·49% C, 9·53% H, 14·76% Si; [h] for $C_7H_{16}O_2Si$ found: 51·98% C, 9·95% H, 17·46% Si; calculated: 52·45% C, 10·06% H, 17·52% Si; [i] for $C_6H_{14}OSi$ found: 55·58% C, 10·92% H, 21·20% Si; calculated: 55·32% C, 10·83% H, 21·56% Si; [j] lit.[31].

vibrations of the methylene groups inserted between the silicon and the oxygen cannot be regarded as characteristic. Their position does not remain constant and the band further frequently overlaps with other bands. The presence of the alkoxy groups in the compounds $(C_2H_5O)_n(CH_3)_{3-n}$.$Si(CH_2)_mOSi(CH_3)_3$ $(n = 0-3)$ $(m = 1-4)$ was confirmed by absorption bands at 945—956 cm^{-1} and 1 164 cm^{-1} and a doublet at 1 083 cm^{-1} and 1 103 cm^{-1}; in the region around 1 100 cm^{-1} there is overlap with $v(Si—O—C)$ of the trimethylsiloxy group ($v(Si—O—C)$ of the compounds $(CH_3)_3Si(CH_2)_nOSi(CH_3)_3$ $(n = 3, 4)$ occur at 1098 cm^{-1}). The spectra of the so far unpublished compounds $(C_2H_5O)_n(CH_3)_{2-n}Si(CH_2)_4O$ $(n = 0-2)$ resemble the spectra of the compounds $(C_2H_5O)_n(CH_3)_{3-n}Si(CH_2)_4OSi(CH_3)_3$. The spectra of the former compounds show characteristic absorption bands of the methyl group and ethoxy groups bonded to the silicon (see above). The compound $(CH_3)_2Si(CH_2)_4O$ showed absorption band at 1 080 cm^{-1}, presumably arising from C—O(Si) ring stretching vibration. In the spectra of other compounds the absorption band due to this vibration overlaps with the bands of the ethoxy groups. The 1-oxa--2-sila-cyclohexanes studied, contrarily to the compounds $(C_2H_5O)_n(CH_3)_{3-n}Si(CH_2)_4OSi$.$(CH_3)_3$ $(n = 1-3)$, all showed absorption maxima at 920 cm^{-1} and in the region of 519—530 cm^{-1} which in accordance with literature[34] can be assigned to the vibration of the heterocycle.

Kinetic measurements of the cyclization. Relative rate constants were calculated from equations derived for Scheme (E)
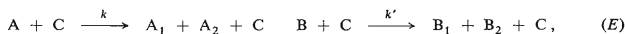
$$A + C \xrightarrow{k} A_1 + A_2 + C \quad\quad B + C \xrightarrow{k'} B_1 + B_2 + C, \quad\quad (E)$$

TABLE IV

Measurements of Relative Rate Constants of Catalysed Decomposition of the Compounds $(C_2H_5O)_n(CH_3)_{3-n}Si(CH_2)_mOSi(CH_3)_3$ $(n = 1-3, m = 3, 4)$

Couple of compounds A and B	Acid-catalysed decomposition			Base-catalysed decomposition		
	mole fraction of HCl	k_A/k_B	$2K_nR^a$	mole fraction of C_2H_5ONa	k_A/k_B	$2K_nR^a$
$(C_2H_5O)_3Si(CH_2)_3OSi(CH_3)_3$ $(C_2H_5O)_2CH_3Si(CH_2)_3OSi(CH_3)_3$	$4\cdot7 \cdot 10^{-4}$	1·21	0·14	0·0255	1·87	0·48
$CH_3(C_2H_5O)_2Si(CH_2)_3OSi(CH_3)_3$ $(CH_3)_2C_2H_5OSi(CH_2)_3OSi(CH_3)_3$	$4\cdot7 \cdot 10^{-4}$	1·38	0·24	0·0255	1·50	0·36
$(C_2H_5O)_3Si(CH_2)_4OSi(CH_3)_3$ $(C_2H_5O)_2CH_3Si(CH_2)_4OSi(CH_3)_3$	$4\cdot3 \cdot 10^{-4}$	0·47	0·04	0·0219	1·38	0·08
$(C_2H_5O)_3Si(CH_2)_3OSi(CH_3)_3$ $(C_2H_5O)_3Si(CH_2)_4OSi(CH_3)_3$	$3\cdot8 \cdot 10^{-4}$	1·44	0·22	0·0241	0·78	0·10

^{a} Ref.[35].

in which one of the starting compounds (catalyst C) is common to both reactions and its concentration remains constant during the reaction. We therefore assumed that the cyclization is pseudo-monomolecular and that its mechanism is the same for all the compounds studied. When conversions of compounds A and B are denoted as x and y, then the relative rate constant is given by equation (I).

$$\frac{k_A}{k_B} = \frac{\ln [1/(1-x)]}{\ln [1/(1-y)]} . \qquad (I)$$

Equimolar amounts of two or three compounds of the type studied and internal standard (dodecane or tridecane) were weighted to 5 ml flask and the reaction was started by adding the catalyst (0·014M benzene solution of sodium ethanolate or hydrogen chloride). The reaction mixture was analysed by g.c.l., by following the changes in the area of elution curve corresponding to the reactant (relative to the peak area of the standard) during the reaction. These analyses were carried out on a chromatograph equipped with thermal-conductivity detector on a column filled with 20% Apiezon on grinded unglazed tiles (carrier gas was hydrogen, column temperature was 145°C). The results are presented in Table IV.

RESULTS AND DISCUSSION

The interpretation of the results of kinetic measurements of the cyclization of terminal ethoxysilyl-substituted butoxy- and propoxyethylsilanes (Table V) was based on the assumption that the rate determining step of the base- and the acid-catalysed cyclization is formation of the transition state, which is preceeded by the interaction of the organosilicon compound (S) with the active part of the catalyst (K).
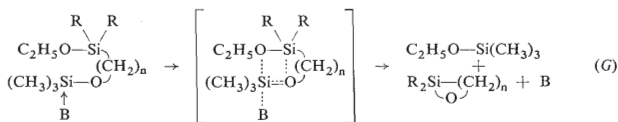
$$S + K \xrightarrow{\text{slow}} S \cdots K \xrightarrow{\text{fast}} \text{products} . \qquad (F)$$

TABLE V

Relative Rate Constants k_{rel} of Decomposition of Terminal Ethoxysilyl-Substituted Butoxy- and Propoxytrimethylsilanes

Compound	A^a	B^b
$(C_2H_5O)_3Si(CH_2)_3OSi(CH_3)_3$	1·67	2·80
$(C_2H_5O)_2(CH_3)Si(CH_2)_3OSi(CH_3)_3$	1·38	1·50
$C_2H_5O(CH_3)_2Si(CH_2)_3OSi(CH_3)_3$	1·00	1·00
$(C_2H_5O)_3Si(CH_2)_4OSi(CH_3)_3$	1·16	3·59
$(C_2H_5O)_2CH_3Si(CH_2)_4OSi(CH_3)_3$	2·47	2·60
$C_2H_5O(CH_3)_2Si(CH_2)_4OSi(CH_3)_3{}^c$	—	—

^{a} The acid-catalysed decomposition. ^{b} The base-catalysed decomposition. ^{c} The compound was extremely unstable; the portion obtained by distillation completely decomposed during 10 h.

In the base-catalysed decomposition (4-ethoxysilylbutoxy)trimethylsilanes react faster than 3-ethoxysilylpropoxy derivatives; the six-membered ring is therefore formed easier than the five-membered one. The reactivity of all the ω-(ethoxysilylalkoxy)trimethylsilanes increases with increasing number of ethoxy groups. The formation of the four-centre transition state (I) of the base-catalyzed cyclization can be assumed to be initiated by nucleophilic attack at the silicon of the trimethylsiloxy group by the base. This attack would increase the electron density at the oxygen and thus also its electron-donor ability so much that the oxygen may form coordination bond with the silicon of the ethoxysilyl group. This attack will induce twofold syn-

$$
\begin{array}{c}
\underset{|}{\overset{R\quad R}{C_2H_5O-Si}} \\
\underset{|}{\overset{|}{(CH_3)_3Si-O}}(CH_2)_n \\
\overset{\uparrow}{B}
\end{array}
\;\rightarrow\;
\left[
\begin{array}{c}
\overset{R\quad R}{C_2H_5O-Si} \\
(CH_3)_3Si\!\cdots\!O(CH_2)_n \\
B
\end{array}
\right]
\;\rightarrow\;
\begin{array}{c}
C_2H_5O-Si(CH_3)_3 \\
+ \\
R_2Si-(CH_2)_n + B \\
\underset{O}{\qquad}
\end{array}
\qquad (G)
$$

chronous nucleophilic substitution of both silicon atoms, which would be completed by the release of the active part of the catalyst. From the reactivity order found it follows that the ease with which the silicon of the ethoxysilyl group is attacked increases with increasing number of the ethoxy groups. This can be explained in terms of the progressive decrease in the electron density of the silicon due to increasing influence of the $-I$ effect of the ethoxy groups in transition state.

In the acid-catalyzed decomposition of (3-ethoxysilylpropoxy)trimethylsilanes, the reactivity difference between individual members is smaller than in the base-catalyzed reaction. In the case of (4-ethoxysilylbutoxy)trimethylsilanes the reactivity order is even reversed. It seems probable that initiation step in this reaction is attack by the catalyst at the oxygen of the ethoxy group. The suggestion of reliable mechanism which would comport with the observed reactivity order is at present difficult and will require the accumulation of further data.

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