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Abstract

Full Text

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On Reactions of Intramolecular Transesterification of Substituted Esters of γ-Hydroxypropylalkoxysilanes

Methylallyloxysilanes readily react in the presence of H_2PtCl_6 with hydridoalkoxy- and hydridoalkylalkoxysilanes according to the known scheme:

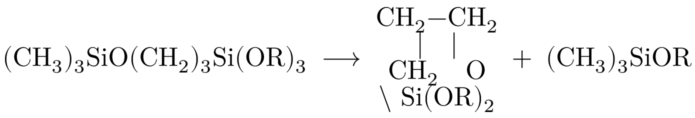
$$R_3SiOCH_2{-}CH{=}CH_2 + HSi(OR)_3 \rightarrow R_3SiOCH_2CH_2CH_2Si(OR)_3.$$

By means of this reaction new compounds were obtained, the properties of which are given in Table 1. In studying the products of the addition of hydridoalkoxysilanes to trimethylallyloxysilane, it was established that they are capable of entering into a reaction of intramolecular interaction of alkoxy groups with trimethylsiloxy groups, forming cyclic compounds, with elimination of trimethylsilyl groups in the form of trimethylalkoxysilanes. The reaction of intramolecular transesterification is expressed by the equation

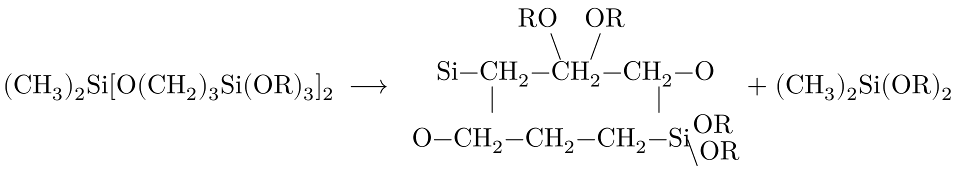
Table 1

Compound	B.p., °C	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
$(CH_3)_2Si\,[O(CH_2)_3Si(OMe)_3]_2$	127–129/2 mm	1.4240	1.039	102.32	102.2
$(CH_3)_2Si\,[O(CH_2)_3SiEt(OMe)_2]_2$	134–135/1 mm	1.4320	0.9808	109.98	109.18
$(CH_3)_2Si\,[O(CH_2)_3SiMe(OEt)_2]_2$	142–143/1 mm	1.4252	0.9558	119.27	118.22
$(CH_3)_2Si\,[O(CH_2)_3Si(OEt)_3]_2$	154–155/1 mm	1.4208	0.9776	130.21	129.8
$(CH_3)_2SiO(CH_2)_3SiMe(OEt)_2$ with OC_3H_5	86–89/1 mm	1.4185	0.9311	84.37	83.3
$(CH_3)_3SiO(CH_2)_3Si(OEt)_3$	81–85/1 mm	1.411	0.918	80.2	79.75
$(CH_3)_3SiO(CH_2)_3SiEt(OMe)_2$	83–85.5/1 mm	1.4190	0.9007	70.08	69.53
$(CH_3)_3SiO(CH_2)_3Si(OBu)_3$	124–128/1–1.5 mm	1.4232	0.8967	108.09	107.61

Compound	B.p., °C	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
$(C_2H_5)_3SiO(CH_2)_3Si(OEt)_3$	118–123/1 mm	1.426	0.9205	94.124	93.51
$(C_2H_5)_2Si[O(CH_2)_3Si(OMe)_3]_2$	152–162/1–2 mm	1.427	1.0288	111.616	111.01



This interesting reaction was also carried out on dimethyl-substituted esters of γ-hydroxypropyltrialkoxysilanes, and was accompanied by the formation of ten-membered rings:



On heating under vacuum, γ-trimethylsiloxypropyltributoxysilane yielded trimethylbutoxysilane and 1,1-dibutoxy-1-sila-2-oxacyclopentane in a yield of 32%. The reaction is accelerated (with an increase in yield) if traces of acid are introduced. If other trimethylsiloxy-γ-pro-

pinylalkoxysilanes, the five-membered rings obtained at room temperature usually polymerize rapidly. Therefore, for them it was possible to establish only the boiling points and elemental composition. On heating the dimethyl-substituted esters of bis-γ-oxypropyltrimethoxysilanes, dimethyldimethoxysilane was split off and 1,1,6,6-tetramethoxy-1,6-disila-5,10-dioxacyclodecane was isolated in 11% yield. Other ten-membered rings were obtained analogously; their properties are given in Table 2. Some five-membered rings are readily converted into ten-membered ones; for example, 1,1-dibutoxy-2-sila-2-oxacyclopentane, on standing

Table 2

Compound	B.p., °C	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
$(BuO)_2Si-(CH_2)_3-O-O-(CH_2)_3-Si(OBu)_2$	141-146/1 mm	1.4282	0.9347	126.26	126.6
cyclic $(BuO)_2Si-(CH_2)_3-O$	80-82/1 mm	1.4282	0.9575	63.13	62.47
$(MeO)_2Si-(CH_2)_3-O-O-(CH_2)_3-Si(OMe)_2$	90-93/1 mm	1.4171	1.0383	70.49	71.88
$MeOEtSi-(CH_2)_3-O-O-(CH_2)_3-SiEtOMe$	94-95/1 mm	1.4184	0.9560	78.14	77.17
cyclic $MeOEtSi-(CH_2)_3-O$	162-165/752 mm	1.4495	–	39.07	–
$(EtO)_2Si-(CH_2)_3-O-O-(CH_2)_3-Si(OEt)_2$	88-91/1 mm	1.412	0.9749	89.08	90.03
cyclic $(EtO)_2Si-(CH_2)_3-O$	195-197/750 mm	1.4175	–	44.54	–

at room temperature is converted into 1,1,6,6-tetrabutoxy-1,6-disila-5,10-dioxacyclodecane. On heating, the reverse reaction may occur.

The mechanism of formation of five-membered rings may be represented as follows:

$$R_3Si-O-CH_2-CH_2-CH_2-Si(OR')_3 \longrightarrow \begin{array}{c}\text{five-membered cyclic}\\ O-Si(OR')_2\end{array} + R_3SiOR'$$

and the formation of ten-membered rings:

$$\begin{gathered}(R'O)_3Si(CH_2)_3O{-}Si(R)_2{-}O{-}CH_2CH_2CH_2\\ \longrightarrow R'(O)OR'{-}Si(CH_2CH_2CH_2O)\ -\ R_2Si{-}OCH_2CH_2CH_2Si(OR')_2\\ \longrightarrow (R'O)_2SiCH_2CH_2CH_2O{-}OCH_2CH_2CH_2Si(OR')_2+R_2Si(OR')_2.\end{gathered}$$

As follows from the schemes given, the formation of five-membered rings requires a stronger deformation of the molecule and therefore should proceed under more severe conditions than the formation of ten-membered rings. Indeed, in the absence of catalysts (for example, traces of H_2PtCl_6), many products of the type $R_3SiO(CH_2)_3Si(OR')_3$ can be distilled without appreciable decomposition at temperatures that cause decomposition of products of the type $R_2Si[O(CH_2)_3Si(OR')_3]_2$, with formation of ten-membered rings. To prove the intramolecular mechanism of the cleavage reaction of the produc-

of the type $R_2Si[O(CH_2)_3Si(OR')_3]_2$ into ten-membered rings and $R_2Si(OR')_2$, a mixture of equimolecular amounts of $(CH_3)_2Si[O(CH_2)_3Si(OC_2H_5)_3]_2$ and $(C_2H_5)_2Si[O(CH_2)_3Si(OCH_3)_3]_2$ was decomposed. In this case, with a purely intramolecular reaction, equimolecular amounts of $(CH_3)_2Si(OC_2H_5)_2$ and $(C_2H_5)_2Si(OCH_3)_2$ should split off, whereas in the case of an intermolecular reaction—a complex mixture of alkylalkoxysilanes should be formed. In reality, depending on the decomposition conditions, the amounts of $(CH_3)_2Si(OC_2H_5)_2$ and $(C_2H_5)_2Si(OCH_3)_2$ amounted to 60-75% of the mixture of dialkyldialkoxysilanes, as was established by rectification of the mixture. In this case a higher yield of $(CH_3)_2Si(OC_2H_5)_2$ and $(C_2H_5)_2Si(OCH_3)_2$ corresponded to milder decomposition conditions. Thus, the intramolecular reaction proves to be predominant.

Preparation of dimethyl-bis-(γ-ethyldimethoxysilylpropoxy)-silane. Into a flask are charged 20 g of dimethyldiallyloxysilane, heated to 125°, 0.2 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol is added, and 32 g of ethyldimethoxysilane is introduced dropwise, taking care that the temperature does not rise above 150°. The product is heated for 2 hours under nitrogen at 140°. Vacuum distillation gave 20 g of dimethyl-bis-(γ-ethyldimethoxysilylpropoxy)-silane, b.p. 134-135°/1 mm, yield 42%. Elemental composition:

Found, %: Si 19.0; 20.00; H 9.55; 9.68; C 46.68; 46.77
$C_{16}H_{40}Si_3O_6$. Calculated, %: Si 20.42; H 9.77; C 46.56

Preparation of dimethyl-bis-(γ-triethoxysilylpropoxy)-silane. In an analogous manner, at 140° for 7-8 hours, from 94 g of triethoxysilane and 42 g of dimethyldiallyloxysilane, 49% of dimethyl-bis-(γ-triethoxysilylpropoxy)-silane was obtained, b.p. 183-185°/6 mm. Elemental composition:

Found, %: Si 16.74; 16.49; C 48.20; 48.27; H 10.36; 10.37
$C_{20}H_{48}Si_3O_8$. Calculated, %: Si 16.83; C 47.96; H 9.66

Preparation of dimethyl-bis-(γ-trimethoxysilylpropoxy)-silane and 1,1-6,6-tetramethoxy-1,6-disila-5,10-dioxacyclodecane. At 140–150° for 4 hours, from 60 g of dimethyldiallyloxysilane and 75.2 g of trimethoxysilane, 39 g of dimethyl-bis-(γ-trimethoxysilylpropoxy)-silane was obtained, b.p. 127–129°/1 mm. Elemental composition:

Found, %: C 39.81; 40.01; H 9.15; 8.98; Si 19.64; 19.84
$C_{14}H_{30}Si_3O_8$. Calculated, %: C 40.35; H 8.71; Si 20.22

and 10.5 g of 1,1-6,6-tetramethoxy-1,6-disila-5,10-dioxacyclodecane, b.p. 90–93°/1 mm. Elemental composition:

Found, %: Si 18.35; 19.01; C 40.12; 39.87; H 7.93; 8.26
$C_{10}H_{24}Si_2O_6$. Calculated, %: Si 18.95; C 40.51; H 8.16

Preparation of dimethyl-bis-(γ-methyldiethoxysilylpropoxy)-silane. From 22 g of dimethyldiallyloxysilane and 40 g of methyldiethoxysilane (7 hours of heating at 140–150°), 25 g of dimethyl-bis-(γ-methyldiethoxysilylpropoxy)-silane was obtained, b.p. 140–143°/1 mm. Elemental composition:

Found, %: Si 19.39; 19.57; C 49.41; 49.55; H 10.47; 10.53
$C_{18}H_{44}Si_3O_6$. Calculated, %: Si 19.12; C 49.04; H 10.06

and 8 g of fraction 86–89°/1 mm, corresponding by analysis to dimethyldiallyloxy-(γ-methyldiethoxysilylpropoxy)-silane. Elemental composition:

Found, %: Si 17.67; 17.55; H 9.95; 10.21; C 49.85; 49.74
$C_{13}H_{30}Si_2O_4$. Calculated, %: Si 18.33; H 9.87; C 50.93

Preparation of 1,1-6,6-tetrabutoxy-1,6-disila-5,10-dioxacyclodecane. 35 g of dimethyldiallyloxysilane and 112 g of tributoxysilane are heated in the presence of H_2PtCl_6 at 140–150° for 10 hours. By distillation under vacuum, 68 g of 1,1-6,6-tetrabutoxy-1,6-disila-5,10-dioxacyclodecane, b.p. 141–146°/1 mm. Elemental composition:

Found, %: C 56.33; 56.06; H 10.60; 10.53; Si 12.11; 12.20
$C_{22}H_{48}Si_2O_6$. Calculated, %: C 56.85; H 10.41; Si 12.09

Preparation of 1,1-dibutoxy-1-sila-2-oxacyclopentane. As a result of rectification on a column (12 theoretical plates), 30 g of 1,1,6,6-tetrabutoxy-1,6-disila-5,10-dioxacyclodecane at 1 mm gave 6 g of 1,1-dibutoxy-1-sila-2-oxacyclopentane, b.p. 80–82°/1 mm. Elemental composition:

Found, %: C 56.53; 56.56; H 10.65; 10.90; Si 11.26; 11.38
$C_{11}H_{24}SiO_3$. Calculated, %: C 56.85; H 10.41; Si 12.09

Molecular weight 281 (cryoscopically) after several days becomes equal to 470 (the monomer converts into the dimer).

Preparation of 1,1,6,6-bis(ethylmethoxy)-1,6-disila-5,10-dioxacyclodecane. Distillation of 42 g of dimethyl-bis-(γ-ethylmethoxysilylpropoxy)-silane at 20 mm gave 13 g of 1,1,6,6-bis-(ethylmethoxy)-1,6-disila-5,10-dioxacyclodecane, b.p. 94-95°/1 mm. Elemental composition:

Found, %: C 48.58; 48.88; H 10.42; 9.84; Si 20.38; 19.76
$C_{12}H_{28}Si_2O_4$. Calculated, %: C 49.26; H 9.65; Si 19.25

Preparation of 1,1,6,6-bis-(diethoxy)-1,6-disila-5,10-dioxacyclodecane. Distillation of 25 g of dimethyl-bis-(γ-triethoxysilylpropoxy)-silane at 14-35 mm led to the formation of 5 g of 1,1,6,6-bis-(diethoxy)-1,6-disila-5,10-dioxacyclodecane, b.p. 88-91.5°/1 mm. Elemental composition:

Found, %: C 48.25; 48.54; H 10.50; 10.25; Si 17.02; 16.86
$C_{14}H_{32}Si_2O_6$. Calculated, %: C 47.89; H 9.15; Si 15.93

Preparation of 1,1-diethoxy-1-sila-2-oxacyclopentane. To 10 g of trimethyl-γ-triethoxysilylpropoxysilane are added traces of acid (sulfuric acid or $H_2PtCl_6 \cdot 6H_2O$). Upon distillation at 750 mm under nitrogen, 3 g of trimethylethoxysilane were isolated, b.p. 72-75°, n_D^{20} 1.3740, and 5 g of 1,1-diethoxy-1-sila-2-oxacyclopentane with b.p. 190-197.5°, which rapidly polymerized. Elemental composition:

Found, %: C 48.18; 48.63; H 9.86; 10.22; Si 15.01; 14.63
$C_7H_{16}SiO_3$. Calculated, %: C 47.69; H 9.15; Si 15.93

Preparation of 1,1-dibutoxy-1-sila-2-oxacyclopentane from trimethyl-γ-tributoxysilylpropoxysilane. By distilling 13 g of trimethyl-γ-tributoxysilylpropoxysilane in the presence of traces of H_2PtCl_6 at 15 mm, 5 g of 1,1-dibutoxy-1-sila-2-oxacyclopentane were obtained, mol. wt. 250; 289, b.p. 83-85°/1 mm. Elemental composition:

Found, %: C 56.25; 25.73; H 10.45; 10.95; Si 11.75; 12.32

Preparation of 1,1-ethylmethoxy-1-sila-2-oxacyclopentane. By distilling 5 g of trimethyl-γ-ethyldimethoxysilylpropoxysilane in the presence of traces of H_2SO_4 at 750 mm under nitrogen, 2.3 g of 1,1-ethylmethoxy-1-sila-2-oxacyclopentane, b.p. 162-165°, and 1.5 g of trimethylmethoxysilane were isolated. Elemental analysis:

Found, %: C 49.37; 50.14; H 10.32; 10.57; Si 19.14; 18.92
$C_6H_{14}SiO_2$. Calculated, %: C 49.26; H 9.65; Si 19.25

Preparation of diethyl-bis-(γ-trimethoxysilylpropoxy)-silane. At 140-150° over 2.5-2 hours, from 72 g of trimethoxysilane and 54.3 g of diethyldiallyloxysilane, 42 g of diethyl-bis-(γ-trimethoxysilylpropoxy)silane were obtained, b.p. 158-162°. Elemental analysis:

Found, %: C 43.92; 43.82; H 9.71; 9.56; Si 18.51; 18.90
$C_{16}H_{40}Si_3O_8$. Calculated, %: C 43.21; H 9.07; S 18.95

Decomposition of a mixture of equimolecular amounts of diethyl-bis-(γ-trimethoxysilylpropoxy)-silane and dimethyl-bis-(γ-triethoxysilylpropoxysilane). From a mixture of 23.2 g of $(CH_3)_2Si[OC_3H_6Si(OEt)_3]_2$ and 20.1 g of

$(C_2H_5)_2Si[OC_3H_6Si(OMe)_3]_2$, which was distilled at 60–70 mm and then at 17 mm, rectification of the low-boiling fractions yielded 5 g of dimethyldiethoxysilane, b.p. 111–115°, and 4.8 g of diethyldimethoxysilane, b.p. 120–126°.

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Note: Figure translations are in progress. See original paper for figures.