

# Monosodiumoxyorganoalkoxysilanes: Synthesis and Properties

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**ABSTRACT:** *The reaction of organoalkoxysilanes with sodium hydroxide was studied in detail. Studies indicate that this reaction involves more than one stage and involves rather complex multistep process, which leads to the formation of both monosodiumoxyorganoalkoxysilanes (MSOAS) and several secondary products. Analysis of experimental evidence makes it possible to advance the mechanism behind this phenomenon and to define the optimum conditions for the preparation of pure MSOAS with high yields. Different MSOAS were synthesized and their basic physicochemical properties were studied. MSOAS are shown to constitute multifunctional reagents with chemically independent functional groups, and their reaction with trimethylchlorosilane selectively proceeds via  $-ONa$  groups, whereas their interaction with triethylesilanol and higher alcohols proceeds exclusively via  $-OAlk$  groups. Exchange interaction between MSOAS and organoalkoxysilanes via  $-ONa$  and  $-OAlk$  groups was found and studied in detail. Temperature corresponding to the onset of thermal degradation of MSOAS was estimated to be equal to  $\sim 180-190^{\circ}C$ . © 2006 Wiley Periodicals, Inc. *Heteroatom Chem* 17:514–541, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20280*

## INTRODUCTION

Monosodium salts of oxyorganoalkoxysilanol (MSOAS) constitute new promising reagents for the controlled synthesis of various functional organosiloxanes with different structures. Earlier [1,2] promising advantages of such reagents have been vividly demonstrated for the most intricate case such as the synthesis of organosiloxane dendrimers. However, properties of MSOAS and procedure of their synthesis have eluded the attention of authors, and only scarce information on this topic has occasionally appeared. This unfortunate scenario had its sad consequences because until now the above reagents have been considered to be quite exotic, hard to get, and rather unstable compounds.

This skeptic approach seemed to be valid and even well justified when considering various historical aspects concerning the general development of the chemistry of alkali metal silanolates and their use as starting reagents for the synthesis of organosiloxanes (instead of the corresponding silanols and siloxanols) [3–24]. Attractive features of this approach are its relative simplicity and its well-defined mechanism of the reaction between  $\equiv SiONa$  and  $\equiv SiCl$  groups, which leads to the formation of a siloxane bond. In classical version, similar reaction of hydroxyl-containing reagents necessarily requires the involvement of third components as acceptors of hydrogen chloride. Furthermore, as compared with the corresponding labile silanols, sodiumoxy derivatives are known to be rather stable compounds. Pioneering experimental data concerning the application of less exclusive

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triorganosilanolates and organosiloxanates containing a single sodiumoxy group led to rather encouraging results [3–5]. In addition, evident advances in this direction have triggered the development of simple and reliable methods of the preparation of sodiumsilanolate reagents with more complex structures. One of the most reasonable and widely used methods involved an interaction of bifunctional and trifunctional organosilanes, usually organoalkoxysilane [6–8], or diorganocyclosiloxanes [9–12], and organosilsesquioxanes [13–20], which were prepared by hydrolytic polycondensation of organoalkoxysilanes with sodium hydroxide in aqueous alcohol solutions. However, even the first experimental trials proved that controlled monitoring over structure and composition of the formed sodiumoxyorganoalkoxysilanes (by varying feed ratio of initial reagents or by changing such parameters as type of solvent and temperature conditions) was not feasible. Due to the specific character of chemical interactions in the reaction system, this process is totally independent of any variations in the above parameters and entails the formation of a set of the most stable and thermodynamically stable sodiumsilanolates. Molecules of sodiumsilanolates contain specified number of sodiumoxy groups and organosiloxy fragments [12–13,15,19,20]. Furthermore, in many cases, this process leads to the formation of nonseparable mixtures of sodium-containing homologs. It is important to note that the lower individual representatives of this homological series are virtually insoluble in all known aprotic organic solvents. Therefore, the total replacement of hydroxyl-containing reagents by their sodiumoxy derivatives is baseless and unsound. Taking into account this unfortunate historical scenario, many scientists involved in the synthesis have lost their interest in such reagents. Evidently, this is the reason why rather scarce publications are devoted to the use of organic sodiumsilanolates for the synthesis of individual functional organosiloxanes and organopolysiloxanes, and all results of the above works did not meet the stated objectives [15,18,19,21,22].

However, many publications have addressed the synthesis of various poly(organometallosiloxanes) from the mixtures of the above-mentioned reagents [13,17–19,25–29]. During the early stages, the authors were likely to be pretty satisfied with the characteristics of newly synthesized compounds. Unfortunately, the problems related to the structure and composition of initial sodium silanolates have escaped their attention. However, snowballing development of this challenging and promising direction of chemistry as well as application of powerful modern physical

methods, such as X-ray analysis, was triggered by stored knowledge on the chemical nature of organosilanolates and improved methods of their synthesis. As a result, general strategy for the preparation of sodium oxyorganoalkoxysilanes has been changed. Presently, all efforts are being focused not on overcoming the natural barriers but also on the development of proper favorable conditions that assist the formation of particular sodium-containing homologs from available compounds directly in the course of synthesis. Evident progress in this direction concerns the preparation of reagents with cyclic structure; their molecules contain one –ONa group at each silicon atom, and the dimensions of siloxane cycles may be appreciably different [30–33]. A stereochemical aspect of this approach also deserves a special interest: most of the synthesized compounds are virtually pure *cis*-isomers.

It should be emphasized that the above-mentioned classical methods were initially directed to take full advantages offered by the functional potential of silicon atoms in the molecules of raw compounds, which are involved in the formation of ≡SiONa groups and siloxane bonds in the molecules of resultant sodiumorganosilanolates at desired proportions. Therefore, they cannot be directly used for the synthesis of such compounds as monosodiumoxyorganoalkoxysilanes (**1**) (MSOAS), whose molecules contain a single silicon atom with attached sodiumoxy and alkoxy fragments (Fig. 1).

According to formal hallmarks, MSOAS belong to a family of sodium salts of the corresponding organosilanols. However, by their molecular design, chemical behavior, and synthetic potential, they may be classified as specific compounds, which are conditionally referred to as “reagents with chemically independent functional groups.” In addition to MSOAS, this small group of compounds includes organoalkoxysilanol (2) [34–43], organohydride silanolate of alkali metals (3) [44–47], lithium organofluorosilanolate (4) [48], and lithium salts of organophenylsilanolate (5) [49,50] (Fig. 2).

Organoalkoxysilanol (Fig. 2, 2) are known to be direct structural precursors of MSOAS. In principle, the above reagents and a well-known procedure

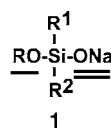
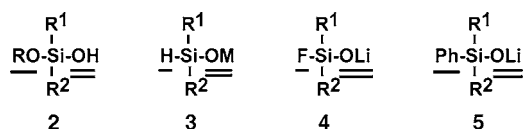


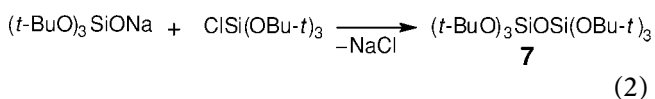
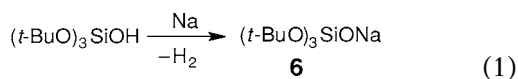
FIGURE 1 Monosodiumoxyorganoalkoxysilanes (MSOAS): R: organic radicals; R<sup>1</sup>, R<sup>2</sup>: organic radicals or alkoxy groups.



**FIGURE 2** Reagents with “chemically independent functional groups”. Organoalkoxysilanols (**2**), Organohydridsilanolates of alkali metals (**3**), Lithium organofluorinesilanolates (**4**), Lithium organophenylsilanolates (**5**). R<sup>1</sup>, R<sup>2</sup>: organic radicals.

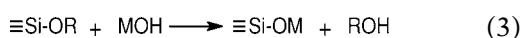
of their synthesis [34–40] may be independently used for the preparation of individual functional organosiloxanes—for example, in the reactions with ≡SiCl groups in the presence of HCl acceptors [35,39–41] or without any acceptors in the reactions with ≡SiNH<sub>2</sub> groups [42,43]. Furthermore, organoalkoxysilanols are rather mobile compounds, which are capable of self-condensation [38,39]. Therefore, as in the above-mentioned classical case, the best scenario involves the use of sodium salts (such as MSOAS) for synthetic purposes.

The simplest method for the transformation of organoalkoxysilanols into the corresponding silanolate derivatives includes their interaction with alkali metals (in particular, with sodium). This procedure has been applied for the pioneering synthesis of MSOAS, which is sodiumoxytris(*tert*-butoxysilane) (**6**) with bulky inert *tert*-butoxy groups (Scheme 1) [51]. Its structure was confirmed by the recovery of disiloxane (**7**) with a yield of ~80% (Scheme 2).



However, the above methods are virtually used to illustrate the feasibility of MSOAS synthesis, rather than being justified as reliable procedures for their preparation because they involve multistage synthesis of initial organoalkoxysilanols, some of which (especially, with methoxy and ethoxy groups) are known to be rather unstable compounds.

In the literature, certain information concerning the formation of compounds with ≡SiOM groups via the interaction of alkoxysilanes with sodium and potassium hydroxides are available [26,32–38]. Formally, the scheme of their preparation may be presented as the reaction of nucleophilic substitution (Scheme 3):



**FIGURE 3** Composition of resulting products from the reaction between tetraethoxysilane and potassium hydroxide.

This method of preparation of sodium and potassium-containing oxyorganoalkoxysilanes seems to be rather attractive, and its advantages over the other methods are as follows: (i) it involves no stage of preliminary synthesis and the formation of organoalkoxysilanols; and (ii) alkali metal hydroxide, rather than alkali metal by itself, is used for the formation of the ≡SiOM group. However, analysis of this reaction (Scheme 3) leads to rather conflicting results. For example, as was shown in [54], structure and composition of the products resulting from the reaction between tetraethoxysilane and potassium hydroxide in tetrahydrofuran are primarily controlled by the feed ratio between initial components: Si(OEt)<sub>4</sub> and KOH. When this ratio is 1:1, potassiumoxytriethoxysilane (**8**) is formed; when ratio is 1:2, dipotassiumoxydiethoxysilane (**9**) is obtained; at 1:3, an insoluble compound of uncertain composition is produced (Fig. 3).

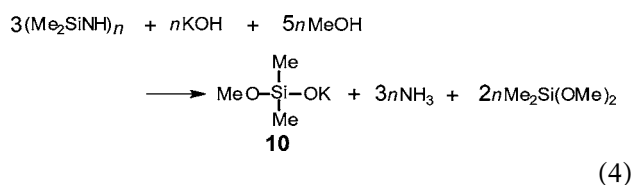
Similar results were obtained when studying the interaction of tetraethoxysilane with sodium hydroxide [55,56]. When Si(OEt)<sub>4</sub>:NaOH ratio is 1:2, the reaction mixture contains unreacted sodium hydroxide (no quantitative data are presented). Evidently, in this case, in addition to disodium oxydiethoxysilane (NaO)<sub>2</sub>Si(OEt)<sub>2</sub>, reaction products contain monosodium oxytriethoxysilane NaOSi(OEt)<sub>3</sub>.

Potassium and sodium oxytriethoxysilanes were synthesized directly in the course of the reaction between tetraethoxysilane and sodium or potassium hydroxides when feed ratio between (Si(OEt)<sub>4</sub> and MOH) is ~2.25:1 [57–59]. The reaction products were deliberately used as reagents for the synthesis of functional aluminum silicates via their reaction with AlBr<sub>3</sub> and with aluminum diethoxy or diisobutylbromides. Analysis of thermal behavior of potassium oxytriethoxysilane shows that its thermal degradation commences at temperatures above 80°C [57]. Volatile products of thermal degradation include tetraethoxysilane (92%), ethanol (5.3%), and ethylene (2.7%). This process is assumed to be accompanied by the disproportionation of potassium oxytriethoxysilane into tetraethoxysilane and dipotassiumoxydiethoxysilane [(KO)<sub>2</sub>Si(OEt)<sub>2</sub>]. However, this assumption was not proved by the analysis of solid residue after thermal degradation. It was found that the structure of degradation

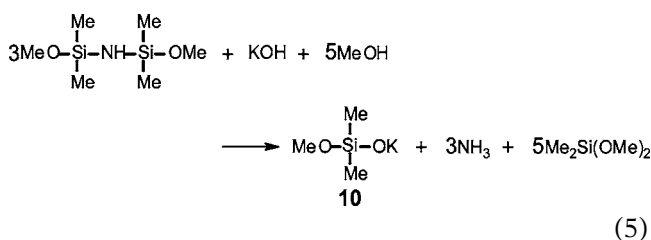
product appears to be far more complex and rather uncertain.

However, quite opposite results were presented in the literature [60,61]. As was shown, sodium and potassium hydroxides react with tetramethoxysilane (under threefold excess of tetramethoxysilane) to produce the adducts with the following composition:  $(\text{MO})_2\text{Si}(\text{OMe})_{2-x}\text{Si}(\text{OMe})_4$  [60]. When the above adducts are heated at  $\sim 155\text{--}230^\circ\text{C}$  in vacuum (20 Torr), they were decomposed into the following components: disodium oxydimethoxysilane, dipotassium oxydimethoxysilane, and tetramethoxysilane. As was reported in [61], this approach has been applied to obtain the following compounds:  $(\text{RO})_2\text{Si}(\text{OM})_2$ , where  $\text{R} = \text{Et}, \text{Pr}, \text{Bu}$ ;  $\text{M} = \text{Na}, \text{K}$ . Possible formation of monosodium and monopotassiumoxytrialkoxysilanes was not discussed.

Interesting results were reported in a brief communication [62], but unfortunately they did not receive any proper attention. Interaction of dimethylcyclosilazanes with methanol solution of potassium hydroxide was shown to produce potassiumoxydimethylmethoxysilane (**10**) (Scheme 4). When  $n = 3$ , yield of compound **10** is equal to 88.5%; at  $n = 4$ , the yield is 72.3%.

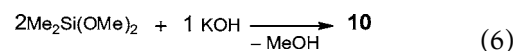


Reaction of 1,3-dimethoxytetramethyldisiloazane with the same reagent at  $100^\circ\text{C}$  also leads to the formation of compound **10** with a yield of 65% (Scheme 5).

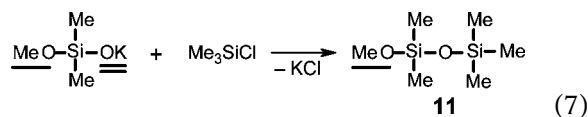


It seems interesting that the resulting potassiumoxydimethylmethoxysilane (**10**) exists in the medium, which does not contain any active hydroxyl-containing products. This is the reason why dimethylsilazanes were used as starting silicon-containing components. However, as was shown, compound **10** may be obtained with a yield of  $\sim 86.9\%$  directly from dimethyldimethoxysilane and potassium hydroxide (Scheme 6). This reaction was carried out without any solvents at  $100^\circ\text{C}$ , and feed

ratio between components was equal to 2:1.



The formation of potassium oxydimethylmethoxysilane was also confirmed by the preparation of the corresponding trimethylsilyl derivative (**11**) (Scheme 7).



The above examples vividly demonstrate that a systematic analysis using the literature as a data source proves that no reliable and approved methods for the preparation of the above compounds are available. In this connection, the objective of this work concerns the development of straightforward and convenient method for the synthesis of sodium salts of oxyorganoalkoxysilanes and characterization of their properties.

## RESULTS AND DISCUSSION

### General Background

Conflicting literature data concerning the formation of organoalkoxysilanolates suggest that no systematic research in this direction has been conducted, and the mechanism of this reaction is still vague (Scheme 3). However, the reaction of organoalkoxysilanes with sodium or potassium hydroxides for the preparation of monoderivatives seems to be rather attractive. Without going into the details behind this process [63], this reaction is assumed to present a typical nucleophilic substitution at the silicon atom. In this case, the hydroxyl ion serves as the primary nucleophilic particle for attacking the silicon atom. Substitution of one alkoxy group in the molecules of initial organoalkoxysilanes by  $\text{MO}^\ominus$  group, which, in turn, presents a rather strong nucleophilic site, decreases the sensitivity of the silicon atoms to the attacks from another  $\text{HO}^\ominus$  ion due to electron density redistribution and, as a result, to the inhibition of further substitution of remaining alkoxy groups by  $-\text{OM}$  groups (Fig. 4).

Therefore, a thorough investigation of this reaction and the specific features of the interaction between the components of the reaction may allow one to select the conditions, which provide high yields of pure organoalkoxysilanolates containing

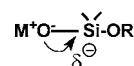


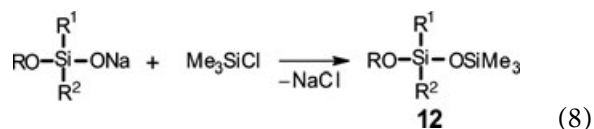
FIGURE 4 Electronic effects in MSOAS molecules.

only one –OM group. In turn, the preferable route is to synthesize monosodiumoxyorganoalkoxysilanes from their potassium analogs. This approach may be justified by the fact that potassium hydroxide contains ~15 wt% of water or 1 mol of water per each 1.8 mol of potassium hydroxide. One may hardly exclude the possibility that this factor may exert its negative effect on the yields and purity of potassiumoxyorganoalkoxysilanes and related organosiloxanes. It is worth mentioning that sodium hydroxide of the same chemical grade is free of this drawback. We also take into account the fact that thermal degradation of potassiumoxytriethoxysilane commences at 80°C [57].

### Interaction of Organoalkoxysilanes with Sodium Hydroxide. Synthesis of Monosodiumoxyorganoalkoxysilanes

Interaction between alkoxy silanes and NaOH takes place in the presence of organic solvents or in the presence of excessive amounts of alkoxy silane at temperatures ranging from –30 to +100°C. The end of this reaction was fixed at the point of total homogenization of the system. In all cases, this reaction is accompanied by an evident exothermic effect and leads to the formation of the corresponding alcohol.

The separation of individual salt-containing products from the reaction mixture and their analysis present a rather complicated and inefficient procedure. Therefore, yields and purity of final products were indirectly controlled by their trimethylsilyl (12) derivatives prepared according to Scheme 8.



Trimethylsilyl derivatives (12) are liquids, which may be readily isolated as individual compounds by rectification or trivial distillation (Table 1). Constants of several compounds (12) prepared by other methods were listed in Ref. 64.

Purity of the resulting compounds was proved by the GLC method; this parameter was not less than ~99%; the structure of the above compounds was confirmed by the <sup>1</sup>H NMR spectroscopy and elemental analysis. As an example, Fig. 5 presents the <sup>1</sup>H NMR spectra of initial dimethyldiethoxysilane (I), sodiumoxydimethylethoxysilane (II), and its trimethylsilyl derivative, 1,1,1,3,3-pentamethyl-3-ethoxydisiloxane (III).

To avoid any additional problems and to prepare the exact copies of sodium-containing products, reaction (8) was carried out from –30 to –40°C in non-

polar organic solvents (*n*-alkanes, aromatic hydrocarbons). Such conditions allow one to prevent any exchange interaction between alkoxy and chlorosilyl groups (Scheme 9) and, hence, preclude the formation of any by-products, which are not typical of the main reaction (Scheme 9).



In addition to instrumental control, trimethylsilylation reaction presents the simplest model for studying the applicability of MSOAS as reagents with “chemically independent” functional groups. The obtained data appeared to be very helpful for selecting the optimum conditions for the synthesis of organosiloxanes with far more complex structures.

Preliminary studies showed that the reaction of NaOH with organoalkoxysilanes is accompanied by the formation of the corresponding alcohol and sodium-containing products. Under certain conditions, monosodiumoxyorganoalkoxysilanes (MSOAS) dominate. Along with this, analysis of the resulting trimethylsilyl derivatives as well as salt-free volatile liquid compounds makes it possible to reveal several secondary concurrent processes. It was also found that the intensity and conversion of the above processes are controlled by external conditions (temperature, feed ratio between starting reagents, solvent, and duration of reaction) as well as the molecular structure of initial organoalkoxysilanes (number and type of alkoxy groups and organic radicals at silicon atoms).

Information listed in Table 2 shows the composition and structure of by-products, which lead to several conclusions concerning the mechanism of their formation. This character of by-products containing more than one silicon atom unequivocally demonstrates the occurrence of condensation processes in the systems. It seems reasonable to speculate that such processes are related to the presence of mobile hydrogen atoms in the composition of reactive alcohol in the reaction volume. In this case, the primary event giving rise to the whole cascade of secondary processes is likely to be related to the transformation of alcohol into silanol hydroxyl according to Schemes 10–12.

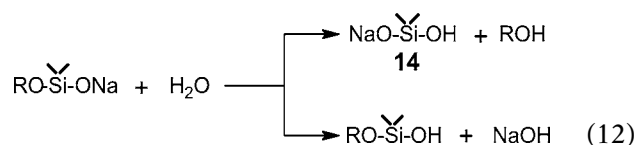
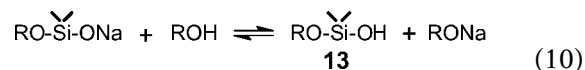


TABLE 1 Properties of Trimethylsilyl Derivatives of MSOAS

No.	Trimethylsilyl Derivative	Starting Reagent	bp (°C)	$n_D^{20}$	Elemental Composition		
					Si	C	H
1	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{Me} \end{array}$	132	1.3825			
2	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	154	1.3865			
3	$\begin{array}{c} \text{OEt} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	$\begin{array}{c} \text{OEt} \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	177	1.3867			
4	$\begin{array}{c} \text{CH}=\text{CH}_2 \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{CH}=\text{CH}_2 \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{Me} \end{array}$	146	1.4037	$\frac{27.65}{27.27}$	$\frac{47.28}{47.01}$	$\frac{9.92}{9.86}$
5	$\begin{array}{c} \text{CH}=\text{CH}_2 \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	$\begin{array}{c} \text{CH}=\text{CH}_2 \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	175	1.4022			
6	$\begin{array}{c} \text{Ph} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	$\begin{array}{c} \text{Ph} \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{OEt} \end{array}$	247	1.4746	$\frac{19.58}{19.74}$	$\frac{54.51}{54.58}$	$\frac{8.42}{8.50}$
7	$\begin{array}{c} \text{Ph} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OEt} \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Ph} \\   \\ \text{NaO}-\text{Si}-\text{OEt} \\   \\ \text{Me} \end{array}$	230	1.4721	$\frac{21.83}{22.07}$	$\frac{56.39}{56.34}$	$\frac{56.39}{56.64}$
8	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OMe} \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OMe} \\   \\ \text{Me} \end{array}$	118	1.3805			
9	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OMe} \\   \\ \text{OMe} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OMe} \\   \\ \text{OMe} \end{array}$	134	1.3841	$\frac{28.92}{28.89}$	$\frac{36.87}{37.08}$	$\frac{9.37}{9.33}$
10	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OBu-}n \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OBu-}n \\   \\ \text{Me} \end{array}$	172	1.3938			
11	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OPr-}n \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OPr-}n \\   \\ \text{Me} \end{array}$	151	1.3891			
12	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OPr-i} \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OPr-i} \\   \\ \text{Me} \end{array}$	145	1.3889	$\frac{27.43}{27.21}$	$\frac{46.39}{46.54}$	$\frac{10.68}{10.74}$
13	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OPr-i} \\   \\ \text{OPr-i} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{OPr-i} \\   \\ \text{OPr-i} \end{array}$	174	1.3911	$\frac{22.27}{22.42}$	$\frac{47.75}{47.95}$	$\frac{10.40}{10.46}$
14	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{OSiMe}_3 \\   \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{ONa} \\   \\ \text{Me} \end{array}$	153	1.3847			
15	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{O}-\text{SiMe}_3 \\   \\ \text{Me} \end{array} \quad 2$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{O}-\text{Na} \\   \\ \text{Me} \end{array} \quad 2$	194	1.3896			
16	$\begin{array}{c} \text{Me} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{O}-\text{SiMe}_3 \\   \\ \text{Me} \end{array} \quad 3$	$\begin{array}{c} \text{Me} \\   \\ \text{NaO}-\text{Si}-\text{O}-\text{Na} \\   \\ \text{Me} \end{array} \quad 3$	231	1.3973			
17	$\begin{array}{c} \text{OEt} \\   \\ \text{Me}_3\text{SiO}-\text{Si}-\text{O}-\text{SiMe}_3 \\   \\ \text{OEt} \end{array} \quad 2$	$\begin{array}{c} \text{OEt} \\   \\ \text{NaO}-\text{Si}-\text{O}-\text{Na} \\   \\ \text{OEt} \end{array} \quad 2$	245	1.3910	$\frac{25.60}{26.07}$	$\frac{39.98}{39.04}$	$\frac{8.87}{8.69}$

Continued

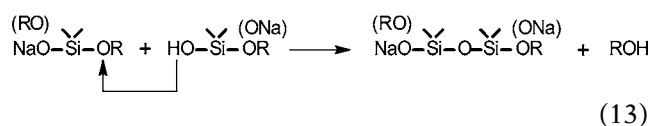
TABLE 1 Continued

No.	Trimethylsilyl Derivative	Starting Reagent	bp (°C)	n <sub>D</sub> <sup>20</sup>	Elemental Composition		
					Si	C	H
18	$\text{Me}_3\text{SiO}-\underset{\text{OSiEt}_3}{\overset{\text{Me}}{\text{Si}}}-\text{OSiEt}_3$	$\text{NaOSi}\underset{\text{OSiEt}_3}{\overset{\text{Me}}{\text{O}}}$	150/10	1.4271	28.23	48.44	10.26
					28.45	48.67	10.72
19	$\text{Me}_3\text{SiO}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{OSiMe}_3$	$\text{NaO}-\underset{\text{Ph}}{\overset{\text{Ph}}{\text{Si}}}-\text{ONa}$	135/6	1.4940			
20	$\text{Me}_3\text{SiO}-\left[ \underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O} \right]_2-\text{Et}$	$\text{NaO}-\left[ \underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O} \right]_2-\text{Et}$	168	1.3841	31.48	40.35	9.80
					31.60	40.56	9.83

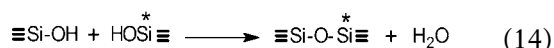
Experimental and calculated values are given in nominator and denominator, respectively. Compound numbers 4, 6, 7, 9, 12, 13, 17, 18, and 20 were synthesized for the first time.

Initiation according to Scheme 10 should dominate at the final stages of the main reaction when initial sodium hydroxide is virtually absent. In the opposite case, at the early stages and with excessive amounts of NaOH, processes (11) and (12) seem to be more probable.

Silanol intermediates **13** and **14** may be involved in further condensation reactions with initial alkoxysilane and formed sodium oxyorganoalkoxysilane, which lead to the formation of siloxane fragments ( $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ ) and regeneration of alcohol as exhausted at stages (10) and (11) (Scheme 13).



One may hardly exclude homocondensation between silanol intermediates (Scheme 14).



Due to the occurrence of thermodynamically favorable condensation processes, silanol intermediates are permanently generated as a result of equilibria (10) and (11). Therefore, repeated exchange (Schemes 10–12) and condensation (Schemes 13 and 14) processes are likely to produce the above-mentioned family of by-products (Table 2). Hence, timescale factor or, namely, duration of contacts between reaction components and alcohol should favor the accumulation of secondary by-products

TABLE 2 Qualitative Composition of Byproducts in Main Reaction

No.	Starting Reagents	Main Product	Byproducts
1	$\text{R}_3\text{SiOR}' + \text{NaOH}$	$\text{R}_3\text{SiONa}$	$\text{R}_3\text{Si}-\text{O}-\text{SiR}'_3, \text{RONa}$
2	$\begin{array}{c} \text{R}^1 \\   \\ \text{R}'\text{O}-\text{Si}-\text{OR}' \\   \\ \text{R}^2 \end{array} + \text{NaOH}$	$\begin{array}{c} \text{R}^1 \\   \\ \text{NaO}-\text{Si}-\text{OR}' \\   \\ \text{R}^2 \end{array}$	$\begin{array}{c} \text{R}^1 \quad \text{R}^1 \\   \quad   \\ \text{R}'\text{O}-\text{Si}-\text{O}-\text{Si}-\text{OR}' \\   \quad   \\ \text{R}^2 \quad \text{R}^2 \end{array}, \text{NaO} \left[ \begin{array}{c} \text{R}^1 \\   \\ \text{Si}-\text{O} \\   \\ \text{R}^2 \end{array} \right]_n \text{Na}$ <p style="text-align: right;"><math>n=2, 3</math></p>
3	$\text{RSi}(\text{OR}')_3 + \text{NaOH}$	$\begin{array}{c} \text{R} \\   \\ \text{NaO}-\text{Si}-\text{OR}' \\   \\ \text{OR}' \end{array}$	$\begin{array}{c} \text{R} \\   \\ \text{R}'\text{O}-\left[ \text{Si}-\text{O} \right]_n \\   \\ \text{ONa} \end{array}$ <p style="text-align: center;"><math>n \geq 2</math></p>
4	$\text{Si}(\text{OR}')_4 + \text{NaOH}$	$\begin{array}{c} \text{OR}' \\   \\ \text{NaO}-\text{Si}-\text{OR}' \\   \\ \text{OR}' \end{array}$	$\begin{array}{c} \text{OR}' \\   \\ \text{R}'\text{O}-\left[ \text{Si}-\text{O} \right]_n \\   \\ \text{ONa} \end{array}$ <p style="text-align: center;"><math>n \geq 2</math></p>

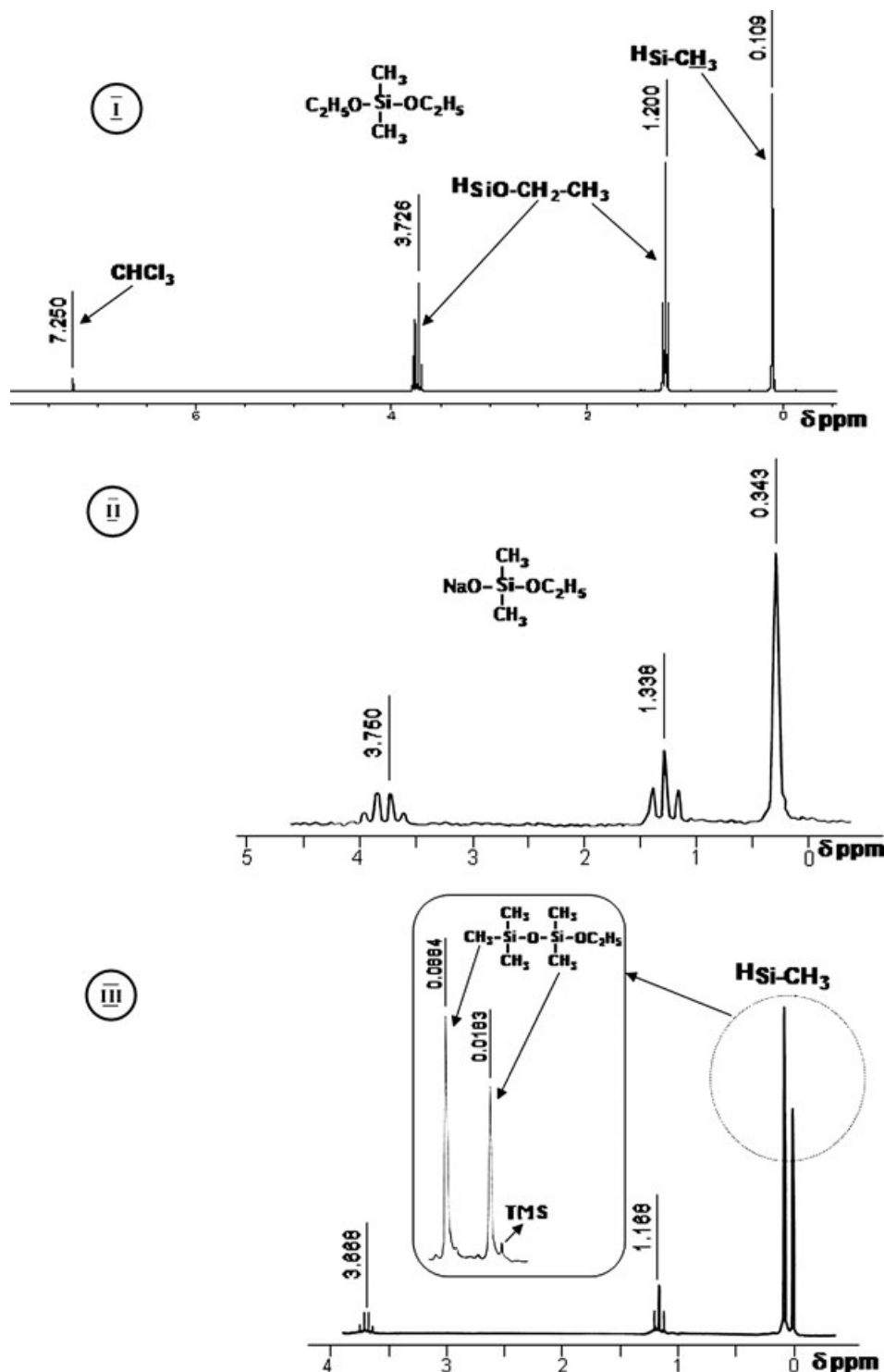


FIGURE 5  $^1\text{H}$  NMR spectra of initial dimethyldiethoxysilane (I), sodiumoxydimethylethoxysilane (II) and its trimethylsilylic derivative: 1,1,1,3,3-pentamethyl and 3-ethoxydisiloxanes (III).

in the system and would inevitably exert its negative effect on the purity of the resulting MSOAS.

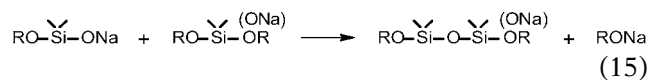
It is also apparent that the rupture of siloxane bonds in intermediate products under the presence

of sodium alcoholates and silanolates also affects the final state of the system.

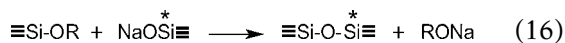
The role of alcohol in the reaction volume is reduced to the initiation of condensation processes. Formally, this conclusion can be drawn by



combining, Schemes 10 (initiation) and 13 (condensation). General Scheme 15 does not involve alcohol:



This reasoning also suggests an alternative alcohol-free mechanism of secondary processes, which includes the direct condensation of alkoxy groups with sodium silanolate fragments according to Scheme 16:



The data presented in the literature either directly [65] or indirectly [66] attest to the possible occurrence of such reactions.

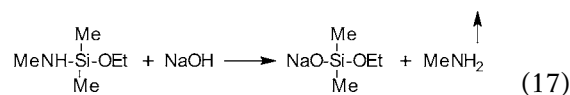
To establish the true nature of secondary processes and to find out the preventive measures for suppressing the above reactions during the synthesis of MSOAS, several model experiments have been carried out; the related results are summarized in Table 3.

This evidence primarily supports the first scenario among the proposed mechanisms of secondary processes, namely, the initiation by alcohols. Indeed, long-term heating of homogeneous solutions of sodium oxytriethoxysilane in perfectly dried organic solvents (toluene and *n*-nonane) and under dry argon at 100–150°C does not lead to any changes in the system (Table 3, nos. 1 and 2). This result was obtained when sodium oxydimethylethoxysilane was heated at 100°C in the medium of dimethyldiethoxysilane (Table 3, no. 3). Similar experiments were performed in the presence of ethanol or water. As was shown, such reactions entail the formation of the above-mentioned products, and their content and conversion of secondary processes are directly proportional to the temperature and duration of contact between reagents. This dependence seems to be quite reasonable because, according to the advanced mechanism of secondary processes, the limiting stage is the stage of initiation. This conclusion is related to the fact that equilibrium (19) is markedly shifted to the left because alkoxy silanols **13** are stronger acids than alcohols.

Due to the negative charge redistribution of the ionic sodium silanolate group in molecules of sodium oxyorganoalkoxysilanes onto neighboring alkoxy groups, sensitivity of the latter groups toward proton attacks from hydroxyl-containing reagents increases. This is the reason why silanol intermediates **13** should primarily react with the formed sodium oxyorganoalkoxysilanes rather than with initial organoalkoxysilanes (Scheme 13). This specific character of chemical interactions in the systems un-

der study has a strong effect on the structure of by-products containing –ONa groups (97%) (except for the reaction between trimethylmethoxysilane with NaOH). This fact can be invoked to explain why, in model experiments, MSOAS (Table 3, nos. 9–11) show high reactivity toward hydroxyl-containing reagents under rather mild conditions.

Taking into account a negative role of alcohol formed in the course of the main reaction, it seems interesting to conduct the synthesis of MSOAS under the conditions of its active binding. In this connection, the reaction of (*N*-methylamino)dimethylethoxysilane with sodium hydroxide was carried out (Table 3, no. 12). At a feed ratio of 1:1, the yield of sodiumoxydimethylethoxysilane was equal to ~80% (Scheme 17).



The specific feature of this reaction (Scheme 17) concerns the fact that the final products do not contain any compounds with hydroxyl groups. Released gaseous methylamine containing hydrogen atoms earlier involved in sodium hydroxide is absolutely indifferent toward all compounds in the system. This fact can be invoked to explain high yields and purity of the target product (yield decreases down to 80% as compared with theoretical level, and this behavior is related to the fact that not all NaOH is involved in the reaction under stoichiometric ratio between components).

Interaction of dimethyldiethoxysilane with NaOH under the same ratio between components (1:1) entails the formation of a complex mixture of resulting products, and the fraction of sodiumoxydimethylethoxysilane is equal to ~40% (Table 3, no. 13). The above evidence vividly illustrates the negative effect of ethanol on the systems containing sodium oxyorganoalkoxysilanes.

Analysis of model experiments allows one to reveal the general features behind the mechanism of seemingly trivial but vague reaction of organoalkoxysilanes with sodium hydroxide (Scheme 3), and this understanding is crucial for solving the problems stated in this work as well as general scientific aspects. One may expect that this reaction involves more than one stage. To gain a deeper insight into this reaction, it seems reasonable to consider the interaction between (*N*-methylamino)dimethylethoxysilane with sodium hydroxide (Scheme 17). This evidence suggests that, at early stages of the reaction, nucleophilic substitution of this ethoxyl group at silicon atoms by hydroxyl groups in the molecules

TABLE 3 Principal Results of Model Experiments

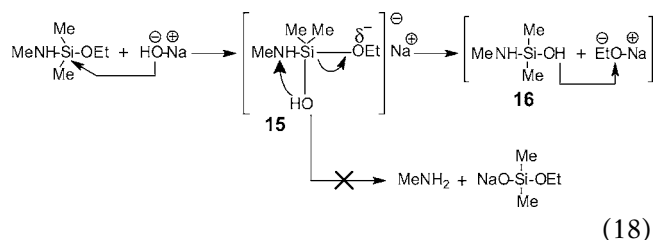
No.	Scheme of Reactions. Conditions	Results of Interaction. The Main Products.
1	$\text{NaOSi}(\text{OEt})_3 \xrightarrow[\text{t} = 100\text{--}110^\circ\text{C}, 8 \text{ h, argon}]{\text{Dry toluene, homogenous medium}}$	No changes in system were detected
2	$\text{NaOSi}(\text{OEt})_3 \xrightarrow[\text{t} = 150^\circ\text{C}, 12 \text{ h, argon}]{\text{Dry } n\text{-nonane, homogenous medium}}$	No changes in system were detected
3	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} + \text{Me}_2\text{Si}(\text{OEt})_2 \xrightarrow[\text{t} = 100^\circ\text{C}, 0.6 \text{ h, argon}]{\text{Homogenous medium, excess}}$	No changes in system were detected
4	$\text{NaOSi}(\text{OEt})_3 \xrightarrow[\text{t} \rightarrow 80\text{--}95^\circ\text{C}, 2.5 \text{ h}]{\text{Wet toluene (0.1\% H}_2\text{O)}}$	precipitate of $\text{EtO}-\left[\underset{\text{ONa}}{\overset{\text{OEt}}{\text{Si}}}-\text{O}-\text{Et}\right]_n$ $n > 2$
5	$\text{NaOSi}(\text{OEt})_3 \xrightarrow[\text{t} = 40\text{--}50^\circ\text{C}, 9 \text{ h}]{n\text{-heptane} + \text{ethanol (5\%)}}$	precipitate of $\text{NaO}-\underset{\text{OEt}}{\overset{\text{OEt}}{\text{Si}}}-\text{O}-\underset{\text{OEt}}{\overset{\text{OEt}}{\text{Si}}}-\text{ONa}$
6	$\text{NaOSi}(\text{OEt})_3 \xrightarrow[\text{t} = 60\text{--}65^\circ\text{C}, 14 \text{ h}]{n\text{-heptane} + \text{ethanol (5\%)}}$	precipitate of $\text{EtO}-\left[\underset{\text{ONa}}{\overset{\text{OEt}}{\text{Si}}}-\text{O}-\text{Et}\right]_n$ $n \geq 2$ $\frac{n=2}{n>2} = \frac{3}{2}$
7	$2 \text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} + 1 \text{H}_2\text{O} \xrightarrow{\text{Azeotropic drying with toluene}}$	precipitate of $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\text{Na}\right]_n$ $n=1, 2, 3$ $n=2(60\%)$
8	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} \xrightarrow[\text{t} = 90\text{--}95^\circ\text{C}]{n\text{-Heptane} + \text{ethanol (5\%)}}$	precipitate of $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\text{Na}\right]_n$ $n = 2, 3$
9	$1 \text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} + 0.5 \text{CH}_3\text{COOH} \xrightarrow[\text{t} = -50 \rightarrow +25^\circ\text{C}]{\text{toluene}}$	mainly precipitate of $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\text{Na}\right]_3$
10	$1 \text{NaO}-\underset{\text{OR}}{\overset{\text{Me}}{\text{Si}}}-\text{OR} + 2 \text{Et}_3\text{SiOH} \xrightarrow[\text{t} = 20\text{--}25^\circ\text{C}, -\text{ROH}]{\text{Ether}}$	$\text{NaO}-\underset{\text{OSiEt}_3}{\overset{\text{Me}}{\text{Si}}}-\text{OSiEt}_3$ $\text{RO} = \text{OMe}$ (24%), $\text{RO} = \text{OEt}$ (55%)
11	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OMe} + \text{ROH} \xrightarrow[\text{t} = 20\text{--}25^\circ\text{C}, -\text{MeOH}]{} $	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OR}$ $\text{RO} = n\text{-Bu}$ (90%), $\text{RO} = i\text{-Amil}$ (93%)
12	$1 \text{EtO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{NHMe} + 1 \text{NaOH} \xrightarrow[\text{t} = 25\text{--}35^\circ\text{C}, -\text{MeNH}_2]{} $	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ (80%)
13	$1 \text{Me}_2\text{Si}(\text{OEt})_2 + 1 \text{NaOH} \xrightarrow{\text{Azeotropic distillation EtOH with toluene}}$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ (40%); $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\text{Na}\right]_n$ $n = 2, 3$
14	$1 \text{Me}_2\text{Si}(\text{NHMe}_2)_2 + 1 \text{NaOH} \xrightarrow[\text{t} = 120^\circ\text{C}, 10 \text{ h}]{} $	No changes in system were detected
15	$\text{Ph}_2\text{Si}(\text{OH})_2 + t\text{-}i\text{-C}_5\text{H}_{11}\text{ONa} \xrightarrow[\text{t} = -10^\circ\text{C}, -t\text{-}i\text{-C}_5\text{H}_{11}\text{OH}]{} $	$\text{Ph}_2\text{Si}(\text{ONa})_2$ (98%)
16	$3 \text{Me}_3\text{SiOMe} + 1 \text{NaOH} \xrightarrow[\text{t} = 0 \rightarrow 30^\circ\text{C}]{} $	$\text{Me}_3\text{SiOSiMe}_3 + \text{MeONa} + \text{Me}_3\text{SiONa} + \text{MeOH}$ (95–97%) (3–5%)

Continued

TABLE 3 Continued

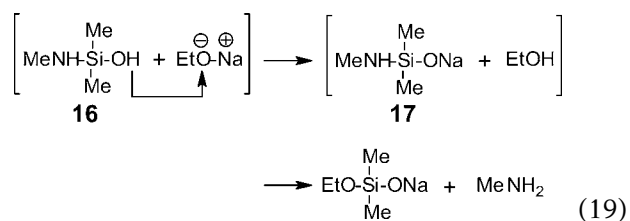
No.	Scheme of Reactions. Conditions	Results of Interaction. The Main Products.
17	$3\text{Si}(\text{OEt})_4 + \text{NaOSi}(\text{Me})_2\text{OEt} \xrightarrow[\text{t} = 70^\circ\text{C}, 100 \text{ tor}]{\text{distillation of Me}_2\text{Si}(\text{OEt})_2}$	$\text{NaOSi}(\text{OEt})_3$ (93%)
18	$3\text{Si}(\text{OEt})_4 + 1\text{NaOH} \xrightarrow[\text{t} = -10 \rightarrow 25^\circ\text{C}]{} \longrightarrow$	$\text{NaOSi}(\text{OEt})_3 + \text{NaO}-\underset{\text{OEt}}{\overset{\text{OEt}}{\text{Si}}}-\text{O}-\underset{\text{OEt}}{\overset{\text{OEt}}{\text{Si}}}-\text{ONa}$ (86%)
19	$3\text{Me}_2\text{Si}(\text{OEt})_2 + 1\text{NaOH} \xrightarrow[\text{t} = 15 \rightarrow 30^\circ\text{C}]{} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ (95%)
20	$5\text{Me}_2\text{Si}(\text{OMe})_2 + 1\text{NaOH} \xrightarrow[\text{t} = 10 \rightarrow 40^\circ\text{C}]{} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OMe}$ (10%) + $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ $n = 2, 3$
21	$1\text{Me}_2\text{Si}(\text{OMe})_2 + 1\text{NaOH} \xrightarrow[\text{t} = 25-30^\circ\text{C}]{\text{ether}} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OMe}$ (80%)
22	$1\text{Me}_3\text{Si}(\text{OMe})_3 + 1\text{NaOH} \xrightarrow[\text{t} = 25-30^\circ\text{C}]{\text{dioxane}} \longrightarrow$	$\text{NaO}-\underset{\text{OMe}}{\overset{\text{Me}}{\text{Si}}}-\text{OMe}$ (79%)
23	$1\text{Me}_2\text{Si}(\text{OEt})_2 + 2\text{NaOH} \xrightarrow{\text{Azeotropic distillation EtOH with toluene}} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ ; $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ $n=2$ (65%), $n=3$ (20%) (5%)
24	$1\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} + 1\text{NaOH} \xrightarrow{\text{Azeotropic distillation EtOH with toluene}} \longrightarrow$	$\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ $n=2, 3$ ; $n=2$ (65%)
25	$1\text{Si}(\text{OEt})_4 + 2\text{NaOH} \longrightarrow$	precipitate of $\text{EtO}-\left[\underset{\text{ONa}}{\overset{\text{OEt}}{\text{Si}}}-\text{O}\right]_n-\text{Et}$ $n \geq 2$
26	$1(\text{Me}_2\text{SiO})_4 + 2\text{MeONa} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OMe}$ ; $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ $n = 2, 3$ (35%)
27	$1(\text{Me}_2\text{SiO})_4 + 1\text{EtONa} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ ; $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ ; $\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ (50%) (5%)
28	$1\text{EtO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} + 1\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} \xrightarrow[\text{- Me}_2\text{Si}(\text{OEt})_2]{\text{t} = 60^\circ\text{C}} \longrightarrow$	$\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ ; $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ ; $\text{NaO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt}$ (25%) $n=2, 3$ (50%) (7%)
29	$1\text{EtO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OEt} + 1\text{NaOH} \xrightarrow[\text{t} = 15 \rightarrow 30^\circ\text{C}]{} \longrightarrow$	$\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_3-\text{Na}$
30	$1.25 \text{Me}_3\text{SiO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{OMe} + 1\text{NaOH} \xrightarrow[\text{t} = 40^\circ\text{C}]{\text{toluene}} \longrightarrow$	$\text{Me}_3\text{SiO}-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{ONa}$ ; $\text{Me}_3\text{SiONa}$ ; $\text{NaO}-\left[\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{O}\right]_n-\text{Na}$ $n=2, 3$ (73%) (7%) (20%)

of methylaminodimethylethoxysilane takes place (Scheme 18) rather than intramolecular transfer of  $\text{OH}^-$  proton to a nitrogen atom in the negatively charged pentacoordinated transition complex (**15**):



In this respect, the absence of any interaction between bis-(dimethylamino)dimethylsilane and sodium hydroxide even after heating for 10 h at  $120^\circ\text{C}$  is to be expected because the leaving group of dimethylamine anion ( $\text{Me}_2\text{N}^-$ ) is a far more stronger nucleophilic agent than the incoming hydroxyl ion ( $\text{HO}^-$ ) (Table 3, no. 14). At the same time, reactivities of ethoxyl ( $\text{EtO}^-$ ) and hydroxyl anions are virtually the same, and the reaction may proceed according to Scheme 18.

It is also evident that the elimination of ethoxyl anion from the transition complex (**15**) is the limiting stage of the whole process. At later stages, the fast interaction of the formed silanol intermediates (**16**) and sodium ethylate is accompanied by the formation of rather reactive sodiumoxydimethylaminosilane (**17**) and ethanol, which in turn quickly react with each other, as the whole system approaches its final state (Scheme 19):

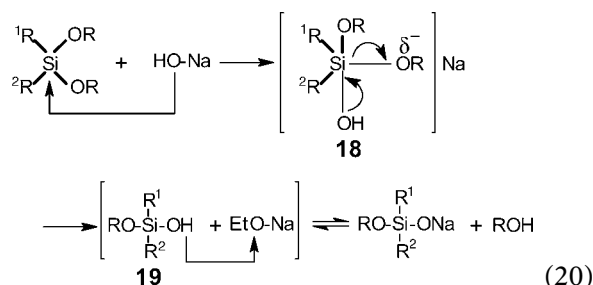


Perfect separation of intermediate compounds shown in Schemes 18 and 19 in square brackets is conditional. It seems probable that the system virtually changes its state, and concurrent processes take place in reaction microvolumes in the vicinity of the nearest silicon atom.

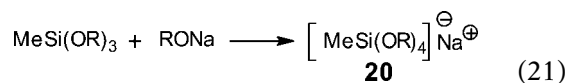
It is necessary to mention that substitution of ethoxyl group (first stage) appears to be the key event for the whole reaction because, in this case, the negatively charged hydroxyl group is transformed into the hydroxyl group of the silanol intermediate (**16**), which shows well-pronounced acidic properties. This process is not involved in General Scheme 3, which is usually offered in the literature.

The above results allow one to conclude that interaction of organoalkoxysilanes with sodium

hydroxide presents not a single-stage but a multi-stage process, whose first stage involves substitution of the ethoxyl group at a silicon atom by a hydroxyl group (Scheme 20).



As was mentioned earlier, the reaction of alkoxy silanes with  $\text{NaOH}$  is accompanied by a well-pronounced exothermic effect. In this connection, the question concerning the driving force of reaction (20) arises (the stage with heat release). As was shown, the thermal effect of the interaction of sodium methylate and ethylate with methyltrimethoxysilane and triethoxysilanes is equal to zero. According to known literature data [67], this interaction entails the formation of pentacoordinated complex compound (**20**) (Scheme 21).

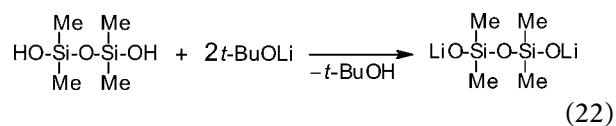


Taking into account the above evidence, one can conclude that the formation of intermediate complex **18** (Scheme 20) also proceeds without any marked thermal effect. Further elimination of alkoxy group requires a certain energy input because the  $\text{EtO}^-$  group is a somewhat stronger nucleophile than the entering  $\text{HO}^-$  group. Finally, when the proposed scheme of this process (Scheme 20) is valid, the observed thermal effect should be controlled by the final stage, which involves the reaction of silanol intermediate **19** with sodium alkoxide.

According to general theoretical speculations, such process is energetically favorable in most cases because organosilanols are stronger acids than alcohols.

Analysis of the model reaction of diphenylsilanediol (prototype of silanol intermediate) with sodium *t*-isoamylate (Table 3, no. 15) shows that this reaction is extensive even at  $-10^\circ\text{C}$  and leads to an almost quantitative formation of bisodium oxydiphenylsilane. Similar results were also reported in the literature. For example, 1,3-bilithium oxytetramethylidisiloxane with a yield of 98% was obtained by the reaction of tetramethyldisiloxanediol with lithium

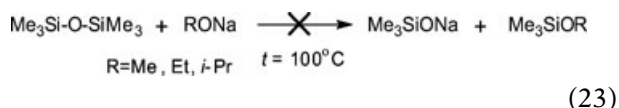
*t*-butylate [68] (Scheme 22).



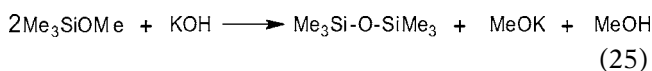
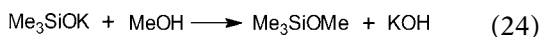
Therefore, the above data suggests that Scheme 20 fairly describes the process leading to the formation of MSOAS from organoalkoxysilanes and sodium hydroxide.

The above analysis shows that silanol intermediates **19** appear in the reaction volume even at the early reaction stages rather than during exchange processes. In this case, when some other energetically favorable processes of the above intermediates can take place, the composition of final products may be appreciably different. In this respect, interaction of trimethylmethoxysilane with NaOH (limiting case) presents a rather interesting case (Table 3, no. 16). The main silicone-containing product of this reaction is hexamethyldisiloxane (95–97%); content of sodium trimethylsilanolate does not exceed 3–5%. This reaction proceeds rather vigorously and completes within 1.5–2 min after mixing the reagents. One may assume that the formation of hexamethyldisiloxane takes place immediately after the stage of nucleophilic substitution of methoxyl by a hydroxyl group during homocondensation of the released trimethylsilanol or during its condensation with excessive trimethylmethoxysilane. In this case, sodium-containing components serve as catalysts. Therefore, to provide unequivocal identification of the formed compounds, sodium-containing reaction products were treated not with trimethylchlorosilane but with triethylchlorosilane or dimethyldichlorosilane.

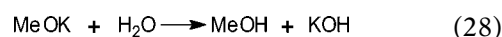
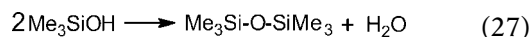
Hexamethyldisiloxane is stable relative to the components of the system under study, and its formation is likely to be energetically more favorable as compared with other possible versions. All attempts to break down the siloxane bond in hexamethyldisiloxane under the action of sodium methylate, ethylate, and isopropylate at 100°C failed (Scheme 23):



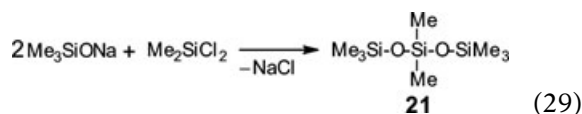
According to the <sup>1</sup>H NMR spectroscopy data in a published report [69], interaction of potassium trimethylsilanolate with methanol can be presented as follows:



In contrast to Scheme 24, reliability of Scheme 25 is supported beyond any doubt. The most feasible route of events taking place in this scheme is as follows (Schemes 26–28):



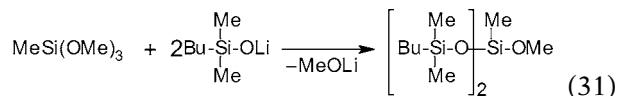
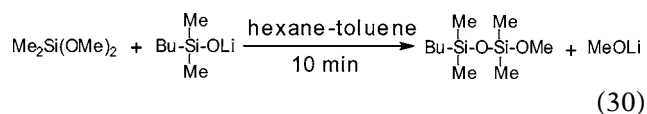
The composition of the products resulting from the reaction between trimethylalkoxysilanes with sodium hydroxide is markedly controlled by the nature of alkoxy group at a silicon atom. As opposed to trimethylmethoxysilane, trimethylethoxysilane interacts with NaOH only upon heating at 70°C in the presence of pyridine. When final products are treated with dimethyldichlorosilane, the yield of octamethyltrisiloxane (**21**) is equal to 48% (Scheme 29). This fact suggests that, at the first stage of the reaction, sodium trimethylsilanolate with the same or higher yield is formed.



This evidence shows that sodium trimethylsilanolate and hexamethyldisiloxane are formed at an equal probability due to a low activity of trimethylethoxysilane in its condensation reaction with trimethylsilanol.

Trimethyl isopropoxysilane and sodium hydroxide do not interact with each other even after boiling for 4 h (*T* ~ 90°C).

Analysis of model reactions with trimethylalkoxysilanes also provides valuable information for gaining a deeper insight into the nature of secondary processes, which accompany the formation of MSOAS. Furthermore, chemical behavior of organosilanes containing three alkyl substituents at the silicon atom appears to be very specific. For example, lithium butyldimethylsilanolate is known to interact with organomethoxysilanes (but not with trimethylmethoxysilane) at room temperature; as a result of this reaction, lithium methylate is obtained, and ≡Si–O–Si≡ group is formed (Schemes 30 and 31) [65].



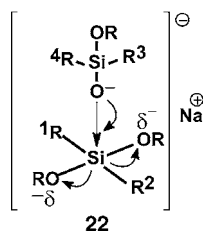
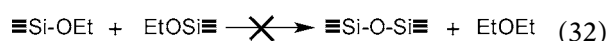


FIGURE 6 Pentacoordinated complex of organoalkoxysilane with MSOAS.

Such reactions are not typical of the systems containing sodium oxyorganoalkoxysilanes, and this observation is proved by the results of model experiments (Table 3, nos. 1–3). This fact also suggests that “ether mechanism” (Scheme 32) of secondary processes in the systems under study does not take place, at least, at temperatures below  $\sim 150^\circ\text{C}$ . In all three above-mentioned experiments, no diethyl ether is formed.



To complete the pattern of chemical reactions in the system under study, it seems necessary to consider the interaction of the formed MSOAS with initial organoalkoxysilanes and to assess its contribution to the final result. According to the literature data [60,67], MSOAS are known to be rather strong  $-\text{O}^-$  nucleophiles, and negative charge in their molecules is primarily localized at the oxygen atom in sodium silanolate group:  $\equiv\text{Si}-\overset{\ominus}{\text{O}}\text{Na}$ ; hence, they should interact with organoalkoxysilanes and form pentacoordinated complex compound (**22**) (Fig. 6):

The formation of this complex was experimentally observed for 30% solution of sodiumoxydimethylethoxysilane in dimethyldiethoxysilane; its cooling down to  $-45^\circ\text{C}$  leads to the precipitation of colorless low-melting crystals ( $T_m \sim -5^\circ\text{C}$ ) with the following composition:  $\text{NaOSi}(\text{Me})_2\text{OEt} \cdot (\text{Me})_2\text{Si}(\text{OEt})_2$ . However, chemical stability of this compound is low; all dimethyldiethoxysilane, including excessive amounts, can be easily and fully removed from the system at  $25 \rightarrow 40^\circ\text{C}$  at a reduced pressure of 1 Torr. Taking into account this fact, all earlier published data [60,61] seem to be unsubstantiated. Let us mention that the interaction of sodium hydroxide with threefold excess of tetraethoxysilane immediately leads to the formation of a stable adduct with the following composition:  $(\text{NaO})_2\text{Si}(\text{OEt})_2 \cdot x\text{Si}(\text{OEt})_4$ ; its separation into individual components takes place only upon heating to  $155\text{--}230^\circ\text{C}$  at a reduced pressure of 20 Torr. The results of model experiments (Table 3, no. 18) unequivocally demonstrate that the main

product of this reaction (at the same feed ratio) is monosodiumoxytriethoxysilane (86% yield). The composition of a hypothetical adduct at  $x=1$  coincides with its composition. Therefore, analysis solely based on the data concerning the composition of the formed adduct leads to invalid conclusions concerning its structure. Furthermore, monosodiumoxytriethoxysilane at  $\sim 190^\circ\text{C}$  degrades to release tetraethoxysilane; this may be a reason behind the ill-judged conclusion concerning the degradation of the above-mentioned adduct. In this case, salt residue presents a heavily condensed polymer rather than disodium oxydiethoxysilane  $[(\text{NaO})_2\text{Si}(\text{OEt})_2]$ , and this reasoning is also proved in [57].

The formation of complex compound **22** during the main reaction course is likely to play its positive role for inhibition of the above secondary processes. The formation of the complex compound during the course of the main reaction assists the inhibition of the above secondary processes and, thus provides a higher purity of target products. Within this compound, delocalization of negative charge of sodium silanolate over several centers (oxygen atoms of alkoxy groups) takes place. This process is naturally accompanied by the decrease in the density of negative charge and nucleophilicity of the complex as compared with pure MSOAS. Thus, its susceptibility to proton attacks from reactive alcohol and silanol intermediates is reduced. This tendency is clearly observed during the synthesis of sodium oxyorganoethoxysilanes when, by increasing the ratio initial reagents (ethoxysilane : NaOH) from 1:1 to 5:1, the yield of target MSOAS markedly increases from 40 to 95%, whereas the content of byproducts decreases. This fact can hardly be explained by a trivial decrease in the concentrations of interacting components in the system due to an increased content of excessive ethoxysilanes. For example, the reaction between dimethyldiethoxysilane and NaOH (1:1) in toluene or dioxane at dilutions comparable to threefold or fivefold excess leads to the formation of sodium oxydimethylethoxysilane with a yield below 40%. However, the formation of complex **22** during the reaction with the excess of ethoxysilane supports the above observations.

Therefore, the formation of complex **22** favors an efficient inhibition of secondary processes, and this complex by itself is not stable to prevent the formation of pure MSOAS.

### Optimization of MSOAS Synthesis Conditions

The results of model experiments provide valuable information for finding optimal conditions in

the reactions of organoalkoxysilane with sodium hydroxide and the preparation of pure MSOAS with maximum yields. Initially, this procedure has been applied for the synthesis of sodium organoethoxysilanes as main reagents for synthetic purposes.

#### Interaction of Organoethoxysilanes with NaOH

**Initial feed ratio.** As was theoretically known, at least, 1 mol of organoethoxysilane is involved in complex **22** and 1 mol is spared to form target MSOAS; therefore, theoretical ratio between organoethoxy silane and NaOH should be equal to 2:1. According to the experimental data, optimal ratio is 3:1, which provides high reaction rates (reaction duration is 3–5 min) and results in a minimum duration of contacts between MSOAS and reactive alcohol.

**Reaction temperature.** Optimal (minimum) reaction temperature depends on the structure of organoethoxysilane and ranges from –30 to –25°C

for Si(OEt)<sub>4</sub> to +30–35°C for PhSi(OEt)<sub>3</sub> and Me(Ph)Si(OEt)<sub>2</sub>. This temperature is experimentally estimated as the temperature at which intensive heat release is observed in the organoethoxysilane–NaOH system. Indeed, this method seems to be rather primitive and not quite reliable for the estimation of optimum reaction temperature; however, its practical value is beyond any doubt.

Removal of reactive alcohol and excessive organoalkoxysilane from the reaction mixture in a 1-Torr vacuum at 20–50°C (depending on the type of initial organoalkoxysilane) leads to the formation of target MSOAS with a yield of ~96%. More detailed information concerning optimization of this reaction will be presented in the section *Experimental* (Table 4).

**Interaction of Organopropoxysilanes, Isopropoxysilanes, and *n*-Butoxysilanes with NaOH.** The above data concerning the optimization of synthesis of monosodiumoxyorganoethoxysilanes and the

**TABLE 4** Conditions of the Reaction between Organoalkoxysilanes and Sodium Hydroxide

Main Reaction							Trimethylsilylation Reaction			
Initial Alcoxysilane			NaOH (g/mol)	Molar Ratio of Reagents	Solvent	<i>t</i> <sub>mix</sub> (°C)	<i>t</i> <sub>dist</sub> (°C/1)	Trimethylsilylic Derivative		
No.	Formula	g/mol						Solvent	Number in Table 1	Yield (g/%)
1.1	Me <sub>2</sub> Si(OEt) <sub>2</sub>	14.8/0.1	4.0/0.1	1:1	Toluene dioxane	25–30	20–25/20	<i>n</i> -Pentane	1	7.7/40
1.2		29.6/0.2	4.0/0.1	2:1	Toluene dioxane	25–30	20–35/20	<i>n</i> -Pentane	1	12.5/65
1.3		44.4/0.3	4.0/0.1	3:1	–	15→25	25–40	<i>n</i> -Pentane	1	18.0/94
1.4		74.0/0.5	4.0/0.1	5:1	–	15→25	25–40	<i>n</i> -Pentane	1	18.03/94
2.1	MeSi(OEt) <sub>3</sub>	53.5/0.3	4.0/0.1	3:1	–	0→25	30–45	<i>n</i> -Hexane	2	21.3/96
2.2		89.2/0.5	4.0/0.1	5:1	–	0→25	30–45	<i>n</i> -Hexane	2	21.34/96
3	Si(OEt) <sub>4</sub>	62.5/0.3	4.0/0.1	3:1	–	–15→25	35–50	<i>n</i> -Heptane	3	21.7/86
4	Me(Vi)Si(OEt) <sub>2</sub>	48.1/0.3	4.0/0.1	3:1	–	20–30	30–40	<i>n</i> -Pentane	4	19.0/93
5	ViSi(OEt) <sub>3</sub>	57.1/0.3	4.0/0.1	3:1	–	5→25	35–45	<i>n</i> -Hexane	5	22.2/95
6	PhSi(OEt) <sub>3</sub>	72.1/0.3	4.0/0.1	3:1	–	30–40	80–100	Toluene	6	27.5/97
7	Ph(Me)Si(OEt) <sub>2</sub>	63.1/0.3	4.0/0.1	3:1	–	30–40	80–100	Toluene	7	24.1/95
8.1	Me <sub>2</sub> Si(OMe) <sub>2</sub>	60.0/0.5	4.0/0.1	5:1	–	10→40	20–30	<i>n</i> -Pentane	8	2.0/10
8.2		12.0/0.1	4.0/0.1	1:1	Ether	10→30		<i>n</i> -Pentane	8	14.2/80
9.1	MeSi(OMe) <sub>3</sub>	41.0/0.3	4.0/0.1	3:1	–	5→25	20–35	<i>n</i> -Pentane	9	14.7/76
9.2		27.2/0.2	8.0/0.2	1:1	Ether	5→25		<i>n</i> -Pentane	9	15.5/40
9.3		27.2/0.2	8.0/0.2	1:1	TGF	5→25		<i>n</i> -Pentane	9	17.1/44
9.4		27.2/0.2	8.0/0.2	1:1	Dioxane	5→30		<i>n</i> -Pentane	9	31.3/80
10	Me <sub>2</sub> Si(OBu- <i>n</i> ) <sub>2</sub>	61.3/0.3	4.0/0.1	3:1	–	65–70	45–60	<i>n</i> -Hexane	10	19.8/90
11	Me <sub>2</sub> Si(OPr- <i>n</i> ) <sub>2</sub>	53.0/0.3	4.0/0.1	3:1	–	60–65	40–55	<i>n</i> -Hexane	11	18.9/91
12	Me <sub>2</sub> Si(OPr- <i>i</i> ) <sub>2</sub>	53.0/0.3	4.0/0.1	3:1	–	65–70	40–50	<i>n</i> -Hexane	12	19.2/93
13	MeSi(OPr- <i>i</i> ) <sub>3</sub>	66.1/0.3	4.0/0.1	3:1	–	60–65	40–55	<i>n</i> -Hexane	13	24.0/96

Items 1, 3, 2.1, 4, 5, 6, 7, 8, 9.4, 11, 12, and 13 correspond to the optimal conditions of synthesis of MSOAS. The resulting reagents were used for the synthesis of various polyalkoxyorganosiloxanes.

interpretation of concurrent processes are also valid for some other compounds such as sodiumoxyorganopropoxysilanes, isopropoxysilanes, and butoxysilanes. As the size of alkoxy radical is increased and as radicals pass from normal to iso radicals in the molecules of organoalkoxysilanes, their activity in the reactions with sodium hydroxide decreases. In turn, temperature corresponding to the onset of reaction and its duration are increased. For example, methyltri-iso-propoxysilane starts to interact with sodium hydroxide only at 60°C; dimethyldibutoxysilane at 65–70°C (for comparison, in the case of methyltriethoxysilane,  $T = \sim 0$  to  $-3^\circ\text{C}$ ). However, secondary processes tend to slow down due to a low activity of the reaction components. The interplay of the above factors leads to the formation of corresponding MSOAS with rather high yields of  $\sim 90$ – $96\%$ .

From the results of model experiments (Table 3, no. 11), it seems expedient to obtain MSOAS with bulky alkoxy groups (from  $-\text{OC}_4$  and higher) from the reaction of realkoxylation of sodiumoxyorganomethoxysilanes with the corresponding alcohols. This process proceeds in one stage without any release of intermediate sodiumoxyorganomethoxysilanes. For example, sodiumoxydimethylbutoxysilane was obtained with a yield of  $\sim 90\%$  due to the interaction of  $(\text{Me})_2\text{Si}(\text{OMe})_2$  with NaOH (1:1) in the medium of butanol at room temperature. In this case, the formed methanol is likely to be deactivated by excessive *n*-butanol due to the formation of hydrogen bonds.

*Interaction of Organomethoxysilanes with NaOH.* Sodiumoxyorganomethoxysilanes occupy a prominent position among various MSOAS. Excessive amounts of organomethoxysilane in the reactions with NaOH do not always exert their positive effect on yields and purity of the formed MSOAS. For example, interaction of  $(\text{Me})_2\text{Si}(\text{OMe})_2$  with NaOH even at a ratio of 5:1 leads to the formation of a complex mixture of resulting products, and the content of target sodiumoxydimethylmethoxysilane does not exceed 10% (Table 3, no. 19). In this case, sodiumoxymethyldimethoxysilane with a yield of  $\sim 76\%$  is formed during the reaction of methyltrimethoxysilane with sodium hydroxide at a ratio of 3:1. In contrast to other organoalkoxysilanes, dimethyldimethoxysilanes and methyltrimethoxy readily react with sodium hydroxide in the medium of linear and cyclic ethers (diethyl ether, tetrahydrofuran, and dioxane) at a ratio of 1:1. In this case, target MSOAS are formed with a yield of  $\sim 80\%$  (Table 3, nos. 21 and 22). The effect of solvent is likely to be related to the solvation of the

formed methanol, stabilization of silanol intermediates, and reduced concentration of reacting compounds; due to high reaction rates, the fraction of secondary by-products is reduced.

*Feasibility of the Formation of Highly Substituted Disodiumoxysilanes and Trisodiumoxysilanes During the Synthesis of MSOAS.* Earlier, the formation of disodiumoxyorganosiloxanes as admixtures containing sodiumoxy groups at different silicon atoms in the course of the main reaction was not given due importance by experts. However, as was reported in several publications, the reaction of organoalkoxy silanes with sodium hydroxide at a ratio of 1:2 [54,55] and even in the presence of excessive alkoxy silane [60,61] can entail the formation of disodiumoxy derivatives  $\text{NaO-Si-ONa}$ , which contain two sodiumoxy groups at one silicon atom. Furthermore, some publications described the formation of trisodium(potassium)oxyorganosilanes [15,16,70]. Certain doubts concerning the reliability of this information arise because such compounds are not identified among all secondary products of the main reaction. According to the proposed mechanism of the interaction of organoalkoxysilanes with sodium hydroxide (Scheme 32), the appearance of such derivatives in the reaction system seems to be highly improbable, at least, under the conditions providing the formation of MSOAS. Indeed, as was expected, the electrophilicity of silicon atom and, hence, its susceptibility to the action of nucleophilic groups such as  $^\ominus\text{OH}$  should be inevitably decreased after the substitution of one alkoxy group in the organoalkoxysilane molecules with negatively charged  $^\ominus\text{ONa}$  group. Therefore, substitution of another alkoxy group with  $^\ominus\text{ONa}$  group in MSOAS requires far more severe conditions. Hence, the appearance of MSOAS in the reaction volume in the course of the interaction between alkoxy silanes and sodium hydroxide serves as a certain barrier for further exhaustive substitution of all alkoxy groups in alkoxy silane molecules  $^\ominus\text{ONa}$  by groups. The above speculations are proved by the results of model experiments (Table 3, nos. 23–25). The reaction of dimethyldiethoxysilane with NaOH at a ratio of 1:2 can be completed only at temperatures of 80–100°C, which are far from the optimum temperature regime (15–25°C). Main reaction products are disodiumoxydimethylsiloxanes, and this fact suggests that secondary processes dominate. The formation of trimethylsilyl derivative corresponding to disodiumoxydimethylsilane is not detected. Similar results were obtained for the reaction between tetraethoxysilane and NaOH at a ratio of 1:2 or 1:3.



Therefore, the reaction of organoalkoxysilanes with sodium hydroxide under optimal conditions presents a simple and convenient way for the synthesis of MSOAS.

### *Interaction of Sodium Hydroxide with Organoalkoxysiloxanes. Prospects of Synthesis of Sodiumoxyorganoalkoxysiloxanes*

In contrast to organoalkoxysilanes, interaction of organoalkoxysiloxanes with sodium hydroxide is unfortunately inapplicable for the introduction of sodiumsilanolate groups into organosiloxane molecules. Even under the above-mentioned optimal conditions, this reaction is usually accompanied by the degradation of siloxane groups, which proceeds along with the exchange reactions between alkoxy and sodiumoxy groups. As a result, a complex mixture of various compounds is formed, and their separation into individual components appears to be impossible. Furthermore, in most cases, final products do not contain any target components. For example, interaction of 1,3-diethoxytetramethyldisiloxane with sodium hydroxide (Table 3, no. 29) and simultaneous azeotropic distillation of the formed ethanol with toluene finally leads to the formation of 1,5-disodiumoxyhexamethyltrisiloxane, instead of the expected 1-sodiumoxy,3-ethoxytetramethyldisiloxane. When this reaction is carried out under mild conditions, trimethylsilyl derivative of target product as 1-ethoxyheptamethyltrisiloxane (Table 1, no. 20) is obtained, and its yield is equal to ~9.7%. In a somewhat complex case, interaction of 3,3-dimethylhexaethoxytrisiloxane with sodium hydroxide does not lead to the formation of any sodiumoxy derivatives, which contain both initial

ethoxysiloxane and three silicon atoms. As was expected, this reaction entails the formation of ethanol and dimethyldiethoxysilane, which presents the central structural fragment of the initial compound. In the case of trimethylsilylation, the following compounds are identified: tetraethoxysilane and 1,1,1-trimethyl,3,3,3-triethoxydisiloxane, which is trimethylsilyl derivative of sodiumoxytriethoxysilane (Table 1, no. 3); most of the final products are involved in the residue, which presents the mixture of nondistillable compounds. This evidence looks rather convincing and does not require any additional comments. In a simpler version, interaction of 1-methoxypentamethyldisiloxane with sodium hydroxide (Table 3, no. 30) leads to the formation of the target compound as 1-sodiumoxy-pentamethyldisiloxane with a yield of ~73%, in addition to sodium trimethylsilanolate (~7%) and virtually equal amounts (10%) of 1,3-disodiumoxytetramethyldisiloxane and its homolog, 1,5-disodiumoxyhexamethyltrisiloxane. Despite the evident progress shown by the latest results, it is too early to use this mixture for synthetic purposes.

### *Properties of Monosodiumoxyorganoalkoxysilanes*

**Physical Properties.** As was shown in our studies, interaction of organoalkoxysilanes with sodium hydroxide allows one to synthesize various MSOAS as well as change the chemical nature of their organic decoration and vary the number of alkoxy groups at silicon atom (from one to three) (Fig. 7). Usually, direct yields of MSOAS are high at 93–97%. The only exception concerns sodiumoxytriethoxysilane, and its yield does not

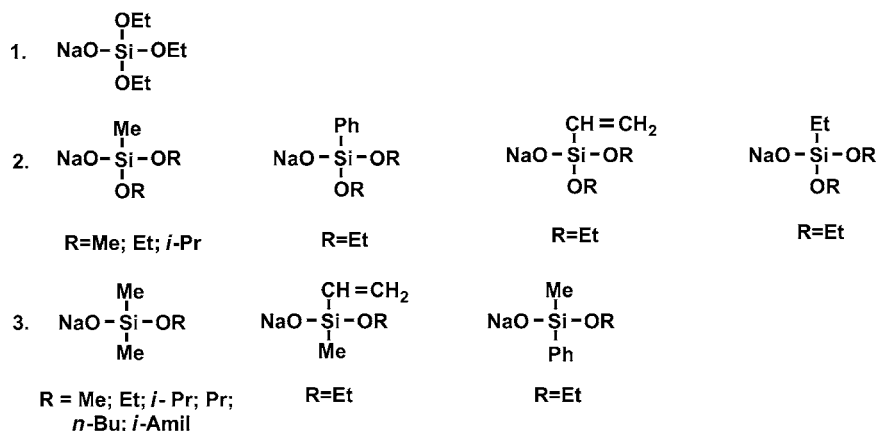


FIGURE 7 A family of synthesized MSOAS.

exceed 86%. However, this yield can be increased up to 93% by using the exchange reaction between tetraethoxysilane and sodiumoxydimethylethoxysilane (Table 3, no. 17), a challenging problem that will be discussed in more detail later.

With the exception of methoxyl derivatives, a combination of ionic sodiumoxy and organic alkoxyl groups in the molecules of most MSOAS is an attractive solution because the above compounds can be dissolved well in both polar and nonpolar organic solvents.

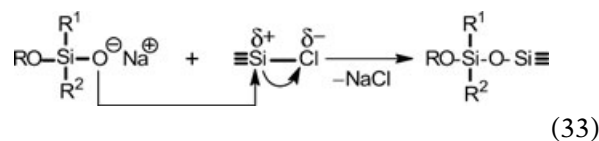
If MSOAS are well dissolved in such nonpolar solvents such as *n*-alkanes and aromatic hydrocarbons, the formed secondary products (primarily, disodiumoxyorganosiloxanes) appear to be virtually insoluble. This fact makes it possible to obtain pure MSOAS by using rather simple techniques such as filtration or decantation of their solutions.

By their appearance, MSOAS present crystalline compounds, and their melts are rather susceptible to supercooling (except for sodiumoxytriethoxysilane, which is infusible).

All MSOAS are known to be thermally stable compounds among various sodiumoxyorganosilanes and siloxanes. For example, thermal degradation of sodiumoxydimethylethoxysilane in its melt ( $T_m \sim 70^\circ\text{C}$ ) or in its *n*-undecane solution takes place at 185–190°C. Among volatile products of thermal degradation, trimethylethoxysilane (~95%) and dimethyldiethoxysilane are identified. Solid salt products are presented by disodiumoxydimethylsilane, sodium ethylate, and sodium trimethylsilanolate (in total, ~25%; other 75% involve the mixture of oligomer polysodiumoxymethylethoxysiloxanes). Analysis of the thermal degradation products primarily suggests that, at intermediate stages, redistribution of methyl (not ethoxyl groups) takes place. This is in contrast to the exchange interaction between MSOAS and organoalkoxysilanes. Thermal degradation of sodiumoxytriethoxysilane commences within the same temperature interval; however, this process proceeds with slower rates. In this case, the only volatile product of thermal degradation is tetraethoxysilane. The salt fraction is presented by three-dimensional polysodiumoxyethoxysiloxane.

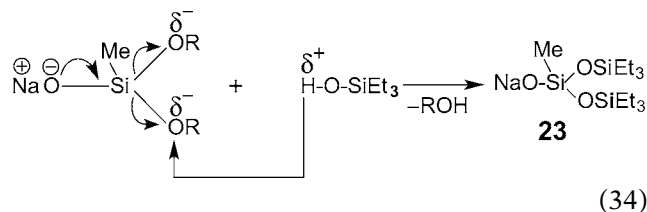
**Chemical Properties.** Chemical behavior of MSOAS is primarily controlled by their molecular structure. Depending on the conditions and type of reagents, they selectively react either with  $-\text{ONa}$  or  $-\text{OR}$  groups. According to this criterion, MSOAS can be classified as reagents with “chemically independent functional groups.”

**Interaction of MSOAS with organochlorosilanes.** Because of the presence of an ionic  $-\text{ONa}$  group, MSOAS are rather strong  $-\text{O}^\ominus$  nucleophiles, which are able to enter the  $\text{S}_\text{N}2$  substitution reactions with organosilicon compounds that contain easily removed groups (for example,  $\text{Hal}^-$  or acyloxy anions) at silicon atoms (Scheme 33):

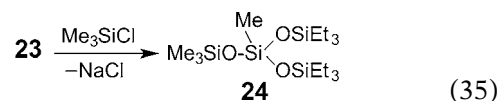


Within the scope of this work, we studied the interaction of MSOAS with trimethylchlorosilane in detail (Scheme 8). This reaction readily proceeds in the medium of nonpolar organic solvents solely through sodiumoxy groups when alkoxyl reactive sites remain intact. This process leads to the formation of the corresponding trimethylsilyl derivatives (Table 1) with almost quantitative yields.

**Interaction of MSOAS with hydroxyl-containing reagents.** Due to the partial redistribution of negative charge of the ionic sodiumsilanolate group in MSOAS molecules over oxygen atoms of neighboring alkoxyl groups, their reactivity toward compounds with mobile hydrogen atoms (for example, hydroxyl-containing reagents) increases. This property was discussed earlier when analyzing the specific features of secondary processes taking place during synthesis. As was shown in model experiments (Table 3, no. 10), sodiumoxymethyldimethoxysilanes and diethoxysilanes readily react with triethylsilanol even at room temperature, and this reaction is accompanied by a moderate exothermic effect (Scheme 34):

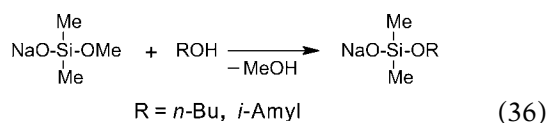


When the reaction products are treated with trimethylchlorosilane, compound **24** (Scheme 35) is obtained, and its yield is equal to 24–55%.

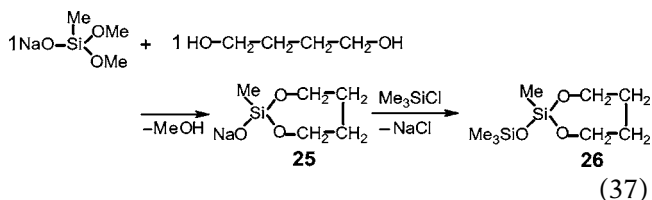


Reactions of realkoxylation of sodiumoxydimethylmethoxysilane with *n*-butanol or isoamyl

alcohol (Table 3, no. 11) proceed virtually quantitatively with the formation of sodiumoxydimethyl-*n*-butoxysilanes and isoamyloxysilanes. This approach offers the best scenario for their preparation (Scheme 36):

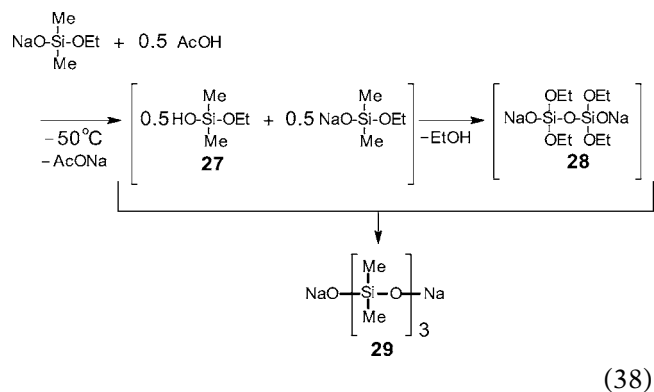


Replacement of monoatomic alcohols from C<sub>4</sub> and higher with its diatomic analogs leads to the formation of more complex mixture of final products. Obviously, it is caused by processing reiterated intermolecular realkoxylation processes in the reactive system. As a result of the interaction of sodiumoxymethyldimethoxysilane with 1,4-butanediol, only the cyclic product of intramolecular condensation (**25**) was successfully identified (Scheme 37). Its trimethylsilyl derivative (**26**) was isolated with the yield ~22%. The main part of obtained products ~64% was undistillable substances (1 Torr).



However, the preparation of realkoxylation products with acceptable yields presents a challenging task. For example, interaction of sodiumoxydimethylmethoxysilane with isopropanol leads to the formation of a complex mixture of compounds, among which the above-mentioned secondary products are predominant (Table 1, no. 3). Positive results of earlier experiments are related to low activity of *n*-butanol and isoamyl alcohol in the above exchange and condensation processes.

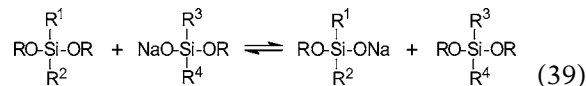
With the internal generation of silanol intermediates (dimethylethoxysilanol **27**) in the medium of sodiumoxydimethylethoxysilane by acetic acid at -50°C and the further increase to room temperature, primary products of reaction **28** are not identified. Exchange and condensation processes proceed rather intensively and finally lead to the formation of 1,5-disodiumoxyhexamethyltrisiloxane **29** with a yield of ~90% (Scheme 38).



The preferential formation of stable compound **29** corresponds to the earlier results obtained for the decomposition reaction of dimethylcyclosiloxanes with sodium hydroxide [12].

*Exchange Interaction of MSOAS with Organoalkoxysilanes.* Interaction of MSOAS with organoalkoxysilanes leads to the formation of pentacoordinated complex compound **22**. More detailed studies show that, under certain conditions, complex **22** experiences internal migration of alkoxy groups from one silicon atom to another, and this migration is likely to proceed via a four-centered transition state (Fig. 8).

Exchange interaction within the transition complex **30** can be presented in a simpler way as the case of limiting separation of components (Scheme 39):



When R<sup>1</sup> = R<sup>3</sup> and R<sup>2</sup> = R<sup>4</sup>, no visible changes in the system take place (Table 3, nos. 2 and 3). Inversely,

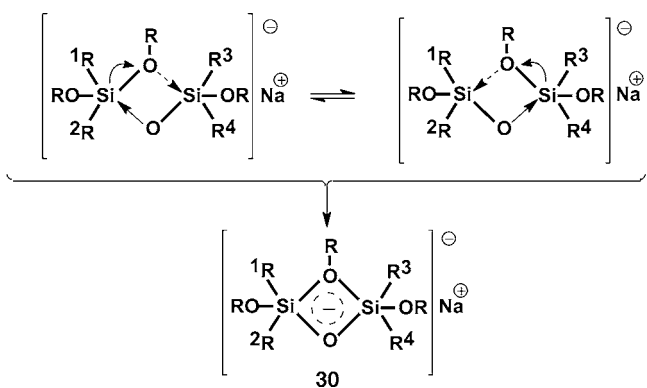
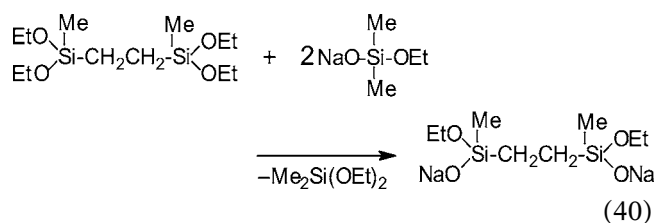


FIGURE 8 Internal interactions of organoalkoxysilane with MSOAS in complex.

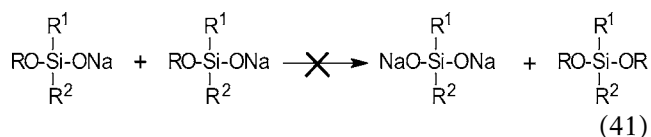
removal of lower boiling alkoxy silane from the reaction volume can fully shift the equilibrium of reaction (38) to a desirable direction. For example, heating of homogeneous solution of  $\text{NaOSi}(\text{Me})_2\text{OEt}$  (33%) in the medium of  $\text{Si}(\text{OEt})_4$  at  $70^\circ\text{C}$  and at 100 Torr entails an almost complete isolation of  $(\text{Me})_2\text{Si}(\text{OEt})_2$  (Table 3, no. 17). In this case, sodiumoxytriethoxysilane ( $\text{NaOSi}(\text{OEt})_3$ ) is formed with a yield of 93%. Purity of this final product is rather high, and this level of purity cannot be attained when this compound is obtained directly from  $\text{Si}(\text{OEt})_4$  and  $\text{NaOH}$  (Table 3, no. 18).

Therefore, the exchange reaction (Scheme 39) offers wide possibilities for the synthesis of various (including MSOAS) organosilicon sodiumoxy derivatives under aprotic conditions. For example, depending on the type of solvent, feed ratio of starting reagents, temperature, and duration of this process, interaction of 1,2-bis-(diethoxymethylsilyl)ethane with sodiumoxydimethylethoxysilane allows a stepwise substitution of ethoxyl groups by sodiumsilanolate groups depending on synthetic requirements (Scheme 40):



Unfortunately, this convenient reaction can hardly be used for the incorporation of sodiumsilanolate groups into organosiloxane molecules because of the concurrent degradation processes, which are accompanied by the rupture of siloxane bond. As a result, a complex mixture of final products is formed (Table 3, no. 28).

Similar exchange reactions (39) but only combined with sodiumoxyorganoalkoxysilanes (Scheme 41) are virtually prohibited:



Such processes can take place only at high temperatures of about  $180\text{--}200^\circ\text{C}$  when the degradation of MSOAS occurs.

## CONCLUSIONS

1. The reaction of organoalkoxysilanes with sodium hydroxide is studied.

- (a) This reaction presents a rather complex process, which proceeds in more than one stage. Specific character of chemical interactions in the reaction systems leads to the formation of various reaction products, which primarily involve target compounds based on monosodiumoxyorganoalkoxysilanes. Electronic effects in the molecules of such compounds prevent further exhaustive substitution of alkoxy groups in their composition by sodiumsilanolate groups. The mechanism for their formation is proposed.
- (b) Composition and structure of secondary reactions or by-products are studied. The most probable reason behind their formation is shown to be related to the presence of alcohol formed in the course of main reaction.
- (c) This study allows us to propose a simple and convenient method for the preparation of pure MSOAS. Various target compounds were synthesized, and their basic physicochemical properties were studied. As is shown, MSOAS are reagents with chemically independent functional groups such as  $\text{NaO}$ — and  $-\text{OEt}$ .

2. The exchange interaction between MSOAS and organoalkoxysilanes is revealed and studied in detail. This process can be used for the synthesis of MSOAS and other organosilicon compounds containing sodiumoxy group.
3. The reaction of MSOAS with trimethylchlorosilane is studied in detail. This reaction proceeds only via sodiumoxy groups. Important information concerning the use of MSOAS for the synthesis of functional organosiloxanes of more complex structure is obtained.

## EXPERIMENTAL

### 1. Initial Compounds. Method of Investigation

Initial compounds such as organochlorosilanes, alcohols, and organic solvents were pretreated according to the adopted procedures [71]. Organoalkoxysilanes, organoaminosilanes, organoalkoxyaminosilanes, organoalkoxysiloxanes, organosilanols, and organocyclosiloxanes were synthesized using the procedures described in [72].

GLC analysis was performed on an LChM-80 chromatograph; length of columns was equal to 1 or 2 m; their internal diameter was equal to 3 mm; catharometer—detector; carrier gas—helium

(30 mL/min), immobile phase: SE-30 deposited onto a Chromatron-N-AW-HMDS (5% SE-30).

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker WP-200 and WP-250 spectrometers in  $\text{CDCl}_3$ ,  $\text{CCl}_4$ , and  $\text{C}_6\text{D}_6$ . Internal reference sample: tetramethylsilane (TMS),  $\text{CHCl}_3$ .

## 2. Reaction of Organoalkoxysilanes with Sodium Hydroxide. Synthesis of Monosodiumoxyorganoalkoxysilanes

**2.1. General Procedure of Trimethylsilylation of Organosodiumsilanates.** 50% solution of trimethylchlorosilane (in 5–10% excess per sodium oxy groups with respect to stoichiometry) was added in drops to a stirred homogeneous solution or suspension of organosodiumsilanates in nonpolar organic solvent (*n*-alkanes, aromatic hydrocarbons) at  $-40$  to  $-30^\circ\text{C}$  in the flow of dry argon. Reaction mixture was stirred for 1 h at  $25^\circ\text{C}$  and for 0.5 h at  $35$ – $60^\circ\text{C}$ . Sodium chloride precipitate was filtered and washed three times with solvent; filtrate was evaporated to remove solvent; residue was separated by a simple distillation or rectification. Purity of the prepared products was controlled by the GLC method, and their structure was confirmed by the  $^1\text{H}$  NMR spectroscopy. For known compounds, their constants were compared with the literature data [64]. Yields of trimethylsilyl derivatives for each case under study are listed below.

**2.2. General Procedure of the Reaction Between Organoalkoxysilanes and Sodium Hydroxide. Synthesis of Monosodiumoxyorganoalkoxysilanes.** A solid sodium hydroxide at temperature  $T_{\text{mix}}$  was added to organoalkoxysilane or its solution in organic solvent. Suspension was mixed in the flow of dry argon to achieve a complete homogenization of the system. Highly volatile liquid components (organic solvent, excessive organoalkoxysilane, and reactive alcohol) were removed in vacuum (1 Torr) at temperature  $T_{\text{dist}}$ . Residue was dissolved or suspended in organic solvent; then, it was subjected to trimethylsilylation according to procedure as described in procedure 2.1. Specific conditions of this reaction and yield of target compounds are listed in Table 4. Yields of trimethylsilyl derivatives of MSOAS were calculated from the data of GLC analysis, which allowed one to estimate their true amounts among other reaction products.

**2.3. Exchange Reaction Between Sodiumoxydimethylethoxysilane and Tetraethoxysilane. Synthesis of Sodiumoxytriethoxysilane.** After its recrystallization from *n*-hexane, sodiumoxy-

dimethylethoxysilane (28.5 g, 0.2 mol) was dissolved at room temperature in tetraethoxysilane (125.0 g, 0.6 mol). The stirred solution was heated to  $70^\circ\text{C}$  at a reduced pressure of 100 Torr. The formed dimethyldiethoxysilane was slowly removed from the system through long fractional distillation column. After the extraction of dimethyldiethoxysilane, the mixture was stirred under the same conditions for 3 h. Excessive tetraethoxysilane was evaporated at a reduced pressure of 1 Torr at  $35$ – $50^\circ\text{C}$ . Solid residue was dissolved in dry *n*-heptane (150 mL) and treated with a solution of trimethylchlorosilane (24.0 g, 0.22 mol) in *n*-heptane (40 mL) according to procedure 2.1. As a result, we obtained 46.8 g (93% yield) of 1,1,1-trimethyl,3,3,3-triethoxydisiloxane (Table 1, no. 3).

## 2.4. Thermostating of Sodiumoxytriethoxysilane Solutions Under Different Conditions

**2.4.1. Solution of sodiumoxytriethoxysilane (24.3 g, 0.12 mol) in dry toluene (100 mL) was heated in the flow of dry argon at  $100$ – $110^\circ\text{C}$  for 8 h. No visible changes in the systems were detected. Toluene was evaporated from the solution at a reduced pressure of 20 Torr; residue was dissolved in *n*-hexane and treated with trimethylchlorosilane (14.5 g, 0.13 mol) in *n*-hexane (30 mL). As a result, we obtained 29.1 g (96% yield) of 1,1,1-trimethyl, 3,3,3-triethoxydisiloxane (Table 1, no. 3).**

**2.4.2. Solution of sodiumoxytriethoxysilane (28.3 g, 0.14 mol) in dry *n*-nonane (120 mL) was stirred under the flow of dry argon at  $150^\circ\text{C}$  for 12 h. No visible changes in the systems were detected. *n*-Nonane was evaporated from the solution at a reduced pressure of 1 Torr; the residue was dissolved in *n*-hexane and treated with trimethylchlorosilane (17.0 g, 0.16 moles) in *n*-hexane (35 mL). As a result, we obtained 33.8 g (96% yield) of 1,1,1-trimethyl,3,3,3-triethoxydisiloxane (Table 1, no. 3).**

**2.4.3. Solution of sodiumoxytriethoxysilane (36.4 g, 0.18 mol) in *n*-heptane (180 mL) containing 5 wt% of ethanol was stirred at  $40$ – $50^\circ\text{C}$  for 9 h. This process led to the precipitation of a white solid. *n*-Heptane was evaporated at a reduced pressure of 20 Torr. To the solid residue was added dry toluene (100 mL), which was also evaporated at 20 Torr. This procedure was repeated three times in order to remove the traces of ethanol. The residue was suspended in *n*-hexane (120 mL) and treated with the solution of trimethylchlorosilane (21.7 g, 0.20 mol) in *n*-hexane (55 mL). As a result, we obtained 21.6 g (47.5% yield) of 1,1,1-trimethyl,3,3,3-triethoxydisiloxane and 16.4 g (42.3% yield)**

of 3,3,5,5-tetraethoxyhexamethyltetrasiloxane, (Table 1, no. 17). Found:  $n_D^{25} = 1.3910$ ,  $d_4^{25} = 0.9548$ ,  $M_D^R = 108.58$ ,  $T_b = 245^\circ\text{C}$ ; Si 25.60, C 39.98, H 8.87. Weight of distillation fractions: 0.8 g (2% with respect to the total amount of isolated products). Calcd:  $M_D^R = 107.19$ ; Si 26.07, C 39.04, H 8.89.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz):  $\delta = 0.050$  (s, 18H),  $\delta = 1.180$  (t, 12H),  $\delta = 3.680$  (q, 8H).

2.4.4. Solution of sodiumoxytriethoxysilane (36.4 g, 0.18 mol) in *n*-heptane (180 mL) containing 5 wt% of ethanol was stirred at  $65^\circ\text{C}$  for 14 h. In this case, the precipitation of a voluminous white solid was observed. All further steps were similar to those described in procedure 2.4.3. As a result, we obtained 17.3 g (38.1% yield) of 1,1,1-trimethyl,3,3,3-triethoxydisiloxane, 15.8 g (40.7% yield) of 3,3,5,5-tetraethoxyhexamethyltetrasiloxane. Weight of distillation fractions: 3.4 g (9.3% with respect to the total amount of isolated products).

2.4.5. Solution of sodiumoxytriethoxysilane (36.4 g, 0.18 mol) in toluene (180 mL) containing 0.1 wt% of water was stirred and heated at 80 to  $95^\circ\text{C}$  for 2.5 h. In this case, the precipitation of a voluminous white solid was observed. All further steps were similar to those described in procedure 2.4.3. As a result, we obtained 3.4 g (7.6% yield) of 1,1,1-trimethyl, 3,3,3-triethoxydisiloxane, 1.1 g (2.8% yield) 3,3,5,5-tetraethoxyhexamethyltetrasiloxane, 8.8 g of mixture of oligomer products:  $T_b = 163\text{--}200^\circ\text{C}$ . Weight of distillation fractions: 17.3 g (56.5% with respect to the total amount of isolated products).  $^1\text{H}$  NMR: Found: ratio of integral intensities of signals from protons of methyl radicals at silicon atoms  $\text{H}_{\text{Si}(\text{CH}_3)}$   $\delta = 0.05$  (s) and ethoxyl groups  $\text{H}_{\text{SiOCH}_2\text{CH}_3}$   $\delta = 1.18$  (t),  $\text{H}_{\text{SiOCH}_2\text{CH}_3}$   $\delta = 3.68$  (q) was equal to 1.65:1. Calcd: for repeat unit  $-\text{Si}(\text{OC}_2\text{H}_5)_3\text{OSi}(\text{CH}_3)_3$ , 1.80:1.

## 2.5. Thermostating of Sodiumoxydimethylethoxysilane Solutions Under Different Conditions

2.5.1. A homogeneous solution of sodiumoxydimethylethoxysilane (28.5 g, 0.20 mol) recrystallized from *n*-hexane was stirred in dimethyldiethoxysilane (148.0 g, 1.0 mol) at  $100^\circ\text{C}$  for 6 h. No visible changes in the systems were detected. To remove dimethyldiethoxysilane, the solution was evaporated at  $25\text{--}35^\circ\text{C}$  and at a reduced pressure of 1 Torr; solid residue was dissolved in dry *n*-hexane (85 mL) and treated with the solution of trimethylchlorosilane (24.0 g, 0.22 mol) in *n*-hexane (55 mL). As a result, we obtained 36.0 g (94% yield) of pentamethylethoxydisiloxane (Table 1, no. 1).

2.5.2. Solution of sodiumoxydimethylethoxysilane (28.5 g, 0.20 moles) in *n*-heptane (120 mL)

containing 5 wt% of ethanol was stirred at  $90\text{--}95^\circ\text{C}$  for 14 h. In this case, the precipitation of a voluminous white solid was observed. All further steps were similar to those described in procedure 2.4.3. As a result, we obtained 5.8 g (15.0% yield) of pentamethylethoxydisiloxane, 9.3 g (30.0% yield) of decamethyltetrasiloxane (Table 1, no. 15), 12.8 g (50.0% yield) dodecamethylpentasiloxane (Table 1, no. 16).

2.6. *Interaction of Sodiumoxydimethylethoxysilane with Water.* A solution of water (1.8 g, 0.10 mol) in dioxane (15 mL) was added to a solution of sodiumoxydimethylethoxysilane (28.5 g, 0.20 mol) in toluene (130 mL) under stirring at  $25^\circ\text{C}$ . Temperature in the system was spontaneously increased to  $35^\circ\text{C}$ ; the solution became brightly crimson and fully homogeneous. The mixture was stirred at  $60^\circ\text{C}$  for 2 h; then, the formed ethanol was removed by azeotropic distillation with toluene. In this case, the precipitation of a white solid based on reaction products was observed. The residue was filtered, washed with dry toluene, dried at a reduced pressure of 1 Torr at  $50^\circ\text{C}$ , suspended in dry *n*-hexane (60 mL), and treated with a solution of trimethylchlorosilane (24.0 g, 0.22 mol) in *n*-hexane (55 mL). As a result, we obtained 19.0 g (60% yield) of decamethyltetrasiloxane (Table 1, no. 15), 5.1 g (20% yield) of dodecamethylpentasiloxane (Table 1, no. 16).

2.7. *Interaction of Sodiumoxydimethylethoxysilane with Acetic Acid.* Acetic acid (6.0 g, 0.10 mol) was added in drops to a solution of sodiumoxydimethylethoxysilane (28.5 g, 0.20 mol) in toluene (130 mL) under stirring at  $-50^\circ\text{C}$ . The mixture was stirred at  $-30^\circ\text{C}$  for 2 h; then, the temperature was increased to room temperature. Residue of sodium acetate was filtered and washed with toluene. Reaction ethanol was removed from the system by the azeotropic distillation with toluene. In this case, the precipitation of a white solid based on reaction products was observed. The precipitate was filtered, dried at  $50^\circ\text{C}$  at a reduced pressure of 1 Torr, and treated with a solution of trimethylchlorosilane (24.0 g, 0.22 mol) in *n*-hexane (55 mL). As a result, we obtained 0.5 g (1.6% yield) of decamethyltetrasiloxane and 15.4 g (60% yield) of dodecamethylpentasiloxane.

## 2.8. Interaction of MSOAS with Alcohols

2.8.1. *Interaction of sodiumoxydimethylmethoxydisilane with *n*-butanol. Synthesis of sodiumoxydimethyl-*n*-butoxysilane.* Sodium hydroxide (4.0 g, 0.10 mol) was added to a solution of

dimethyldimethoxysilane (12.0 g, 0.10 mol) in *n*-butanol (26.0 g, 0.35 mol), under stirring at 20°C. The mixture was stirred until its complete homogenization was achieved; then, excessive *n*-butanol and formed methanol were removed at a reduced pressure of 1 Torr at 80°C. Residual *n*-butanol was removed by azeotropic distillation with toluene at a reduced pressure of 20 Torr. The resulting product was colorless viscous liquid, which was dissolved in dry *n*-hexane (45 mL) and treated with a solution of trimethylchlorosilane (12.0 g, 0.11 mol) in *n*-hexane (40 mL). As a result, we obtained 19.8 g (90% yield) of *n*-butoxypentamethyldisiloxane (Table 1, no. 10).

2.8.2. *Interaction of sodiumoxydimethylmethoxysilane with isoamyl alcohol. Synthesis of sodiumoxydimethylisoamylloxysilane.* Sodium hydroxide (5.4 g, 0.135 mol) was added to a solution of dimethyldimethoxysilane (21.0 g, 0.175 mol) in isoamyl alcohol (41.67 g, 0.472 mol) under stirring at 20°C. Temperature in the system was spontaneously increased to 40°C. The mixture was stirred until its complete homogenization was achieved; then, the excess isoamyl alcohol and formed methanol were removed at a reduced pressure of 1 Torr at 85°C. Residual isoamyl alcohol was removed by azeotropic distillation with toluene at a reduced pressure of 20 Torr. The resulting product was a colorless viscous liquid, which was dissolved in dry *n*-hexane (65 mL) and treated with a solution of trimethylchlorosilane (15.3 g, 0.141 mol) in *n*-hexane (40 mL). As a result, 29.4 g (93% yield) of isoamylxypentamethyldisiloxane was obtained (Table 1, no. 10).

2.8.3. *Interaction of sodiumoxymethylmethoxysilane with 1,4-butanediol.* Solution of 20.98 g (0.154 mol) methyltrimethoxysilane in dioxane (15 mL) was added to a suspension of 5.60 g (0.140 mol) sodium hydroxide in dioxane (15 mL) under stirring at 15°C. The mixture was stirred for 0.5 h until its complete homogenization was achieved. To the resulting solution, the solution of 12.62 g (0.140 mol) 1,4-butanediol in dioxane (15 mL) was added under stirring at 10°C. The mixture was stirred for 1 h at 20°C; then, dioxane and formed methanol were removed at a reduced pressure of 1 Torr at 40–50°C. The suspension of insoluble residue was treated with a solution of trimethylchlorosilane (16.3 g, 0.150 mol) in *n*-hexane (40 mL) at –30°C. The mixture was stirred at 25°C for 1 h and at 60°C for 0.5 h. As a result, 6.69 g (22%) 1-methyl, 1-trimethylsiloxy-1-sila-2,7-dioxacycloheptane and 19.4 g of undistillable products were obtained. Found:  $T_b = 63\text{--}65^\circ\text{C}/2$  Torr.  $^1\text{H NMR}$  ( $\text{CCl}_4$ , 200 MHz):  $\delta = 0.096$  (s, 9H),  $\delta = 0.035$  (s, 3H),  $\delta = 1.74$  (d, 4H),  $\delta = 3.62$  (m, 4H).

2.9. *Interaction of Dimethyldimethoxysilane with Sodium Hydroxide in *n*-propanol.* According to procedure 2.8, 12.0 g (0.10 mol) of dimethyldimethoxysilane, 4.0 g (0.10 mol) of sodium hydroxide, 21.0 g (0.35 mol) of *n*-propanol, and 12.6 g (0.12 mol) of trimethylchlorosilane yield 2.0 g (10%) of *n*-propoxypentamethyldisiloxane (Table 1, no. 11).

#### 2.10. Interaction of MSOAS with Triethylsilanol

2.10.1. *Interaction of sodiumoxydimethylethoxysilane with triethylsilanol.* A solution of triethylsilanol (12.2 g, 0.092 mol) in ether (16 mL) was added in drops to a solution of sodiumoxydimethylethoxysilane (7.9 g, 0.045 mol) in dry diethyl ether (20 mL), under stirring at 10°C. Temperature in the reaction system was spontaneously increased to 25°C. The mixture was stirred at 25°C for 1 h and allowed to stay at a reduced pressure of 20 Torr and then at 1 Torr and at 35–40°C until constant weight was attained (15.2 g). The resulting residue was a colorless viscous liquid, which was dissolved in dry *n*-hexane (45 mL) and treated with a solution of trimethylchlorosilane (5.6 g, 0.052 mol) in *n*-hexane (20 mL). As a result, we obtained 10.01 g (53.3% yield) of 3-methyl,3-(trimethylsiloxy)hexaethyltrisiloxane (Table 1, no. 18). Found:  $T_b = 150\text{--}151^\circ\text{C}/10$  Torr,  $n_D^{25} = 1.4271$ ; Si 28.23, C 48.44, H 10.76. Calcd: Si 28.45, C 48.67, H 10.72.  $^1\text{H NMR}$  ( $\text{CCl}_4$ , 200 MHz):  $\delta = 0.275$  (s, 3H),  $\delta = 0.353$  (s, 9H),  $\delta = 0.823$  (q, 4H),  $\delta = 1.212$  (t, 6H).

2.10.2. *Interaction of sodiumoxydimethylmethoxysilane with triethylsilanol.* A solution of triethylsilanol (11.0 g, 0.083 mol) in ether (15 mL) was added in drops to a suspension of sodiumoxydimethylmethoxysilane (6.0 g, 0.042 mol) in dry diethyl ether (20 mL) under stirring at 10°C. The solution was stirred until its complete homogenization was achieved. All further steps were similar to those described in procedure 2.10.1. As a result of treatment with a solution of trimethylchlorosilane (5.8 g, 0.053 moles) in *n*-hexane (20 mL), 3.94 g (24% yield) of 3-methyl,3-(trimethylsiloxy)hexaethyltrisiloxane was obtained.

#### 2.11. Interaction of Diphenylsilanediol with Sodium Tert-Isoamylate

2.11.1. Sodium *tert*-isoamylate was prepared via the reaction of *tert*-isoamyl alcohol and metallic sodium in dry toluene. When needed, the solution was evaporated from toluene at a reduced pressure of 1 Torr; residue was dissolved in dry ether.

2.11.2. A solution of diphenylsilanediol (12.0 g, 0.555 mol) with its mixture with ether (100 mL) and pyridine (5 mL) was added in drops to a stirred solution of sodium *tert*-isoamylate (12.76 g, 0.116 mol) in dry ether (100 mL) at  $-10^{\circ}\text{C}$ . The mixture was stirred for 1.5 h and heated to  $25^{\circ}\text{C}$ . After evaporation of ether, the formed *tert*-isoamyl alcohol was removed by azeotropic distillation with toluene. The precipitated residue of disodiumoxydiphenylsilane was filtered and dried at a reduced pressure of 1 Torr and at  $50^{\circ}\text{C}$  (content of sodium in the residue was equal to 17.20%; theoretical content, 17.69%), suspended in dry toluene (85 mL), and treated with a solution of trimethylchlorosilane (16.4 g, 0.15 mol) in toluene (50 mL). As a result, we obtained 19.61 g (98% yield) of 3,3-diphenylhexamethyltrisiloxane (Table 1, no. 19).

2.12. *Interaction of Trimethylmethoxysilane with Sodium Hydroxide (3:1)*. Sodium hydroxide (2.6 g, 0.065 mol) was added to trimethylmethoxysilane (20.3 g, 0.195 mol) under stirring at  $0^{\circ}\text{C}$ . Temperature in the system was spontaneously increased to  $30\text{--}35^{\circ}\text{C}$ . After a complete homogenization within 3 min, crystalline precipitate of sodium methylate was obtained. Reaction mixture was evaporated at a reduced pressure of 1 Torr; the resulting condensate was collected in a liquid nitrogen cooled trap. As a result of rectification of the condensate, 10.0 g (95% yield) of hexamethyldisiloxane was obtained. Found:  $T_b = 4100^{\circ}\text{C}$ ,  $n_D^{20} = 1.3772$ .

Solid residue (3.6 g) was treated with a solution of triethylchlorosilane (10.8 g, 0.072 moles) in dry *n*-pentane (40 mL). According to the GLC data, a mixture based on triethylmethoxysilane (95%) and 1,1,1-triethyl, 3,3,3-trimethyldisiloxane (5%) was obtained.

2.13. *Interaction of Trimethylethoxysilane with Sodium Hydroxide (3:1)*. Sodium hydroxide (2.0 g, 0.05 mol) was added to a mixture of trimethylethoxysilane (17.7 g, 0.15 mol) and pyridine (3.9 g, 0.05 mol). The mixture was stirred for 1.5 h at  $70^{\circ}\text{C}$  until its complete homogenization was attained. Liquid components of the system were evaporated at a reduced pressure of 1 Torr. The residue was dried by azeotropic distillation with benzene and treated with a solution of dimethyldichlorosilane (3.2 g, 0.025 mol) in benzene (15 mL). As a result, we obtained 5.70 g (48% yield) of octamethyltrisiloxane (Table 1, no. 14).

2.14. *Interaction of Trimethyl-Iso-Propoxysilane with Sodium Hydroxide (3:1 ratio)*. The suspension

of sodium hydroxide (2.0 g, 0.05 mol) in trimethyl-*iso*-propoxysilane (19.8 g, 0.15 mol) was stirred at  $90^{\circ}\text{C}$  for 4 h. No visible changes in the systems were detected: system remained heterogeneous. The mixture was evaporated at a reduced pressure of 1 Torr; the distilled fraction was collected in a liquid nitrogen cooled trap. This fraction (19.5 g) was based on a pure trimethyl-*iso*-propoxysilane ( $T_b = 90^{\circ}\text{C}$ ,  $n_D^{25} = 1.3749$ ).

2.15. *Interaction of Hexamethyldisiloxane (HMDS) with Sodium Methylate, Ethylate, and Isopropylate*

2.15.1. Sodium alcoholates were prepared by the interaction of the corresponding alcohol with metallic sodium in dry toluene.

2.15.2. Suspension of sodium methylate (4.67 g, 0.086 mol) in HMDS (69.80 g, 0.43 mol) was stirred at  $100^{\circ}\text{C}$  for 6 h. No visible changes in the systems were detected: system remained heterogeneous. The mixture was evaporated at a reduced pressure of 1 Torr; the distilled fraction was collected in a liquid nitrogen cooled trap. This distilled fraction (69.60 g) was based on a pure HDMS ( $T_b = 100^{\circ}\text{C}$ ,  $n_D^{20} = 1.3772$ ).

2.15.3. Similar results were obtained when mixtures of HDMS (46.80 g, 0.29 mol) HMDS with sodium ethylate (3.92 g, 0.057 mol) and HDMS (40.70 g, 0.25 mol) with sodium isopropylate (4.11 g, 0.05 mol) were boiled.

2.16. *Interaction of (N-methylamino)dimethylethoxysilane with Sodium Hydroxide (1:1)*

2.16.1. Sodium hydroxide (8.0 g, 0.20 mol) was added to (N-methylamino)dimethylethoxysilane (26.65 g, 0.20 mol) under stirring at room temperature. Within 10 min, temperature in the system was spontaneously increased to  $35^{\circ}\text{C}$ , and this led to an intensive formation of methylamine, which was titrated by 0.1 N HCl using the Tishchenko titration cell. The mixture was stirred at  $35^{\circ}\text{C}$  for 8 h and evacuated at a reduced pressure of 1 Torr and at  $40^{\circ}\text{C}$  for 1.5 h. White solid residue was dissolved in dry *n*-pentane (85 mL); the solution was filtered from unreacted sodium hydroxide and treated with a solution of trimethylchlorosilane (23.8 g, 0.22 mol) in *n*-pentane (55 mL). As a result, we obtained 30.8 g (80%) of pentamethylethoxydisiloxane (Table 1, no. 1).

2.16.2. Similar reaction of (N-methylamino)dimethylethoxysilane (79.9 g, 0.6 mol), sodium hydroxide (8.0 g, 0.2 mol), and trimethylchlorosilane



(23.8 g, 0.22 mol) gave 36.9 g (96% yield) of pentamethylethoxydisiloxane.

2.16.3. Sodiumoxydimethylethoxysilane was synthesized according to procedure 2.16.2 and recrystallized from *n*-pentane. The formed crystals were filtered, washed with cooled *n*-pentane, and dried at a reduced pressure of 1 Torr at 30°C. Found: Na 16.10. Calcd: Na 16.19. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, internal reference sample—TMS):  $\delta = 0.343$  (s, 6H),  $\delta = 1.338$  (t, 3H),  $\delta = 3.750$  (q, 2H).

2.17. *Interaction of bis(dimethylamino)dimethylsilane with Sodium Hydroxide.* The suspension of sodium hydroxide (4.0 g, 0.1 mol) in bis(dimethylamino)dimethylsilane (43.8 g, 0.6 mol) was stirred at 120°C for 10 h. No visible changes in the systems were detected: system remained heterogeneous. The mixture was evaporated at a reduced pressure of 1 Torr; the distilled fraction was collected in a liquid nitrogen cooled trap. The distilled fraction (43.6 g) was based on a pure bis(dimethylamino)dimethylsilane ( $T_b = 127^\circ\text{C}$ ,  $n_D^{25} = 1.4158$ ).

2.18. *Interaction of Dimethyldiethoxysilane with Sodium Hydroxide (1:2).* Sodium hydroxide (24.0 g, 0.6 mol) was added to a solution of dimethyldiethoxysilane (44.4 g, 0.3 mol) in dry toluene (55 mL). The mixture was stirred at 80°C for 1.5 h and at 100°C for 1 h. The formed ethanol was removed from the system by its azeotropic distillation with toluene. The mixture was evaporated from toluene at a reduced pressure of 1 Torr; solid residue was dried at a reduced pressure of 1 Torr at 50°C, suspended in dry *n*-pentane (120 mL), and treated with a solution of trimethylchlorosilane (107.4 g, 0.93 mol) and pyridine (23.7 g, 0.31 mol) in *n*-pentane (240 mL). As a result, we obtained 48.0 g of hexamethyldisiloxane, 2.9 g (5%) of pentamethylethoxydisiloxane (Table 1, no. 1), 30.3 g (65%) of decamethyltetrasiloxane (Table 1, no. 15), and 7.7 g (20%) dodecamethylpentasiloxane (Table 1, no. 16).

2.19. *Interaction of Sodiumoxydimethylethoxysilane with Sodium Hydroxide (1:1).* Sodium hydroxide (8.0 g, 0.20 mol) in 70 mL of dry toluene was added under stirring to a solution of sodiumoxydimethylethoxysilane (28.5 g, 0.20 mol) prepared according to procedure 2.2 (Table 4, no. 1.3). The mixture was stirred at 90 → 100°C for 6.5 h. In this case, the precipitation of a voluminous white solid was observed. After azeotropic drying with toluene, the precipitate was filtered

and dried at a reduced pressure of 1 Torr at 50°C. As a result, we obtained 27.0 g of white powder (%Na = 29.23); after its treatment with a solution of trimethylchlorosilane (71.6 g, 0.61 mol) and pyridine (17.4 g, 0.21 mol) in *n*-hexane (180 mL), we obtained 17.3 g of hexamethyldisiloxane, 20.2 g (65%) of decamethyltetrasiloxane (Table 1, no. 15), and 2.5 g (10%) of dodecamethylpentasiloxane (Table 1, no. 16).

2.20. *Interaction of Tetraethoxysilane with Sodium Hydroxide (1:2).* Sodium hydroxide (8.0 g, 0.20 mol) was added to a solution of tetraethoxysilane (20.8 g, 0.10 mol) in toluene (50 mL), under stirring at 15°C. Temperature in the system was spontaneously increased to 40°C. In this case, the precipitation of a voluminous white solid was observed. The mixture was stirred at 25°C for 3 h and then heated to 75°C. Within 1 h of stirring, the mixture became fully homogeneous. After treatment with a solution of trimethylchlorosilane (23.0 g, 0.21 mol) and pyridine (17.4 g, 0.21 mol) in toluene (80 mL) at -40°C, we obtained 6.1 g (28.4%) of 3,3,5,5-tetraethoxyhexamethyltetrasiloxane (Table 1, no. 17) and 10.8 g undistillable fractions. Found: <sup>1</sup>H NMR of undistillable fractions (CCl<sub>4</sub>, 200 MHz, internal reference sample—TMS): ratio between integral intensities of signals from protons of methyl radical at silicon atoms H<sub>Si(CH<sub>3</sub>)</sub>  $\delta = 0.05$  (s) and ethoxyl groups H<sub>SiOCH<sub>2</sub>CH<sub>3</sub></sub>  $\delta = 1.18$  (t), H<sub>SiOCH<sub>2</sub>CH<sub>3</sub></sub>  $\delta = 3.68$  (q) was equal to 1.7:1. Calcd: for repeat unit -Si(OC<sub>2</sub>H<sub>5</sub>)OSi(CH<sub>3</sub>)<sub>3</sub> 1.80: 1.

### 3. Reactions of Organoalkoxysiloxanes with Sodium Hydroxide and MSOAS

#### 3.1. Interaction of 1,3-diethoxytetramethyldisiloxane with Sodium Hydroxide

3.1.1. Sodium hydroxide (1.8 g, 0.045 mol) was added to a solution of 1,3-diethoxytetramethyldisiloxane (10.0 g, 0.045 mol) in toluene (25 mL) under stirring at 15°C. The mixture was stirred at room temperature until its complete homogenization was attained. The formed ethanol was removed from the system by azeotropic distillation with toluene at a reduced pressure of 10 Torr and at 25–30°C. White powder residue was suspended in *n*-pentane (30 mL) and treated with a solution of trimethylchlorosilane (5.4 g, 0.05 mol) in *n*-pentane (15 mL) at -55°C. As a result, we obtained 8.15 g (98% with respect to the total amount of formed products) of dodecamethylpentasiloxane (Table 1, no. 16).

3.1.2. Sodium hydroxide (2.65 g, 0.066 mol) was added to 1,3-diethoxytetramethyldisiloxane (44.10 g,

0.198 mol) under stirring at 15°C. The mixture was stirred at 26°C until complete homogenization was attained; then, the mixture was evaporated at a reduced pressure of 1 Torr at 30 → 55°C. Distilled fraction (25.7 g) was collected in a liquid nitrogen cooled trap. According to the GLC data, in addition to ethanol, distilled fraction contained dimethyldiethoxysilane (95%) and initial 1,3-diethoxytetramethyldisiloxane (5%). The amount of the formed ethanol agreed with theoretical estimates (3.1 g).

After evaporation, the resulting residue was dissolved in dry *n*-pentane (80 mL) and treated with a solution of trimethylchlorosilane (7.9 g, 0.073 mol) in *n*-pentane (20 mL) at -50°C. As a result, we obtained 8.8 g (69.5%) of pentamethylethoxydisiloxane (Table 1, no. 1), 1.7 g (9.7%) of 1-ethoxyheptamethyltrisiloxane (Table 1, no. 20), and 9.8 g of undistillable fractions.

**3.2. Interaction of 1,3-diethoxytetramethyldisiloxane with Sodiumoxydimethylethoxysilane.** Sodiumoxydimethylethoxysilane (32.0 g, 0.225 mol) prepared according to procedure 2.2 (Table 4, no. 1.3) was dissolved in 1,3-diethoxytetramethyldisiloxane (50.0 g, 0.225 mol). The solution was stirred at a reduced pressure of 40 Torr at 55 → 65°C for 6 h and then for 1 h at 1 Torr and at 55°C. In this case, we obtained 28.7 g (88%) of distilled dimethyldiethoxysilane. The resulting residue was dissolved in *n*-hexane (120 mL) and treated with a solution of trimethylchlorosilane (26.8 g, 0.247 mol) in *n*-hexane (60 mL) at -30°C. As a result, we obtained 10.8 g (25%) of pentamethylethoxydisiloxane (Table 1, no. 1), 4.19 g (7%) of 1-ethoxyheptamethyltrisiloxane (Table 1, no. 20), 5.33 g (15%) of decamethyltetrasiloxane (Table 1, no. 15), and 15.2 g (35%) of dodecamethylpentasiloxane (Table 1, no. 16).

**1-Ethoxyheptamethyltrisiloxane:** <sup>1</sup>H NMR (CCl<sub>4</sub>, 200 MHz, internal reference sample—TMS) δ = 0.377 (s, 6H), δ = 0.400 (s, 6H), δ = 0.486 (s, 9H), δ = 1.500 (t, 3H), δ = 4.08 (q, 2H).

**3.3. Interaction of 1-methoxypentamethyldisiloxane with Sodium Hydroxide.** Solid sodium hydroxide (5.8 g, 0.145 mol) was added to a solution of 1-methoxypentamethyldisiloxane (28.3 g, 0.159 mol) in toluene (50 mL). The mixture was stirred at 40°C for 3.5 h until a complete homogenization of the system was attained. The solution was evaporated from toluene at a reduced pressure of 1 Torr. The resulting residue was colorless viscous liquid, which was dissolved in *n*-hexane (55 mL) and treated with a solution of trimethylchlorosilane

(17.3 g, 0.159 mol) in *n*-hexane (40 mL). As a result, we obtained 1.9 g (7%) of hexamethyldisiloxane, 20.2 g (73%) of octamethyltrisiloxane, 2.7 g (10%) of decamethyltetrasiloxane, and 2.7 g (10%) of dodecamethylpentasiloxane. Yields were calculated with respect to the total amount of isolated trimethylsilyl derivatives (27.6 g).

### 3.4. Interaction of 3,3-dimethylhexaethoxytrisiloxane with Sodium Hydroxide

**3.4.1. Synthesis of 3,3-dimethylhexaethoxytrisiloxane.** A solution of dimethyldichlorosilane (33.5 g, 0.26 mol) in *n*-hexane (80 mL) was added in drops to a solution of sodiumoxytriethoxysilane (105.0 g, 0.52 mol) prepared according to procedure 2.3 in dry *n*-hexane (450 mL) under stirring at -40°C. The mixture was stirred at 25°C for 1 h and at 60°C for 0.5 h. The precipitated residue of sodium chloride was filtered and washed with *n*-hexane; the resulting filtrate was evaporated from *n*-hexane; residue was rectified at a reduced pressure of 1 Torr. As a result, we obtained 60.7 g (56%) of 3,3-dimethylhexaethoxytrisiloxane. Found: *T*<sub>b</sub> = 99°C/1 Torr, *n*<sub>D</sub><sup>25</sup> = 1.3957, *d*<sub>4</sub><sup>25</sup> = 0.9946, *M*<sub>D</sub><sup>R</sup> = 100.59. Si 20.48, C 40.33, H 8.58. Calcd: *M*<sub>D</sub><sup>R</sup> = 100.74, Si 20.22, C 40.31, H 8.71. <sup>1</sup>H NMR (CCl<sub>4</sub>, 200 MHz, internal reference sample—TMS): δ = 0.153 (s, 6H), δ = 1.180 (t, 18H), δ = 3.680 (q, 12H).

**3.4.2. Suspension of sodium hydroxide (0.98 g, 2.45 × 10<sup>-2</sup> mol) in 3,3-dimethylhexaethoxytrisiloxane (10.25 g, 2.45 × 10<sup>-2</sup> mol) was stirred at -35°C for 1 h. No visible indications of the reaction were observed. The mixture was stirred at 15°C for 0.5 h until its homogenization was attained. Volatile reaction products were removed from the system at a reduced pressure of 1 Torr at 20–25°C and collected in a liquid nitrogen. Distilled fraction contained 1.15 g of mixture of ethanol and dimethyldiethoxysilane. The resulting residue was dissolved in *n*-hexane (35 mL) and treated with a solution of trimethylchlorosilane (2.9 g, 2.67 × 10<sup>-2</sup> moles) in *n*-hexane (15 mL). After vacuum fractionation at 1 Torr, we obtained 2.9 g of mixture of 1,1,1-trimethyl,3,3,3-triethoxydisiloxane and tetraethoxysilane. The weight of nonfractionated residue was equal to 5.4 g.**

## 4. Thermal Behavior of MSOAS

### 4.1. Thermal Degradation of Sodiumoxydimethylethoxysilane

**4.1.1. Stirred melt of sodiumoxydimethylethoxysilane (*T*<sub>b</sub> = 70°C) (56.9 g, 0.40 mol) was**

slowly heated under argon from 70 to 200°C. At 185–190°C, an intensive thermal degradation was accompanied by the release of volatile liquid products, which were collected in an ice-cooled trap. After thermal degradation, the system was heated at a reduced pressure of 1 Torr at 190°C for 1 h. Condensate was collected in a liquid nitrogen cooled trap. In total, we obtained 19.1 g of degradation products, which were fully distilled at 45–130°C. According to the GLC data, the condensate contained two compounds: trimethylethoxysilane (95%) and dimethyldiethoxysilane (5%).

After thermal degradation, solid residue (31.3 g, %Na = 27.2) was suspended in *n*-pentane (130 mL) and treated with a solution of trimethylchlorosilane (44.2 g, 0.41 mol) in *n*-pentane (100 mL) at –30°C. As a result, we obtained 40.7 g of trimethylsilyl derivatives, which involved 5.90 g (14.6%) of trimethylethoxysilane, 2.80 g (6.9%) of hexamethyldisiloxane, 1.91 g (4.7%) of octamethyltrisiloxane, 1.02 g (2.5%) of pentamethylethoxydisiloxane, and 29.07 g of distilled fractions.

4.1.2. Solution of sodiumoxydimethylethoxysilane (28.44 g, 0.20 moles) in *n*-undecane (100 mL) was stirred at 185–190°C for 7 h. According to the GLC data, distilled fraction (9.20 g) contained trimethylethoxysilane (95%) and dimethyldiethoxysilane (5%).

The precipitated residue was filtered, washed with dry *n*-hexane, and dried at a reduced pressure of 1 Torr at 60°C. The resulting white powder (16.20 g, %Na = 26.9) was suspended in dry *n*-pentane (75 mL), and treated with a solution of trimethylchlorosilane (23.9 g, 0.22 mol) in *n*-pentane (50 mL) at –30°C. As a result, we obtained 20.9 g of trimethylsilyl derivatives, which contained 3.10 g (14.8%) of trimethylethoxysilane, 1.40 g (6.7%) of hexamethyldisiloxane, 0.90 g (4.3%) of octamethyltrisiloxane, 1.00 g (4.8%) of pentamethylethoxydisiloxane, and 14.50 g of distilled fractions.

4.2. *Thermal Degradation of Sodiumoxytriethoxysilane.* Solution of sodiumoxytriethoxysilane (35.8 g, 0.178 mol) in *n*-undecane (100 mL) was stirred at 180–190°C with slow distillation of the mixture of *n*-undecane and formed tetraethoxysilane for 20 h. In total, 15.8 g of tetraethoxysilane was obtained. The precipitated residue was filtered, washed with dry *n*-pentane, and dried at a reduced pressure of 1 Torr at 100°C (%Na = 20.5). The suspension of the resulting powder in *n*-pentane (70 mL) was treated with a solution of trimethylchlorosilane (21.2 g, 0.195 mol) in *n*-pentane (45 mL) at 35°C. As a result, we obtained

1.5 g of 3,3,5,5-tetraethoxyhexamethyltetrasiloxane (Table 1, no. 17) and 2.3 g of high-boiling liquid fractions ( $T_b > 350^\circ\text{C}$ ). Unreacted precipitate was washed with dimethylsulfoxide to remove sodium chloride; as a result, we obtained 13.2 g of white powder (%Na = 12.1).

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