filter into a calibrated Schlenk flask, and the precipitate was washed with THF (20 mL). According to the data of determination of hydride hydrogen, the solution contained 5.3 g of GaH_3 (0.078 mol) in 160 mL of THF.

Reaction of GaH_3 with isopropyl alcohol. ***A.*** *Ratio of reagents 1 : 1.* A solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL) was introduced into a three-neck flask equipped with a magnetic stirrer, thermometer, addition funnel, and reflux condenser connected with a calibrated buret. Then a solution of Pr^iOH (1.09 g, 0.018 mol) in THF (20 mL) was poured slowly at −10 °C to the mixture; this resulted in a vigorous reaction. The temperature was raised to 20 °C, H_2 (401 mL, 0.018 mol) was released (0 °C, 760 Torr), and the reaction ceased. The THF was evaporated *in vacuo* (1 Torr), and the residue was heated at 50 °C to a constant weight. A viscous product (2.33 g, 98.3% with respect to H_2GaOPr^i) with m.p. 50—60 °C was obtained. IR, ν/cm^{-1}: 1913—1943. Found (%): Ga, 53.01; H, 1.50. Ratio Ga : H = 1 : 1.96. C_3H_9GaO. Calculated (%): Ga, 53.33; H, 1.54. The substance obtained (2 g) was distilled at 80—90 °C and 0.5 Torr. The product (1.4 g) with the ratio Ga : H = 1 : 1.85 was isolated.

B. *Ratio of reagents 1 : 2.* Pr^iOH (2.18 g, 0.036 mol) in THF (40 mL) was added to a solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL) at −5 °C. The reaction rate was retarded after the addition of 1 equiv. alcohol. The reaction proceeded to completion upon heating the reaction mixture to boiling. H_2 (798 mL) was released. The solvent was distilled off *in vacuo*. The yield of the product was 3.4 g (99% with respect to $HGa(OPr^i)_2$). Found (%): Ga, 37.16; H, 0.58. Ratio Ga : H = 1 : 1.02. $C_6H_{15}GaO_2$. Calculated (%): Ga, 36.94; H, 0.53. The substance was distilled at 110—120 °C (1 Torr); purity with respect to H^- was 96% of the theoretical value.

Reaction of GaH_3 with *tert*-butyl alcohol. ***A.*** *Ratio of reagents 1 : 1.* A solution of Bu^tOH (1.33 g, 0.018 mol) in THF (20 mL) was added to a solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL) for 20 min at −5 °C. The reaction mass was gradually heated to 40 °C to release 390 mL of H_2. The solvent was evaporated *in vacuo* (1.0 Torr) at 50 °C. A product in the form of a viscous semitransparent mass was obtained (2.65 g, 99%). Found (%): Ga, 47.86; H, 1.30. Ratio Ga : H = 1 : 1.96. $C_4H_{11}GaO$. Calculated (%): Ga, 48.17; H, 1.39. IR, ν/cm^{-1}: 1942. The substance was distilled *in vacuo* (1.0 Torr) at 80—90 °C with decomposition. The content of H^- in the distillate was 85% of the theoretical value.

B. *Ratio of reagents 1 : 2.* A solution of Bu^tOH (2.66 g, 0.036 mol) in THF (20 mL) was added dropwise at −5 °C to a solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL). The reaction was retarded after the addition of 1 equiv. alcohol; the reaction mixture was heated to boiling, and H_2 (800 mL) was released. The solvent was removed *in vacuo*. A product in the form of a crystalline mass with m.p. 70—80 °C was obtained in 99.5% yield (4.11 g). IR, ν/cm^{-1}: 1942. Found (%): Ga, 31.91; H, 0.44. Ratio Ga : H = 1 : 0.96. $C_8H_{19}GaO_2$. Calculated (%): Ga, 32.17; H, 0.46. The substance was distilled at 80—90 °C and 1 Torr. Purity with respect to H^- was 93% of the theoretical value.

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Unusual exchange of functional groups at the silicon and metal atoms

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Reactions of α,ω-dichlorooligosilanes with metal hydroxides in the presence of pyridine results in the exchange of halogen and oxygen atoms and the formation of cyclic siloxyoligosilanes and pyridine complexes of metal halides. The metallosiloxane groups are not formed. A scheme for the transformations observed is proposed.

Key words: exchange reactions, metal complexes, polysilanes.

In all cases studied so far,[1] reactions of organochlorosiloxanes with metal hydroxides resulted in the formation of a metallosiloxane fragment according to the scheme

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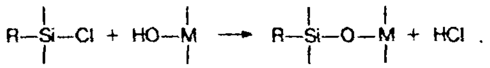
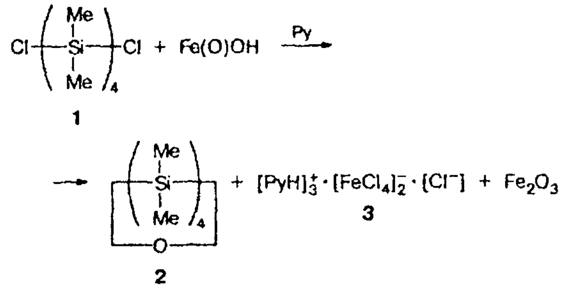


$$\mathrm{R{-}Si{-}Cl + HO{-}M \rightarrow R{-}Si{-}O{-}M + HCl}\ .$$

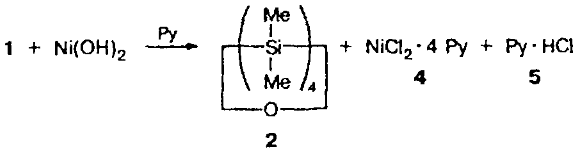
The study of analogous reactions for the cases where the silicon atom is incorporated into a polysilane chain is the purpose of this work.

Results and Discussion

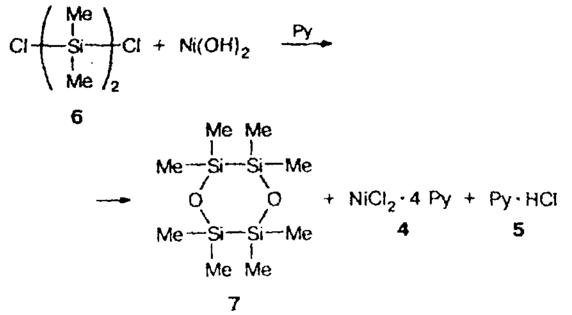
We established that the reactions of permethyl-α,ω-dichlorooligosilanes with iron and nickel hydroxides occur in a different way. An exchange of functional groups at the silicon and metal atoms occurs, which is accompanied by the formation of cyclosilanes containing siloxane fragments and complex compounds of metal halides. The reaction of 1,4-dichlorooctamethyltetrasilane (**1**) with iron oxide-hydroxide in the presence of pyridine results in the formation of octamethyloxatetrasilacyclopentane (**2**) and iron chloride complex (**3**).



The reaction of dichlorooligosilane **1** with nickel hydroxide leads to heterocycle **2**, complex **4**, and pyridine hydrochloride (**5**).

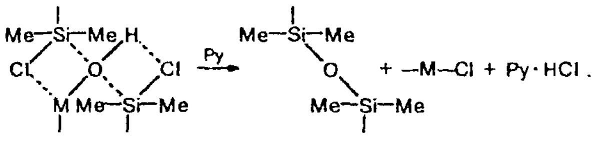


In the case of 1,2-dichlorotetramethyldisilane (**6**) as the starting compound, the reaction with nickel hydroxide results in 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxatetrasilacyclohexane (**7**).



The formation of compounds containing both silicon and metal atoms was observed in neither case. These transformations do not occur in the absence of pyridine.

The nontraditional direction of the reaction is possibly explained by the fact that the conjugation of the σ-type[2] exists in the polysilane chain, which results in the tendency of the silicon atom to coordination with the nucleophilic centers. The simultaneous formation of the siloxane fragment SiOSi and HCl can be represented by a scheme involving an intermediate spirocyclic complex:



Spirocyclic complexes consisting of four-membered cyclic fragments of this type are most typical of organic and inorganic metal compounds and of metalloorganosiloxanes.[3] The transformation is observed only in the presence of Py. This indicates that the decomposition of the transition complex in the direction of exchange of functional groups occurs due to the shift of the equilibrium owing to the binding of HCl in the form of Py · HCl.

Thus, we have established the unusual direction of the reactions of dichlorooligosilanes with iron and nickel hydroxides involving the exchange of oxygen and halogen atoms between the metal- and silicon-containing fragments.

Experimental

IR spectra were obtained on a Specord M-82 spectrometer (suspensions in Nujol between KBr plates), and UV spectra were obtained on a Specord M-40 spectrometer in the 180—500 nm range in a 0.1-cm cell.

The starting dichlorooligosilanes **1** and **6** were obtained by the known procedure.[4] Pyridine (1.6 g, 20 mmol) was added to a suspension of anhydrous Fe(O)OH [5] (0.9 g, 10 mmol) in a MeCN—toluene (1 : 1) mixture (10 mL), and then a solution of oligosilane **1** (3 g, 10 mmol) in toluene (10 mL) was added with stirring. The reaction mixture was refluxed until dichlorooligosilane disappeared (the absence of the acid reaction in an aqueous extract of the reaction mixture), and cooled. The unconsumed Fe(O)OH was filtered off. The precipitate of Fe_2O_3 formed in the reaction remains insoluble (yield 0.1 g, 55%) after dissolution of Fe(O)OH in a concentrated alkali solution at 70 °C. Yellow crystalline product **3** (1.06 g, 72%) was isolated on slow concentration of the filtrate obtained after separation of Fe(O)OH and Fe_2O_3. The concentration was performed until the precipitation of **3** ceased and the reaction solution became colorless. The product obtained after recrystallization from a toluene—*n*-butanol (1 : 1) mixture forms large single crystals. The unit cell parameters determined by X-ray diffraction analysis corresponded exactly to the previously published[6] data for compound **3**. After the complete removal of the solvents from the reaction mixture, a colorless product slowly crystallizing at 0 °C was obtained. Compound **2** was obtained in 68% yield (1.69 g), m.p. 44—

46 °C (*cf.* Ref. 7: m.p. 45 °C). Found (%): Si, 44.80. $C_8H_{24}OSi_4$. Calculated (%): Si, 45.19. IR (KBr), ν/cm^{-1}: 1050 (SiOSi). UV (hexane), λ_{max}/nm: 236.

The reaction of dichlorooligosilane **1** (3 g, 10 mmol) with anhydrous $Ni(OH)_2$ [5] (0.92 g, 10 mmol) and Py (3.2 g, 40 mmol) was performed in a similar way. Green crystalline product **4** (64% yield, 1.43 g) corresponds in composition to the complex described previously.[8] Found (%): Cl, 16.21; N, 11.97; Ni, 13.80. $C_{20}H_{20}Cl_2N_4Ni$. Calculated (%): Cl, 15.89; N, 12.56; Ni, 13.15. Heterocycle **2** (1.61 g, 65%) was obtained after product **4** was separated from the reaction mixture and the solvents were removed. Compound **5** (0.66 g, 57%) was isolated by aqueous extraction from the remained solid residue. IR (KBr), ν/cm^{-1}: 2600 (≡N · HCl).

The reaction of dichlorodisilane **6** (1.87 g, 10 mmol) with $Ni(OH)_2$ (0.93 g, 10 mmol) and Py (3.2 g, 40 mmol) gave compound **4** (1.95 g, 87.4%), heterocycle **7** (0.91 g, 69%), and compound **5** (0.82 g, 70.6%). The compounds were isolated from the reaction mixture by a similar scheme. Found (%): C, 35.80; H, 8.92; Si, 41.93. $C_8H_{24}O_2Si_4$. Calculated (%): C, 36.30; H, 9.14; Si, 42.45. IR (KBr), ν/cm^{-1}: 1050 (SiOSi). UV (hexane), λ_{max}/nm: 200.

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Reaction of 5-allyl-2,5-dichloro-4,4-dimethoxy-3-morpholinocyclopent-2-enone with Me_3SiI

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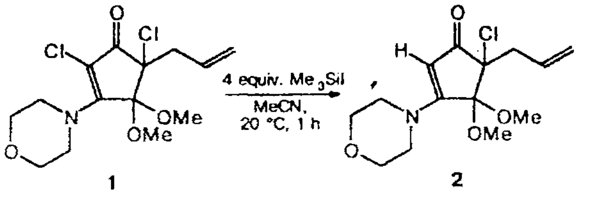
5-Allyl-2,5-dichloro-4,4-dimethoxy-3-morpholinocyclopent-2-enone reacts with Me_3SiI in MeCN to give the corresponding product of reductive vinylic monodechlorination.

Key words: α,α′-dichlorocyclopentenone, iodotrimethylsilane, reductive monodechlorination.

The reaction of dichloroenamineketone (**1**)[1] with Me_3SiI in a solution of MeCN occurs as reductive dechlorination to form compound **2** in ~80% yield.



1 **2**

Note that the chloroenaminoketone fragment in compound **1** and related cyclopentenones differs from that in the corresponding systems devoid of Cl by its pronounced chemical "inertness." Among the transformations studied of this class of compounds,[2—9] transformation **1**→**2** is the first example of the reaction involving the vinylic Cl atom. It is of interest to study the mechanism of formation of **2**. This reaction extends the synthetic potentialities of Me_3SiI as the reagent. The known variants of application of Me_3SiI in the synthesis include the cleavage of ethers and esters, ketals, preparation of

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