Letters to the Editor

Compounds containing the structural fragment O—Si—O, generators of silanones

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We discovered a new liquid-phase reaction making it possible to generate silanones with different substituents at normal or higher pressure in the presence of catalytic additives (2—5 mol. %) such as cation exchange resins, Lewis acids, KOH, *etc.* from compounds containing the structural fragment O—Si—O.

Thermolysis of these compounds does not occur in the absence of catalysts. The thermolysis products were identified by GLC and mass-spectroscopy techniques.

It was established that during the thermolysis of tetraethoxysilane (TEOS) in the presence of the catalyst at normal or higher pressure, conversion of TEOS ranges from 16 % to 50 % after 3—6 hs.

Besides the initial TEOS, diethyl ether (10—16 %), hexaethoxysilane (11—17 %), octaethoxytrisiloxane (6—11 %), and high-boiling compounds (HBC) (4—6 %) were found in the reaction mixture. The products of thermolysis were isolated and identified, except HBC.

$$\mathrm{Si(EtO)_4 \longrightarrow EtOEt + (EtO)_3SiOSi(OEt)_3 + (EtO)_3SiOSi(OEt)_2OSi(OEt)_3 + HBC}$$

Diethyl ether and probably the unstable unsaturated compound diethoxysilanone (**1**) are formed during catalytic thermolysis of TEOS. Compound **1** is inserted at the Si—O bond of the initial TEOS to give the corresponding siloxanes:

$$\mathrm{Si(OEt)_4 \longrightarrow EtOEt + \underset{\mathbf{1}}{[(EtO)_2Si{=}O]}}$$

$$\mathrm{[(EtO)_2Si{=}O] + Si(OEt)_4 \longrightarrow (EtO)_3SiOSi(OEt)_3 \xrightarrow{\mathbf{1}} \longrightarrow (EtO)_3SiOSi(OEt)_2OSi(OEt)_3}$$

Cothermolysis of TEOS and hexamethyldisiloxane (HMDS) used as a trapping reagent for **1** was carried out in order to confirm generation of **1** from TEOS. In addition to the compounds usually formed by the homothermolysis of TEOS, we found products of the interaction between silanone and the Si—O bond of HMDS:

$$n\mathrm{[O{=}Si(EtO)_2] + Me_3SiOSiMe_3 \longrightarrow Me_3Si[OSi(OEt)_2]_{\mathit{n}}OSiMe_3} \quad (n = 1, 2)$$

Diethyl ether and ethoxysiloxanes were also produced during thermolysis of various organoethoxysilanes. Ethoxysiloxanes presumably resulted from the insertion

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of the generated silanone into the Si—O bonds of the initial and new compounds:

$$(EtO)_{4-n}SiR_n \longrightarrow [(EtO)_{2-k}R_kSi{=}O] + EtOEt$$

R = Me, Vin, Ph;
$n = 0, 1, 2$; $k = 1, 2$

Using GLC and mass-spectrometry, we showed that simple ethers and silanones are formed as a result of the catalytic thermolysis of organyloxysiloxanes. Reaction of silanones with the Si—O bond of the initial compound leads to the corresponding siloxanes and makes it possible to synthesize various inaccessible siloxanes.

$$(R'O)_{4-n}SiR_n \longrightarrow [(R'O)_{2-k}R_kSi{=}O] + R'OR'$$

R = Me, Vin; R′ = Me, Ph;
$n = 0, 1, 2$; $k = 0, 1$

Conversion of the initial organyloxysilane was found to depend on both the substituent at silicon atom and the type of catalyst.

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Symmetrization of carboranyl derivatives of tin in the course of synthesis of carboranyltinphenylsiloxane

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Introduction of tin atoms bonded to σ ligands (Me or Ph) into the siloxane framework is not accompanied by side reactions.[1,2] We studied the possibility of synthesis of tinorganosiloxanes containing the carboranyl group at the Sn atom by the reaction of a butanol solution of organosilanolate $C_6H_5Si(ONa)_3 \cdot 6Pr^nOH$ (see Ref. 3) with a benzene solution of $(o\text{-}C_2H_2B_{10}H_9\text{-}9)SnCl_3$ (see Ref. 4) at an equimolar ratio of Na^+ and Cl^- in the reaction system. The experimental data unambiguously confirm that when organosilanolate —Si—ONa groups react with halides of polyvalent metals, the metallosiloxane —Si—O—M— group is formed.[5] However, we obtained dicarboranyltin oxide (**1**)[6] and tinphenylsiloxane (**2**) instead of the expected carboranyltinphenylsiloxane. Apparently, the carboranyltinphenylsiloxane formed initially undergoes conversions resulting in symmetrization of the ligand environment about Sn. A number of Sn atoms (which do not contain carboranyl groups) are incorporated into the siloxane framework. The process may be represented by the following scheme:

$$PhSi(ONa)_3 + (o\text{-}C_2H_2B_{10}H_9\text{-}9)SnCl_3 \xrightarrow{-3NaCl}$$
$$\longrightarrow (PhSiO_{1.5})[(o\text{-}C_2H_2B_{10}H_9\text{-}9)SnO_{1.5}] \longrightarrow$$
$$\longrightarrow \underset{\mathbf{1}}{0{,}5[(o\text{-}C_2H_2B_{10}H_9\text{-}9)_2SnO]} + \underset{\mathbf{2}}{0{,}5(PhSiO_{1.5})(SnO_2)}$$

After the removal of NaCl, which was separated out from the organic medium, the reaction mixture was concentrated. The crystals of **1** were separated and recrystallized from benzene. The yield of **1** was 58 %. Found (%): B, 51.12; Sn, 28.75, Si is absent. $C_4H_{22}B_{20}SnO$. Calculated (%): B, 51.34; Sn, 28.19. IR, ν/ cm^{-1}: 2598—26039 (C—H in carborane); 1140 (δ(C—H) in B-substituted *o*-carborane); 726—729 (icosahedral skeleton). The bands were assigned based on the data reported previously.[7—9] Distillation of the reaction solution after the removal of **1** affords amorphous product **2**, which was purified by reprecipitation from the benzene solution with hexane. The yield of **2** was 66 %. Found (%): Si, 15.78; Sn, 32.68. $C_{12}H_{10}Si_2O_5Sn$. Calculated (%): Si, 15.46; Sn, 33.13. IR, ν/cm^{-1}: 1130 (P—Si), 1050—1000 (S—O—Si), 950—958 (Si—O—Sn).

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