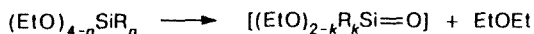
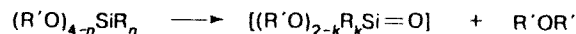


of the generated silanone into the Si—O bonds of the initial and new compounds:



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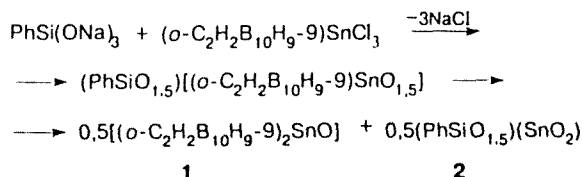
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Symmetrization of carboranyl derivatives of tin in the course of synthesis of carboranyltinphenylsiloxane

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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 $\text{C}_6\text{H}_5\text{Si}(\text{ONa})_3 \cdot 6\text{Pr}^n\text{OH}$ (see Ref. 3) with a benzene solution of (*o*- $\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9$ -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 metallo-siloxane —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:



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. $\text{C}_4\text{H}_{22}\text{B}_{20}\text{SnO}$. Calculated (%): B, 51.34; Sn, 28.19. IR, ν/cm^{-1} : 2598—26039 (C—H in carborane); 1140 ($\delta(\text{C—H})$ 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. $\text{C}_{12}\text{H}_{10}\text{Si}_2\text{O}_5\text{Sn}$. 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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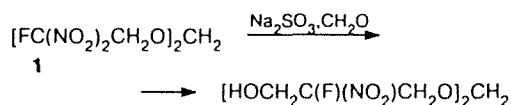
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Effect of the nucleophile on the direction of denitration of compounds with two fluorodinitromethyl groups

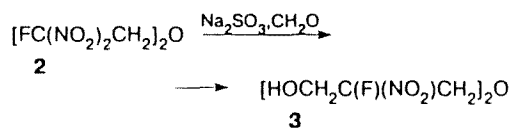
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Previously,¹ it was demonstrated that both fluorodinitromethyl groups are involved in the reaction of 1,7-difluoro-1,1,7,7-tetranitro-3,5-dioxaheptane (**1**) with Na₂SO₃ in an aqueous-methanolic solution of formaldehyde:

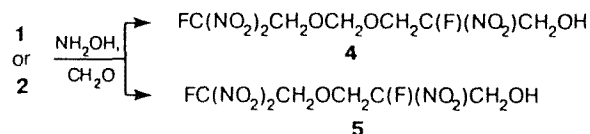


The reaction with 1,5-difluoro-1,1,5,5-tetranitro-3-oxapentane (**2**) proceeds in a similar fashion:²



We isolated and identified the previously unknown 2,6-difluoro-2,6-dinitro-4-oxa-1,7-heptanediol (in the form of diacetate); the yield was 80 %.

In this work we found that, unlike Na₂SO₃, NH₂OH denitrates compounds **1** and **2** at only one of the fluorodinitromethyl groups:



Examples of this direction of denitration of compounds with two fluorodinitro- or trinitromethyl groups have not been described until now.

2,6-Difluoro-2,6-dinitro-4-oxa-1,7-heptanediol. M.p. 62–64 °C, the purity grade was 99.1 % (GLC). ¹H NMR (CD₃CN), δ: a mixture of optical isomers: 2.04 (s, 6 H, CH₃); 4.00–4.43 (m, 4 H, CF(NO₂)CH₂O, AB is the portion of the ABX spectrum); 4.50–4.70 (m, 4 H, CH₂OC(O)CH₃, AB is the portion of the ABX spectrum). IR, ν/cm⁻¹: 803, 847 (NO₂); 1059, 1221 (C–O); 1146 (C–F); 1312, 1589 (C–NO₂); 1756(C=O); 2920, 2943 (CH₂).

2,8-Difluoro-2,8,8-trinitro-4,6-dioxa-1-octanol (**4**) was formed in a yield of 37–38 % under the action of NH₂OH (9-fold excess, 0–5 °C, 1 h) on **1**. The reaction mixture was poured into water, and unreacted **1** was isolated and extracted with Et₂O. Then the solvent was removed, and compound **4** was identified in the form of acetate (colorless oil, n_D²⁰ 1.4463). Found (%): C, 27.44; H, 3.01; F, 10.64; N, 11.97. C₈H₁₁F₂N₃O₁₀. Calculated (%): C, 27.66; H, 3.17; F, 10.95; N, 12.10. ¹H NMR (CD₃CN), δ: 1.99 (s 3 H, CH₃); 4.18 (2 H, OCH₂CF(NO₂), AB is the portion of the ABX spec-