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trans-Silylation of silatranes and 1,2-dimethyl-2-azasilatran-3-one by Si-substituted trimethoxysilanes

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Abstract

trans-Silylation of silatranes by Si-substituted trimethoxysilanes has been found to be a reversible reaction, the equilibrium of which is shifted towards the formation of the silatrane bearing a stronger (shorter) transannular N→Si bond. A related reaction of 1,2-dimethyl-2-azasilatran-3-one with Si-substituted trimethoxysilanes leads to products in good yields only when phenyltrimethoxysilane is used. © 2000 Elsevier Science Ltd. All rights reserved.

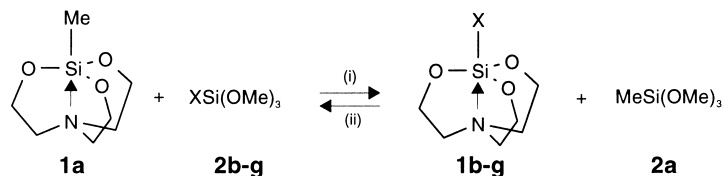
Keywords: silicon; trialkoxysilanes; silatranes; *trans*-silylation; transannular bond.

The transannular N→Si bonding and the cage structure determine a number of features of chemical and physical properties of silatranes including methods for their preparation.^{1–3} The gain in energy due to the formation of the intramolecular N→Si bond affords a high yield of monomeric silatranes instead of polymeric products in the classical route to these compounds, i.e. reactions of trifunctional silanes with tris-(2-hydroxyalkyl)amines or their derivatives. A fine balance between the energy of transannular and conjugative interactions in the reactants and products results in a high yield of 1-hydro- and 1-organylsilatranes in reactions of boratrane with triethoxysilane,⁴ organyltriethoxysilanes⁵ and even some tetraorganylsilanes.⁵ Similarly, treatment of 2,8,9-triazaalumatrane with methyltriethoxysilane leads to 1-methyl-2,8,9-triazasilatrane.⁶ These data stimulated our interest in the previously unknown *trans*-silylation of silatranes and their poorly studied analogs, 2-azasilatran-3-ones,⁷ by Si-substituted trialkoxysilanes.

We found that *trans*-silylation of silatranes by trialkoxysilanes is generally a reversible and highly chemoselective process. Thus, forward reactions (i) between 1-methylsilatrane **1a** and Si-substituted trimethoxysilanes **2b–g** lead to nearly the same resultant equilibrium mixtures as those

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produced in the reverse reactions (ii) between silatranes **1b–g** bearing the corresponding substituent X and methyltrimethoxysilane **2a** (Scheme 1). Under MeONa catalysis, these reactions, occurring at 150°C in dry CDCl₃ in sealed ampoules, reach equilibrium within 1.5 h, by-product formation being negligible.⁸ The **1b–g:1a** ratio in equilibrium mixtures was found to be dependent on the nature of the Si-substituent and, hence, on the strength of the transannular Si←N bonding in both reacting and forming silatranes.



Scheme 1. X = ClCH₂ (**b**), Cl₂CH (**c**), vinyl (**d**), Ph (**e**), MeO (**f**), Cl (**g**)

Table 1 displays the Si←N bond lengths (d_{SiN}) of silatranes **1b–g** in CDCl₃[†] and the results of reacting silatranes **1a–g** with trimethoxysilanes **2a–g**.¹⁰ The data obtained demonstrate a regular trend towards a shift of equilibrium of the *trans*-silylation reactions (i) and (ii) towards the formation of the silatranes with the shorter transannular N→Si bond (for **1a**, $d_{\text{SiN}} = 2.24$ Å).

Table 1
The Si→N bond lengths of silatranes **1b–g** in CDCl₃ and their relative content (**1b–g:1a**) in equilibrium mixtures as well as isolated yields in reactions (i)

Silatranes	d_{SiN} , Å	1b–g:1a	% isolated yield
1b	2.14	96:4	89
1c	2.10	100:0	81
1d	2.19	80:20	52
1e	2.18	91:9	78
1f	2.12	95:5	91
1g	2.05	100:0	58

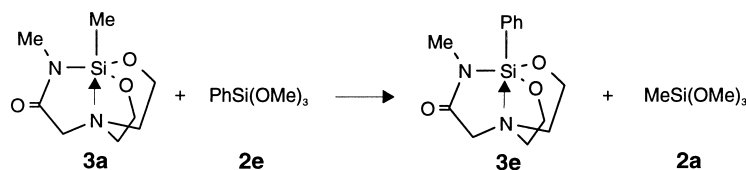
Similar results were obtained when these reactions were performed without solvent and when trimethoxysilanes **2a–g** were replaced by the corresponding triethoxysilanes. In the absence of the catalyst, *trans*-silylation proceeds more slowly.

The efficient *trans*-silylation of 1-methylsilatranes by trialkoxysilanes having a more electro-negative substituent X than a methyl group is of interest. This reaction not only demonstrates the

[†] The d_{SiN} values for silatranes in CDCl₃ solutions were estimated from their ¹⁵N NMR chemical shifts, δ , using the previously established⁹ linear correlation: $d_{\text{SiN}} = -4.30 - 1.82 \times 10^{-2} \delta$. The latter is based on the corresponding solid-state and gas-phase data and is interpolated on the solutes.

key role of the N→Si bond in the formation of silatranes, it also opens a new route to these compounds which are inclined to undergo a Si–X bond cleavage under routine synthetic procedures.^{2,3}

trans-Silylation of 1,2-dimethyl-2-azasilatran-3-one **3a** by trimethoxysilanes **2b–g** under similar conditions appears to be a less chemoselective process. According to NMR, reactions of azasilatranone **3a** with most of the trimethoxysilanes are plagued by a number of side-reactions to give complex mixtures of by-products with non-cage structures together with just a small amount of the target compounds. Only the use of phenyltrimethoxysilane **2e** resulted in a good (60%) yield and moderate (38%) isolated yield of the expected azasilatranone **3e** (Scheme 2).¹¹ These results probably reflect a weaker transannular N→Si bonding in azasilatranones than in related silatranes and the high sensitivity of their amido Si–N bond to both electrophile and nucleophile attack.



Scheme 2.

Acknowledgements

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- Typical procedures: A 1:1 mixture of the reagent **1a–f** and **2a–f** families (0.05 mol) and a few drops of the catalyst (MeONa in MeOH) in 10 mL of dry CDCl₃ were kept for 1.5 h in sealed ampoules at 150°C (oil bath). The resultant solution was then analyzed by ¹H and ²⁹Si NMR spectroscopy methods before isolation of their components, the relative amounts of which were determined by integration of the corresponding ¹H NMR peaks. The reaction mixtures containing 1-chlorosilatranone **1g**, which is poorly soluble in CDCl₃, were analyzed by ¹H NMR after the isolation and dissolving of the crystalline material in D₂O. The NMR parameters observed for silatranes **1a–g** were consistent with those published earlier: see, for example, Refs. 1 and 2.
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- The isolated yields of silatranes **1b–g** in forward reactions (i) were determined after purification of the crude products. The purification procedure included removal of the solvent and the well sublimating initial silatranone **1a**

from the reaction mixtures under a high vacuum at 80°C and recrystallization of the solid residue using appropriate solvents. Melting points of the isolated compounds agree with those found previously.^{1,2}

11. Synthesis of 1-phenyl-2-methyl-2-azasilatran-3-one **3e**: Phenyltrimethoxysilane (4.32 g, 0.02 mol) was added to a solution of azasilatranone **3a** (3.96 g, 0.02 mol) in 25 mL of dry CDCl₃. The reaction mixture was kept for 2 h in sealed ampoule at 100°C (oil bath). The resultant solution was analyzed by NMR spectroscopy. It was then concentrated under vacuum and the solid residue was recrystallized three times from a mixture of benzene:Et₂O (3:1) to give **3e** (2.11 g, 38%) as a cream-colored, sensitive to moisture, powder. Compound **3e**: m.p. 238–239°C; δ_{H} (400.1 MHz, CDCl₃) 2.41 (s, 3H), 2.91 (dt, ²*J* = 12.0 Hz, ³*J* = 5.9 Hz, 2H), 3.08 (dt, ²*J* = 12.0 Hz, ³*J* = 5.9 Hz, 2H), 3.49 (s, 2H), 3.96 (t, ³*J* = 5.9 Hz, 4H), 7.26 (m, 3H), 7.70 (m, 2H); δ_{C} (100.6 MHz, CDCl₃) 32.1, 53.1, 55.9, 57.6, 127.4, 128.2, 135.0, 141.9, 172.5; δ_{Si} (79.5 MHz, CDCl₃) -79.0. Found: C, 55.78; H, 6.13; N, 10.23; Si, 9.57. C₁₃H₁₈N₂O₃Si requires: C, 56.09; H, 6.52; N, 10.06; Si, 10.09.