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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on his 70th anniversary

Reaction of Sodium Amide with 1-Chloromethylsilatrane

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Abstract—The reaction of 1-chloromethylsilatrane with sodium amide in benzene is accompanied by ring expansion with formation of 1-amino-2-carba-3-oxahomosilatrane.

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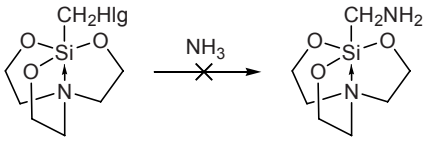
Anomalously high reactivity of amines $RR'NCH_2Si(OCH_2CH_2)_3N$ containing a silatrane fragment in the α-position [1–3] suggests that the primary amine $H_2NCH_2Si(OCH_2CH_2)_3N$ could reveal unusual chemical properties. Unfortunately, synthesis of this compound has not been reported. A classical method for building up C–N bond is based on reactions of alkyl halides with ammonia and amines, which are widely used in organosilicon chemistry for the synthesis of aminoalkylsilanes $RR'N(CH_2)_nSiX_3$ [4, 5]. 1-Haloalkylsilatranes are known to react with tertiary amines to give the corresponding ammonium salts [6, 7]. The goal of the present work was to study the amination of 1-halomethylsilatranes with NH_3 and sodium amides.

1-Chloromethylsilatrane failed to react with ammonia at 60–80°C under pressure over a period of 6 h, and attempts to catalyze the process using NaI, KI, or $(n\text{-Bu})_4N^+ I^-$ were unsuccessful (Scheme 1).

Scheme 1.



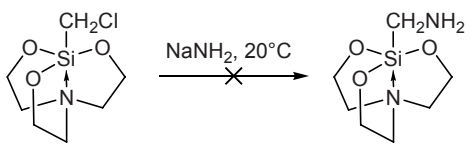
Hlg = Cl, I.

Even traces of the desired product, 1-aminomethylsilatrane, were not detected in the reaction mixtures, while 1-chloromethylsilatrane was recovered almost quantitatively. In the reaction with more reactive 1-iodomethylsilatrane, ~95% of the initial compound was recovered from the reaction mixture, and a small amount of oligomeric products was obtained, but their ^1H NMR spectra contained no signals assignable to silatrane fragment. Halogen substitution in primary alkyl halides usually follows S_N2 mechanism which is also operative in the amination of chloromethyl(alkoxy)silanes [8]. Presumably, 1-halomethylsilatrane is inactive toward amination due to reduced positive charge on the $ClCH_2Si$ carbon atom as a result of strong donor effect of the silatrane fragment [9, 10].

Higher reactivity of anions compared to neutral molecules in nucleophilic substitution reactions was successfully utilized in the chemistry of silatranes. For example, 1-haloalkylsilatranes reacted with alkali metal thiolates RSM (M = Na, K) to give the corresponding 1-(organylsulfanyl)alkylsilatranes [11], while reactions with alkali metal amides were successfully used to obtain a series of 1-aminoazasilatranes [12]. We anticipated that amination of 1-chloromethylsilatrane with sodium amide will produce the desired 1-aminomethylsilatrane.

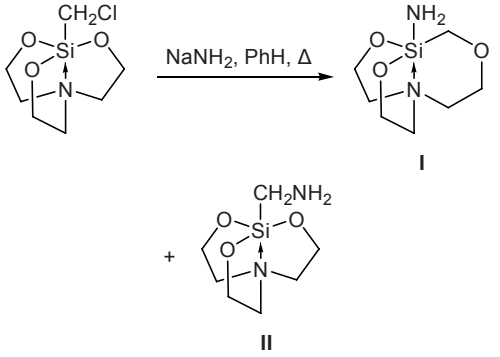
However, 1-chloromethylsilatrane failed to react with sodium amide in benzene at room temperature (Scheme 2); even after 3 days, the NMR spectra of the reaction mixture contained only signals of the initial silatrane and ~5% of tris(2-hydroxyethyl)amine formed as a result of decomposition of the atrane

Scheme 2.



skeleton. Analysis of the reaction mixtures by NMR spectroscopy on different nuclei showed the presence of a considerable amount of initial 1-chloromethylsilatrane even after heating for 28 h under reflux, and the major product was 1-amino-2-carba-3-oxahomosilatrane (1-amino-3,9,10-trioxa-6-aza-1-silabicyclo[3.3.4]-dodecane) (**I**). The target 1-aminomethylsilatrane (**II**) was formed in a poor yield (Scheme 3).

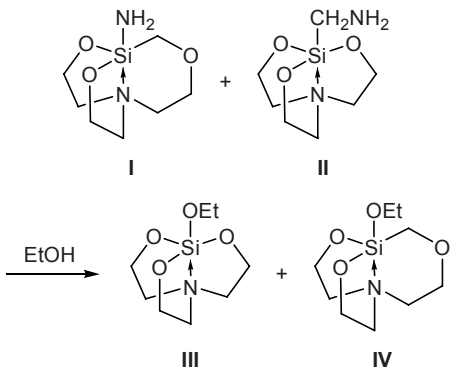
Scheme 3.



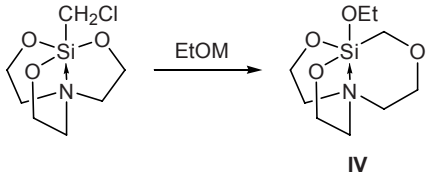
Initial 1-chloromethylsilatrane separated almost completely from the reaction solution on cooling; therefore, it can be readily removed from the reaction mixture. Unfortunately, all our attempts to isolate compounds **I** and **II** as individual substances by recrystallization or column chromatography were unsuccessful. Both these compounds turned out to be unstable to hydrolysis, and they readily formed solvate complexes with such solvents as DMF, DMSO, and HMPA. By heating silatrane mixture **I**/**II** in anhydrous ethanol we obtained 1-ethoxysilatrane **III** (product of Si–C bond cleavage in compound **II**; its spectral parameters were identical to those given in [13]) and compound **IV** which was identified as 1-ethoxy-2-carba-3-oxahomosilatrane [14] (Scheme 4).

Expansion of the atrane ring in 1-chloromethylsilatrane with formation of 1-alkoxy-2-carba-3-oxahomosilatranes by the action of alkoxides in dioxane was reported for the first time in 1986 [14] (Scheme 5).

Scheme 4.



Scheme 5.



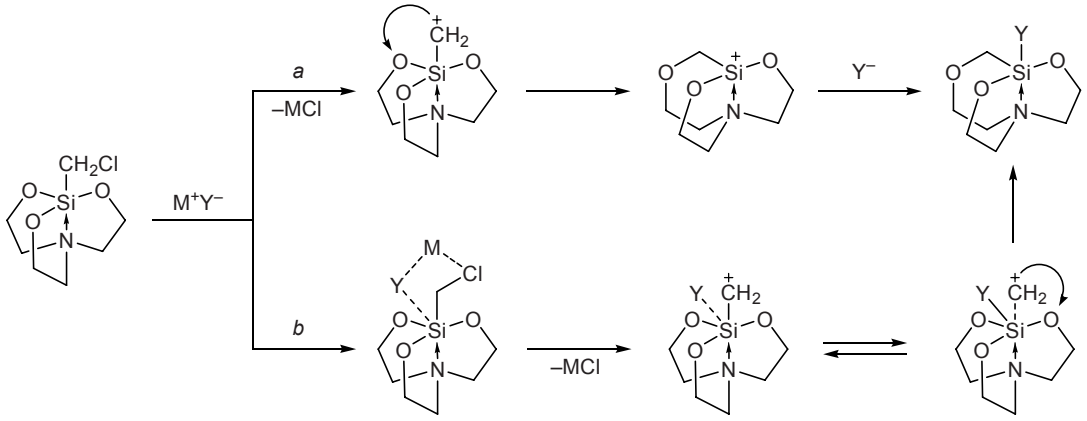
The structure of the products was proved [14, 15], but no assumption were made on the reaction mechanism. Several possible mechanisms for the observed ring expansion may be proposed (Scheme 6). One of these involves initial elimination of MCl with formation of $CH_2^+Si(OCH_2CH_2)_3N$ cation which then undergoes rearrangement into stable homosilatrane cation $^+Si(OCH_2CH_2)_2(CH_2OCH_2CH_2)N$ with migration of the cationic center to the silicon atom (path *a*). This reaction path is substantiated by the fact that silyl cation $CH_3SiH_2^+$ is more stable than carbenium ion $^+CH_2SiH_3$ [16]. Addition of alkoxide or amide ion to the silyl cation completes the process. Another possible mechanism is synchronous (path *b*). Cleavage of the Si–O–C bond by the action of alkali metal alkoxide, followed by intramolecular nucleophilic substitution, as proposed in [6], seems to be less probable. This reaction path does not agree with the fact that reactions of 1-iodosilatrane with alkali metal alkoxides or thiolates RZM (Z = O, S; M = Na, K) give the corresponding alkoxy- or alkylsulfanylsilatranes in high yields, whereas no products resulting from cleavage of the atrane skeleton were detected.

EXPERIMENTAL

The NMR spectra were recorded from 20% solutions in $CDCl_3$ or CD_3CN on a Jeol-90Q spectrometer using tetramethylsilane as internal reference. The IR spectra were obtained on a Specord 75IR instrument. The solvents used were dehydrated according to standard procedures [17]. Liquid ammonia was dehydrated by treatment with metallic sodium and subsequent distillation. All reactions were carried out under dry argon.

Reaction of 1-chloromethylsilatrane with sodium amide in liquid ammonia. 1-Chloromethylsilatrane, 2.23 g (0.01 mol), was added under stirring to a solution of sodium amide prepared according to the procedure described in [18] from 0.23 g of sodium and

Scheme 6.



50 ml of anhydrous liquid ammonia in the presence of 0.001 g of $Fe(NO_3)_3 \cdot 6H_2O$. Ammonia was evaporated, 100 ml of benzene was added to the residue, and the mixture was stirred for 28 h on heating under reflux. The mixture was filtered while hot, the precipitate was treated with anhydrous benzene (2×50 ml), and the extracts were combined with the filtrate. The undissolved material (0.3 g) was initial 1-chloromethylsilatrane, mp 203–205°C. ^{1}H NMR spectrum, δ, ppm: 2.62 (2H, $ClCH_2$), 2.90 (6H, NCH_2), 3.86 (6H, CH_2O). ^{29}Si NMR spectrum: δ_{Si} –77.9 ppm. The filtrate was kept for 24 h at 10°C in a refrigerator, and the precipitate was filtered and dried. According to the ^{1}H and ^{29}Si NMR data, it was initial 1-chloromethylsilatrane (1.33 g, 60%). The mother liquor was concentrated to a volume of 10 ml (until it became turbid) and was kept for 3 days at 10°C in a refrigerator. The precipitate was filtered off, washed with anhydrous diethyl ether, and dried under reduced pressure. We thus isolated 0.42 g of a product which, according to the ^{1}H, ^{13}C, and ^{29}Si NMR data, was a mixture of compounds **I** and **II** at a ratio of ~10:1. IR spectrum, ν, cm^{-1}: 460, 615, 770, 800, 820, 910, 945, 1070, 1100, 1130, 1280, 1620, 2700, 2870, 2900, 2930, 3430, 3500.

3,9,10-Trioxa-6-aza-1-silabicyclo[4.3.3]dodecan-1-amine (I). ^{1}H NMR spectrum, δ, ppm: 2.21 (2H, CH_2O), 3.05 (2H, CH_2N), 3.12 (4H, CH_2N), 3.68 (4H, OCH_2), 3.99 (2H, OCH_2). ^{13}C NMR spectrum, δ_C, ppm: 53.94 (CH_2N), 59.64 (CH_2O), 60.09 (OCH_2), 67.86 (CH_2N), 68.12 (OCH_2). ^{29}Si NMR spectrum: δ_{Si} –83.8 ppm.

2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-ylmethanamine (II). ^{1}H NMR spectrum, δ, ppm: 1.97 (2H, CH_2), 2.84 (6H, CH_2N), 3.78 (6H, OCH_2). ^{13}C NMR spectrum, δ_C, ppm: 50.37 (CH_2), 51.69 (CH_2N), 58.12 (OCH_2). ^{29}Si NMR spectrum: δ_{Si} –79.7 ppm.

Reaction of a mixture of compounds I and II with ethanol. A 0.3-g portion of the mixture of compounds **I** and **II** isolated as described above was dissolved in 5 ml of anhydrous ethanol, and the solution was heated for 2 h under reflux. The mixture was evaporated to dryness, and the residue was recrystallized from 10 ml of heptane to isolate 0.02 g of 1-ethoxy-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (**III**). ^{1}H NMR spectrum, δ, ppm: 1.15 (3H, CH_3), 2.91 (6H, CH_2N), 3.72 (2H, CH_2), 3.83 (6H, OCH_2). ^{29}Si NMR spectrum: δ_{Si} –94.3 ppm. The mother liquor was evaporated by half, and anhydrous pentane was added until the solution turned turbid (~3 ml). After 24 h, the precipitate was filtered off and dried. Yield of 1-ethoxy-3,9,10-trioxa-6-aza-1-silabicyclo[4.3.3]dodecane (**IV**) 0.21 g, mp 68–69°C; published data [14]: mp 67°C. ^{1}H NMR spectrum, δ, ppm: 2.65 (2H, CH_2O), 2.92 (2H, CH_2N), 3.06 (4H, CH_2N), 3.78 (6H, OCH_2). The ^{13}C NMR spectrum of **IV** was identical to that given in [14].

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