

Si—C-Bond cleavage in 1-organylsilatrane by bromine or iodine chloride

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The Si—C bond in 1-organylsilatrane is cleaved by bromine or iodine chloride to yield 1-bromo- or 1-chlorosilatrane respectively. In the presence of Et₂O or THF and under the action of dioxane dibromide, 1-halosilatrane is formed together with 1-alkoxy- and 1-(ω-haloalkoxy)silatrane.

Key words: Si—C bond, electrophilic cleavage, halogens, 1-organylsilatrane, 1-halosilatrane.

The tendency of the Si—C bond in organysilanes RSiR₃ to undergo electrophilic cleavage through the action of halogens increases with an increase in the nucleophilicity of the leaving group R, polarity of the medium, and the electron-donating effect of the SiR₃ group, which favors the effective charge separation in the transition state.^{1–10}

When organypentafluorosilicates or diorganyl(phthalocyaninato)silane are treated with Br₂, ICl, *N*-bromosuccinimide (NBS), or CuX₂, both aryl and alkyl groups are eliminated from the silicon atom.^{9,10} Upon treatment with ICl, Si—Ar bonds are selectively cleaved to give Si—Cl and C—I derivatives, whereas in the case of Si—C₈H₁₇, a mixture of chloro- and iodoctanes is formed.¹⁰ The Si-bromination of pentafluorosilicates in nonpolar solvents occurs with the retention of the configuration, while as the polarity of the medium increases, a tendency to its inversion arises.⁹

The silatranyl group in 1-organylsilatrane possesses a strong electron-donating effect¹¹ and readily undergoes electrophilic Si-halogenation through the action of heavy metal halides.^{12,13} However, the reaction of 1-vinylsilatrane and its 3,7,10-trimethyl derivative with NBS in an aqueous medium leads smoothly to the corresponding 1-silatranylethylenebromohydrins.¹⁴

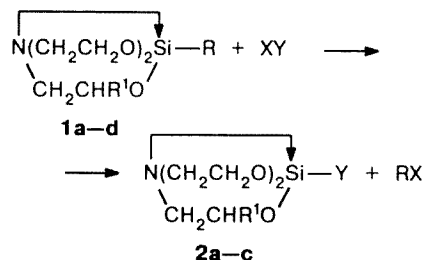
We studied reactions of 1-organylsilatrane with Br₂, ICl, and their complexes with ethers.

The reaction of 1-organylsilatrane (**1a–d**) with Br₂ or ICl in CH₂Cl₂ or CHCl₃ proceeds smoothly even at –50 °C and involves cleavage of the Si—R bond (Scheme 1).

The highest yield of 1-halosilatrane was attained in the case of 1-phenylsilatrane (**1d**), and the lowest yield was obtained in the case of 1,3-dimethylsilatrane (**1b**) (Table 1). The substantial resinification indicates that reactions involving destruction of the silatrane framework occur.

In the reactions with ICl, the formation of 1-iodosilatrane is in principle possible; the latter compound is

Scheme 1



R = Me, R¹ = H (**1a**); R = R¹ = Me (**1b**);
R = CH₂=CH, R¹ = H (**1c**); R = Ph,
R¹ = H (**1d**); XY = Br₂, ICl; Y = Cl, R¹ = H (**2a**);
Y = Cl, R¹ = Me (**2b**); Y = Br, R¹ = H (**2c**)

known¹⁵ to readily cleave Si—O—C and C—O—C bonds. However, only the corresponding C—I derivatives were detected among the volatile products obtained according to Scheme 1. This indicates that the substituent R is electrophilically attacked only by the I atom.

It is also noteworthy that the yields of the cleavage products in the reactions with Br₂ are not higher than those in the reactions with ICl.

Amines, ethers, and alkoxy silanes are known^{16,17} to form complexes with halogens. The basicity of the O atoms of the silatrane framework in 1-organylsilatrane is substantially higher than that in ethers or in alkoxy silanes,¹⁸ whereas the basicity of the N atom is low, since it participates in the intramolecular Si—N coordination.¹⁹ It has been assumed that the formation of complexes of 1-organylsilatrane with Lewis acids involves the O atoms of the silatrane framework.²⁰ The interaction of HCl with 1-organylsilatrane in CHCl₃ or CH₂Cl₂ results in the reversible cleavage of the Si—O bond.²¹

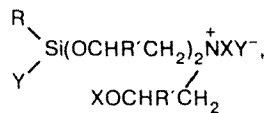
1-Chloro- and 1-bromosilatrane **2a** and **2c** do not react with ICl under the conditions studied; they are

Table 1. Conditions and products of the cleavage of 1-organylsilatrane

Silatrane	Cleaving reagent	Reaction temperature/ ^o C (solvent)	Identified reaction products (yields of compounds 2a—c; 3a—c, %)
1a	ICl	20 (CH ₂ Cl ₂)	2a (38.0), MeI
1a	ICl	20 (CHCl ₃)	2a (32.2), MeI
1b	ICl	20 (CH ₂ Cl ₂)	2b (11.3), MeI
1a	Br ₂	-5 (CH ₂ Cl ₂)	2c (30.1), MeBr
1c	ICl	20 (CH ₂ Cl ₂)	2a (19.2), CH ₂ =CHI
1c	ICl	20 (CHCl ₃)	2a (19.0), CH ₂ =CHI
1c	Br ₂	-5 (CHCl ₃)	2c (25.0), CH ₂ =CHBr
1d	ICl	22 (CH ₂ Cl ₂)	2a (42.0), PhI
1d	ICl	22 (CHCl ₃)	2a (42.8), PhI
1d	Br ₂	-5 (CH ₂ Cl ₂)	2c (38.0), PhBr
1d	ICl + Et ₂ O	20 (CH ₂ Cl ₂)	2a (38.4), 3a (9.2), PhI, EtCl
1d	Br ₂ + Et ₂ O	-5 (CH ₂ Cl ₂)	2c (32.0), 3a (9.1), PhBr, EtBr
1d	ICl + THF	20 (CH ₂ Cl ₂)	2a (19.1), 3b (16.1), PhI
1d	O(CH ₂ CH ₂) ₂ O · Br ₂	20 (CH ₂ Cl ₂)	2c (39.0), 3c (11.7), PhBr
1c	O(CH ₂ CH ₂) ₂ O · Br ₂	20 (CH ₂ Cl ₂)	2c (16.4), 3c (14.6), CH ₂ =CHBr

also inert with respect to HCl in nonaqueous media. This precludes the possibility that 1-halosilatrane 2a—c formed by Scheme 1 are involved in consecutive processes leading to the destruction of the silatrane framework.

It may be assumed that during the interaction of 1-organylsilatrane with electrophilic reagents, the O atoms in the silatrane framework as well as the substituent R can act as the sites at which the primary electrophilic attack occurs. The reaction of 1-organylsilatrane 1a—d with Br₂ and ICl leads apparently to the cleavage of the Si—N and Si—O bonds and to the formation of unstable haloammonium quaternary salts with a hypohalogenite fragment:

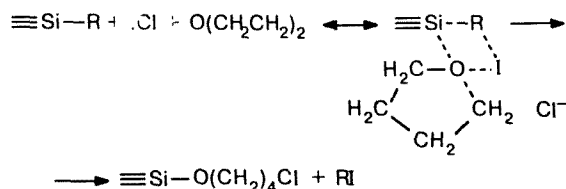


where R is organyl; R' = H, Me; XY = Br₂, ICl

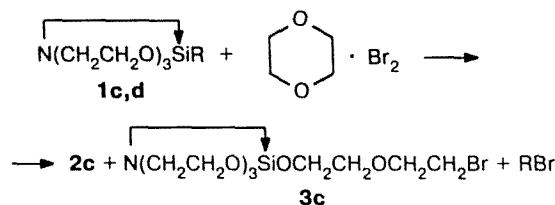
In order to study the effect of the formation of complexes of free halogens with ethers on the cleavage of the Si—C bond we carried out the reaction of 1-organylsilatrane (1c,d) with ICl and Br₂ in the presence of Et₂O or THF at a molar ratio of 1 : 3—5. We found that in this case, the yields of 1-chloro (or bromo)silatrane (2a,c) decrease and new products, 1-ethoxy- and 1-(4-chlorobutoxy)silatrane 3a,b, appear; the latter are formed *via* the cleavage of the C—O—C bonds in ethers (see Table 1) (Scheme 2).

The use of dioxane dibromide as the brominating reagent also leads to bromo- and alkoxy-silatrane (Scheme 3).

Scheme 2



Scheme 3



Experimental

¹H NMR spectra were recorded on a BS-487C spectrometer in CDCl₃ using tetramethylsilane as the internal standard.

Volatile reaction products were identified by GLC on an LKhM-8MD chromatograph. A 2-m column with 5 % XE-30 on Chezasorb AW-HMDS was used; the rate of the carrier gas (He) was 60 mL min⁻¹.

The solvents and bromine were dried by standard procedures. Ether and THF were freed from peroxides and dried immediately before use. Dioxane dibromide was prepared in light petroleum by a previously reported procedure,²² and ICl was obtained from I₂ and dry liquefied Cl₂²² and purified by crystallization. The initial 1-organylsilatrane were synthesized by a known procedure.²³

Reactions of 1-organylsilatrane (1a—d) with ICl and Br₂.

A. A solution of ICl or Br₂ (10 mmol) in 15 mL of CH₂Cl₂ or CHCl₃ was added dropwise to a stirred solution of 1-organylsilatrane (10 mmol) in 40 mL of CH₂Cl₂ or CHCl₃; during the addition, the mixture rapidly decolorized and warmed up (by 5–10 °C), and a friable yellowish precipitate formed. The precipitate was filtered off and recrystallized from CH₂Cl₂ or from a PrⁱOH—CHCl₃ mixture (1 : 1). The resulting 1-halosilatrane (2a—c) were identified based on the decomposition points and on the ¹H NMR spectral data.¹⁵ The filtrate was analyzed by GLC. It was combined with the mother liquor obtained from recrystallization and concentrated until crystallization began. The solution was cooled to 20–22 °C, and compound 2a, 2b, or 2c was filtered off. The mother liquor was concentrated under reduced pressure (5–10 Torr) to give a thick orange oil as the residue.

B. A solution of ICl or Br₂ (10 mmol) in 15 mL of CH₂Cl₂ or CHCl₃ was added dropwise to a stirred solution of 1-phenylsilatrane (2.51 g, 10 mmol) and a threefold molar excess of Et₂O or THF. The precipitated 1-halosilatrane 2a or 2c was recrystallized from CH₂Cl₂. The filtrate was analyzed by GLC. It was combined with the mother liquor obtained in the recrystallization of 2a,c and concentrated until 2a or 2c, respectively, began to crystallize, and the crystals were filtered off. Evaporation of the filtrate to dryness and extraction with heptane gave 1-ethoxy- (3a) or 1-(4-chlorobutoxy)silatrane (3b), respectively. The yields of 3a,b are listed in Table 1. 3a. M.p. 100–101 °C; ¹H NMR, δ: 3.92 (t, 6 H, OCH₂); 2.83 (t, 6 H, NCH₂); 3.78 (q, 2 H, OCH₂); 1.17 (t, 3 H, Me) (cf. lit.¹⁹). 3b. ¹H NMR, δ: 3.81 (t, 6 H, OCH₂); 2.83 (t, 6 H, NCH₂); 3.57 (m, 2 H, OCH₂); 1.77 (m, 4 H, CH₂CH₂); 1.19 (t, 2 H, ICH₂). Found (%): Cl, 12.21; N, 5.13. C₁₀H₂₀ClNO₄Si. Calculated (%): Cl, 12.58; N, 4.97.

C. Dioxane dibromide (1.62 g, 10 mmol) was added to a stirred solution of 1-phenyl- or 1-vinylsilatrane (1d or 1c) (10 mmol) in 40 mL of CH₂Cl₂. 1-Bromosilatrane (2c) was recrystallized from a PrⁱOH—CHCl₃ mixture (1 : 2). 1-[2-(2-Bromoethoxy)ethoxy]silatrane (3c) was extracted with heptane from the dry residue obtained from mother liquors. M.p. 88–90 °C. ¹H NMR, δ: 3.80 (t, 6 H, OCH₂); 2.85 (t, 6 H, NCH₂); 3.59 (m, 6 H, OCH₂CH₂OCH₂); 1.25 (t, 2 H, CH₂Br).

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