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Scheme of Hydrolysis of Five-Coordinate Chlorosilanes by X-Ray Diffraction Data

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Abstract—Hydrolysis of monochelate five-coordinate chlorosilanes $MeC(O)N(Me)CH_2SiMe_2Cl$ (**Ia**), $L^7CH_2SiMe_2Cl$ (**Ib**), $L^8CH_2SiMe_2Cl$ (**Ic**), $PhtImCH_2SiMe_2Cl$ (**Id**), $MeC(O)N(Me)CH_2SiMePhCl$ (**IIa**), and $Im^5CH_2SiMePhCl$ (**IIe**), containing a monoanionic C,O-chelating ligand LCH_2 [L is an amide, *n*-membered lactam (L^n), imide (Im^n), or phthalimide (PhtIm) residue]. The structures of the starting chlorides and their hydrolysis products were established by means of X-ray diffraction analysis. Based on experimental and published data, a general scheme of hydrolysis of mono-C,O-chelate chlorosilanes was suggested, including initial formation of silyloxonium chlorides **III** and subsequent formation of disiloxane dihydrochlorides **IV**.

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Typical representatives of silicon compounds with nonstandard coordination, specifically neutral monochelate five-coordinate monochlorosilanes containing monoanionic amidomethyl and related C,O-chelating ligands (LCH_2), have been studied in sufficient detail [1–3]. Effective synthetic approaches to such compounds [2, 4–6] and, on their basis, to other five-coordinate silicon derivatives with widely varied O→Si coordination bond strength have been developed [1–3, 6–8]. This made it possible to gain insight into the structural features of compounds with a SiC_3OX coordination entity (X = Hlg, OAlk, OAr, 0.5O, OTf) [7–11] and their stereodynamic behavior [12, 13], as well as to use them as models for studying the hypervalence problem [2, 14] and S_N reactions at the silicon atom [1–3, 10, 11, 15–18].

However, active research in this field has been continued. For example, five-coordinate [(2-oxopiperidin-1-yl)methyl]-R-hydrochlorosilanes (R = Me, Ph, Bn) have been synthesized [19]. Cationic polymerization with silacycle opening in sila[1]ferrocenophane [20] in the presence of a salt containing a silylium cation $[MeC(O)NCH_2SiMe_2]^+B[(3,5\text{-}CF_3)_2C_6H_3]_4^-$, has been used to prepare a poly(ferrocenylsilane) with a five-coordinate Si atom in the polymeric chain [21]. Novel Si-substituted *N*-(dimethylsilyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams with a SiC_3OX coordination entity (X = Hlg, OTf) and a chiral carbon atom in the amide or lactam fragment have been synthesized, and their stereodynamic behavior has been studied [13].

At the same time, one of the most important reactions of mono-C,O-chelate chlorosilanes, viz. hydrolysis, have still scarcely been studied. Note that the hydrolysis process can be complicated due to the ability of the donor oxygen atom for additional coordination. In the present paper we describe hydrolysis products of first synthesized and known C,O-chelate chlorosilanes $LCH_2Si(R)MeCl$ **I** and **II** with a SiC_3OCl coordination entity in the absence and in the presence of HCl acceptors. Based on the X-ray diffraction and NMR data for the intermediate reaction products: silyloxonium chlorides $[LCH_2Si(R)MeOH_2]Cl$ **III** and disiloxane dihydrochlorides $[LCH_2Si(R)Me]_2O{\cdot}2HCl$ **IV**, as well as the final hydrolysis products: disiloxanes $[LCH_2Si(R)Me]_2O$ **V** and **VI**, a general scheme of hydrolysis of five-coordinate chlorosilanes **I** and **II** [here and hereinafter, R = Me (**I, III–V**), Ph (**II, VI**)] is considered.

Mono-*C,O*-chelate chlorosilanes I and II and their final hydrolysis products disiloxanes V and VI. As objects for hydrolysis study we chose five-coordinate monochelate complexes of the general formula $LCH_2Si(R)MeCl$ [R = Me (**I**), Ph (**II**)], specifically chlorides $MeC(O)N(Me)CH_2SiMe_2Cl$ (**Ia**), $L^7CH_2SiMe_2Cl$ (**Ib**), $L^8CH_2SiMe_2Cl$ (**Ic**), $PhtImCH_2 \cdot SiMe_2Cl$ (**Id**), $MeC(O)N(Me)CH_2SiMePhCl$ (**IIa**), and $Im^5CH_2SiMePhCl$ (**IIe**), which contain a monoanionic amidomethyl or related C,O-chelating ligand LCH_2 [L is an amide, *n*-membered lactam (L^n), imide (Im^n), or phthalimide (PhtIm) residue].

The previously described chlorides **Ia** [4], **Ib** [6], and **IIa** [13] were prepared by a common procedure for neutral monochelate five-coordinate silicon complexes, i.e. by the reaction of trimethylsilyl derivatives of the corresponding amides, lactams, and imides $L{-}SiMe_3$ with $ClCH_2SiMe_2Cl$ or $ClCH_2SiMePhCl$ [reaction (1), route *a*]. The reactions were performed under thermodynamic control, and only final N-silylmethylation products **I** and **II** were isolated (a more detailed scheme is given in [19]).

$$L{-}SiMe_3 \xrightarrow[-Me_3SiCl]{a,\ ClCH_2Si(R)MeCl} \underset{\textbf{Ia–Ic, IIa, IIe}}{LCH_2Si(R)MeCl} \xrightarrow[(NaHCO_3)]{b,\ H_2O} \underset{\textbf{Va, Vc, Vd, VIa, VIe}}{[LCH_2Si(R)Me]_2O,} \qquad (1)$$

R = Me, L = MeC(O)N(Me) (**a**), L^7 (**b**), L^8 (**c**), PhtIm (**d**); R = Ph, L = Im^5 (**e**).

In a similar was we synthesized chloride **Ic**, the first representative of five-coordinate monochelate complexes containing an eight-membered lactam (enantolactam) fragment incorporated into a chelate ligand, as well as chloride **IIe** (yields 87 and 95%, respectively).

The reaction of $ClCH_2SiMe_2Cl$ with *N*-$SiMe_3$-phthalimide gave, against expectations, no chloride **Ie**. A substance isolated in 43% yield was identified as its hydrolysis product disiloxane **Vd**. In an analogous experiment in the presence of a base ($NaHCO_3$) the yield of disiloxane **Vd** was 50.5%. Chloride **Id** could not also be prepared by a method of silylation of imides we described previously: reaction of phthalimide with $ClCH_2SiMe_2Cl$ and hexamethyldisilazane. Instead of the target chloride **Ic** we isolated *N*-(dimethylphthalimidosilylmethyl)phthalimide (**VII**) [22].

The pentacoordination of silicon in chloride **Ib** was established by X-ray diffraction analysis in our previous work [10] and in chlorides **Ia, Ic**, and **IIa**, in the present work.

Attempted recrystallization of chloride **IIe** (a hot benzene solution was poured into hexane) gave crystals of its hydrolysis product disiloxane $(Im^5CH_2 \cdot SiMePh)_2O$ (**VIe**). The structure of the latter was confirmed by X-ray diffraction analysis.

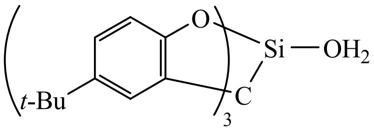
The previously unknown final hydrolysis products of chlorides **Ia, Ic, IIa**, and **IIe**, specifically disiloxanes **Va, Vc, VIa, VIe**, were prepared in high yields by treatment of the starting chlorides with water in the presence of $NaHCO_3$ [reaction (1), route *b*]. Disiloxane **Vc** was, too, prepared by hydrolysis of siloxonium chloride **IIIc** in the presence of ammonium carbonate.

Products of incomplete hydrolysis of chlorides I. A characteristic feature of five-coordinate silicon compounds [1, 3], including those containing Si–Cl bonds [23], is that they exhibit enhanced reactivity compared with four-coordinate Si atom. Therefore, it is not surprising that chlorosilanes **I** and **II** are easily hydrolyzed and not infrequently are quite sensitive to atmospheric moisture.

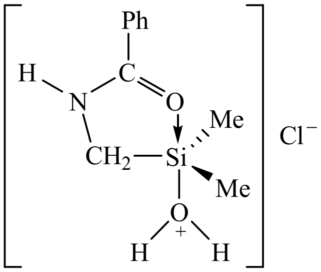
It can be stated with assurance that the structure of two types of intermediate hydrolysis products of mono-C,O-chelate chlorosilanes LCH_2SiMe_2Cl **I**:silyloxonium chlorides $[LCH_2SiMe_2OH_2]Cl$ **III** [24] and disiloxane dihydrohydrochlorides $(LCH_2SiMe_2)_2O \cdot 2HCl$ **IV** [25], was reliably established by X-ray diffraction. Five-coordinate silanols LCH_2SiMe_2OH can also be considered as intermediates. The formation of their analogs: hydrosilanol $L^6CH_2SiMe(H)OH$ and chlorosilanol $L^6CH_2SiMe(OH)Cl$, as primary hydrolysis products of chlorosilane $L^6CH_2Si(H)MeCl$ (**VIII**) was suggested on the basis of ^1H and ^{29}Si NMR spectra [19]. These products were detected in a fraction of ~10% in the NMR spectrum of chlorosilane **VIII**, which was explaned by the presence of traces of water in the solvent ($CDCl_3$).

By X-ray diffraction we established the structure of a five-coordinate silicon compound on the basis of quite a ridig tetradentate ligand, substituted 1-aqua-5-

carbasilatrane (**IX**), obtained by hydrolysis of its C_2H_5OH analog [26]. Nevertheless, the possibility of detection of five-coordinate intermediates in which a molecule of water is coordinated with silicon, namely neutral aqua complexes like $LCH_2SiMe_2OH_2$, seems very unlikely in our case.

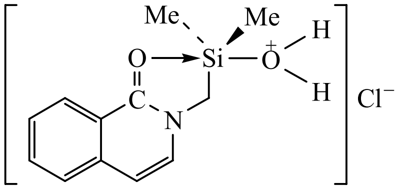


IX

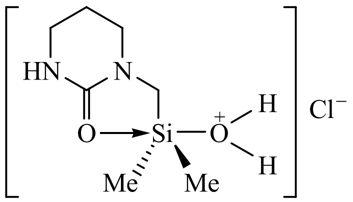


X

The Cambridge Structural Database [27] contains data for two silyloxonium chlorides **X** [24, 28] and **XI** [29]. Furthermore, the structure of bromide [PhC(O)$NHCH_2SiMe_2OH_2$]Br, a Br analog of compound **X**, was established [24, 28]. An urea derivative, silyloxonium chloride **XII**, was synthesized and structurally characterized [30].

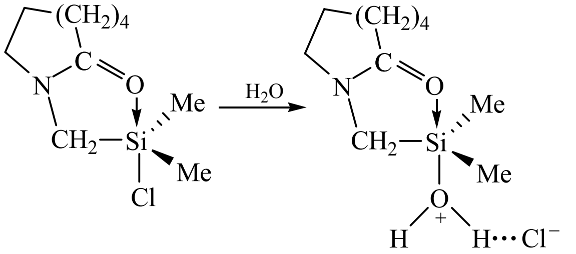


XI



XII

In the present work we determined an X-ray diffraction structure of one more representative of this quite a rare class of compounds, silyloxonium chloride [$L^8CH_2SiMe_2OH_2$]Cl (**IIIc**). It was isolated as a hydrate **IIIc**·H_2O upon recrystallization of chloride **Ic** without special protection from atmospheric moisture.



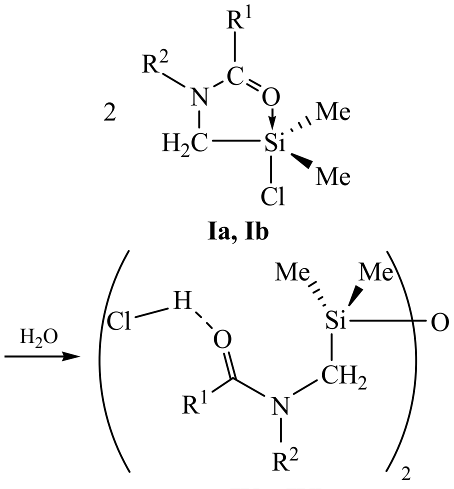
(2)

Ic **IIIc**

When the starting chloride **Ic** was prepared in hexane and then crystallized from the same solvent, we obtained, according to the elemental analysis, hydrochloride **IIIc**. If benzene was used as a solvent, the isolated product was assigned, by X-ray diffraction and elemental analysis data, the structure of solvate **IIIc**·H_2O.

In the present work we also prepared different-type intermediate hydrolysis products of mono-C,O-chelate chlorosilanes, namely disiloxane dihydrochlorides $[LCH_2SiMe_2]_2O{\cdot}2HCl$ **IV**. Thus, dihydrochlorides **IVa** and **IVb** were isolated, after hydrolysis of chlorides Ia and **Ib** in air in the absence of bases (benzene solutions of chlorides **Ia** and **Ib** were left in air at room temperature until the solvent evaporated almost completely).

Thus, disiloxanes function as bases binding HCl in reaction (3). The structure of dihydrochloride **IVa** was established by X-ray diffraction.



Ia, Ib

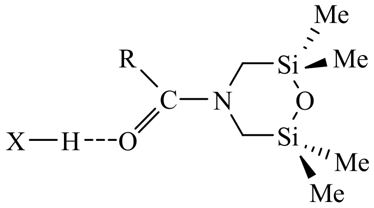
IVa, IVb

(3)

$R^1 = R^2 = Me$ (**a**); $R^1 = R^2 = (CH_2)_5$ (**b**).

Note that adducts of disiloxanes with C,O-chelating ligands have been described. In particular, the X-ray diffraction structures of adduct $(L^5CH_2SiMe_2)_2O\cdot 2CCl_3COOH$ (**XIII**) synthesized from the corresponding disiloxane and CCl_3COOH [31], as well as of dihydrochloride $(L^5CH_2SiMe_2)_2O\cdot 2HCl$ (**XIV**) were established, even though the synthesis of the latter compound was not reported [25]. Thus, our described dihydrochlorides **IVa** and **IVb** are the first compounds of this type prepared by hydrolysis of five-coordinate mono-C,O-chelate chlorosilanes.

It should be added that the protonation of an amide rather than disiloxane oxygen was observed in adducts of 2,6-disilamorpholines **XV** with HCl (**XV**·HCl), and CF_3COOH (**XV**·CF_3COOH) [32]. The structure of the latter adduct was confirmed by X-ray diffraction.



XV·HX

XV·HX, R = Me, X = Cl, CF_3COO; R = $ClCH_2$, X = CF_3SO_3.

In the case of imidomethylchlorosilanes **Id** (in situ) and **IIe**, compounds in which the O→Si intramolecular interaction is almost lacking (see below), no intermediate hydrolysis products could be obtained. As mentioned above, after hydrolysis of these compounds at ~50–60°C by moisture contained in air or solvent, we isolated as final productsdisiloxanes **Vd** and **VIe**, respectively, rather than compounds **III** or **IV**.

Thus, the reduced donor ability of the oxygen atom in the imide derivatives studied compared with their amide and lactam analogs, leads, on the one hand, to the lack of O→Si coordination in their molecules and, on the other, excludes their involvement as acceptors of HCl formed on hydrolysis.

No intermediate hydrolysis products could also be obtained in the case of chloride **IIa**, which differentiates them from chloride Ia containing a Ph group on silicon. Chloride **IIa** is not hydrolyzed at room temperature in the absence of a base; under more rigid conditions (long-term boiling with water), Si–C (Ph) bond cleavage takes place. Such cleavage under the action of strong acids is characteristic of four-coordinate silicon compounds. For example, the reaction of hydrosilane $PhSiHMe_2$ with CF_3SO_3H gave triflate $Me_2Si(H)OTf$ in a 86% isolated yield [33].

The composition and structure of previously unknown five-coordinate monochelates **I–III** and four-coordinate disiloxane dihydrochlorides and disiloxanes **IV–VI** were established by means of elemental analysis and IR and NMR spectroscopy; the structure of compounds **Ia, Ic, IIa, IIIc, IVa, Vd**, and **VIe** was confirmed by X-ray diffraction analysis.

IR spectroscopy. Like with earlier described mono-C,O-chelate chlorosilanes, specifically amide and lactam derivatives [5, 6], including chlorides **Ia** [4], **Ib** [6], and **IIa** [13] used in the hydrolysis study, the IR spectrum of chloride **Ic** contains in the range 1700–1400 cm^{-1} two absorption bands of associated stretching vibrations ν(C=O) and ν(C=N) which relate to the $N\overset{\cdots}{—}C\overset{\cdots}{—}O$ fragment of the chelate ligand (a strong band at 1600 cm^{-1} and a medium band at 1510 cm^{-1}). These observables provide evidence showing that the Si atom in chloride **Ic** is five-coordinate due to O→Si coordination.

At the same time, in the derivative of a five-membered imide, chloride **IIe**, the coordination interaction O→Si in solution may well be lacking. Stretching vibrations of the carbonyl groups in **IIe** appear as bands peaking at 1775 [ν_s(C=O)] and 1700 cm^{-1} [ν_{as}(C=O)]. Their positions are close to those in the spectrum of the $ClMe_2$ analog $Im^5CH_2SiMe_2Cl$ (1750 and 1690 cm^{-1} [34]). These absorption bands are appreciably shifted to high frequencies compared to those of the six-membered imide derivative $Im^6CH_2\cdot SiMe_2Cl$ (1717 and 1670 cm^{-1}), where a fairly weak but reliably detected O→Si coordination takes place [34].

Evidence for the five-coordinate state of silicon in silanol hydrochloride **IIIc** due to O→Si coordination comes from the IR spectrum which contains in the range 1700–1400 cm^{-1}, like with chlorosilanes **I**, two absorption bands of the $N\overset{\cdots}{—}C\overset{\cdots}{—}O$ fragment of the chelate ligand (1580 and 1510 cm^{-1}), similar to those observed previously in silyloxonium chloride **X** [24, 28]. Note also quite a broad strong absorption at 3200–2900 cm^{-1} with maxima about 3040 and 2980 cm^{-1}, associated with intermolecular H-bonds involving Cl atoms.

A similar broad strong absorption band at 3200–3100 cm^{-1} with its maximum about 3160 cm^{-1} is observed in disiloxane dihydrochlorides **IVa** and **IVb**

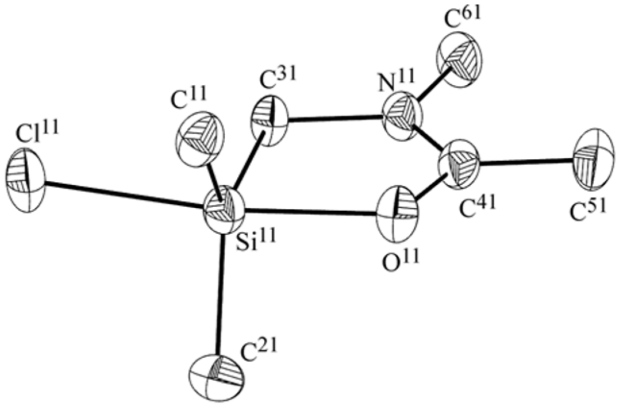


Fig. 1. General view of a molecule of chloride **Ia** in crystal (2 independent molecules) (H atoms are not shown).

(O–H stretching vibrations perturbed by intermolecular H-bonding). However, in these cases we observed in the carbonyl stretching vibration region a single strong band at 1600 and 1640 cm^{-1}, respectively (protonated carbonyl), which implies lacking O→Si intramolecular interaction.

Like with chloride **IIe**, the IR spectra of imidomethyl-substituted disiloxanes **Vd** and **VIe** show two carbonyl absorption bands (1765–1780 and 1685–1680 cm^{-1}), whose position implies lacking O→Si coordination. Such bonding is also lacking in disiloxanes **Va** and **Vc**: Their spectra contain a single strong absorption band at 1630–1615 cm^{-1} [ν(C=O)] {compare with the position of this band (1635 cm^{-1}) in a seven-membered lactam derivative $(L^7CH_2SiMe_2)_2O$ [8]}. Therewith, no additional absorption at 1600–1500 cm^{-1}, characteristic of C,O-chelate ligand LCH_2, is observed.

NMR spectroscopy. The ^1H, ^{13}C, and ^{29}Si NMR spectra of compounds **I–VI** are consistent with the suggested structures. As known, the NMR spectra of five-coordinate silicon compounds differ from those of model four-coordinate derivatives by enhanced ^{29}Si shielding [1, 2, 12]. For our studied chlorides **Ia–Ic** and **IIa** and most known mono-C,O-chelate monochlorosilanes like **I**, an upfield shift of the ^{29}Si NMR signal (δ_{Si} from –32 to –54 ppm) compared to their closest tetrahedral analog $ClCH_2SiMe_2Cl$ (23.7 ppm) [35] suggests quite a strong O→Si coordination bond in these compounds in the liquid phase [1, 2, 12, 13].

The signals of chloride $Im^5CH_2SiMePhCl$ (**IIe**) and its Me_2Si analog $Im^5CH_2SiMe_2Cl$ [34] in the ^{29}Si NMR spectrum in $CDCl_3$ (δ_{Si} 15.2 and 25.4 ppm, respectively) are close to those of $ClCH_2SiMe_2Cl$ [35], which points to the lack of any appreciable O→Si coordination in **IIe** in solutions.

The ^{29}Si NMR signals of dihydrochlorides **IVa** and **IVb** and disiloxanes **Va–Vd** are observed at δ_{Si} –3.5 to 15 ppm, which corresponds to their position in ordinary siloxanes {for example, the δ_{Si} of $(Me_3Si)_2O$ is 7.4 ppm [12]}, providing evidence for the four-coordinate state of silicon in these compounds in solution. Note that the silicon signal of adduct **XV**·HCl protonated by the amide oxygen was observed at 10.7 ppm [32].

X-ray diffraction study. The geometry of the coordination entity of Si in the three neutral five-coordinate C,O-chelate chlorosilanes **Ia, Ic**, and **IIa** (Table 1, Figs. 1 and 2) is a distorted trigonal bipyramid with the Si atom deviating from the equatorial plane by 0.026–0.068 Å towards Cl. The replacement of the methyl group on silicon by phenyl in going from compound **Ia** to **IIa** does not affect essentially the Si–O coordination bond length. Therewith, the Si–Cl bond gets longer by 0.03 Å, which can be explained by repulsion between the phenyl substituent and chlorine atom (the CSiCl angle in **IIa** is larger by ~2° than the respective angle in **Ia**).

More appreciable are differences between complexes **Ia** and **Ic**. Replacement of methyl substituents by a more donor eight-membered lactam ring results in strengthening of the Si–O bond and weakening of the Si–Cl bond (the corresponding distances have changed by 0.03 and 0.04 Å). The bulky substituent in complex Ic disturbs planarity of the chelate ring. The chelate rings in complexes Ia and IIa are in fact planar, whereas that in compound Ic is an *envelope* with the Si atom deviating by 0.1003(6) Å.

The structure of the coordination polyhedron of the Si atom in the hydrolytic intermediate of chloride **Ic**, silyloxonium chloride **IIIc** (Fig. 3), is slightly different from that in complex **Ic**. Replacement of Cl by H_2O slightly changes the Δ_{Si} value [from 0.0261(6) to 0.0158(4) Å]. The axial $Si^1–O^1$ and $Si^1–O^2$ bond orders are almost equal to each other [the corresponding interatomic distances are 1.9129(15) and 1.9140(16) Å]. The chlorine atom resides in the outer sphere with respect to Si and does not form interatomic contacts with it (the shortest Si···Cl distance is 4.084 Å).

The cation and anion in silyloxonium chloride **IIIc** are associated by O–H···Cl hydrogen bonds. Furthermore, the crystal of **IIIc** contains an uncoordinated water molecule which, too, forms hydrogen bonds with

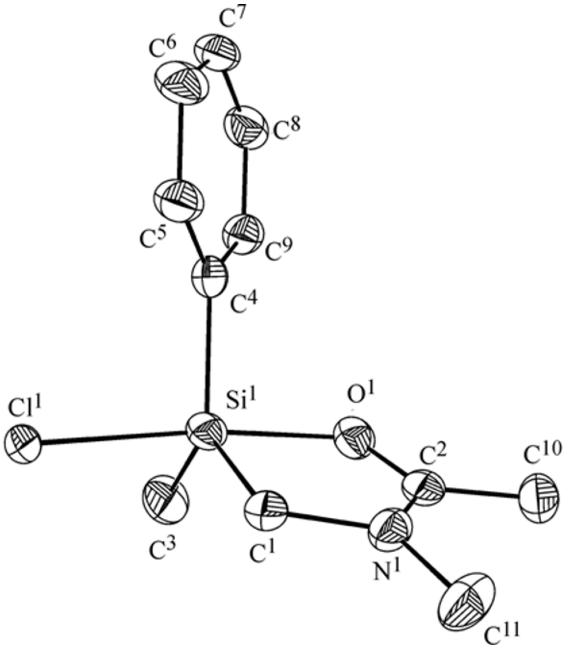


Fig. 2. General view of a molecule of chloride **IIa** in crystal (H atoms are not shown).

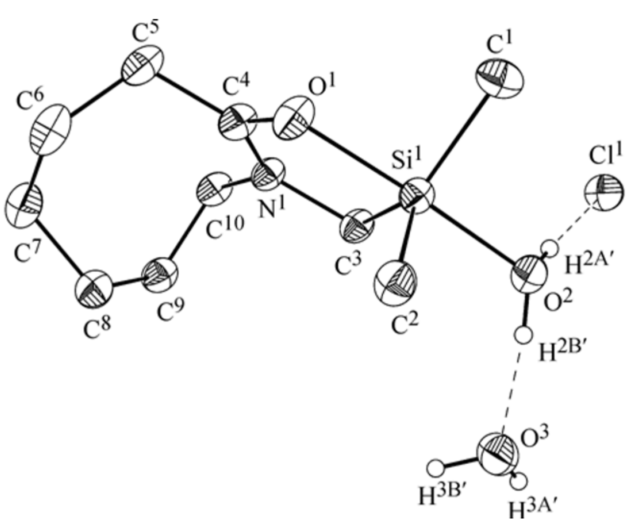


Fig. 3. General view of a molecule of silyloxonium chloride hydrate **IIIc**·H_2O in crystal (H atoms of water molecules are only shown). Principal bond lengths (Å) and bond angles (deg): $Si^1–O^1$ 1.9129(15), $Si^1–O^2$ 1.9140(16), $O^1–C^4$ 1.285(2), $Si^1–C^1$ 1.860(2), $Si^1–C^2$ 1.855(2), $Si^1–C^3$ 1.8964(18), $O^1Si^1O^2$ 173.23(6).

the cation and anion. An analogous structure has been earlier discussed for two salts with a (benzoylamido) methyl ligand [24]). The $Si^1–O^2$ bonds are longer by about 0.1 Å than in complex **IIIc**, whereas the $Si^1–O^1$ bond length is almost the same. The latter fact can be explained by an effect of crystal packing, since both chloride X and its Br analog [24] contains no uncoordinated water molecule, which entails considerable differences the H-bond systems.

Disiloxane dihydrochloride **IVa** (Fig. 4) can be considered as one of the possible intermediates of hydrolysis of chloride Ia, whereas disiloxanes **Vd** and **VIe** as final hydrolysis products of complexes with a $OSiC_3Cl$ coordination entity. Actually, these complexes contain no endocyclic Si–O coordination bond (the Si···O interatomic distance is longer than the sum of the van der Waals radii) (Table 2).

The shortest Si···Cl distance in salt **IVa** is 4.110 Å, which points to lacking interaction between these two atoms. Not being involved in Si···Cl contacts, the chlorine atom forms O–H···Cl and C–H···Cl hydrogen bonds with the *N*-(methylacetamido)methyl fragment (Table 3). Unlike salt **IVa**, compounds **Vd** and **VId** (Fig. 5) are not ionic crystals and contain no chlorine atom and protonated oxygen atom of the amide fragment. In their structures, weak C–H···O hydrogen bonds could only be localized.

EXPERIMENTAL

The IR spectra of 5% solutions were registered on a Specord IR-75 instrument in KBr cells. The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of CD_2Cl_2 and $CDCl_3$ solutions were obtained on a Varian XL-400 spectrometer (400.1, 100.6, 396, and 79.5 MHz, respectively). The ^{1}H, ^{13}C, and ^{29}Si chemical shifts were measured against internal Me_4Si.

Table 1. Principal geometric parameters (Å, deg) of the Si coordination entity and the chelate rings in complexes **Ia, Ic,** and **IIa** containing a $OSiC_3Cl$ coordination entity

Parameter	**Ia**	**Ic**	**IIa**
Si–Cl	2.309(1)	2.3470(8)	2.3392(13)
Si–O	1.944(2)	1.9091(16)	1.939(2)
$Si–C_{eq}$ [a]	1.866(3)	1.861(2)	1.867(4)
$Si–C_{endo}$	1.888(3)	1.897(2)	1.885 (4)
O–C	1.269(4)	1.280(2)	1.278(4)
$N–C_{endo}$ [a]	1.310(4)	1.310(3)	1.300(4)
OSiCl	170.79(8)	171.68(5)	171.02(9)
Δ_{Si} [b]	0.0565(8)	0.0261(6)	0.068(1)

[a] C_{eq} relate to the equatorial carbon atoms and C_{endo}, to the carobn atom in the chelate ring. [b] Deviation of the Si atom from the equatorial plane towards Cl.

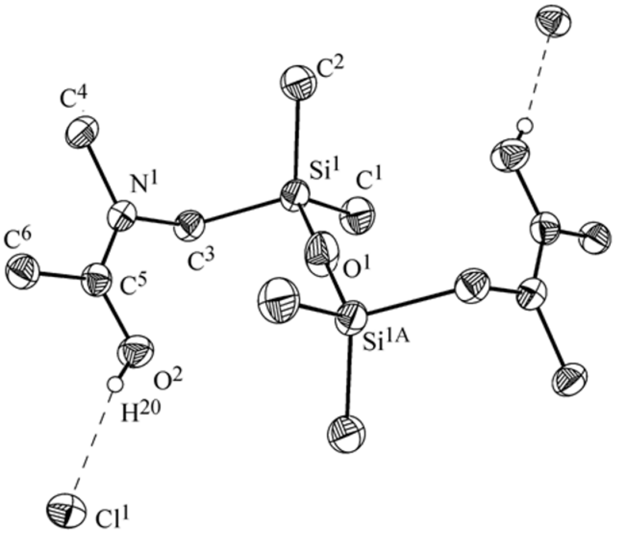


Fig. 4. General view of the molecule of dihydrochloride **IVa** in crystal (H-bonded hydrogen atoms are only shown).

N-Methyl-*N*-SiMe$_3$-acetamide [36], *N*-SiMe$_3$-enantolactam [37], *N*-SiMe$_3$-succinimide [38], *N*-SiMe$_3$-phthalimide [39], chloro(chloromethyl)phenylsilane [40], *N*-(dimethylchlorosilylmethyl)-*N*-methylacetamide (**Ia**) [4], *N*-(dimethylchlorosilylmethyl)-hexahydroazepin-2-one (**Ib**) [6], as well as *N*-methyl-*N*-[chloro(methyl)phenylsilylmethyl)acetamide (**IIa**) [22] were prepared by known procedures, and their physicochemical and spectral characteristics were consistent with published data.

To obtain single crystals for X-ray diffraction analysis, chloride **Ia** and dihydrochloride **IVa** were crystallized from a 1:1 ether–hexane mixture, chlorides **Ic, IIa**, and silyloxo-nium chloride **IIIc**, from benzene, disiloxanes **Vd** and **VIe**, from 3:1 and 1:1 hexane–benzene mixtures, respectively.

Crystal data and details of X-ray diffraction experiments are presented in Table 4. The X-ray diffraction measurements were performed on a Bruker Smart 1000 CCD instrument at 120 K. The structures were solved by the direct method and refined by fill-matrix least squares on F^2 in the anisotropic approximation for non-hydrogen atoms. Absorption was included using SADABS software [41]. The absolute structure of **Ia** was established by the Flack parameter [42], equal to –0.14(8). In disiloxanes **IVa, Vd**, and **VIe**, the independent part is half of the molecule, whereas the bridging O^1 atom occupies a special position. In the crystal of **Ia**, there are two independent molecules. The crystal of **Ic** contains a solvate benzene molecule, the lactam ring is disordered in two positions (C^7 and C^8), with the occupancies 0.6 and 0.4. The unit cell of **IIIc** contains a solvate water molecule.

The principal bond lengths and bond angles in the studied structures are listed in Tables 1 and 2. All calculations were performed using SHELXTL 5.10 software [43].

Synthesis of *N*-(dimethylchlorosilylmethyl)-*N*-methylacetamide (Ia) and 1,1,3,3-tetramethyl-1,3-bis(*N*-methylacetamidomethyl)-1,3-disiloxane dihydrochloride (IVa). *a.* A mixture of 7 g of *N*-methyl-*N*-SiMe$_3$-acetamide and 7 g of ClCH$_2$SiMe$_2$Cl was

Table 2. Principal geometric parameters (Å, deg) of compounds **IVa, Vd**, and **VIe**

Angle, bond	**IVa**	**Vd**	**VIe**
Si^1–O^1	1.6195(6)	1.6122(8)	1.6150(5)[a]
Si^1–C^1	1.845(2)	1.843(2)	1.8608(15)
Si^1–C^2	1.855(2)	1.847(3)	1.8446(19)
Si^1–C^3	1.892(2)	1.887(2)	1.8881(16)
O^1–Si^{1i}	1.6195(6)	1.6122 (8)	1.6149(5)
Si^1···O^2	3.6726(18)	3.8549(3)	3.6496(18)[a]
Si^1···Cl^1	4.110		
$Si^1O^1Si^1$	180.0	180.00 (3)	180.0

[a] The values for structure **VIe** relate to the Si^1–O^2 bond and $Si^{1\cdot}$···O^{11} distance.

Table 3. Parameters of hydrorgen bonds in structures **Ic** and **IVa**

Hydrogen bond	**Ic**			
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (deg)
O^2–$H^{2A'}$···Cl^1	0.85(2)	2.13(2)	2.9820(17)	175.8(5)
O^2–$H^{2B'}$···O^3	0.850(13)	1.696(16)	2.541(2)	172(2)
O^3–$H^{3A'}$···Cl^{1i}	0.85(3)	2.288(19)	3.122(2)	167(2)
O^3–$H^{3B'}$···Cl^{1ii}	0.844(14)	2.255(11)	3.0976(18)	176(3)
	IVa			
O^2–H^{2O}···Cl^1	0.850(4)	2.018(4)	2.8558(19)	168.9(4)

heated in a distillation flask for 15 min until chlorotrimethylsilane no longer distilled. After a few days the residue crystallized to give 8.2 g (95%) of crude chloride **Ia**, mp 84–86°C (mp 64–66°C [4], purified by sublimation). Crystallization of the crude product from a 1:1 ether–hexane mixture gave two types of crystals: on the flask bottom under a layer of solvent and on the flask walls in contact with air. According to X-ray diffraction data, the first crystals belong to chloride **Ia** and the second, to dihydrochloride **IVa**.

b. To 24.7 g of *N*-methyl-*N*-$SiMe_3$-acetamide we added dropwise 23 g of $ClCH_2SiMe_2Cl$, and the mixture was heated until complete removal of chlorotrimethylsilane (15.5 g, 89%). The residue crystallized to give 26.7 g (87%) of chloride **Ia**. The physiochemical and spectral parameters of the product were consistent with those reported in [4, 44]. Crude chloride **Ia** (14.5 g) was dissolved in 80 ml of benzene, and the solution was left to stand in an open vessel in a hood at room temperature. The crystals that remained after the solvent evaporated almost completely were suspended in 20 ml of hexane and filtered off to obtain 14 g (93%) of dihydrochloride **IVa**, mp 99–103°C (dioxane). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3200–3100 br (CH, OH), 1600 s (C=O). ^1H NMR spectrum ($CDCl_3$), δ_H, ppm: 0.22 s (12H, $SiMe_2$), 2.14 s (6H, CH_3C), 2.80–2.90 m (4H, $SiCH_2$), 3.09 s (6H, CH_3N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 4.52 ($SiMe_2$), 17.35 [MeC(O)], 37.91 (NCH_2), 43.07 (NMe_2), 173.12 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –3.1 ppm. Found, %: C 38.05; H 8.14; N 7.81. $C_{12}H_{30}Cl_2N_2O_3Si_2$. Calculated, %: C 38.18; H 8.01; N 7.42.

Hydrolysis of *N*-(dimethylchlorosilylmethyl)-*N*-methylacetamide Ia in the presence of a base. 1,1,3,3-Tetramethyl-1,3-bis(*N*-methylacetamidomethyl)-1,3-disiloxane (Va). To a solution of 13 g of chloride Ia in 40 ml of $CHCl_3$ we added dropwise with stirring a solution of 6.1 g of $NaHCO_3$ in 20 ml of water, and the mixture was stirred for 3 h. After a day the organic layer was separated, and the aqueous layer was extracted with chloroform (3×10 ml). The combined organic extracts were dried over calcinated K_2CO_3, chloroform was removed by distillation, anв the residue was fractionated to obtain 9 g (85%) of disiloxane **Va**, mp 197–201°C (7 mm), n_D^{20} 1.4725. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1630 s (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.22 s (12H, $SiMe_2$), 2.14 s (6H, CH_3C), 2.80–2.90 m (4H, $SiCH_2$), 3.09 s (6H, CH_3N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –0.01 ($SiMe_2$), 23.50 [MeC(O)], 26.93 (NCH_2), 41.02 (NMe_2). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 3.2 ppm. Found, %: C 47.33; H 9.27; N 9.20. $C_{12}H_{28}N_2O_3Si_2$. Calculated, %: C 47.09; H 9.63; N 9.42.

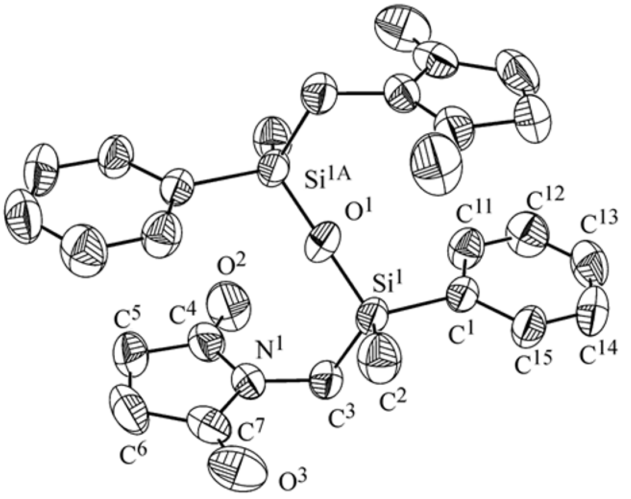


Fig. 5. General view of a molecule of disiloxane **VIe** in crystal (H atoms are not shown).

1,1,3,3-Tetramethyl-1,3-bis[(2-oxohexahydroazepin-1-yl)methyl]-1,3-disiloxane dihydrochloride ($[L^7CH_2SiMe_2]_2O\cdot 2HCl$) (IVb). Chloro(dimethyl)[(2-oxohexahydroazepin-1-yl)methyl]silane (**Ib**), 1.7 g, was dissolved in 20 ml of benzene, and the solution was left to stand in an open vessel in a hood at room temperature. The crystals that remained after the solvent evaporated almost completely were suspended in 5 ml of heptanes and filtered off to obtain 1.6 g (89%) of dihydrochloride **IVb**, mp 99–103°C (ether). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3200–3100 br (CH, OH), 1640 s (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.42 s (12H, $SiMe_2$), 2.89 s (4H, NCH_2), 2.52 m (4H, H^3), 1.51–1.83 m (12H, H^{4-6}), 4.54 m (4H, H^7), 6.54 br.s (2H, HCl). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –3.2 ppm. Found, %: C 47.08; H 8.43; Si 12.22. $C_{18}H_{38}N_2O_3Si_2$. Calculated, %: C 47.25; H 8.37; Si 12.22.

Synthesis of *N*-(chlorodimethylsilylmethyl)-2-azocanone (Ic) and dimethyl[(2-oxoazpcan-1-yl)methyl]-silyloxonium chloride (IIIc). *a*. To a solution of 2 g of *N*-$SiMe_3$-enantolactam [37] in 8 ml of absolute benzene we added dropwise with stirring 1.43 g of $ClCH_2SiMe_2Cl$ (the reaction mixture warmed up to ~50°C). After a day part of crystals that formed was taken for X-ray diffraction analysis which showed that they belong to chloride **Ic**. The remaining crystals

Table 4. Principal measurement and refinement parameters for structures **I–VI**

Parameter	**Ia**	**Ic**	**IIa**	**IIIc**	**IVa**	**Vd**	**VIe**
Brutto formula	$C_6H_{14}ClNOSi$	$C_{16}H_{26}ClNOSi$	$C_{11}H_{16}ClNOSi$	$C_{20}H_{48}Cl_2N_2O_6Si_2$	$C_{12}H_{30}Cl_2N_2O_3Si_2$	$C_{22}H_{24}N_2O_5Si_2$	$C_{24}H_{28}N_2O_5Si_2$
Molecular weight	179.72	311.92	241.79	539.68	377.46	452.61	480.66
Space group	$I4_1$	$P2(1)/c$	$P2_1/c$	$C2/c$	$P2_1/n$	P-1	$P2_1/n$
Z	16	4	4	4	2	1	2
a, Å	20.985(6)	9.9024(17)	12.174(5)	29.564(7)	6.5023(10)	7.687(4)	9.0743(16)
b, A	20.985(6)	21.877(4)	11.914(4)	6.6436(15)	13.771(2)	8.309(3)	13.937(2)
c, A	8.773(2)	8.7971(15)	8.693(3)	16.692(4)	11.6576(19)	10.077(5)	10.1789(17)
α, deg	90.00	90.00	90.00	90.00	90.00	106.87(3)	90.00
β, deg	90.00	115.333(4)	92.253(7)	117.841(4)	104.452(3)	90.95(3)	105.883(4)
γ, deg	90.00	90.00	90.00	90.00	90.00	108.92(3)	90.00
V, Å^3	3863.3(18)	1722.5(5)	1259.8(8)	2899.0(12)	1010.8(3)	578.3(5)	1238.2(4)
d_{calc}, g cm^{-3}	1.236	1.203	1.275	1.237	1.240	1.300	1.289
μ, cm^{-1}	4.63	2.88	3.74	3.41	4.49	1.88	1.8
F(000)	1536	672	512	1168	404	238	508
2θ_{max}, deg	60	60	57	60	60	56	60
Reflections measured	22793	12677	12546	8463	11856	4376	12107
Unique reflections	5602	4933	3210	4108	2938	2695	3601
Reflections with $I > 2\sigma(I)$	4630	3424	1770	3191	2206	2241	2231
Number of refined parameters	181	199	139	241	157	142	152
R_1	0.0576	0.0709	0.0642	0.0622	0.0596	0.0696	0.0470
wR_2	0.1466	0.1918	0.1263	0.1685	0.1488	0.2085	0.1430
GOOF	1.009	0.995	0.991	0.998	1.062	1.090	0.980
Residual electron density, e A^{-3} (d_{min}/d_{max})	0.960/–0.399	1.867/–0.293	0.672/–0.360	1.613/–0.432	1.664/–0.326	1.385/–0.404	0.419/–0.145

were filtered off to isolate 2 g (87%) of chloride **Ic**, mp 109–114°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1600 s, 1510 m (NCO). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.55 s (6H, $SiMe_2$), 1.39–1.78 m (8H, H^{4-7}), 2.46 m (2H, H^3), 2.76 s (2H, NCH_2), 3.50 m (2H, H^8). Since chloride **Ic** fairly rapidly hydrolyzed in $CDCl_3$, we could not obtain ^{13}C and ^{29}Si NMR spectra of a pure sample.

Recrystallization of part of the synthesized chloride **Ic** from benzene without special protection from air moisture gave, according to X-ray diffraction and elemental analysis data, hydrate **IIIc**·H_2O, mp 73–75°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 s, 2980 w (CH, OH), 1580 s, 1500 m (NCO). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.38 s (6H, $SiMe_2$), 1.35–1.76 m (8H, H^{4-7}), 2.48 m (2H, H^3), 2.75 s (2H, NCH_2), 3.49

m (2H, H^8), 4.9 br.s (2H, O^+H_2Cl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 3.76 ($SiMe_2$), 23.77 (C^7), 25.50 (C^4), 27.43 (C^6), 28.28 (C^5), 29.9 (C^3), 39.50 (NCH_2), 48.35 (C^8), 177.56 (C=O). ^{29}Si NMR spectrum (CPMAS): δ_{Si} –47.1 ppm. Found, %: C 44.64; H 9.00; N 5.17. $C_{10}H_{24}ClNO_3Si$. Calculated, %: C 44.51; H 8.96; N 5.19.

b. The reaction of 4 g of *N*-$SiMe_3$-enantolactam and 2.9 g of $ClCH_2SiMe_2Cl$ in hexane gave 4.2 g (90%) of chloride **Ic**. The product was recrystallized from benzene to obtain, according to the elemental analysis, silyloxonium chloride **IIIc**, mp 87–94°C. Found, %: C 48.09; H 8.86; N 5.62. $C_{10}H_{22}ClNO_2Si$. Calculated, %: C 47.70; H 8.80; N 5.56.

1,1,3,3-Тетраmethyl-1,3-bis[(2-oxoazocan-1-yl)-methyl]disiloxane (Vc). *a*. To a solution of 8 g of *N*-$SiMe_3$-enantolactam in 20 ml of benzene we added drowise 5.7 g of $ClCH_2SiMe_2Cl$, and the reaction mixture was stirred for 2 h. In doing so, we observed formation of a small amount of crystals. After a day the reaction mixture was diluted with 20 ml of $CHCl_3$, a solution of 7 g of $NaHCO_3$ in 40 ml of water was then added, and the resulting mixture was stirred for 6 h. The organic layer was separated, the solvent was removed in a rotary evaporator, and the residue was fractionated to obtain siloxane 4.8 g of disiloxane **Vc**, mp 260–261°C (4 mm), n_D^{20} 1.5000. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1615 s (C=O). ^1H NMR spectrum ($CDCl_3$) δ, ppm: 0.07 s (12H, $SiMe_2$), 2.59 s (4H, NCH_2), 3.40 m (4H, H^8), 2.39 m (4H, H^3), 1.34–1.68 m (16H, H^{4-7}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 174.57 (C=O), 0.64 ($SiMe_2$), 23.71 (C^7), 25.97 (C^4), 27.85 (C^6), 28.53 (C^5), 33.10 (C^3), 38.19 (NCH_2), 48.71 (C^8). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 1.0 ppm. Found, %: C 58.14; H 9.87; N 6.71. $C_{20}H_{40}N_2O_3Si_2$. Calculated, %: C 58.20; H 9.77; N 6.79.

b. To a mixture of 3.9 g of ammonium carbonate, 0.8 g of water, and 40 ml of CH_2Cl_2 we added with stirring a solution of 2 g of **IIIc**·H_2O in 40 ml of CH_2Cl_2. After 5 days excess ammonium carbonate was filtered off, the organic layer was separated and dried over calcinated K_2CO_3, the solvent was removed in a rotary evaporator, and the resdue was filtered off to obtain 1.55 g (94%) of disiloxane **Vc** as an oil, n_D^{20} 1.4990.

Tteramethyl-1,3-bis(phthalimidomethyl)disiloxane (Vd). *a*. To chloro(chloromethyl)dimethylsilane, 16.2 g, heated to 50°C we added dropwise a solution of 15.35 g of *N*-$SiMe_3$-phthalimide [39] in 15 ml of CH_2Cl_2. In 30 min after chlorotrimethylsilane had stopped to evolve and the reaction mixture cooled down to room temperature, it was diluted with 30 ml of hexane. Crystals formed and were filtered off to obtain 6.81 g (43%) of disiloxane **Vd** (per *N*-$SiMe_3$-phthalimide), mp 135–137°C (hexane–benzene, 3:1). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1765 w, 1685 s (C=O), 1617 w (Ar). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.12 s (12H, $SiMe_2$), 3.11 s (4H, NCH_2), 7.61–7.75 m (8H, Ar). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.35 ($SiMe_2$), 29.89 (NCH_2), 132.41, 133.66, 122.95, 168.42 (C_{Ar}). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 0.7 ppm. Found, %: C 58.43; H 5.19; N 6.24. $C_{22}H_{24}N_2O_5Si_2$. Calculated, %: C 58.38; H 5.34; N 6.19.

b. To chloro(chloromethyl)dimethylsilane, 14.3 g, heated to 50°C were added dropwise 15.35 g of *N*-$SiMe_3$-phthalimide [39] in 20 ml of CH_2Cl_2, and the mixture was heated until the solvent (CH_2Cl_2) and the chlorotrimethylsilane formed (~29 ml) had been removed completely. After a day the residue was diluted with 50 ml of chloroform and then a solution of 12.6 g of $NaHCO_3$ in 30 ml of water was added in small portions with stirring. The resulting mixture was stirred for 2 h and left to stand for a day, after which the organic layer was separated, and the aqueous layer was extracted with chloroform (3×10 ml). The combined organic extracts were dried over calcinated K_2CO_3, chloroform was removed in a rotary evaporator, the crystals that remained were washed with 125 ml of water, filtered off, and dried in air to obtain 8 g (50.5%) of disiloxane **Vd** (per *N*-$SiMe_3$-phthalimide), mp 138–140°C (hexane–benzene, 1:1). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1765 w, 1685 s (C=O), 1617 w (Ar). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.12 s (12H, $SiMe_2$), 3.11 s (4H, NCH_2), 7.61–7.75 m (8H, Ar).

Hydrolysis of *N*-methyl-*N*-[chloro(methyl)phenyl-silylmethyl]acetamide (IIa). *a*. *In the presence of a base*. To a solution of 8.94 g of chloride **IIa** in 35 ml of $CHCl_3$ we added with stirring a solution of 4.32 g of $NaHCO_3$ in 60 ml of water, and the reaction mixture was stirred for 4 h. After a day the organic layer was separated, the aqueous layer was extracted with $CHCl_3$ (3×15 ml), the chloroform extracts were evaporated in a rotary evaporator, and the residue was fractionated to obtain 3.79 g (48%) of 1,3-dimethyl-1,3-diphenyl-1,3-bis(*N*-methylacetamidomethyl)-1,3-disiloxane (**VIa**), mp 258–260°C (1 mm), n_D^{20} 1.5448. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1620 s (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.47 s (6H, SiMe), 1.89 s (6H,

CH_3C), 2.81 s (6H, CH_3N), 2.98 s (4H, $SiCH_2$), 7.30–7.60 m (10H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –0.01 ($SiMe_2$), 23.50 [MeC(O)], 26.93 (NCH_2), 41.02 [$N(CH_3)_2$]. ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 3.2 ppm. Found, %: C 61.62; H 7.52; N 6.56. $C_{22}H_{32}\cdot N_2O_3Si_2$. Calculated, %: C 61.64; H 7.52; N 6.54.

b. In chloroform. Chloride **IIa**, 1 g, was dissolved in a conical flask in 10 ml of wet chloroform, and the solution was left to stand in air. Chloroform evaporated within 5 days. The IR spectrum of the residue and its melting point (120–124°C) were the same as those of the starting chloride **IIa**.

c. On heating in water. A mixture of 1 g of chloride **IIa** and 10 ml of water were refluxed for 9 h in a conical flask equipped with a reflux condenser. Water was then evaporated to obtain 0.45 g of an oily liquid whose ^1H NMR spectrum showed four groups of broadened singlets assignable to methyl and methylene protons of a mixture of oligosiloxanes HO–{Me[MeC·(O)N(Me)CH_2]SiO}$_n$H and/or cyclosiloxanes {Me[MeC(O)N(Me)CH_2]SiO}$_n$. The lack in the spectrum of aromatic proton signals suggests the hydrolytic cleavage of the Si–C(Ph) bond under these conditions.

Chloro(methyl)(phenyl)(succinimidomethyl)silane (IIe). To chloro(chloromethyl)(methyl)phenylsilane, 12.3 g, heated to 50°C, we added dropwise 8.6 g of *N*-$SiMe_3$-succinimide; distillation of chlorotrimethylsilane was observed. After Me_3SiCl had stopped to distill (5.2 g, 95%), the reaction mixture was fractionated to obtain 12.75 g (95%) of chloride **IIe**, bp 212–214°C (8 mm), n_D^{20} 1.5610. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1775 w, 1700 s (C=O), 1590 w (Ph). Found, %: C 53.80; H 5.35; N 5.14. $C_{12}H_{14}ClNO_2Si$. Calculated, %: C 53.82; H 5.27; N 5.23.

1,3-Dimethyl-1,3-diphenyl-1,3-bis(succinimidomethyl)disiloxane (VIe). *a*. Part of chloride **IIe** isolated in the previous experiment was boiled in benzene, the hot solution was poured into hexane, and the solution was cooled to ~4°C. X-ray analysis of the crystals that formed showed that they belong to disiloxane **VIe**.

b. To a solution of 6.6. g of chloride **IIe** in 50 ml of $CHCl_3$ we added dropwise with stirring a solution of 4.2 g of $NaHCO_3$ in 50 ml of H_2O. After a day the layers were separated, the organic layer was evaporated in a rotary evaporator, the thick oily residue was poured with 20 ml of hexane, and the crystals that formed on the next day were filtered off to obtain 5.9 g (98%) of disiloxane **VIe**, mp 158–160°C (benzene). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1780 w, 1680 s (C=O), 1600 w (Ar). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 s (3H, SiMe), 3.33 д (2H, NCH_2, $^2J_{HH}$ 15.4 Hz), 2.57 s (4H, H^3, H^4), 7.37–7.63 m (5H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.76 (SiMe), 27.71 (C^3, C^4), 30.31 (NCH_2), 128.32 (C^o), 133.85 ($C^{\text{м}}$), 131.09 (C^n), 133.31 (C^u), 177.52 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} 15.2 ppm. Found, %: C 59.81; H 5.84; N 5.81. $C_{14}H_{28}N_2O_5Si_2$. Calculated, %: C 59.97; H 5.87; N 5.83.

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REFERENCES

1. Kost, D. and Kalikhman, I., *The Chemistry of Organic Silicon Compounds*, Chichester: Wiley, 1998, vol. 2, p. 1339.
2. Voronkov, M.G., Pestunovich, V.A., and Baukov, Yu.I., *Metalloorg. Khim*., 1991, vol. 4, no. 6, p. 1210.
3. Chuit, C., Corriu, R.J.P., Reye, C., and Young, J.C., *Chem. Rev*., 1993, vol. 93, p. 1371.
4. Hillard, R.W., Ryan, C.M., and Yoder, C.H., *J. Organomet. Chem*., 1978, vol. 153, p. 369.
5. Yoder, C.H., Ryan, C.M., Martin, G.F., and Ho, P.S., *J. Organomet. Chem*., 1980, vol., 190, p. 1.
6. Baukov, Yu.I., Kramarova, E.P., Shipov, A.G., Oleneva, G.I., Artamkina, O.B., Albanov, A.I., Voronkov, M.G., and Pestunovich, V.A., *Zh. Obshch. Khim*., 1989, vol. 59, no. 1, p. 127.
7. Artamkina, O.B., Kramarova, E.P., Shipov, A.G., Baukov, Yu.I., Macharashvili, A.A., Ovchinnikov, Yu.E., and Struchkov, Yu.T., *Zh. Obshch. Khim*., 1993, vol. 53, no. 10, p. 2289.
8. Artamkina, O.B., Kramarova, E.P., Shipov, A.G., Baukov, Yu.I., Macharashvili, A.A., Ovchinnikov, Yu.E., and Struchkov, Yu.T., *Zh. Obshch. Khim*., 1994, vol. 64, no. 2, p. 263.
9. Onan, K.D., McPhail, A.T., Yoder, C.H., and Hillyard, R.W., *J. Chem. Soc., Chem. Commun*., 1978, no. 5, p. 209.
10. Macharashvili, A.A., Shklover, V.E., Struchkov, Yu.T., Oleneva, G.I., Kramarova, E.P., Shipov, A.G., and Baukov, Yu.I., *J. Chem. Soc., Chem. Commun*., 1988, no. 10, p. 683.
11. Bassindale, A.R., Parker, D.J., Taylor, P.G., Auner, N., and Herrschaft, B., *J. Organomet. Chem*., 2003, vol. 667, p. 66.

12. Negrebetskii, V.V. and Baukov, Yu.I., *Izv. Akad. Nauk, Ser. Khim.*, 1997, no. 11, p. 1912.
13. Negrebetsky, V.V., Taylor, P.G., Kramarova, E.P., Bylikin, S.Yu., Belavin, I.Yu., Shipov, A.G., Bassindale, A.R., and Baukov, Yu.I., *J. Organomet. Chem.*, 2006, vol. 691, p. 3976.
14. Sidorkin, V.F., Belogolova, E.F., and Pestunovich, V.A., *J. Mol. Struct. (Teochem)*, 2001, vol. 538, p. 59.
15. Sidorkin, V.F., Vladimirov, V.V., Voronkov, M.G., and Pestunovich, V.A., *J. Mol. Struct. (Theochem)*, 1991, vol. 228, p. 1.
16. Ovchinnikov, Yu.E., Macharashvili, A.A., Struchkov, Yu.T., Shipov, A.G., and Baukov, Yu.I., *Zh. Strukt. Khim.*, 1994, vol. 35, no. 1, p. 100.
17. Bassindale, A.R., Borbaruah, M., Glynn, S.J., Parker, D.J., and Taylor, P.G., *J. Chem. Soc., Perkin Trans.*, 1999, vol. 2, p. 2099.
18. Bassindale, A.R., Glynn, S.J., Taylor, P.G., Auner, N., and Herrschaft, B., *J. Organomet. Chem.*, 2001, vol. 619, p. 132.
19. Pestunovich, V.A., Kirpichenko, S.V., Lazareva, N.F., Albanov, A.I., and Voronkov, M.G., *J. Organomet. Chem.*, 2007, vol. 692, p. 2160.
20. El-Sayed, I., Hatanaka, Y., Muguruma, C., Shimada, S., Tanaka, M., Koga, N., and Mikami, M., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 5095.
21. Hatanaka, Y., Okada, S., Minami, T., Goto, M., and Shimada, K., *Organometallics,* 2005, vol. 24, p. 1053.
22. Shipov, A.G., Kramarova, E.P., Murasheva, T.P., Artamkina, O.B., Negretskii, V.V., Pogozhikh, S.A., Baukov, Yu.I., Pogozhikh, S.A., Ovchinnikov, Yu.E., Voronkov, M.G., Bassindale, A.R., and Taylor, P.G., *Izv. Akad. Nauk, Ser. Khim.*, 2006. no. 3, p. 558.
23. Shipov, A.G., Kramarova, E.P., Artamkina, O.B., and Baukov, Yu.I., *Metalloorg. Khim.*, 1991, vol. 4. no. 5, p. 1101.
24. Korlyukov, A.A., Pogozhikh, S.A., Ovchinnikov, Yu.E., Lyssenko, K.A., Antipin, M.Yu., Shipov, A.G., Zamyshlyaeva, O.A., Kramarova, E.P., Negrebetsky, V.V., Yakovlev, I.P., and Baukov, Yu.I., *J. Organomet. Chem.*, 2006, vol. 691, p. 3962.
25. Shklover, V.E., Burgi, H.-B., Raselli, A., Armbruster, T., Hummel, W., *Acta Crystallogr., Sect. B,* 1991, vol. 47, p. 544.
26. Kobayashi, J., Kawaguchi, K., and Kawashima, T., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 16318.
27. *Cambridge Structural Database*, Release 2010.
28. Pogozhikh, S.A., Zamyshlyaeva, O.A., Kramarova, E.P., Antipin, M.Yu., Ovchinnikov, Yu.E., and Baukov, Yu.I., *Izv. Akad. Nauk, Ser. Khim.*,, 1999. no. 8, p. 1617.
29. Bassindale, A.R., Parker, D.J., Taylor, P.G., Auner, N., and Herrschaft, B., *Chem. Commun.*, 2000, p. 565.
30. Lazareva, N.F., *Doctoral (Chem.) Dissertation*, Irkutsk, 2009.
31. Shipov, A.G., Kramarova, E.P., Artamkina, O.B., Negrebetskii, V.V.,, Kalashnikova N.A., Ovchinnikov, Yu.E., Pogozhikh, S.A., Baukov, Yu.I., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 6, p. 954.
32. Shipov, A.G., Kramarova, E.P., Mamaeva, E.A., Zamyshlyaeva O.A., Negrebetsky, V.V., Ovchinnikov, Yu.E., Pogozhikh, S.A., Bassindale, A.R., Taylor, P.G., and Baukov, Yu.I., *J. Organomet. Chem.*, 2001, vol. 620, p. 139.
33. Bassindale, A.R. and Stout, T., *J. Organomet. Chem.*, 1984, vol. 271, p. C1.
34. Pogozhikh, S.A., Ovchinnikov, Yu.E., Kramarova, E.P., Negrebetskii, V.V., Shipov, A.G., Albanov, A.I., Voronkov, M.G., Pestunovich, V.A., and Baukov, Yu.I., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 10, p. 1617.
35. Pestunovich, V.A., Albanov, A.I., Larin, M.F., Voronkov, M.G., Kramarova, E.P., and Baukov, Yu.I., *Izv. Akad. Nauk, Ser. Khim.*, 1980. no. 9, p. 2178.
36. Fedotov, N.S., Kozyukov, V.P., Goler, G.E., and Mironov, V.F., *Zh. Obshch. Khim.*, 1972, vol. 42, no. 3, p. 358.
37. Hua, D.H., Miao, S.W., Bharathi, S.N., Katsuhira, T., and Bravo, A.A., *J. Org. Chem.*, 1990, vol. 55, p. 3682.
38. Birkofer, L., Dickop, H., and Majlis, S.H., *Chem. Ber.*, 1969, vol. 102, p. 3094.
39. Basenko, S.V. and Voronkov, M.G., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 4, p. 596.
40. Tamao, K. and Kumada, M., *J. Organomet. Chem.*, 1971, vol. 30, p. 349.
41. Sheldrick, G.M., *SADABS*, Version 2.01. Bruker Analytical X-ray Instruments, Madison, 1998.
42. Flack, H.D., *Acta Crystallogr., Sect. A*, 1983, vol. 39, p. 876.
43. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2007, vol. 64, p. 112.
44. Negrebetsky, Vad.V., Negrebetsky, V.V., Shipov, A.G., Kramarova, E.P., and Baukov, Yu.I., *J. Organomet. Chem.*, 1995, vol. 496, p. 103.