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The reaction of *N*-trimethylsilyl-amides and -lactams with dimethyl(chloromethyl)chlorosilane. Kinetically controlled formation of (N–Si) chelate intermediates, *O*-[(dimethylchlorosilyl)methyl]imidates and their rearrangement to final(O–Si) chelate *N*-[(dimethylchlorosilyl)-methyl]amides and lactams

I.D. Kalikhman, A.I. Albanov, O.B. Bannikova, L.I. Belousova, M.G. Voronkov, V.A. Pestunovich *,

Institute of Organic Chemistry, Siberian Division, USSR Academy of Sciences, 664033 Irkutsk (USSR)

A.G. Shipov, E.P. Kramarova and Yu.I. Baukov

N.I. Pirogov 2nd Moscow Medical Institute, 117437 Moscow (USSR)

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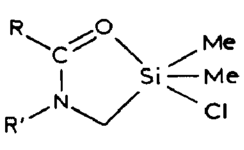
Abstract

The multistage character of the reaction of dimethyl(chloromethyl)chlorosilane (I) with *N*-trimethylsilyl-amides and -lactams (II) was shown by NMR monitoring. Interaction of the reactants starts with transsilylation, leading to Me_3SiCl and the corresponding *N*-[dimethyl(chloromethyl)silyl]amide or -lactam (III). The second stage, intramolecular (dimethylchlorosilyl)methylation of unstable III, proceeds in two directions. A kinetically controlled transformation of III affords previously unknown *O*-(dimethylchlorosilyl)methylated intermediates, *O*-[(dimethylchlorosilyl) methyl]imidates (IV) containing a hypervalent Cl–Si–N bond. The already known products, (O–Si) chelate *N*-[(dimethylchlorosilyl)methyl]amides (V), arise from the reaction carried out under thermodynamic control. The same compounds are also formed via the Chapman rearrangement of the intermediates (IV).

Introduction

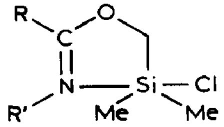
The reaction of $ClCH_2SiMe_2Cl$ with *N*- or *O*-trimethylsilyl-amides [1], -lactams [2,3], -diacetylamine [4,5], -ureas [6] and -acylhydrazines [7–9] provides a convenient route to (O–Si) chelate pentacoordinate silicon derivatives of type **A**:



(A)

R and R' = Alk , Ar ;
$R = R' = CH_2(CH_2)_nCH_2$
R = Me , R' = Ac ;
$R = NAlk_2$, R' = Alk ;
R = Alk , Ar , $R' = NMe_2$

The main mechanistic features of this process were disclosed by NMR. Any possibility for the existence of (N–Si) chelate derivatives **B**, as alternative isomers of compounds **A**, has not been discussed until now.



(B)

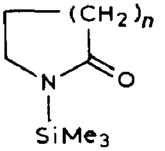
Meanwhile, germanium and tin analogues of compounds **B** have recently been found as products of the kinetically controlled stage of the reaction of $ClCH_2MMe_2Cl$ (M = Ge, Sn) with trialkyl-silylated, -germylated or -stannylated amides and lactams [10]. These are sufficiently stable and can be transformed to the thermodynamically more favourable (O–M) chelate heterocycles, similar to compounds **A**, only when heated to 60–100 °C. This promoted us to study, in more detail, the reaction pathway of dimethyl(chloromethyl)chlorosilane (I) with *N*-trimethylsilyl-amides and -lactams by NMR monitoring.

Results and discussion

As the starting *N*-trimethylsilyl-amides and -lactams, the corresponding *N*-methylacetamide (IIa), pyrrolidone (IIb), piperidone-2 (IIc) and hexahydroazepinone-2 (IId) derivatives were chosen:

$MeC(O)N(Me)(SiMe_3)$

(IIa)



n = 1 (IIb)
n = 2 (IIc)
n = 3 (IId)

This choice was made based on the fact that the spectral characteristics of the final products and some intermediates of their reaction with dimethyl(chloromethyl)chlorosilane are well known [2,3].

Taking into account the limited thermal stability of the intermediates [3], solutions of I and II in a mixture of chloroform and methylene chloride were mixed at −100 °C. The ampoule containing the reaction mixture was placed in the thermostatted NMR probe. The sample temperature was raised by 10 °C every 30 min until signals of new compounds appeared in the ^1H NMR spectrum. When these compounds were formed in sufficient quantities, the reaction was slowed down by cooling the solutions to −40 or −50 °C, and the ^{13}C and ^{29}Si NMR spectra of the reaction mixture were accumulated. The next cycle of NMR monitoring was performed at higher solution temperatures.

Table 1

^1H, ^{13}C and ^{29}Si NMR chemical shifts of *N*-trimethylsilyl-*N*-methylacetamide (IIa) and its derivatives

Compound	$T_{obs.}$ (°C)	$\delta(^1H)$				$\delta(^{13}C)$					$\delta(^{29}Si)$
		*Si*Me	Me*C*	Me*N*	CH_2	*Si*Me	Me*C*	Me*N*	CH_2	NCO	
IIa	25	0.25	2.04	2.79	–	−0.80	21.41	31.54		177.0	8.8
IIIa	−70	0.33	2.05	2.84	3.06	−3.36	22.48	32.83	29.95	179.37	6.2
IVa	−50	0.49	2.12	2.94	3.81	5.32	16.20	31.95	62.51	170.00	−51.4
Va	25	0.56	2.16	3.15	2.73	6.68	17.78	37.60	43.57	174.40	−40.3

Table 2

^1H, ^{13}C and ^{29}Si NMR chemical shifts of *N*-trimethylsilylpiperidone (IIc) and its derivatives

Compound	$T_{obs.}$ (°C)	$\delta(^1H)$					$\delta(^{13}C)$						$\delta(^{29}Si)$
		MeSi	CH_2-4,5	CH_2-3	CH_2-6	$SiCH_2$	SiMe	C-4,5	C-3	C-6	$SiCH_2$	NCO	
IIc	25	0.24	1.74	2.33	3.22	–	−0.22	23.35 20.86	32.56	44.15	–	176.99	8.8
IIIc	−80	0.34	1.76	2.32	3.23	3.08	−3.47	23.08 21.02	32.50	44.80	30.45	177.58	5.3
IVc	−40	0.55	1.85	2.43	3.39	3.82	5.42	22.10 19.12	25.68	43.01	61.98	172.87	−53.8
Vc	−40	0.55	1.85	2.43	3.39	2.75	7.69	22.15 19.88	27.90	48.86	43.01	173.20	−41.8

Table 3

^1H, ^{13}C and ^{29}Si NMR chemical shifts of *N*-trimethylsilylhexahydroazepinone (IId) and its derivatives

Compound	$T_{obs.}$ (°C)	δ(^1H)					δ(^{13}C)							δ(^{29}Si)
		Me	CH_2-4,5,6	CH_2-3	CH_2-7	$SiCH_2$	Me	C-4	C-5,6	C-3	C-7	$SiCH_2$	NCO	
IId	25	0.22	1.66	2.45	3.19	–	0.16	23.78	30.77 30.12	37.98	44.69	–	183.06	8.8
IIId	−90	0.34	1.75	2.56	3.21	3.07	−2.87	23.57	30.55 30.07	37.71	44.75	30.07	184.14	6.0
IVd	−40	0.60	1.74	2.52	3.35	3.88	5.74	22.37	30.12 31.53	27.30	44.80	63.17	178.88	−50.7
Vd	−40	0.60	1.74	2.52	3.52	2.92	7.42	22.70	32.45	26.49	50.92	45.02	178.78	−39.7

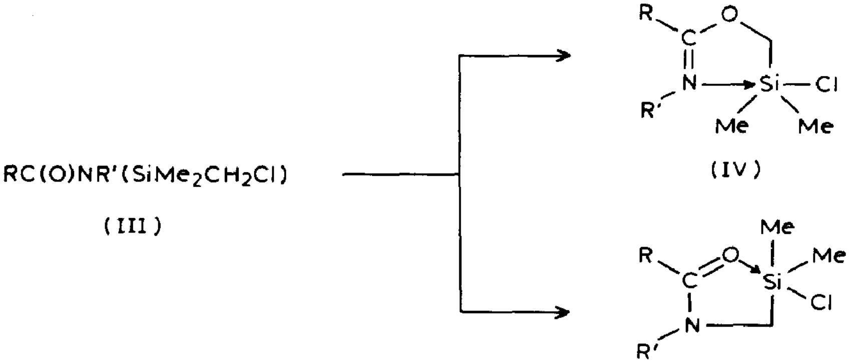
The results obtained can be summarized as follows. In the reaction with dimethyl(chloromethyl)chlorosilane under mild conditions, each of the *N*-trimethylsilylamides IIa–IId is quantitatively converted to the corresponding product of transsilylation (III):

$$\begin{array}{cccc} \mathrm{ClCH_2SiMe_2Cl} + & \mathrm{RC(O)NR'(SiMe_3)} \rightarrow & \mathrm{RC(O)NR'(SiMe_2CH_2Cl)} + & \mathrm{Me_3SiCl} \\ \mathrm{(I)} & \mathrm{(IIa\text{–}IId)} & \mathrm{(IIIa\text{–}IIId)} & \end{array}$$

The temperature conditions for the formation of and the upper limit for the existence of dimethyl(chloromethyl)silyl derivatives IIIa, IIIc, IIId are virtually the same. At −80 °C, transsilylation of IIa, IIc, IId is completed within some minutes. A noticeable subsequent conversion of intermediates IIIa, IIIc, IIId is observed as low as −30 °C. At −10 °C the lifetime of IIIa, IIIc, IIId does not exceed 10 min. *N*-Trimethylsilylpyrrolidone (IIb) undergoes rapid transsilylation at a higher temperature (about 25 °C), the intermediate IIIb formed becoming unstable at 60 °C.

The NMR spectra parameters of dimethyl(chloromethyl)silyl derivatives IIIa–IIId (Tables 1–3) indicate an *N*-silyl structure. For possible *O*-tautomers one should expect lower values for the ^{29}Si screening constants ($\delta > 16$) [11,12].

Within a temperature range of −30 to −20 °C, compounds IIIa, IIIc, IIId start a gradual conversion to the already known final (O–Si) chelate products V as well as to unstable *O*-dimethylchlorosilylmethyl derivatives IVa, IVc, IVd observed for the first time.

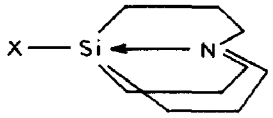


After completion of the conversion of III (30 min at −10 °C), the IV/V ratio is 1/4 (a), 1/4 (c) and 1/1 (d).

The *O*-[(dimethylchlorosilyl)methyl]imidate structure of intermediates IVa, IVc, IVd is confirmed by characteristic values of the ^{1}H and ^{13}C NMR chemical shifts of the OCH_2 fragments of these molecules. The high ^{29}Si screening constants of compounds IVa, IVc, IVd provide evidence for the Si atom pentacoordination [13]. On the basis of the known rules of apicophilicity of substituents attached to the trigonal–bipyramidal silicon atom [14], it is suggested that in molecules IVa, IVc, IVd three carbon atoms adjacent to the silicon atom occupy the equatorial positions, whereas the more electronegative nitrogen and chlorine prefer axial positions.

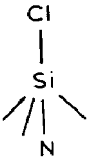
Thus, derivatives IV are new representatives of pentacoordinate silicon compounds with a hypervalent Cl–Si–N bond.

A temperature decrease from 0 to −45 °C causes a linear low frequency shift of the ^{29}Si NMR signal from δ −50.5 to δ −51.9 ppm. This is characteristic of compounds with the Si–N bond being the weakest ("coordinative") component of the hypervalent X–Si–N bond [15–17]. Therefore, IVa should be referred to a fairly rare class of (N–Si) chelate pentacoordinate silicon derivatives with three sp^3-hybridized carbons bound to the central TBP atom. Until recently, compounds of this kind were represented only by tricyclic derivatives [18]:

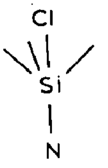


Compounds IVc, IVd are characterized by an opposite temperature dependence of the ^{29}Si chemical shifts. Cooling of solutions of IVc, IVd from −40 to −80 °C is accompanied by a visible ^{29}Si NMR signal shift to higher frequency. The δ(Si) values change from −53.8 to −52.9 ppm for IVc and from −50 to −48 ppm for IVd. A similar decrease in ^{29}Si screening constants is common in pentacoordinate silicon derivatives exhibiting a coordinative Si←Cl bond [7,8,13].

Thus, the Cl–Si bond order should be higher than the Si–N bond order in molecules VIa but lower in molecules IVc, IVd. According to the Bürgi-Dunitz principle [19], bond order ratios of this kind should be displayed at a molecular level by displacement of the TBP silicon atom out of the equatorial plane of three adjacent carbon atoms toward the chlorine atom in molecule IVa and toward the nitrogen atom in molecules IVc, IVd:



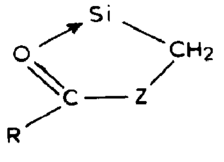
(IVa)



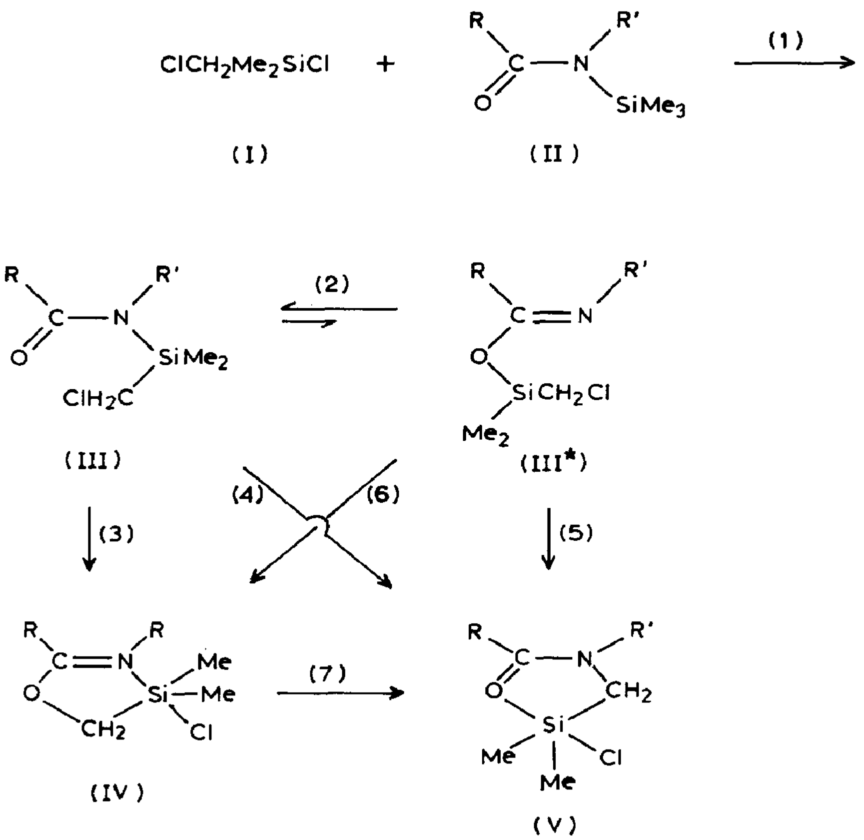
(IVc,d)

This consideration, as well as the lower ^{29}Si shielding and its more pronounced temperature dependence for IVd as compared with those for IVc, suggest [13] contraction of the Si–N bond length and lengthening of the Cl–Si bond on going from IVa to IVc to IVd.

The nitrogen and silicon bonding in compounds IVa, IVc, IVd causes a considerable deshielding in their sp^2-hybridized carbon atom with respect to that observed in *O*-alkylated imidate derivatives. The δ(C(2)) value for IVd, for example, is 9 ppm higher than for the product of hexahydroazepinone *O*-alkylation [20]. In this respect, the involvement of the nitrogen atom of the imidate fragments in the hypervalent bonding with silicon in IVd leads to effects similar to those known for the (O–Si) chelate (acyloxymethyl)silyl [21]] or (amidomethyl)silyl [22] fragments:



Z = O or NR

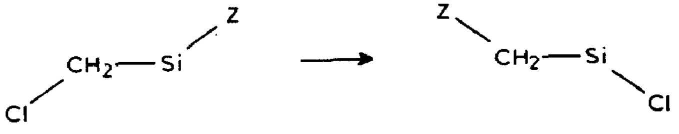


Scheme 1

Compounds IV are stable in solution at 0 °C. At 20–25 °C they transform completely to the (O–Si) chelate compounds V within 5–10 min.

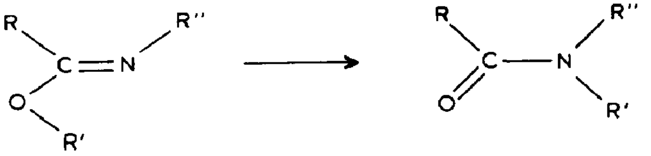
N-[Dimethyl(chloromethyl)silyl]pyrrolidone (IIIb) behaves differently from the related intermediates IIIa, IIIc, IIId. At 60 °C, IIIb immediately transforms to a (O–Si) chelate bicycle Vb. Its (N–Si) chelate analogue IVb does not form, even in trace amounts, according to NMR.

So, the reaction of dimethyl(chloromethyl)chlorosilane with N-trimethylsilylamides and -lactams can be represented by Scheme 1. Stage 1, transsilylation, needs no explanation. The tautomeric equilibrium (2) for both compounds IIIa–IIId and initial IIa–IId [11–13] are almost completely shifted toward the *N*-silyl form. This does not make it impossible, however, for the participation of the less stable *O*-silyl tautomer in further transformations. The intramolecular conversion of *N*- and *O*-tautomers can, in principle, occur in two ways. The first way is intramolecular *O*- or *N*-alkylation, followed by migration of the chlorine anion to the silicon atom (reactions 3 and 5). The second way is a 1,2-shift, with further formation of hypervalent bonds of the silicon atom with chlorine and the sp^2-hybridized hetero-



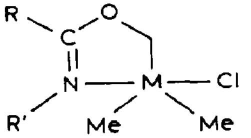
atom of the amide (reaction 4) or imidate (reaction 6) fragment. The latter seems less probable since 1,2-diatropic rearrangements of Si-substituted chloromethylsilanes take place under more rigid conditions [23], whilst the thermodynamic gain from an expansion of the silicon atom coordination number is, naturally, unable to lower the barrier of this isomerization.

Isomerization (7) is analogous to the Chapman rearrangement, well known in organic chemistry [24]:



But it proceeds under milder conditions. The transformation of caprolactam *O*-methylimidate to *N*-methylcaprolactam, for example, occurs as high as 300 ° C [25].

The (N–Si) chelate intermediates IVa, IVc, IVd also undergo rearrangement more readily than their germanium and tin analogues [10]. The latter can be isolated from the reaction mixture individually. In solution, their transition to thermodynamically more favourable (O–M) chelate derivatives occurs upon heating to 60–100 ° C. The reasons for the exclusive facility of the Chapman rearrangement of IVa, IVc, IVd have to be explained. The nearest task is to investigate the possibility of isolating these substances individually.



(M = Ge , Sn)

Experimental

^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.55, 22.49 and 17.85 MHz, respectively. ^{13}C and ^{29}Si NMR spectra were recorded with proton decoupling, the latter being obtained by the use of the INEPT pulse sequence.

Chemical shifts were measured relative to internal TMS for 0.5 *M* solutions of the samples in a 1/1 mixture of $CDCl_3$ and CH_2Cl_2 in 5-mm ampoules, the accuracy being ±0.01 ppm for ^1H and ±0.05 ppm for ^{13}C and ^{29}Si.

The starting compounds IIa, IIc, IId were prepared by routine techniques [26]. The degree of purity was checked by NMR. The NMR parameters of IIa, IIc, IId are given in Tables 1–3 and coincide with literature data. All the experiments with substances and reaction mixtures were carried out under dry argon, with anhydrous solvents distilled just before use. For preparing the reaction mixtures, use was made of equimolar solutions of the initial compounds, which were mixed in equal volumes. Any effect of reagent concentration on the reaction course and rate has not been observed.

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