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The synthesis and NMR spectra of new pentacoordinate silicon compounds, (O–Si)- and (Cl–Si)-chloro[1-(1,1-dimethyl-2-acylhydrazonium)methyl]dimethylsilanes and (O–Si)chloro-[2-(1,1-dimethyl-2-acylhydrazino)methyl]dimethylsilanes

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Abstract

Pentacoordinate silicon compounds containing a "chelate" six-membered silacarbofunctional ring, such as the chloro[1-(1,1-dimethyl-2-acylhydrazonium)methyl]-dimethylsilanes, $Me_2ClSiCH_2NMe_2NC(O)R$ with $R = CF_3$ (Ib), C_6H_5 (Ic), 4′-MeC_6H_4 (Id), 4′-$MeOC_6H_4$ (Ie), 4′-$NO_2C_6H_4$ (If) have been synthesized for the first time and were studied by NMR spectroscopy.

In contrast to Ib in molecules of Ia (R = Me), Ic–If the Cl–Si bond rather than O–Si bond is the weaker component of the hypervalent O–Si–Cl bond, which implies the possibility of Cl → Si coordinative interaction.

An irreversible rearrangement of compounds I upon heating leads to (O–Si)chloro[2-(1,1-dimethyl-2-acylhydrazino)methyl]dimethylsilanes, $Me_2ClSiCH_2N[C(O)R]NMe_2$ (II), and was used for preparative purposes.

Introduction

Pentacoordinate silicon derivatives with an intramolecular Si ← O bond in the silacarbofunctional fragment have for a long time been represented by a few five-membered (O–Si)chelate heterocycles [1–15] (see **A–F**).

The existence of their six-membered analogs has only been shown recently [16], with an unusual bipolar chelate silacycle (Ia) being formed along with a five-membered isomer (IIa) in the reaction of the *O*-trimethylsilyl derivative of 1,1-dimethyl-2-acetylhydrazine with dimethyl(chloromethyl)chlorosilane. Compound Ia is unstable and could only be identified in the reaction mixture, by NMR spectroscopy. Attempts to isolate Ia led to an unexpected rearrangement Ia → IIa. Meanwhile the

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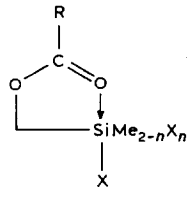
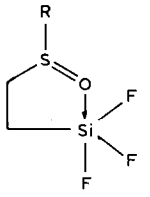


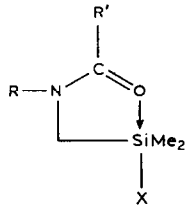
(A) [3-6]

(X = F ; R = Alk , Ar ;
n = 0-2)



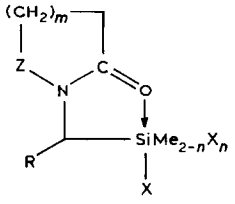
(B) [7]

(R = Alk , $ArCH_2$)



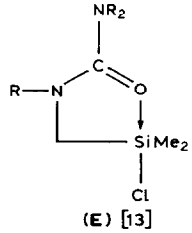
(C) [8]

(X = Cl ; R = Me , Ar ; R' = H , Me ;
R = $Me_2(Cl)SiCH_2$, $Me_2(Et_2N)SiCH_2$;
R' = Me ; X = Br ; R = Me , Me_3Si ; R' = Me)



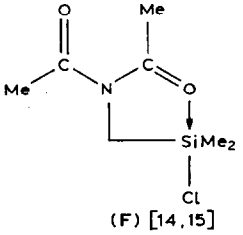
(D) [9-12]

(X = Hal , OSO_2R' , OCOR' ;
R = H , Me ; Z = CH_2 , C(O) ;
n = 0-2 ; m=1-3)



(E) [13]

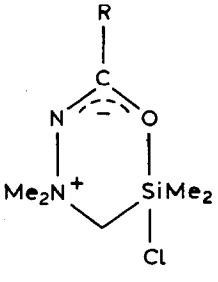
(R = Alk)



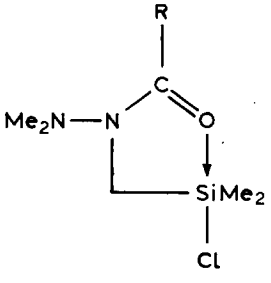
(F) [14,15]

(X = Hal , OCOMe , $OCOCF_3$)

structural features of molecules like Ia and their comparison with those of the five-membered (O–Si)chelate silacycle are of considerable interest.



(I)



(II)

(R = Me (a) , CF_3 (b) , C_6H_5 (c) , 4'-MeC_6H_4 (d) ,
4'-$MeOC_6H_4$ (e) , 4'-$NO_2C_6H_4$ (f))

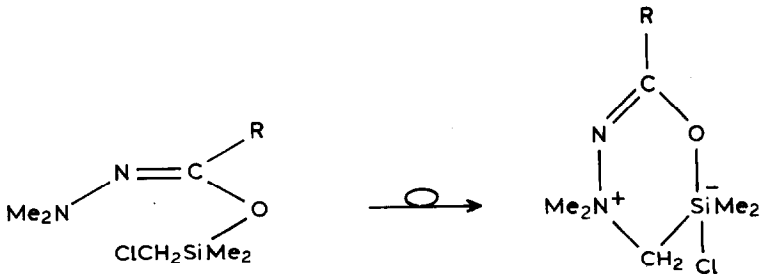
Here we describe the synthesis and NMR spectroscopy of the more stable (relative to Ia) chloro[1-(1,1-dimethyl-2-acylhydrazonium)methyl]dimethylsilanes (Ib–If), and their thermal isomerization to the corresponding (O–Si)chloro[2-(1,1-dimethyl-2-acylhydrazino)methyl]dimethylsilanes (IIb–IIf).

Results and discussion

The six-membered (O–Si)chelate silacycles (Ib–If) resulted after the reaction of dimethyl(chloromethyl)chlorosilane (III) with 1,1-dimethyl-2-acylhydrazine *O*-trimethylsilyl derivative, $Me_2NNC(R)OSiMe_3$ (R = CF_3 (IVb), C_6H_5 (IVc), 4′-MeC_6H_4 (IVd), 4′-$MeOC_6H_4$ (IVe) and 4′-$NO_2C_6H_4$ (IVf)). The reaction is analogous to that previously used for the synthesis of Ia from *O*-trimethylsilylated 1,1-dimethyl-2-acetylhydrazine (R = Me (IVa)). It was found that whereas molecules of IVa exist as an equilibrium mixture of *Z*- and *E*-conformers [16], their analogs IVb–IVf have, judging from their NMR data [17,18], a single conformation which could be identified only by structural analysis of the products of the reaction of these compounds with III. The reaction of IV with III is regioselective and leads to the formation of final products of type I and/or II depending on whether the initial reagents IV have *E*- or *Z*-conformation [16–19]. This is caused by the intramolecular rearrangement of the unstable transsilylation products V formed at the first stage (eq. 1).

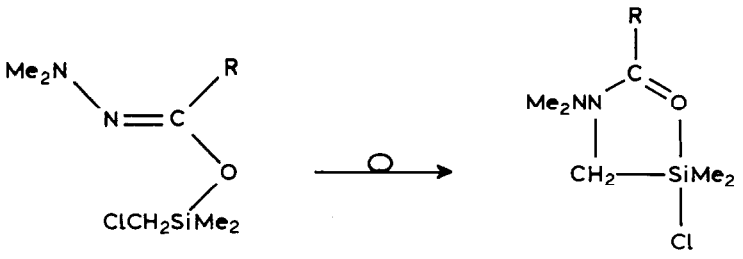
$$\underset{\text{(III)}}{Me_2(ClCH_2)SiCl} + \underset{\text{(IV-}Z,\ E\text{)}}{Me_2NN{=}C(R)OSiMe_3} \rightarrow Me_3SiCl + \underset{\text{(V-}Z,\ E\text{)}}{Me_2NN{=}C(R)OSiMe_2CH_2Cl} \qquad (1)$$

This rearrangement involves siliconmethylation of an accessible nitrogen atom, migration of the chlorine atom to silicon, and displacement of the NCO fragment π-bonds. In the case of *Z*-conformation of the intermediate V it is the N(1) atom which, owing to steric factors, undergoes intramolecular siliconmethylation to give six-membered (O–Si) silacycle I (eq. 2):



(V-Z) (I) (2)

If molecules of V are *E*-conformers electrophilic attack by chloromethylsilyl groups can occur at only the N(2) atom which results in the five-membered (O–Si)chelate compound II (eq. 3):



(V-*E*) (II) (3)

The above scheme of the formation of I and II has been simplified considerably since it ignores the possibility of V-*Z* → V-*E* isomerization during the reaction. The free energy of activation of these transformations should not exceed 30 kcal/mol from NMR data [20]. The above scheme does not take into account the I → II rearrangement either. In the reaction of III with IVa the ratio of final products (Ia/IIa = 3/4) is higher than that expected from the isomer composition of initial IVa (*Z*/*E* = 1/4) [16]. On the other hand, the reaction of III with 1-phenyl-2-acetylhydrazine *O*-trimethylsilyl derivative existing as only the *E*-conformer does not involve *E*–*Z* isomerization, which leads to only the five-membered analog of II, (O–Si)chloro[2-(1-phenyl-2-acetylhydrazino)methyl]dimethylsilane [19].

The tentative results of the reaction of III with IVb and IVc [18] and the similarity of the ^{29}Si chemical shifts in the NMR spectra of IVc–IVf [17] provide evidence for the *Z*-structure in derivatives IV. This allows the formation of six-membered silacycles Ib–f from IV, which has been confirmed experimentally.

Immediately after the introduction of equimolar quantities of III and IVb–IVf in $CDCl_3$ into an NMR tube thermostated at −60 °C we were able to fix the instant quantitative conversion of the starting reagents to trimethylchlorosilane and the corresponding dimethyl(chloromethyl)silyl derivatives Vb–Vf by monitoring with ^1H and ^{29}Si NMR spectroscopy. The most characteristic feature of Vb–Vf is an increase of 9–10 ppm in the ^{29}Si screening constants as compared with those observed for the corresponding trimethylsilyl derivatives (IV). This increase is quite typical of Si-substituted dimethyl(chloromethyl)silanes [21].Compounds Vb–Vf are extremely unstable and even at −60 °C undergo rearrangement to final reaction products within 30 min.

At room temperature the rearrangement of Vb–Vf is accelerated when it approaches completion within 1–2 min (^1H NMR data). The ^1H, ^{13}C and ^{29}Si NMR spectra show, that apart from trimethylchlorosilane, the corresponding six-membered silacycle I is the only final product of the reaction of III with IVb–IVf. NMR spectroscopy did not reveal the presence of another possible product, five-mem-

Table 1

^{29}Si NMR chemical shifts (δ (ppm)) of compounds $Me_2NNC(R)OSiMe_3$ (IV) and $Me_2NNC(R)O$-$SiMe_2CH_2Cl$ (V)

Compound	R				
	CF_3	C_6H_5	4′-MeC_6H_4	4′-$MeOC_6H_4$	4′-$NO_2C_6H_4$
IV [17]	27.8	18.8	18.6	18.4	21.5
V [a]	18.3	9.7	9.5	9.7	11.2

[a] At −60 °C.

bered (O–Si)chelate silacycle II, in the reaction mixture after it had been kept at room temperature. Mixing of the initial reagents at room temperature does not change the final composition of the reaction mixture. However, due to the high reaction rate the intermediates V could not be observed under these conditions not even by the rather sensitive method of ^{1}H NMR spectroscopy.

Unlike Ia, compounds Ib–If can be isolated individually by distillation and collection of the more volatile components, and recrystallization of the solid residue from ether or hexane. These compounds are white crystals which are sensitive to atmospheric moisture. The spectra of preparatively isolated Ib–If (Table 2) are identical with those observed for the compounds in the reaction mixture.

Similar to Ia described previously [16], Ib–If display low ^{1}H and ^{13}C nuclear shielding constants for their CH_2NMe_2 fragments. This indicates an "ammonium" character of the N(1) atoms in their molecules. The positive charge on this atom seems also to influence the ^{13}C chemical shifts of the NCO group. This influence as well as the coordinative interaction effect are responsible for both the delocalization of the excessive negative charge at the NCOSi fragment and the "one-and-a-half-bond" character of the N⋯C⋯O bonds. As a result, the corresponding signal in the ^{13}C NMR spectra of Ib–If is shifted by 10–20 ppm upfield with respect to the one observed for the CO group of the initial compounds IV [17]. The ^{29}Si chemical shifts in the NMR spectra of compounds I are typical of hypervalent silicon derivatives. In pentacoordinate silicon compounds the ^{29}Si nuclear shielding constants are considerably higher than in the tetrahedral analogs with covalently bonded substituents of similar electronegativity [6,22]. This is caused by an increasing of diamagnetic contribution to the ^{29}Si shielding constant with increasing coordination number of this atom [23]. According to Flygare, this contribution value is determined by the expression [24]:

$$\sigma^d(A) = \sigma_d^\circ(A) + \frac{e^2}{3mc^2} \sum_{K \neq A} \frac{Z_K}{r_{AK}}$$

where $\sigma_d^\circ(A)$ is the diamagnetic term of free atom A and the second term is a molecular or Madelung potential term in which the sum includes all other nuclei with the atomic number Z and at a distance r_{AK} from A. Thus, the approaching of the donating partner in the coordinative interaction towards the silicon atom should enhance the σ^d(Si) value.

For isostructural compounds with one or two highly electronegative substituents at the pentacoordinate silicon atom the increase in ^{29}Si shielding constants is proportional to the strengthening of coordinate interaction [6]. Hence, comparison of the σ(Si) values for the derivatives Ib–If indicates that the coordination bonding weakens in the order: Ib ≃ If ≫ Ic > Ie > Id. At first glance, this weakening with increasing electron-donating ability of substituent R is abnormal.

The decrease in the ^{29}Si shielding constants for Ic–If when solutions of these are cooled is also unusual. The effect of temperature on the ^{29}Si chemical shifts is more clearly defined for the compounds with less-shielded ^{29}Si nuclei. It is rather symptomatic that the temperature decrease accounts for downfield shifts of the carbon nuclei adjacent to O and Si atoms in the ^{13}C NMR spectra of Ic–If. All of this is indicative of a decreased participation by the silicon atom in coordinative interaction when the temperature of the solution decreases. An analogous regularity was observed by us in the ^{29}Si and ^{13}C NMR spectra of Ia [16]. Only for compound

Table 2

^{13}C and ^{29}Si NMR chemical shifts (δ (ppm)) of compounds $Me_2(Cl)\overline{SiCH_2NMe_2NC(O)}R$ (I) at 25 °C [a]

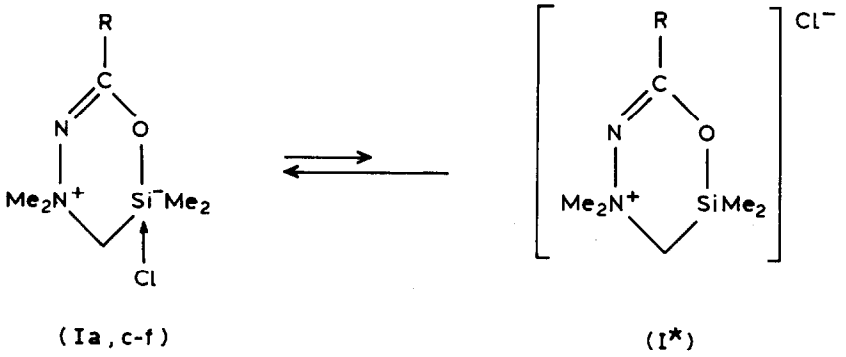
Compound	R	^{29}Si	^{13}C								
			Me_2Si	NMe_2	CH_2	C=O	$C_R(1)$	$C_R(2)$	$C_R(3)$	$C_R(4)$	4′-R′
Ia [16]	Me	−33.5	4.8	58.0	56.9	169.2	22.0				
		(−14.0)									
Ib	CF_3	−42.9	7.6	57.5	63.8	160.0	117.2				
		(−46.8)	(7.6)	(57.4)	(62.8)	(160.0)	(117.2)				
Ic	C_6H_5	−20.8	5.3	58.3	59.1	165.7	132.6	127.9	128.8	130.0	
		(−3.6)	(3.4)	(58.3)	(56.9)	(164.0)					
Id	4′-MeC_6H_4	−16.3	4.7	58.5	59.4	165.5	143.5	129.3	127.9	128.3	21.6
		(2.1)	(2.6)	(58.6)	(56.3)	(163.8)					(21.7)
Ie	4′-$MeOC_6H_4$	−17.4	4.4	58.5	58.5	165.0	163.4	129.8	113.9	123.1	55.5
		(−1.3)	(2.7)	(58.5)	(56.5)	(163.5)					
If	4′-$NO_2C_6H_4$	−43.1	7.6	58.1	60.9	165.5	149.8	128.9	123.5	137.4	
		(−31.4)	(6.6)	(58.1)	59.6	(164.3)					

[a] The δ values shown in parentheses are determined at −40 °C, Ia at −70 °C.

Ib is cooling of the sample accompanied by upfield shifts of the ^{29}Si NMR signal, a feature which is typical of most compounds with a coordinate Si ← O bond [6,12,15].

The above experimental data can be explained in terms of the hypervalent bonding model [6,25] in the axial O–Si–Cl fragment of molecule I. Indeed, it is quite reasonable to admit the evident increase in the degree of interaction (bond order) between the silicon and oxygen atoms as the electron-donating abilities of substituent R increase in the order: Ib ≪ If < Ic < Id < Ie < Ia. Owing to a common property of pentacoordinate silicon compounds, i.e., constancy of the total order of the hypervalent bond [6,26] the O–Si bond strengthening should be accompanied by weakening of the Si–Cl bond. In molecules of Ib the ^{29}Si shielding constant and, consequently, the degree of silicon atom pentacoordination are practically coincident with those for related (O–Si)chloro(*N*-amidomethyl)dimethylsilane (C) [8a]. Meanwhile, the silicon atom in crystals of the latter is nearly trigonal-bipyramidal [8a]. Strengthening of the Si–O bond, weakening of the Si–Cl bond and decrease in the degree of coordinative interaction on going from compounds Ib and C to derivatives Ia and Ic–If can be explained on the assumption that the Cl–Si rather than the O–Si bond is the weakest component of hypervalent O–Si–Cl bond in the latter molecules. This implies the possibility of coordinative Cl → Si interaction not observed previously.

Indeed, from the analysis of the Flygare formula, it follows that a significant lengthening of the Si–Cl bond with a slight shortening of the O–Si bond length can induce the observed lowering of the ^{29}Si shielding constants of molecules Ia, Ic–If as compared with those of Ib and C. Cooling solutions of Ia, Ic–If probably causes weakening or even partial dissociation of the Si ← Cl bond (eq. 4):



(Ia, c-f) (I*) (4)

This is due to an increase in the dielectric constant of the medium at low temperatures, which facilitates charge separation in the dissolved molecule. The weaker the Si ← Cl interaction, the greater will be the shift to the right of the I ⇌ I* equilibrium.

So, among the six-membered silacycles I obtained by us only Ib is a true (O–Si)chelate derivative. In molecules of other compounds of this series the silicon atom is involved in the six-membered heterocycle to form a "coordinate bond" with the chlorine anion, the bond becoming stronger with temperature elevation.

The weaker interaction of silicon with the halogen rather than with the oxygen

Table 3

^{13}C and ^{29}Si NMR chemical shifts (δ (ppm)) of compounds $Me_2ClSiCH_2N[C(O)R]NMe_2$ (II) at 25 °C [a]

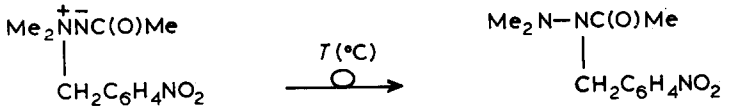
Compound	R	^{29}Si	^{13}C								
			Me_2Si	CH_2	NMe_2	C=O	$C_R(1)$	$C_R(2)$	$C_R(3)$	$C_R(4)$	4′-R′
IIa [16]	Me	−35.9 (−38.3)	7.4	27.9	43.1	175.5	16.9				
IIb	CF_3	11.9 (9.0)	3.9 (4.3)	30.4 (27.5)	43.1 (43.0)	160.6 (160.1)	117.6 (117.0)				
IIc	C_6H_5	−34.1 (−37.9)	6.9 (7.0)	29.6 (29.9)	43.2 (43.3)	171.7 (171.3)	129.5 (128.2)	129.6 (129.9)	128.1 (128.0)	132.2 (132.7)	
IId	4′-MeC_6H_4	−36.3 (−38.1)	7.3 (7.4)	29.6 (29.2)	43.2 (43.2)	171.6 (171.2)	126.0 (125.7)	130.1 (130.1)	128.8 (128.7)	143.3 (143.6)	21.7 (21.7)
IIe	4′-$MeOC_6H_4$	−38.1 (−38.9)	7.3 (7.4)	29.7 (29.4)	43.0 (43.1)	170.3 (170.0)	120.2 (119.2)	132.7 (132.9)	113.4 (113.2)	163.1 (162.9)	55.5 (55.5)
IIf	4′-$NO_2C_6H_4$	−23.9 (−30.7)	6.7 (7.0)	29.4 (29.0)	43.2 (43.4)	170.2 (169.9)	126.1 (126.0)	130.2 (130.6)	123.3 (123.1)	149.4 (149.1)	

[a] The δ values shown in parentheses are determined at −40 °C.

atom in the axial fragment O–Si–Hal and the ability of the Si–Hal bond to dissociate in solutions is rare but known properties of pentacoordinate silicon cyclic derivatives. They first became apparent while studying the ^{29}Si NMR spectra, electrical conductivity and X-ray diffraction of dimethyl(*N*-2-piperidonomethyl)-silane bromo- and iodo derivatives (**D**) [6,12,27].

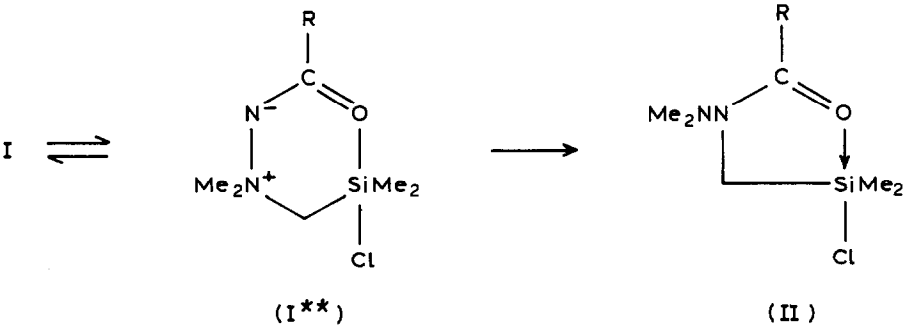
Short heating of Ib–If at melting temperature causes an irreversible rearrangement to the corresponding (O–Si)chloro[2-(1,1-dimethyl-2-acetyhydrazino)methyl]-dimethylsilanes II. This rearrangement is analogous to the one observed previously [16] with Ia → IIa conversion. In the case of Ib–If, however, their thermal isomerization is still the only preparative route to the five-membered silacycles IIb–IIf because of the *E*-configuration of starting IVb–IVf [17]. The relative rate and the degree of I → II conversion increases in the order: Ib < If < Ic < Id ≃ Ie ≪ Ia.

Outwardly it resembles the known Wawsonek rearrangement [28] first revealed for ylide:



This is the first such rearrangement ever observed in organosilicon compounds.

At melting temperature molecule I could first undergo transition to the ylide form (I**) and then to convert to II under migration of the dimethyl(chloro)silyl-



methyl group from N(1) to N(2).

The proposed scheme thus accounts for the relative rate sequence for the rearrangement to II observed in the series Ia–If. The lower the electronegativity of substituent R, the more likely is the structure I** and the more facile the conversion I → II.

The structure of compounds II was confirmed by ^{13}C and ^{29}Si NMR spectroscopy (Table 3). The ^{29}Si shielding constants for compounds II are also considerably higher than for a model derivative of tetracoordinate silicon, $ClCH_2Si(Me)_2Cl$, which has similar electronegativity of the covalently bonded substituents. Participation of the silicon atom in coordination bonding in molecules II is evidenced by a characteristic 5 ppm increase of the ^{13}C chemical shifts of the N–CO group in the NMR spectra compared with those of the corresponding 1,1-dimethyl-2-acylhydrazines, $Me_2NNHC(O)R$. According to ^{29}Si NMR spectroscopy, the strength of Si ← O bonding decreases as the electron-withdrawing properties of substituent R increase in the sequence IIe > IId > IIc > f ≫ IIb. On cooling, in solutions of the

compounds strengthening of the Si ← O bond is observed, this effect is most noticeable for compounds with the weakest coordinative interaction.

Comparison of the ^{29}Si chemical shifts in the NMR spectra of five-membered (O–Si)chelate *N*-dimethylchlorosilylmethyl derivatives **C–F** and II indicates an increase in the degree of Si ← O bonding in their molecules in the order **F** ≃ **E** < IIb–IIf ⩽ **D** < **C**.

The greater degree of Si–O interaction in the six-membered heterocycles I is due to a higher basicity of their negatively charged oxygen atom in comparison with the "amidic" group oxygen in their five-membered analogs.

Experimental

^{1}H, ^{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. All ^{13}C and ^{29}Si NMR spectra were recorded with proton decoupling, the latter being obtained by use of the INEPT pulse sequence.

Chemical shifts are reported relative to internal TMS for 10–20% solutions of the samples in $CDCl_3$, the accuracy being ±0.01 ppm for ^{1}H and 0.05 ppm for ^{13}C and ^{29}Si.

The NMR mixtures were placed in septum cap 5 mm NMR tubes. NMR spectroscopy of the isolated compounds I and II was carried out on samples in evacuated sealed ampules which were inserted into 10 mm NMR tubes.

The preparative method and physico-chemical parameters of the starting 1,1-dimethyl-2-aroylhydrazines (IV) have been reported previously [17].

(O–Si)chloro[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)methyl]dimethylsilane (Ib) *

^{1}H NMR: δ 0.73 (s, 6H, $SiMe_2$), 3.46 (s, 2H, CH_2), 3.36 (s, 6H, NMe_2).

(Cl–Si)chloro[1-(1,1-dimethyl-2-benzoylhydrazonium)methyl]dimethylsilane (Ic)

Dimethyl(chloromethyl)chlorosilane (2.47 g, 17.3 mmol) was added to frozen (by liquid nitrogen) solution of 3.21 g (13.6 mmol) of dimethylhydrazone-1-trimethylsiloxyphenone (IVc) in 15 ml of dry ether. The reaction mixture was elevated stepwise (1–3 h) to room temperature, with continuous stirring. After 6 h at 20 °C the readily volatile products were distilled off in vacuum. The residue, Ic, white crystalline powder was washed with dry ether (2 × 10 ml), dried in vacuum (0.5 mmHg) at 20 °C. The yield of Ic 2.90 g (79%), m.p. 164 °C (vacuumized capillary). Found: C, 53.16; H, 7.26; N, 10.05; Si, 9.79; Cl, 13.55. $C_{12}H_{19}N_2OSiCl$ calc: C, 53.22; H, 7.07, N, 10.34; Si, 10.37; Cl, 13.09%.

Compounds Id, Ie and If were prepared similarly by the reaction of $ClMe_2SiCH_2Cl$ with dimethylhydrazone-1-trimethylsiloxy-4′-methylphenone (IVd), dimethylhydrazone-1-trimethylsiloxy-4′-methoxyphenone (IVe) or dimethylhydrazone-1-trimethylsiloxy-4′-nitrophenone (IVf), respectively, in dry CH_2Cl_2.

(Cl–Si)chloro[1-(1,1-dimethyl-2-(4′-methylbenzoyl)hydrazonium)methyl]dimethylsilane (Id)

Yield 80%, m.p. 159–160 °C (vacuumized capillary). Found: C, 55.00; H, 7.49;

* Details of the synthesis and physico-chemical parameters of Ib are given in ref. 29.

N, 9.99; Si, 9.63; Cl, 12.99. $C_{13}H_{21}N_2OSiCl$ calc: C, 54.81; H, 7.43; N, 9.83; Si, 9.86; Cl, 12.45%. ^1H NMR: δ 0.80 (s, 6H, $SiMe_2$), 3.92 (s, 2H, CH_2), 2.41 (s, 3H, Me), 3.60 (s, 6H, NMe_2), 7.29 and 7.80 (m, 4H, C_6H_4).

(Cl–Si)chloro[1-(1,1-dimethyl-2-(4'-methoxybenzoyl)hydrazonium)methyl]dimethylsilane (Ie)

Yield 81%, m.p. 161.5–162.8°C (vacuumized capillary). Found: C, 51.29; H, 7.12; N, 9.89; Si, 9.89; Cl, 12.41. $C_{13}H_{21}N_2O_2SiCl$ calc: C, 51.90; H, 7.04; N, 9.31; Si, 9.34; Cl, 11.78%. ^1H NMR: δ 0.79 (s, 6H, $SiMe_2$), 3.85 (s, 2H, CH_2), 3.58 (s, 6H, NMe_2), 3.90 (s, 3H, OMe), 6.62 and 7.80 (m, 4H, C_6H_4).

(Cl–Si)chloro[1(1,1-dimethyl-2-(4'-nitrobenzoyl)hydrazonium)methyl]dimethylsilane (If)

Yield 71%, m.p. 159–160°C (vacuumized capillary). Found: C, 44.44; H, 5.77; N, 13.24; Si, 9.93; Cl, 10.95. $C_{12}H_{18}N_3O_3SiCl$ calc: C, 45.64; H, 5.74; N, 13.31; Si, 8.94; Cl, 8.94%. ^1H NMR: δ 0.82 (s, 6H, $SiMe_2$), 3.70 (s, 2H, CH_2), 3.46 (s, 6H, NMe_2) 8.23 (m, 4H, C_6H_4).

(O–Si)chloro[2-(1,1-dimiethyl-2-benzoylhydrazino)methyl]dimethylsilane (IIc)

1 g of compound Ic was heated for half an hour at 170°C in an evacuated sealed ampule. To the substance formed 30 ml of hexane was added. The mixture was heated to 65°C. The solution was decanted, and after cooling to room temperature crystals of IIc precipitated. The mother solution was decanted, and the crystals dried in vacuum (0.5 mmHg) at 20°C. Yield of IIc 0.60 g (60%), m.p. 116–117°C (vacuumized capillary). Found: C, 53.24; H, 6.98; N, 10.36; Si, 10.42; Cl, 12.96. $C_{12}H_{19}N_2OSiCl$ calc: C, 53.22; H, 7.07; N, 10.34; Si, 10.37; Cl, 13.09%. ^1H NMR: δ 0.70 (s, 6H, $SiMe_2$), 2.57 (s, 6H, NMe_2), 2.96 (s, 2H, CH_2), 7.84 and 7.90 (m, 5H, C_6H_5).

(O–Si)chloro[2-(1,1-dimethyl-2-(4'-methoxybenzoyl)hydrazino)methyl]dimethylsilane (IIe) was prepared in a way similar to that for compound IIc. Yield IIe 70%, m.p. 123.5–124°C (vacuumized capillary). Found: C, 52.04; H, 6.85; N, 9.31; Si, 9.60; Cl, 12.29. $C_{13}H_{21}N_2SiCl$ calc: C, 51.90; H, 7.04; N, 9.31; Si, 9.34; Cl, 11.78%. ^1H NMR: δ 0.70 (s, 6H, $SiMe_2$), 2.59 (s, 6H, NMe_2), 2.97 (s, 2H, CH_2), 3.87 (s, 3H, OMe), 6.93 and 8.00 (m, 4H, C_6H_4).

Compounds IId, IIf and IIb were prepared analogously from Id, If and Ib, respectively.

(O–Si)chloro[2-(1,1-dimethyl-2-(4'-methylbenzoyl)hydrazino)methyl]dimethylsilane (IId)

^1H NMR: δ 0.71 (s, 6H, $SiMe_2$), 2.57 (s, 6H, NMe_2), 2.96 (s, 2H, CH_2), 2.41 (s, 3H, Me), 7.26 and 7.81 (m, 4H, C_6H_4).

(O–Si)chloro[2-(1,1-dimethyl-2-(4'-nitrobenzoyl)hydrazino)methyl]dimethylsilane (IIf)

^1H NMR: δ 0.70 (s, 6H, $SiMe_2$), 2.58 (s, 6H, NMe_2), 2.97 (s, 2H, CH_2), 7.94 and 8.23 (m, 4H, C_6H_4).

(O–Si)chloro[2-(1,1-dimethyl-2-trifluoroacetylhydrazino)methyl]dimethylsilane (IIb)

^1H NMR: δ 0.65 (s, 6H, $SiMe_2$), 2.56 (s, 6H, NMe_2), 2.89 (s, 2H, CH_2).

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