The hindered inversion of the seven-membered ring in *N*-(chlorodimethylgermylmethyl)- and *N*-(chlorodimethylstannylmethyl)hexahydroazepin-2-ones

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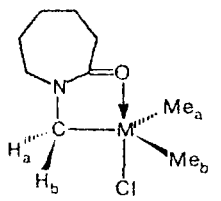
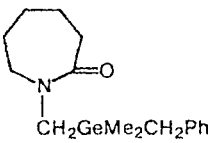
The stereochemical flexibility of *N*-(chlorodimethylgermylmethyl)- and *N*-(chlorodimethylstannylmethyl)hexahydroazepin-2-ones was studied by dynamic NMR spectroscopy. Protons of the NCH_2M and MMe_2 groups (M = Ge, Sn) were shown to be anisochronic at low temperatures (<−70 °C). The free activation energy of the process resulting in chemical equivalence of the protons indicated was determined. The anisochronicity of signals observed is due to the restricted inversion of the seven-membered cycle.

Key words: pentacoordinated germanium and tin compounds; stereochemical flexibility; intramolecular coordination; dynamic NMR spectroscopy.

Stereochemical flexibility is the characteristic feature of penta- and hexacoordinated (hypervalent) compounds of silicon, germanium, and tin.[1,2] In this work, continuing our studies on stereochemistry of hypervalent compounds of these elements with amidomethyl and related C,O-coordinating ligands,[2] we discuss the results of studying stereodynamic transformations of hexahydroazepin-2-one derivatives, chlorides **1** and **2**, containing pentacoordinated germanium and tin atoms by dynamic ^{1}H NMR spectroscopy (^{1}H DNMR). *N*-(Benzyldimethylgermylmethyl)hexahydroazepin-2-one (**3**), in which the Ge atom is tetracoordinated, was studied for comparison. The spectral (^{1}H and ^{13}C NMR) parameters of compounds **1**—**3** are presented in Table 1. The synthesis of chlorogermane **1** has been described previously.[3] The data on methods of preparation of compounds **2** and **3** will be presented elsewhere.



1: M = Ge
2: M = Sn



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Pentacoordination of the tin atom in chloride **2** is indicated by the upfield shift of the signal in the ^{119}Sn NMR spectrum (in $CDCl_3$ $\delta(^{119}Sn)$ −35.3, *cf.*: −40.6 ppm for *N*-methyl-*N*-(chlorodimethylstannylmethyl)acetamide[4]) as compared, for example, to chlorodimethylchloromethylstannane (in $CDCl_3$ $\delta(^{119}Sn)$ 112.3) taken as the model compound.

The trigonal-bipyramidal structure of the central coordination node in chloride **1** in the crystalline state was established by X-ray diffraction analysis.[5] According to the IR spectroscopy data, the germanium atom in compound **3** is tetracoordinated (the 1500—1750 cm^{-1} region contains one intense absorption band νC=O at 1620 cm^{-1}, $CHCl_3$).

The ^{13}C NMR spectrum of compound **2** at room temperature exhibits the spin-spin coupling of the tin atom with carbon atoms of the NCH_2Sn ($^1J(^{118}SnC)$ = 550.4 Hz and $^1J(^{117}SnC)$ = 527.3 Hz) and $Sn(Me)_2$ groups ($^1J(^{118}SnC)$ = 543.2 Hz and $^1J(^{117}SnC)$ = 518.6 Hz), which is retained at low temperatures. Note that, unlike bis(lactamomethyl)dichlorostannanes containing hexacoordinated tin atoms,[6] no spin-spin coupling of tin and carbon atoms of the carbonyl group were detected. Perhaps, this is related to an increase in the coordination bond length in compounds of pentacoordinated tin compared to that in compounds of hexacoordinated tin. In the ^{1}H NMR spectra, the direct constants of spin-spin interaction of the tin atom with protons of the $SnMe_2$ and NCH_2Sn groups are not so high (70.5 and 61.6 Hz in $CDCl_3$, respectively). In this case, the temperature decrease does not result in their change as well.

At low temperatures (down to −100 °C), only one set of signals is detected in the NMR spectra of chlorides **1** and **2**. This is their difference from the Si analog, whose low-temperature ^{1}H, ^{13}C, and ^{29}Si NMR spectra, as in the case of several other pentacoordinated silicon chlorides, exhibit two sets of signals with differ-

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Table 1. Chemical shifts of signals in ^1H and ^{13}C NMR spectra of compounds **1**—**3**

Compound	Solvent	Chemical shift, δ							
		H(3), C(3)	H(4), C(4)	H(5), C(5)	H(6), C(6)	H(7), C(7)	NCH_2	MMe	C=O
1	$CDCl_3$	2.52 m, 29.63	1.65 m, 22.85	1.69 m, 26.76	1.77 m, 34.13	3.51 m, 51.77	3.03 s, 45.16	0.92 s, 8.52	 178.14
2	$CDCl_3$	2.50 m, 29.46	1.61 m, 22.80	1.68 m, 26.46	1.75 m, 34.67	3.55 m, 53.55	2.88 s, 39.86	0.69 s, 0.67	 179.32
	$(CD_3)_2CO$	2.44 m, 29.77	1.63 m, 23.02	1.69 m, 26.53	1.75 m, 34.46	3.49 m, 53.28	2.89 s, 39.34	0.62 s, 0.49	 179.72
	$(CD_3)_2CO$ [a]	30.38	22.78	26.05	34.03	52.93	38.56	0.48	179.87
	CD_2Cl_2	2.53 m, 29.79	1.65 m, 23.18	1.71 m, 26.79	1.77 m, 34.96	3.59 m 54.03	2.91 s, 40.02	0.69 s, 0.65	 179.75
	CD_2Cl_2 [b]	29.89	23.02	26.57	34.94	53.86	39.59	1.17	180.00
3[c]	$CDCl_3$	2.49 m, 30.24	1.56 m, 23.70	1.65 m, 25.59	1.69 m, 30.24	3.17 m, 52.33	3.09 s, 40.72	0.16 s, −3.29	 174.77

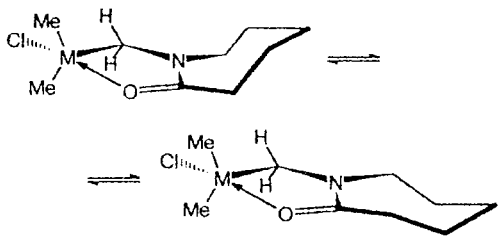
[a] The ^{13}C NMR spectrum was obtained at −95 °C.
[b] The ^{13}C NMR spectrum was obtained at −85 °C.
[c] Chemical shifts of ^1H NMR signals, δ: 2.30 (s, 2 H, CH_2Ph); 7.21 (t, 2 H, H_{ortho}, C_{ortho}, $^1J_{HH}$ = 7.6 Hz); 7.03 (t, 2 H, H_{meta}, C_{meta}, $^1J_{HH}$ = 7.6 Hz); 7.01 (d, 1 H, H_{para}, C_{para}, $^1J_{HH}$ = 7.6 Hz). Chemical shifts of ^{13}C NMR signals, δ: 37.29 (CH_2Ph), 128.52 (C_{ortho}), 124.27 (C_{meta}), 127.99 (C_{para}), 141.02 (C_{ipso}).

ent intensities.[7] This fact was explained by the dynamic equilibrium between the monomer and hexacoordinated homoassociate with bridge chlorine atoms.[7]

At ~20 °C, signals of protons of the NCH_2M and MMe_2 groups of compounds **1** and **2** in the ^1H NMR spectra are recorded as singlets. The singlet of the NCH_2M group is transformed into a quartet of the AB system with $^1J_{HH}$ = 13—14 Hz. In the case of compound **2**, at low temperatures (<−70 °C), we observed nonequivalence of the signals of the MMe_2 groups, which are detected as two singlets with equal intensities. The temperature increase to room temperature is accompanied by recovering of the spectral pattern.

The values of the free activation energy ($\Delta G^{\neq}$, kcal mol^{-1}) in an equimolar mixture of $CDCl_3$ and CD_2Cl_2 were determined by the ^1H DNMR method at the temperature of coalescence (T_c) of the signals from MMe_2 and NCH_2M and equaled: 9.4±0.2 (T_c = −79.1 °C, NCH_2Ge) for chloride **1**; 9.6±0.2 (T_c = −73.3 °C, NCH_2Sn) and 9.3±0.1 (T_c = −87.8 °C, $SnMe_2$) for chloride **2**. In the accessible temperature range (below −100 °C), we failed to observe anisochronicity of the signals of the $GeMe_2$ group in the ^1H NMR spectra of compound **1**.

Taking into account the conformational uniformity of the seven-membered cycle at low temperatures (Table 1), which was established by the ^{13}C NMR method, we can assume that the nonequivalence of the ^1H signals of the indicatory groups observed in the NMR spectra of compounds **1** and **2** is due to the restricted inversion of the lactam cycle. As a result, hydrogen atoms and methyl groups in the five-membered chelate cycle are arranged at either the same or opposite sides from the plane of this cycle relative to the C(5) atom of the seven-membered lactam. In the conformational equilibrium presented below, the seven-membered lactam cycle is shown in the "chair" conformation observed for chloride **1** in the crystalline state.[5]



The calculated $\Delta G^{\neq}$ values of chlorides **1** and **2** are close to the inversion barrier of the cycloheptane ring (8.1 kcal mol^{-1}).[5] Note that diastereomers existing due to the asymmetrical conformation of the seven-membered lactam cycle and the chiral pentacoordinated silicon atom in the molecule were observed in the crystalline state by X-ray diffraction method for *N*-(dichloromethyldichlorosilylmethyl)hexahydroazepin-2-one, in which one chlorine atom is in the axial position, and the methyl group and the second chlorine atom are in two different (with respect to the seven-membered cycle) equatorial positions.[8]

In the case of compound **3** in which the Ge atom is tetracoordinated, no stereodynamic process analogous to that under discussion is observed, which indicates that the presence of the intramolecular chelate cycle in addition to the seven-membered lactam cycle in chlorides **1** and **2** results in anisochronicity of protons of the NCH_2M and MMe_2 groups.

The chemical shift of the Sn atom in chloride **3** ($\delta(^{119}Sn)$ −33.3, $CDCl_3$ −60 °C) is temperature-independent, which indicates that the central atom retains its coordination state. Therefore, a nonregular mechanism of the stereodynamic process observed involving the cleavage if the coordination O→M bond seems improbable.

Experimental

^1H, ^{13}C, and ^{119}Sn NMR spectra of compounds studied were obtained on a Varian XL-400 spectrometer (400.1, 100.6, and 149.2 MHz, respectively) in a pulse mode followed by the Fourier transformation and ^2H-stabilization of resonance conditions. Low-temperature studies were carried out in an equimolar mixture of $CDCl_3$ and CD_2Cl_2. ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane as the internal standard. ^{119}Sn chemical shifts were measured relative to tetramethylstannane as the external standard. Free activation energies were determined by the modified Eyring equation.[9]

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Selective dehydrogenation of isopropyl alcohol on low-percentage supported bimetallic rhenium-containing catalysts

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The activity and selectivity of mono- and bimetallic sibunite-supported Re-, Cu-, Ni-, and Pd-containing catalysts in dehydrogenation of isopropyl alcohol to acetone (T = 200—275 °C, v = 1.1 h^{-1}) were studied. The bimetallic Re,Cu-, Re,Ni-, and Re,Pd-catalysts containing 1 or 2% of the metal possess the higher activity and stability than monometallic catalysts.

Key words: supported monometallic Re-, Cu-, Ni-, and Pd-catalysts, bimetallic rhenium-containing catalysts; isopropyl alcohol, dehydrogenation.

The high activity of the carbon-supported rhenium-containing catalysts (30% Re/C) has been observed previously[1] in the dehydrogenation of isopropyl alcohol to acetone. However, this catalyst was rapidly deactivated. In this work, we attempted to develop selective low-percentage rhenium-containing catalysts and found conditions for the dehydrogenation of isopropyl alcohol to acetone.

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