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SYNTHESIS AND ^{1}H, ^{13}C, ^{15}N, ^{29}Si NMR SPECTRA OF SIL- AND GERM-ATRANONES

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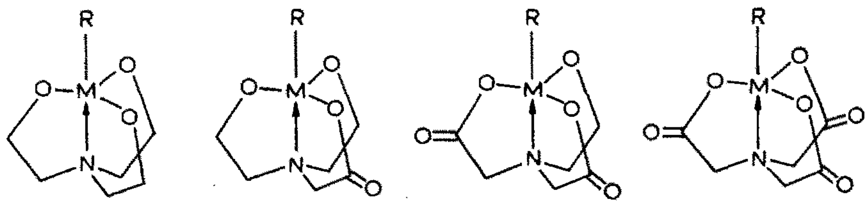
Summary

A novel technique using trimethylsilyl aminoacetic acid derivatives and trialkoxy or trichloro derivatives of silicon and germanium has been employed to prepare sil- and germ-atranones. The ^{1}H, ^{13}C, ^{15}N and ^{29}Si NMR spectroscopy data obtained for the synthesized compounds indicate that an increase in the number of carbonyl groups in the atrane framework enhances charge transfer along the donor–acceptor N → M bond. Because of the prominent electron-acceptor properties of the central atom, the atrantriones tend to bind electron-donor solvents. This is accompanied by an increase in the coordination number of silicon and germanium in these complexes, reaching six. A substitution in the equatorial position of the title compounds has been found to affect more readily charge transfer along the N → M bond than in the axial one. The steric structure of the compounds under study is discussed.

Introduction

Contrary to the widely studied metallatranes of the Group IV elements (I), their carbonyl-containing derivatives have received only scant attention so far. Ionic-type complexes of nitrilotriacetic acid with lead, titanium and zirconium were obtained which were provisionally assigned the structure of atrantriones [1,2].



(I) (II) (III) (IV)

M = Si(a), Ge(b)

Among the carbonyl-containing silatranes [3–5], silatran-3-ones (IIa) originally synthesized by Popowsky [3] in 1973 have been described. We are not aware of any reports in the literature concerning silatran-3,7-diones (IIIa) and -3,7,10-triones (IVa), except for our preliminary communication [6]. Germatranones (II–IVb) were synthesized only recently [7–9]. The PMR spectroscopy [4] and X-ray analysis data [10] reveal the presence of a coordinative N → Si bond in silatranones IIa. According to [8], the N → Ge bond in 1-phenylgermatran-3-one (IIb) is somewhat shorter, as compared to that in germatranes (Ib); however, the ^{13}C NMR spectra are suggestive of decreased donor properties of the germatranyl framework in compounds IIb. The above works represent the only evidence available on the atranones of the Group IV elements. The main obstacle on the way to their more detailed analysis is the difficulty encountered during their synthesis by the existing method [3–5,7] from aminoacetic acids $(HOCOCH_2)_nN(CH_2CH_2OH)_{3-n}$ (n = 1–3) and trialkoxy derivatives of the elements arising from the low solubility of the starting acids and the end products: atranones.

The present study was aimed at the synthesis and detailed comparison by means of NMR spectroscopy of all types of sil- and germ-atranones (II–IV).

Results and discussion

The above difficulties during the syntheses of II–IV were overcome successfully by using, instead of poorly soluble amino acids, their liquid trimethylsilyl derivatives (V^n) [6,9]. The synthesis was conducted after the scheme:

$$\underset{(V^n)}{N\left\langle\begin{matrix}(CH_2COOSiMe_3)_n\\(CH_2CH_2OSiMe_3)_{3-n}\end{matrix}\right.} + X_3MR \rightarrow \underset{(II\text{–}IV)}{N\left\langle\begin{matrix}(CH_2COO)_n\\(CH_2CH_2O)_{3-n}\end{matrix}\right\rangle MR} + 3Me_3SiX$$

X = halogen, alkoxyl; n = 1–3
R = organic radical, halogen

The reaction proceeds in an organic solvent (DMFA, xylene, chloroform) with slight heating or during continuous standing of the mixture at room temperature. If moisture-induced hydrolysis of the silylated acids (V^n) is prevented, the end product, being the only solid component in the reaction mixture, can be readily isolated. Besides the alkoxy derivatives, the procedure can also use the more readily accessible halogen-silanes and -germanes as starting products. Our method is applicable to the preparation of all types of sil- and germ-atranones, as well as -atranes (I, n = 0).

The ^{1}H, ^{13}C, ^{15}N and ^{29}Si NMR chemical shifts (CS) of the compounds studied are given in Tables 1 and 2. It is advisable to begin their analysis with ^{15}N NMR data, since the nitrogen atom is directly involved in the formation of the donor-acceptor (DA) N → M bond.

The data obtained for the model compounds (V^n) have demonstrated that introduction of CO groups into the molecule only affects slightly the position of resonance of ^{15}N nuclei causing an upfield shift of the signal with increasing number of carbonyl groups (see Table 1). The effect of cyclization in aliphatic amines also enhances the screening of ^{15}N [11]. A shift of ^{15}N resonance to the strong field in some silatranes and germatranes [12–14] with respect to the model compounds is accounted for by increased steric hindrance due to cyclization, because protonation of the nitrogen atom in aliphatic amines leads to a low-field shift of ^{15}N resonance up to 18 ppm [15,16], whereas the transition from trimethylamine to tetramethylamonium decreases nitrogen screening by 32 ppm [10]. Hence, a dramatic shift of the ^{15}N resonance to low fields in the metallatrane sequence: I < II < III < IV is indicative of enhanced charge transfer along the N → M bond in the above order [12,18]. It has been found, at the same time, that the CS of ^{15}N depend on the Taft's parameters $\sigma^\star$ of substituents at the silicon atom in the IIa series of compounds:

$$\delta(^{15}N) = -344.6 + 3.68\,\sigma^\star \quad r = 0.96 \qquad (1)$$

and IIIa series:

$$\delta(^{15}N) = -335.0 + 1.71\,\sigma^\star \quad r = 0.98 \qquad (2)$$

It is apparent that an increase in electron-acceptor properties of the central atom with increasing number of CO groups would diminish the effect of substituents R on the CS of ^{15}N and, hence, on the energy of the DA bond N → M. The compounds of the IV series exhibit a weak, but appreciable inverse correlation between the CS of ^{15}N and $\sigma^\star$.

It should be noted that the range of CS changes ($\Delta\delta(^{15}N)$) for the studied germatranes I–IVb is significantly greater (if $R = CH_3$, $\Delta\delta(^{15}N) = 57.0$ ppm) than for the corresponding Si derivatives (36.5 ppm). The ^{15}N CS changes in germatranones are about −20 ppm per one CO group, whereas in silatranones they are about −10 ppm. This considerably overrides the effect of the axial substituent R and indicates that the equatorial substituent on the trigonal-bipyramidal polyhedron of the central atom in the studied series of compounds influences the charge transfer along the N → M bond more appreciably than the axial one. The increase in electron-acceptor properties of the M atom upon introduction of the CO groups in the molecule may be due to the significantly weakened *dp–π* interaction between the lone electron pair (1*p*) of the oxygen atom and the vacant *d* orbitals of the central atom because of the competitive conjugation M–O–C=O [19]. This is indicated by the elongation of the M–O bond following the replacement of the OCH_2 group by OCO in IIa [10] and IIb [8]. A more notable effect of equatorial substitution in the given series may be explained by the symmetry of *d* orbitals inplying effective *dp–π* interaction for d^0 only with equatorial substituents [20].

Extended coordination of the silicon atom during DA N → M bond formation in silatranes and their analogues leads to a stronger screening of the ^{29}Si nuclei as compared to the model compounds containing a tetracoordinated Si atom [21–27]. It is known [28] too that the signal of the tetracoordinated Si in ethoxysilanes $R_{4-n}Si(OC_2H_5)_n$ (VI) is shifted more upfield than in the corresponding acetoxysilanes $R_{4-n}Si(OCOCH_3)_n$ (VII). Therefore, increase in the shift of the ^{29}Si resonance to the stronger field in the sequence: Ia < IIa < IIIa < IVa should be considered as an indication of stronger coordination of the silicon following the same order. This agrees reasonably well with the conclusions reached on the basis of ^{15}N data. It must be pointed out that upfield displacement of the ^{29}Si signal in compounds Ia–IIIa amounts approximately only to 4–6 ppm for every CO group (cf. ^{15}N data).

At the same time, this displacement is by an order of magnitude higher for compounds IVa (52 to 59 ppm), as compared to IIIa. Taking into account the ^{15}N data as well as the fact that the ^{29}Si signal in IVa is observed within the region (−135 to −206 ppm) which is characteristic of hexacoordinated silicon [29], one can

(Continued on p. 21)

TALBE 1

CHEMICAL SHIFTS OF ^{13}C, ^{15}N AND ^{29}Si NMR OF SIL- AND GERM-ATRANONES $RM<^{(OCOCH_2)_n}_{(OCH_2CH_2)_{3-n}}>N$ (I–IV) AND MODEL COMPOUNDS $N<^{(CH_2COOSiMe_3)_n}_{(CH_2CH_2OSiMe_3)_{3-n}}$ (V^n) IN DMSO-d_6 AT 30°C

Compound	R	n	δ (^{13}C) (ppm)								δ (^{15}N) (ppm)	δ (^{29}Si) (ppm)
			C=O	$COCH_2$	OC	NC	R					
							α-	o-	m-	p-		
Ia	CH_3	0	–	–	57.84	51.09	1.33				−356.3	−69.7
	CH_2CH	0	–	–	57.68	50.91	144.14	127.36(β)			−354.2	−84.6
	C_6H_5	0	–	–	57.99	51.09	146.01	135.33	127.18	127.54	−354.5	−83.9
	CH_2Cl	0	–	–	57.58	51.20	33.10				−352.2	−83.1
IIa	CH_3	1	169.92	55.75	58.22	53.60	1.15				−344.3	−73.2
	CH_2CH	1	169.84	55.88	58.22	53.67	141.41	129.45(β)			−342.2	−88.5
	C_6H_5	1	170.01	55.91	58.57	53.70	143.25	135.33	127.85	128.76	−343.0	−87.6
	CH_2Cl	1	169.26	56.10	58.30	54.04	31.70				−340.1	−85.6
IIIa	CH_3	2	168.63	58.15	58.87	57.24	0.82				−335.0	−77.2
	CH_2CH	2	169.31	58.29	58.87	57.38	138.88	131.14(β)			−334.2	−93.4

	C_6H_5	2	168.81	58.61	59.21	57.57	140.83	135.24	128.28	128.58	−333.8	−93.6
	CH_2Cl	2	168.21	58.68	58.94	57.77	30.73				−333.2	−90.3
IVa	CH_3	3	169.13	64.58	–	–	4.78				−319.9	−135.8
	CH_2CH	3	168.90	64.67	–	–	143.10	130.02(β)			–	−146.5
	C_6H_5	3	169.16	64.79	–	–	143.82	135.69	128.22	129.19	–	−146.0
	CH_2Cl	3	168.91	64.53	–	–	34.96				−320.6	−144.7
Ib	CH_3 *	0	–	–	57.28	52.33	0.85				−366.8	
	C_2H_5 *	0	–	–	57.31	52.47	12.05	9.07(β)			−367.1	
	Cl	0	–	–	58.54	51.85			–		−359.5	
IIb	CH_3	1	170.22	55.45	57.53	54.15	2.68				−346.9	
	C_2H_5	1	170.48	55.52	57.47	54.22	13.47	9.31(β)			−346.4	
	Cl	1	168.73	55.91	59.15	54.74			–		−344.9	
IIIb	CH_3	2	170.09	61.33	58.09	62.31	8.16				−324.4	
IVb	CH_3	3	169.24	63.86	–	–	7.51				−309.8	
	C_2H_5	3	169.38	64.09	–	–	18.86	9.89(β)			−310.1	
	Cl	3	168.79	63.64	–	–			–		−311.9	
V^{na}		0	–	–	62.00	58.56	−0.06		–		−350.7	
		1	172.43	57.99	62.47	57.66	−0.05	0.28(2)			−352.0	
		2	172.37	57.40	62.67	56.56	0.28	−0.05(2)			−354.0	
		3	171.59	56.10	–	–	0.21				−358.5	

[a] In $CDCl_3$ solution.

TABLE 2

CHEMICAL SHIFTS (IN PPM) OF ^{1}H NMR OF SIL- AND GERM-ATRANONES $RM\langle^{(OCOCH_2)_n}_{(OCH_2CH_2)_{3-n}}\rangle N$ (I–IV) IN DMSO-d_6 at 20°C

Compounds	R	n	$COCH_2$	OCH_2 (X)	OCH_2 (Y)	NCH_2 (A)	NCH_2 (B)	R	$^{2}J(COCH_2)$ (Hz)
Ia	CH_3 [a]	0	–	3.63		2.81		−0.35	
	CH_2CH [a]	0	–	3.62		2.82		[c]	
	C_6H_5 [a]	0	–	3.72		2.90		7.53(o) 7.11 (m,p)	
	CH_2Cl [a]	0	–	3.66		2.88		2.36	
IIa	CH_3	1	3.632	3.689	3.717	3.047	2.838	−0.241	
	CH_2CH	1	3.700	3.733	3.764	3.095	2.891	[c]	
	C_6H_5	1	3.781	3.859	3.820	3.165	2.970	7.559(o) 7.197(m,p)	
	CH_2Cl	1	3.780	3.795	3.771	3.156	2.960	2.478	
IIIa	CH_3	2	3.873	3.831		3.122		−0.074	
	CH_2CH	2	3.922 3.919	3.860		3.165		[c]	−18.1
	C_6H_5	2	3.995 3.992	3.942		3.235		7.618(o) 7-281(m,p)	−18.0
	CH_2Cl	2	4.003 3.996	3.887		3.236		2.627	−17.8
IVa	CH_3 [a]	3	3.92	–		–		0.14	
	CH_2CH [a]	3	3.93	–		–		[c]	
	C_6H_5 [a]	3	3.99	–		–		7.73(o) 7.31(m,p)	
	CH_2Cl	3	3.98	–		–		2.95	
Ib	CH_3 [b]	0	–	3.65		2.83		0.13	
IIb	CH_3	1	3.578	3.671	3.700	3.038	2.826	0.331	
	C_2H_5 [a]	1	3.46	3.85		3.07	2.87	1.16(CH_2,CH_3)	
	Cl [a]	1	3.80	3.80		3.23	3.08	–	
IIIb	CH_3	2	3.685 3.698	3.590		3.085		0.724	−16.9
IVb	CH_3	3	3.87	–		–		0.85	
	C_2H_5	3	3.86	–		–		1.42(CH_2) 1.19(CH_3)	
	Cl	3	3.89	–		–		–	

[a] At 90 MHz. [b] Taken from ref. 8. [c] See Table 3.

infer that the coordination number of the central atom in IV has assumed a six-valent state (this issue will be discussed in more detail below).

The study of one-bond spin-spin coupling constants between ^{15}N and ^{29}Si nuclei can provide additional information concerning the character of the N → Si bond.

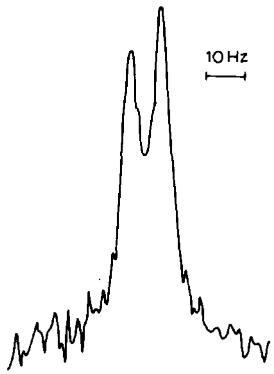


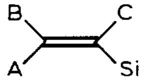
Fig. 1. ^{29}Si NMR spectrum of ^{15}N-enriched 1-methylsilatran-3,7,10-trione in DMSO-d_6 at 17.88 MHz. Temperature 30°C; SW, 1.2 KHz: proton noise decoupling.

Although the coupling between these nuclei has been only scarcely studied so far [15], the values of coupling constants between covalently bonded nuclei in $(SiH_3)_3N$, $^1J(^{15}N-^{29}Si) = 6$ Hz, and between the nuclei involved in the formation of DA bond in silatranes Ia, $^1J(^{15}N-^{29}Si) = 0-3$ Hz, are known [12,30,31].

Bearing in mind the corresponding values of ^{15}N CS, the values $^1J(^{15}N-^{29}Si) = 8.2$ Hz and 10.9 Hz obtained by us for ^{15}N-enriched samples of IVa, $R = CH_3$ and CH_2Cl, respectively, (see Fig. 1) indicate the extremely high order of the N → M bond in compounds IV.

The characteristic feature of ^1H and ^{13}C NMR spectra of Ia and Ib [14,21,32,34] as well as of their analogues [24,25] is a significant shift of the α-carbon signals of substituent R to the low fields, whereas the signals of the protons bonded to the α-carbon are shifted upfield following the N → M bond formation. This is due to the alterations in the electronic structure and geometry of the central atom with respect to the tetracoordinated derivatives. Introduction of CO groups in the title compounds invariably shifts the α-proton resonance of substituents R to the low fields. This may indicate accumulation of positive charge on the central atom. The lack of additivity observed for proton CS and the more complicated pattern of changes of the α-carbon CS in ^{13}C NMR spectra suggest significant contribution of several factors such as electronic effects and anisotropy of CO groups, steric interactions, electrostatic field of the N → M bond, etc. For additional information we have carried out a more detailed analysis of PMR spectra of the Si-vinyl systems (see Table 3). Most typically, there is a decrease in the geminal $^2J_{AB}$ coupling in the sequence Ia > IIa > IIIa > IVa. At the same time, increase in the negative charge on the Si atom in Ia with respect to the corresponding VI ($n = 3$) derivative is known [21] to cause a reverse change in $^2J_{AB}$ value (see also Table 3). Analysis of the CS of *meta-* and *para-*carbons in 1-phenylsilatrane also reveals rise in σ-donor ability of the silatranyl group, as compared to the triethoxysilyl one [34]. However, the reactivity constants σ_I calculated for the tricyclic substituent (see Table 4) using the expression

TABLE 3



THE ^{1}H NMR SPECTRAL PARAMETERS OF THE Si VINYL GROUPS IN COMPOUNDS Ia–IVa AND VI (n = 3)

Compound	Solvent	δ_A (ppm)	δ_B (ppm)	δ_C (ppm)	$^2J_{AB}$ (Hz)	$^3J_{BC}$ (Hz)	$^3J_{AC}$ (Hz)
VI [a] (n = 3)	$CDCl_3$	6.002	6.107	5.888	3.87	14.97	20.70
Ia [a]	$CDCl_3$	5.775	5.730	5.959	4.82	14.54	20.28
IIa	$CDCl_3$	5.916	5.858	5.952	4.35	14.67	20.26
Ia	DMSO-d_6	5.494	5.441	5.756	5.38	14.49	20.13
IIa	DMSO-d_6	5.625	5.588	5.783	4.96	14.50	20.16
IIIa	DMSO-d_6	5.766	5.736	5.842	4.52	14.55	20.07
IVa [b]	DMSO-d_6	5.759	5.799	6.090	4.37	14.46	20.15

[a] At 220 MHz; taken from ref. 22. [b] At 50°C.

proposed previously [34] suggest diminished σ-donor properties of the tricyclic framework with increasing number of CO groups. As the sum of constants $\sigma_I + \sigma_R$ is related to the charge induced on the reaction centre [35], the experimental evidence indicates an increased positive charge on atom M in the sequence Ia < IIa < IIIa < IVa. The above facts taken together and the ^{15}N findings demonstrate that the recently found constancy of the total bond order N $\rightarrow$ Si–R in silatranes [36] presents a particular case and is observed only in compounds with invariable equatorial substituents. It should be noted that the explanation of the electronic and steric structure of silatranes [37,38] based on the theory of hypervalent bonding [39,40] fails to take into account the effect of equatorial substituents on the N $\rightarrow$ M interaction. However, substitution in the equatorial position may essentially alter the electron-acceptor properties of the central atom. As could be seen above, increase in the positive charge on M in the case of strong equatorial acceptors causes an increase in the order of the N $\rightarrow$ M bond eventually leading to extended coordination of the central atom. This is accompanied, at the same time, by the significantly diminished dependence of charge transfer along the N $\rightarrow$ M bond on the axial

TABLE 4
REACTIVITY CONSTANTS σ_i CALCULATED FOR THE TRICYCLIC FRAMEWORK OF COMPOUNDS Ia–IVa AND VI (n = 3) USING THE PROPOSED RELATIONSHIP [34]

Compound	Solvent	σ_I	σ_R	σ_R^0	σ_R^+	σ_R^-	σ^*	$\sigma_I + \sigma_R$
VI (n = 3) [a]	$CDCl_3$	−0.08	0.10	0.08	0.25	0.15	0.02	0.02
Ia [a]	$CDCl_3$	−0.40	0.02	0.02	−0.09	0.17	−0.89	−0.38
Ia	DMSO-d_6	−0.32	0.00	0.01	−0.07	0.13	−0.71	−0.32
IIa	DMSO-d_6	−0.08	0.01	0.01	0.06	0.08	−0.18	−0.07
IIIa	DMSO-d_6	0.04	−0.04	−0.02	0.04	0.00	0.09	0.00
IVa	DMSO-d_6	0.04	0.00	−0.03	0.10	0.04	0.09	0.04

[a] Taken from ref. 34.

substituent. The *trans* influence of the axial substituent widely employed for modelling the S_N2 mechanism of substitution reactions is apparently most effective in compounds with weak acceptors in the equatorial position.

The shift of NC carbon signals of unsubstituted cycles to low field in response to increased strength of DA bond in the sequence I < II < III < IV appears rather unexpected, since protonation of amines commonly leads to the displacement of α-carbons to the strong field [41,42]. In compounds III and IV, all the NC carbons are considerably less screened than in the model compounds V^n (see Table 1). Furthermore, in IIIb, inversion of NC and OC carbon signals is even observed in the unsubstituted cycle. This may be due, in part, to diminished steric hindrance upon replacement of CH_2 group for CO [43]. On the other hand, it is known [42] that the extent and direction of signal shifts of the α-carbon in aliphatic amines depend on the orientation of $1p$ of the nitrogen. The OC and OCO carbon resonances are significantly less susceptible to the introduction of the CO groups into the molecule.

The methylene protons of the OCH_2CH_2N chains in IIa and IIb are not equivalent and form an ABXY system at room temperature. The centres of NCH_2 and OCH_2 proton signals are displaced to lower fields than in unsubstituted analogues I [8]. According to Tandura et al. [44], this implies strengthening of the N → M bond which is in agreement with the ^{15}N NMR data. Simulation of spectra (Fig. 2) allowed us to obtain all the coupling constants for the spin system of the OCH_2CH_2N moiety. The results obtained for 1-methyl derivatives are presented in Table 5. Analysis of Dreiding's models revealed that it is equality, but not difference, as claimed [8], between *trans* couplings J_{AX} and J_{BY} that are indicative of the enantiomeric conformations A and A′ being predominant in solution. Exchange between them possibly occurs through the intermediate state C (see Fig. 3), where unsubstituted semi-cycles form an eight-membered heterocycle having the chair-chair (CC) conformation. The intermediate state B, as demonstrated by the calculations

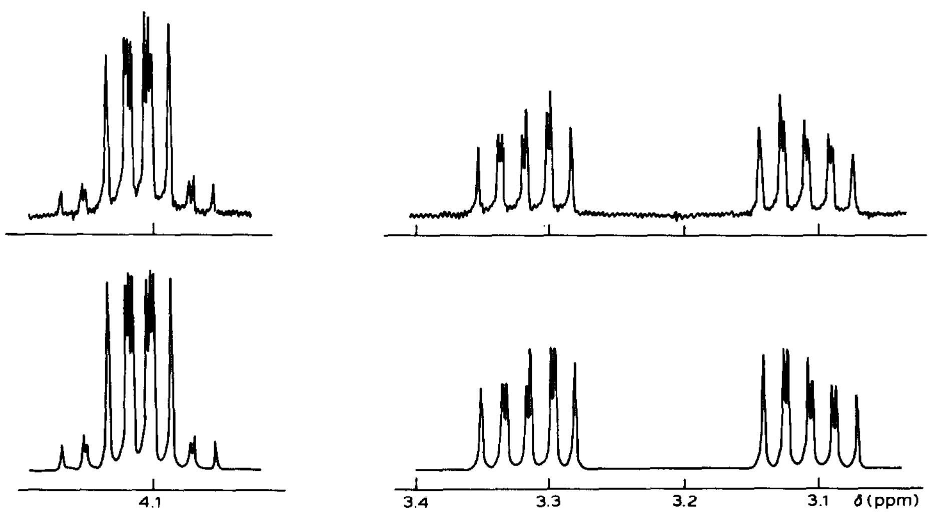


Fig. 2. ^1H NMR spectrum of OCH_2CH_2N region of 1-methylgermatran-3-one solution of $CDCl_3$ (~ 0.01 *M*), recorded at 360 MHz. The computer-simulated spectrum is the bottom one. Temperature 20°C, SW, 1.8 KHz, PW = 5 μs (~ 45°).

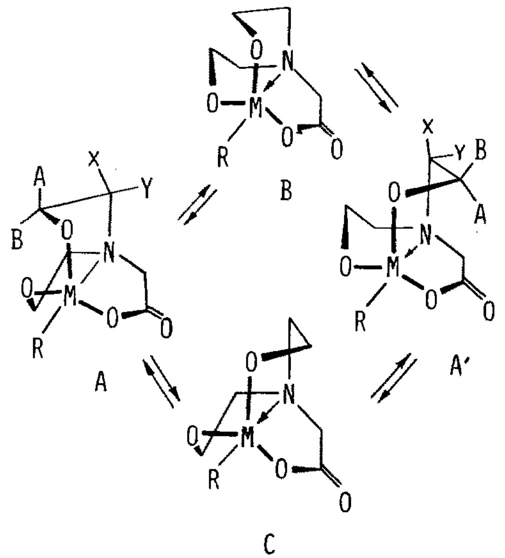


Fig. 3. Exchange paths between the enantiomeric conformations A and A′ in atran-3-ones (IIa,b).

for conformations of the boat family [45] are less favourable than C. Difference in *trans* coupling constants characteristic of these conformations [46] allows us to determine their relative population in solution. According to equations obtained previously [46], the conformation C in this case predominates over B only by ~ 3%.

The values of dihedral angle ϕ_{ON} formed by the planes O–C–C and C–C–N estimated using the R-factor method [47,48] are in fairly good agreement with the X-ray finding [8] and for 1-phenylgermatran-3-one constitute 41° and 46° (cf. data in Table 5). Increase in ϕ_{ON} in the sequence: solid state < DMSO < $CDCl_3$ reflects the weakening of the N → M bond during solvation and even with decreasing solvent polarity. Decrease in ϕ_{ON} in 1-methylsilatran-3-one, as compared to the

TABLE 5

PROTON SPIN-SPIN COUPLING CONSTANTS OF THE OCH_2CH_2N FRAGMENT IN 1-METHYLSILATRAN-3-ONE AND 1-METHYLGERMATRAN-3-ONE

Compound	Solvent	$^2J_{AB}$ (Hz)	$^3J_{AX}$ (Hz)	$^3J_{AY}$ (Hz)	$^3J_{BX}$ (Hz)	$^3J_{BY}$ (Hz)	$^2J_{XY}$ (Hz)	ϕ_{ON} (°)
1-Methylsilatran-3-one	DMSO-d_6	−11.00	6.28	5.64	5.57	6.23	−12.42	47.1
	$CDCl_3$	−11.45	6.49	5.42	5.35	6.22	−12.41	48.1
1-Methylgermatran-3-one	DMSO-d_6	−10.94	6.40	5.12	5.05	6.26	−12.49	49.0
	$CDCl_3$	−11.31	6.48	5.04	4.90	6.36	−12.27	49.7

corresponding Ge derivative, suggest that the N → M distance is shorter in the former case. This results from the weaker N → M bond in IIb or the greater Van der Waals' radius of Ge. Increase in temperature to 120°C leads to the fusion of OCH_2 proton signals and degeneration of the spin system ABXY to A_2XY for the 1-methyl derivatives of II.

The shift of the signals of OCH_2, NCH_2 and $COCH_2$ protons to low field in compounds III with respect to the corresponding derivatives of compounds II demonstrates a further strengthening of the N → M bond in accordance with the conclusions reached on the basis of ^{15}N and ^{29}Si spectra. Inequivalence of $COCH_2$ protons depends on the substituent at the central atom and, consequently, on the N → M bond length. The greater extent of inequivalence of $COCH_2$ protons in IIIb, as compared to IIIa, and the ^{15}N signal being shifted further downfield for the former compound suggest the stronger N → M bond in Ge derivatives. At the same time, the geminal coupling between the $COCH_2$ protons is diminished in the same sequence. The increased inequivalence of protons in substituted cycles is possibly due to the enchanced puckering around the NC carbon of the five-membered cycle in compounds with a shorter N → M bond.

A characteristic feature of compounds IV is their tendency to complex with electron-donating solvents. As a rule, these compounds are isolated from the reaction mixture as complexes (1:1) with DMFA or DMSO. Addition of slightly polar solvents or heating result in decomposition of IV.

The positive charge on the central atom in this series of compounds shows that the negative charge arising during the N → M bond formation is distributed on stronger accepting equatorial substituents. Increased ionicity of the M–O bonds explains the observed instability of these compounds. Extension of the coordination number of the central atom is possibly due to complexing with electron-donating solvents. It appears most likely that the structure of bonds at the central atom of IV is close to tetragonal bipyramid. Equivalency of all side chains in NMR spectra at

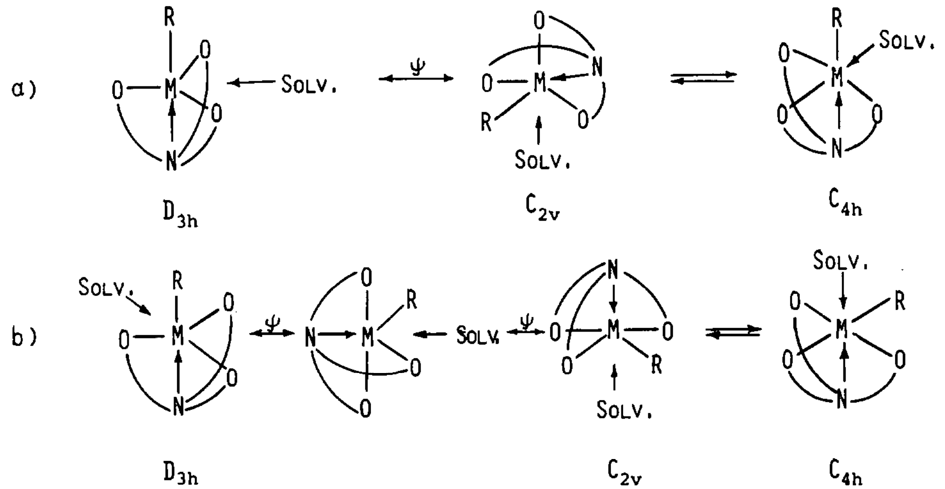


Fig. 4. The mechanisms of equatorial (a) and facial (b) attack at the central atom of metalatran-3,7-10-triones.

room temperature denotes rapid (on the NMR time scale) delocalization of the complexed solvent. Two exchange mechanisms can be proposed: equatorial and facial attack on the central atom by the solvent molecule (see Fig. 4). The intermediate state, tetragonal pyramid (C_{2v}), occurs as a result of partial permutational isomerization of the trigonal-bipyramidal (D_{3h}) structure of the central atom [49,50]. Keeping this in mind, the mechanism postulating equatorial attack appears sterically less rigid.

Experimental

^{1}H, ^{13}C, ^{15}N and ^{29}Si NMR spectra were recorded using Bruker WH-90 and WM-360 spectrometers operating in the FT mode. Either DMSO-d_6 or $CDCl_3$ was dried over molecular sieves (4 Å) and used as solvent and internal ^{2}H lock material. The ^{1}H, ^{13}C and ^{29}Si spectra were referenced to TMS as internal standard, and ^{15}N spectra to nitromethane as external standard. All spectra were measured at ambient temperature.

^{1}H NMR spectra were obtained at 90 MHz and 360 MHz in 5 mm sample tubes; solution concentration was about 0.01 *M*. A complete second order iterative fit of the four spin systems of OCH_2CH_2N fragments was performed using the Bruker Instruments PANIC.81 NMR simulation program. The agreement between the simulated and experimental spectra was excellent, with a rms error in the peak positions within 0.05 Hz.

^{13}C NMR spectra were determined at 22.63 MHz and 90.56 MHz in 10 mm sample tubes containing ca. 0.1 *M* solutions. The delay time at 60° pulse was 1–3 seconds together with proton broad-band noise decoupling. The OC and NC carbon signals were assigned by selectively decoupling the proton resonances while observing the ^{13}C NMR spectra.

^{29}Si NMR spectra were obtained at 17.68 MHz and 71.55 MHz with the same samples using inverse gated ^{1}H-decoupled mode as well as by the pulse sequence INEPT [51]. Typically, the delay time was 3–10 seconds at 60° irradiation pulse in the inverse gated mode and 2 seconds in the INEPT experiment.

^{15}N NMR spectra were obtained at 9.12 MHz and 36.48 MHz in 10 mm and 15 mm sample tubes using solutions of maximal concentration. Time between 60° pulse was 10 seconds.

The accuracy of measurements was 0.001 ppm for ^{1}H spectra at 360 MHz and 0.01 ppm at 90 MHz. The chemical shifts of ^{13}C were determined with 0.01 ppm accuracy and those of ^{15}N and ^{29}Si with 0.1 ppm accuracy.

Synthetic procedures

1-Chloromethylsilatran-3-one (IIa, R = CH_2Cl). Following the addition of the tristrimethylsilyl derivative of *N,N*-bis(hydroxyethyl)aminoacetic acid (V^1) (5.6 g, 0.015 mol) to the solution of chloromethyltriethoxysilane (4.2 g, 0.02 mol) in anhydrous DMFA (6 ml) the mixture was heated for 2 h at 40–50°C preserving it from atmospheric moisture. The crystalline sediment formed was filtered under vacuum. Yield: 2.3 g (64%), m.p. 254–255°C.

Analogously, the other earlier known silatran-3-ones (IIa) with R = CH_3, CH_2=CH, C_6H_5 were obtained with 60–70% yield.

1-Vinylsilatran-3,7-dione (IIIa, R = CH_2=CH). The mixture of vinyltriethoxysilane (1.9 g, 0.01 mol), *N*-(2-hydroxyethyl)iminodiacetic acid tristrimethylsilyl derivative (2.9 g, 0.075 mol) (V^2) and DMFA (3 ml) was allowed to stand for 2–3 h at room temperature to give a crystalline sediment (1.1 g, 64%) undergoing decomposition above 200°C.

Analogously, silatran-3,7-diones (IIIa) with R = CH_3, CH_2Cl, C_6H_5 were obtained, for the first time, with 65–70% yield as crystalline substances decomposing above 200°C.

1-Methylsilatran-3,7-10-trione (IVa, R = CH_3): DMFA complex (1:1)

As in the above example, a crystalline substance (1.3 g, 85%) undergoing decomposition above 240°C was sedimented from the solution of methyltriethoxysilane (1.8 g, 0.01 mol) and nitrilotriacetic acid tristrimethylsilyl derivative (2.0 g, 0.005 mol) (V^3) in 3 ml DMFA.

The previously unknown silatran-3,7-10-trione dimethylformamide complexes (IVa) where R = CH_2Cl, CH_2=CH, C_6H_5 were similarly obtained with ca. 70% yield. They all are crystalline substances that decompose at heating above 240°C.

1-Chlorogermatran-3-one (IIb, R = Cl)

Silylated acid V^1 (1.9 g, 0.005 mol) was added to tetrachlorogermane (1.1 g, 0.005 mol) solution in 20 ml anhydrous chloroform. A crystalline deposit (1.0 g, 75%) was immediately formed, whose melting point following recrystallization from DMFA was 265–268°C.

The heating of the xylene solution of the starting reagents for 2 – 3 h gave 1-ethylgermatran-3-one (IIb, R = C_2H_5), m.p. 132–135°C, yield 60% and the methyl derivative (IIb, R = CH_3), yield 62%, described previously.

1-Methylgermatran-3,7-diones (IIIb, R = CH_3)

A mixture of methyltrichlorogermane (1.9 g, 0.01 mol) and silylated acid V^2 (3.9 g, 0.01 mol) in DMFA (6 ml) was heated at 100°C for 1 h. A crystalline sediment was formed by concentrating the solution under vacuum. Yield: 1.6 g (62%), m.p. 262–265°C.

Analogously, 1-chlorogermatran-3,7-dione (IIIb, R = Cl) decomposing above 220°C was obtained in chloroform solution with 85% yield.

1-Methylgermatran-3,7-trione (IVb, R = CH_3): DMFA complex (1:1)

Methyltrichlorogermane (1.0 g, 0.005 mol) and silylated acid V^3 (2.0 g, 0.005 mol) in 3 ml DMFA were heated at 100°C for 1 h. Evaporation of the reaction mixture under vacuum yielded 1.0 g (57%) of a crystalline substance undergoing decomposition above 240°C.

1-Chloro-(IVb, R = Cl), 1-ethyl-germatrane-3,7,10-trione (IVb, R = C_2H_5) complexes with DMFA were similarly obtained with 50–60% yield, decomp. above 240°C.

The structures of the synthesized atranes was substantiated, apart from the NMR spectra discussed here, by elemental analysis and from mass spectroscopy data.

The sil- and germ-atranes (Ia, b) employed in the study were also prepared by the above method using silylated triethanolamine (V, $n = 0$).

References

1 M.G. Voronkov and S.V. Mihkailova, Khim. Geterotsikl. Soedin., (1969) 795.
2 M.G. Voronkov, S.V. Mikhailova, L.A. Ritevskaya and Ya.A. Eidus, Khim. Geterotsikl. Soedin., (1972) 753.
3 E. Popowski, DDR Patent 106389, 1974; Chem. Abstr., 81 (1974) 169626s.
4 E. Popowski, M. Michalik and H. Kelling, J. Organomet. Chem., 88 (1975) 157.
5 Y. Wu., K. Lu and G. Wu, Huaxue Shiji, (1981) 202; Chem. Abstr., 96 (1982) 162799b.
6 G.I. Zelchan, A.F. Lapsina and E. Lukevics, Zh. Obshch. Khim., (1983) 465.
7 T.K. Gar, N.Yu. Khromova, S.N. Gurkova, A.I. Guseva and V.F. Mironov, Zh. Obshch. Khim., 50 (1980) 1894.
8 N.V. Alekseev, S.N. Gurkova, S.N. Tandura, V.M. Nosova, A.I. Gusev, T.K. Gar, I.P. Segelman and N.Yu. Khromova, Zh. Strukt. Khim., 22 (1981) 135.
9 G.I. Zelchan, A.F. Lapsina, I.P. Urtane, E. Lukevics, E.E. Liepins and E.L. Kupce, II All-Union Conference on Organometallic Chemistry (Abstracts), Gorki, 1982, p. 75.
10 L. Parkanyi, P. Hencsei and E. Popowski, J. Organomet. Chem., 197 (1980) 275.
11 R.O. Duthaler, K.L. Williamson, D.D. Gianini, W.H. Beardon, and J.D. Roberts, J. Amer. Chem. Soc., 99 (1977) 840.
12 E.E. Liepins, I.S. Birgele, G.I. Zelchan and E. Lukevics, Zh. Obshch. Khim., 49 (1979) 1537.
13 V.A. Pestunovich, S.N. Tandura, B.Z. Shterenberg, V.P. Baryshok and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2159.
14 G.I. Zelchan, A.F. Lapsina, I.I. Solomennikova, E. Lukevics, E.E. Liepins and E.L. Kupce, Zh. Obshch. Khim., in press.
15 G.C. Levy and R.L. Lichter, Nitrogen-15 NMR Spectroscopy, Willey, New York, 1979, p. 33.
16 G.J. Martin, M.L. Martin and J.P. Gouesnard, N-15 NMR Spectroscopy, in NMR Basic Principles and Progress, vol. 18, Springer-Verlag, Berlin, 1981, p. 108.
17 M. Witanowski and G.A. Webb (Eds.), Nitrogen NMR, Plenum, New York, 1973.
18 E.E. Liepins, A.F. Lapsina, G.I. Zelchan and E. Lukevics, Izv. Akad. Nauk Latv. SSR, Ser. Khim., (1980) 371.
19 A.N. Egorochkin, G.A. Domrachev, N.S. Vyazankin, S.Ya. Khorshev, O.S. Dyakovskaya and V.T. Bichkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 164.
20 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
21 R.K. Harris, J. Jones and S.Ng, J. Magn. Reson., 30 (1978) 521.
22 V.A. Pestunovich, S.N. Tandura, M.G. Voronkov, G. Engelhardt, E. Lippmaa, T. Pehk, V.F. Sidorkina, G.I. Zelchan and V.P. Baryshok, Dokl. Akad. Nauk SSSR, 240 (1978) 914.
23 V.A. Pestunovich, B.Z. Shterenberg, S.N. Tandura, G.I. Zelchan, V.P. Baryshok, I.I. Solomennikova, I.P. Urtane, E. Lukevics and M.G. Voronkov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., (1981) 467.
24 S.N. Tandura, V.A. Pestunovich, M.G. Voronkov, G.I. Zelchan, I.I. Solomennikova and E. Lukevics, Khim. Geterotsikl. Soedin., (1977) 1063.
25 E.E. Liepins, I.S. Birgele, I.I. Solomennikova, A.F. Lapsina, G.I. Zelchan and E. Lukevics, Zh. Obshch. Khim., 50 (1980) 2462.
26 S.N. Tandura, V.A. Pestunovich, M.G. Voronkov, G.I. Zelchan, V.P. Baryshok and Yu.A. Lukina, Dokl. Akad. Nauk SSSR, 235 (1977) 406.
27 E. Liepins, Yu. Popelis, I. Birgele, I. Urtane, G. Zelchan and E. Lukevics, J. Organometal. Chem., 201 (1980) 113.
28 H. Marshmann, ^{29}Si-NMR Spectroscopic Results, in NMR Basic Principles and Progress, Vol. 17, Springer-Verlag, Berlin, 1981, p. 65.
29 H.C. Marshmann and R. Lowör, Chem. Z., 97 (1973) 660.
30 D.W.W. Anderson, J.E. Bentham and D.W.H. Rankin, J. Chem. Soc., Dalton Trans., (1973) 1215.
31 V.A. Pestunovich, B.Z. Shterenberg, M.G. Voronkov, M. Maegi and A.V. Samoson, Izv. Akad. Nauk SSSR, (1982) 1435.
32 V.A. Pestunovich, M.G. Voronkov, G.I. Zelchan, E. Lukevics, L.I. Libert, A.N. Egorochkin and A.I. Burov, Khim. Geterotsikl. Soedin., sb. 2, (1970) 339.
33 M.G. Voronkov, S.N. Tandura, B.Z. Shterenberg, A.L. Kuznetsov, R.G. Mirskov, G.I. Zelchan, N.Yu. Khromova, T.K. Gar, V.F. Mironov and V.A. Pestunovich, Dokl. Akad. Nauk SSSR, 248 (1979) 134.
34 V.I. Glukhikh, S.N. Tandura, G.A. Kuznetsova, V.V. Keiko, V.M. Dyakov and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 239 (1978) 1129.

35 W.J. Hehre, R.W. Taft and R.D. Topsom, in Progress in Phys. Org. Chem., Vol. 12, Wiley, New York, 1976, p. 159.
36 V.A. Pestunovich, V.F. Sidorkin, O.B. Dogaev and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 251 (1980) 1440.
37 V.F. Sidorkin, V.A. Pestunovich and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 235 (1977) 1363.
38 V.F. Sidorkin, V.A. Pestunovich and M.G. Voronkov, Usp. Khimii, 49 (1980) 789.
39 J.J. Musher, Angew. Chem., Int. Ed., 8 (1969) 54.
40 D.A. Bochvar, N.P. Gambaryan and L.M. Epshtein, Usp. Khimii., 45 (1976) 1316.
41 J.B. Stothers, Carbon-13 NMR Spectroscopy, Acad. Press, New York, 1972, p. 196.
42 I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa and K. Goto, J. Amer. Chem. Soc., 95 (1973) 165.
43 A.S. Shashkov and O.S. Chizhov, Bioorg. Khim., 2 (1976) 437.
44 S.N. Tandura, V.A. Pestunovich, G.I. Zelchan, V.P. Baryshok, Yu.A. Lukina, M.S. Sorokin and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 295.
45 F.A.L. Anet and J. Krane, Tetrahedron Lett., (1973) 5029.
46 E. Kupce, E. Liepins and E. Lukevics, J. Organomet. Chem., 248 (1983) 131.
47 J.B. Lambert, Acc. Chem. Res., 4 (1971) 87.
48 J.B. Lambert, J. Amer. Chem. Soc., 89 (1967) 1836.
49 R.S. Berry, J. Chem. Phys., 32 (1960) 933.
50 V.I. Sokolov, Vvedeniye v teoreticheskuyu stereokhimiyu, Nauka, Moscow, 1979, chap. 4.
51 G.A. Morris and R. Freeman, J. Amer. Chem. Soc., 101 (1979) 160.