THE SYNTHESIS AND STRUCTURE OF SOME TRIMETHYLGERMYL AMIDES

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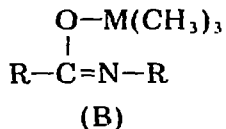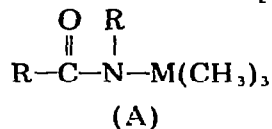
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Summary

A series of trimethylgermyl amides of the type $RC-N-Ge(CH_3)_3$ (where R = H, CH_3; R' = H, aryl) were prepared and the amide structures established by IR and NMR measurements. The barriers to rotation and isomer ratios were determined and are discussed in relation to those for the carbon and silicon homologs.

In contrast to trimethylsilyl amides, whose structures and properties have been explored in some detail [1-5], little is known about amides containing a trimethylgermyl group as the substituent at nitrogen. Indeed, only a few trimethylgermyl amides have been reported [6].

The structures of these compounds are of particular interest. Trimethylsilyl amides exist in either the amide A or imidate B form, or as equilibrium mixtures of both [2-5]. The tautomeric behavior of the silicon derivatives is

$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-M(CH_3)_3 \qquad\qquad R-\overset{\overset{O-M(CH_3)_3}{|}}{C}=N-R$$

$$(A) \qquad\qquad\qquad\qquad (B)$$

understandable in view of the high Si—O bond energy, which presumably increases the thermodynamic stability of the imidate form. The difference between the Ge—O and Ge—N bond energies is apparently smaller, however, than the difference between the Si—O and Si—N bond energies [7], and it might be anticipated, therefore, that trimethylgermyl amides would exist in the amide form. Thus, the objectives of the present work were to prepare a series of mono(trimethylgermyl) amides of the type $R-\overset{\overset{O}{\|}}{C}-\overset{\overset{R'}{|}}{N}-Ge(CH_3)_3$ (R = H, CH_3; R' = H, aryl), and to determine their structures.

Experimental

Syntheses

All operatiuns were carried out under nitrogen, N-Trimethylgermylacet-amide (I) was prepared by refluxing equimolar amounts of acetamide and trimethylbromogermane with excess triethylamine in dioxane; b.p. 93-94°/8mm. (Found: C, 35.37; H, 7.94; N, 7.75. $C_5H_{13}GeNO$ calcd.: C, 34.16; H, 7.43; N, 7.95%.) N-Trimethylgermylformamide (II) was prepared by transamination of trimethylgermyl-tert-butylamine (III) with formamide in benzene according to the procedure of Horwitz and deBenneville [8]. The starting material III was obtained by addition of an equimolar amount of n-butyllithium in hexane to tert-butylamine followed by reflux with an equimolar amount of trimethylbro-mogermane. II b.p. 85-87°/9mm, yield 30%. (Found: C, 29.70; H, 7.05; N, 10.02. $C_4H_{11}GeNO$ calcd.: C, 29.71; H, 6.81; N, 8.66%.) III b.p. 136-137°, yield 54%. (Found: C, 44.71; H, 10.17; N, 6.28. $C_7H_{19}GeN$ calcd.: C, 44.28; H, 10.07; N, 7.38%.)

para-Substituted N-trimethylgermylformanilides were prepared by refluxing the appropriate formanilide with an equimolar amount of trimethylbromo-germane and excess triethylamine in THF. IV p-H, b.p. 70°/0.18mm, yield 51%. (Found: C, 49.80; H, 6.41; N, 5.63. $C_{10}H_{15}GeNO$ calcd.: C, 50.50; H, 6.36; N, 5.89%.) V p-Cl, b.p. 131-132°/0.67mm, yield 60%. (Found: C, 44.87; H, 5.38; N, 5.35. $C_{10}H_{14}ClGeNO$ calcd.: C, 44.11; H, 5.18; N, 5.14%.) VI p-N(CH$_3$)$_2$, b.p. 155-156°/0.54 mm, yellow solid, m.p. 45-47°, yield 57%. (Found: C, 51.34; H, 7.42; N, 10.54. $C_{12}H_{20}GeN_2O$ calcd.: C, 51.31; H, 7.18; N, 9.97%.)

para-Substituted N-trimethylgermylacetanilides were prepared by refluxing the appropriate acetanilide with an equimolar amount of trimethylbromogermane and excess triethylamine in THF. VII p-H, b.p. 129°/8 mm, white solid, m.p. 31-33°, yield 50%. (Found: C, 52.92; H, 6.80; N, 5.71. $C_{11}H_{17}GeNO$ calcd.: C, 52.46; H, 6.81; N, 5.56%.) VIII p-Cl, b.p. 106°/0.15 mm, white solid, m.p. 55.5-57°, yield 46%. (Found C, 47.43; H, 5.33; N, 4.77. $C_{11}H_{16}ClGeNO$ calcd.: C, 46.15; H, 5.63; N, 4.89%.) IX p-OCH$_3$, b.p. 176.5°/ 8 mm, white solid, m.p. 31-32.5°, yield 54%. (Found: C, 51.14; H, 6.73; N, 4.92. $C_{12}H_{19}GeNO_2$ calcd.: C, 51.13; H, 6.79; N, 4.97%.)

NMR and IR spectra of the above compounds were consistent with proposed structures.

NMR measurements

NMR spectra were recorded on a Varian A-60D spectrometer equipped with variable temperature accessory V-4341/V-6057. Calibration was achieved by standard side-banding techniques using a Hewlett-Packard 200 CD audio oscillator and Model 522B electronic counter. Probe temperatures were determined from peak separations of standard methanol and ethylene glycol samples and the equations of Van Geet [9].

Spectra used for calculation of free energies of activation were obtained from 30% w/v or v/v solutions in p-xylene (except I and II which were 20% v/v in C_6H_5Cl). At least three traces of the trimethylgermyl region at 50 Hz sweep width were recorded for each of a minimum of three different temp-

eratures in the slow exchange region. Populations of isomers were determined by weighing peaks traced and cut from good grade paper. Free energies of activation were determined by the method of Shanan-Atidi and Bar-Eli [10] utilizing Δv's and populations extrapolated to coalescence temperatures. This method has been shown to yield values of $\Delta G^{o\ddagger}$ for the unequal population case in good agreement with total line shape analysis [11]. The dependence of the free energy on solution concentration was checked and found to be within the estimated experimental error ($\pm$ 0.3 kcal mol^{-1}).

Structural assignments for isomers were based on the method of differential chemical shifts on dilution in aromatic solvents [12]. Chemical shifts for formanilides and acetanilides were measured at 0° ($\pm$ 2°) as 30% v/v or w/v solutions in p-xylene and C_6H_5Cl respectively, relative to internal TMS.
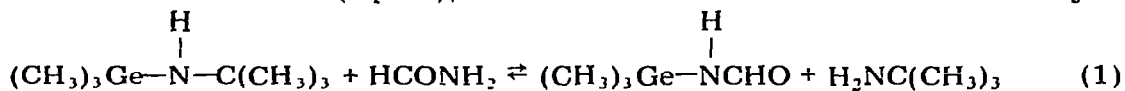
Chemical grade C_6H_5Cl and p-xylene used as spectral solvents were dried over molecular sieves (Linde type 4Å).
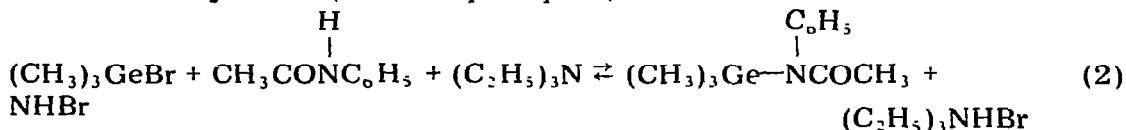
IR measurements

Infrared spectra of N-trimethylgermylformanilides and acetanilides were taken as 2% w/v solutions in spectroquality grade CCl_4 on a Perkin-Elmer 621 spectrometer. N-trimethylgermylacetamide was obtained as a 2% w/v solution in spectroquality grade $CHCl_3$ (shaken with alumina to remove ethanol).

Results and discussion

The trimethylgermyl amides were prepared by two routes: trimethylgermylformamide was obtained by transamination of tert-butyltrimethylgermyl amine with formamide (eqn. 1), while the other derivatives were obtained by

$$(CH_3)_3Ge\underset{|}{\overset{\overset{\displaystyle H}{|}}{N}}C(CH_3)_3 + HCONH_2 \rightleftarrows (CH_3)_3Ge\overset{\overset{\displaystyle H}{|}}{N}CHO + H_2NC(CH_3)_3 \qquad (1)$$

reaction of trimethylbromogermane with the appropriate amide in the presence of triethylamine (for example eqn. 2).

$$(CH_3)_3GeBr + CH_3CONC_6H_5 + (C_2H_5)_3N \rightleftarrows (CH_3)_3Ge\overset{\overset{\displaystyle C_6H_5}{|}}{N}COCH_3 + \qquad (2)$$
$$NHBr \qquad\qquad (C_2H_5)_3NHBr$$

The NMR spectral characteristics of the compounds are shown in Table 1. The trimethylgermyl region of the NMR spectra of the formyl derivatives II, IV-VI contains two peaks of unequal intensity, while the same region for the acetyl derivatives I, VII-IX contains only one peak. The two trimethylgermyl peaks in the spectrum of each of the formyl derivatives coalesce to a single peak as the temperature is increased. The rate of the process responsible for this temperature dependent behavior is concentration independent. The free energies of activation as well as parameters necessary for their calculation are also given in Table 1.

The spectral behavior of the formyl compounds is consistent with either hindered rotation about the carbonyl—nitrogen bond of the amide structure A, which would produce rotational isomers of unequal abundance, or taut-

TABLE 1

CHEMICAL SHIFTS, ISOMER RATIOS, AND ROTATIONAL PARAMETERS

$$O \quad Ge(CH_3)_3$$
$$\| \quad |$$
$$R_1{-}C{-}N{-}R_2$$

| | R_1 | R_2 | Chem. shift $(CH_3)_3Ge$ (Hz)[a] | | T(°C)[b] | % Abundance (±2)[c] | T_c(°C)[d] | $\Delta G^{\ddagger}$(±0.3 kcal mol⁻¹)[e] | |
			Major	Minor				$A \to B$	$B \to A$
I	CH_3	H	26.4		−20	100			
II	H	H	25.7	17.0	−20	83	61	19.3	18.3
IV	H	C_6H_5	24.1	10.4	0	94	27	17.7	15.0
V	H	$p\text{-}ClC_6H_3$	23.8	13.4	0	96	37	18.1	16.2
VI	H	$p\text{-}N(CH_3)_2C_6H_3$	26.0	8.5	0	97	49	19.0	16.7
VII	CH_3	C_6H_5	23.5		0	100			
VIII	CH_3	$p\text{-}ClC_6H_4$	21.3		0	100			
IX	CH_3	$p\text{-}OCH_3C_6H_4$	24.8		0	100			

[a] Chemical shifts recorded as v/v or w/v dilutions downfield from TMS at 60 MHz: I-II, 20% C_6H_5Cl; IV-VI, 30% p-xylene; VII-IX, 30% C_6H_5Cl. [b] Temperature in slow rotation region at which populations and chemical shifts were measured. [c] Abundance of isomer represented by structural formula at left. [d] Temperature at which $(CH_3)_3$Ge peaks coalesce. [e] Free energies of activation for conversion of major isomer A to minor isomer B in 30% w/v or v/v solutions in p-xylene except for II which was 20% v/v in C_6H_5Cl.

omeric exchange of trimethylgermyl groups between the imidate B and amide forms (also present in unequal amounts). The structures can be assigned by comparison of the activation parameters, populations and free energies of activation for the germyl derivatives with those of analogous compounds of known structure, the carbon and silicon derivatives.

The relative population (83%) of the major peak in the trimethylgermyl region of the NMR of compound II is close to the populations of the analogous peaks in the NMR of tert-butylformamide (72%) and N-trimethylsilylformamide (73%), both of which have the amide structure [1]. The free energy of activation for I is also similar to the rotational free energies of the carbon (20.4 kcal mol^{-1}) and silicon (18.15 kcal mol^{-1}) analogs [1].

Moreover, the strengths of the Ge—N and Ge—O bonds relative to the strengths of the Si—N and Si—O bonds as discussed above argues for the amide structure for II because the carbon and silicon analogs have the amide structure. The $\Delta G^{\ddagger}$ for II, which is intermediate between that of the carbon and silicon analogs, can be rationalized by assuming that the lower $\Delta G^{\ddagger}$ for the silicon compound is a result of the stabilization of the rotational transition state by $(p—d)\ \pi$ interaction between nitrogen and silicon [1]. The value of $\Delta G^{\ddagger}$ for II is therefore presumably indicative of an intermediate degree of such interaction (assuming that the electronegativities of silicon and germanium are similar). The assignment of the major isomer for II as that in which the trimethylgermyl group is *cis* to the oxygen is also in agreement with the rotamer assignments for N-tert-butyl and N-trimethylsilylformamide [1]. The somewhat larger percentage of major isomer relative to that of the carbon and silicon analogs may be a result of the lower steric requirement of the trimethylgermyl group or of nonbonded germanium—oxygen interaction.

In contrast to the spectral behavior of II, the NMR spectrum of the acetyl derivative I contains a single sharp peak in the trimethylgermyl region even at −50°. This behavior also parallels that of the carbon and silicon homologs and is probably a result of a very low abundance of the minor isomer [1].

The NMR spectra of the anilides parallel those of the formamides and acetamides: the formanilides exhibit two peaks of unequal intensities in the trimethylgermyl region at lower temperatures which coalesce to a single peak at higher temperatures, while the acetanilides have only one peak in this region even at −80°C. The populations of the minor peak in the spectra of the formanilides are rather insensitive to substitution on the aromatic ring. This is in distinct contrast to the behavior of the trimethylsilyl formanilides and acetanilides in which a change in phenyl substituent from p-OCH$_3$ to p-Cl results in a drastic shift in populations [4] but is the same as the behavior of N-methylformanilides [13]. Since the N-methylformanilides exist in the amide form and trimethylsilyl anilides exist as tautomeric mixtures of amide and imidate, the lack of significant variation in the population of the minor peak is evidence for the existence of the amide form for the trimethylgermylformanilides. The amide form is also substantiated by free energies of activation for the formanilides which vary in an order similar to that observed for the N-methylformanilides, but opposite to that found for the exchange of trimethylsilyl groups in the trimethylsilylacetanilides [14].

A third piece of evidence for the amide form is the magnitude of the free

energies of activation for the trimethylgermylformanilide. The $\Delta G^{\ddagger}$ for the p-H derivative is 0.7 kcal mol^{-1} lower than that of N-tert-butylformanilide [13], in agreement with the effect of the trimethylgermyl group on the rotational barrier observed with the formamides. A final observation supportive of the amide form is the single peak found for the trimethylgermyl region of the NMR spectra of the trimethylgermyl acetanilides. The same behavior has been observed for N-alkylacetanilides [12] but trimethylsilylacetanilides exhibit two peaks in this region due to the two tautomers [4].

Dilution of the trimethylgermylformanilides with xylene reveals that the minor isomer has the $Ge(CH_3)_3$ group *trans* to oxygen in agreement with the previous rotamer assignments for the N-alkylformanilides [13]. The large population of the major isomer relative to N-tert-butylformanilide (73%) can again be attributed to either a smaller steric requirement of the $Ge(CH_3)_3$ group or sizeable nonbonded interactions between germanium and oxygen.

Assignment of structure on the basis of C=O or C=N absorption in the infrared is unreliable because of the proximity of the two absorption bands [15]. The IR spectra of the trimethylgermylformanilides and acetanilides show an absorption of medium intensity at 829 cm^{-1} (± 2) which could be assigned to the Ge—N mode. No Ge—O absorptions indicative of the imidate form were observed.

Acknowledgements

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