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THE PREPARATION AND STRUCTURES OF SOME SIMPLE TRIALKYLSTANNYLAMIDES

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Summary

Trialkylstannylamides of the type $HC(=O)N(SnR_3)R'$ ($R = CH_3$, C_2H_5; $R' = H$, CH_3, C_6H_5 were prepared by the reaction of a trialkylmethoxystannane with the appropriate amide at 110—120°C. Trimethylstannylformamide is an associated liquid and exists in only one conformation. Trimethylstannyl-*N*-methylformamide is unassociated in benzene and exists primarily (70%) in the conformation with the trimethylstannyl group *cis* to the carbonyl group. The average free energy of activation for rotation is 22 kcal/mole. The other derivatives exist in only one conformation and are unassociated in benzene.

Although a variety of organostannylamides have been prepared, relatively little is known about their structural characteristics such as conformations, hindrance to rotation, association, etc. [1—3]. Moreover, the trimethylstannyl derivatives apparently have not been reported. The present study of a series of simple trialkylstannylamides is a continuation of our investigation of the structural determinants of organometallic amides [4—6].

Experimental

All operations were carried out under a nitrogen atmosphere using oven-dried glassware and dry reagents. Trimethylmethoxystannane was obtained from the reaction of trimethyldiethylaminostannane with methanol [7]. Likewise, triethylmethoxystannane was obtained from triethyldimethylaminostannane [8]. Trimethylstannylformamide was formed in the neat reaction of trimethylmethoxystannane (4.5 g, 0.023 mol) with formamide (0.9 g, 0.020 mol) at 110-120°C. Removal of the liberated methanol by distillation was followed by fractionation of the product: b.p. 130°C/3 mmHg, yield 67%. (Found: C, 24.41; H, 5.55. $C_4H_{11}NOSn$ calcd.: C, 23.12; H, 5.33%.) The product underwent partial solidification over a period of time. A solid residue in the pot was not conclusively identified, but the NMR spectrum (ClC_6H_5) showed a peak in the formyl

region and a peak (with tin satellites) in the $SnCH_3$ region with an integration ratio of 1 to 18. There was no evidence of an NH peak.

In another preparation at 150°C the product obtained by distillation partially solidified in the receiver. The spectral and analytical data for the solid were nearly identical to those of the liquid obtained at 120°C. (Found: C, 24.14; H, 5.55. $C_5H_{11}NOSn$ calcd.: C, 23.12; H, 5.33%.) In each preparation difficulty was experienced in freeing the product from small amounts of unreacted formamide.

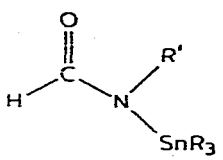
Trimethylstannyl-*N*-methylformamide and trimethylstannylformanilide were formed in neat reactions of trimethylmethoxystannane with the appropriate amide at 120°C. The liberated methanol was removed by distillation. The *N*-methyl derivative was separated by distillation; m.p. 73—75°C, yield 34%. (Found: C, 27.18; H, 6.14. $C_5H_{13}NOSn$ calcd.: C, 27.07; H, 5.91%) while the phenyl derivative was recrystallized from cyclohexane; m.p. 112—117°C; yield 47%. (Found: C, 41.94; H, 5.43. $C_{10}H_{15}NOSn$ calcd.: C, 42.30; H, 5.32%.)

Triethylstannylformamide was prepared by neat reaction of triethylmethoxystannane and formamide at 120°C. Removal of methanol was followed by distillation of product: b.p. 105°C/2 mmHg, yield 65%. (Found: C, 33.70; H, 6.91. $C_7H_{16}NOSn$ calcd.: C, 33.65; H, 6.86%.)

Infrared spectra were recorded with Perkin—Elmer 621 and 137 spectrometers on liquid smears or Nujol mulls. NMR spectra were obtained on a Varian A-60D spectrometer equipped with variable temperature accessory V-4341/V-6057.

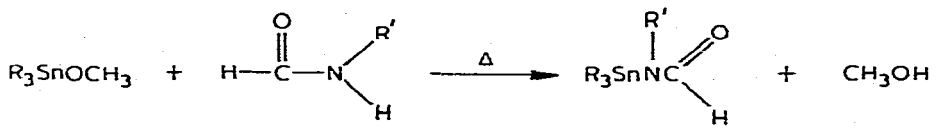
Results

A series of trimethylstannyl and triethylstannyl amides (I—IV) were prepared



(I: $R = CH_3, R' = H$)
(II: $R = CH_3, R' = CH_3$)
(III: $R = CH_3, R' = C_6H_5$)
(IV: $R = C_2H_5, R' = H$)

by the reaction of the trialkylmethoxystannane and the appropriate amide at 110—120°C. Compound I was also obtained by transamination.



Trimethylstannylformamide (I) is a liquid with an apparent molecular weight (cryoscopic, benzene) that increases from 208 at low concentrations (0.06 *M*) to 303 at a concentration of 0.12 *M*. If this liquid is allowed to sit at room temperature a solid slowly forms that has a molecular weight similar to that of the liquid measured at low concentrations. The infrared and NMR spectra of this solid in chlorobenzene solution are also virtually identical to those of the liquid. The experimentally determined molecular weights of the other compounds did not vary significantly with concentration and were consistent with unassociated monomers (in solution in C_6H_6).

The infrared spectrum of each of the compounds contains an intense peak at

about 1600 cm^{-1} (±15 cm^{-1}) which has been assigned to the C=O mode in other trialkylstannylamides [1—2]. The spectra also contain a shoulder at ca. 1680 cm^{-1} that increases upon exposure of the compound to air and is therefore probably a result of hydrolysis. The N—H stretching vibrations in compounds I and IV occur at 3385 and 3310 cm^{-1}, respectively.

The NMR spectrum of I in chlorobenzene contains a singlet with $^{117,119}Sn$ satellites (J 63 Hz) at 0.43 ppm and single broad peaks at 6.29 and 8.12 ppm. This spectrum is unaffected by a change in temperature from —60 to +100°C, but the peaks in the formyl and NH region are definitiely altered by a change in concentration. As the concentration increases the formyl and NH peaks sharpen considerably. There are no satellite peaks visible for the formyl and NH protons.

The NMR spectrum of II in chlorobenzene contains a singlet (and $^{117,119}Sn$ satellites, J 60 Hz) at 0.40 ppm with an upfield shoulder, two doublets at 2.59 and 2.69 ppm of unequal intensity, and a broad peak at 7.96 ppm. The low field doublet has a splitting of 1.1 Hz and is somewhat less than half as intense as the upfield doublet which is just barely resolved (splitting ca. 0.5 Hz). At ca. 106°C the two doublets coalesce to one broad peak.

The NMR spectra of III and IV are temperature invariant and contain broad singlets for the formyl protons at 8.30 and 8.32 ppm, respectively. The NMR spectrum of III exhibits a singlet at 0.44 ppm, with satellites for the $SnCH_3$ peaks (J 57 Hz) while the spectrum of IV shows a multiplet centered at 1.18 ppm for the SnC_2H_5 group.

An attempt to prepare trimethylstannylthioformanilide by the reaction of trimethylmethoxystannane and thioformanilide produced a liquid that upon fractional distillation was separated into two fractions, one of which was identified as $[(CH_3)_3Sn]_2S$ from its IR and NMR spectra, boiling point, and refractive index. The IR and NMR spectra and refractive index of the other fraction indicate that it is a mixture of $[(CH_3)_3Sn]_2S$ and $C_6H_5N{=}C(OCH_3)H$. The formation of $[(CH_3CH_2)_3Sn]_2S$ was observed previously in the reaction of triethylmethoxystannane and thioformanilide [2].

Discussion

The reaction of a trialkylmethoxystannane with an amide affords a convenient method for the preparation of a variety of tin amides [2]. Several of the compounds were also obtained by transamination but separation of the product was more difficult.

The structures of the compounds are of interest because of the possibility of amide—imidate tautomerism. While such tautomerism has been amply documented for trimethylsilyl "amides" [4—6], the NMR spectrum of II provides convincing evidence for the amide structure for these compounds. The two doublets of unequal intensities and couplings in the *N*-methyl region must be a result of methyl groups in magnetically nonequivalent positions. This nonequivalence could result of course from an amide—imidate equilibrium or from *syn,anti* isomerism in the imidate form, but the similarity in couplings to those observed for trimethylsilyl-*N*-methylformamide which exists in the amide form [9], is indicative of the amide structure. The amide structure has also been suggested for several triethylstannylanilides [2].

The free energy of activation for the coalescence process calculated by the method of Shanan-Atidi and Bar-Eli [10] (T_c 106°C, $\Delta\nu_c$ 1.9 Hz, P_a 0.215, $\Delta G_a^{\ddagger}$ 21.3 kcal/mol, $\Delta G_b^{\ddagger}$ 22.3 kcal/mol) is higher than that for the silyl analog. This increase in free energy of activation for rotation about the CO—N bond follows the trend observed for the germanium analogs [5] and is perhaps a result of a decrease in $(p—d)\pi$ overlap in the transition state. It is also possible that there is less steric hindrance in the ground state of the tin amides (because of the longer Sn—N and Sn—C bonds) which would produce a higher $\Delta G^{\ddagger}$.

Conformational assignments for II can be made from the magnitude of the *N*-methyl—formyl couplings. The less intense *N*-methyl doublet has the greater coupling and can therefore be assigned to the methyl group *trans* to the formyl proton. At room temperature this doublet constitutes 30% of the total area under both doublets. Hence the favored conformation has the $Sn(CH_3)_3$ *cis* to the carbonyl. This is in sharp contrast to the most populated (87%) conformation for the silicon analog which has the trimethylsilyl group *cis* to the carbonyl. This reversal of conformation could be attributed to the different steric requirement of the $Sn(CH_3)_3$ group or to dative carbonyl—tin interactions.

The NMR spectra of I and III do not provide evidence for more than one conformational isomer for each compound down to —60°C. While this could be a result of rapid rotation, the fairly high barrier observed for II and the known effect on the barrier of substituting H or C_6H_5 for CH_3 at nitrogen [4,5,9], suggest that it is more likely due to 100% population of one isomer. The populations of the more stable isomer for $(CH_3)_3MN(C_6H_5)CHO$ vary therefore: M = C, 0.74 [11]; Si, 0.81 [4]; Ge, 0.94 [5]; Sn, 1.00; and for $(CH_3)MNHCHO$, M = C, 0.72 [9]; Si, 0.73 [9]; Ge, 0.83 [5]; Sn, 1.00. Thus, in these derivatives the relative stability of the isomer with $(CH_3)_3M$ *cis* to carbonyl increases from carbon to tin.

The absence of the three bond coupling of tin to the *N*-methyl protons in II and to the formyl protons in I—IV could be a result of quadrupolar relaxation at the ^{14}N nucleus as has been suggested for some organostannyl amines [12] or to intermolecular exchange of trimethylstannyl groups. The exchange hypothesis seems unlikely at least for II because the exchange would have to occur less rapidly than rotation (because rotamers are observed). Yet exchange at this rate would not destroy the tin *N*-methyl and formyl satellites.

Cryoscopic molecular weight determinations in benzene clearly indicate an increase in association of I as the concentration of the solution increases. The variation of the NMR spectrum as a function of concentration can also be explained in this way. Indeed, it would appear that the solid that forms in liquid I (and also perhaps the solid that forms at higher temperatures) is a dimeric or polymeric form of I that dissociates in solution. This association could exist in several ways: through intermolecular hydrogen bonding of the N—H group to a carbonyl group, hydrogen bonding of NH to amide nitrogen, dative bonding of C=Ö: to tin, or dative bonding of nitrogen to tin. The similarity of the NH stretching vibrations in both I and IV (which is not associated in solution) suggests that the association of I does not occur through hydrogen bonding. The effect of substituents at nitrogen in blocking the association indicate that the association may occur by dative bonding from nitrogen to tin. Evidence for carbonyl—tin association in a variety of tin amides, carbamates, etc., has been obtained from Mössbauer spectroscopy [13].

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