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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS XXIV*. ADDITION AND SUBSEQUENT ELIMINATION REACTIONS OF BIS(TRIMETHYLGERMYL) METHYLAMIDE OXIDE AND SULPHIDE

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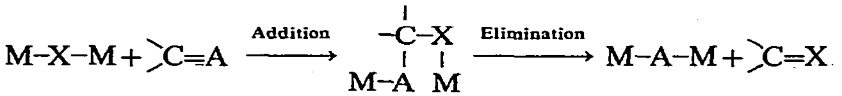
SUMMARY

The addition reactions of polar unsaturated compounds with various organogermanium compounds *i.e.*, $(Me_3Ge)_2X$ (X = NMe, O and S), have been studied. The relative order of reactivities was found to be NMe > O ≫ S. When phenyl isothiocyanate was used as an acceptor with $(Me_3Ge)_2NMe$ and $(Me_3Ge)_2O$, β-elimination of $(Me_3Ge)_2S$ was observed with the formation of phenylmethylcarbodiimide and phenyl isocyanate, respectively. This behaviour suggests that the reactivity of the trimethylgermyl group is similar to that of the corresponding trimethyltin group although the reactivity in both cases is generally low. For this reason the affinity of the trimethylgermyl group to the above heteroatoms must follow the sequence $S < O \approx N$.

INTRODUCTION

Bis(triorganometallyl) amides and oxides; M–X–M (X = NR or O), have been reported as inducing addition–elimination reactions. Thus, such reactions have been reported for $(R_3M)_2NR'$ (M = Si and Sn)[2-10], $(R_3Sn)_2O$[11,12], $Bu_3Sn{-}O(CH_2)_n{-}O{-}SnBu_3$[13] and $Bu_3Sn{-}O(CH_2)_2NR{-}SnBu_3$[14], and in addition, an extension of this type of reaction to organoaluminium chemistry has recently been studied by our group[15] for $(Et_2Al)_2S$.



$$\text{M–X–M} + \rangle C{=}A \xrightarrow{\text{Addition}} \begin{array}{cc} -\overset{|}{\underset{|}{C}} & -\underset{|}{X} \\ \text{M–A} & \text{M} \end{array} \xrightarrow{\text{Elimination}} \text{M–A–M} + \rangle C{=}X$$

The driving force of this sort of reaction has been considered to be the relative stabilities of M–A–M and M–X–M bonds. Although qualitative empirical orders of bond strength have been generally elucidated for R_3Si(O > S ≥ N) and R_3Sn (S > O >

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* For part XXIII, see ref. 1.

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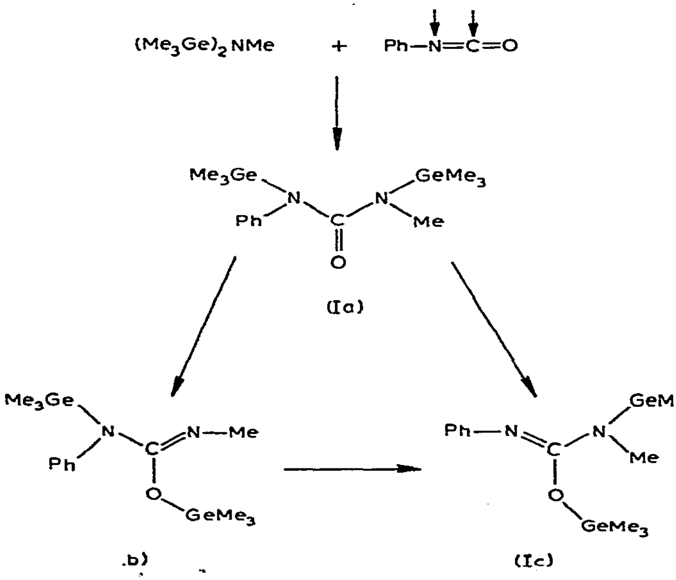
N) groups[1], no information is available for the corresponding triorganogermanium compounds.

Simple addition reactions resulting in the corresponding insertion products have already been reported for Ge–N[16], Ge–O[17], and Ge–S[18], but the relative chemical behaviour of these groups on the basis of the addition–elimination reactions of bis(trimethylgermyl) amides, oxide and sulphide have not been studied at all. For this reason, some addition and subsequent β-elimination reactions of the organogermanium compounds containing unsaturated bonds have been studied in this investigation. A comparison of the addition–elimination reactions of these compounds with those of the corresponding organosilicon or organotin compounds is also made.

RESULTS AND DISCUSSION

Reactions of heptamethyldigermazane; $(Me_3Ge)_2NMe$

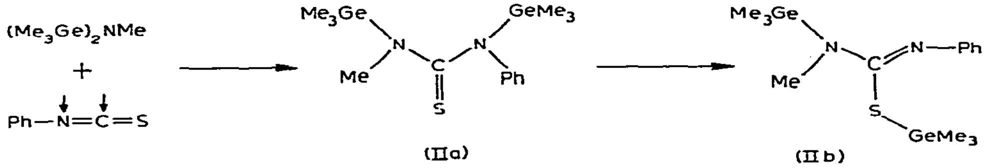
The addition reaction of phenyl isocyanate with heptamethyldigermazane occurred instantaneously and a 1/1 addition product (I) was isolated by distillation. Three possible isomers, (Ia)–(Ic), exist for the structure of (I) . NMR spectroscopic studies of (I) show the presence of only one of these three possible isomeric structures. Thus, the two kinds of CH_3–Ge proton signals at τ 9.65 and 9.62, as well as one CH_3–N signal at τ 7.84, observed in the spectrum have values very similar to those observed for adduct (IIId), mentioned in the preceding paper and obtained by the reaction between phenyl isocyanate and Me_3Ge–NMe–$SiMe_3$.



In addition, the infrared spectrum of (I) showed a strong ν(C=N) absorption at 1588 cm^{-1} which, when taken together with the above NMR spectroscopic evidence, strongly suggests that the predominant structure of (I) is (Ic) which is presumably derived by the one-step Me_3Ge migration (Ia) → (Ic) or by two step migrations involving two Me_3Ge groups *i.e.*, (Ia) → (Ib) → (Ic).

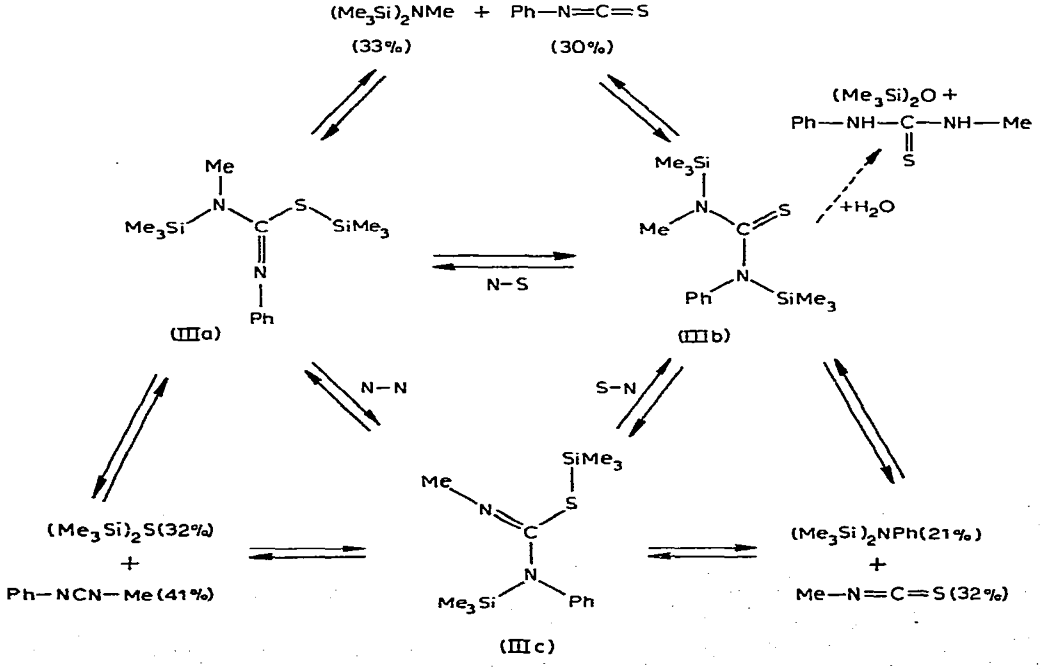
In a similar fashion the addition reaction of heptamethyldigermazane and phenyl isothiocyanate also occurs instantaneously at room temperature. In this case, however, the adduct (I) could only be successfully isolated by distillation in high vacuum because of its ready decomposition.

The existence of a low field chemical shift at τ 9.53 for one of the CH_3–Ge protons suggests the formation of a Ge–S bond in the predominant structure of this compound. The infrared spectrum of (II) possesses ν(C=N) at 1560 cm^{-1} and the similarities between the NMR and infrared spectra of this adduct with those of the adduct obtained from the reaction of phenyl isothiocyanate with Me_3Ge–NMe–$SiMe_3$ [(VII) in the preceding paper] support (IIb) as the predominant structure in this system.



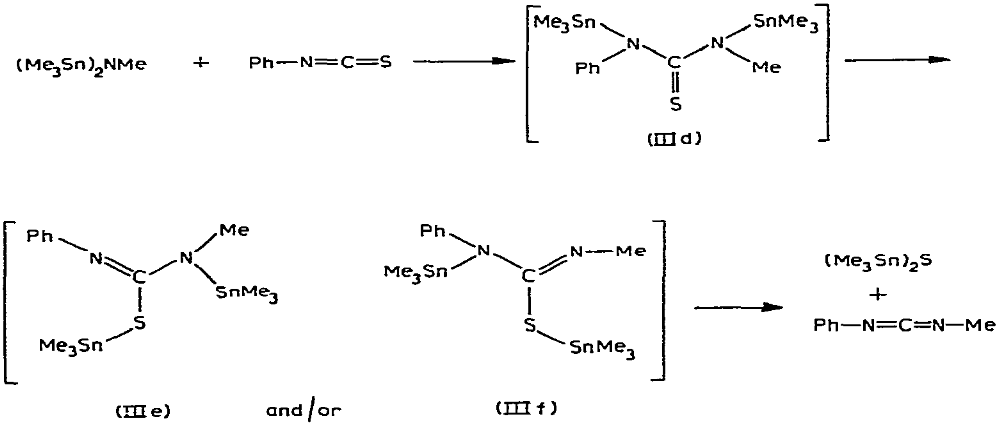
Adduct (II) decomposes completely around 100° to give methylphenylcarbodiimide and bis(trimethylgermyl)sulphide as the main products, thus providing further evidence in favour of structure (IIb) since methylphenylcarbodiimide may be formed from this structure through a selective β-elimination reaction involving $(Me_3Ge)_2S$[27].

SCHEME 1

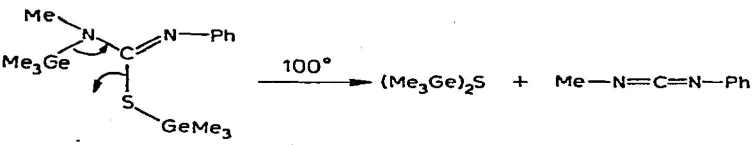


The above elimination process may be compared with the addition–elimination reactions of the corresponding trimethylsilyl and trimethylstannyl analogues. We have previously reported[3] the reaction of heptamethyldisilazane with phenyl isothiocyanate at 150° over a period of ten days resulting in the following series of observations; (1) the reaction products consisted of a mixture of $(Me_3Si)_2NMe$ (recovered 33%), PhNCS(recovered 30%); $(Me_3Si)_2NPh$(21%), MeNCS(32%); $(Me_3Si)_2S$(32%)and Ph–NCN–Me(41%)and(2)when the two components were allowed to react in the presence of moisture at room temperature, the quantitative formation of methylphenylthiourea occurred, this being the hydrolysis product of the intermediate 1/1 adduct (III). These observations were explained in terms of an addition–elimination process as in Scheme 1. The completely random distribution of products may be ascribed to the similarity in the Si–N and Si–S bond strengths in the intermediate (III), so that all three possible isomers, (IIIa), (IIIb) and (IIIc) play similar roles in the subsequent elimination reactions.

The addition–elimination reactions of heptamethyldistannazane with phenyl isothiocyanate, on the other hand, led to the selective formation of bis(trimethyltin) sulphide and methylphenylcarbodiimide[2,7], since Sn–S bonds are much more stable than Sn–N bonds. For this reason, β-elimination in this reaction should occur via either (IIIe) and/or (IIIf) in the following manner.



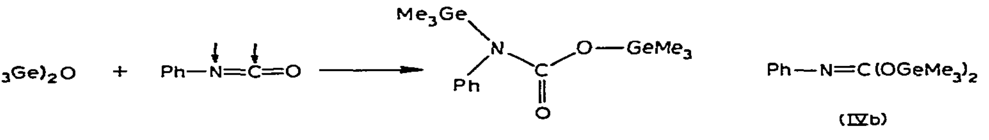
The selective formation of methylphenylcarbodiimide and bis(trimethylgermyl) sulphide from the metastable 1/1 adduct (IIb), reported in this study, indicates that the Me_3Ge group shown is much more closely related to the corresponding Me_3Sn group in its behaviour than to the Me_3Si group.



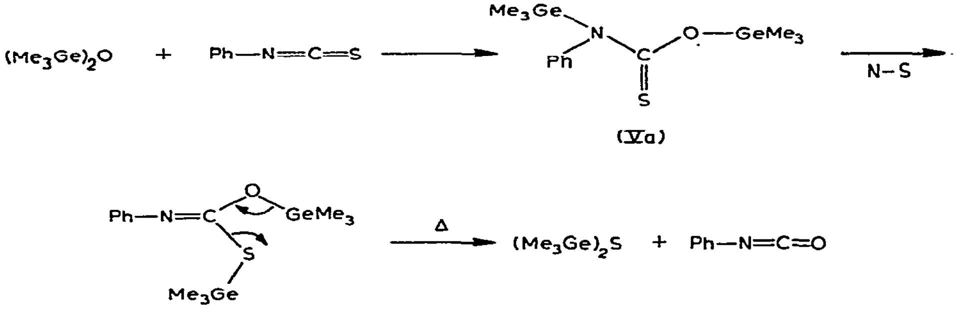
Reactions of hexamethyldigermoxane; $(Me_3Ge)_2O$

The simple insertion reactions of isocyanate, chloral and β-propiolactone into

Bu_3Ge–OMe have been reported previously by us[17]. A similar addition reaction of phenyl isocyanate into one of the Ge–O bonds in hexamethyldigermoxane took place at room temperature over a period of 1.5 h, indicating that the reactivity of hexamethyldigermoxane is considerably less than that of heptamethyldigermazane and suggesting that the reactivity order should be Ge–N>Ge–O. Adduct (IV), isolated as colourless crystals, showed two independent CH_3–Ge proton signals with equal intensities at τ 9.65 and 9.49 respectively, and with ν(C=O) absorptions at 1637 and 1662 cm^{-1} in the IR spectrum. This spectroscopic evidence supports structure (IVa) rather than (IVb), the latter would be eliminated on the basis of the above NMR results, since it should only exhibit one CH_3–Ge signal.


(IVa) (IVb)

As mentioned previously[1], isothiocyanates are weaker acceptors than the corresponding isocyanates, because the polarity of C=S bonds is much lower than that of C=O bonds making isothiocyanates less electrophilic. Phenyl isothiocyanate does not react at all with hexamethyldigermoxane at room temperature, and even under much more drastic conditions, *i.e.*, 150° for 200 h, the expected simple insertion product (V) was not isolated. The sole reaction which occurred was an elimination reaction which yielded bis(trimethylgermyl) sulphide and phenyl isocyanate as the products. This suggests that the following addition–elimination mechanism occurs in which Me_3Ge prefers the soft sulphur to the hard oxygen atom, the similarity of the Me_3Ge group to the R_3Sn group again being demonstrated[11,12].

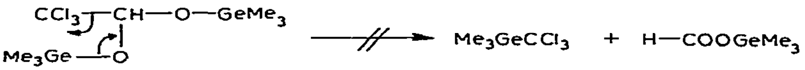

(Va)

(Vb)

Hexamethyldigermoxane does, however, react instantaneously with chloral, even at room temperature, to given the insertion product (VI).

$$(Me_3Ge)_2O + Cl_3C\text{–}CH\text{=}O \rightarrow \underset{\text{(VI)}}{Cl_3C\text{–}CH(OGeMe_3)_2}$$

The structure of adduct (VI) was identified by the presence of the characteristic C–H proton signal at τ 4.93 [*cf.* Cl_3C–CH(SEt)($OSiMe_3$) at τ 500[19], and the equivalent CH_3–Ge proton signal at τ 9.50 as a singlet]. Elimination of Me_3GeCCl_3 from (VI) was not observed in the present investigation, although such elimination has been well established for organotin and organolead oxides[20,21].



Attempted reactions involving bis(trimethylgermyl) sulphide; $(Me_3Ge)_2S$

Attempts to react bis(trimethylgermyl) sulphide with chloral or phenyl isothiocyanate were unsuccessful the starting materials being recovered unchanged. When bis(trimethylgermyl) sulphide was treated with phenyl isocyanate under drastic conditions, *i.e.*, 150° for 264 h, trace amounts of triphenyl isocyanurate, the cyclic trimer of phenyl isocyanate, were identified as the sole product. The formation of triphenyl isocyanurate in excellent yield at room temperature has already been reported as a result of the reaction of bis(trimethyltin) sulphide with phenyl isocyanate[19]. On the basis of Abel's basicity order[22], the basicity of Group IV organometallyl sulphides should lie in the series Sn–S > Ge–S > Si–S; our results, however, indicate the somewhat unexpected sequence, Sn–S > Si–S $\geqslant$ Ge–S. The decreased nucleophilicity of Ge–S bonds to unsaturated polar double bonds may possibly be explained in terms of the electronegativity difference between Group IV metals and the sulphur atom on the basis of the Allred–Rochow scale[23]; Si, 1.74; Ge, 2.02; Sn, 1.72 and S, 2.44.

CONCLUSIONS

The basicity of $(Me_3Ge)_2X$ (X = NMe, O and S) towards unsaturated compounds follows the order $(Me_3Ge)_2NMe > (Me_3Ge)_2O \gg (Me_3Ge)_2S$, which was quite consistent with Abel's basicities[22]; $\Delta\nu$(C–D) (cm^{-1}) for $(Me_3Ge)_3N$, 72 and $Me_3Ge–NEt_2$, 82; $(Me_3Ge)_2O$, 55; $(Me_3Ge)_2S$, 38.

The addition–elimination reactions of heptamethyldigermazane or hexamethyldigermoxane with phenyl isothiocyanate led to the selective formation of bis(trimethylgermyl) sulphide, a behaviour quite similar to that of the corresponding organotin analogues. Thus, on the basis of addition–elimination reactions the bond strength of Ge–X lies in the order Ge–S > Ge–O $\approx$ Ge–N, which differs from that of both the organosilicon and organotin compounds, *viz.*, Si–O > Si–S $\geqslant$ Si–N and Sn–N > Sn–O > Sn–S[1].

EXPERIMENTAL

Heptamethyldigermazane[24], hexamethyldigermoxane[25] and bis(trimethylgermyl) sulphide[26] were prepared as described in the literature. NMR and infrared spectra were measured using JEOL Model C60-HL and JASCO Model DS-403G spectrometers, respectively. All the reactions described were performed under an atmosphere of dry argon.

Addition reaction of heptamethyldigermazane with phenyl isocyanate (I)

Phenyl isocyanate (345 mg; 2.88 mmoles) was added dropwise to heptamethyldigermazane (840 mg; 3.18 mmoles) at room temperature. The addition reaction was completed instantaneously and the 1/1 adduct(I) was isolated by distillation under reduced pressure in 63% yield; b.p. 76–78°/0.05 mm. (Found: C, 43.87; H, 6.73; $C_{14}H_{26}Ge_2N_2O$ calcd.: C, 43.84: H, 6.83%.) IR(CCl_4) 1588 (C=N)(vs) and 1651 (C=O)(vw) cm^{-1}. NMR (CCl_4): τ 9.65 and 9.62 CH_3–Ge; with $J(^{13}C–H)$ 125 Hz, τ 7.84(CH_3–N) and τ 2.8–3.2 (m) (C_6H_5).

Addition reaction of heptamethyldigermazane with phenyl isothiocyanate (II)

Phenyl isothiocyanate (488 mg; 3.61 mmoles) was added to heptamethyldigermazane (923 mg; 3.50 mmoles) at room temperature. Instantaneous reaction occurred and the 1/1 adduct(II) was obtained following distillation under high vacuum in 60% yield; b.p. 92–94°/5×10^{-1} mm. (Found: C, 42.22; H, 6.49. $C_{14}H_{26}Ge_2N_2S$ calcd.: C, 42.08; H, 6.56%.) IR(CCl_4), ν(C=N) 1560 (vs) and ν(C=S) 1330 (vw) cm^{-1}. NMR (CCl_4): τ 9.76 [CH_3–Ge with $J(^{13}C–H)$ 126 Hz], τ 9.53 [CH_3–Ge with $J(^{13}C–H)$ 127 Hz], and τ 7.04 (CH_3–N), τ 2.8–3.1 (m)(C_6H_5).

Pyrolysis of adduct (II). Heating adduct (II) (3 mmoles) under an atmosphere of argon at 150° for 150 h, led to the formation of bis(trimethylgermyl) sulphide (75% yield) and the polymer of methylphenylcarbodiimide (80% yield), both products being identified by the comparison of their NMR and infrared spectra with those of authentic samples.

Addition reaction of hexamethyldigermoxane with phenyl isocyanate (IV)

A mixture of phenyl isocyanate (391 mg; 3.28 mmoles) and hexamethyldigermoxane (911 mg; 3.63 mmoles) was allowed to stand for 1.5 h at room temperature. The whole solidified and evaporation of the low boiling materials *in vacuo* led to the isolation of the crude 1/1 adduct (IV) in 97% yield. Recrystallization from n-hexane gave (IV) in 73% yield, m.p. 61–62° (in sealed tube). (Found: C, 41.94; H, 6.38. $C_{13}H_{23}Ge_2NO_2$ calcd.: C, 42.14; H, 6.26%.) IR(CCl_4); 1637 and 1662 (vs) cm^{-1} due to ν(C=O). NMR(CCl_4), τ 9.65 [CH_3–Ge with $J(^{13}C–H)$ 126 Hz, τ 9.49 [CH_3–Ge with $J(^{13}C–H)$ 124 Hz] and the multiplets between 2.7–3.0 (C_6H_5).

Reaction of hexamethyldigermoxane with phenyl isothiocyanate

Phenyl isothiocyanate (503 mg; 3.73 mmoles) and hexamethyldigermoxane (996 mg; 3.97 mmoles) were placed in a sealed tube under an atmosphere of argon. The mixture was kept at 150° for 200 h, when distillation gave bis(trimethylgermyl) sulphide (33%) and phenyl isocyanate (40%), both characterized by comparison of their spectra with those of authentic samples.

Addition reaction of hexamethyldigermoxane with chloral (VI)

Chloral (647 mg; 4.39 mmoles) was gradually added to hesamethyldigermoxane (840 mg; 3.35 mmoles) at room temperature. The addition reaction was completed in a few minutes and the 1/1 adduct (VI) was isolated by distillation in 63% yield; b.p. 72°/0.2 mm. (Found: C, 24.12; H, 4.88. $C_8H_{19}Cl_3Ge_2O_2$ calcd.: C, 24.10; H, 4.88%.) NMR (CCl_4), τ 9.50 [CH_3–Ge with $J(^{13}C–H)$ 127 Hz] and τ 4.93 (–CH–).

Reaction of bis(trimethylgermyl) sulphide with phenyl isocyanate

A mixture of phenyl isocyanate (10 mmoles) and bis(trimethylgermyl) sulphide

(10 mmoles) was heated at 150° for 48 h in a sealed tube filled with argon. Distillation of the reaction mixture gave the initial starting materials. Recrystallization of the residue of the distillation process from an acetone/petroleum mixture (2/1 v/v) gave triphenyl isocyanurate in 3% yield; m.p. 290–292°.

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