Addition Reactions of Alkoxygermanes

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RECENTLY there has been great interest in the addition reactions of M–N, M–O compounds with a variety of multiply-bonded reagents. Although aminometallation reactions had been well established for Group IV compounds (Si,[1] Ge,[2] Sn,[3] and Pb[4]), alkoxymetallation was known so far only in the case of Sn–O compounds.[5] But a recent report[6] of the reaction of Si–O compounds with hexafluoroacetone to give adducts prompts us to disclose our results of the addition reactions of the Ge–O bond in tributylmethoxygermane and tributylethoxygermane with phenyl isocyanate, phenyl isothiocyanate, chloral, and di-*p*-tolylcarbodi-imide.

When tributylmethoxy- or tributylethoxy-germane and phenyl isocyanate were mixed, a mildly exothermic reaction occurred, and the corresponding germylcarbamates were obtained as distillable liquids: Bu$^{n}_{3}$GeNPh·CO$_2$Me, b.p. 125—127°/0·08 mm., ν(C=O) 1690 cm.$^{-1}$, τ (OCH_3) 6·33 (singlet); Bu$^{n}_{3}$GePh·CO$_2$Et, b.p. 134—135°/0·10 mm., ν(C=O) 1680 cm.$^{-1}$, τ (OCH_2·Me) 5·91 (quartet). These esters could be hydrolyzed readily by atmospheric moisture to give methyl and ethyl *N*-phenylcarbamate, respectively.

Phenyl isothiocyanate was much less reactive, but the reaction took place in 1·5 hr. at 80° to give the adduct [it is now in question which formula should be assigned to the adduct, Bu$_3$Ge,NPh·CS·OR or C$_6$H$_5$N=C(OR)S,GeBu$_3$], which could be hydrolyzed in air to the corresponding methyl or ethyl phenylthiocarbamate (Me, m.p. 93·3—93·6°, Et, m.p. 67·0—68·5°).

Tributylmethoxygermane reacted slowly at room temperature with chloral, but the reaction was complete after heating the mixture at 80° for 5 min. The carbonyl group peak of chloral was lost from the infrared spectrum, and the aldehyde proton signal at τ 0·98 shifted up to τ 5·12, characteristic of an acetal CH. The methoxy-group signal, originally at τ 6·45 shifted to τ 6·36. Therefore, simple addition of the Ge–O bond occurs across the carbonyl group of chloral to give methylgermyl trichloroacetal.

Di-*p*-tolylcarbodi-imide did not react with Bu$_3$GeOMe at room temperature, but slow addition occurred at 100° over 7 days, giving the adduct Bu$_3$Ge·N(*p*-Tol)C(=N-*p*-Tol)·OMe, ν(C=N) 1665 cm.$^{-1}$.

No reaction could be observed when tributylmethoxygermane and carbon disulphide were heated at 80° for 15 hr.

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