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Stabilisation of Germanium(II) Dialkoxide Intermediates by Solvent Coordination

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Introduction

There is current intensive activity in the area of bivalent compounds of the main group IV elements owing to their demonstrated use as intermediates in the formation of unusual heterocyclic compounds [1, 2], as ligands in transition metal complexes [3, 4], and as precursors for oxidative addition reactions [5, 6]. Thus far the emphasis has been on the chemistry of tin(II). There is a paucity of both synthetic and characterisation data for the congener, Ge(II), although the transient existence of some bivalent germanium intermediates have been deduced from sealed tube experiments in which Ge(IV) products are trapped by oxidative addition reactions [7, 8]. We now wish to report preliminary information on the synthesis and characterisation of germanium(II) dialkoxides and their behaviour in non-aqueous, donor solvents.

Experimental

GeI_2 (5 g) was added to EtOH (300 ml) containing an excess (3%) of freshly prepared NaOEt. After 30 min the solution was filtered and EtOH was removed under vacuum. The residual white solid (product (*1*) + NaI) was vacuum dried for 1 hr and dissolved in C_6H_5Cl (50 ml). The by-product, NaI was removed by filtration. ^1H NMR spectrum of *1* (60 MHz, 30 °C): $\delta(OCH_2)$, 3.95 ppm, q, 7Hz; $\delta(CH_3)$, 1.30 ppm, t, 7Hz.

1 (2 g) in pentane (50 ml) was immersed in a bath at –76 °C. After several minutes a white solid, *2* precipitates; MS (m/e (^{74}Ge)): 255 (59%), 210 (6%), 209 (14%), 165 (7%), 164 (11%), 149 (30%), 135 (15%), 120 (17%), 119 (96%), 91 (81%).

1 (2 g) was added to an excess of MeI in toluene and refluxed overnight. The solution was filtered and the voltaile materials were removed under vacuum. The ^1H-NMR (FT 220 MHz) spectrum of the residual liquid in $CDCl_3$: δ(GeMe), 0.72s, 1.26s, 1.95s, 2.80s.

Results and Discussion

Germanium(II) diethoxide ethanolate, $Ge(OEt)_2 \cdot xEtOH$ (*1*), is generated in ethanol solution by the reaction of NaOEt and GeI_2. *1* is stabilised in hydrocarbon solutions by the presence of small amounts of ethanol and can be used as an intermediate in transesterification or oxidative addition reactions. Removal of ethanol under vacuum leads to irreversible association of *1* to an insoluble, intractable material.

The 60 MHz proton NMR spectrum of *1* extracted into benzene after one hour exposure to vacuum following removal of ethanol from the reaction mixture, displays a quartet (3.95 ppm) and triplet (1.15 ppm) [9]. These peaks are shifted downfield from those of ethanol by a comparable magnitude to absorptions of analogous $Sn(OEt)_2$ [10]. The absorptions broaden with decreasing temperature which is consistent with exchange between multiple ethoxide environments. The absorptions move upfield with added ethanol indicating rapid exchange of all species.

When *1* is left under vacuum one day it continues to lose ethanol as the only volatile product and its solubility in hydrocarbon solvents decreases. An FT-220 MHz NMR spectrum of the slightly soluble fraction of this dealcoholated product displays two broad absorptions (4.0 and 1.3 ppm, $w_{1/2} \approx 0.27$ ppm) with fine structure suggestive of many ethoxide environments on an associated species. An upfield quartet (3.95), triplet (1.21) [9] is assigned to the terminal ethoxides on the oligomeric structure, (A). The absorptions sharpen and coalesce at 94 °C (4.13 q, 1.39 t, $w_{1/2} \approx 0.13$ ppm) indicating bridge-terminal exchange. This compound, unlike *1*, does not exchange rapidly with added ethanol at ambient temperatures.

Evidence for a specific alcoholate complex was obtained from a white powder precipitated at –76 °C from a saturated pentane solution of *1*. The material is formulated as $Ge(OEt)_2 \cdot 2EtOH$ (*2*) by thermogravimetric analysis and mass spectrometry. The TGA indicates weight loss of two moles of ethanol. The DSC shows that the transition is endothermic. Importantly ethanol is the only volatile product. Although sublimation of *2* does not compete favourably with desolvation, small amounts of solid do sublime at 10^{-6} torr and 90 °C. The mass spectrum of *2*, which is identical to that of its sublimate, is consistent with the $Ge(OEt)_2 \cdot 2EtOH$ formulation with relevant peaks at m/e 255, 210, and 164 which have masses corresponding to the ions $[(^{74}Ge(OEt)_2 \cdot 2EtOH)-H]^+$, $[^{74}Ge(OEt)_2 \cdot EtOH]^{+\cdot}$, and $[^{74}Ge(OEt)_2]^{+\cdot}$, respectively. The infrared spectrum of *2* displays characteristic ethoxide CH, CO and CCO modes. Bands at 635 cm^{-1} and 585 cm^{-1} are assigned to GeO stretching

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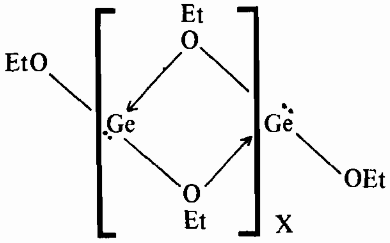
modes by analogy to similar absorptions (*e.g.* ν(SnO)) in $Sn(OEt)_2$ [8].

Structure (A)



1 can be transesterified with n-propanol to yield germanium(II) dipropoxide. *1* can also undergo oxidative addition with MeI (eq. 1) followed by redistribution of labile substituents on the methyl germanium moiety (eqs. 2 and 3):

$$Ge(OEt)_2 \cdot xEtOH + MeI \rightarrow MeGe(OEt)_2I + xEtOH \quad (1)$$

$$2MeGe(OEt)_2I \rightleftharpoons MeGe(OEt)_3 + MeGe(OEt)I_2 \quad (2)$$

$$2MeGe(OEt)I_2 \rightleftharpoons MeGeI_3 + MeGe(OEt)_2I \quad (3)$$

The proton NMR spectrum of the volatile products displays a singlet, quartet, and triplet for each ethoxide containing species with appropriate area ratios and a singlet for $MeGeI_3$ (*Me*GeI_3, 2.8 ppm; *Me*$Ge(OEt)I_2$, 1.95 ppm; *Me*$Ge(OEt)_2I$, 1.26 ppm; *Me*$Ge(OEt)_3$, 0.72 ppm). The positions of methyl absorptions and equilibrium constants for equations (2) and (3) based upon methyl peak areas are in agreement with the $MeGe(OMe)_3$–$MeGeI_3$ redistribution reaction studies of Moedritzer and Van Wazer [11]. Further information will be reported later.

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