Facile Synthesis of Digermyl and Methyl Germyl Ether

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The preparation of germyl ethers, *i.e.* ethers containing the GeH_3 moiety, has so far been accomplished in only two cases; $(GeH_3)_2O$ is obtained from $(GeH_3)_3N–H_2O$ [1] and $(GeH_3)_2S–HgO$ [2] reactions and GeH_3OCH_3 is formed in Hg-sensitized CH_3OH–GeH_4 photolyses [3] and GeH_3Cl–$NaOCH_3$ reactions [4]. Product yields, especially of $(GeH_3)_2O$, have been low. Direct reactions of germyl halides with water or alcohols is known to result only in formation of the hydrogen halide and intractable producs [5]. Since GeH_3-containing ethers are highly reactive, they may offer viable routes to $(GeH_2)_x$ [6, 7], germanium subhydrides of potential interest in inorganic synthesis, and to amorphous germanium hydrides $(GeH_{<2})_x$ [7]. This potential has led us to study novel syntheses of GeH_3-containing compounds. We now wish to report a new highly efficient method for the preparation of compounds of type GeH_3OR (where R = GeH_3 or CH_3) which makes use of the reagent $(CH_3)_3N$-GeH_3Br [8] as a germylating agent.

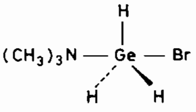
Typically to GeH_3Br (0.45 mmol) dissolved in 10–15 mmol $(CH_3)_2O$, $(CH_3)_3N$ (0.40 mmol) was added at −196 °C. Reactants were warmed to −78 °C for 20 min to form $(CH_3)_3N{\cdot}GeH_3Br{\cdot}(CH_3)_2O$ and excess GeH_3Br were removed *in vacuo*, H_2O (or D_2O; 0.18 mmol) or CH_3OH (0.24 mmol) were condensed into the reactor, and reaction materials were warmed to −63 °C for 4–5 hr. Removal of volatile reaction materials *in vacuo*, and separation of them by low temperature high-vacuum distillation, yielded $(GeH_3)_2O$ [2] and GeH_3OCH_3 [4] in 90–97% and 55–62% yields, respectively. The $(CH_3)_3N{\cdot}GeH_3Br–D_2O$ reaction yielded $(CH_3)_3NDBr$ (N–D present, N–H absent in infrared spectrum [9]) and pure $(GeH_3)_2O$. Traces of GeH_4, Ge_2H_6, and Ge_3H_8, and $(GeH_3)_2O$ were observed as products of some $(CH_3)_3N{\cdot}GeH_3Br–CH_3OH$ reactions.

The $(CH_3)_3N{\cdot}GeH_3Br$ adduct reactions with H_2O (or D_2O) or CH_3OH proceed smoothly in $(CH_3)_2O$ solvent to form $(GeH_3)_2O$ or GeH_3OCH_3 as shown in eqns. 1 and 2.

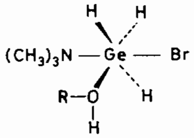
$$2(CH_3)_3N{\cdot}GeH_3Br + H_2O \rightarrow 2(CH_3)_3NHBr + (GeH_3)_2O \qquad (1)$$

$$(CH_3)_3N{\cdot}GeH_3Br + CH_3OH \rightarrow (CH_3)_3NHBr + GeH_3OCH_3 \qquad (2)$$

The mechanism by which $(CH_3)_3N{\cdot}GeH_3Br$ and H_2O or CH_3OH react is of interest, in order to understand how $(CH_3)_3N$ coordination of GeH_3Br moderates reaction of the latter with H_2O or alcohols. We have determined [8] that $(CH_3)_3N{\cdot}GeH_3Br$ at −78 °C to −63 °C is most likely an amine adduct of GeH_3Br, a species containing a five-coordinate germanium atom, I.



I



II

Because GeH_3Br is coordinated to $(CH_3)_3N$, and dissolution of the adduct appears slight, (eqn. 3a), reaction may be moderated simply because the GeH_3Br concentration is kept low during the subsequent reaction steps (eqns. 3b and 3c).

$$(CH_3)_3N{\cdot}GeH_3Br \rightleftharpoons (CH_3)_3N + GeH_3Br \qquad (3a)$$

$$GeH_3Br + ROH \rightarrow GeOR + HBr \qquad (3b)$$

$$(CH_3)_3N + HBr \rightarrow (CH_3)_3NHBr \qquad (3c)$$

Alternatively, $(CH_3)_3N$-coordination to GeH_3Br may appreciably lower the Lewis acidity of the latter, greatly lowering its electrophilicity and tendency towards formation of a key reaction intermediate such as II. Involvement of intermediate species containing GeH_2 moieties, ionized species such as $(CH_3)_3NGeH_2Br^-$ or $(CH_3)_3N(ROH)GeH_2Br^-$, or coordinated germylene species like $(CH_3)_3NGeH_2$, seems unlikely since in reactions of $(CH_3)_3N{\cdot}GeH_3Br$ with D_2O no evidence for incorporation of deuterium into the $(GeH_3)_2O$ product is obtained.

The use of base-coordinated germyl halides in a variety of processes to achieve syntheses that are otherwise difficult or unachievable offers considerable potential for further study. This potential is being pursued by us currently.

Acknowledgements

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