

Facile Synthesis of Digermyl and Methyl Germyl Ether

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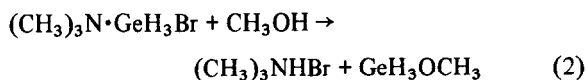
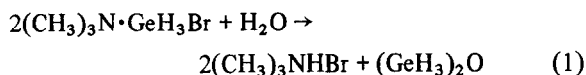
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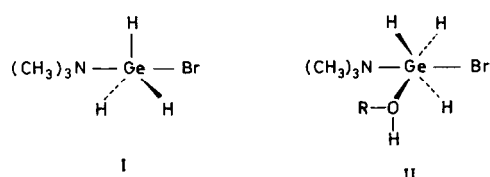
The preparation of germyl ethers, *i.e.* ethers containing the GeH_3 moiety, has so far been accomplished in only two cases; $(\text{GeH}_3)_2\text{O}$ is obtained from $(\text{GeH}_3)_3\text{N}-\text{H}_2\text{O}$ [1] and $(\text{GeH}_3)_2\text{S}-\text{HgO}$ [2] reactions and GeH_3OCH_3 is formed in Hg-sensitized $\text{CH}_3\text{OH}-\text{GeH}_4$ photolyses [3] and $\text{GeH}_3\text{Cl}-\text{NaOCH}_3$ reactions [4]. Product yields, especially of $(\text{GeH}_3)_2\text{O}$, 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 products [5]. Since GeH_3 -containing ethers are highly reactive, they may offer viable routes to $(\text{GeH}_2)_x$ [6, 7], germanium subhydrides of potential interest in inorganic synthesis, and to amorphous germanium hydrides $(\text{GeH}_{<2})_x$ [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 $\text{R} = \text{GeH}_3$ or CH_3) which makes use of the reagent $(\text{CH}_3)_3\text{N}-\text{GeH}_3\text{Br}$ [8] as a germylating agent.

Typically to GeH_3Br (0.45 mmol) dissolved in 10–15 mmol $(\text{CH}_3)_2\text{O}$, $(\text{CH}_3)_3\text{N}$ (0.40 mmol) was added at -196°C . Reactants were warmed to -78°C for 20 min to form $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}\cdot(\text{CH}_3)_2\text{O}$ 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 $(\text{GeH}_3)_2\text{O}$ [2] and GeH_3OCH_3 [4] in 90–97% and 55–62% yields, respectively. The $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}-\text{D}_2\text{O}$ reaction yielded $(\text{CH}_3)_3\text{N}-\text{DDBr}$ ($\text{N}-\text{D}$ present, $\text{N}-\text{H}$ absent in infrared spectrum [9]) and pure $(\text{GeH}_3)_2\text{O}$. Traces of GeH_4 , Ge_2H_6 , and Ge_3H_8 , and $(\text{GeH}_3)_2\text{O}$ were observed as products of some $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}-\text{CH}_3\text{OH}$ reactions.

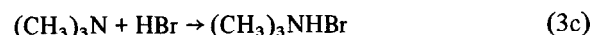
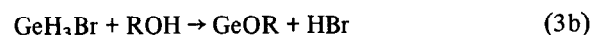
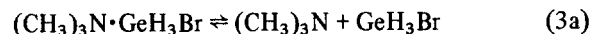
The $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}$ adduct reactions with H_2O (or D_2O) or CH_3OH proceed smoothly in $(\text{CH}_3)_2\text{O}$ solvent to form $(\text{GeH}_3)_2\text{O}$ or GeH_3OCH_3 as shown in eqns. 1 and 2.



The mechanism by which $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}$ and H_2O or CH_3OH react is of interest, in order to understand how $(\text{CH}_3)_3\text{N}$ coordination of GeH_3Br moderates reaction of the latter with H_2O or alcohols. We have determined [8] that $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}$ at -78°C to -63°C is most likely an amine adduct of GeH_3Br , a species containing a five-coordinate germanium atom, I.



Because GeH_3Br is coordinated to $(\text{CH}_3)_3\text{N}$, 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).



Alternatively, $(\text{CH}_3)_3\text{N}$ -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 $(\text{CH}_3)_3\text{NGeH}_2\text{Br}^-$ or $(\text{CH}_3)_3\text{N}(\text{ROH})\text{GeH}_2\text{Br}^-$, or coordinated germylene species like $(\text{CH}_3)_3\text{NGeH}_2$, seems unlikely since in reactions of $(\text{CH}_3)_3\text{N}\cdot\text{GeH}_3\text{Br}$ with D_2O no evidence for incorporation of deuterium into the $(\text{GeH}_3)_2\text{O}$ 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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References

- 1 D. W. H. Rankin, *Chem. Comm.*, 194 (1969).
- 2 T. D. Goldfarb and S. Sujishi, *J. Am. Chem. Soc.*, 86, 1679 (1964).
- 3 G. A. Gibbon, Y. Rousseau, C. H. van Dyke and G. J. Mains, *Inorg. Chem.*, 5, 114 (1966).
- 4 G. A. Gibbon, J. T. Wang and C. H. van Dyke, *Inorg. Chem.*, 6, 1989 (1967).
- 5 A. D. Norman and C. A. Heil, unpublished results; F. Glockling, 'The Chemistry of Germanium', Academic Press, New York, N.Y., 1969 and references therein.
- 6 S. N. Glarum and C. A. Kraus, *J. Am. Chem. Soc.*, 72, 5398 (1950);
H. Satge, M. Massol and P. Riviere, *J. Organometal. Chem.*, 56, 1 (1973).
- 7 D. S. Rustad and W. L. Jolly, *Inorg. Chem.*, 7, 213 (1968);
R. M. Dreyfuss and W. L. Jolly, *Inorg. Chem.*, 10, 2567 (1971).
- 8 C. A. Heil and A. D. Norman, submitted for publication.
- 9 K. Nakamoto, 'Infrared Spectra of Inorganic Compounds', Wiley, New York, 1963.