

Thermal Generation of Dimethylgermylene and its Insertion into the Germanium-Hydrogen Bond

By ERIC C.-L. MA, DON P. PAQUIN, and PETER P. GASPAR*

(*Department of Chemistry, Washington University, Saint Louis, Missouri 63130*)

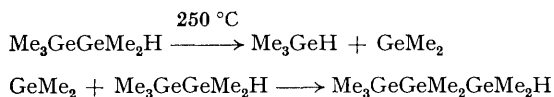
Summary Pyrolysis of pentamethyldigermane leads to the formation of dimethylgermylene as a short-lived intermediate that inserts into a germanium-hydrogen bond of its precursor.

CONSIDERING the brisk pace of activity in the chemistry of molecules containing divalent silicon atoms, silylenes,¹ relatively little is known about the reactions of their germanium analogues. The problem is not a lack of data,²

but the difficulty of differentiating between reactions of complexes or oligomers of germanium(II), *i.e.* species only formally divalent, and the reactions of monomeric divalent germanium compounds. It is the latter molecules for which the term germylene should be reserved.

The few well documented thermally induced reactions of germylenes include insertion of GeH_2 into Ge-H bonds,³ and insertion by GeEt_2 into Ge-Cl bonds.⁴ Insertion into Ge-H bonds of PhGeH and EtGeH formed by α -elimination of methanol from the corresponding methoxygermane RGeH_2OMe has also been reported.⁵

To these reactions should now be added the insertion of dimethylgermylene into the Ge-H bonds of its precursor, reported in this communication. This appears to be the first observation of the insertion by a diorganogermylene GeR_2 into a Ge-H bond.



When pentamethyldigermane⁶ is pyrolysed in the liquid phase at $250 \pm 5^\circ\text{C}$, half of the starting material is consumed in 12 h. At low conversions the only products detected are trimethylgermane Me_3GeH and heptamethyltrigermane $\text{Me}_3\text{GeGeMe}_2\text{GeMe}_2\text{H}$. The latter product was identified by its ^1H n.m.r. and mass spectra. The n.m.r. spectrum consists of a heptet at δ 3.93 (GeH, J 4 Hz, 1H) and a group of four peaks at δ 0.38, 0.37, 0.32, and 0.30 (GeMe, 21H) whose ratio of areas is *ca.* 1:2:1:3. Spin decoupling by irradiation of the GeH heptet leads to a collapse of the two peaks at δ 0.38 and 0.32 to a single peak at δ 0.35, thus establishing the presence of the HGeMe_2 unit.

The mass spectrum displayed M^+ m/e 324 (2%) and 119 (100%).

The absence of radical recombination products $\text{Me}_3\text{GeGeMe}_3$ and $\text{Me}_2\text{HGeGeHMe}_2$ suggests that molecular elimination producing dimethylgermylene is the initial step in the thermolysis of pentamethyldigermane. A simple kinetic study supports this view. Over three half-lives a plot of $\ln[\text{Me}_3\text{Ge}_2\text{H}]$ *vs.* time is linear, its slope yielding a first-order rate constant $-0.075 \pm 0.008 \text{ h}^{-1}$. The curve of growth $\ln[\text{Me}_3\text{GeH}]$ was also linear over the same period, with slope $0.071 \pm 0.011 \text{ h}^{-1}$. The initial rate of formation of heptamethyltrigermane was 0.9 times that of the trimethylgermane, but it decreased at longer times ($>12 \text{ h}$), and after 24 h the yield of heptamethyltrigermane decreased owing to secondary decomposition. Further products were then also observed, including nonamethyltetragermane $\text{Me}[\text{GeMe}_2]_4\text{H}$. That the decomposition of pentamethyldigermane is a first-order process followed by rapid attack of the reactive intermediate on its precursor was indicated by a series of dilution experiments. Neither the rate of thermolysis nor the product yields were altered by dilution (up to eightfold) with 1-methylnaphthalene.

Both the initial products formed and the preliminary examination of the reaction kinetics suggest that pyrolysis of pentamethyldigermane is a relatively clean source of dimethylgermylene that can insert efficiently into a Ge-H bond of its precursor under the reaction conditions.

We are grateful to the United States Department of Energy for support of this work, Ms. Becky Cornett for advice and assistance, and the Eagle-Picher Mineral Company for a gift of germanium compounds.

(Received, 10th January 1980; Com. 021.)

¹ P. P. Gaspar in 'Reactive Intermediates,' Vol. 1, eds. M. Jones, Jr. and R. A. Moss, Wiley-Interscience, N.Y., 1978, ch. 7, p. 229.

² J. Satge, M. Massol, and P. Riviere, *J. Organomet. Chem.*, 1973, **56**, 1.

³ M. D. Sefcik and M. A. Ring, *J. Organomet. Chem.*, 1973, **59**, 167.

⁴ E. J. Bulten and J. G. Noltes, *J. Organomet. Chem.*, 1969, **16**, 8.

⁵ M. Massol, J. Satge, P. Riviere, and J. Barrau, *J. Organomet. Chem.*, 1970, **22**, 599.

⁶ Pentamethyldigermane was prepared by lithium aluminium hydride reduction of chloropentamethyldigermane, synthesized according to E. J. Bulten and J. G. Noltes, *J. Organomet. Chem.*, 1968, **15**, 18.