Novel Formation of Polygermanes

By PHILLIP C. ANGUS and STEPHEN R. STOBART*
(*Department of Chemistry, Queen's University, Belfast* BT9 5AG)

Summary Reaction of germylcyclopentadiene in the presence of primary or secondary amines provides a synthetic route to digermane and trigermane.

ACCESSIBILITY of the higher germanes depends upon their formation as minor products in hydrolysis reactions[1] used to prepare monogermane, or by silent electric discharge synthesis[2] from the latter. We now report a novel formation of Ge–Ge bonds, providing the first example of conversion of a monogermyl derivative into polygermanes.

On warming to room temperature in the presence of a primary or secondary amine, germylcyclopentadiene[3] reacts smoothly to give Ge_2H_6 and Ge_3H_8 but remarkably no GeH_4 [equation (1)]. A typical experiment

$$C_5H_5GeH_3 \xrightarrow[\text{or } R_2NH\ (R = Et \text{ or } Bu^n)]{RNH_2\ (R = Me, Et, \text{ or } CH_2Ph)} C_5H_6 + Ge_2H_6 + Ge_3H_8 \quad (1)$$

using 0·5 mol. equiv. of diethylamine gave, after 10 min at 20 °C, *ca.* 45% conversion into trigermane with *ca.* 20% of digermane. The germanes were identified by their gas-phase i.r. spectra[4] and by mass spectroscopy (parent-ion multiplets, found *m/e*: Ge_2H_6, 142—156; Ge_3H_8, 210—234). An orange, involatile residue remained, which from its i.r. spectrum contained polymeric germanium hydride, GeH_x. With larger mol. ratios of amine, yields were lower and more involatile material was formed. With ammonia, reaction was slow leaving unchanged $C_5H_5GeH_3$ and forming only traces of Ge_3H_8 while with NEt_3 even slower formation of a hard, orange solid was accompanied by a little GeH_4, C_5H_6, and unchanged base as the only volatile products.

Reaction (1) thus constitutes a convenient route to trigermane, rendering its availability comparable with that of trisilane, which although not preparable by any related method can be obtained[5] by reduction of Si_3Cl_8.

(*Received*, 13*th December*, 1972; *Com.* 2086.)

[1] L. M. Dennis, R. B. Corey, and R. W. Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657.
[2] J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 1962, 2807; K. M. Mackay and K. J. Sutton, *J. Chem. Soc.* (*A*), 1968, 2312; K. M. Mackay, S. T. Hosfield, and S. R. Stobart, *ibid.*, 1969, 2937.
[3] S. R. Stobart, *J. Organometallic Chem.*, 1971, **33**, C11.
[4] E. A. Clark and A. Weber, *J. Chem. Phys.*, 1966, **45**, 1759; K. M. Mackay and P. Robinson, *J. Chem. Soc.*, 1965, 5121.
[5] P. P. Gasper, C. A. Levy, and G. M. Adair, *Inorg. Chem.*, 1970, **9**, 1272.