

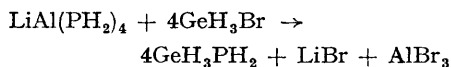
## A New Synthesis of Germylphosphine

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GERMYLPHOSPHINE ( $\text{GeH}_3\text{PH}_2$ ) has been prepared previously by the relatively tedious methods of acid hydrolysis of germanide-phosphide alloys<sup>1,2</sup> and by the ozonizer discharge reaction of a germane-phosphine mixture.<sup>3</sup> Because of the low product yields and the difficulties of product separation, neither of these methods is satisfactory for the synthesis of reasonable quantities of  $\text{GeH}_3\text{PH}_2$ . In view of the recent interest in the chemistry of germanes and germane derivatives,<sup>4-7</sup> we report a new, highly efficient synthesis of  $\text{GeH}_3\text{PH}_2$ .

Germylphosphine can be prepared from the reaction of lithium tetrakis(dihydrogenphosphinido)aluminate [ $\text{LiAl}(\text{PH}_2)_4$ ] and germyl bromide.



Typically, 5.4 mmoles of  $\text{LiAl}(\text{PH}_2)_4$ <sup>8</sup> and 3.6 mmoles of  $\text{GeH}_3\text{Br}$  in an ether solvent are allowed to react for 1 hr. at  $-45^\circ$  followed by slow warming of the reaction mixture to room temperature.

High-vacuum column distillation of the reaction mixture results in the isolation of 3.2 mmoles of  $\text{GeH}_3\text{PH}_2$  (88% yield). The product was identified by its i.r., <sup>31</sup>P n.m.r., and mass spectra and by comparison of its <sup>1</sup>H n.m.r. spectrum with that previously reported.<sup>9</sup> In reactions in which the  $\text{GeH}_3\text{Br}:\text{LiAl}(\text{PH}_2)_4$  ratio is greater than 4.0:1.0, small quantities of higher-molecular-weight germylphosphines, which have not yet been characterized, are obtained.

It is interesting that  $\text{GeH}_3\text{PH}_2$  can be isolated from the reaction of  $\text{LiAl}(\text{PH}_2)_4$  and  $\text{GeH}_3\text{Br}$  since it has been reported recently than an analogous reaction between potassium dihydrogenphosphinide ( $\text{KPH}_2$ ) and  $\text{GeH}_3\text{Br}$  does not yield any germylphosphine products.<sup>6</sup> Further studies of the synthetic potential of  $\text{LiAl}(\text{PH}_2)_4$  are in progress and will be reported later.

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<sup>1</sup> P. Royen, C. Rocktäschel, and W. Mosch, *Angew. Chem. Internat. Edn.*, 1964, **3**, 703.

<sup>2</sup> P. Royen and C. Rocktäschel, *Z. anorg. Chem.*, 1966, **346**, 290.

<sup>3</sup> J. E. Drake and W. L. Jolly, *Chem. and Ind.*, 1962, 1470.

<sup>4</sup> S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc. (A)*, 1967, 12.

<sup>5</sup> S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc. (A)*, 1967, 1226.

<sup>6</sup> S. Cradock, E. A. V. Ebsworth, G. Davidson, and L. A. Woodward, *J. Chem. Soc. (A)*, 1967, 1229.

<sup>7</sup> S. Cradock, G. A. Gibbon, and C. H. Van Dyke, *Inorg. Chem.*, 1967, **6**, 1751.

<sup>8</sup> A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, and E. Jacobsen, *Inorg. Chem.*, 1963, **3**, 504.

<sup>9</sup> J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, 1963, **38**, 1033.