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TRIALKYLGERMYL ALKALI METAL DERIVATIVES*

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Various methods are available for the synthesis of triarylgermyl alkali metal derivatives, e.g. the cleavage of the Ge-Ge bond of hexaphenyldigermane with Li in ether solvents$^{(1)}$ (1, R = Ph; M = Li):

$$R_6Ge_2 + 2\,M \longrightarrow 2\,R_3GeM \qquad (1)$$

However, reaction (1) does not take place under comparable conditions if R = alkyl$^{(2)}$. Only one successful, but rather unattractive route to the alkyl derivatives has been reported: Kraus and Flood obtained Et_3GeK by shaking Et_6Ge_2 with potassium in ethylamine for several weeks in a sealed tube$^{(3)}$. Liquid ammonia is an unsuitable medium, because it does not dissolve Alk_6Ge_2 compounds.

We wish to report that trialkylgermyl alkali metal derivatives may be conveniently prepared according to (1) in hexamethylphosphortriamide (HMPT) which is a good solvent both for alkali metals$^{(4)}$ and for hexaalkyldigermanes.

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Upon stirring R_6Ge_2 (R = alkyl) with potassium in dry HMPT at room temperature reaction is complete in 3-5 hours. R_3GeK is formed in quantitative yield as appeared from hydrolysis of the clear reddish--brown reaction mixture and subsequent determination by g.l.c. of the amount of R_3GeH formed.

Solutions of R_3GeK in HMPT are stable, *e.g.* the strength of a 0.7 N solution of Et_3GeK in HMPT remained unchanged on storage for 3 weeks at 0°C.

An alternative procedure involves the reaction of R_3GeCl with two equivalents of potassium in HMPT according to (2). The reddish-brown color of R_3GeK is observed only after complete conversion of the chloride into the digermane (3), the latter being subsequently cleaved according to (1):

$$\begin{array}{lcll} R_3GeCl + 2\,K & \longrightarrow & R_3GeK + KCl & (2)\\ R_3GeCl + R_3GeK & \longrightarrow & R_6Ge_2 + KCl & (3)\\ \hline 2\,R_3GeCl + 2\,K & \longrightarrow & R_6Ge_2 + 2\,KCl & (4)\end{array}$$

Symmetrically substituted digermanes can be prepared according to (4), *e.g.* Et_6Ge_2 (b.p. 130-132°C/16mm Hg, n_D^{20} = 1,4973) and Bu_6Ge_2 (b.p. 131°C/0,2 mm Hg, n_D^{20} = 1,4858) were obtained in 75-80% yield*.

Trialkylgermyl alkali metal derivatives are reactive nucleophilic compounds. According to (5) the hitherto rather inaccessible asymmetric digermanes $R_3GeGeR'_3$ (R, R' = alkyl) can be readily prepared in 60-70% yield (see Table I), the reaction being completed within a few seconds

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* With Li instead of K the same results were obtained. The digermanes were isolated by extraction with a non-polar solvent after the addition of water.

even at -60°C* .

$$R_3GeK + R'_3GeCl \longrightarrow R_3GeGeR'_3 + KCl \qquad (5)$$

Halogen-metal exchange and subsequent coupling leading to symmetrically substituted digermanes can be suppressed to a great extent by carrying out the reaction at low temperatures.

By reacting R_3GeK derivatives with trialkylmetal chlorides of other IV B group elements compounds of the type $R_3GeMR'_3$ may be obtained in about 60% yield (see Table I).

TABLE I

Some coupling reactions of R_3GeK

Reactants		Product*	B.p.($^{\circ}C/_{mm\ Hg}$)	n_D^{20}
Et_3GeK	Me_3SiCl	$Et_3GeSiMe_3$	89-91/30	1,4670
Et_3GeK	Me_3GeCl	$Et_3GeGeMe_3$	80-82/14	1,4804
Bu_3GeK	Me_3GeCl	$Bu_3GeGeMe_3$	78-80/0,07	1,4800
Et_3GeK	Me_3SnCl	$Et_3GeSnMe_3$	90-93/14	1,5040

* Satisfactory analyses, I.R. and N.M.R. data have been obtained for all compounds reported.

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* Reactions performed below -20°C require dilution of the reaction mixture, e.g. with THF, in order to prevent HMPT from freezing.

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