

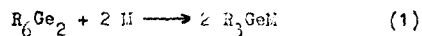
TRIALKYLGERMYL ALKALI METAL DERIVATIVES\*

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Various methods are available for the synthesis of triarylgemyl alkali metal derivatives, e.g. the cleavage of the Ge-Ge bond of hexa-phenyldigermene with Li in ether solvents<sup>(1)</sup> (1, R = Ph; M = Li):



However, reaction (1) does not take place under comparable conditions if R = alkyl<sup>(2)</sup>. 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<sup>(3)</sup>. 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 hexamethylphosphorotriamide (HMPT) which is a good solvent both for alkali metals<sup>(4)</sup> and for hexa-alkyldigermenes.

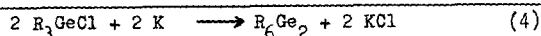
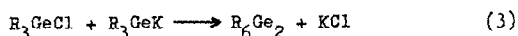
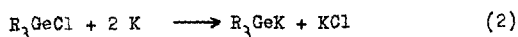
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\* Part VI in the series "Investigations on Organogermanium Compounds";  
Part V: E.J.Bulten and J.G.Noltes, Tetrahedron Letters, in the press.

Upon stirring  $R_6Ge_2$  ( $R = \text{alkyl}$ ) 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  $0^\circ C$ .

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):



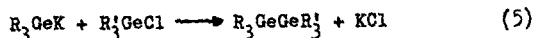
Symmetrically substituted digermanes can be prepared according to (4), e.g.  $Et_6Ge_2$  (b.p.  $130-132^\circ C/16\text{mm Hg}$ ,  $n_D^{20} = 1,4973$ ) and  $Bu_6Ge_2$  (b.p.  $131^\circ C/0,2\text{ mm Hg}$ ,  $n_D^{20} = 1,4858$ ) were obtained in 75-80% yield\*.

Trialkylgermyl alkali metal derivatives are reactive nucleophilic compounds. According to (5) the hitherto rather inaccessible asymmetric digermanes  $R_3GeGeR'_3$  ( $R, R' = \text{alkyl}$ ) 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  $-60^{\circ}\text{C}^*$ .



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  $\text{R}_3\text{GeK}$  derivatives with trialkylmetal chlorides of other IV B group elements compounds of the type  $\text{R}_3\text{GeMR}'_3$  may be obtained in about 60% yield (see Table I).

TABLE I

Some coupling reactions of  $\text{R}_3\text{GeK}$ 

Reactants		Product*	B.p. ( $^{\circ}\text{C}/\text{mm Hg}$ )	$n_D^{20}$
$\text{Et}_3\text{GeK}$	$\text{Me}_3\text{SiCl}$	$\text{Et}_3\text{GeSiMe}_3$	89-91/30	1,4670
$\text{Et}_3\text{GeK}$	$\text{Me}_3\text{GeCl}$	$\text{Et}_3\text{GeGeMe}_3$	80-82/14	1,4804
$\text{Bu}_3\text{GeK}$	$\text{Me}_3\text{GeCl}$	$\text{Bu}_3\text{GeGeMe}_3$	78-80/0,07	1,4800
$\text{Et}_3\text{GeK}$	$\text{Me}_3\text{SnCl}$	$\text{Et}_3\text{GeSnMe}_3$	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  $-20^{\circ}\text{C}$  require dilution of the reaction mixture, e.g. with THF, in order to prevent HMPT from freezing.

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