

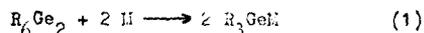
TRIALKYLGERMYL ALKALI METAL DERIVATIVES*

E.J.Bulten and J.G.Noltes

Institute for Organic Chemistry TNO, Utrecht, the Netherlands

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



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.

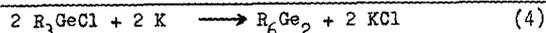
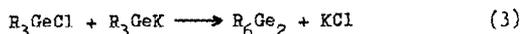
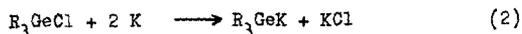
We wish to report that trialkylgermyl alkali metal derivatives may be conveniently prepared according to (1) in hexamethylphosphorotriamide (HMPT) which is a good solvent both for alkali metals⁽⁴⁾ and for hexa-alkyldigermenes.

* 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):

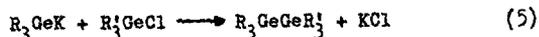


Symmetrically substituted digermanes can be prepared according to (4), e.g. Et_6Ge_2 (b.p. $130-132^\circ C/16\text{mm Hg}$, $n_D^{20} = 1,4973$) and Bu_6Ge_2 (b.p. $131^\circ C/0,2\text{ mm Hg}$, $n_D^{20} = 1,4858$) were obtained in 75-80% yield*.

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

* 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^* .



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 $\text{R}_3\text{GeMR}'_3$ may be obtained in about 60% yield (see Table I).

TABLE I

Some coupling reactions of R_3GeK

Reactants		Product*	B.p. ($^{\circ}\text{C}/\text{mm Hg}$)	n_D^{20}
Et_3GeK	Me_3SiCl	$\text{Et}_3\text{GeSiMe}_3$	89-91/30	1,4670
Et_3GeK	Me_3GeCl	$\text{Et}_3\text{GeGeMe}_3$	80-82/14	1,4804
Bu_3GeK	Me_3GeCl	$\text{Bu}_3\text{GeGeMe}_3$	78-80/0,07	1,4800
Et_3GeK	Me_3SnCl	$\text{Et}_3\text{GeSnMe}_3$	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°C require dilution of the reaction mixture, e.g. with THF, in order to prevent HMPT from freezing.

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