

THE REACTIVITY OF TRIALKYLGERMYL ALKALI METAL DERIVATIVES*

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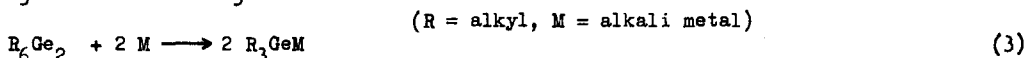
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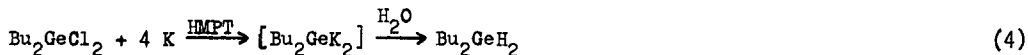
Recently two routes to trialkylgermyl alkali metal derivatives have been disclosed. Vyazankin *et al.*⁽¹⁾ prepared Et_3GeLi according to:



Bulten and Noltes⁽²⁾ obtained such compounds by reacting an alkali metal either with a trialkylchlorogermane (2) or with a hexaalkyldigermane (3) in HMPT**.



Further investigations revealed that a 100% conversion according to (3) can be obtained in 3-5 hours at 20°C with Li or K, whereas reaction with Na takes 6-8 hours. The prolonged reaction time necessary for M=Na probably is due to the lower solubility of this metal in HMPT as compared with that of K or Li⁽³⁾. Upon hydrolysis of the brown reaction mixture obtained according to (4) Bu_2GeH_2 was isolated in 22% yield.



This result indicates the intermediate formation of dibutylgermyldipotassium, presumably according to (5):



Further investigations have shown that the trialkylgermyl alkali metal derivatives are very reactive nucleophiles (cf. ref.2), which can be used for the preparation of a range of

* Part VII in the series "Investigations on Organogermanium Compounds".

Part VI: E.J.Bulten and J.G.Noltes, Tetrahedron Letters, 1966, 4389.

** Hexamethylphosphorictriamide.

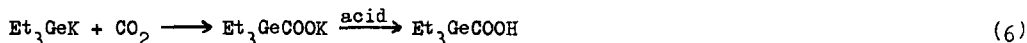
new organogermanium derivatives. The reactions mentioned in Table I take place instantaneously.

TABLE I

Some coupling reactions with Et ₃ GeK				
reactant	product	b.p. (°C/mm Hg)	n _D ²⁰	yield (%)
CO ₂	Et ₃ GeCOOH ^a	-	1,4632	30
CH ₂ Cl ₂	Et ₃ GeCH ₂ GeEt ₃	138-139/14	1,4822	65
Et ₅ Ge ₂ Cl	Et ₈ Ge ₃	152-156/0,08	1,5350	60
Me ₂ GeCl ₂	Et ₃ GeGeMe ₂ GeEt ₃	175-176/18	1,5256	50
(ClEt ₂ Ge) ₂	Et ₁₀ Ge ₄	155-160/5.10 ⁻⁴	1,5748	40

^a NMR: δ_{COOH} 11,78 ppm downfield from TMS

Carboxylation and subsequent careful neutralisation of the reaction mixture obtained according to (6) gave Et₃GeCOOH, the first representative of a trialkylgermylcarboxylic acid.



Its thermal degradation into CO and (Et₃Ge)₂O (glc) starts already at ~100°C. Slow decomposition was also observed (glc) on treatment with dilute mineral acid solutions, with concentrated acids the reaction was vigorous (7). No gas evolution was observed on treatment with a 7 N solution of NaOH.



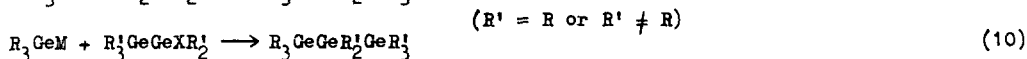
Addition of Et₃GeK to a solution of CH₃Cl in THF resulted in the formation (glc) of 94% of Et₃GeMe.

From the reaction mixture obtained according to (8) 65% of Et₃GeCH₂GeEt₃ was isolated.



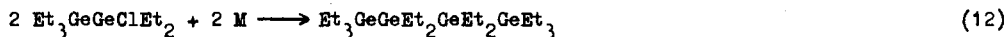
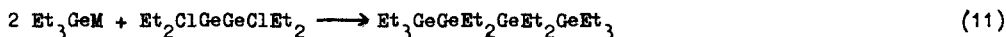
However, reaction with CHCl₃ as well as with CCl₄ resulted in the formation of Et₆Ge₂ and carbon black.

Various types of substituted trigermanes may be prepared conveniently by reacting a trialkylgermyl alkali metal derivative with either a dihalomonogermane (9) or a monochalodigermane⁽⁴⁾ (10).



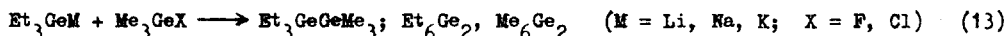
Tetragermanes can be prepared in a similar way as was demonstrated by the preparation of

$\text{Et}_{10}\text{Ge}_4$ according to (11). The latter compound was prepared also according to (12).

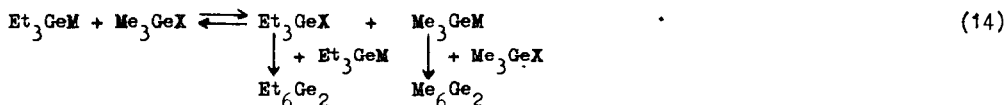


Coupling of a trialkylgermyl alkali metal derivative R_3GeM with an organic or organo-metallic halide $\text{R}'\text{X}$ (R' = organic or organometallic radical) to give $\text{R}_3\text{GeR}'$, always goes attended with the formation of varying amounts of R_6Ge_2 and R'_2 .

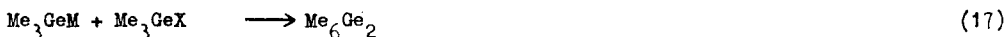
On the basis of reaction (13) some factors influencing the ratio direct coupling product/by-products have been investigated in more detail.



The formation of the symmetrically substituted digermanes Et_6Ge_2 and Me_6Ge_2 can be explained either by halogen-metal exchange and subsequent coupling according to (14) or by a nucleophilic



attack of the germyl-metal compound on the metal-metal bond of the asymmetrically substituted digermane formed on coupling (15, 16, 17)*.



As can be seen from the results given in Table II the nature of X has no appreciable influence on the amounts of by-products formed. On the other hand the sequence of addition is of prime importance, e.g. addition of Me_3GeCl to Et_3GeK gave only 55% of the coupling product $\text{Et}_3\text{GeGeMe}_3$ as compared with 83% on the reverse order of addition. These observations can not easily be explained by a mechanism involving a halogen-metal exchange and point to a nucleophilic attack of Et_3GeK on the Ge-Ge bond of the primary coupling product.

* It was found that in the absence of R_3GeM disproportionation according to (18) does not take place under our conditions.

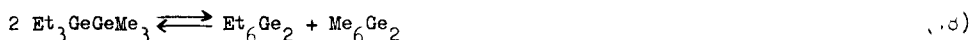
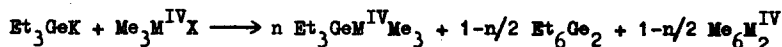


TABLE II



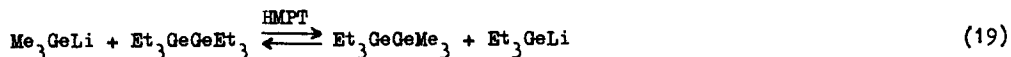
reactants ^a	mode of addn.	solvent	T (°C)	n.10 ²
Me ₃ GeCl	→	HMPT	+20	77
Me ₃ GeCl	→	THF	+20	83
Me ₃ GeCl	→	THF	0	90
Me ₃ GeCl	→	THF	-60	93
Me ₃ GeCl	←	THF	+20	55
Me ₃ GeCl	⇒	THF	+20	88
Me ₃ GeF	→	THF	+20	85
Me ₃ GeF	→	THF	-60	93
Me ₃ SiCl	→	THF	+20	82
Me ₃ SiCl	→	THF	-60	91

^a → : 5 ml of a 0,68 N solution of Et₃GeK in HMPT was added to 15ml of a 0,27 N solution of the halide in the solvent indicated.

← : addn. of 5 ml 0,81 N halide/solvent to 5ml of a 0,68 N solution of Et₃GeK/HMPT diluted with 10 ml solvent.

⇒ : simultaneous addn. of 5 ml 0,68 N Et₃GeK/HMPT and 5 ml 0,81 N halide/solvent to 10 ml of solvent.

Gilman and co-workers⁽⁵⁾ have presented strong arguments for the occurrence of the same type of reaction in organosilicon chemistry. Evidence that metal-metal bond cleavage by germyl alkali metal derivatives actually takes place under these conditions was obtained from a gaschromatographic study of reaction (19).



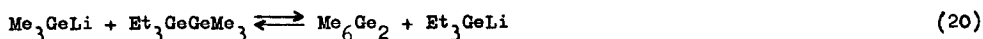
The data given in Table III were obtained on decomposition of the reaction mixture (19) with NH₄Cl and subsequent determination of the amounts of Et₃GeGeEt₃, Et₃GeGeMe₃ and Et₃GeH present. Equilibrium appeared to be reached instantaneously.

TABLE III

$$\text{Me}_3\text{GeLi} + \text{Et}_6\text{Ge}_2 \rightleftharpoons \text{Et}_3\text{GeGeMe}_3 + \text{Et}_3\text{GeLi}$$

molar ratio $\text{Me}_3\text{GeLi}/\text{Et}_6\text{Ge}_2$	percentage conversion of Et_6Ge_2 into $\text{Et}_3\text{GeGeMe}_3$
1	50
2	70
5	90
9-10	~100

The formation of only traces of Me_6Ge_2 even when a large excess of Me_3GeLi is used indicates that contrary to expectation equilibrium (20) lies completely to the left.



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