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THE REACTIVITY OF TRIALKYLGERMYL ALKALI METAL DERIVATIVES*

E.J.Bulten and J.G.Noltes

Institute for Organic Chemistry TNO, Utrecht, The Netherlands

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

$$(Et_3Ge)_2Cd + 2\ Li \xrightarrow{THF} 2\ Et_3GeLi + Cd \qquad (1)$$

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

$$R_3GeCl + 2\ M \longrightarrow R_3GeM + MCl \qquad (2)$$

(R = alkyl, M = alkali metal)

$$R_6Ge_2 + 2\ M \longrightarrow 2\ R_3GeM \qquad (3)$$

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.

$$Bu_2GeCl_2 + 4\ K \xrightarrow{HMPT} [Bu_2GeK_2] \xrightarrow{H_2O} Bu_2GeH_2 \qquad (4)$$

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

$$Bu_2GeCl_2 \xrightarrow{2\ K} [Bu_2Ge] \xrightarrow{2\ K} Bu_2GeK_2 \qquad (5)$$

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

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* 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_3GeK

reactant	product	b.p. (°C/mm Hg)	n_D^{20}	yield (%)
CO_2	$Et_3GeCOOH^a$	-	1,4632	30
CH_2Cl_2	$Et_3GeCH_2GeEt_3$	138-139/14	1,4822	65
Et_5Ge_2Cl	Et_8Ge_3	152-156/0,08	1,5350	60
Me_2GeCl_2	$Et_3GeGeMe_2GeEt_3$	175-176/18	1,5256	50
$(ClEt_2Ge)_2$	$Et_{10}Ge_4$	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 $Et_3GeCOOH$, the first representative of a trialkylgermylcarboxylic acid.

$$Et_3GeK + CO_2 \longrightarrow Et_3GeCOOK \xrightarrow{acid} Et_3GeCOOH \qquad (6)$$

Its thermal degradation into CO and $(Et_3Ge)_2O$ (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.

$$Et_3GeCOOH + HCl \longrightarrow Et_3GeCl + CO + H_2O \qquad (7)$$

Addition of Et_3GeK to a solution of CH_3Cl in THF resulted in the formation (glc) of 94% of Et_3GeMe.

From the reaction mixture obtained according to (8) 65% of $Et_3GeCH_2GeEt_3$ was isolated.

$$2\ Et_3GeK + CH_2Cl_2 \longrightarrow Et_3GeCH_2GeEt_3 \qquad (8)$$

However, reaction with $CHCl_3$ as well as with CCl_4 resulted in the formation of Et_6Ge_2 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 monohalodigermane$^{(4)}$ (10).

$$2\ R_3GeM + R'_2GeX_2 \longrightarrow R_3GeGeR'_2GeR_3 \qquad (9)$$

$$(R' = R \text{ or } R' \neq R)$$

$$R_3GeM + R'_3GeGeXR'_2 \longrightarrow R_3GeGeR'_2GeR'_3 \qquad (10)$$

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

$Et_{10}Ge_4$ according to (11). The latter compound was prepared also according to (12).

$$2\ Et_3GeM + Et_2ClGeGeClEt_2 \longrightarrow Et_3GeGeEt_2GeEt_2GeEt_3 \tag{11}$$

$$2\ Et_3GeGeClEt_2 + 2\ M \longrightarrow Et_3GeGeEt_2GeEt_2GeEt_3 \tag{12}$$

Coupling of a trialkylgermyl alkali metal derivative R_3GeM with an organic or organometallic halide $R'X$ (R' = organic or organometallic radical) to give R_3GeR', 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.

$$Et_3GeM + Me_3GeX \longrightarrow Et_3GeGeMe_3;\ Et_6Ge_2,\ Me_6Ge_2 \quad (M = Li,\ Na,\ K;\ \ X = F,\ Cl) \tag{13}$$

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

$$\begin{tikzcd}
Et_3GeM + Me_3GeX \arrow[r, shift left] & Et_3GeX \arrow[l, shift left] \arrow[d, "+ Et_3GeM"] & + & Me_3GeM \arrow[d, "+ Me_3GeX"] \\
& Et_6Ge_2 & & Me_6Ge_2
\end{tikzcd} \tag{14}$$

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

$$Et_3GeM + Me_3GeK \longrightarrow Et_3GeGeMe_3 \tag{15}$$

$$Et_3GeM + Et_3GeGeMe_3 \rightleftharpoons Et_6Ge_2 + Me_3GeM \tag{16}$$

$$Me_3GeM + Me_3GeX \longrightarrow Me_6Ge_2 \tag{17}$$

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 $Et_3GeGeMe_3$ 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.

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

$$2\ Et_3GeGeMe_3 \rightleftharpoons Et_6Ge_2 + Me_6Ge_2 \tag{18}$$

TABLE II

$$Et_3GeK + Me_3M^{IV}X \longrightarrow n\ Et_3GeM^{IV}Me_3 + 1\text{-}n/2\ Et_6Ge_2 + 1\text{-}n/2\ Me_6M^{IV}_2$$

reactants[a]	mode of addn.	solvent	T (°C)	n.10^2
Me_3GeCl	→	HMPT	+20	77
Me_3GeCl	→	THF	+20	83
Me_3GeCl	→	THF	0	90
Me_3GeCl	→	THF	-60	93
Me_3GeCl	←	THF	+20	55
Me_3GeCl	⇉	THF	+20	88
Me_3GeF	→	THF	+20	85
Me_3GeF	→	THF	-60	93
Me_3SiCl	→	THF	+20	82
Me_3SiCl	→	THF	-60	91

[a] → : 5 ml of a 0,68 N solution of Et_3GeK 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 Et_3GeK/HMPT diluted with 10 ml solvent.

⇉ : simultaneous addn. of 5 ml 0,68 N Et_3GeK/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).

$$Me_3GeLi + Et_3GeGeEt_3 \overset{HMPT}{\rightleftarrows} Et_3GeGeMe_3 + Et_3GeLi \qquad (19)$$

The data given in Table III were obtained on decomposition of the reaction mixture (19) with NH_4Cl and subsequent determination of the amounts of $Et_3GeGeEt_3$, $Et_3GeGeMe_3$ and Et_3GeH present. Equilibrium appeared to be reached instantaneously.

TABLE III

$$Me_3GeLi + Et_6Ge_2 \rightleftharpoons Et_3GeGeMe_3 + Et_3GeLi$$

molar ratio Me_3GeLi/Et_6Ge_2	percentage conversion of Et_6Ge_2 into $Et_3GeGeMe_3$
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.

$$Me_3GeLi + Et_3GeGeMe_3 \rightleftharpoons Me_6Ge_2 + Et_3GeLi \qquad (20)$$

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