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PRELIMINARY COMMUNICATION

Investigations on organogermanium compounds
VIII*. Base-catalyzed disproportionation of compounds containing a germanium–germanium bond

Mixed alkylsubstitute digermanes of the type $R_3GeGeR'_3$ can be readily obtained[1] by reacting trialkylhalogermanes R_3GeX with trialkylgermyl alkali metal derivatives R'_3 GeM (prepared[2] by alkali metal cleavage of hexaalkyldigermanes in hexamethylphosphoric triamide, HMPT[3]). This coupling reaction is always accompanied by the formation of varying amounts of the symmetrical compounds R_6Ge_2 and R'_6Ge_2. Previous studies[1] suggested that nucleophilic attack of the germyl alkali metal compound on the metal–metal bond of the mixed coupling product (reactions 2 and 3) rather than halogen–metal exchange (*i.c.* nucleophilic attack on halogen) is involved in the formation of these symmetrically substituted digermanes:

$$Et_3Ge^-Li^+ + Me_3GeX \rightarrow Et_3GeGeMe_3 \tag{1}$$

$$Et_3Ge^-Li^+ + Et_3GeGeMe_3 \overset{K_1}{\leftrightarrows} Et_6Ge_2 + Me_3Ge^-Li^+ \tag{2}$$

$$Me_3Ge^-Li^+ + Et_3GeGeMe_3 \overset{K_2}{\leftrightarrows} Me_6Ge_2 + Et_3Ge^-Li^+ \tag{3}$$

or
$$Me_3Ge^-Li^+ + Me_3GeX \rightarrow Me_6Ge_2 \tag{4}$$

A closer study of equilibria (2) and (3), which were approached from both sides using various ratios of the reactants, has now revealed (*cf.* ref. 1) that these equilibria are reached instantaneously on mixing the reactants in HMPT.

The equilibrium constants K_1 and K_2 have been determined**:

$$K_1 = \frac{[Me_3GeLi][Et_6Ge_2]}{[Et_3GeLi][Et_3GeGeMe_3]} = 0.59 \pm 0.01$$

$$K_2 = \frac{[Et_3GeLi][Me_6Ge_2]}{[Me_3GeLi][Et_3GeGeMe_3]} = 0.20 \pm 0.01$$

Summation of equations (2) and (3) gives

$$2\,Me_3GeGeEt_3 \underset{HMPT}{\overset{K_3}{\rightleftharpoons}} Me_6Ge_2 + Et_6Ge_2 \tag{5}$$

with an equilibrium constant

$$K_3 = \frac{[Me_6Ge_2][Et_6Ge_2]}{[Me_3GeGeEt_3]^2} = K_1 \times K_2 = 0.12 \pm 0.02$$

* For part VII see ref. 1.

** The equilibrated reaction mixtures were decomposed and the amounts of hydrides and digermanes present were determined gaschromatographically using a silicone oil column (15% silicone oil "Embaphase" on 60–80 mesh Diatoport S).

Since pure $Me_3GeGeEt_3$ was shown to be perfectly stable towards disproportionation in HMPT solution the approach to equilibrium (5) must be kinetically controlled.

It was found that (5) is catalyzed by trialkylgermyl alkali metal derivatives or in general by nucleophilic species. Equilibrium (5) is re·.ched instantaneously at room temperature (in HMPT) in the presence of 5–10 mole % of catalyst (see Table 1).

TABLE 1

BASE-CATALYZED DISPROPORTIONATION OF 1,1,1-TRIMETHYL-2,2,2-TRIETHYLDIGERMANE

$$2\ Me_3GeGeEt_3 \overset{cat}{\rightleftharpoons} Me_6Ge_2 + Et_6Ge_2$$

Catalyst	Solvent	K_3
Et_3GeLi	HMPT	0.12
Et_3GeLi	THF/HMPT ~7	0.12
EtOK	HMPT	0.13
PhLi	HMPT	0.13
PhLi	THF	0

In accordance with the above it was found that hexaalkyldigermanes react instantaneously with potassium ethoxide or phenyllithium in HMPT at room-temperature:

$$EtOK + Et_3GeGeEt_3 \xrightarrow{HMPT} Et_3GeK + Et_3GeOEt \quad (6)$$

$$PhLi + Et_3GeGeEt_3 \xrightarrow{HMPT} Et_3GeLi + Et_3GePh \quad (7)$$

Reaction (7) fails to take place in dimethylformamide or tetrahydrofuran at room temperature or in tetrahydrofuran after several hours at 50°.

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Institute for Organic Chemistry TNO E. J. BULTEN
Utrecht (The Netherlands) J. G. NOLTES

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