

PRELIMINARY COMMUNICATION

INVESTIGATIONS ON ORGANOGERMANIUM COMPOUNDS

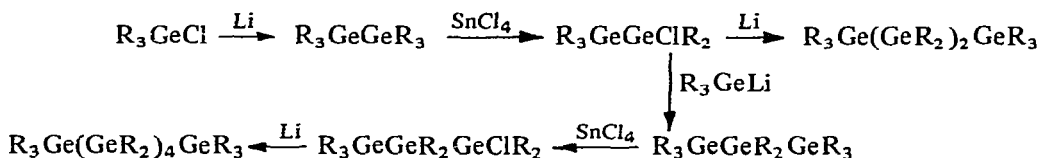
X*. CATENATED ORGANOGERMANIUM COMPOUNDS. EVIDENCE FOR DIVALENT ORGANOGERMANIUM SPECIES

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(Received November 20th, 1968; in revised form December 2nd, 1968)

Investigations into linear alkylpolygermanes containing more than one Ge—Ge bond have been hampered by lack of suitable preparative routes. The development of satisfactory methods for the preparation of trialkylgermyl alkali metal derivatives¹⁻³ and of alkylhalodi- and -trigermanes^{4,5} allows the planned synthesis of linear alkylpolygermanes. Several such compounds have now been prepared (see Table 1) as follows:



In the Wurtz-type couplings an excess of organogermanium halide must be used in order to minimize Ge—Ge bond cleavage, which leads to a mixture of polygermanes. For example reaction of an excess of $Et_3GeGeClEt_2$ with lithium in xylene yields $Et_3Ge(GeEt_2)_2GeEt_3$ as the main product. When the same reaction is performed with an excess of alkali metal in HMPA a mixture of polygermanes is formed. From such a mixture a compound was isolated which in an earlier communication³ was considered to be $Et_3Ge(GeEt_2)_2GeEt_3$. However, the analytical data, UV absorption spectrum and refractive index (Table 1) of the latter product are in better agreement with linear $Et_{12}Ge_5$. In addition to this compound a considerable amount of Et_8Ge_3 was isolated, which points to a metal—metal bond cleavage by the excess of lithium applied or by an intermediately formed germyl—lithium compound^{3,6}.

The perethylpolygermanes display a characteristic UV absorption. The absorption maximum shifts to longer wavelength with increasing chain length (Table 1). Similar observations have been reported for peralkylpolysilanes⁷ and -stannanes^{8,9}. The perethylpolygermanes are stable in air and have considerable thermal stability, e.g. linear $Et_{14}Ge_6$ was recovered in better than 80% yield after heating for 8 h at 250° (under N_2).

*For Part IX see ref. 5.

TABLE 1

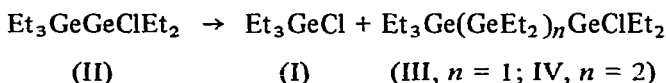
PHYSICAL DATA FOR SOME PERETHYLPOLYGERMANES^a

Compound	B.p. (°C/mm)	n_D^{20}	λ_{\max} (nm)
Et ₃ GeGeEt ₃	130–132/16	1.4985	~ 202
Et ₃ GeGeEt ₂ GeEt ₃ ^b	127–128/0.3	1.5350	217.5
Et ₃ Ge(GeEt ₂) ₂ GeEt ₃ ^c	– ^d	1.5561	233.5
Et ₃ Ge(GeEt ₂) ₃ GeEt ₃ ^c	155–160/5 · 10 ⁻⁴	1.5748	248
Et ₃ Ge(GeEt ₂) ₄ GeEt ₃	– ^d	1.5912	258

^aSatisfactory analyses have been obtained for all compounds reported. ^bRef. 3. ^cSee text.

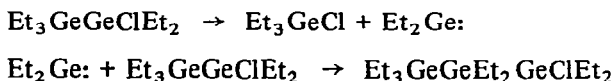
^dPurified by column chromatography (Al₂O₃).

Introduction of functional groups bound to germanium decreases the thermal stability. As reported previously Et₂ClGeGeClEt₂ decomposes above 200° to give Et₂GeCl₂ and a catenated germanium species⁴. Using gas chromatography it has now been found that Et₂ClGeGeClEt₂ disproportionates fairly rapidly at 230–250° to give predominantly Et₂GeCl₂ and Et₂ClGeGeEt₂GeClEt₂^{*}. Under the same conditions Et₃GeGeClEt₂ disproportionates according to:



The formation of tetragermane, presumably IV, was observed only after conversion of about 50% of the starting material into monogermane (I) and trigermane (III). A similar disproportionation has recently been reported for Me₃SiSi(CN)Me₂¹⁰ and Me_{6-n}Si₂(OMe)_n¹¹.

Kinetic experiments revealed that the decomposition of Et₃GeGeClEt₂ is very nearly independent of concentration, which demonstrates that the reaction is predominantly unimolecular (*cf.* ref. 11). These results point to a mechanism involving the formation and subsequent insertion of a divalent germanium species:



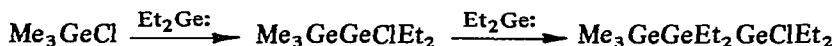
The first order kinetics demonstrate that the formation of Et₂Ge: is the rate-determining step.

The formation of Et₃GeCl as the sole monogermane on thermolysis of Et₃GeGeClMe₂ indicates that a chlorine shift takes place, not an alkyl shift.

Insertion of Et₂Ge: into the Ge–Cl bond seems highly plausible in view of the following results. Thermolysis of a 1:1 mixture of Et₃GeGeClEt₂ and Me₃GeCl gives Me₃GeGeClEt₂^{★★}, in addition to Et₃GeCl and Et₃GeGeEt₂GeClEt₂. A small amount of another trigermane, presumably Me₃GeGeEt₂GeClEt₂ is also formed.

^{*}Identified as Et₈Ge₃ after treatment with EtMgBr.

^{★★}Identified as Me₃GeGeEt₃ after ethylation¹.



Thermolysis of a 1:1 mixture of $\text{Et}_3\text{GeGeClEt}_2$ and Et_6Ge_2 gives only Et_3GeCl and $\text{Et}_3\text{GeGeEt}_2\text{GeClEt}_2$, with no trace of Et_6Ge_3 .

So far attempts to trap $\text{Et}_2\text{Ge:}$ with carbon-carbon unsaturated systems (e.g. tolane) have been unsuccessful, insertion into the Ge-Cl bond taking place instead.

Detailed information will be given at a later date¹².

ACKNOWLEDGEMENTS

Financial support by the Germanium Research Committee is gratefully acknowledged. The authors are much indebted to Professor G.J.M. van der Kerk for his stimulating interest, to Dr. W. Drenth for valuable suggestions and to Mr. K.P. Ligtoet for able experimental assistance.

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J. Organometal. Chem., 16 (1969) P8-P10