

INVESTIGATIONS ON ORGANOGERMANIUM COMPOUNDS XI*. PREPARATION AND STRUCTURE OF TRIALKYLGERMANYL ALKALI METAL COMPOUNDS IN HEXAMETHYLPHOSPHORIC TRIAMIDE (HMPT)**

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(Received December 31st, 1970)

SUMMARY

In this paper a full report is given of our investigations into the preparation of trialkylgermyl alkali metal compounds^{2,3}. The most satisfactory route to these compounds involves the cleavage of hexaalkyldigermanes with alkali metals in HMPT at room temperature. The structure, thermal stability and basicity of trialkylgermyl alkali metal compounds in HMPT solution are discussed. Synthetic aspects will be dealt with in subsequent papers^{4,5}.

INTRODUCTION

Until recently investigations into germanium-alkali metal compounds had concentrated mainly on the triphenylgermyl alkali metal compounds. These can be readily prepared by cleavage of hexaphenyldigermane with alkali metals, preferably lithium, in ether solvents (for a review see refs. 6 and 7).

In contrast, hexaalkyldigermanes are not cleaved by alkali metals in ether solvents such as diethyl ether, THF or DME⁸⁻¹⁰. Up to 1966 only one successful but rather laborious preparation of a trialkylgermyl alkali metal compound had been reported; in this, Kraus and coworkers¹¹ prepared triethylgermylpotassium by treating hexaethyl digermane with potassium in ethylamine for six weeks in a sealed tube:



Digermane cleavage was also obtained with lithium, but the germyllithium derivative was largely ammonolyzed by the solvent, and completely so by liquid ammonia.



Although triethylgermylpotassium was found to be fairly stable in liquid ammonia this solvent is an unsuitable reaction medium because of the very low solubility of hexaethyl digermane.

* For part X see ref. 1

** Taken from the Ph. D thesis of E.J.B., State University of Utrecht, 1969.

As found by Normant *et al.* (*cf.* ref. 12) alkali metals are fairly soluble in the virtually aprotic solvent HMPT. Since we observed that hexaalkyldigermanes are also soluble in HMPT, efforts were directed towards the preparation of trialkylgermyl alkali metal compounds in this medium.

During the course of our investigations^{2,3} Vyazankin *et al.*¹³⁻¹⁵ reported that triethylgermyllithium may be obtained according to the rather complex reaction sequence:

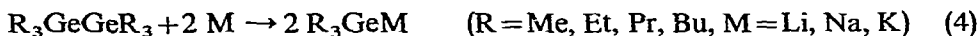


It was not stated whether the corresponding sodium and potassium derivatives can be obtained in the same way.

RESULTS AND DISCUSSION

Cleavage of hexaalkyldigermanes by alkali metals

When a solution of a hexaalkyldigermane in HMPT is stirred vigorously with a slight excess of an alkali metal at room temperature, a very weakly exothermal reaction occurs according to eqn. (4).



Depending on the concentration a clear orange or reddish-brown solution is obtained, which gives a positive Gilman test¹⁶. In this way the trialkylgermyl alkali metal compounds are formed in a quantitative yield. This was proved by decomposition of a sample of the solution with water or solid ammonium chloride and subsequent gas chromatographic determination of the amount of trialkylgermane formed. As shown by PMR spectrometry no hydride was present in the reaction mixture prior to hydrolysis.

In view of the rather low stability of the alkali metal solutions in HMPT¹² reactions were performed in the presence of the substrate, *viz.* by addition of the metal to a solution of the digermane in HMPT. A 5–10% excess of the metal was used in order to make up for small losses, which presumably result from solvent cleavage.

At no time during the reaction are blue colours or trails—characteristic for solutions of the metal as such in HMPT—formed under these conditions. This indicates that the rate of germanium–germanium bond cleavage is greater than, and consequently limited by, the rate of dissolution of the metal. With lithium and potassium the preparation of about 0.8 *M* solutions of the germyl metal compound is complete at room temperature, whereas reaction with sodium takes 6–8 hours. In the latter case the prolonged reaction time is probably due to the lower rate of dissolution of the metal in HMPT as compared with that of lithium¹⁷. The concentration of the germyl metal solutions is limited to about one mmole/ml. This also seems to be the maximum concentration which can be obtained for alkali metals in HMPT¹⁸.

In contrast with those in phenylgermanium compounds¹⁹, the germanium–carbon bonds in alkylgermanium compounds are completely resistant towards alkali metal cleavage in HMPT. For instance, tetraethylgermane was recovered unchanged after prolonged treatment with potassium in HMPT at room temperature or at 50°.



Triethylgermyl potassium and potassium likewise gave no diethylgermyldipotassium.

Attempts to prepare bis(trialkylgermyl)calcium and -magnesium in a similar way failed. This may be due to the low rate of dissolution of the metals in HMPT. In a different approach, a solution of calcium in liquid ammonia was diluted with HMPT and freed from ammonia by evaporation at room temperature. After addition of hexaethyldigermane the resulting suspension gave a slightly positive Gilman test¹⁶. However, on hydrolysis no triethylgermane could be detected.

Hexaalkyldisilanes are also cleaved by lithium in HMPT, but the reaction is much slower than with the digermanes. When a solution of hexabutyldisilane was stirred with lithium in HMPT the mixture remained blue as long as the metal was present. On removal of the metal the color gradually changed to orange-brown and a positive Gilman test was obtained. Apparently cleavage of the Si-Si bond is slower than the rate of dissolution of the metal in HMPT. Treatment of the mixture with methyl iodide and subsequent hydrolysis gave a liquid consisting (PMR) of tributylhydroxysilane together with a minor quantity of methyltributylsilane. The formation of the hydroxysilane can be explained in terms of cleavage of the HMPT by tributylsilyllithium and subsequent hydrolysis of the Si-P and/or Si-N bonds formed.



Reaction of trialkylchlorogermanes with alkali metals

Trialkylgermyl alkali metal compounds can also be prepared by treating a trialkylchlorogermane with two equivalents of an alkali metal in HMPT:



When a trialkylchlorogermane was slowly added under vigorous stirring to small alkali metal pieces in HMPT a strongly exothermic reaction took place. The reaction mixture was kept at room temperature. As long as any chlorogermane was present the reaction mixture remained colourless and failed to give a positive Gilman test. After complete conversion of the trialkylchlorogermane the reaction slowed down markedly and the reddish-brown colour, characteristic for the trialkylgermyl alkali metal species was developed. At this stage the Gilman test became positive. These observations point to the following reaction sequence:



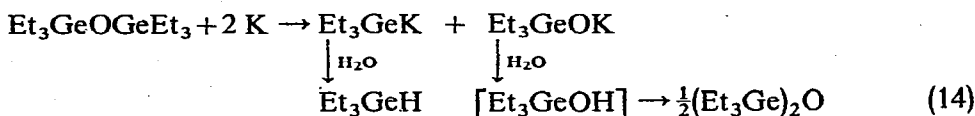
Apparently reaction (9) is much faster than reactions (8) and (10). The yields obtained never exceeded 85–90%, owing to the formation of side-products, presumably germanium-nitrogen and/or germanium-phosphorus derivatives, along with reactions (8) and (9)⁵.

In a similar way dialkylgermyl dialkali metal compounds can be obtained. When dibutyldichlorogermane was treated with four equivalents of potassium in HMPT a brown solution was obtained. Hydrolytic work-up of the reaction mixture and distillation gave dibutylgermane in a 22% yield. This result points to the following reaction sequence:



Miscellaneous preparations

Trialkylgermyl alkali metal compounds can also be obtained by cleavage of a germanium–oxygen bond in oxybis(trialkylgermanes) with alkali metals in HMPT. On bringing stoichiometric amounts of oxybis(triethylgermane) and potassium into reaction, the reddish-brown colour characteristic of triethylgermylpotassium was developed:



Gas chromatographic analysis of a hydrolized sample of the reaction mixture revealed the presence of oxybis(triethylgermane) and triethylgermane in the ratio one to two. Apparently reaction (14) proceeds quantitatively. Addition of two further equivalents of potassium gave no further reaction. Since 50% of the starting material



is converted into reactive alkali metal germanolate, this reaction is less attractive for the preparation of trialkylgermyl alkali metal compounds.

The study of the reactivity of the germanium–germanium bond⁵ revealed another possible route to trialkylgermyl alkali metal compounds, *viz.* cleavage of hexaalkyldigermanes by suitable nucleophiles in the solvent HMPT:



The reactions proceed quantitatively. However, since only half of the starting material is converted into a trialkylgermyl alkali metal compound this method cannot compete with the cleavage of hexaalkyldigermanes by alkali metals. Reactions (16) and (17) do not take place in DMF at room temperature or in THF at 50°.

Structure and reactivity

The unusual charge distribution in trialkylgermyl alkali metal compounds is reflected in their PMR spectra. In HMPT solution the methyl protons of $\text{Me}_3\text{Ge}^{\delta+}\text{-Cl}^{\delta-}$ have a chemical shift* $\delta(\text{CH}_3\text{Ge}) + 0.73$ ppm, whereas in $\text{Me}_3\text{Ge}^{\delta-}\text{-Li}^{\delta+}$ $\delta(\text{CH}_3\text{Ge}) - 0.19$ ppm. As shown in Fig. 1, substitution of the chlorine atom in $\text{Et}_3\text{-GeCl}$ [$\delta(\text{C}_2\text{H}_5\text{Ge}) \sim +1.14$ ppm; unresolved signal] by lithium likewise causes a considerable upfield shift of the α -hydrogen atoms [$\delta(\text{CH}_2\text{Ge}) + 0.29$ ppm; quartet; J 8 Hz]. The influence on the β -hydrogens is small [$\delta(\text{CH}_3\text{CGe}) + 1.08$ ppm, triplet; J 8 Hz].

* Downfield from TMS.

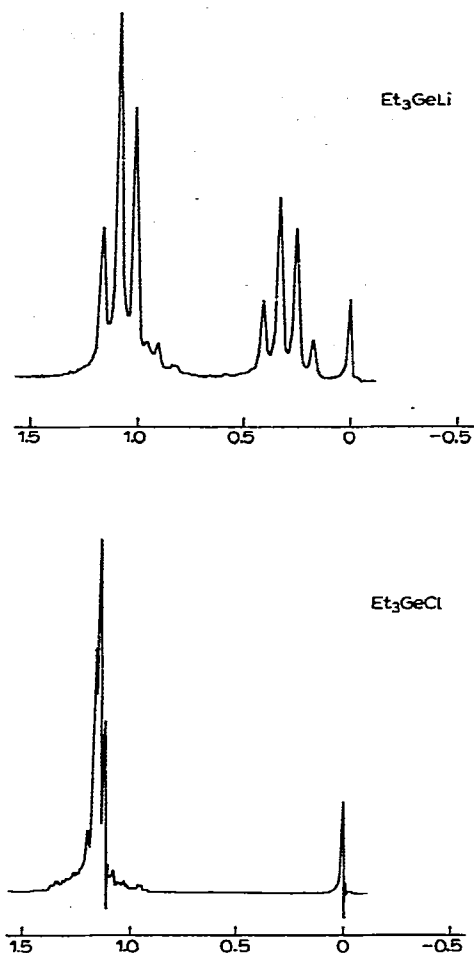


Fig. 1. PMR spectra of Et_3GeCl (0.75 mmole/ml) and Et_3GeLi (0.68 mmole/ml) in HMPT. Internal standard TMS.

TABLE I

CONDUCTIVITY DATA FOR TRIETHYLGERMYLPOTASSIUM AND SOME REFERENCE COMPOUNDS IN HMPT

Compound	Concentration (Mole/l)	Molar conductance ^a , ($\text{mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$) Λ_m
HMPT		$(0.73 \times 10^{-6})^b$
Et_3GeK	0.645	2.5
Et_3GeK	0.064	10.8
Et_3GeK	0.044	12.0
Me_3GeCl	0.050	0.44
LiCl^c	0.028	18.20 ^d

^a At 20°. ^b Specific conductance, κ ($\text{mho} \cdot \text{cm}^{-1}$); lit.²² $\kappa = 0.4 \times 10^{-6} \text{ mho} \cdot \text{cm}^{-1}$. ^c Dried for 6 h at 200° in vacuo. ^d Lit.²² Λ_m 18.6 $\text{mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$, concn. 0.025 mole/l in HMPT.

So far no comparative studies have been made on the relative basicity of triphenyl- and trialkylgermyl alkali metal compounds. According to Kraus²⁰ the latter are susceptible to aminolysis by ethylamine whereas the former are stable in this solvent, and even so in liquid ammonia. In order to obtain information on the degree of ionic dissociation of the Ge-M bond in trialkylgermyl alkali metal compounds in HMPT solution, a few conductivity experiments were carried out (cf. Table 1). The conductance at infinite dilution has not been determined in view of the relatively great experimental error introduced by diluting the germyl alkali metal solutions as result of hydrolysis, oxidation etc. As shown by a comparison with lithium chloride, triethylgermylpotassium behaves, at least in HMPT, as a strong electrolyte²¹. Its molar conductance increases with decreasing concentration. Trimethylchloro-germane shows a much lower conductivity in the same solvent. In a comparative experiment the molar conductance (at 20°C) of a 0.054 molar solution of Me₃GeCl in acetonitrile was found to be 0.05 mho · cm² · mole⁻¹; thus the molar conductance of Me₃GeCl is about eight times greater in HMPT than in acetonitrile. The conductance of Me₃GeCl in benzene was too small to be measured. From these results it can be concluded that when considering the physical and chemical properties of trialkylgermyl alkali metal compounds in HMPT, account must be taken of their virtually ionic structures.

Trialkylgermyl alkali metal compounds are very sensitive towards air and moisture and consequently have to be prepared and handled with extreme care. Under proper conditions their solutions in HMPT are rather stable, e.g. the strength of a 0.7 N solution of triethylgermylpotassium had not changed (GLC, PMR) after three weeks at 0°C. At higher temperatures decomposition occurs to give the corresponding digermene. Indeed, this thermal decomposition so far has prevented the isolation of the germyl alkali metal compounds as such. When a solution of triethylgermyllithium was freed from HMPT by distillation *in vacuo* (b.p. 50–55°C/0.001 mm), the colour gradually changed from reddish-brown to dark-green. Gas chromatographic analysis of a hydrolyzed sample of the resulting slurry revealed the presence of only hexaethyldigermene. The absence of triethylgermane indicates that the germanium-alkali metal bond had been destroyed. In order to gather more information on this decomposition reaction a solution of triethylgermyllithium in HMPT was

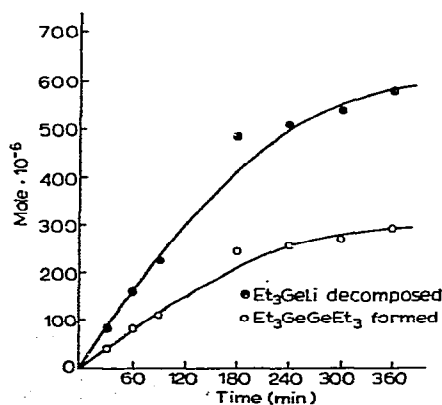
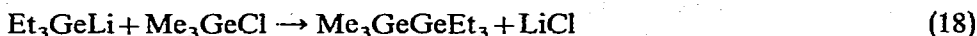


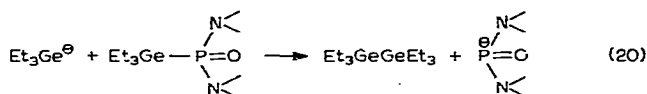
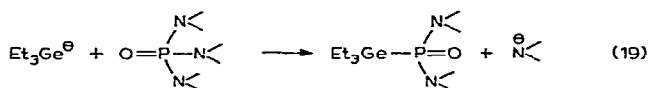
Fig. 2. Thermal decomposition of a 0.7 N solution of Et₃GeLi in HMPT at 100°C.

heated for several hours at 100°. At regular intervals the product composition was determined by GLC analysis following treatment of samples with a 100% excess of trimethylchlorogermane followed by an equivalent amount of water.



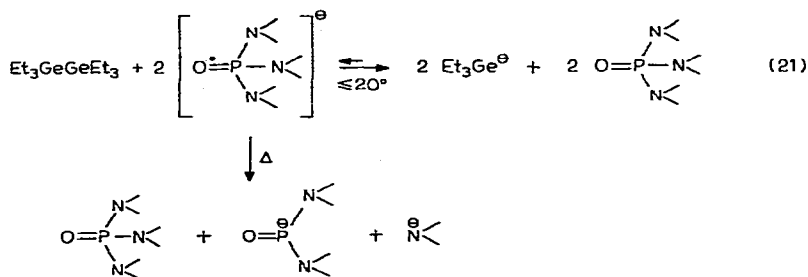
In each case 1,1,1-trimethyl-2,2,2-triethyldigermane and hexaethyldigermane were the only ethylgermanium derivatives present*. As can be seen in Fig. 2., the molar increase of hexaethyldigermane is equal to half the molar decrease of triethylgermyllithium and it is clear that two molecules of triethylgermyllithium are transformed into one molecule of hexaethyldigermane. The half-life time of this reaction at 100° is about 2½ hours.

No data are available in the literature on the mechanism of the cleavage of HMPT by nucleophiles. A nucleophilic attack by the germyl anion on phosphorus (eqn. 19), followed by a nucleophilic attack of another germyl anion on the germanium-phosphor intermediate to give the digermane (eqn. 20) is a possibility.



If this mechanism is operative, reaction (20) must be much faster than reaction (19), since the hydrolyzed samples of the reaction mixture were not found to contain oxybis(triethylgermane).

On the other hand, a mechanism involving the formation of free-radical intermediates could also be operative. In principle both the formation and the decomposition of the germyl alkali metal compounds in HMPT can be explained by an overall equilibrium reaction which is governed completely by the low thermal stability of the radical-anion of HMPT^{12,17}.



* As will be discussed in a separate paper⁵ reaction (18) is accompanied by the formation of small amounts of the symmetrical digermanes $\text{Me}_3\text{GeGeMe}_3$ and $\text{Et}_3\text{GeGeEt}_3$. The experimental section gives details on the calculations of the net amounts of $\text{Et}_3\text{GeGeEt}_3$ formed by thermal degradation of Et_3GeLi .

At room temperature the equilibrium is shifted completely to the right, whereas at elevated temperatures decomposition of the radical-anion causes a shift to the left.

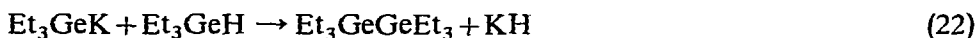
Trialkylgermyl alkali metal compounds are extremely susceptible to protolysis, leading to the corresponding germanium hydride. In fact, their strongly basic character was found to preclude several types of reactions (*cf.* ref. 4). For instance, reaction of Et_3GeK with acetone gives exclusively Et_3GeH instead of the adduct expected, *viz.* 2-(triethylgermyl)-2-propanol. Therefore, some investigations were made into the basicity of Et_3GeK in HMPT. As can be seen from the results given in Table 2,

TABLE 2
REACTIONS OF Et_3GeK WITH WEAK ACIDS

Acid	pKa ^a	Products (%)
$\text{CH}_3\text{C(O)CH}_3$	20	Et_3GeH (100)
Ph_3CH	32	Et_3GeH (~ 70); $\text{Et}_3\text{GeGeEt}_3$ (~ 30)
Ph_2CH_2	35	Et_3GeH (~ 70); $\text{Et}_3\text{GeGeEt}_3$ (~ 30)
NH_3^b	39	Et_3GeH (~ 100); $\text{Et}_3\text{GeGeEt}_3$ (trace)
PhCH_3	40	0

^a Values cited in ref. 23 (aqueous solutions). ^b Large excess.

Et_3GeK is rapidly protolyzed even by such weak acids as diphenylmethane and liquid ammonia. The formation of hexaethyldigermene along with triethylgermane in these experiments is due to reaction (22). In a blank experiment, treatment of triethylgermyl-



potassium and triethylgermane gave 40% of hexaethyldigermene after one hour at room temperature. Recently Vyazankin *et al.*¹⁵ reported that a similar reaction with triethylgermyllithium in THF gives a 42% yield of hexaethyldigermene after heating at 70° for 7 hours.

According to Kraus and Flood²⁰, triethylgermyllithium (prepared in ethylamine) is rapidly ammonolyzed in liquid ammonia, whereas triethylgermylpotassium can be handled in this solvent without appreciable decomposition. We have found that solutions of triethylgermyllithium as well as -potassium in HMPT are decolorized immediately when added to an excess of liquid ammonia at -70°C. These results point to considerable influence of the solvent on the chemistry of germlyl alkali metal derivatives. Both the nucleophilicity and degree of ionization of compounds are strongly enhanced by solvating media. Thus the reactivity of alkali metal compounds will be greater in the strongly basic solvent HMPT than in THF or liquid ammonia. The same holds true for the ionization of weak acids.

EXPERIMENTAL

General

All reactions involving trialkylgermyl alkali metal compounds were performed with rigorously dried apparatus in an atmosphere of dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. Unless indicated otherwise experiments with trialkylgermyl alkali metal compounds were performed with 0.6–0.7 *N*

solutions of these reagents in HMPT, prepared by cleavage of the corresponding hexaalkyldigermanes with alkali metals.

NMR spectra were recorded by Miss. L. Veldstra and Mr. J. W. Marsman, using a Varian Associates HA-100 NMR spectrometer. GLC analyses, performed by Mrs. G. G. Versluis-de Haan, were made by means of F&M gas chromatographs models 500 and 810 with katharometer detection, using helium as the carrier gas.

Purification of HMPT

Commercial HMPT, dried on molecular sieves, was stirred with a small amount of lithium shavings at room temperature until the blue colour—characteristic for alkali metal solutions in HMPT—persisted. Excess of lithium was removed by decantation (under nitrogen) and the HMPT was distilled in vacuo, b.p. 80–81°/3 mm, n_D^{20} 1.4572 (lit. b.p.¹² 115°/15 mm, n_D^{20} 1.4582.) The solvent was stored on molecular sieves under nitrogen.

Preparation of germyl alkali metal compounds in HMPT

Cleavage of hexaalkyldigermanes with alkali metals. The preparation of triethylgermylpotassium in HMPT will be described as an example of the general procedure used for the synthesis of R_3GeM ($R = Me, Et, Pr, Bu$; $M = Li, Na, K$.)

Finely cut potassium (5.1 g, 130 mmoles) was stirred at high speed by means of a Hershberg stirrer (nichrome wire) in 160 ml of HMPT. As soon as the blue colour persisted—which took generally less than one minute, depending on the degree of purity of the solvent, the nature of the alkali metal, the speed of stirring and the size of the metal pieces—hexaethyldigermane (19.3 g, 60.0 mmoles) was added at once by means of a syringe. The blue colour of the solution turned instantly into orange-yellow, and gradually intensified to orange or reddish-brown, depending on the concentration. By means of a syringe a sample of 5 ml was transferred into another vessel and decomposed by addition of a 100% excess of water or of solid ammonium chloride. Finally the decolourized sample was transferred into a calibrated vessel containing a weighed amount of an internal standard (generally nonane or decane was used) and adjusted with HMPT to a volume of 25 ml. GLC analysis revealed the presence of 0.64 mmole/ml of triethylgermane as the sole organogermanium compound. By PMR spectrometry it was established that the triethylgermylpotassium solution contained no triethylgermane (*i.e.* prior to hydrolysis).

Dibutylgermyldipotassium. To 3.3 g (80 mmoles) of finely cut potassium in 30 ml of HMPT was added slowly a solution of 5.1 g (20 mmoles) of dibutyldichlorogermane in 10 ml of HMPT. The reaction mixture was kept at room temperature by external cooling. In about 2½ hours the potassium had been consumed completely to give a dark-brown solution. The mixture was hydrolyzed carefully, diluted with 100 ml of water and extracted with benzene. The combined benzene layers were treated with 25 ml of water, subsequently with 25 ml of concentrated hydrochloric acid and dried. Distillation gave 0.85 g (22%) of Bu_2GeH_2 .

Reaction of oxybis(triethylgermane) with potassium. Oxybis(triethylgermane) (6.6 g, 20.9 mmoles) was added slowly to potassium (1.6 g, 41.0 mmoles) in 25 ml of HMPT. After stirring for 5 h the potassium had been consumed to give a clear orange-brown solution. A 1 ml sample was decomposed with 30 μ l of water, and subsequently analyses by GLC showed the presence of triethylgermane and oxybis(triethylgermane) in the molar ratio 2/1.

Addition of another quantity of potassium (1.6 g, 41 mmoles) and subsequent stirring for another 11 h, did not change the ratio triethylgermane/oxybis(triethylgermane) obtained on hydrolysis.

Reaction of hexaethyldigermene with phenyllithium and with potassium ethoxide. A solution of phenyllithium in THF (1.5 ml, 1.0 mmole of reagent) was added at once to a solution of 0.32 g (1.0 mmole) of hexaethyldigermene in 1 ml of HMPT. After stirring for 2 min the reddish-brown solution was decomposed with solid ammonium chloride. GLC analysis revealed the presence of 0.91 mmole (91%) of triethylgermane and 0.045 mmole of hexaethyldigermene. In addition one more component was observed, which had a retention time identical with that of triethylphenylgermane (prepared from triethylchlorogermene and phenyllithium in THF). Cleavage of hexaethyldigermene by phenyllithium in THF could not be accomplished. Reaction with potassium ethoxide was performed in a similar way with 3 mmoles of potassium ethoxide, 3 mmoles of hexaethyldigermene and 1 ml of HMPT. GLC analysis of a hydrolyzed sample of the reaction mixture revealed the presence of triethylgermane and oxybis(triethylgermane) in the molar ratio 2/1.

Structure and reactivity of trialkylgermyl alkali metal compounds in HMPT

Conductivity experiments (Table 1). The conductivity experiments have been performed at room temperature (20°) by means of a Philipscope II universal measuring bridge, type GM 4144, using a Philips conductivity cell type GM 4221, cell constant of 0.7 cm^{-1} . Prior to each measurement the vessel was flushed repeatedly with the solution to be measured. Measurements were performed in triplo. In order to get an impression of the accuracy of the measurements, the molar conductance of an 0.025 M solution of potassium chloride in water (redistilled twice, specific conductance $3.10 \cdot 10^{-6} \text{ mho} \cdot \text{cm}^{-1}$) was measured. The value obtained for A_m ($127.2 \text{ mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$ at 20°) is in fair agreement with the value cited in the literature²¹ for an 0.020 M solution of potassium chloride in water ($138.34 \text{ mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$ at 25°)*. The molar conductance of potassium chloride in HMPT could not be determined because of the low solubility.

Thermal decomposition of trialkylgermyllithium in HMPT at 100°. A 0.7 M solution of triethylgermyllithium in HMPT was heated at 100°. With the progress of the reaction the colour changed from reddish-brown to dark-green. At regular time intervals one ml samples were decomposed by treating them with a 100% excess of trimethylchlorogermene and subsequently with an equivalent amount of water. By means of gas chromatography the amounts of digermenes formed—hexamethyldigermene, hexaethyldigermene and 1,1,1-trimethyl-2,2,2-triethyldigermene—were determined. In addition to these products, only trimethylchlorogermene and small amounts of oxybis(trimethylgermane)—presumably formed by hydrolysis of trimethylchlorogermene—were detected. Oxybis(triethylgermane) was not observed. Reaction of triethylgermyllithium with excess of trimethylchlorogermene gives, in addition to 1,1,1-trimethyl-2,2,2-triethyldigermene (ME_c), small equal molar amounts of hexamethyldigermene (M_c) and hexaethyldigermene (E_c)⁵. Since the thermal decomposition of triethylgermyllithium also gives hexaethyldigermene (E_d), the total

* The temperature coefficient of conductance is about 2% per degree for most ions²¹.

amount of hexaethyldigermane (E_t) present in the decomposed reaction samples originates partly (E_d) from the thermal decomposition reaction, and partly (E_c) from the coupling reaction with trimethylchlorogermane. The molar amounts of triethylgermyllithium and of hexaethyldigermane actually present in the reaction mixture (before treatment with trimethylchlorogermane) may then be calculated as follows:

$$[\text{Et}_3\text{GeLi}] = ME_c + M_c + E_c = ME_c + 2 M_c$$

$$[\text{Et}_3\text{GeGeEt}_3] (E_d) = E_t - E_c = E_t - M_c$$

ACKNOWLEDGEMENTS

Financial support by the "Germanium Research Committee" is gratefully acknowledged. The authors wish to thank Professor G. J. M. van der Kerk for his stimulating interest in the present subject. Thanks are also due to Mr. K. P. Ligtoet for able experimental assistance.

REFERENCES

- 1 E. J. BULTEN AND J. G. NOLTES, *J. Organometal. Chem.*, 16 (1969) P8.
- 2 E. J. BULTEN AND J. G. NOLTES, *Tetrahedron Lett.*, (1966) 4389.
- 3 E. J. BULTEN AND J. G. NOLTES, *Tetrahedron Lett.*, (1967) 1443.
- 4 E. J. BULTEN AND J. G. NOLTES, *J. Organometal. Chem.*, 29 (1971) 409.
- 5 E. J. BULTEN AND J. G. NOLTES, to be published.
- 6 F. RIJKENS, *Organogermanium Compounds*, Institute for Organic Chemistry TNO, Utrecht, 1960.
- 7 G. E. COATES, *Organometallic Compounds*, Vol. I, Methuen, London, 3rd edn., 1967.
- 8 H. GILMAN, M. B. HUGHES AND C. W. GEROW, *J. Org. Chem.*, 24 (1959) 352.
- 9 C. W. GEROW, Ph.D. Thesis, Ames, Iowa, Iowa State College Library, 1956.
- 10 M. B. HUGHES, Ph.D. Thesis, *Dissertation Abstr.*, 19 (1959) 1921.
- 11 C. A. KRAUS AND L. S. FOSTER, *J. Amer. Chem. Soc.*, 49 (1927) 457.
- 12 H. NORMANT, *Angew. Chem.*, 16 (1967) 1046.
- 13 N. S. VYAZANKIN, E. N. GLADYSHEV, G. A. RAZUVAEV AND S. P. KORNEVA, *Zh. Obshch. Khim.*, 36 (1966) 952; *Chem. Abstr.*, 65 (1966) 8955.
- 14 N. S. VYAZANKIN, G. A. RAZUVAEV, V. I. BICHKOV AND V. L. ZVEZDIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 562; *Chem. Abstr.*, 65 (1966) 5483.
- 15 N. S. VYAZANKIN, G. A. RAZUVAEV, E. N. GLADYSHEV AND S. P. KORNEVA, *J. Organometal. Chem.*, 7 (1967) 353.
- 16 H. GILMAN AND F. J. SCHULZE, *J. Amer. Chem. Soc.*, 47 (1925) 2002.
- 17 H. NORMANT, T. CUVIGNY, J. NORMANT AND B. ANGELO, *Bull. Soc. Chim. Fr.*, (1965) 3441.
- 18 F. FRAENKEL, S. ELLIS AND D. T. DIX, *J. Amer. Chem. Soc.*, 87 (1965) 1406.
- 19 H. NORMANT, T. CUVIGNY, J. NORMANT AND B. ANGELO, *Bull. Soc. Chim. Fr.*, (1965) 3446.
- 20 C. A. KRAUS AND E. A. FLOOD, *J. Amer. Chem. Soc.*, 54 (1932) 1635.
- 21 T. SHEDLOVSKY, in A. WEISSBERGER (Ed.), *Technique of Organic Chemistry*, Vol. I, Part IV, Interscience, New York, 1960, p. 1011.
- 22 J. F. NORMANT AND H. DESHAYES, *Bull. Soc. Chim. Fr.*, (1969) 1001.
- 23 W. L. JOLLY, *J. Chem. Educ.*, 44 (1967) 304.