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# INVESTIGATIONS ON ORGANOGERMANIUM COMPOUNDS

## XIV*. NON-CATALYZED REDISTRIBUTION REACTIONS OF ALKYLMONO- AND -POLYGERMANES WITH GERMANIUM AND TIN TETRACHLORIDE**

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## SUMMARY

A full report is given of studies into non-catalyzed redistribution reactions of alkylmono- and -polygermanes with germanium and tin tetrachloride resulting in the development of a fast, high-yield synthesis of alkylmono- and -polygermanes of the types $R(R_2Ge)_nCl\,(n \geqq 1)$ and $Cl(R_2Ge)_nCl\,(n > 1)$.

The high selectivity of these reactions enables the facile preparation of mixed alkyl-substituted mono- and polygermanes.

On the basis of observed substituent and solvent effects these reactions are concluded to proceed by an electrophilic substitution at carbon through transition states in which considerable charge separation has occurred.

## INTRODUCTION

One of the most satisfactory methods for the preparation of alkylhalogermanes is the so-called redistribution reaction. With organogermanium compounds two different processes can be distinguished:

(*a*). Reactions catalyzed by Lewis acids such as $AlCl_3$, involving the overall transfer of two alkyl groups, the second alkyl-transfer being faster than the first, *e.g.*[3-5]:

$$R_4Ge + GeCl_4 \xrightarrow[AlCl_3]{slow} R_3GeCl + RGeCl_3 \xrightarrow[AlCl_3]{fast} 2\,R_2GeCl_2 \tag{1}$$

(*b*). Reactions involving the rapid transfer of one alkyl group, with the second alkyl-transfer proceeding markedly slower and generally not taking place at all even under vigorous conditions, *e.g.*:

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[*] For Part XIII see ref. 2.
[**] Taken in part from the Ph.D. thesis of E. J. Bulten[1].
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$$R_4Ge+SnCl_4 \xrightarrow{\text{fast}} R_3GeCl+RSnCl_3 \overset{200°}{\not\longrightarrow} R_2GeCl_2+R_2SnCl_2 \quad (2)$$

Although in fact most familiar in organometallic chemistry, reactions of type (*b*) with germanium were only observed originally with other Group IV derivatives[6-8].

$$R_4M+M'Cl_4 \rightarrow R_3MCl+RM'Cl_3 \quad M=Ge, M'=Sn; M=Sn, Pb, M'=Ge \quad (3)$$

More recently, type (*b*) redistributions were also observed between tetraalkylgermanes and germanium tetrachloride catalyzed by divalent germanium species (*e.g.* $GeI_2$[1,9]) and between hexaalkyldigermanes with germanium tetrachloride in the absence of catalysts[10].

This paper deals with further studies of non-catalyzed redistribution reactions as a general route to alkylhalomono- and -polygermanes.

## RESULTS*

### *Reactions of tetraalkylgermanes with $GeCl_4$ and with $SnCl_4$***

Redistributions between germanium compounds and between germanium and tin compounds have been tentatively explained by a mechanism involving electrophilic substitution at carbon[9]. Therefore, it seemed pertinent to determine whether or not these reactions are accelerated by polar solvents.

$$R_4M+M'Cl_4 \rightarrow R_3MCl+RM'Cl_3 \quad M=Ge, M'=Ge, Sn; M=Sn, M'=Ge \quad (4)$$

Tin tetrachloride forms insoluble solid complexes with the most commonly-used polar solvents, however acetyl chloride ($\varepsilon \approx 16$) and nitromethane ($\varepsilon \approx 36$) were found to be suitable. In acetyl chloride the reaction mixtures are homogeneous, whereas in nitromethane two layers are frequently formed (*cf.* Experimental part). Nevertheless, reactions proceed much faster in the latter solvent. The results given in Table 1 show that reactions of all three systems, *viz.* $R_4Ge/GeCl_4$, $R_4Ge/SnCl_4$ and $R_4Sn/GeCl_4$, are accelerated by polar solvents, the rate increasing with increasing dielectric constant of the solvent (expts. 1–4, 7–12). In nitromethane the reaction rate of the system $R_4Ge/SnCl_4$ is at least 100 times faster than in benzene. Tin tetrachloride is more reactive than germanium tetrachloride, tetraalkyltins are more reactive than tetraalkylgermanes, but the system $R_4Sn/GeCl_4$ reacts slower than the system $R_4Ge/SnCl_4$ (expts. 8 and 16, 9 and 17). In none of the three systems even under drastic conditions could the transfer of more than one alkyl group be accomplished.

In view of the very moderate conditions and short reaction times the system $R_4Ge/SnCl_4$ is quite attractive as a general route to trialkylchlorogermanes (*cf.* Experimental).

In both $R_4Ge/SnCl_4$ and $R_4Sn/GeCl_4$ systems reactions proceed faster with R=Et than with R=Bu (*cf.* expts. 7 and 5, 15 and 13). Comparative experiments in nitromethane ($R_4Ge/SnCl_4$) showed the reaction rate to decrease in the order: $Me > Et > Pr \geqslant Bu \geqslant Pent$

Dealkylation of mixed-substituted tetraalkylgermanes by tin tetrachloride was found to be very selective, the rate of dealkylation decreasing in the order Me >

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* For details *cf.* ref. 1.

** For a preliminary paper, see ref. 11.

TABLE 1

NON-CATALYZED REDISTRIBUTIONS BETWEEN GERMANIUM AND TIN COMPOUNDS

| *Expt. nr.* | *Reactants* | | | | *Reaction conditions* | | | |
|---|---|---|---|---|---|---|---|---|
| | *$R_4Ge$* | *$R_4Sn$* | *$GeCl_4$* | *$SnCl_4$* | *Solvent*[a] | *Time (h)* | *Temp.*[b] *(°C)* | *Reaction (%)*[c] |
| 1 | Et | | + | | Neat | 6 | 200 | 0 |
| 2 | Et | | + | | $C_6H_6$ | 3 | 200 | 0 |
| 3 | Et | | + | | MeCOCl | 3 | 200 | $\approx 50^d$ |
| 4 | Et | | + | | $MeNO_2$ | 3 | 200 | 72 |
| 5 | Bu | | | + | Neat | 6 | 110 | $0^e$ |
| 6 | Bu | | | + | Neat | 1 | 210 | $100^{e,f}$ |
| 7 | Et | | | + | Neat | 2 | 100 | ≈12 |
| 8 | Et | | | + | Neat | 2 | 150 | $100^f$ |
| 9 | Et | | | + | $C_6H_6$ | 2 | 100 | ≈9 |
| 10 | Et | | | + | MeCOCl | 17 | 50 | 65 |
| 11 | Et | | | + | $MeNO_2$ | ≈0.8 | 50 | 100 |
| 12 | Et | | | + | $MeNO_2$ | 1 | 20 | 75 |
| 13 | | Bu | + | | Neat | 6 | 110 | $0^e$ |
| 14 | | Bu | + | | Neat | 1 | 210 | $100^{e,f}$ |
| 15 | | Et | + | | Neat | 2 | 100 | ≈6 |
| 16 | | Et | + | | Neat | 2 | 150 | 42 |
| 17 | | Et | + | | $C_6H_6$ | 2 | 150 | 22 |
| 18 | | Et | + | | $MeNO_2$ | $\leqslant 2$ | 150 | $100^f$ |

[a] Equimolar amounts of reactants were used, each of concentration (for reactions performed in solutions) 0.56 mole/l. [b] Experiments above $100^c$ were performed in Carius tubes. [c] Determined by GLC. [d] Inhomogeneous black mixture. [e] Ref. 6. [f] The minimal reaction time required was not determined.

Et > Pr > Bu. For instance, reaction of diethylpropylbutylgermane with tin tetrachloride gave exclusively (GLC) ethyltin trichloride and ethylpropylbutylchlorogermane:

$$Et_2PrBuGe + SnCl_4 \xrightarrow{(MeNO_2)} EtPrBuGeCl + EtSnCl_3 \quad (5)$$

Another example of the high selectivity of these reactions involves the synthesis and subsequent dealkylation of methylethylpropylbutylgermane (eqns. 7–11). As demonstrated by GLC in each of the separate dealkylation steps methyltin trichloride was the

$$Me_3BuGe + SnCl_4 \xrightarrow{(MeNO_2)} Me_2BuGeCl + MeSnCl_3 \quad (6)$$

$$Me_2BuGeCl \xrightarrow{PrMgBr} Me_2PrBuGe \quad (7)$$

$$Me_2PrBuGe + SnCl_4 \xrightarrow{(MeNO_2)} MePrBuGeCl + MeSnCl_3 \quad (8)$$

$$MePrBuGeCl \xrightarrow{EtMgBr} MeEtPrBuGe \quad (9)$$

$$MeEtPrBuGe + SnCl_4 \xrightarrow{(MeNO_2)} EtPrBuGeCl + MeSnCl_3 \quad (10)$$

sole organotin product (>98%). Reaction of both tributylcyclohexylgermane and dibutylcyclohexylhexylgermane with $GeCl_4$ in the presence of $GeI_2$ (no solvent) at 200° gave exclusive debutylation. However, the analogous reaction with butylcyclohexyldihexylgermane yielded roughly equal amounts of butyltrichlorogermane and

$$Bu_3(\text{cyclo-Hex})Ge + GeCl_4 \rightarrow Bu_2(\text{cyclo-Hex})GeCl + BuGeCl_3 \quad (11)$$

$$Bu_2Hex(\text{cyclo-Hex})Ge + GeCl_4 \rightarrow BuHex(\text{cyclo-Hex})GeCl + BuGeCl_3 \quad (12)$$

an unidentified product, probably hexyltrichlorogermane or cyclohexyltrichlorogermane. The physical constants and yields for a series of mixed-substituted alkylgermanium compounds are listed in Table 4.

### *Reactions of alkylpolygermanes with $GeCl_4$ and with $SnCl_4$*[1,10,11]

The results of a series of redistributions between different alkylpolygermanes and $GeCl_4$ are compiled in Table 2. As mentioned previously in the absence of catalysts, tetraalkylgermanes do not react with $GeCl_4$ at 200°. In contrast, under the same conditions, hexaalkyldigermanes react smoothly with $GeCl_4$ according to eqn. (13) (expts. 1, 2, 8, 9).

$$R_3GeGeR_3 + GeCl_4 \rightarrow R_3GeGeClR_2 + RGeCl_3 \quad (13)$$

Substitution of a second alkylgroup proceeds slower, the ethyl compound being more reactive than the butyl compound (expts. 3, 10). As determined by chlorine cleavage and subsequent GLC analysis of the chlorogermanes formed, the symmetrical 1,2-dichlorodigermanes are formed exclusively.

TABLE 2

REDISTRIBUTIONS BETWEEN $GeCl_4$ AND ALKYLDIGERMANES

| *Expt. nr.* | *Reactants (molar ratio)* | | *Other compounds* | *R* | *Time (h)* | *Temp. (°C)* | *Composition (mole %) of the digermane fraction*[a] | | *Total recovery of digermanes (%)* |
|---|---|---|---|---|---|---|---|---|---|
| | $R_6Ge_2$ | $GeCl_4$ | | | | | $R_3Ge$–$GeClR_2$ | $R_2ClGe$–$GeClR_2$ | |
| 1 | 1.00 | 1.03 | | Et | 6 | 200 | 96 | 4 | 81 |
| 2 | 1.00 | 1.00 | | Et | 6 | 190[b] | ≈100 | | 88 |
| 3 | 1.00 | 1.96 | | Et | 6 | 200 | 19 | 81 | 82 |
| 4 | 1.00 | 1.99 | | Et | 24 | 200 | | 100 | 78 |
| 5 | 1.00 | 1.99 | 0.02 $GeI_2$ | Et | 6 | 200 | | 100 | 76 |
| 6 | 1.00 | 2.92 | | Et | 24 | 200 | | 100 | 63 |
| 7 | | 1.00 | 1.00 $R_8Ge_3$ | Et | 3 | 200 | 42[c] | | |
| 8 | 1.00 | 1.09 | | Bu | $6\frac{1}{2}$ | 200 | 92 | 8 | 94 |
| 9 | 1.00 | 1.00 | | Bu | $4\frac{1}{2}$ | 220–230[b] | 100 | | 100[d] |
| 10 | 1.00 | 2.02 | | Bu | $6\frac{1}{2}$ | 200 | 80 | 20 | 100[d] |
| 11 | 1.00 | 2.97 | | Bu | $6\frac{1}{2}$ | 200 | | 100 | 86 |
| 12 | | 2.00 | 1.00 $(R_2ClGe)_2$ | Bu | $6\frac{1}{2}$ | 180–190 | | 100 | 100[d] |
| 13 | | 2.16 | 1.00 $(R_2ClGe)_2$ | Bu | $6\frac{1}{2}$ | 250 | | | 0[e] |
| 14 | 1.00 | 2.00 | 0.2 $AlCl_3$ | Bu | $6\frac{1}{2}$ | 205 | | | 0 |

[a] Separated by distillation; determined by refractive index measurements, chlorine analysis and GLC. [b] Expts. at atmospheric pressure (see *Experimental*). [c] Mainly $Et_3GeGeEt_2GeClEt_2$. [d] Determined only by GLC. [e] Dec. giving $R_3GeCl$, $R_2GeCl_2$ and metallic germanium.

Reaction (14) can be achieved by using prolonged reaction times (expt. 4), or

$$R_3GeGeClR_2 + GeCl_4 \xrightarrow{200^\circ} R_2ClGeGeClR_2 + RGeCl_3 \tag{14}$$

with $GeI_2$ as catalyst (expt. 5) or with excess of $GeCl_4$ (expt. 11). An increase in reaction temperature (250°) or catalysis by $AlCl_3$ resulted in complete cleavage of the Ge–Ge bond (expts. 13, 14). Introduction of more than two chlorine atoms could not be achieved (expts. 6, 11–13).

Reaction of octaethyltrigermane with one equivalent of $GeCl_4$ at 200° (expt. 7) gave only a moderate yield of 1-chloroheptaethyltrigermane, the structure of which was determined by chlorine cleavage and subsequent GLC product analysis. Ge–Ge bond cleavage had occurred to a considerable extent.

$$Et_3GeGeEt_2GeEt_3 + GeCl_4 \rightarrow Et_3GeGeEt_2GeClEt_2 + EtGeCl_3 \tag{15}$$

Like alkylmonogermanes, alkylpolygermanes react faster with $SnCl_4$ than with $GeCl_4$, the reactions being markedly accelerated in polar solvents (*cf.* Table 3). For example, reaction between hexaethyldigermane and $SnCl_4$ in nitromethane (heterogeneous system) is complete in about twenty minutes at room temperature (expt. 7). A comparison of the systems $Et_6Ge_2/SnCl_4$ and

$$Et_3GeGeEt_3 + SnCl_4 \rightarrow Et_3GeGeClEt_2 + EtSnCl_3 \tag{16}$$

$Et_4Ge/SnCl_4$ in acetyl chloride solution (homogeneous system) shows (*cf.* Table 3, expt. 4 and Table 1, expt. 10) that reaction with the digermane proceeds appreciably faster than with the monogermane.

Kinetic studies of the system $Et_6Ge_2/SnCl_4$ in acetyl chloride solution (Fig. 1) demonstrated the reaction to be second order overall; first order in each

TABLE 3

REDISTRIBUTIONS BETWEEN $MCl_4$ AND HEXAETHYLDIGERMANE IN POLAR SOLVENTS

| *Expt. nr.* | *M* | *Ratio* | *Solvent*[a] | *Reaction conditions* | | *Reaction*[b] (%) |
|---|---|---|---|---|---|---|
| | | | | *Time* (*h*) | *Temp.* (°*C*) | |
| 1 | Sn | 1 | Neat | 7 | 20 | 50 |
| 2 | Sn | 1 | $C_6H_6$ | 6 | 20 | trace |
| 3 | Sn | 1 | $C_6H_6/MeCOCl \approx 8$[c] | 6 | 20 | <2 |
| 4 | Sn | 1 | MeCOCl[c] | 6 | 20 | 61 |
| 5 | Sn | 1 | MeCOCl[c] | 2 | 53 | 100[d] |
| 6 | Sn | 1 | $MeNO_2$ | 3 | 20 | >90 |
| 7 | Sn | 1 | $MeNO_2$ | ≈0.3 | 50 | 100 |
| 8 | Ge | 1 | Neat | 7 | 20 | 0 |
| 9 | Ge | 1 | $MeNO_2$ | 2 | 50 | 0 |
| 10 | Ge | 1 | $MeNO_2$ | 2 | 100 | 50[e] |
| 11 | Ge | 2 | $MeNO_2$ | 7 | 100 | 100[d,e] |

[a] Concentration of reactants 0.50 mole/l, unless indicated otherwise. [b] Determined by GLC; $Et_3GeGeClEt_2$. [c] Concentration of reactants 0.40 mole/l. [d] The minimal reaction time was not determined. [e] $Et_2ClGeGeClEt_2$.

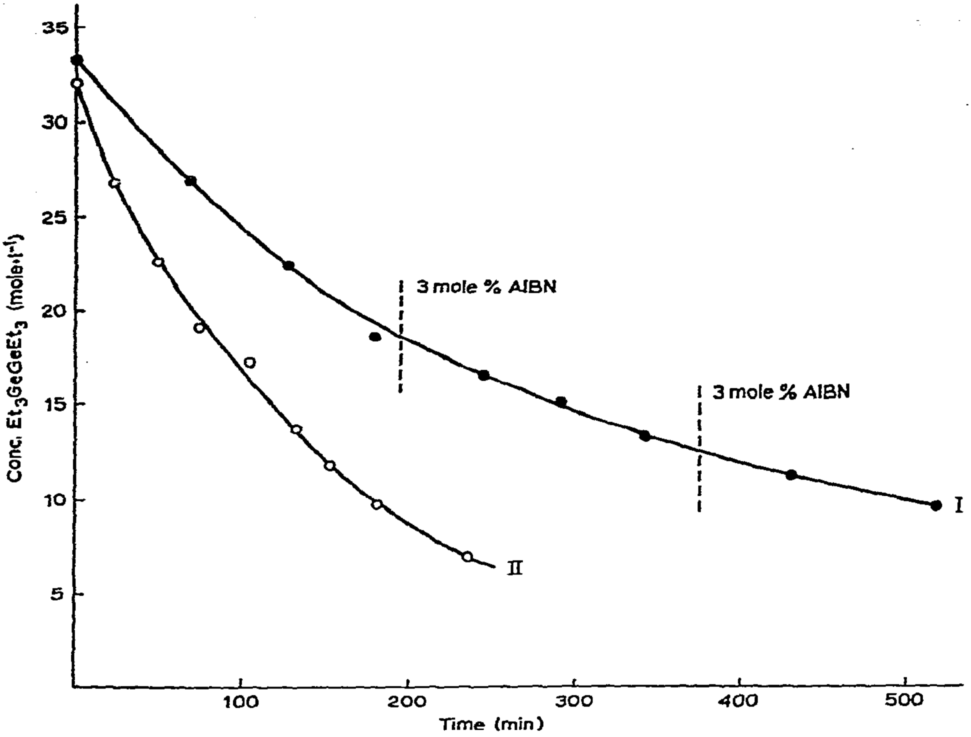


Fig. 1. Reaction of tin tetrachloride with hexaethyldigermane in acetyl chloride at 20°. Concentration ratio $SnCl_4/Et_3GeGeEt_3$: I, 1/1; II, 2/1.

reactant, the second-order rate constant at 20° for the process being $2.0 \times 10^{-6}$ $l \cdot mole^{-1} \cdot sec^{-1}$. As expected, addition of the free radical initiator, 2,2'-azobisisobutyronitrile (AIBN), does not affect the rate. From comparative studies the second-order rate constant for the system $Me_6Ge_2/SnCl_4$ was found to be ca. $2.5 \times 10^{-4}$ $l \cdot mole^{-1} \cdot sec^{-1}$, *i.e.* about 125 times greater than that for the system $Et_6Ge_2/SnCl_4$. Reaction with $Bu_6Ge_2$ proceeds about 4 times slower than with $Et_6Ge_2$, the second order rate constant being $0.5 \times 10^{-6}$ $l \cdot mole^{-1} \cdot sec^{-1}$.

Reaction of $SnCl_4$ with mixed-substituted alkylpolygermanes also proceeds in a very selective way.

For example, reaction of 1,1,1-trimethyl-2,2,2-triethyldigermane with one equivalent of $SnCl_4$ in nitromethane was found to give exclusively methyltin trichloride and 1-chloro-1,1-dimethyl-2, 2,2-triethyldigermane:

$$Me_3GeGeEt_3 + SnCl_4 \xrightarrow{(MeNO_2)} Me_2ClGeGeEt_3 + MeSnCl_3 \quad (17)$$

On the other hand, dealkylation of (trimethylsilyl)triethylgermane with $SnCl_4$ takes place exclusively at germanium:

$$Me_3SiGeEt_3 + SnCl_4 \xrightarrow{(MeNO_2)} Me_3SiGeClEt_2 + EtSnCl_3 \quad (18)$$

Reaction of butylpentaethyldigermane with $SnCl_4$ gave exclusively (GLC >

99%) ethyltin trichloride. Chlorine cleavage and subsequent GLC analysis of the mixture of chlorogermane products, revealed that in fact two chlorodigermanes had been formed, *viz.* 1-chloro-1-butyltetraethyldigermane and 1-chloro-2-butyltetraethyldigermane, in the ratio 2/3. Apparently a statistical deethylation of butylpentaethyldigermane had occurred.

$$\mathrm{Et_3GeGeBuEt_2 + SnCl_4} \begin{cases} \xrightarrow{(2)} \mathrm{Et_3GeGeClEtBu + EtSnCl_3} \\ \xrightarrow{(3)} \mathrm{Et_2ClGeGeBuEt_2 + EtSnCl_3} \end{cases} \tag{19}$$

In the reaction of octaethyltrigermane with one as well as with two equivalents of $SnCl_4$ in nitromethane resulted in exclusive terminal substitution (eqn. 20). In

$$\mathrm{Et_3GeGeEt_2GeEt_3} \begin{cases} \xrightarrow{1\ \mathrm{SnCl_4}} \mathrm{Et_3GeGeEt_2GeClEt_2 + EtSnCl_3} \\ \xrightarrow{2\ \mathrm{SnCl_4}} \mathrm{Et_2ClGeGeEt_2GeClEt_2 + EtSnCl_3} \end{cases} \tag{20}$$

contrast, reaction of 2,2-dimethylhexaethyltrigermane with $SnCl_4$ gave predominantly methyl substitution when performed in acetyl chloride, whereas in nitromethane solution ethyl substitution prevailed:

$$\mathrm{Et_3GeGeMe_2GeEt_3 + SnCl_4} \begin{cases} \xrightarrow{(a)} \mathrm{Et_3GeGeClMeGeEt_3 + MeSbCl_3} \\ \xrightarrow{(b)} \mathrm{Et_3GeGeMe_2GeClEt_2 + EtSnCl_3} \end{cases} \tag{21}$$

$$\mathrm{AcCl}: >90\%\ (a), <10\%\ (b);$$

$$\mathrm{MeNO_2}: <5\%\ (a), >95\%\ (b)$$

Physical constants and yields of some alkylhalomono- and -polygermanes obtained by transalkylation reactions are compiled in Table 4.

ABLE 4

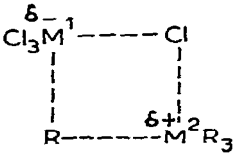
LKYLHALOMONO- AND -POLYGERMANES PREPARED VIA TRANSALKYLATION REACTIONS[a]

| ompound | *B.p.* (*°C/mmHg*) | $n_D^{20}$ | *Yield*[b] (%) | *Compound* | *B.p.* (*°C/mmHg*) | $n_D^{20}$ | *Yield* (%) |
|---|---|---|---|---|---|---|---|
| $e_2BuGeCl$ | 168 | 1.4490 | 54 | $Me_3GeGeClMe_2$ | 62–63/18 | 1.4911 | 47 |
| $e_2PrBuGe$ | 170–171 | 1.4350 | 82 | $Et_3GeGeClMe_2$ | 108/14 | 1.5011 | 82 |
| ePrBuGeCl | 104/26 | 1.4567 | 57 | $Et_3GeGeClEt_2$ | 146–147/18 | 1.5090 | 78 |
| eEtPrBuGe | 104/47 | 1.4431 | 80 | $Et_4BuGe_2Cl$[e] | 114–116/0.5 | 1.5042 | 80 |
| tPrBuGeCl | 86–89/12 | 1.4611 | 55 | $Pr_2GeGeClPr_2$ | 110–112/0.4 | 1.5007 | 75 |
| $t_2BuGeCl$ | 81–83/16 | 1.4611 | 79 | $Bu_3GeGeClBu_2$ | 130/0.06 | 1.4932 | 60 |
| $t_2PrBuGe$ | 91–92/13 | 1.4499 | 82 | $Et_2ClGeGeClEt_2$ | 144–146/18 | 1.5191 | 86 |
| $u_3$cyclo-HexGe | 172/13 | 1.4790 | 43 | $Bu_2ClGeGeClBu_2$ | 133–138/0.16 | 1.5027 | 86 |
| $u_2$Hex-cyclo-HexGe[c] | 122–125/0.15 | [d] | 61 | $Et_3GeGeEt_2GeClEt_2$ | $62–64/5 \cdot 10^{-4}$ | 1.5410 | 68 |
| uHex$_2$-cyclo-HexGe[c] | 131–132/0.06 | 1.4929 | 82 | $Et_2ClGeGeEt_2GeClEt_2$ |  | 1.5468 | 65 |
|  |  |  |  | $Me_3SiGeClEt_2$ | 126/65 | 1.4819 | 72 |

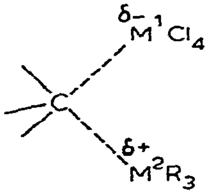
Satisfactory analysis data have been obtained for all compounds, see ref. 1. [b] After distillation. [c] See ref. 1. [d] M.p. 21–22°.
Mixture of $Et_3GeGeClEtBu_4$ and $Et_2ClGeGeEt_2Bu$, see text.

## DISCUSSION

Several related reactions in organometallic chemistry have been accounted for in terms of electrophilic attack of the metal atom of the halide on the first carbon atom of the alkyl group to be transferred[12-14]. This mechanism also applies to our results, and the following transition state may be envisaged.



As regards the accelerating effect by the polar solvents acetyl chloride and nitromethane, it is known that these solvents complex strongly with tin tetrachloride[15], resulting in a species of lower energy than the non-complexed tin tetrachloride. Thus, in our reactions the accelerating factor is even larger than appears from the solvent effect. This very large acceleration suggests an appreciable charge separation in the transition state, therefore in the transition state the interaction $M^2$–Cl is of minor importance. Consequently, in polar solvents our reactions will proceed by the $S_E2$ (open) rather than by the $S_E2$ (cyclic) mechanism[12,13].



The observed reactivity order $R_4Ge < R_5Ge_2Cl < R_6Ge_2$ can be explained by the increasing electron donation to $M^2$ in the series $R < R_2GeCl < R_3Ge$. As a matter of course the electron withdrawing chlorine atom in ${}^{\delta+}M^2ClR_2$ retards the rate enormously and the difficulty of introducing a second chlorine atom becomes understandable. Also in accordance with this picture chloropentaalkyldigermanes dealkylate to give 1,2-dichlorodigermanes instead of 1,1-dichlorodigermanes. Similar arguments account for the selectivity observed in the dealkylation of mixed-substituted tetraalkylgermanes; ${}^{\delta+}M^2$ is better stabilized by larger alkyl groups $Me < Et < Pr < Bu$. Thus, the methyl group is preferentially removed, however, the easier accessibility of the methyl group may play an important role as well. The importance of such a steric effect is also revealed in recent studies of the bimolecular electrophilic substitution of tetraalkyltins by mercuric salts in methanol/water mixtures[12,13]. Probably, steric effects are also dominant in the rates of homogeneously substituted tetraalkylgermanes $R_4Ge$, $R = Me > Et > Pr \geqslant Bu \geqslant Pent$.

The alkylating capacity increases in the order $R_4Si < R_4Ge < R_4Sn$. In addition to a decreasing metal–carbon bond strength in this sequence, this order can be ascribed to a better accommodation of positive charge on $M^2R_3$ for $M^2 = Si < Ge < Sn$.

The dealkylating capacity is larger for tin tetrachloride than for germanium tetrachloride because the former reagent is the more electrophilic or, in terms of our transition state picture, the negative charge is better accommodated on $(M^1=)$Sn than on Ge.

## EXPERIMENTAL

All reactions were performed under nitrogen. GLC analyses were carried out by Mrs. G. G. Versluis-De Haan by means of F & M gas chromatograph models 500 and 810 with katharometer detection, using helium as the carrier gas. The following columns were used:

1. 12′ stainless steel $\frac{1}{4}$″ OD, packed with 20% Silicone Fett Bayer/H on Chromosorb WAW 60–80 mesh.
2. 6′ stainless steel $\frac{1}{4}$″ OD, packed with 15% Polyphenyl Ether on Diatoport S 60–80 mesh.
3. 2′ copper $\frac{1}{4}$″ OD, packed with 20% Silicone Gum Rubber SE 30 on Chromosorb W 60–80 mesh.
4. 6′ stainless steel $\frac{1}{4}$″ OD, packed with 15% Polyphenyl Ether on Diatoport WAW 60–80 mesh.
5. 6′ stainless steel $\frac{1}{4}$″ OD, packed with 15% Silicone Oil Embaphase on Diatoport S 60–80 mesh.

*General procedures applied in the experiments compiled in Table* 1.

Experiments above 100° were performed in closed systems. Reactions were carried out on a very small scale (1–3 mmoles of each reactant) in "mini" Carius tubes (volume ≈ 8 ml), which were wrapped in nichrome gauze and agitated whilst submerged in an oil bath at constant temperature.

Reactions below 100° were performed in conventional glass vessels fitted with reflux condenser and nitrogen inlet. Unless indicated otherwise reaction mixtures were analyzed by gas chromatography.

*Reaction between tetraethylgermane and tin tetrachloride in acetyl chloride at* 50° (*Table* 1, *expt.* 10). A mixture of tetraethylgermane (0.95 g, 5.03 mmoles), tin tetrachloride (1.260 g, 4.85 mmoles) and acetyl chloride (8 ml) were heated at 50° for 17 h. GLC analysis (column 1) of the clear, deep-brown reaction mixture revealed the presence of tetraethylgermane, triethylchlorogermane, ethyltin trichloride and acetyl chloride. Tin tetrachloride could not be separated from acetyl chloride. From the molar ratio tetraethylgermane/triethylchlorogermane it appeared that reaction had proceeded to 65% completion.

*Reaction between tetraethylgermane and tin tetrachloride in nitromethane at* 50° (*Table* 1, *expt.* 11). Tetraethylgermane (0.950 g, 5.03 mmoles), tin tetrachloride (1.30 g, 5.00 mmoles) and nitromethane (8 ml) were allowed to react. At room temperature a two-layer system was obtained, however on heating at 50°, the mixture became instantly homogeneous. GLC analysis (column 2) of samples taken from the clear, faintly yellowish reaction mixture revealed that during 50 minutes reaction had been completed to give triethylchlorogermane and ethyltin trichloride as the sole products.

*Tripentylchlorogermane.* Tetrapentylgermane (35.7 g, 0.10 mole), tin tetrachloride (28.7 g, 0.11 mole) and 125 ml of nitromethane were refluxed together for 2 h. The mixture remained inhomogeneous throughout. The clear, colourless upper-layer, consisting nearly exclusively of tripentylchlorogermane (GLC, column 3), was separated and the brown lower-layer was extracted twice with pentane. The upper-layer and the pentane layers were combined and freed from solvent by evaporation *in vacuo*, yielding 36.6 g of high boiling residue. Fractionation gave 28.1 g (88%) of tripentylchlorogermane, b.p. 96–98°/0.1 mmHg, $n_D^{20}$ 1.4651 (lit.[16] b.p. 110–114°/0.3 mmHg, $n_D^{20}$ 1.4656. (Found: Cl, 11.2. $C_{15}H_{33}ClGe$ calcd.: Cl, 11.03%.)

*Diethylbutylchlorogermane* (*Table* 4). To a solution of 5.5 g (15.7 mmoles) of butylpentaethyldigermane[10] in 10 ml of carbon tetrachloride at 0° was added slowly 14 ml of a 1.12 *M* solution of chlorine in carbon tetrachloride which yellow solution decolourized immediately upon addition. GLC analysis (column 2) of the reaction mixture showed that the digermane had been cleaved completely to give two products, one of which had a retention time similar to that of triethylchlorogermane.

Careful fractionation gave 2.6 g (85%) of triethylchlorogermane, b.p. 57°/16 mmHg, $n_D^{20}$ 1.4590 and 2.75 g (79%) diethylbutylchlorogermane, b.p. 81–83°/16 mmHg, $n_D^{20}$ 1.4611.

*Diethylpropylbutylgermane* (*Table* 4). A solution of propylmagnesium bromide, prepared from 0.7 g (30 mmoles) of magnesium and 3.7 g (30 mmoles) of propyl bromide in 15 ml of diethyl ether, was added dropwise to a solution of 2.3 g (10.3 mmoles) of diethylbutylchlorogermane in 15 ml of diethyl ether. After refluxing for 4 h the mixture was hydrolyzed with dilute hydrochloric acid and extracted with diethyl ether. Distillation of the ether extract gave 1.9 g (82%) of diethylpropylbutylgermane, b.p. 91–92°/13 mmHg, $n_D^{20}$ 1.4499 (GLC column 2). In a similar way were prepared dimethylpropylbutylgermane, methylethylpropylbutylgermane, tributylcyclohexylgermane, dibutylhexylcyclohexylgermane and butyldihexylcyclohexylgermane.

*Ethylpropylbutylchlorogermane* (Table 4). Diethylpropylbutylgermane (1.8 g, 7.8 mmoles) and tin tetrachloride (2.05 g, 7.9 mmoles) were refluxed together for 1 h in 13 ml of nitromethane. According to GLC analysis (column 2) ethyltin trichloride was the only organotin compound present. The reaction mixture was extracted three times with 20 ml of pentane, the combined pentane layers were treated with 10 ml of water, subsequently with 10 ml of dilute sodium hydroxide and finally with 10 ml of concentrated hydrochloric acid. Distillation of the organic extract gave 1.0 g (55%) of ethylpropylbutylchlorogermane (GLC $>$92% of one peak). By means of preparative gas chromatography a product was obtained which analyzed correctly for ethylpropylbutylchlorogermane, b.p. 86–89°/12 mmHg, $n_D^{20}$ 1.4611. In a similar way were prepared dimethylbutylchlorogermane and methylpropylbutylchlorogermane.

*General procedures applied in the experiments compiled in Table* 3.

*Reaction between hexaethyldigermane and germanium tetrachloride at* 200° (*Table* 2, *expt*. 4). Hexaethyldigermane (6.15 g, 19.1 mmoles) and germanium tetrachloride (8.2 g, 38.2 mmoles) were heated together at 200° for 24 h in a Carius tube. Distillation of the colourless reaction mixture gave 66% of ethyltrichlorogermane (GLC, column 4, $>$98% pure) and 80% of 1,2-dichlorotetraethyldigermane (GLC, column 4, 98% containing of 2% ethyltrichlorogermane).

*Reaction between hexaethyldigermane and germanium tetrachloride at atmospheric pressure* (*Table* 2, *expt.* 2). To hexaethyldigermane (6.7 g, 21.0 mmoles), heated at 200°, was added under reflux 4.5 g (21.0 mmoles) of germanium tetrachloride. Addition was performed at such a rate that the internal temperature did not fall below the range 150–170°. Distillation then gave 2.5 g (53%) of ethyltrichlorogermane and 6.0 g (88%) of >98% pure (GLC, column 4) chloropentaethyldigermane.

*Reaction of hexaethyldigermane with tin tetrachloride in nitromethane at* 20° (*Table* 3, *expt.* 6). A mixture of hexaethyldigermane (1.6 g, 5.0 mmoles) and tin tetrachloride (1.3 g, 5.0 mmoles) in 8 ml of nitromethane was stirred for 3 h at 20°. The reaction mixture then consisted of two layers. GLC analysis (columns 4 and 5) of the homogeneous solution obtained on addition of 6 ml of toluene, showed that about 91% of the hexaethyldigermane had been converted into chloropentaethyldigermane.

*Rate constant determination for the reaction between hexaethyldigermane and tin tetrachloride in acetyl chloride at* 20° (*Fig.* 1). Tin tetrachloride (294 μl, 0.65 g, 2.5 mmoles) and 0.379 g of decane (internal standard) were dissolved in 6 ml of acetyl chloride. The reaction flask was thermostatted at 20.0° and 0.80 g (2.5 mmoles) of hexaethyldigermane was added at once. At appropriate time intervals samples of the reaction mixture were withdrawn and were analyzed by means of gas chromatography (columns 4 or 5).

### *Preparative examples*

*Chloropentabutyldigermane* (*Table* 2, *expt.* 8). Germanium tetrachloride (5.8 g, 27.0 mmoles) and hexabutyldigermane (12.2 g, 27.0 mmoles) were heated together in a Carius tube at 200° for 6½ h. Fractionation gave 6.0 g (25.4 mmoles) of butyltrichlorogermane, b.p. 74–80°/13 mmHg, $n_D^{20}$ 1.4742, slightly contaminated (GLC, column 1) with traces of tributylchlorogermane and dibutyldichlorogermane. The residue (11.2 g) obtained after removal of the monogermanes by distillation, consisted mainly of chloropentabutyldigermane (chlorine content 9.1%, calcd. 7.61%). Purification by distillation failed. Therefore, 23 g of combined residues obtained from several experiments, were treated at room temperature for ½ h with 0.3 of potassium hydroxide (equivalent to the chlorine surplus) and one drop of water. Fractionation of the organic phase gave 21.0 g (60% calculated on the basis of hexabutyldigermane applied) of pure chloropentabutyldigermane, b.p. 130°/0.06 mmHg, $n_D^{20}$ 1.4932.

1,2-*Dichlorotetrabutyldigermane* (*Table* 2, *expt.* 11). Germanium tetrachloride (12.9 g, 60.0 mmoles) and hexabutyldigermane (9.9 g, 20.0 mmoles) were heated together in a Carius tube for 6½ h at 200°. Fractionation gave 8.84 g of butyltrichlorogermane, 1.33 g of tributylchlorogermane, 0.4 g of dibutyldichlorogermane and 7.7 g (86%) of 1,2-dichlorotetrabutyldigermane, b.p. 133–138°/0.16 mmHg, $n_D^{20}$ 1.5027.

1,2-*Dichlorotetraethyldigermane*. Hexaethyldigermane (5.7 g, 17.9 mmoles) and tin tetrachloride (9.9 g, 38.0 mmoles) were heated for 6 h at 180° in a Carius tube. Fractionation gave 5.1 g (86%) of 1,2-dichlorotetraethyldigermane, b.p. 130–132°/16 mmHg, $n_D^{20}$ 1.5197. The product gave a single peak in the gas chromatogram (columns 4 and 5).

*Chloropentaethyldigermane*. A mixture of hexaethyldigermane (31.9 g, 0.1 mole) and tin tetrachloride (26.2 g, 0.1 mole) in 110 ml of nitromethane was refluxed for 2½ h. Benzene (100 ml) was added and the mixture was extracted twice with 25 ml of water and subsequently with 25 ml of 4 *N* sodium hydroxide, with 25 ml of water and with 25 ml of concentrated hydrochloric acid. The combined benzene layers were dried and evaporated *in vacuo* and distillation of the residue obtained (26.1 g, $n_D^{20}$ 1.5085) gave 24.3 g (75%) of chloropentaethyldigermane, b.p. 146–147°/18 mmHg, $n_D^{20}$ 1.5090. The product showed a single peak in the gas chromatograms (columns 2 and 4).

In a similar way were obtained chloropentamethyldigermane (47%), 1-chloro-1,1-dimethyltriethyldigermane (82%), chloropentapropyldigermane (75%), 1-chloroheptaethyltrigermane (68%), 1,3-dichlorohexaethyltrigermane (65%) and (trimethylsilyl)diethylchlorogermane (72%).

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