

PRELIMINARY COMMUNICATION

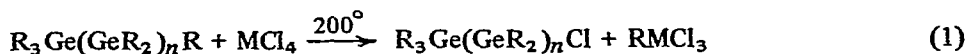
INVESTIGATIONS ON ORGANOGermanium COMPOUNDS IX*. THE SELECTIVE DEALKYLATION OF ALKYL MONO- AND -POLYGERMANES BY TIN TETRACHLORIDE IN POLAR SOLVENTS

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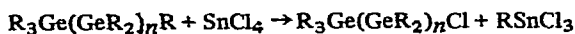
The dealkylation of tetraalkylgermanes and hexaalkyldigermanes, respectively, by GeCl_4 ^{1,2} and SnCl_4 ^{2,3} offers an excellent method for the preparation of compounds of the type R_3GeCl and $\text{R}_3\text{GeGeClR}_2$:



(R = alkyl, $n = 0-1$, M = Ge, Sn**)

For this reaction a polar mechanism involving electrophilic attack by the metal atom of the tetrahalide on carbon has been proposed^{1,2}. In accordance with such a polar mechanism these reactions were found to be accelerated considerably by polar solvents.

TABLE I
 INFLUENCE OF POLAR SOLVENTS ON REACTIONS OF THE TYPE:



R	n	Solvent	Time (h)	Temp. (°C)	% Reaction
Et	0	-	1	210	100 ^a
Et	0	-	5	20	0
Et	0	MeCOCl	22	50	75
Et	0	MeNO ₂	1	20	75
Et	0	MeNO ₂	1	50	100
Pent	0	MeNO ₂	2	100	100 ^a
Et	1	benzene	6	20	trace
Et	1	MeCOCl	6	20	61
Et	1	MeCOCl	2	52	100 ^a
Et	1	MeNO ₂	<0.5	50	100
Et	2	MeNO ₂	4	100	100 ^a

^aMinimal time required for complete reaction was not determined.

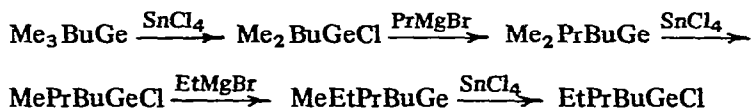
*For Part VIII see ref.6.

**With $n = 0$ and M = Ge a catalyst is required¹.

SnCl_4 forms insoluble solid complexes with most of the commonly used polar solvents, but acetylchloride ($\epsilon \sim 16$) and nitromethane ($\epsilon \sim 36$) were found to be suitable solvents. Whereas in nitromethane generally two layers are formed upon adding the organogermans, homogeneous reaction mixtures are obtained in acetylchloride. However, the reactions are much faster in the first solvent. Relevant results are given in Table 1.

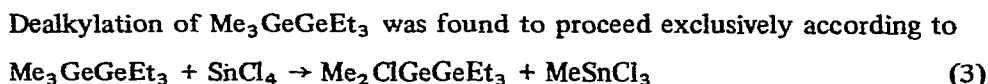
The ease of dealkylation of compounds R_4Ge tends to decrease in the series $\text{Et} > \text{Pr} \approx \text{Bu} \approx \text{Pent}$. Nevertheless even with Pent_4Ge reaction is complete in less than two hours at 100° in nitromethane. After distillation gaschromatographically pure Pent_3GeCl was obtained in 88% yield. Hexaalkyldigermans react faster than tetraalkylgermanes. Under the conditions employed side-reactions, such as metal-metal bond cleavage do not occur. Reaction of Et_6Ge_2 with SnCl_4 in acetylchloride was found to be first order in each of the reactants with a bimolecular rate constant of approximately $2 \times 10^{-6} \text{ l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$.

The dealkylation of mixed alkyl substituted mono- and polygermanes was found to be very selective e.g. dealkylation of Et_2PrBuGe with SnCl_4 gave exclusively EtSnCl_3 and EtPrBuGeCl . The high selectivity of these dealkylation reactions allows the facile preparation of mixed substituted mono- and polygermanes. The following reaction sequence involving the synthesis and subsequent dealkylation of methylethylpropylbutylgermane is given as an example:

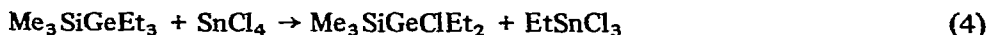


In each of the separate dealkylation steps MeSnCl_3 was the only ($> 98\%$) organotin product formed (GLC).

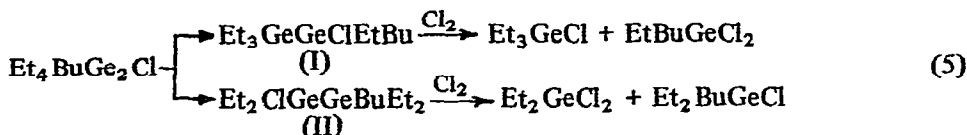
In organotin chemistry recently the selective dealkylation of tetraalkyltin compound by bromine in methanol has been reported⁴.



In contrast reaction with $\text{Me}_3\text{SiGeEt}_3$ gave EtSnCl_3 and $\text{Me}_3\text{SiGeClEt}_2$ as the sole reaction products:



Dealkylation of $\text{Et}_3\text{GeGeEt}_2\text{Bu}$ afforded almost exclusively EtSnCl_3 ($> 99\%$ GLC) and 80% (after distillation) of a digermane which analyzed correctly for $\text{Et}_4\text{BuGe}_2\text{Cl}$ (cf. Table 2). Although this product showed a single peak upon GLC analysis, chlorine cleavage gave Et_3GeCl , EtBuGeCl_2 , Et_2GeCl_2 and Et_2BuGeCl in the ratio 2:3:2:3. These results point out that the digermane isolated consists of a mixture of $\text{Et}_3\text{GeGeClEtBu}$ (I) and $\text{Et}_2\text{ClGeGeBuEt}_2$ (II) in the ratio 2:3, which is indicative of a statistical dealkylation of the digermane.



The versatility of the tin tetrachloride-dealkylation reaction for the preparation of various types of alkylmono- and -polygermanes is illustrated by the new compounds listed in Table 2. Detailed information on this subject will be given at a later date⁵.

TABLE 2
SOME NEW ORGANOGERMANES

Compound	Analysis						B _o p. (°C/mm Hg)	²⁰ n _D
	Found			Calcd.				
	C	H	Cl	C	H	Cl		
Et ₂ PrBuGe	57.6	11.4	—	57.22	11.35	—	91–92/13	1.4499
EtPrBuGeCl	45.7	9.0	15.1	45.55	8.99	14.94	86–89/12	1.4611
Me ₂ BuGeCl	36.7	7.7	18.2	36.91	7.74	18.16	168	1.4490
Me ₂ PrBuGe	53.0	11.0	—	53.29	10.93	—	170–171	1.4350
MePrBuGeCl	43.1	8.6	16.0	43.03	8.57	15.88	104/26	1.4567
MeEtPrBuGe	54.9	11.1	—	55.38	11.15	—	104/47	1.4431
Me ₃ GeGeClMe ₂	23.5	6.1	13.8	23.48	5.91	13.86	62–63/18	1.4911
Et ₃ GeGeClMe ₂	32.1	7.2	12.0	32.25	7.10	11.91	108/14	1.5011
Me ₃ SiGeClEt ₂ ^a	34.7	8.1	15.4	35.13	8.0	14.8	126/65	1.4819
Et ₃ GeGeBuEt ₂	48.5	9.7	—	48.37	9.86	—	84–88/0.03	1.4947
Et ₄ BuGe ₂ Cl ^b	41.0	7.9	10.2	40.72	8.25	10.01	114–116/0.5	1.5042
Et ₃ GeGeEt ₂ GeClEt ₂	36.6	7.8	8.1	36.83	7.72	7.77	62–64/5 · 10 ⁻⁴	1.5410

^aContained about 2% of EtSnCl₃. ^bSee text.

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