

THE PREPARATION OF ALKYLDIGERMANE HALIDES\*

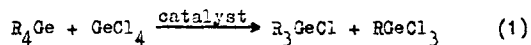
E.J.Bulten and J.G.Noltes

Institute for Organic Chemistry TMO, Utrecht, the Netherlands

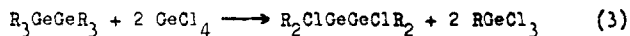
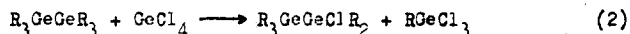
(Received 18 May 1966)

Only a few data are available in the literature on alkyldigermane halides. A compound with the composition  $Bu_4Ge_2I_2$  was isolated by Jacobs from the reaction of  $GeI_2$  with  $Bu_2Hg$ <sup>(1)</sup>. Vyazankin<sup>(2)</sup> isolated impure  $Et_3GeGeBrEt_2$  in about 50% yield by reacting  $Et_3GeGeEt_3$  with *i*-PrBr in the presence of  $AlCl_3$ .

Our investigations on transalkylation reactions between alkyldigermanium derivatives<sup>(3)</sup> according to:



have been extended to hexaalkyldigermanes. It appeared that compounds of the type  $R_3GeGeClR_2$  and  $R_2ClGeGeClR_2$  are readily accessible according to:



\* Part V in the series "Investigations on Organogermanium Compounds";  
Part IV: ref. 3.

As can be seen from Table I pentaalkyldigermene halides can easily be prepared in high yields according to (2). The introduction of a second chlorine atom according to (3) can only be performed either by prolonged reaction times or by using  $\text{GeI}_2^{(3)}$  as a catalyst.

TABLE I  
Reaction of  $\text{Et}_3\text{GeGeEt}_3$  with  $\text{GeCl}_4$  at  $200^\circ\text{C}$

Molar ratio $\text{GeCl}_4:\text{Et}_3\text{GeGeEt}_3$	Total recovery of digermenes <sup>a</sup> (moles)	Composition (%) of the digermene fraction <sup>b</sup>		Reaction time, hrs.	Loss of digermene by decomp. <sup>c</sup>
		$\text{Et}_3\text{GeGeClEt}_2$	$\text{Et}_2\text{ClGeGeClEt}_2$		
1,03 <sup>e</sup>	0,81	~100	trace	6	trace
1,00 <sup>f</sup>	0,88	100	0	6	-
1,95 <sup>e</sup>	0,82	20	80	6	trace
2,92 <sup>e</sup>	0,77	14	86	6	trace
3,98 <sup>e</sup>	0,73	4	96	6	+
1,59 <sup>d,e</sup>	0,76	0	100	6	+
1,59 <sup>e</sup>	0,78	0	100	24	+

<sup>a</sup> The reaction mixtures were separated by distillation in a monogermene and a digermene fraction. Only the latter was analyzed; <sup>b</sup> Determined by gaschromatography and chlorine analyses;  $\text{Et}_3\text{GeGeEt}_3$  was completely converted; <sup>c</sup> Mainly  $\text{Et}_2\text{GeCl}_2$ ; <sup>d</sup> Catalyzed by  $\text{GeI}_2^{(3)}$ ; <sup>e</sup> Sealed tube; <sup>f</sup> Expts. at atmospheric pressure<sup>(4)</sup>.

The dichlorodigermenes isolated have a symmetric structure as appears from the halogen cleavage reaction (4), a dialkylgermanium dihalide being the sole reaction product.



Reaction between a hexaalkyldigermene and one or two equivalents of either  $\text{CCl}_4$  or  $\text{SiCl}_4$  results in appreciable decomposition.  $\text{SnCl}_4$  reacts essentially in the same way as  $\text{GeCl}_4$ , but is much more reactive than the latter. The reaction with  $\text{SnCl}_4$  is especially suited for the preparation of tetraalkyldigermene halides (see Table II).

Both the observation that substitution of a second alkyl group by halogen takes place preferably at the germanium atom with the highest degree of alkylation and the greater reactivity of  $\text{SnCl}_4$  as compared with  $\text{GeCl}_4$  are in agreement with a mechanism involving electrophilic attack by chlorine on carbon (cf. ref. 3).

The composition of the digermene mixtures obtained was determined by gas chromatography, since a mixture of  $\text{R}_3\text{GeGeR}_3$ ,  $\text{R}_3\text{GeGeClR}_2$  and  $\text{R}_2\text{ClGeGeClR}_2$  can not be separated by distillation. Therefore, the conditions which give rise to the formation of either  $\text{R}_3\text{GeGeClR}_2$  or  $\text{R}_2\text{ClGeGeClR}_2$  as the sole reaction product have been determined.

Digermene halides differ markedly from their ditin analogs in thermal and oxidative stability. Whereas compounds of the type  $\text{R}_2\text{ClSnSnClR}_2$  are highly susceptible towards oxydation<sup>(5)</sup>, the chlorinated digermenes are relatively inert. Pentaethyliditin chloride is stable at  $-20^\circ\text{C}$  but decomposes at room temperature with formation of triethyltin chloride<sup>(6)</sup>. On the other hand  $\text{Et}_3\text{GeGeClEt}_2$  was recovered unchanged after heating for 6 hrs. at  $200^\circ\text{C}$  (under nitrogen). Under the same conditions  $\text{Et}_2\text{ClGeGeClEt}_2$  was decomposed for about 8 % into  $\text{Et}_2\text{GeCl}_2$  and some polymeric material, possibly according to:

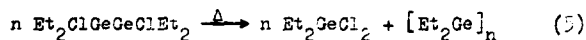
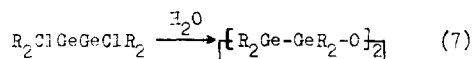
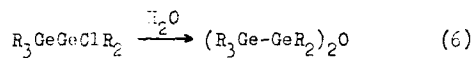


TABLE II  
Reaction of  $\text{Et}_3\text{GeGeEt}_3$  with  $\text{MCl}_4$  at  $200^\circ\text{C}$

M	Molar ratio $\text{MCl}_4:\text{Et}_3\text{GeGeEt}_3$	Total recovery of digermans <sup>a</sup> (moles)	Composition (%) of the digermans fraction		Reaction time, hrs.	Loss of digermans by recomb. <sup>c</sup>
			$\text{Et}_3\text{GeGeEt}_3$	$\text{Et}_2\text{ClGeGeClEt}_2$		
C	1,06 <sup>e</sup>	0,53	47	53	6	++
Si	0,95 <sup>e</sup>	0,23	91	9	6	++
Ge	1,03 <sup>e</sup>	0,91	0	~100	6	trace
Sn <sup>d</sup>	1,00 <sup>e</sup>	0,80	0	93	7	trace
C	2,08 <sup>e</sup>	0,22	0	69	31	++
Si	2,00 <sup>e</sup>	0,10	0	2	98	++
Ge	1,90 <sup>e</sup>	0,82	0	20	80	trace
Sn <sup>d</sup>	2,12 <sup>e</sup>	0,20	0	0	100	trace
Sn <sup>d</sup>	2,09 <sup>f</sup>	0,64	0	0	100	+

<sup>a</sup> See note a table I; <sup>b</sup> Determined by gaschromatography and chlorine analyses; <sup>c</sup> Variable amounts of  $\text{Et}_3\text{GeCl}$  and  $\text{Et}_2\text{GeCl}_2$ ; <sup>d</sup> Occasionally small amounts of  $\text{SnCl}_2$  were formed; <sup>e</sup> Sealed tube; <sup>f</sup> Expt. at atmospheric pressure (4).

A variety of reactions can be performed with the digermane halides without rupture of the metal-metal bond. Hydrolysis affords the oxides (6, 7), the dichlorodigermane yielding the cyclic dimer.



Reduction of  $\text{Bu}_3\text{GeGeClBu}_2$  with  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  affords  $\text{Bu}_3\text{GeGeHBu}_2$  as an air-sensitive liquid. Alkylation of  $\text{Bu}_3\text{GeGeClBu}_2$  with  $\text{MeMgBr}$  gives  $\text{Bu}_3\text{GeGeMeBu}_2$ .

The physical constants and yields for some new digermanes are summarized in Table III.

TABLE III  
New digermanes prepared<sup>a</sup>

Compound	b.p. (°C/mm Hg)	$n_D^{20}$	yield (%)
$\text{Et}_3\text{GeGeClEt}_2$	126-127/16	1,5092	88
$\text{Et}_2\text{ClGeGeClEt}_2$	130-132/16	1,5197	86
$\text{Pr}_3\text{GeGeClPr}_2$	110-112/ 0,4	1,5007	60
$\text{Bu}_3\text{GeGeClBu}_2$	130-132/ 0,06	1,4932	87
$\text{Bu}_2\text{ClGeGeClBu}_2$	133-138/ 0,16	1,5027	86
$(\text{Et}_3\text{GeGeEt}_2)_2\text{O}$	162-165/ 0,3	1,5185	70
$\left[ \text{Bu}_2\text{Ge}-\text{GeBu}_2-\text{O} \right]_2$	130-132/ $5 \cdot 10^{-5}$	1,4993	80
$\text{Bu}_3\text{GeGeHBu}_2$	115-116/ 0,09	1,4851	50
$\text{Bu}_3\text{GeGeMeBu}_2$	125-126/ 0,1	1,4841	84

<sup>a</sup> Satisfactory analyses have been obtained for all compounds reported.

Acknowledgement. The authors gratefully acknowledge the "Germanium Research Committee" for support of this work and for permission to publish the results. They wish to thank Professor G.J.M. van der Kerk for his stimulating interest. Thanks are also due to Mr. J.Q. Mol and Miss G.G. de Haan for able experimental assistance.

## REFERENCES

1. G. Jacobs, Compt. rend. 238, 1825 (1954).
2. N.S. Vyazankin, E.N. Gladyshev, S.P. Korneva and G.A. Razuvaev, Zh. Obshch. Khim. 34, 1645 (1965).
3. F. Rijkens, W. Drenth, E.J. Bulten and G.J.M. van der Kerk, Rec. Trav. Chim., in the press.
4. F. Rijkens and G.J.M. van der Kerk, Rec. Trav. Chim. 83, 723 (1964).
5. A.J. Gibbon, A.K. Sawyer and A. Ross, J. Org. Chem. 26, 2304 (1961).
6. H.M.J.C. Creemers and J.G. Noltes, unpublished results.