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THE PREPARATION OF ALKYLDIGERMANE HALIDES*

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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(1). Vyazankin(2) 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 alkylgermanium derivatives(3) according to:

$$R_4Ge + GeCl_4 \xrightarrow{catalyst} R_3GeCl + RGeCl_3 \qquad (1)$$

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

$$R_3GeGeR_3 + GeCl_4 \longrightarrow R_3GeGeClR_2 + RGeCl_3 \qquad (2)$$

$$R_3GeGeR_3 + 2\ GeCl_4 \longrightarrow R_2ClGeGeClR_2 + 2\ RGeCl_3 \qquad (3)$$

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As can be seen from Table I pentaalkyldigermane 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 GeI_2(3) as a catalyst.

TABLE I

Reaction of $Et_3GeGeEt_3$ with $GeCl_4$ at 200°C

Molar ratio $GeCl_4:Et_3GeGeEt_3$	Total recovery of digermanes[a] (moles)	Composition (%) of the digermane fraction[b]		Reaction time, hrs.	Loss of digermane by decomp.[c]
		$Et_3GeGeClEt_2$	$Et_2ClGeGeClEt_2$		
1,03[e]	0,81	~100	trace	6	trace
1,00[f]	0,88	100	0	6	-
1,95[e]	0,82	20	80	6	trace
2,92[e]	0,77	14	86	6	trace
3,98[e]	0,73	4	96	6	+
1,99[d,e]	0,76	0	100	6	+
1,99[e]	0,78	0	100	24	+

[a] The reaction mixtures were separated by distillation in a monogermane and a digermane fraction. Only the latter was analyzed; [b] Determined by gaschromatography and chlorine analyses; $Et_3GeGeEt_3$ was completely converted; [c] Mainly Et_2GeCl_2; [d] Catalyzed by GeI_2(3); [e] Sealed tube; [f] Expts. at atmospheric pressure(4).

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

$$R_2ClGeGeClR_2 + X_2 \longrightarrow 2\ R_2GeClX \qquad (4)$$

Reaction between a hexaalkyldigermane and one or two equivalents of either CCl_4 or $SiCl_4$ results in appreciable decomposition. $SnCl_4$ reacts essentially in the same way as $GeCl_4$, but is much more reactive than the latter. The reaction with $SnCl_4$ is especially suited for the preparation of tetraalkyldigermane 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 $SnCl_4$ as compared with $GeCl_4$ are in agreement with a mechanism involving electrophilic attack by chlorine on carbon (cf. ref. 3).

The composition of the digermane mixtures obtained was determined by gaschromatography, since a mixture of R_3GeGeR_3, $R_3GeGeClR_2$ and $R_2ClGeGeClR_2$ can not be separated by distillation. Therefore, the conditions which give rise to the formation of either $R_3GeGeClR_2$ or $R_2ClGeGeClR_2$ as the <u>sole</u> reaction product have been determined.

Digermane halides differ markedley from their ditin analogs in thermal and oxidative stability. Whereas compounds of the type $R_2ClSnSnClR_2$ are highly susceptible towards oxydation(5), the chlorinated digermanes are relatively inert. Pentaethylditin chloride is stable at -20°C but decomposes at room temperature with formation of triethyltin chloride(6). On the other hand $Et_3GeGeClEt_2$ was recovered unchanged after heating for 6 hrs. at 200°C (under nitrogen). Under the same conditions $Et_2ClGeGeClEt_2$ was decomposed for about 8 % into Et_2GeCl_2 and some polymeric material, possibly according to:

$$n\ Et_2ClGeGeClEt_2 \xrightarrow{\Delta} n\ Et_2GeCl_2 + [Et_2Ge]_n \qquad (5)$$

TABLE II

Reaction of $Et_3GeGeEt_3$ with MCl_4 at 200°C

M	Molar ratio MCl_4:$Et_3GeGeEt_3$	Total recovery of digermanes[a] (moles)	Composition (%) of the digermane fraction $Et_3GeGeEt_3$	$Et_3GeGeClEt_2$	$Et_2ClGeGeClEt_2$	Reaction time, hrs.	Loss of digermane by decomp.[c]
C	1,06[e]	0,53	47	53	0	6	+ +
Si	0,95[e]	0,23	91	9	0	6	+ +
Ge	1,03[e]	0,81	0	~100	trace	6	trace
Sn[d]	1,00[e]	0,80	0	93	7	6	trace
C	2,08[e]	0,22	0	69	31	6	+ +
Si	2,00[e]	0,10	0	2	98	6	+ +
Ge	1,96[e]	0,82	0	20	80	6	trace
Sn[d]	2,12[e]	0,86	0	0	100	6	trace
Sn[d]	2,09[f]	0,64	0	0	100	3	+

[a] See note a table I; [b] Determined by gaschromatography and chlorine analyses; [c] Variable amounts of Et_3GeCl and Et_2GeCl_2; [d] Occasionally small amounts of $SnCl_2$ were formed; [e] Sealed tube; [f] 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.

$$R_3GeGeClR_2 \xrightarrow{H_2O} (R_3Ge\text{-}GeR_2)_2O \qquad (6)$$

$$R_2ClGeGeClR_2 \xrightarrow{H_2O} \underline{\{R_2Ge\text{-}GeR_2\text{-}O\}_2} \qquad (7)$$

Reduction of $Bu_3GeGeClBu_2$ with $LiAlH_4$ in Et_2O affords $Bu_3GeGeHBu_2$ as an air-sensitive liquid. Alkylation of $Bu_3GeGeClBu_2$ with MeMgBr gives $Bu_3GeGeMeBu_2$.

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

TABLE III

New digermanes prepared[a]

Compound	b.p.(^oC/mm Hg)	n_D^{20}	yield (%)
$Et_3GeGeClEt_2$	126-127/16	1,5092	88
$Et_2ClGeGeClEt_2$	130-132/16	1,5197	86
$Pr_3GeGeClPr_2$	110-112/ 0,4	1,5007	60
$Bu_3GeGeClBu_2$	130-132/ 0,06	1,4932	87
$Bu_2ClGeGeClBu_2$	133-138/ 0,16	1,5027	86
$(Et_3GeGeEt_2)_2O$	162-165/ 0,3	1,5185	70
$\underline{\{Bu_2Ge\text{-}GeBu_2\text{-}O\}_2}$	130-132/ 5.10^{-5}	1,4993	80
$Bu_3GeGeHBu_2$	115-116/ 0,09	1,4851	50
$Bu_3GeGeMeBu_2$	125-126/ 0,1	1,4841	84

[a] Satisfactory analyses have been obtained for all compounds reported.

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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.