

## STUDIES IN THE FIELD OF ORGANIC GERMANIUM COMPOUNDS

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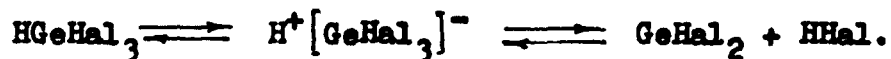
Our studies in the field of organic chemistry of germanium presented in more than 200 issues (including two monographs) were commenced in 1955 and are still in progress.

The comparative studies of chemical conversions of analogous compounds within the Group IVB elements in single-type reactions made it possible to conclude that in the chemistry of Group IVB elements (C, Si, Ge, Sn, Pb), after obvious substantial change between chemical properties during transition from carbon to silicon there is another, less pronounced, change between germanium and tin, i.e. the chemistry of germanium and silicon derivatives despite the fact that it has much common features differs greatly from the chemistry of organic derivatives of tin and lead.

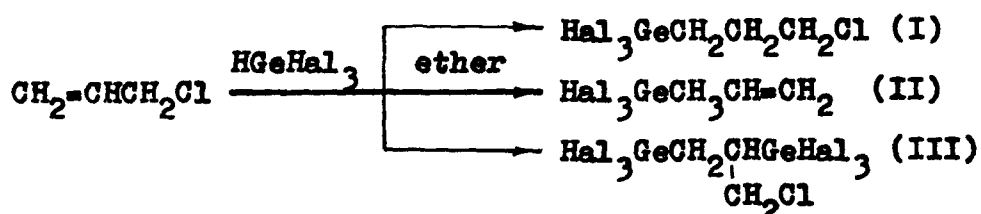
Initially the chemistry of trihalogermanes ( $\text{HGeHal}_3$ ) received primary emphasis. It has been found that with conjugated dienes the reaction proceeds as follows:



i.e. it was for the first time found that trihalogermanes can be a source for reactive germanium dihalogenides of carbene-type:

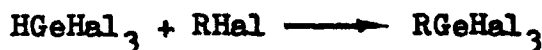


With ethers or amines in reaction medium giving ethers or aminates with  $\text{HGeHal}_3$  the above equilibrium moves to the right and the hydrogermylation reaction (I) for example, in the case of allyl chloride is displaced by hitherto unknown condensation (II), double germylation (III) and polymerization (IV) reactions:

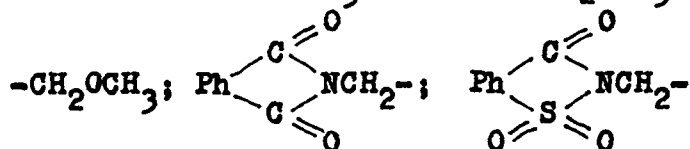


Hydrogermylation reaction proceeds essentially with any compounds containing multiple bonds. It opened the broad possibilities to obtain carbofunctional organic germanium compounds previously unknown. The tendency to reactions (II), (III) and (IV) increases from Cl to I. These reactions proceed often without ether or amine.

Iodides and other organohalogenides capable to reaction according to  $\text{S}_{\text{N}}1$  mechanism enter actively into condensation reaction (II):

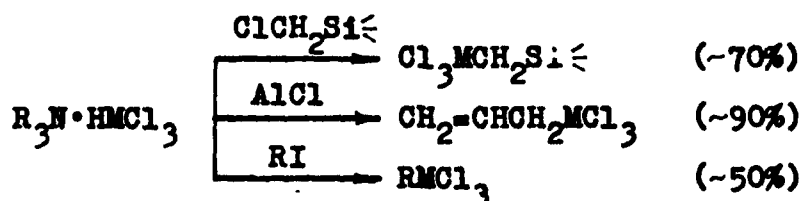


where R = t-Bu;  $\text{Ph}_3\text{C}-$ , Ad-;  $-\text{CH}_2\text{SiR}_3$ ;  $\text{CH}\equiv\text{CCH}_2-$ ;  $\text{PhCH}_2-$ ;



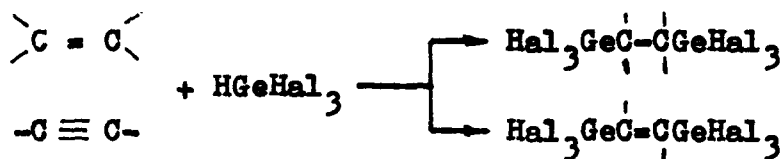
The amine complexes of trihalogermanes can also enter in this reaction.

The comparative studies of  $\text{HGeCl}_3 \cdot \text{R}_3\text{N}$  and  $\text{HSiCl}_3 \cdot \text{R}_3\text{N}$  revealed their close similarity and opened new preparative methods for the germanium and silicon compounds hitherto non-available:

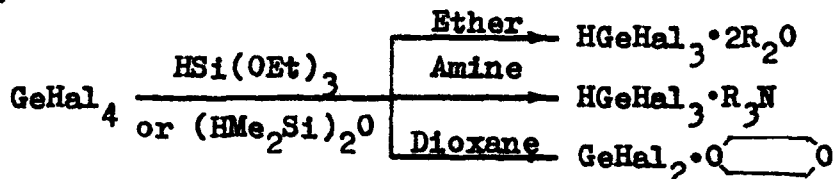


where M = Ge and Si.

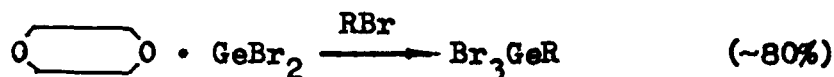
The original double germylation reaction (III) proved also to be enough conventional, it proceeds with some olefinic and acetylenic compounds:



The simple preparative methods for trihalogermane etherates and aminates obtaining as well as  $\text{GeHal}_2$  dioxanates from available hydrosilanes and  $\text{GeHal}_4$  have been found:

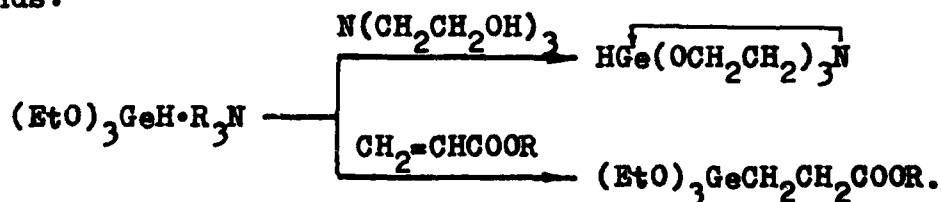


Dibromogermanium dioxanate became to be the most convenient one in series of synthesis. It is established that it reacts with practically any organobromides:

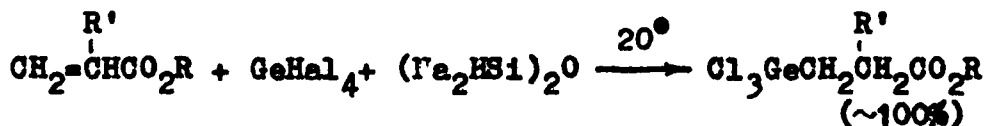


where  $\text{R} = \text{Ad-}; \text{Ar-}; -\text{CH}_2\text{Br}; -(\text{CH}_2)_n\text{COOMe}; -\text{CH}=\text{CH}_2; -\text{CH}=\text{CHPh}; -\text{CH}=\text{CHBr}$  etc.

Trialkoxygermane aminates (new complex germanium compounds) have substantially extended the synthetic possibilities in the chemistry of germanium organic compounds:



In the case of  $\alpha, \beta$ -unsaturated carbonyl compounds it is unnecessary to prepare separately trichlorogermanes and their etherates; it is sufficient to mix three starting reagents:



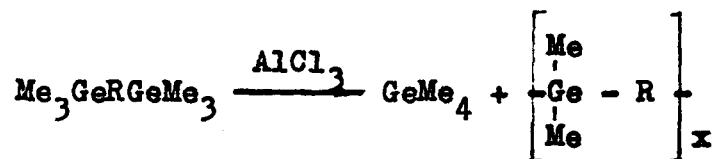
where  $\text{R} = \text{H}, \text{Alk}, \text{Cl}; \text{R}' = \text{H}, \text{Me}; \text{Hal} = \text{Cl}, \text{Br}.$

$$\begin{array}{c}
 \text{Hal}_3\text{GeCH}_2\text{CH}_2\text{OH} \xleftarrow{\text{CH}_2-\text{O}-\text{CH}_2} \text{Hal}_3\text{GeH} \xrightarrow{\text{H}_2\text{CO}} \text{Hal}_3\text{GeCH}_2\text{OH} \xrightarrow{\text{PCl}_5} \text{Hal}_3\text{GeCH}_2\text{Cl} \\
 \text{Hal}_3\text{GeC}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_2\text{OH} \xleftarrow{\text{MeC}(\text{O})\text{Me}} \text{Hal}_3\text{GeH} \xrightarrow{\text{MeC}(\text{O})\text{H}} \text{Hal}_3\text{GeC}(\text{Me})_2\text{CHOCH}(\text{Me})_2\text{GeHal}_3
 \end{array}$$
$$\text{Cl}_3\text{GeCH}_2\text{OH} + \text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \text{O} \longrightarrow \text{GeCl}_2 \cdot \text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \text{O}$$

$\text{CH}_2\text{Cl}_2 \xrightarrow{\text{Ge}} \text{Cl}_2\text{Ge}-\text{CH}_2-\text{GeCl}_2-\text{CH}_2-\text{GeCl}_2-\text{CH}_2-\text{GeCl}_2 \xrightarrow{\text{AlCl}_3} \text{Cyclohexane-1,3,5-triyl tris(germyl)chloride}$

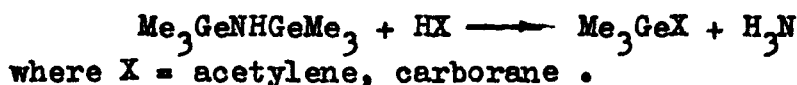
$$\begin{array}{ccc} & \text{CH}_2 & \\ \text{Me}_2\text{Ge} & \diagup \quad \diagdown & \text{MMe}_2 \\ & (\text{CH}_2)_n & \end{array}$$

The bridged germanium compounds in contrast to their silicon analogues showed more tendency to the following reactions:

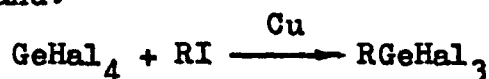



where R = CH<sub>2</sub>; C<sub>2</sub>H<sub>4</sub>; O; NH .

Germazanes are proved to be more reactive than silazanes with protonated compounds:

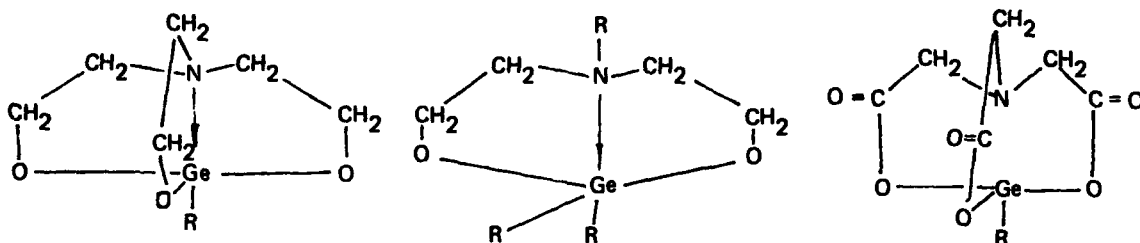


Finally, one more new reaction for Ge-C bond formation has been found:

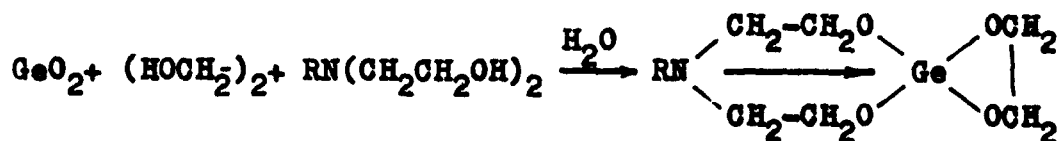


where R = Me, Pr, CH<sub>2</sub>I, Ph , n-PhI, Bu, All, α-Naf, m-MePh-.

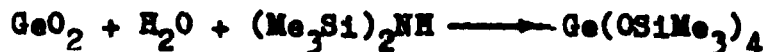
The chemistry of biological active five-coordinated germanium compounds (so-called germatranes and their analogues) as well as germyladamantanes and C-germylcarboxylic and hydroxamic acids received the particular attention.



Involving germanium dioxide in synthesis has substantially simplified the preparation of some germatranes and germacynes, for example:



Germanium dioxide react also with hexamethyldisilazane:



The extensive studies of biological activity of organic germanium compounds have been showed that because of low toxicity they exhibit high biological activity and favourably affect the different living organisms. Besides, in contrast to silicone compounds germanium compounds turned to be less toxic among the structure-like compounds.

Quite possibly germanium plays an independent role as a biochemical trace element and its deficiency could doubtlessly make itself felt in all living organisms as well as that among organic germanium compounds will be find that ones of great value for use in medical preparations.