

RECENT ADVANCES IN TRICHLOROGERMANE CHEMISTRY

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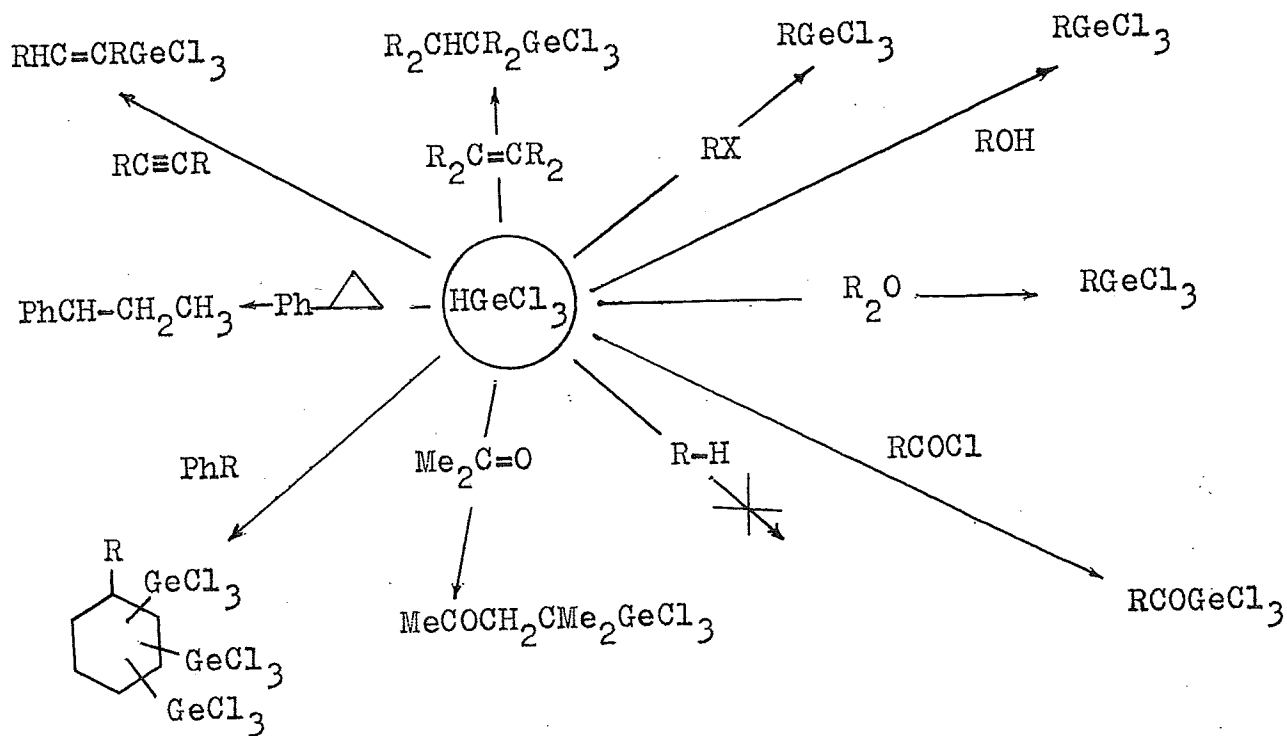
High reactivity and great variety of chemical properties of trichlorogermane determine its special place in organogermanium chemistry. Reactions of hydrogermylation of various unsaturated compounds and cyclopropane derivatives by trichlorogermane are widely known. Condensation and double germylation reactions are of preparative importance. In the course of many reactions trichlorogermane behaves as a source of dichlorogermylene, the studies in this direction having important influence on chemistry of carbene analogues. Finally, strong acidic properties of trichlorogermane made it possible to characterise it as a new superacid, which has interesting perspectives for the investigation of various aspects of ionic reactions.

Superacidic properties of HGeCl_3 and the mechanism of its interaction with aromatics

The exact determination of trichlorogermane acidic properties involves experimental difficulties. First of all, trichlorogermane in its pure state, being a covalent compound, cannot be considered an acid. Its ionization takes place only in the presence of substrates or some other substances, for instance,

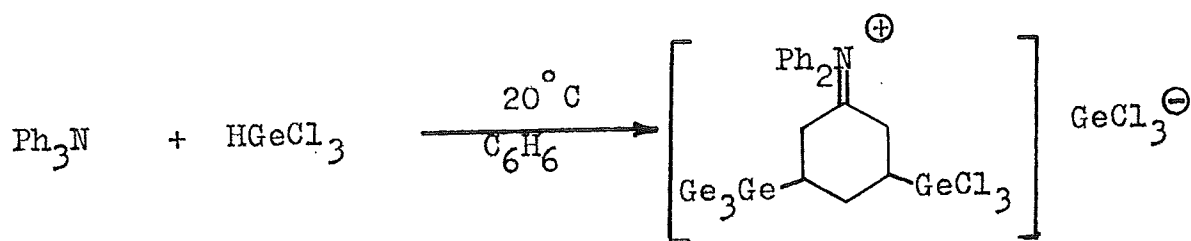
n-donor bases, i.e. ethers, amines or phosphines. So only indirect estimation of acidic properties of $\text{H}^+ \text{Ge}^{\text{II}}\text{Cl}_3^-$ in a solvated form can be made. Such estimation was given using IR-spectroscopy /1/. The method is based on the fact that via strong interactions of acids AH and base B a protonated form BH^+ is regarded as a standard acid which forms a hydrogen bond in ionic pairs $\text{BH}^+ \dots \text{A}^-$. Herein a frequency shift of B-H vibrations is used for the comparative estimation of strength of bases A^- or, in other words, effective values of pK_a of corresponding acids AH. It was found that the Hammett acidity function H_0 for trichlorogermane was equal to ≈ -13.0 and close to that of HClO_4 .

In consideration of superacidity a surprising reactivity of trichlorogermane, exceeding the reactivity of other hydrides of elements of the group IV B, becomes quite comprehensible. Fig. shows certain trichlorogermane reactions proceeding at room temperature and moderate heating in the absence of catalysts.



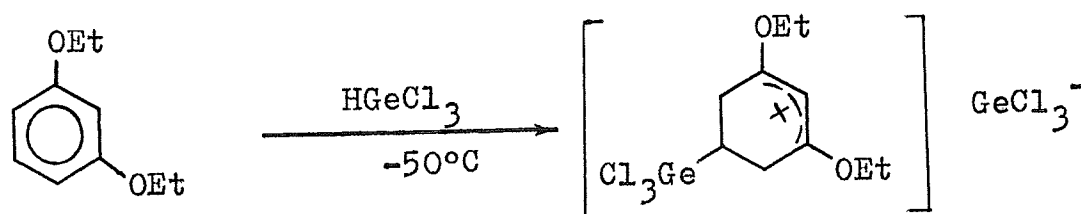
The formation of products here can be referred to the intermediate participation of carbocations, arenonium ions, acylcations and oxonium ions. The temptation arises to notice a surprising similarity of this illustration with the scheme of the formation of stable carbocations in superacids given in Olah's review /2/. Trichlorogermane is unsufficiently strong acid only for the activation of the C-H bond in hydrocarbons. A principal distinction of HGeCl_3 from other superacids lies in the properties of the GeCl_3^- counter-ion. It is known that counter-ions of conventional superacids have an exceptionally low nucleophilicity being widely use for obtaining and study of stable carbocations. On the contrary, HGeCl_3 is considered an example of a superacid, the counter-ion ^{of} which tends to a rapid recombination with many organic cations with the formation of stable covalent compounds with a rather stable Ge-C bond (bond energy 57-59 kcal/mol). At the same time, as it will be seen below, GeCl_3^- anion does not recombine with some cations. Thus, trichlorogermane represents an uncommon example of an acid with the anion of an moderate nucleophilicity, protonating properties of which correspond to those of superacids.

Stable iminium salt with the GeCl_3^- anion. The ability of trichlorogermane as an acid to form stable organic salts with the GeCl_3^- anion was for the first time observed in the study of the reaction of HGeCl_3 with triphenylamine. It was found that at room temperature their interaction lead to the formation of an unusual salt of iminium, i.o. trichlorogermanate 3,5-bis(trichlorogermyl)cyclohexylidendiphenyliminium in the 92% yield /3,4/.



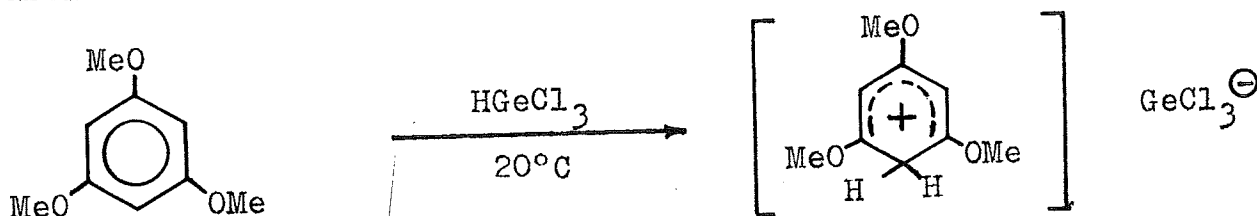
Crystalline salt of iminium was isolated in pure state and fully characterized. Conformation features of this salt cation were also studied.

Cyclohexenyl cation with the GeCl_3^- anion. A principal result was obtained in the study of HGeCl_3 reaction with 1,3-diethoxybenzene. In this reaction at -50°C in CD_2Cl_2 the 1,3-diethoxy-5-trichlorogermylcyclohexenyl cation stable under these conditions during many hours was formed /5/.



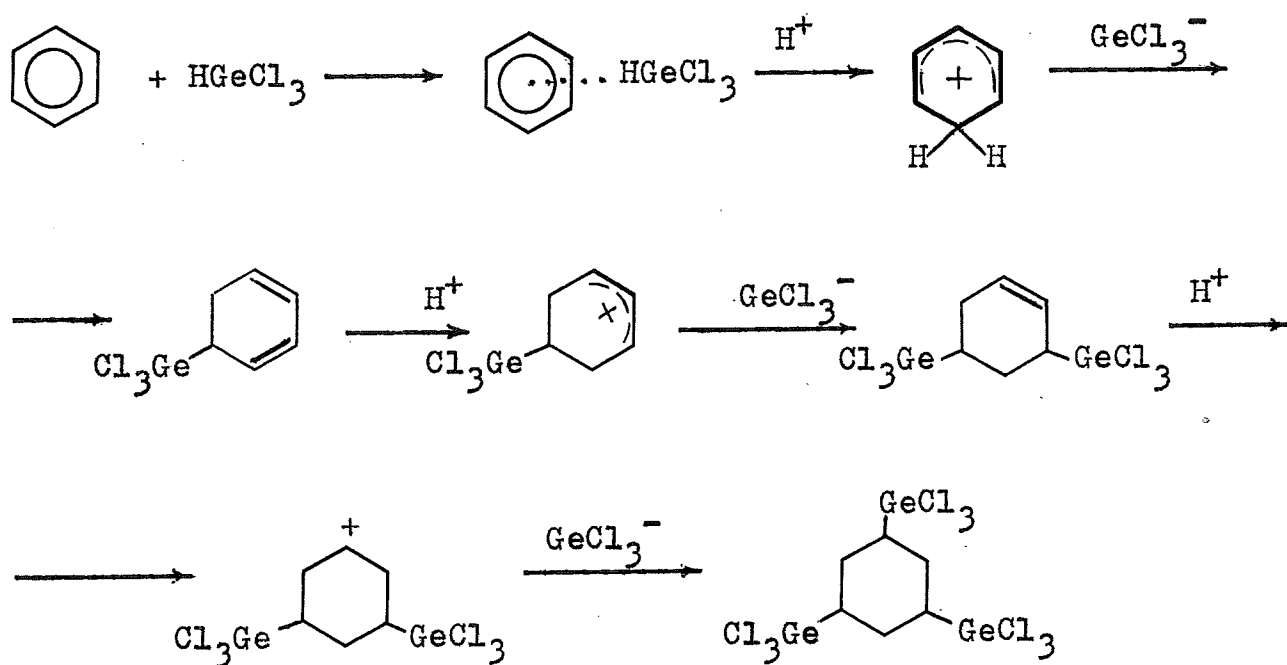
The first carbocation of the allyl type stabilized by GeCl_3^- anion, being formed in the yield close to the quantitative, was characterized at -50°C by IR, UV, NMR ^1H and ^{13}C spectra.

Stable σ -complex with GeCl_3^- anion. In the case of the reaction of HGeCl_3 with 1,3,5-trialkoxybenzene we hoped to detect the σ -complex experimentally. Actually, in the course of this reaction in the CD_2Cl_2 solution a quantitative formation of the arenonium ion was observed.



The obtained arenonium ion, stable for an hour even at room temperature /6/, was characterized by IR, UV, NMR ^1H and ^{13}C spectra.

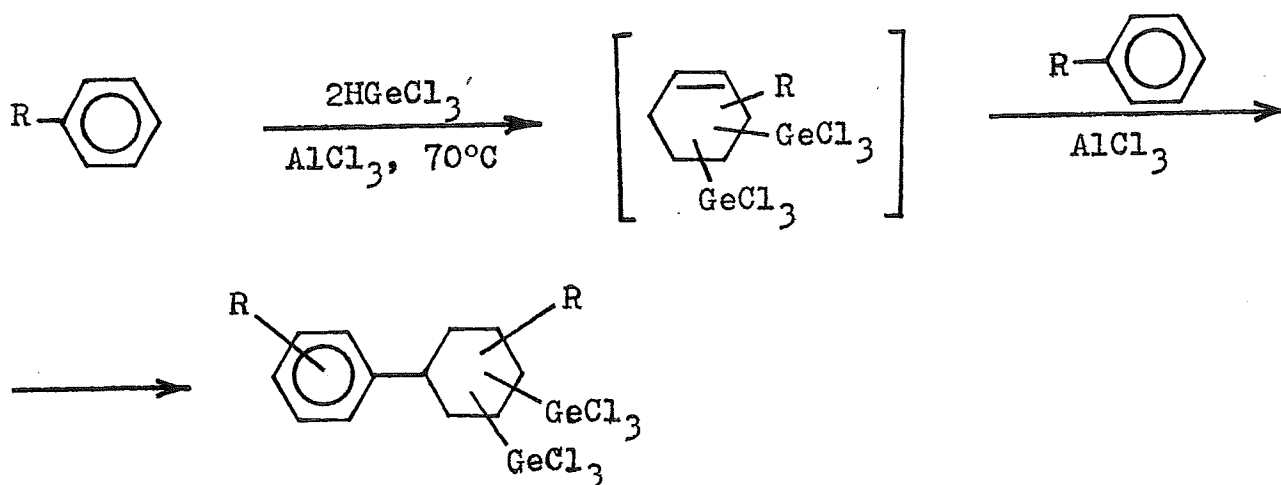
A general scheme of hydrogermylation of aromatics by trichlorogermane. The general scheme vividly reflects a sequence of heterolytic stages of exhaustive hydrogermylation of the aromatic rings.



Limitating stages are undoubtedly represented here by stages of σ -complex and cyclohexadiene derivative formation. We suggested that a protonating ability of HGeCl_3 could be increased by the addition of strong Lewis acids thus making it reactive to those aromatic compounds to which it was inert.

It is known that trichlorogermane does not hydrogermylate benzene and toluene when refluxed for many hours, though a deuterium exchange reaction occurs /7/. Only under drastic conditi-

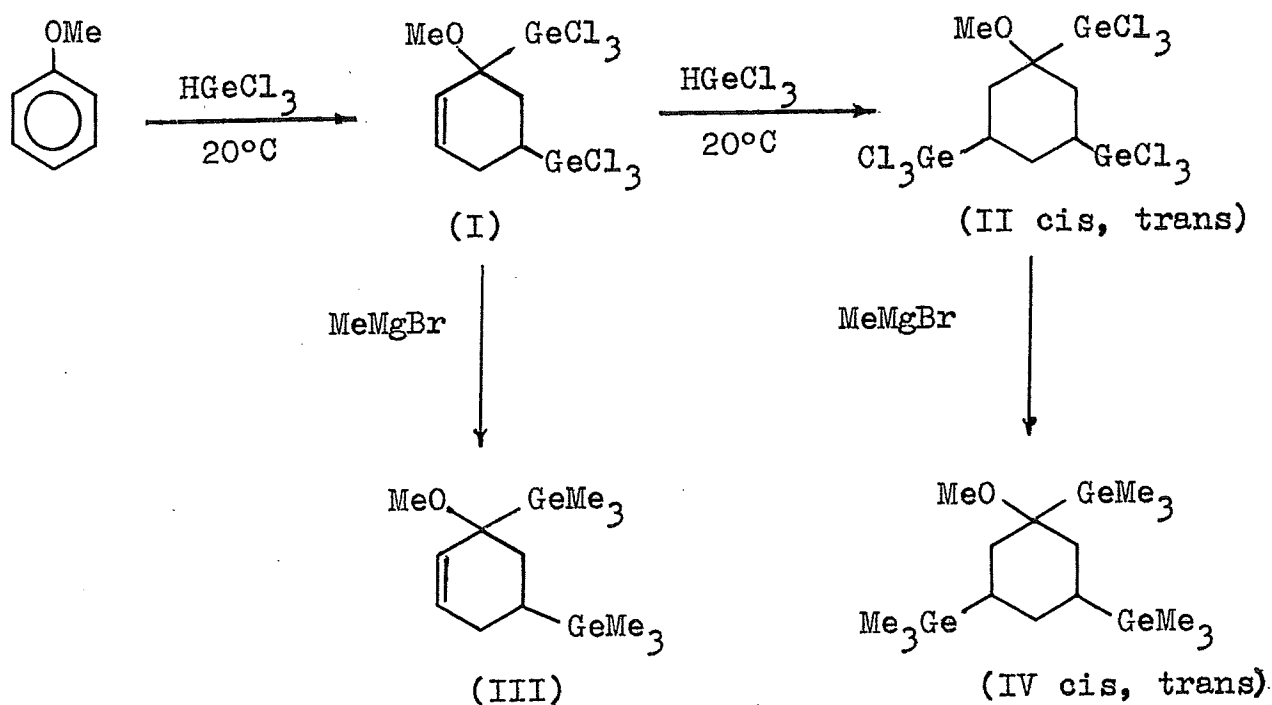
ons (8-14 kbar and at 80-140°C) the reaction leads to the formation of isomeric bis(trichlorogermyl)-cyclohexenes /8/. It was found that in the presence of catalytic amounts of AlCl_3 in sealed glass tube at 70°C during 3-5 days benzene and toluene undergo the interaction with HGeCl_3 according to the hydrogermylation scheme /9/.



However, not only acidic properties of HGeCl_3 or systems on its basis determine the addition to aromatic carbon-carbon bonds in contrast to the other HX acids. Specific features of HGeCl_3 are probably manifested at the stage of the cyclohexadiene derivative formation. The energy loss is obvious during the conversion from σ -complex to cyclohexadiene. The formation of the cyclohexadiene- GeCl_2 complex (the latter existing in the reaction mixture as a result of the well-known $\text{HGeCl}_3 \rightleftharpoons \text{HCl} + \text{GeCl}_2$ equation) is likely to be responsible for the equilibrium shift in the direction of cyclohexadiene.

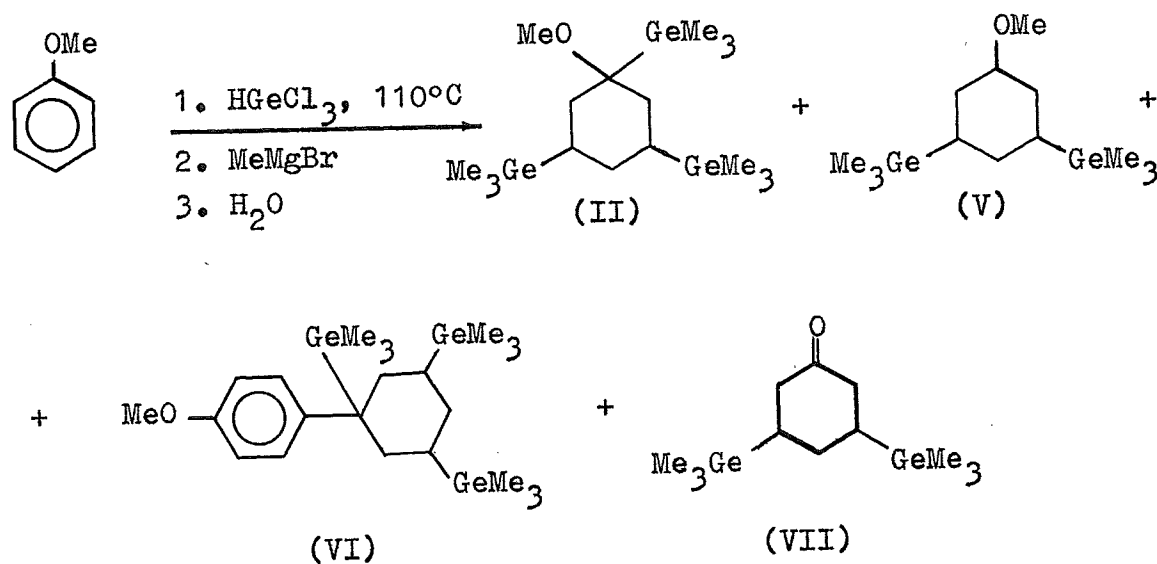
Reactions of HGeCl_3 with aromatic compounds

Anisole. A detailed study of HGeCl_3 interaction with anisole displayed a strong dependence of the character and ratio of the products from the reaction conditions /10/. The interaction of the HGeCl_3 excess with anisole (molar ratio 3:1) proceeds most selectively at room temperature, leading to 1-methoxy-1, cis-3, trans-5-trans(trichlorogermyl)cyclohexane (II cis, trans) in the 82% yield in 72 hours. According to the NMR ^1H spectra in the course of the reaction an intermediate compound is being formed, the concentration of which reaches its maximum value of 22% in 12-16 hours and then drops down. This is the product of double hydrogermylation of anisole - 3-methoxy-3,5-bis(trichlorogermyl)cyclohexene (I), which was isolated and identified as a methylated derivative (III).



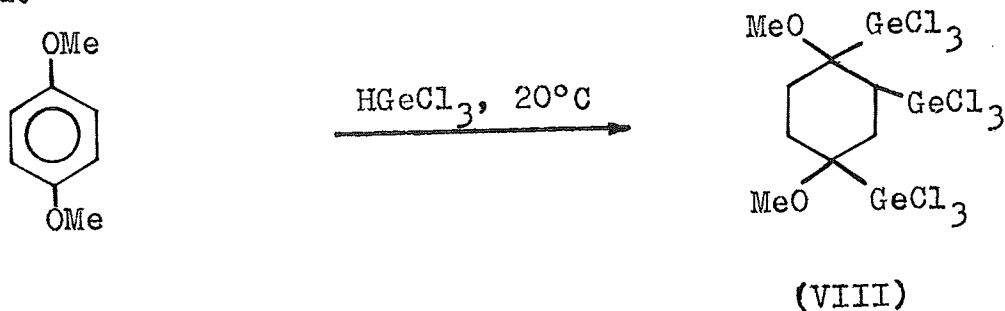
This reaction proceeds considerably less selectively at 110°C. In this case another isomer - 1-methoxy-*r*-1, *cis*-3, *cis*-5-tris(trichlorogermeryl)cyclohexane (II *cis*, *cis*), isolated in the form of a methylated derivative, yield 23%, is mainly formed.

Along with (II) 1-methoxy-3,5-bis(trimethylgermyl)cyclohexane (V) (yield 15%), 1-(4-methoxyphenyl)-*r*-1, *cis*-3, *cis*-5-tris(trimethylgermyl)cyclohexane (VI) (yield 20%), as well as 3,5-bis(trimethylgermyl)cyclohexanone (VII) (yield 15%, the ratio of *cis*- to *trans*-isomers here is 3:1) were isolated from the reaction mixture.

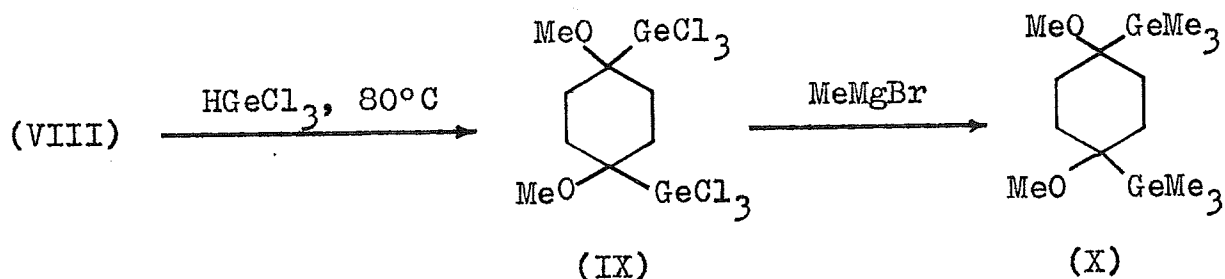


1,4-Dimethoxybenzene. As expected, the presence of the second electrono-donor group in 1,4-dimethoxybenzene noticeably increases the rate of its interaction with HGeCl_3 as compared with anisole /10/. With the triple excess of HGeCl_3 at room temperature the interaction is completed during 4-5 hours leading to 1,4-dime-

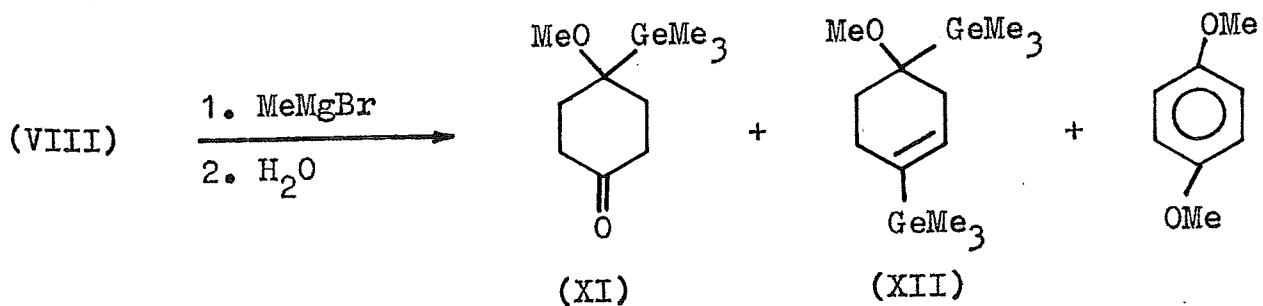
thoxy-1,2,4-tris(trichlorogermyl)cyclohexane (VIII) in the 85% yield.



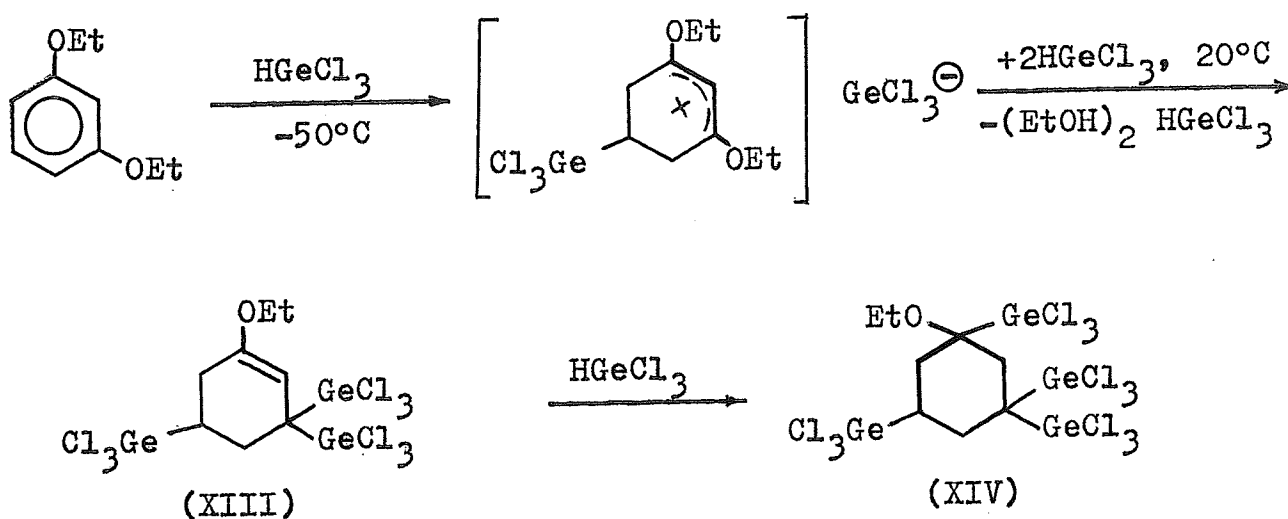
The presence of bulky trichlorogermyl groups in the geminal and neighbouring positions in (VIII) causes its easy hydrogenolysis (protodegermylation) under the action of the trichlorogermene excess at 80°C. The yield of (IX) achieves 43%.



The treatment of (VIII) by the excess of MeMgBr in ether followed by hydrolysis does not lead to the corresponding tris-trimethylgermyl derivative, but yields the mixture of 4-methoxy-4-trimethylgermylcyclohexanone (XI) (35%), 4-methoxy-1,4-bis(trimethylgermyl)cyclohexene (XII) (17%) and 1,4-dimethoxybenzene (21%).

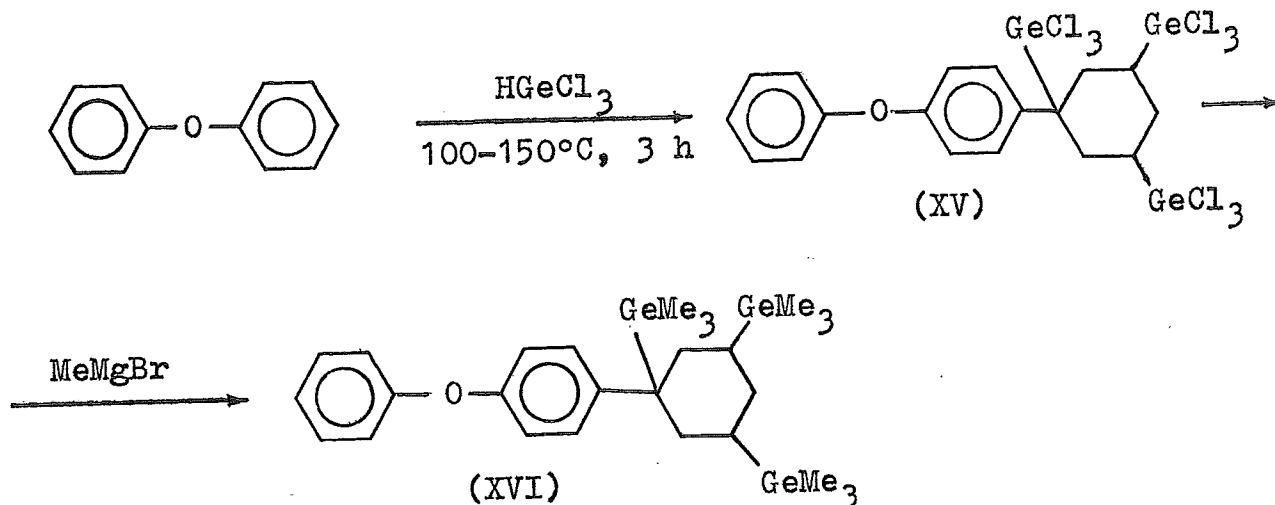


1,3-Diethoxybenzene. A cyclohexenyl cation resulting from the reaction of HGeCl_3 with 1,3-diethoxybenzene at -50°C during the heating of the reaction mixture to room temperature undergoes the following conversions:

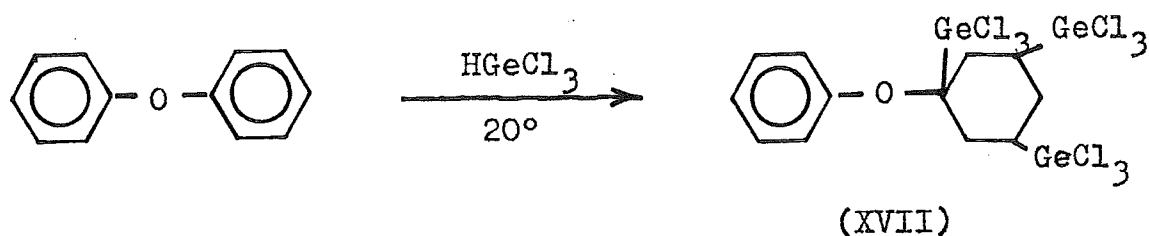


The compound (XIV) (yield 85%) was characterized by complete X-ray analysis /11/.

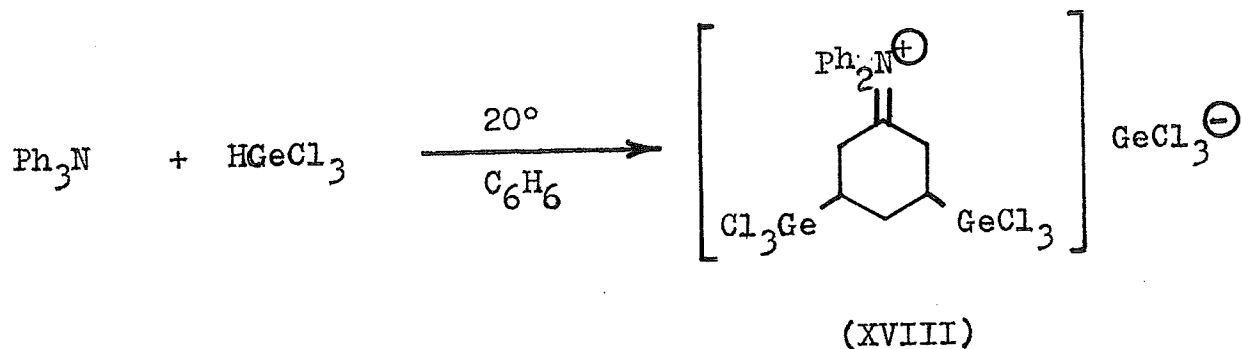
Diphenyl ether. Alkylation takes place during the HGeCl_3 interaction with the excess of diphenyl ether at $100\text{--}150^\circ\text{C}$, along with hydrogermylation of the aromatic ring /12/.



1,3,5-Tris(trimethylgermyl)-1-(p-phenoxyphenyl)cyclohexane (XVI) was characterized by X-ray analysis data (total yield 70%). The structure of (XVI) indicates that the interaction of HGeCl_3 with diphenyl ether should include the stages of total hydrogermylation of one ring of diphenyl ether, cleavage of the ether C-O bond and alkylation another molecule of diphenyl ether into para-position by the carbenium ion formed at the previous stage. We confirmed the existence of the first stage by the isolation of product (XVII) when reaction runs at 20°C .



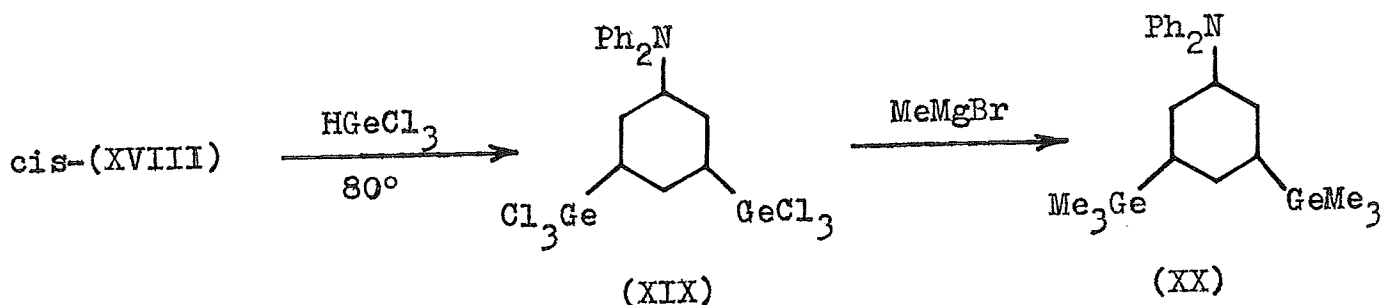
Triphenylamine. As it was mentioned above, triphenylamine with HGeCl_3 at 20°C forms iminium salt - trichlorogermanate of 3,5-bis(trimethylgermyl)cyclohexylidene diphenyliminium (XVIII) (yield 92%) /3,4/.



A detailed study of the reaction using NMR ^{13}C spectroscopy showed that initially formed (XVIII) was an isomer with trans-

configuration of germyl groups (in relation to the conditional plane of the cyclohexane ring which existed in twist-conformation). Trans-isomer (XVIII) isomerises into cis-isomer (XVIII) for 85% at 25°C in 2 hours. This ratio does not further change. Crystall cis-isomer (XVIII) was isolated in a pure state and completely identified.

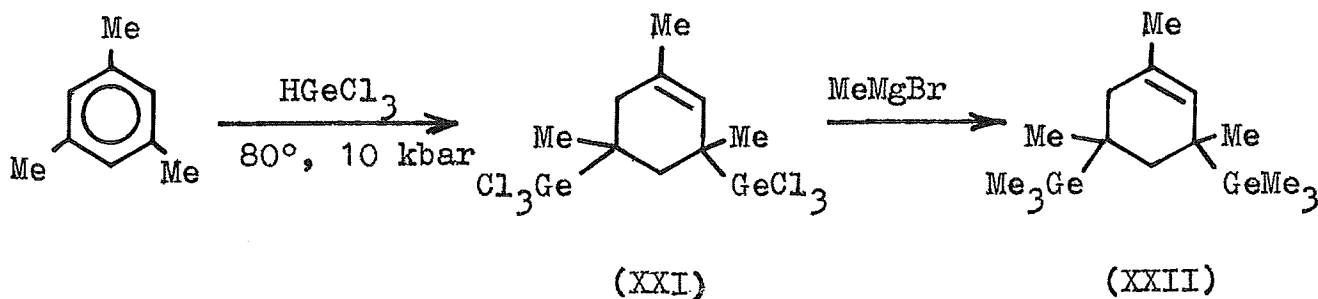
The change of the reaction conditions of triphenylamine with HGeCl_3 leads to the formation of some other products. With the increase of reaction temperature from 20 to 80°C and a 4-5 fold molar excess of HGeCl_3 the initially formed cis-(XVIII) converts into a product of formal hydration - 1-diphenylamino-3,5-bis(trichlorogermyl)cyclohexane (XIX) isolated in the 58% yield as a methylated derivative (XX).



Cyclohexane (XX) represents a mixture of two geometric isomers in the ratio of 2:1, having different positions, i.e. axial and equatorial, of the diphenylaminogroup. Both germyl group in (XX) are equatorial thus preserving the configuration of initial cis-(XVIII). Methylation of cis-(XVIII) salt by the excess of MeMgBr in ether leads to the cleavage of the carbon-nitrogen bond with the formation of diphenylamine (83%) and 3,5-bis(trimethylgermyl)cyclohexanon (VII) (12%).

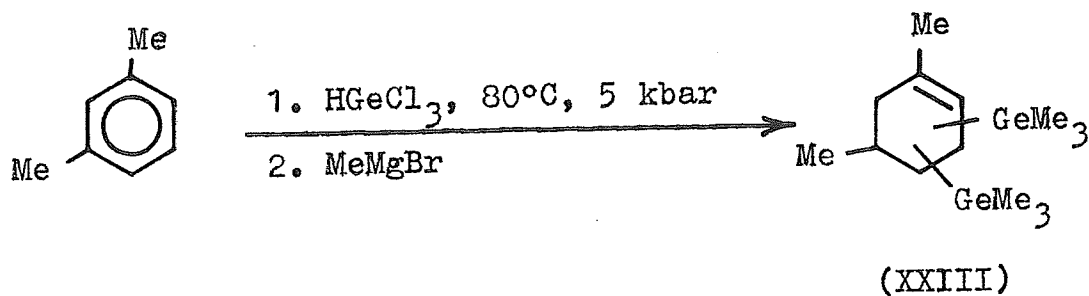
Methylbenzenes. Under 5-14 kbar methylbenzenes easily add HGeCl_3 /8/. Since ionic reactions, in the course of which the number of ions does not change, are slightly accelerated by pressure hydrogermylation of methylbenzenes by trichlorogermane obviously includes here a slow stage according to the molecular mechanism.

Mesitylene undergoes hydrogermylation most easily and selectively. In the molar ratio of HGeCl_3 :mesitylene=2:1 the conversion of both compounds at 80°C and 10 kbar for 2 hours results in 100%. The product of double hydrogermylation, a corresponding cyclohexene (XXI) (93%), is the main one. The products of three HGeCl_3 molecules addition are not observed even when a considerable excess of the HGeCl_3 is used.

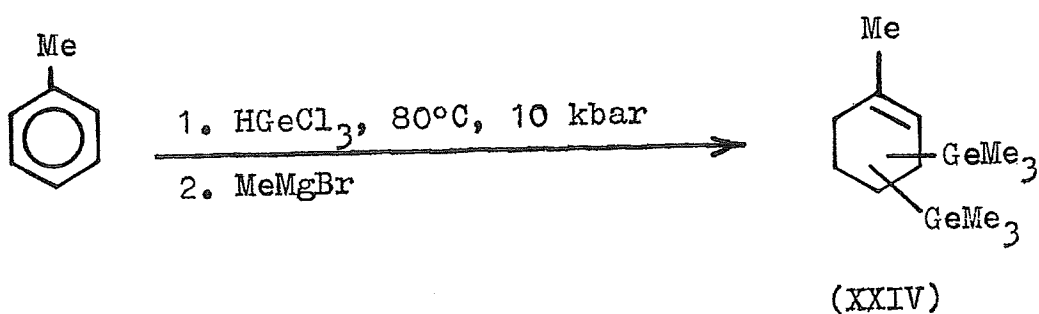


Both compounds (XXI) and (XXII) were isolated and identified.

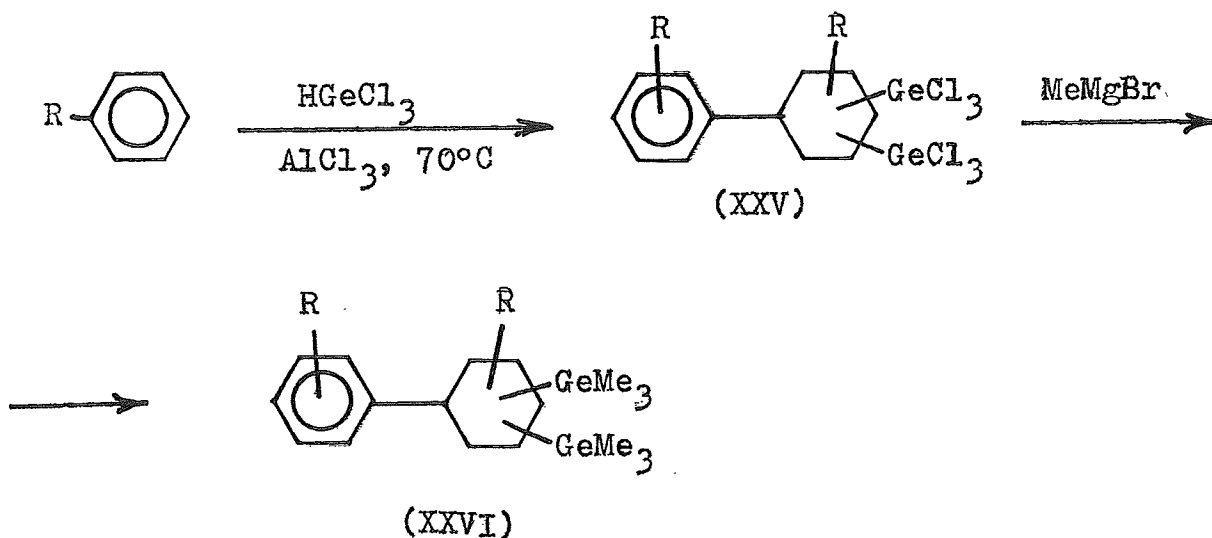
In the reaction of m-xylene with HGeCl_3 independently of their molar ratio main products are also those of double germylation - isomeric cyclohexenes obtained in the form of methylated derivatives (XXIII) (total yield 50%).



The interaction of HGeCl_3 with tolylene proceeds in a similar way.

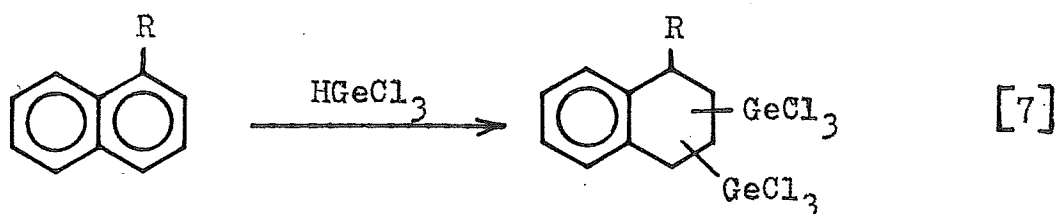


In the presence of catalytic amounts of AlCl_3 at 70°C benzene and tolylene interact with HGeCl_3 under usual pressure (75-80% conversion for 3-5 days). Herein a complicated reaction mixture in which compounds of type (XXV) are predominant, is formed.

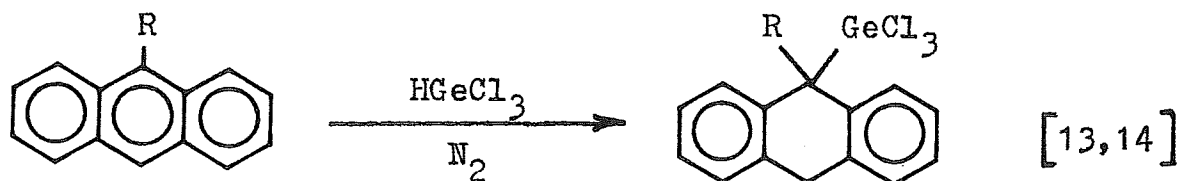


Compounds (XXV) obtained in the form of the mixture of isomers (2 isomers for R=H and 4 isomers for R=Me) were isolated and identified /9/.

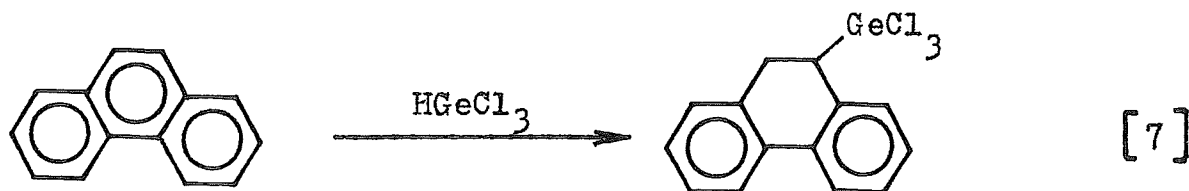
Condensed aromatics. Naphthalene, anthracene and phenanthrene easily add HGeCl_3 according to the schemes:



(XXVII)



(XXVIII)



(XXIX)

Thus, hydrogermylation of aromatic compounds by trichlorogermane is a new effective method of synthesis of organogermane-

mium derivatives. A possibility of the exchange of germil groups for other functional ones allows to consider this reaction as perspective in organic synthesis. A search of selective reactions of Ge-C bond cleavage is an urgent problem.

Finally, the introduction of germyl groups into an organic compound often increases the biological activity of the latter. In this connection the search of Ge-containing drugs, especially antitumor and antiviral ones, has good prospects. On the bases of trichlorogermane reactions we are studying possible ways of synthesis and looking for biological activity of polynucleus germanes, carboxygermaniumsesquioxanes, Ge-containing 2'-desoxyuridines and antibiotics.

References

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