

REACTIVE INTERMEDIATES IN ORGANOGERMANIUM CHEMISTRY

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Abstract - New aspects of germylene reactivity are reported. The insertion reactions of halogermynes into metal-metal bonds of various organometallic compounds lead to trimetallated compounds. The insertion reaction into silicon-transition metal bonds usually leads to unstable adducts which decompose by an α -elimination process to give the first germynes with germanium-transition metal bonds. These new divalent germanium species give specific germylene reactions. Cycloaddition with 2,3-dimethylbutadiene leads to germacyclopentene and shows unusual thermal reversibility. Insertion of these new germynes into transition metal-transition metal bonds gives polymetallated compounds.

The reactions of germynes with small organic or organometallic heterocycles such as : oxiranes, thiranes, oxaziranes and 1,3-cycloaddition with nitrones lead to unstable four-membered germaheterocycles which give, by β -elimination, germanium doubly bonded intermediates ($\text{Ge}=\text{Y}$, $\text{Y}=\text{O}, \text{S}, \text{NR}$).

The reactions of germynes with diazoderivatives (or carbenes) and organic azides (or nitrenes) are a new and interesting route to germylenes and germa-imines, i.e. species with germanium doubly bonded to carbon and nitrogen.

Digermylenes (α -digermyl radicals) $\text{Ge}=\text{Ge} \rightleftharpoons \text{Ge}-\text{Ge}$ generated by photolysis of polygermylmercury compounds or cyclopolygermanes have been characterized by several trapping reactions with dimethyl disulfide, biacetyl and 2,3-dimethylbutadiene.

INTRODUCTION

During the last years, considerable interest and numerous investigations have concerned organometallic intermediates with a metal with an unusual degree of coordination. The interest of these intermediates is great from the fundamental, theoretical and synthetic points of view. Several general articles or reviews recently published have shown the rapid development of research in the field of organometallic intermediates of IV_b group (Ref. 1, 2 & 3). The interest devoted to carbene chemistry (Ref. 4 & 5) has given rise to the great development of studies into divalent species of IV_b group germynes (Ref. 1 & 6-10), silylenes (Ref. 2, 4, 10 & 11) and stannynes (Ref. 3, 10 & 12).

Germyl radicals ($\text{R}_3\text{Ge}\cdot$) and monovalent species of germanium (germynes), analogs of carbynes, have been characterized in the photolytic oxido-reduction of germynes (Ref. 1 & 13) and in the photolysis of organogermanium-mercury compounds (Ref. 14).

Moreover, short-lived and highly reactive germanium doubly bonded intermediates have been recently obtained, mainly from germynes (Ref. 15 & 16).

All these species (germynes, germynes, germanium doubly bonded intermediates, germyl radicals and germylanions) appear as powerful synthetic agents in organometallic chemistry (Ref. 1, 6-10 & 14-18). The germynes and particularly the halogermynes (GeX_2 and RGeX) have a strong electrophilic activity (Ref. 1 & 6). Ab initio calculations show that the germynes have singlet ground state (Ref. 19).

The germynes exhibit properties analogous to those of carbenes (Ref. 4 & 5) and silylenes (Ref. 2 & 11) and have been shown to insert in various σ bonds of organic and organometallic compounds and to add to various π bonds (Ref. 1 & 6-10).

New aspects of the reactivity of germynes towards metal-metal bonds, small organic and organometallic heterocycles and electron-deficient species such as carbenes and nitrenes (or their precursors: diazo-derivatives and organic azides respectively) are described.

Generation and characterization of new digermynes (or α -digermyl radicals) are also described.

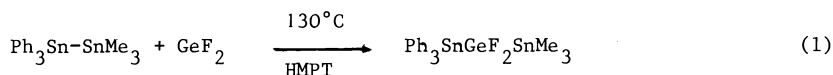
INSERTION REACTIONS OF GERMYLENES INTO METAL-METAL BONDS

Insertion reactions of divalent metal (IV_b) species into metal-metal bonds provide an easy route to various polymetallated compounds (Ref. 1) $\text{X}_2\text{MIV}_b(\text{M}'\text{Ln})_2$.

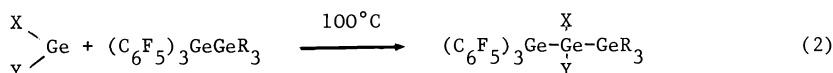
Insertion reactions of germynes into metal-metal bonds have been described in the literature (Ref. 1, 6 & 20).

Insertion into metal-IVb-bonds

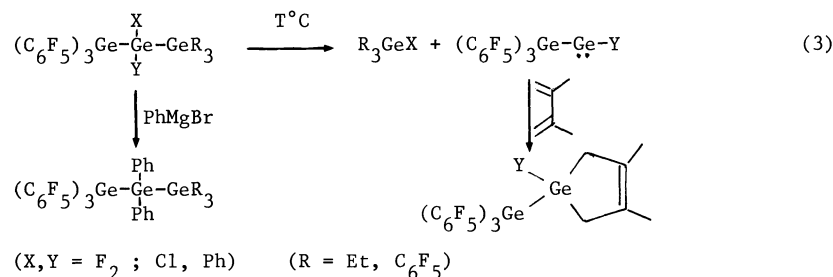
Difluorogermylene which has a strong electrophilic activity inserts into the Sn-Sn bond of triphenyltrimethyldistannane (Ref. 21) (equation 1)



Difluorogermylene and phenylchlorogermylene insert into the very reactive germanium-germanium bonds of pentafluorophenyldigermene (equation 2)

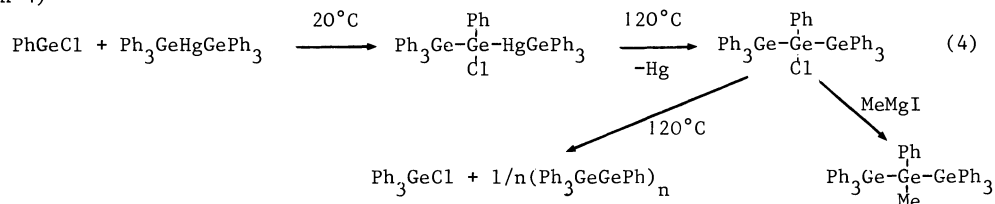


The trigermanses so obtained are stable at room temperature but decompose through a thermally induced α -elimination process to give the corresponding halogermanses and germylgermylenes (Ref. 22) (equation 3)

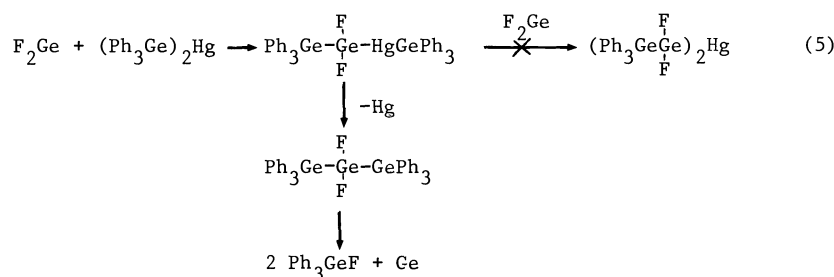


Insertion reactions into the germanium-mercury bond

Insertion reactions of germynes into the germanium-mercury bond of germylmercury compounds lead to digermylmercury compounds. The photolytic or thermal decomposition of these compounds allows, through a demercuration reaction, the formation of various polygermanes (Ref. 23) (equation 4)

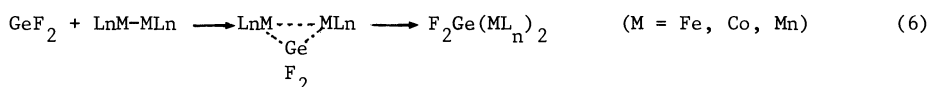


Even in the case of difluorogermylene only the monoinsertion derivative is observed without formation of tetragermene (Ref. 23) (equation 5)



Reactions with metalcarbonyl dimers (Fe, Co, Mn)

Depending on the nature of the halogen, the different dihalogermynes show different reactivities towards transition metal-transition metal bonds such Fe-Fe, Co-Co, Mo-Mo and Mn-Mn (Ref. 1, 6, 20 & 24). In order to determine the reactivity of difluorogermylene within the series GeI₂, GeBr₂, GeCl₂, GeF₂ we studied its reaction with transition metal complexes containing symmetrical or unsymmetrical transition metal-transition metal bonds or metal(IVb)-transition metal bonds (Ref. 25). Various polymetallated compounds have been obtained by insertion of pure difluorogermylene or of its complexes GeF₂.OR₂ (R₂O = ether, THF, dioxane) into metal-metal bonds of transition metal complexes (equation 6)



The products thus synthesized are shown in Table 1.

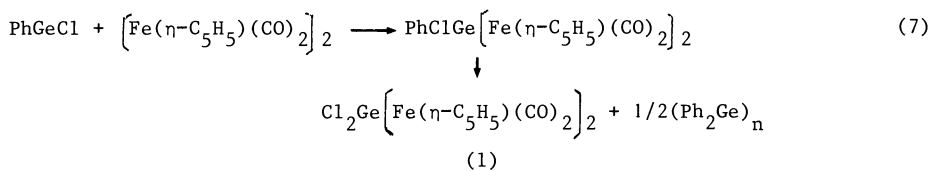
Table 1. Adducts from the insertion of GeF_2 into metal carbonyl dimers

Products	Yield %
$\text{F}_2\text{Ge}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]_2^*$	47
$\text{F}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	18
$\text{F}_2\text{Ge}[\text{Co}(\text{CO})_3\text{PPh}_3]_2$	45
$\text{F}_2\text{Ge}[\text{Co}(\text{CO})_3\text{P(OPh)}_3]_2$	32
$\text{F}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$	8

* (Ref. 26)

GeBr_2 does not insert into the Co-Co bond of $\text{Co}_2(\text{CO})_8$ or into the Mn-Mn bond of $\text{Mn}_2(\text{CO})_{10}$ (Ref. 24).

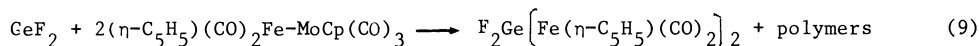
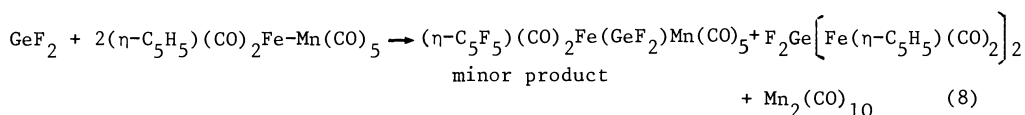
The results show that in these reactions difluorogermylene appears to have the greatest reactivity within the halogermylene series (Ref. 25). The less reactive organohalogermynes also give derivatives in thermally induced reactions. However, under these conditions a redistribution of ligands on germanium was observed leading to a symmetrization reaction with formation of stable (1) (Ref. 26) (equation 7)



Reactions with unsymmetrical complexes

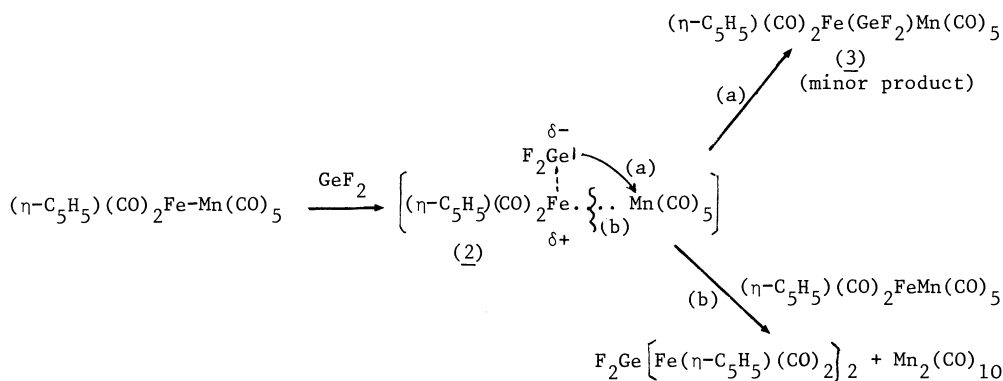
To date insertion reactions of germynes into unsymmetrical transition metal-transition metal bonds have not been reported.

Difluorogermylene, however, reacts with such complexes to give mainly symmetrical derivatives (Ref. 25) (equations 8 and 9)



The redistribution observed seems due to the decomposition of the reaction intermediate (2) formed. After initial electrophilic attack of the gerylene on the iron followed by the interaction between germanium and manganese reaction a would lead, through a bridged intermediate $\text{Cp}(\text{CO})_2\text{Fe} \cdots \underset{\text{GeF}_2}{\text{Mn}}(\text{CO})_5$, to the unsymmetrical adduct (3) which has been detected in

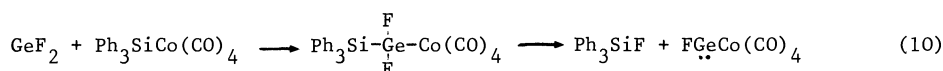
the reaction mixture by means of mass spectrometry. However, the breaking of the unsymmetrical Fe... Mn bond in (2) (reaction b) would lead to the observed symmetrization (Ref. 25) (Scheme 1).



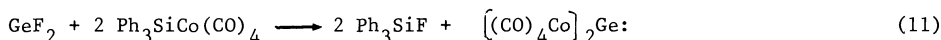
Scheme 1

Insertion into Metal(IVb)-transition metal bonds

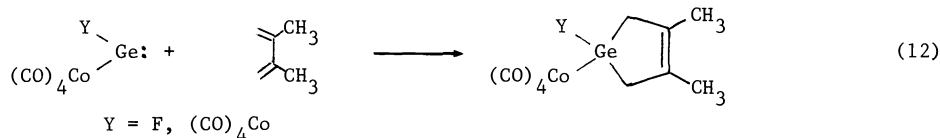
The insertion of difluorogermylene into the silicon-cobalt bond of $\text{Ph}_3\text{SiCo}(\text{CO})_4$ which leads to a polymetallated derivative of low stability has been studied (Ref. 25). The rapid decomposition of this intermediate via α -elimination gave the first halogermylene with a germanium-transition metal bond (equation 10)



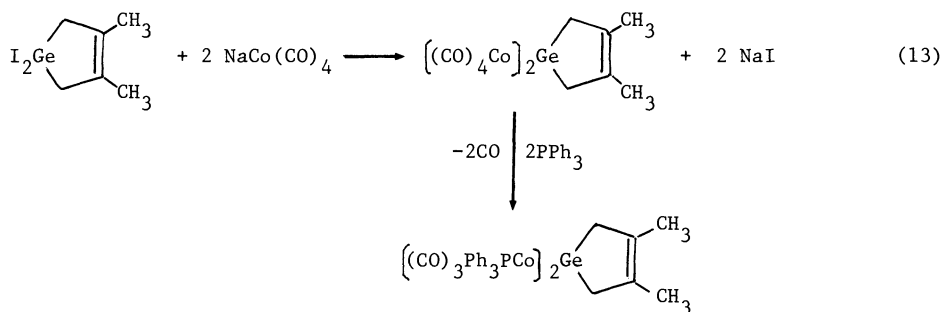
When an excess of $\text{Ph}_3\text{SiCo}(\text{CO})_4$ was used successive insertion and α -elimination reactions gave a novel germylene with two germanium-transition metal bonds (equation 11)



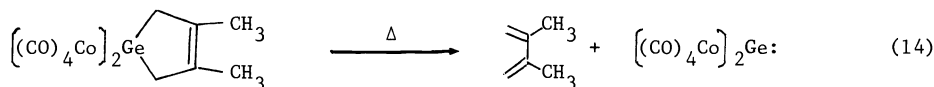
These hitherto unknown germynes gave a characteristic cycloaddition reaction (1) with 2,3-dimethylbutadiene (Ref. 25) (equation 12)



The germacyclopentenes thus formed in these reactions also can be synthesized, using substitution reactions, from 3,4-dimethyl 1,1-diodogermacyclopent-3-ene. Crystalline products were obtained with substitution of a carbonyl ligand by triphenylphosphine (equation 13)

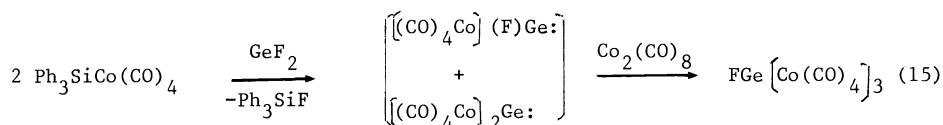


Such substituted germacyclopentenes decompose readily when heated with release of the diene to give the original germylene (equation 14)



Thus the two latter reactions could provide a general route to germynes with germanium-transition metal bonds starting from dihalogermacyclopentenes and transition metal anions (Ref. 25).

Such a germylene with a germanium-transition metal bond has also been characterized in the insertion reaction into octacarbonyldicobalt (Ref. 25) (equation 15)

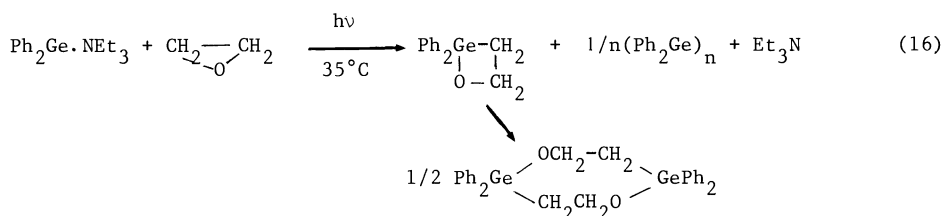


The adduct corresponding to the symmetrical germylene has not been detected. These insertion reactions of germylenes into M-M' metal bonds (M, M' = transition metal, metal_{IVb}) are of great interest. They lead to the formation of polymetallic compounds and previously unknown unsymmetrical and symmetrical germylenes with germanium-transition metal bonds. The chemistry and applications of these polymetallic compounds are under investigation.

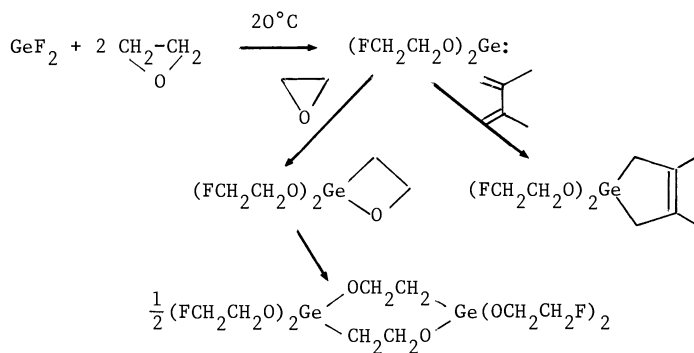
REACTIVITY OF GERMYLENES TOWARDS SMALL ORGANIC HETEROCYCLES

Germylenes and oxiranes

Insertion reactions in the oxirane ring are observed in the reaction of germylenes Ph_2Ge , PhGeX (X=F, Cl), GeF_2 with ethylene oxide (Ref. 27). These reactions lead to germaoxetanes which dimerise and give digermadioxocanes (equation 16)

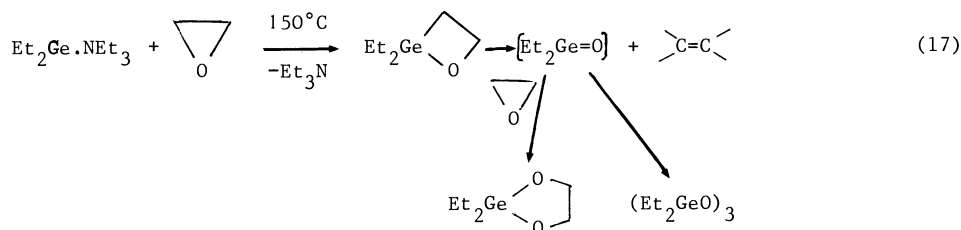


In the case of halogermynes, the first reaction is the cleavage of the oxirane ring followed by its insertion into the germanium-halogen bond. The newly formed haloethoxygermylenes react further by insertion into the oxirane ring (Ref. 27) (Scheme 2)

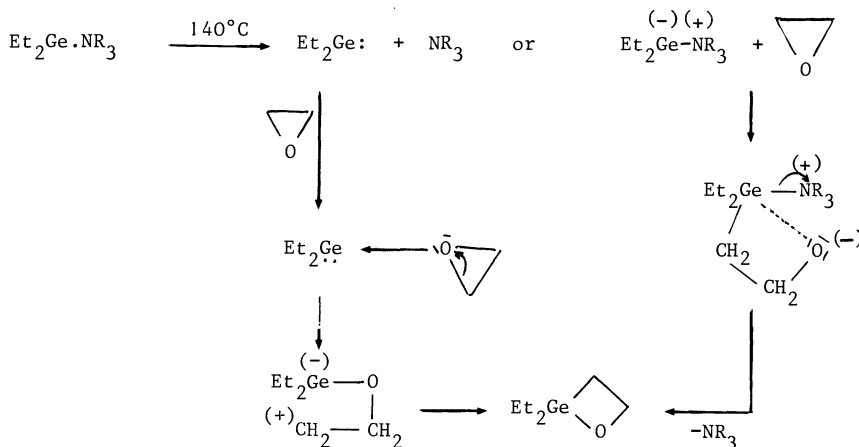


Scheme 2

Condensation of complexed dialkylgermylenes $\text{R}_2\text{Ge} \cdot \text{NEt}_3$ with various oxiranes (oxirane, phenyloxirane, 1,2-dimethyloxirane), gave, by insertion and ring expansion, the corresponding oxagermacyclobutanes. These thermally unstable heterocycles led via β -elimination reactions to transient dialkylgermanones which, by insertion into oxirane ring, formed germa-dioxolanes (Ref. 28) (equation 17)

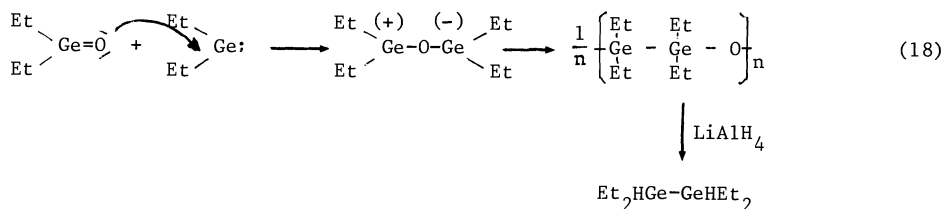


The insertion reactions of germylenes into the oxirane ring begin by complexation of germylene by oxirane followed by ring opening and ionic cyclisation. But the complexed germylene can also be the reactive intermediate (Ref. 28) (Scheme 3).

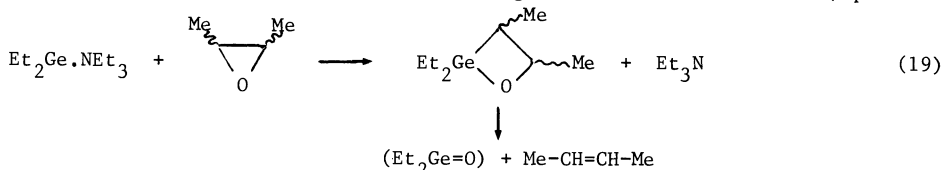


Scheme 3

Besides the main reaction, the formation of $\{\text{GeEt}_2\text{-GeEt}_2\text{-O}\}_n$ can be explained by nucleophilic attack of germylene by germanone (equation 18)

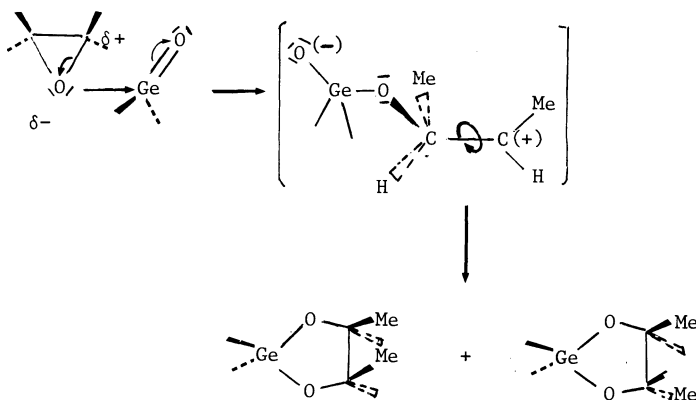


In the condensation reaction of complexed diethylgermylene with butene oxide in the presence of an excess of triethylamine: $\text{Et}_2\text{Ge} \cdot \text{NEt}_3/2\text{Et}_3\text{N}$, the almost exclusive formation of cis germadioxolane is observed (Ref. 29). The first step of the reaction is the formation of diethylgermanone after β -decomposition of unstable germaoxetane intermediate (equation 19)

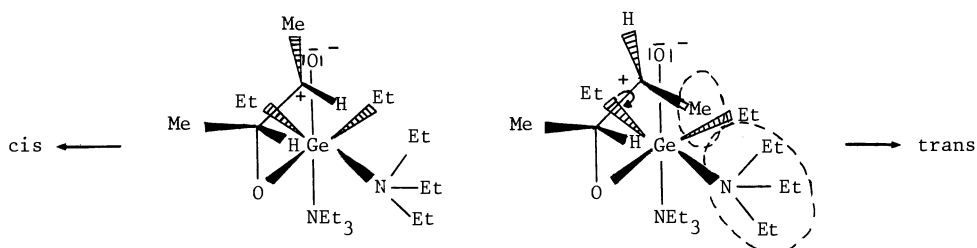


Diethylgermanone should lead to a mixture of cis and trans adducts (Ref. 29) (Scheme 4a). This high stereoselectivity in the presence of triethylamine seems to pass, after nucleophilic attack of oxygen on germanium followed by ring opening, by a complex with a germanium hexacoordinated by two molecules of triethylamine.

The study of molecular models shows very strong steric hindrance between the methyl group and the triethylamino group in the equatorial position in the bipolar intermediate during the cyclization process. The position of least hindrance is that where the two methyls are in the cis position opposite to the triethylamino group, leading to the cis isomer (Ref. 29) (Scheme 4b)



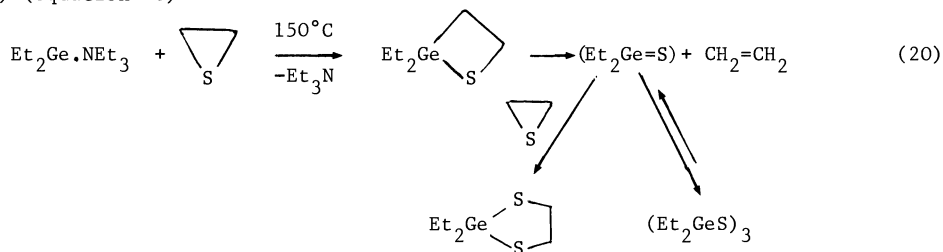
Scheme 4a



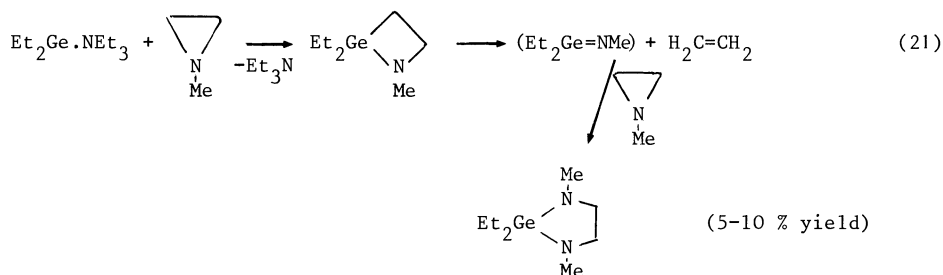
Scheme 4b

Germynes and thiirane

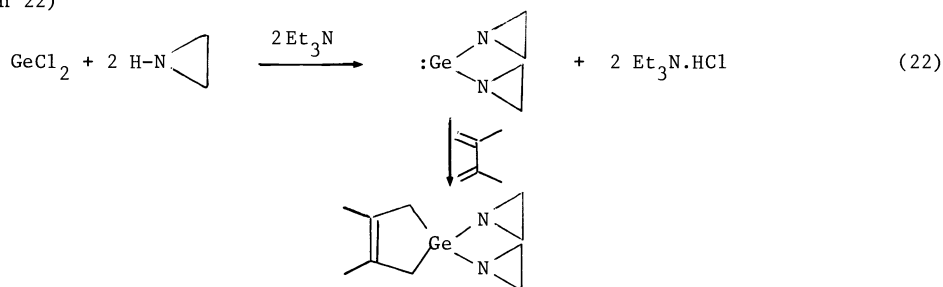
The action of complexed diethylgermylene on thiirane leads to germadithiolane via the formation of unstable germathiacyclobutane. The equilibrium between monomeric diethylgermathione and its trimeric form can explain the rather good yield of germadithiolane (60%) (Ref. 28) (equation 20)

Germynes and aziridines

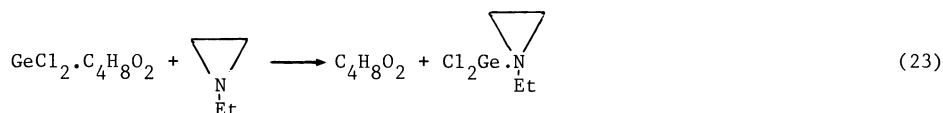
The reaction between diethylgermylene and N-methylaziridine leads to germadiazolidine in low yields probably via an unstable germaazetidine intermediate (Ref. 28) (equation 21)



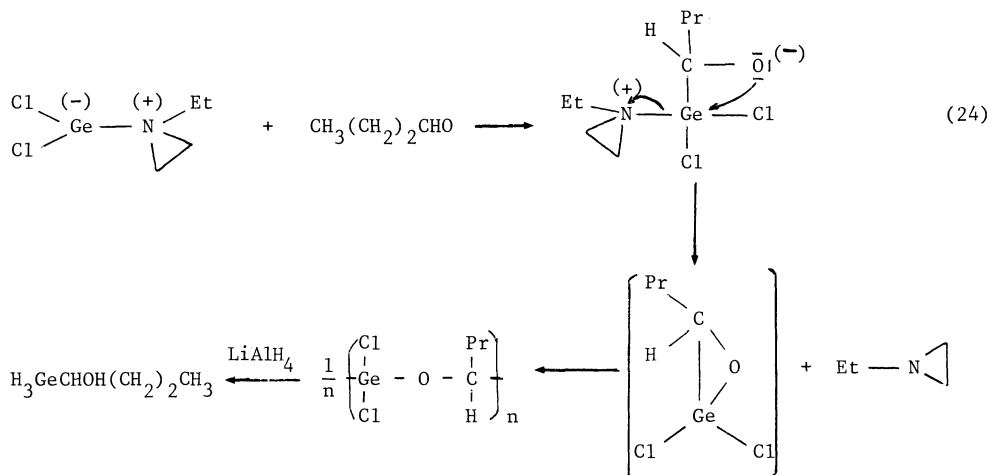
With the halogermynes, ammonolysis or complexation are mainly observed (Ref. 28 & 30) (equation 22)



Dichlorogermylene and N-ethylaziridine give complexation reactions (equation 23)

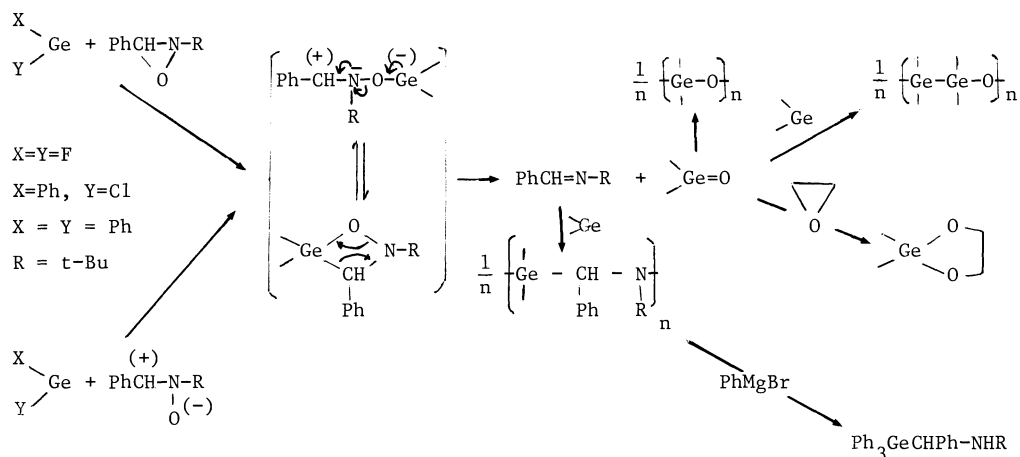


This complex or its ylide form, shows reactions characteristic of germynes (Ref. 1), insertion reaction in the C-Br bond of EtBr (Ref. 28) and condensation reactions on the carbonyl group (Ref. 28 & 31) (equation 24)



Germynes and oxaziridine and isomeric nitron

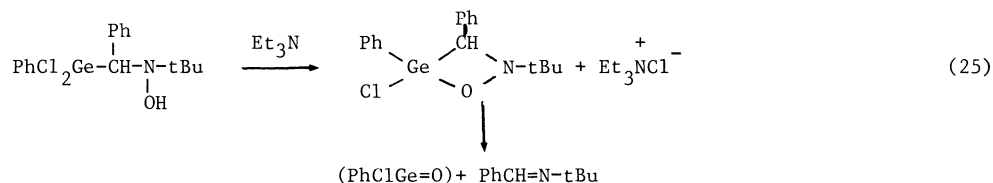
The reactions of germynes with phenyl N-t-butyloxaziridine show an increasing germenyl reactivity according to their electrophilic character $\text{Ph}_2\text{Ge} < \text{PhGeCl} < \text{F}_2\text{Ge}$. Thus it is possible to postulate an electrophilic attack of germenyl on the oxygen of the oxaziridine which leads to a polar C-O cleavage with formation of germaoxazetidine which is also obtained by 1,3-cycloaddition of the same germynes with phenyl-N-t-butyl nitron isomer (Ref. 32) (Scheme 5)



Scheme 5

The germaoxazetidine structure is confirmed chemically and by NMR analysis.

The action of triethylamine removing HCl from C-chlorogermylhydroxylamine leads to the same oxazetidine structure (equation 25)



This phenylchlorogermyl oxazetidine gives rise to two signals in the NMR spectrum (in C_6H_6) at $\delta : 0.97$ and $\delta : 0.94$ ppm(s) (N-tBu) which show that the germaoxazetidine (X=Ph, Y=Cl) (equation 25) exists in two diastereoisomeric forms.

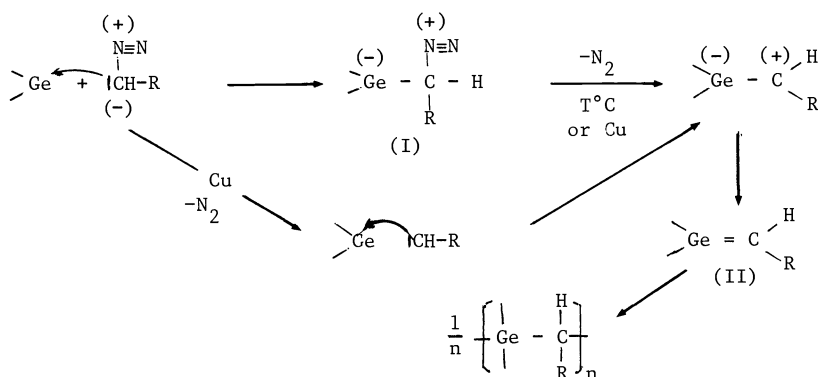
The rapid decomposition of these germaoxazetidines leads to the corresponding imines and germanones. The adducts of the initial germenyl with the formed imine lead to oligomers which, treated by Grignard reagents, lead to α -germanium amines (Ref. 31). The germanone intermediates have been characterized either as their adducts with the starting germenyl or as their insertion products with ethylene oxide leading to germadioxolane (Ref. 32).

Organohalo- and difluorogermynes insert easily into germanium-oxygen, -sulfur, -nitrogen and -phosphorus bonds with formation of functional digermanes (Ref. 1 & 6). The insertion reactions of germynes into the germanium-oxygen bond of diastereoisomeric oxagermacycloalkanes are stereospecific and can be interpreted by a concerted mechanism (Ref. 21). In contrast the insertion of difluorogermylene into the germanium-phosphorus bond of the diastereoisomers of 2-methylphenylgerma-1-phenylphospholane which has chiral germanium and phosphorus atoms is not stereospecific and can be interpreted by formation of a dipolar intermediate (Ref. 21 & 33).

$$\text{Me}_2\text{Ge} \begin{array}{c} \diagup \quad \diagdown \\ \text{S} \end{array} + \text{EtClGe:} \longrightarrow \text{Me}_2\text{Ge} \begin{array}{c} \diagup \quad \diagdown \\ \text{S} \end{array} \begin{array}{c} \text{C} \text{---} \text{GeEtCl} \\ (+) \quad (-) \end{array} \longrightarrow \text{Me}_2\text{Ge} \begin{array}{c} \diagup \quad \diagdown \\ \text{S} \\ \text{GeEtCl} \end{array} \quad (26)$$

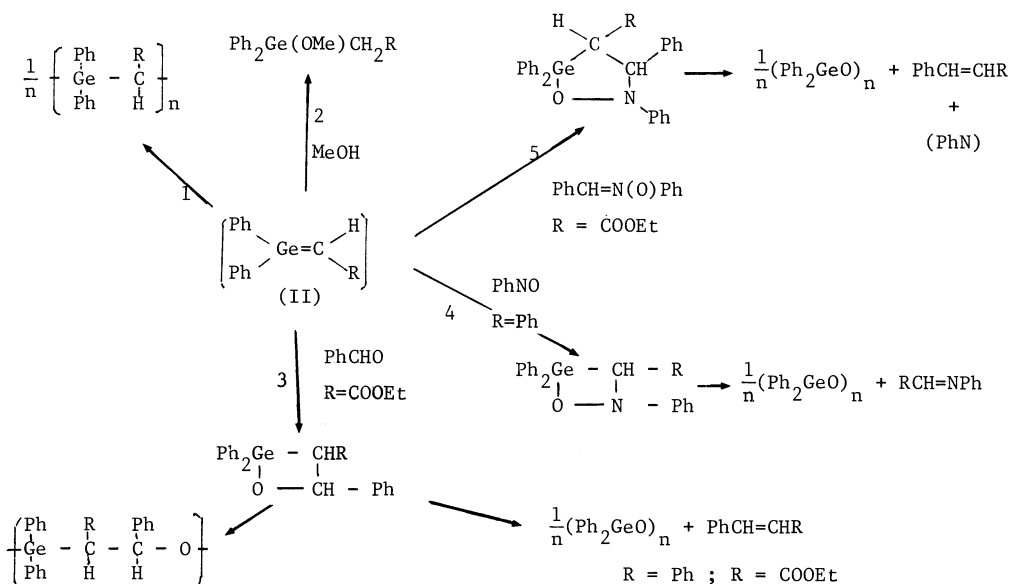
Germynes and diazoderivatives

The reactions of gerymylenes $\text{Ge}(\text{Ph}_2\text{Ge}, \text{PhGeCl}, \text{F}_2\text{Ge})$ with diazo compounds (PhCHN_2 , EtOOCCHN_2) in C_6H_6 show an increasing gerymylene reactivity according to their relative electrophilic character (Ref.35). Thus, it is possible to postulate an initial nucleophilic attack of gerymylene by the diazo compound which leads to a complex of ylide type I. Complex I proceeds, with release of nitrogen, to germene II through a transient zwitterionic form. Moreover, when copper is used as catalyst in these reactions, germene II can also be produced by a direct interaction between gerymylene and generated carbene (Ref. 35) (Scheme 6)



Scheme 6

Intermediates obtained from Ph_2Ge mainly polycondense leading to oligomers (Scheme 7 reaction 1). However, strong chemical evidence for the formation of II has been obtained :

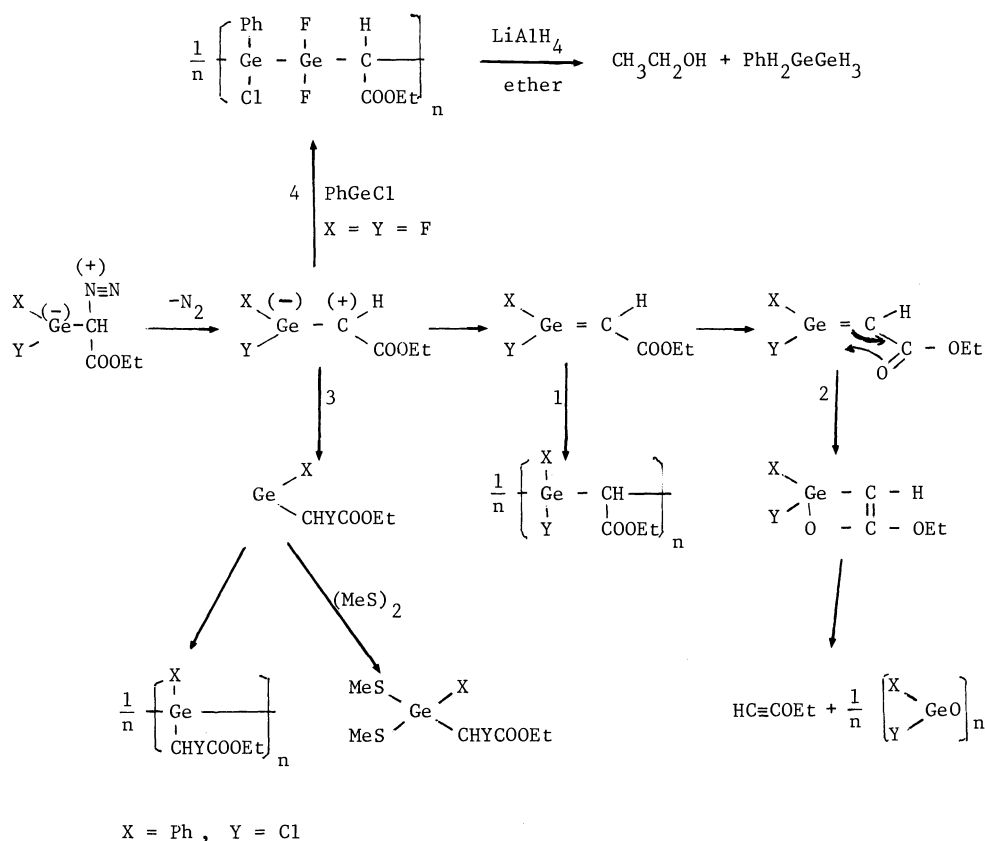


Scheme 7

- addition to methanol leading to the corresponding methoxygermanes (Scheme 7 reaction 2)
- pseudo-Wittig reactions with benzaldehyde leading transitorily to germaoxetane (Scheme 7 reaction 3)
- cycloaddition of II to nitrosobenzene, formation of germaoxaazetidine and finally germoxane and imine (Scheme 7 reaction 4)
- cycloaddition reaction is also observed with α -diphenylnitrone with transitory formation of germaoxaazolidine which decomposes to germanone, alkene and phenylnitrene (Scheme 7 reaction 5).

In the case of the reaction of halogermynes (difluorogermylene and phenylchlorogermylene) with ethyldiazoacetate the formed intermediates react in three different ways :

- 1) the transient germene partially polycondenses to oligomers (Scheme 8 reaction 1)
- 2) rearrangement of germene through a germanotropic transposition. The transient 2-germa-3-oxacyclobutene then formed decomposes readily through a β -elimination process with formation of germoxane and ethoxyacetylene (Scheme 8 reaction 2)
- 3) the migration of halogen from the metal to the carbonium in the α -position (Scheme 8 reaction 3) leads to a new germylene partly trapped with dimethyldisulfide. Digermylated oligomers can also be formed in this reaction when it is carried out with an excess of germylene (Scheme 8 reaction 4).

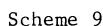


Scheme 8

The characterization of these halogenated germaalkenes with previously used trapping reagents (alcohol, nitrosobenzene or nitrones) is impossible due to the high reactivity of the starting halogermynes and the germanium-halogen bonds with these reagents.

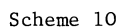
The only trapping reagent which could be used was benzaldehyde. It does not give the expected pseudo-Wittig reaction, but a far more complex reaction for which we propose the following interpretation (Scheme 9).

In the reaction between phenylchlorogermylene and ethyldiazoacetate the first step seems to be the nucleophilic attack of the germylanion on the carbonyl group of benzaldehyde which leads to phenylbenzoylchlorogermane which loses HCl by the action of the diazo compound leading to phenylbenzoylgermylene and the haloester (chloroethylacetate). Phenylbenzoylgermylene decomposes into diphenyldigermylene which is characterized by condensation on dimethylbutadiene and formation of benzil (Ref. 35) (Scheme 9)



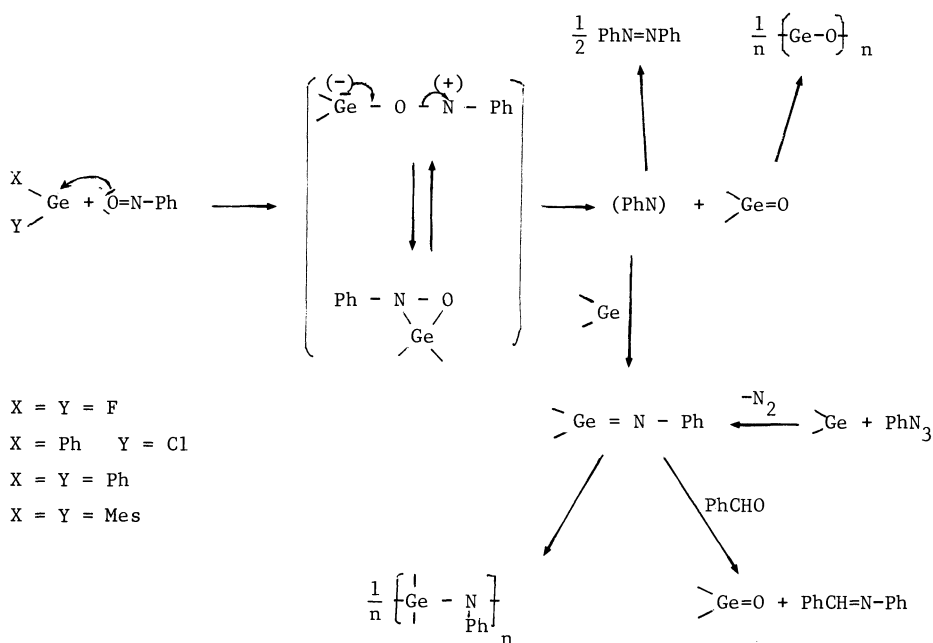
Germynes and organic azides
Germynes were obtained by a quite analogous route through the action of phenyl or methylazides on the germynes. In this case, too, the azides react better with the more electrophilic germynes. This fact is consistent with a nucleophilic attack of azide on germylene leading to a bipolar intermediate which decomposes generating nitrogen and forming the germa-imine (Ref. 36).

Germa-imines are characterized in the form of polygermazanes, by insertion into a tetrahydrofuran ring and formation of a seven-membered heterocycle, as well as by pseudo-Wittig reaction with benzaldehyde and formation of unstable germaoxazetidine (Ref. 36) (Scheme 10)



Germynes and nitrosobenzene

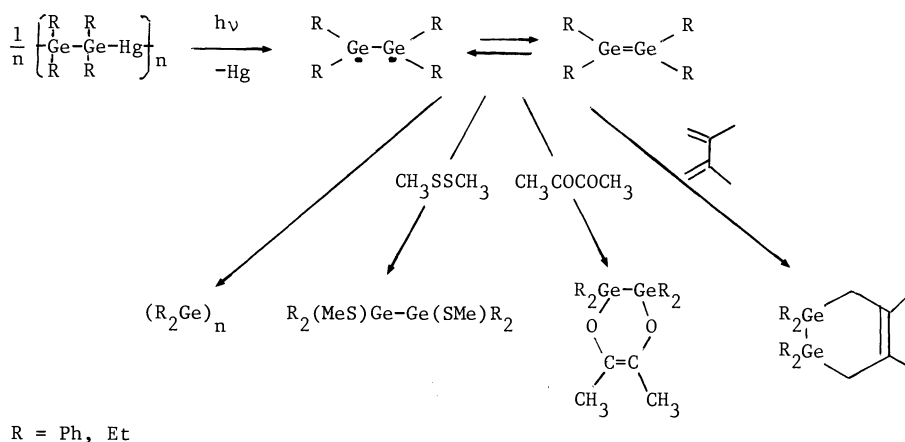
Germa-imines can also be formed by direct interaction between germynes and nitrenes. The reactions of germynes with nitrosobenzene lead to nitrene and >Ge=O intermediates via the zwitterionic form of the appropriate germaoxa-aziridine (Ref. 32). Interactions between the germynes and the nitrenes generated in the reactions give new >Ge=N- intermediates which polycondense to the corresponding cyclogermazanes. Furthermore the germa-imines have been characterized by a pseudo-Wittig reaction with benzaldehyde (Ref. 36) (Scheme 11)



Scheme 11

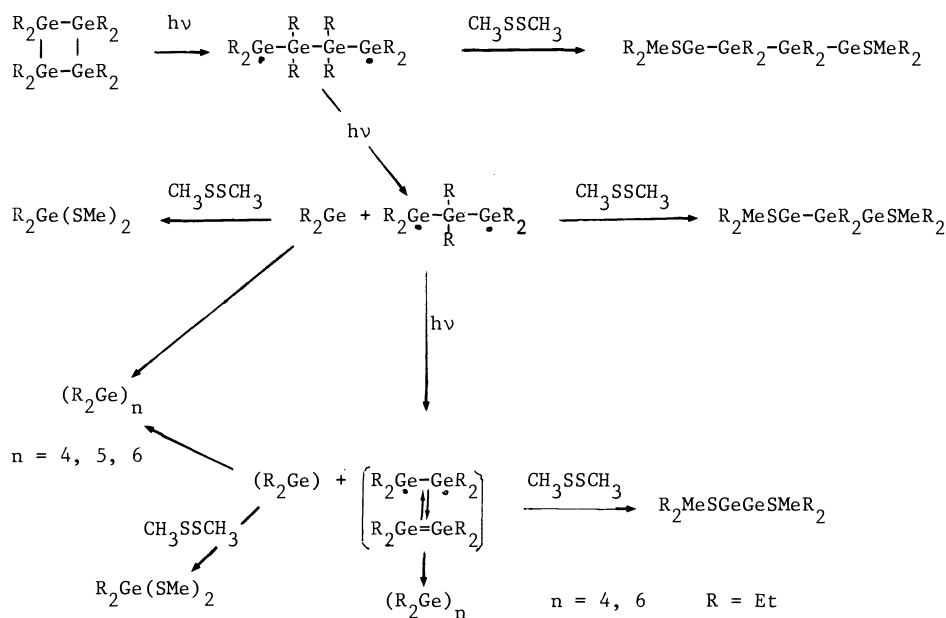
Digermenes

Digermenes (or α -digermyl radicals) whose formation can be postulated as occurring in some cases through germylene dimerisation reactions (Ref. 37) were generated in good yields by photolysis of polydigermylmercury compounds (Ref. 14 & 37). These intermediates have been characterized by several trapping reactions with biacetyl (Ref. 14 & 37), dimethyldisulfide (Ref. 37) or 2,3-dimethylbutadiene (Ref. 37 & 38) but in very low yields in this latter case (Scheme 12)



Scheme 12

Digermenes can also be characterized among other germanium centered radicals and germylenes, in the photolysis of octaethylcyclotetra- and decaethylcyclopentagermanes (Ref. 37) (Scheme 13)



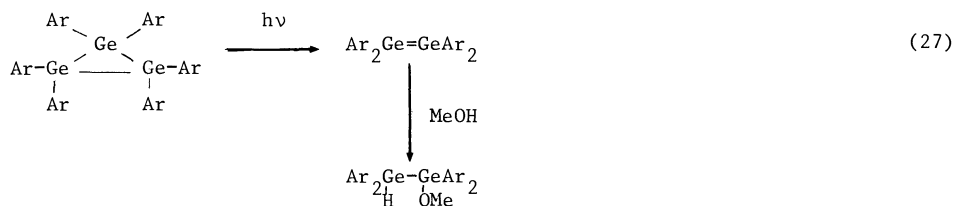
The main results in the photolysis of alkylcyclopolygermanes are reported in the following Table 2

Table 2. Photolysis of alkylcyclopolygermanes

$(\text{Et}_2\text{Ge})_n$	Reactant	t(h)	% *	Identified products
n = 4	CH_3SSCH_3	1	76	$\text{Et}_2\text{Ge}(\text{SMe})_2$ (33%), $(\text{Et}_2\text{MeSGe})_2$ (28%) $(\text{Et}_2\text{MeSGe})_2\text{GeEt}_2$ (26%) $(\text{Et}_2\text{MeSGe})_2(\text{GeEt}_2)_2$ (13%)
n = 5	CH_3SSCH_3	6	56	$\text{Et}_2\text{Ge}(\text{SMe})_2$ (55%), $(\text{Et}_2\text{MeSGe})_2$ (32%) $(\text{Et}_2\text{MeSGe})_2\text{GeEt}_2$ (13%) $(\text{Et}_2\text{MeSGe})_2(\text{GeEt}_2)_2$ (traces)

* Percentage decomposition of initial polygermane

Let us recall, in the field of digermenes, the photoconversion of a cyclotrigermene to digermene recently published by Masamune (Ref. 39) (equation 27)



Ar = 2,6-dimethylphenyl

and the recent report of Sakurai et al (Ref. 40) on tetramethyldigermene generated by pyrolysis of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo 2.2.2 octadiene. The digermene was trapped by (4+2) cycloaddition with anthracene and a silacyclopentadiene.

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