ХИМИЯ ГЕТЕРОЦИКЛИЧЕСКИХ СОЕДИНЕНИЙ. — 1999. — № 9. — С. 1155—1175

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GERMYLENES AND GERMANIUM DOUBLY BONDED SPECIES IN HETEROCYCLIC ORGANOGERMANIUM CHEMISTRY. SOME RESULTS FROM THE TOULOUSE GROUP*

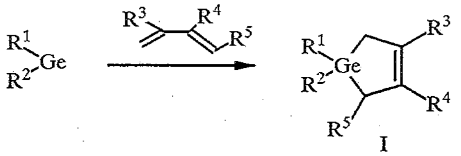
(REVIEW)

Germylenes, divalent germanium species, and germanium derivatives with Ge=Y double bonds (Y = C=, O, S, N—, P—) are powerful synthetic reagents in organometallic chemistry. The germylenes exhibit properties analogous to those of carbenes and have been shown to insert into various σ-bonds such as: carbon-hetero element, metal-carbon, metal-hetero element of heterocyclic derivatives with the ring expansion. The addition of germylenes to various unsaturated compounds (dienes, orthoquinones, carbonyl compounds, imines, nitrosobenzene) leads, as a rule to cycloadducts with low stability except for dienes and quinones. The doubly bonded germanium species are highly reactive and widely used in organometallic synthesis in various types of reactions such as:
— addition (or insertion reactions) to various σ-bonds of organometallic compounds;
— insertion reactions with ring expansion of small organic rings;
— cycloaddition reactions with 1—2, 1—3, 1—4 dipolar reagents.
The mechanism and stereochemistry of some reactions are discussed.

During the last years considerable interest and numerous investigations have been devoted to organometallic derivatives or intermediates having a metal with an unusual degree of coordination. In this field of organometallic chemistry the germylenes, divalent germanium species, and the doubly bonded germanium species are powerful synthetic agents. Our purpose is to describe some applications of germylenes and doubly bonded germanium species in heterocyclic organogermanium chemistry developed in the Toulouse group.

GERMYLENES

The first application of germylenes studied in our group was the addition of mixed germylenes $R(R^1)Ge$ (R = alkyl, phenyl, R^1 = F, Cl, Br, I, H or MeO) to conjugated dienes such as isoprene, 2,3-dimethyl-1,3-butadiene or 1,3-pentadiene (eq. 1).



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(1)

R^1 = alkyl, phenyl, R^2 = F, Cl, Br, I, H or MeO;
R^2 =Me , $R^4 = R^5$ = H; $R^3 = R^4$ = Me, R^5 = H;
$R^3 = R^4$ = H, R^5 = Me

The 1,4-addition of germanium diiodide to butadiene, isoprene and 2,3-dimethyl-1,3-butadiene also led to the diiodogermacyclopentene derivatives I [1].

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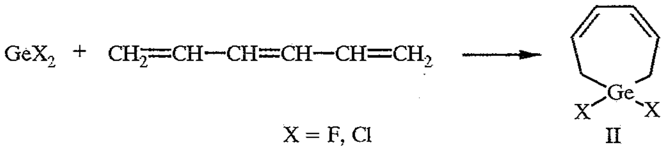
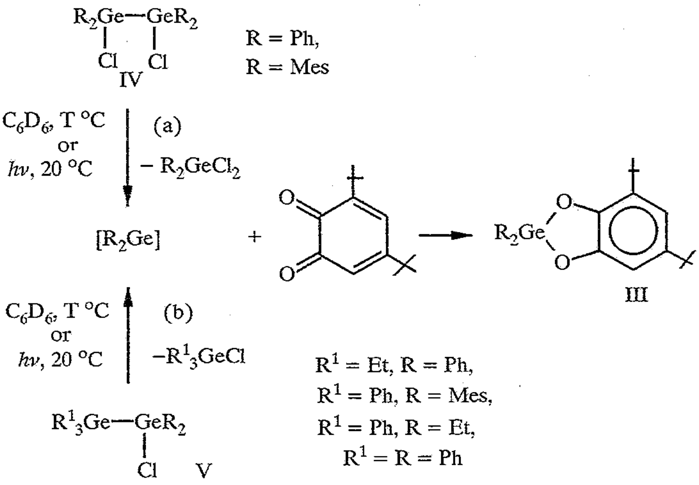
* In commemoration of 100 years of Academician A. N. Nesmeyanov birth. Homage at his memory.

The difluorogermylene reacts, like $GeCl_2$, with conjugated trienes (hexa-1,3,5-triene) to give the 1,6-cycloadduct II [2, 3] (eq. 2).



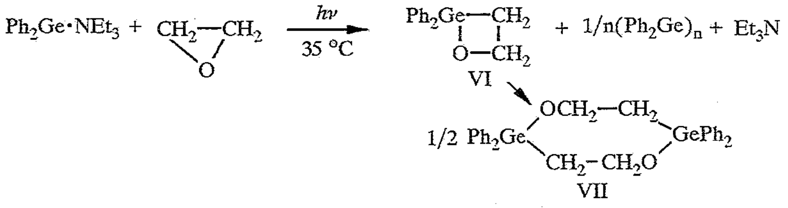
(2)

Cycloaddition of germylenes to 3,5-di-*t*-butylorthoquinone affording 2-germa-1,3-dioxolanes III is also an excellent tool for characterization of these divalent species [4—9] (eq. 3); germylenes being generated using thermolysis or photolysis of suitable digermanes IV, V [10].



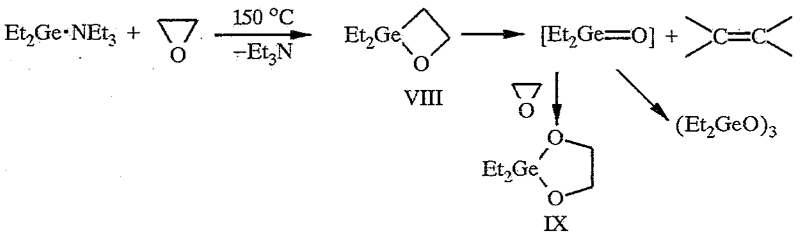
(3)

Insertion reactions in the oxirane ring are observed on interactions of germylenes Ph_2Ge, PhGeX (Y = F, Cl), GeF_2 with ethylene oxide. These reactions lead to germaoxetanes VI which dimerise and give digermadioxocanes VII [11] (eq. 4).



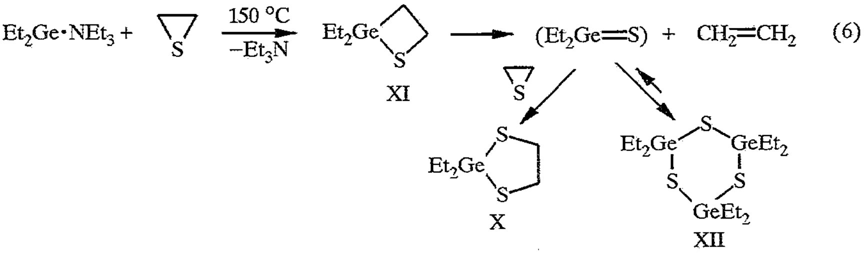
(4)

Condensation of complexed dialkylgermylenes $R_2Ge{\cdot}NEt_3$ with various oxiranes (oxirane, phenyloxirane, 1,2-dimethyloxirane) give, by insertion with ring expansion, the corresponding oxagermacyclobutanes VIII. These thermally unstable heterocycles transform *via* β-elimination reactions to transient dialkylgermanones which, by insertion into the oxirane ring, form germadioxolanes IX [11] (eq. 5).

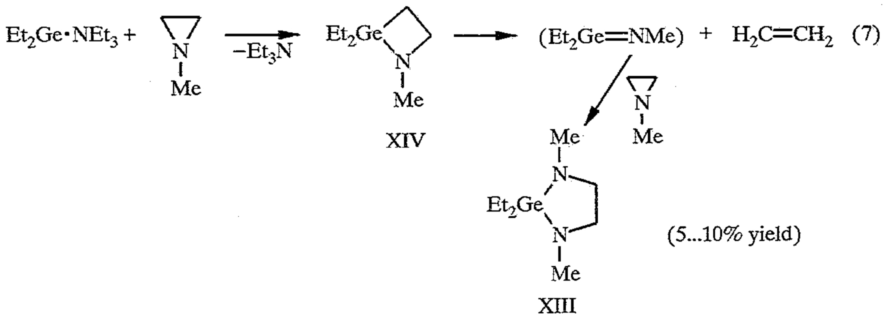


(5)

The treatment of complexed diethylgermylene with thiirane leads to germadithiolane X *via* the formation of unstable germathiacyclobutane XI. The equilibrium between monomeric diethylgermathione and its trimeric form XII can explain the rather good yield of germadithiolane [11] (eq. 6).

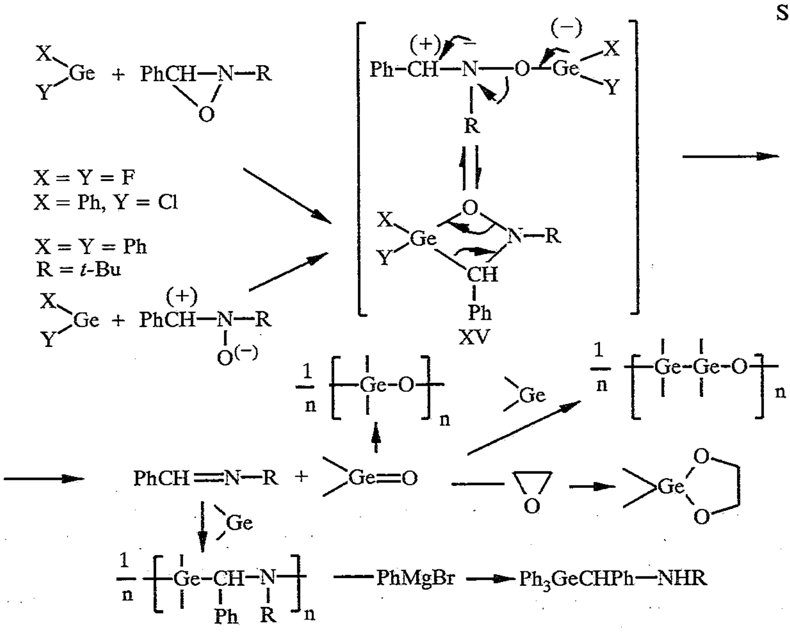


The reaction between diethylgermylene and N-methylaziridine leads to germadiazolidine XIII in low yields probably *via* an unstable germazetidine intermediate XIV [11] (eq. 7).

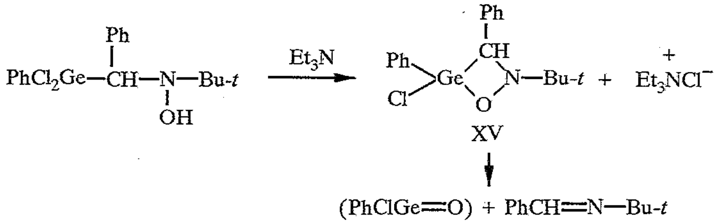


The reaction of germylenes with phenyl N-*t*-butyloxaziridine reveals an increasing germylene reactivity in the row Ph2Ge<PhGeCl<F2Ge, which is due to their electrophilic character. Thus, it can be postulated that an electrophilic attack of germylene at the oxaziridine oxygen leads to a polar C—O cleavage and formation of germaoxaazetidine XV. The latter can be also obtained by 1,3-cycloaddition of the same germylenes to phenyl-N-*t*-butylnitrone [11] (Scheme 1).

Scheme 1



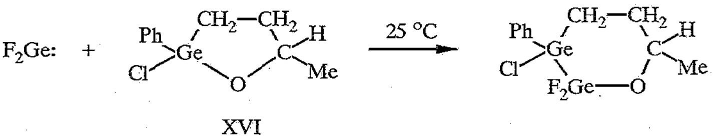
The structure of germaoxaazetidine is confirmed chemically and by NMR analysis. Removing HCl from a phenyldichlorogermyl-substituted hydroxylamine leads to the same germaoxaazetidine structure XV (X = Ph, Y = Cl, R = *t*-Bu) [11] (eq. 8).



(8)

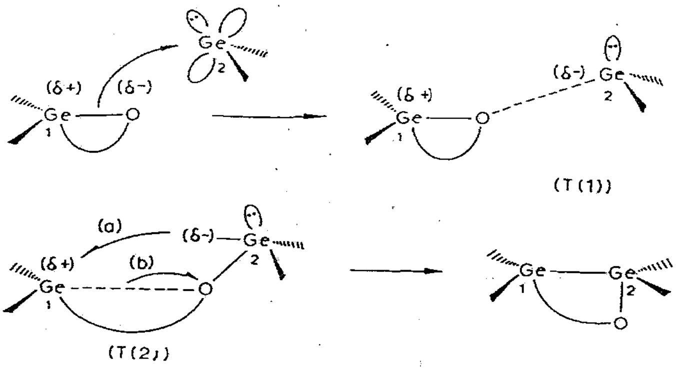
The NMR spectrum of phenylchlorogermaoxaazetidine shows two signals at δ: 0.97 and 0.94 (N—Bu-*t*) of two diastereoisomeric forms.

Organohalogermylenes and difluorogermylene insert easily into the germanium-oxygen bond of diastereoisomeric oxagermacycloalkanes, e. g. XVI. The insertion reaction is stereospecific and can be interpreted by a concerted mechanism [10] (eq. 9 and Scheme 2).



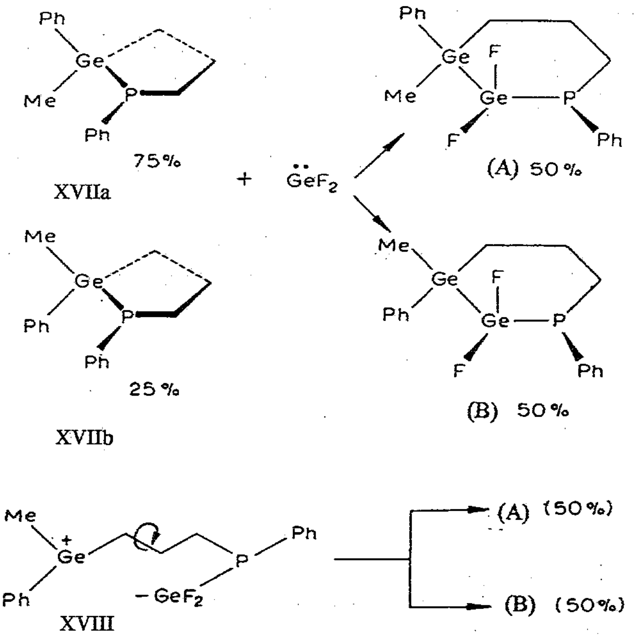
(9)

Scheme 2



In contrast, the insertion of difluorogermylene into the germanium-phosphorus bond of the 2-dimethyl-1,2-diphenyl-2-germaphospholane diastereoisomers XVII having chiral germanium and phosphorus atoms, is not stereospecific and can be interpreted by the formation of a dipolar intermediate XVIII [11, 12] (Scheme 3).

Scheme 3

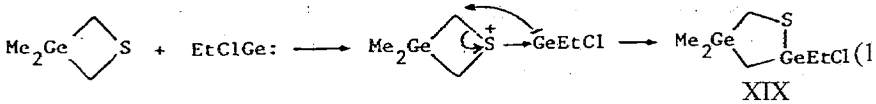


XVIIa

XVIIb

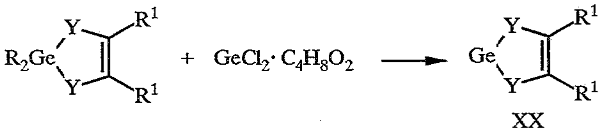
XVIII

Ethylchlorogermylene inserts, into C—S bond of 3,3-dimethyl-3-germathietane to a stable ring expansion adduct XIX [11] (eq. 10).


(10)

XIX

New stable cyclic germylenes XX can be obtained by exchange reactions with cyclic difunctional derivatives of germanium (IV) following the general pattern [9] (eq. 11).

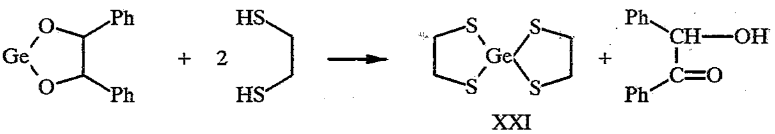

(11)

XX

$Y = S, R^1 = H, CN, R = Me, Et, Ph$
$Y = O, R^1 = Ph, R = Et, Ph$

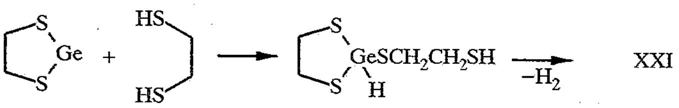
The germylene XX ($Y = S, R^1 = CN$) can also be obtained by the reaction of $GeCl_2$-dioxan with NaS—C(C=N)=C(C=N)—SNa [9].

The 4,5-diphenyl-1,3-dioxagermole XX ($Y = O, R^1 = Ph$) has been characterized by mass spectroscopy and by the reaction with ethanedithiol [9] (eq. 12).


(12)

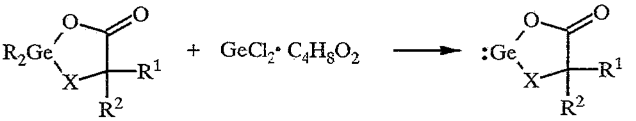
XXI

The intermediate formation of 2-germa(II)-1,3-dithiolane XX (Y = S, R^1 = H) is proved by the direct reaction of this germylene with ethanedithiol giving the same *spiro*-germanium compound XXI [9] (eq. 13).



(13)

The exchange reactions of germa(IV)oxazolidones and -dioxolones XXII with dichlorogermylene lead to the corresponding germylenes XXIII [13] (eq. 14).



(14)

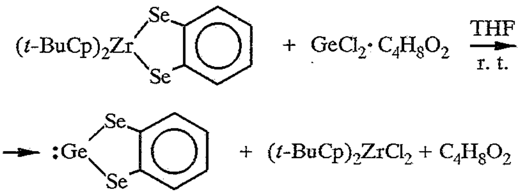
$X = NPh, R^1 = R^2 = H;\quad X = O, R^1 = R^2 = Me, R^1 = R^2 = Ph$

These stable germylenes are characterized by the cycloaddition to dimethylbutadiene or di-*t*-butyl-*o*-quinone and by the condensation with dimethyl disulfide [13, 14].

The benzodiselenagermylene XXIV is obtained easily by exchange reaction between diselenaphenylene zirconocene and dichlorogermylene [13, 15] (eq. 15).

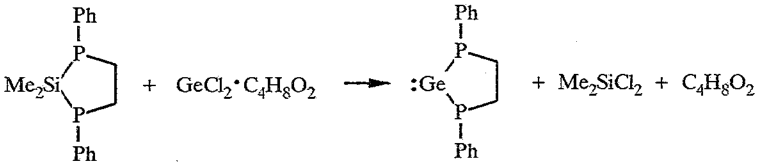
This new stable germylene XXIV is characterized by mass spectrometry, ^1H and ^{77}Se NMR and by the cycloaddition to 2,3-dimethyl-1,3-butadiene.

The same type of exchange reaction yields stable 2-germa(II)-1,3-diphospholane XXV [4, 16] (eq. 16).



(15)

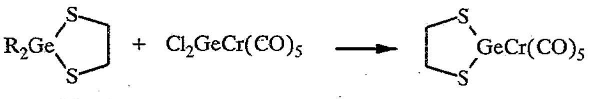
XXIV



(16)

XXV

Germylene complexes XXVI are obtained by exchange reactions of functionalized organogermanes XXVII with $Cl_2GeCr(CO)_5 \cdot THF$ [5, 17] (eq. 17).



(17)

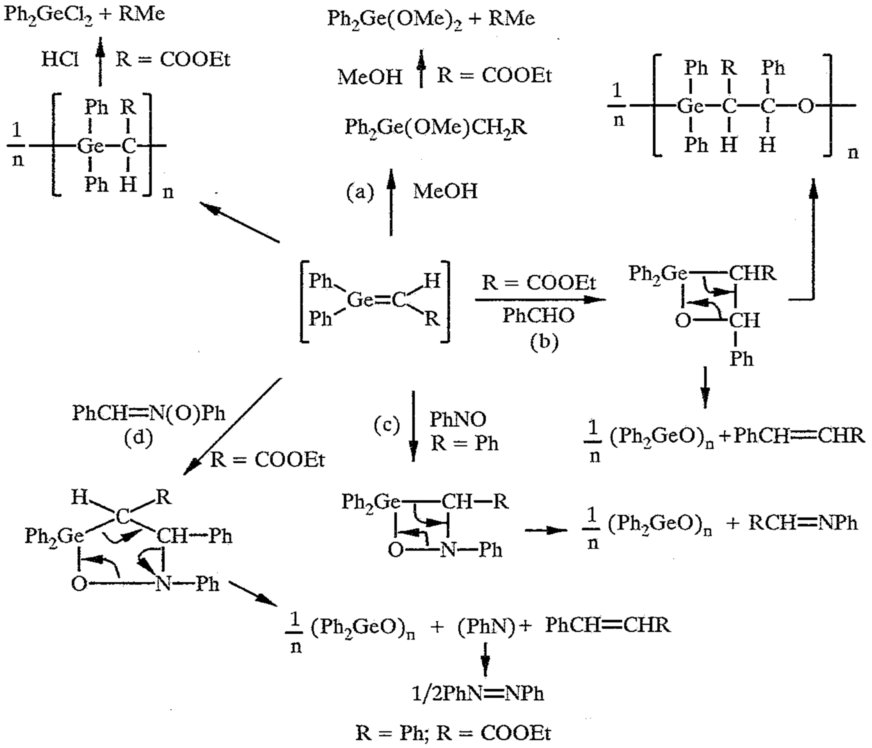
XXVII XXVI

The synthesis and characterization of doubly bonded germanium species: germenes =Ge=C=, germaimines =Ge=N—, germaphosphenes =Ge=P, germanones and germathiones =Ge=X (X = O, S)are largely described in Refs. [2, 4, 5, 9, 12, 13, 18—27].

Germenes

The first results concerning formation of heterocycles from germenes appeared in 1980 [28]. Germenes obtained from condensation of diazo derivatives and germylenes were characterized: a) by methanol addition, b) by the pseudo-Wittig reactions with benzaldehyde leading at their first step to germaoxetane and, finally, to germanone (which undergoes polycondensation to cyclic germoxane); c) by the cycloaddition reaction with nitrosobenzene to form germaoxaazetidine, and, finally germoxane and imine. A cycloaddition reaction (d) of diphenylnitrone forms germaoxaazolidine decomposing to germanone, alkene and phenylnitrene characterized by the formation of azobenzene (Scheme 4).

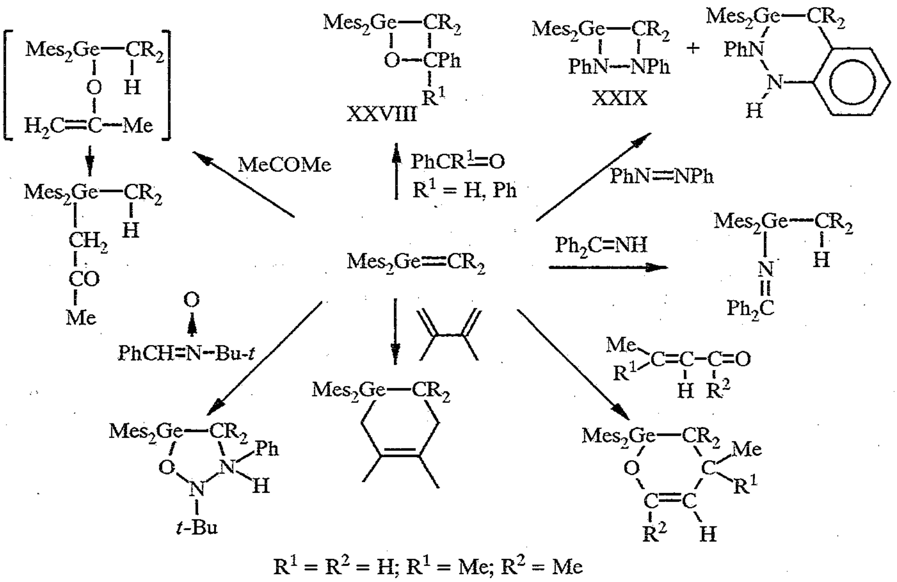
Scheme 4



Various [2 + 2], [2 + 3] and [2 + 4] cycloadditions occur with participation of dimesitylfluorenylgermene $Mes_2Ge = CR_2$. Four-membered rings are obtained from this germene and aldehydes or ketones. The germaoxetanes XXVIII are highly stable probably due to steric hindrances [29, 30]. Diphenylketimine reacts with the same germene as a protic reagent but when reacting with azobenzene a stable four-membered ring XXIX with Ge—N—N linkage is obtained. In this case the steric hindrance also plays a very important role for the stabilization.

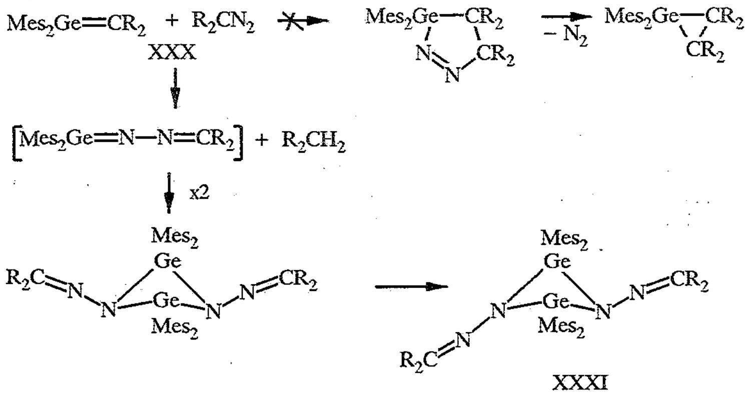
Nearly quantitative [2 + 3] cycloadditions have been observed with nitrones. [2 + 4] Cycloadditions occur with 1,3-dienes and α-ethylenic aldehydes and ketones [20, 29—31] (Scheme 5).

Scheme 5



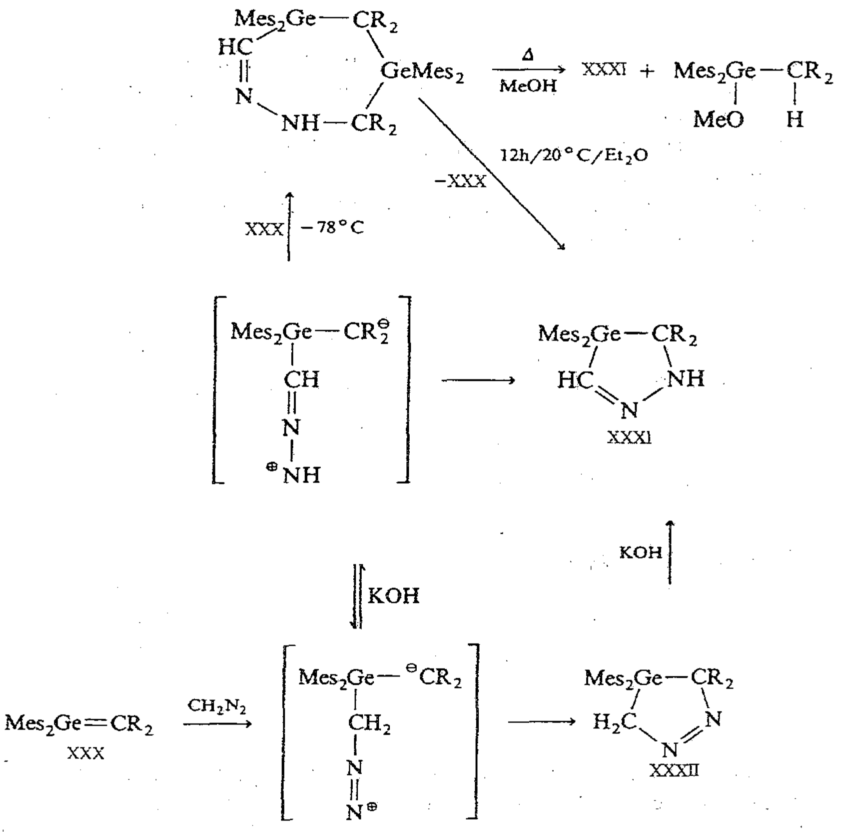
Reactions of diazo compounds R_2CN_2 (R_2C = fluorenylidene) or R = CN with germene $Mes_2Ge{=}CR_2$ (XXX) lead to cyclodigermadiazetidines XXXI probably *via* transient germaimines with evolution of carbene CR_2 [20, 32] (Scheme 6).

Scheme 6



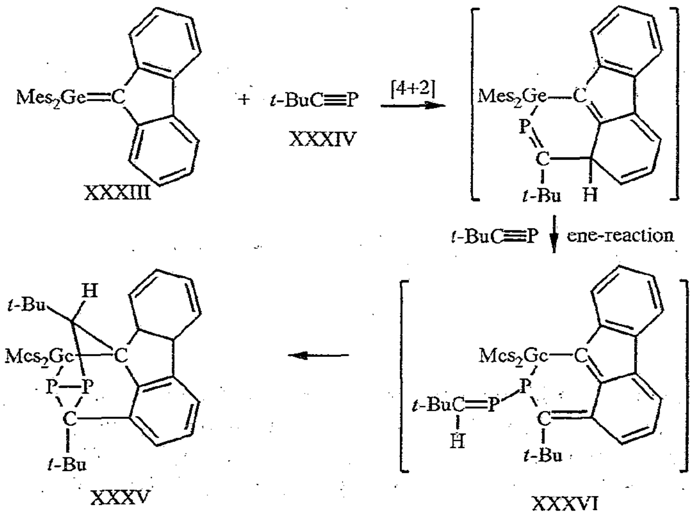
The reaction with diazomethane is very dependent on experimental conditions. When a large excess of an ethereal solution of diazomethane was added to a solution of germene XXX in Et_2O at −78 °C the only observable product was the germapyrazoline XXXI. When the reaction was carried out with a solution of distilled diazomethane isomeric 4-germa-1-pyrazoline XXXII was obtained [33, 34] (Scheme 7).

Scheme 7



The reaction of dimesitylfluorenylidenegermene XXXIII and *tert*-butylphosphoalkyne XXXIV gives a polycyclic derivative XXXV. The mechanism leading to this compound involves of the first step a Diels—Alder reaction, in which germene reacts as 1,3-diene with participation of one aromatic carbon-carbon bond of the fluorenylidene group. This cycloaddition step is followed by an ene-reaction with *t*-BuC ≡ P acting as an enophile which affords XXXVI. The latter undergoes an intramolecular Diels—Alder reaction to give the final product XXXV [26, 35] (Scheme 8).

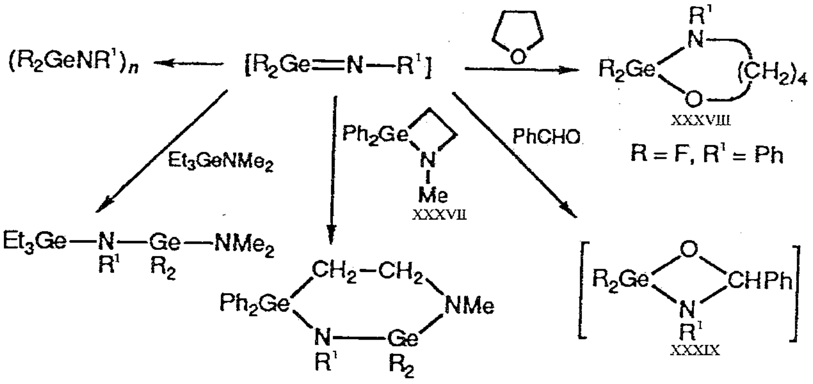
Scheme 8



Germaimines

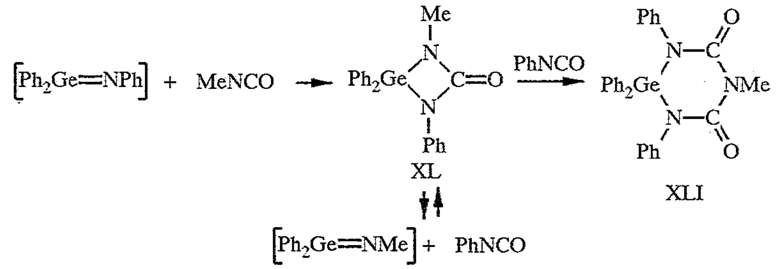
Syntheses of germaimines are described in Refs. [4, 18, 20, 23]. Germaimines are characterized as cyclic polygermazanes $(R_2GeNR^1)_n$, insertion into the germanium-nitrogen bond of germylazetidine XXXVII and dimethyl(triethylgermyl)amine, by insertion into the tetrahydrofuran ring with the formation of a seven-membered heterocycle XXXVIII as well as by the pseudo-Wittig reaction with benzaldehyde to form unstable germaoxaazetidine XXXIX [20, 23] (Scheme 9).

Scheme 9

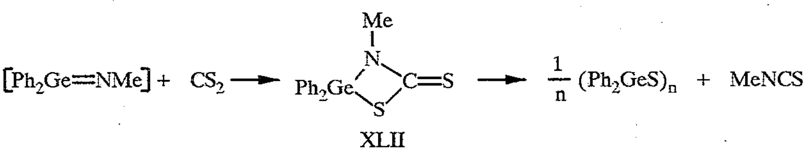


The [2+2] cycloadditions of germaimines with phenyl or methyl isocyanates produce unstable oxogermadiazetidine XL, which reacts with phenyl isocyanate to give 4,6-dioxo-2-germaperhydro-1,3,5-triazine XLI [20, 23, 36] (Scheme 10).

Scheme 10



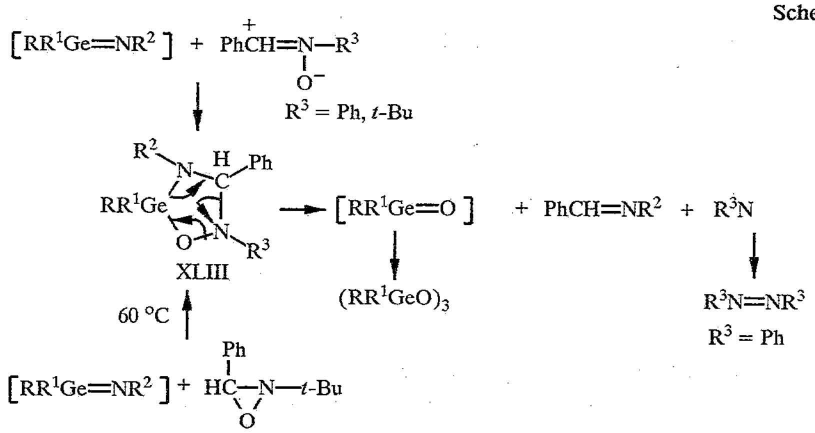
N-Methyldiphenylgermaimine adds CS_2 with the formation of unstable 2-germa-4-thioxo-2-germa-1,3-thiaazetidine XLII [20, 23, 36] (eq. 18).



(18)

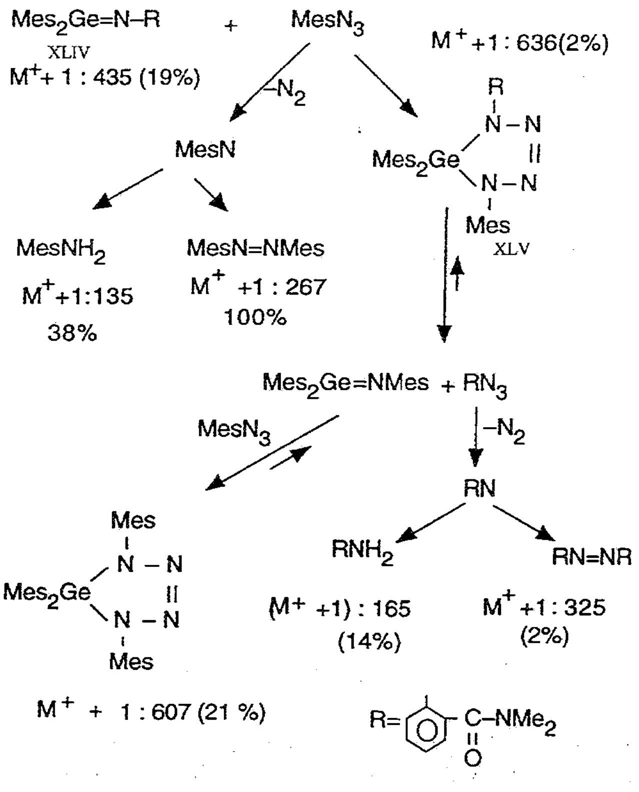
The [2+3] cycloadditions of germaimine $RR^1Ge{=}NR^2$ (R = Ph, R^1 = Ph, Cl, R^2 = Me, Ph, *t*-Bu) with diphenyl- or phenyl-*t*-butylnitrones as well as their insertion reactions with oxaziridines lead to germanones ($RR^1Ge = O$), imines and nitrenes probably *via* transient 2-germa-1-oxa-3,5-diazolidines XLIII [20, 23, 36, 37] (Scheme 11).

Scheme 11

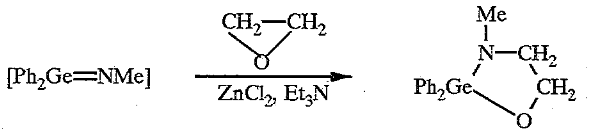


Reaction of germaimines XLIV with 1,3 dipole as mesitylazide leads to the expected cyclic tetrazene XLV in accordance with Wiberg's results [38]. However, the (2+3) cycloadducts are unstable and at room temperature give an equilibrum in which all components were detected and characterized by CI mass spectrometry (CH_4 as reagent gas [23, 39] (Scheme 12).

Scheme 12



Germaimines insert into ethylene oxide with the formation of 2-germa-1,3-oxazolidine XLVI [23, 36] (eq. 19).

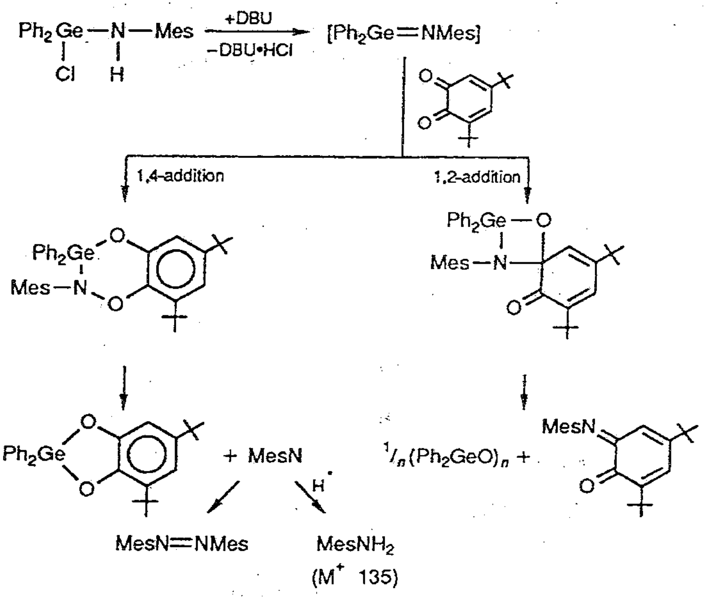


XLVI

(19)

The transient diphenyl-N-mesitylgermaimine Ph2Ge=NMes gives unstable 1,4- and 1,2-adducts with di-*t*-butyl-3,5-*o*-quinone [20, 23] (Scheme 13).

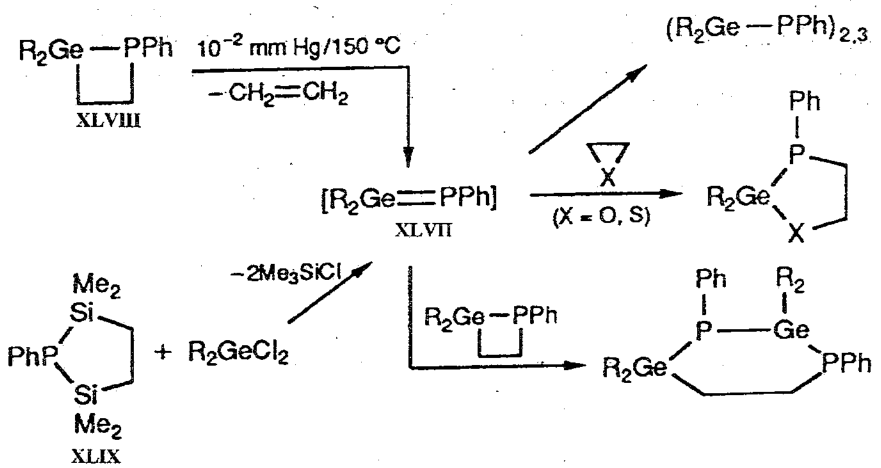
Scheme 13



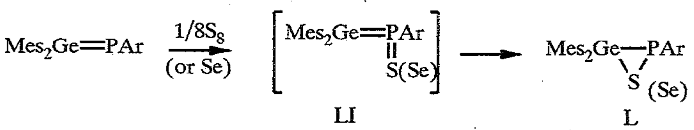
Germaphosphenes

Transient germaphosphenes XLVII obtained by thermal decomposition of 2-germaphosphetanes XLVIII or by reaction between dialkyldichlorogermanes and disilaphosphole XLIX were clearly characterized by the formation of dimeric or trimeric cyclic germylphosphine and by the insertion and ring expansion reactions of strained three or four membered heterocycles [20, 40, 41] (Scheme 14).

Scheme 14

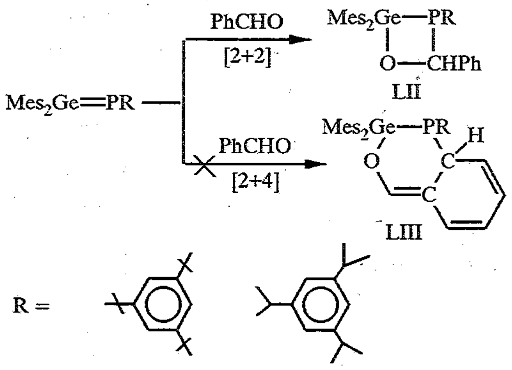


Reactions of an equivalent sulfur or selenium with germaphosphene lead to the stable three membered heterocycles L, germathiaphosphirane and germaselenaphosphirane. The first step of the reaction is probably the formation of germaphosphene sulfide (or selenide) LI [20, 21, 42] (eq. 20).



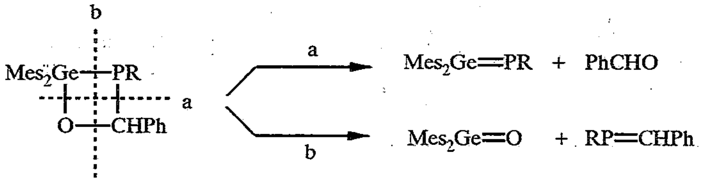
(20)

Germaphosphenes react readily with benzaldehyde by [2+2] cycloaddition to give the corresponding four-membered ring heterocycles LII. The products of [2 + 4] cycloadditions LIII are never obtained [21, 43] (eq. 21).



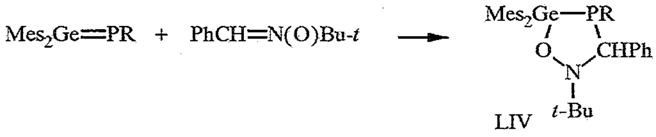
(21)

In the mass spectrum of germaphosphaoxetanes LII the classical [2+2] decomposition of organometallic four-membered heterocycles has been observed, the most important route (a/b 95 : 5) regenerating the starting material [21, 43] (eq. 22).



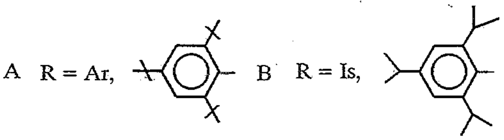
(22)

Reactions of N-phenyl-N-*tert*-butylnitrone with germaphosphenes afford the corresponding five-membered heterocycles LIV; whilst two diastereoisomeres are obtained for B and only one is observed for A probably due to the high steric hindrance imposed by the 2,4,6-tri-*tert*-butyl group [21, 43] (eq. 23).



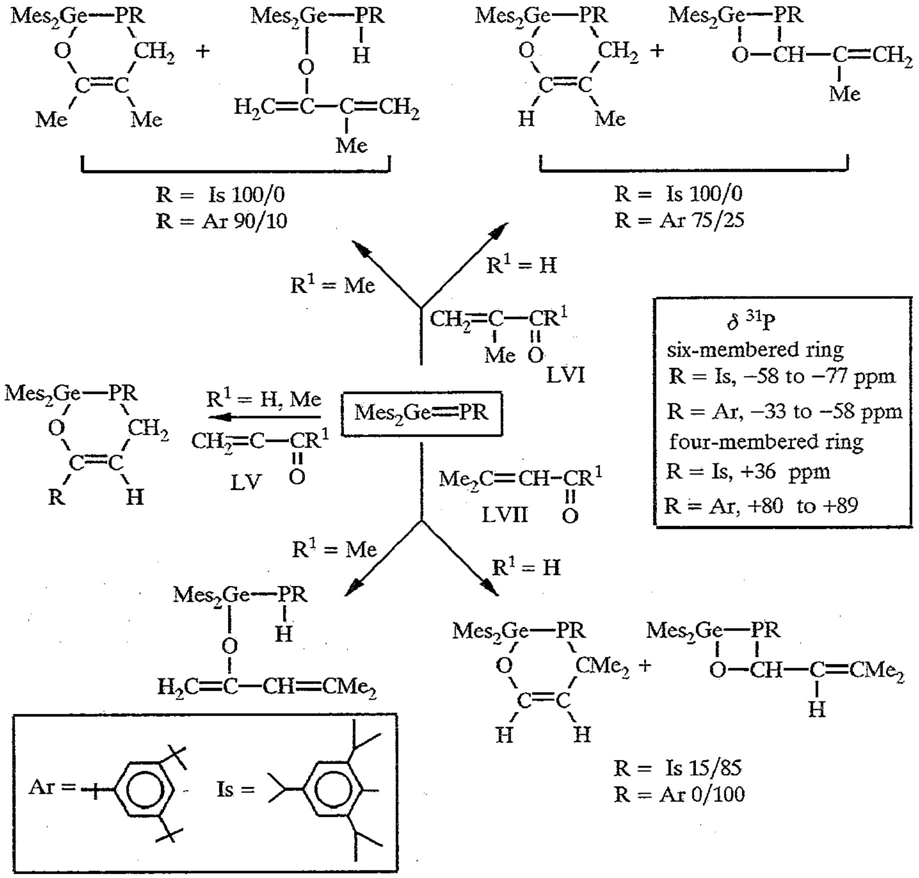
LIV

(23)



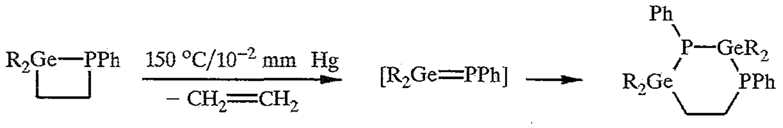
Germaphosphenes react with α,β-unsaturated aldehydes and ketones LV to produce six-membered dihydro germaoxaphosphorines according to a [2+4] cycloaddition [33]. However, four-membered ring compounds, the [2+2] cycloaddition and open-chain products are also obtained with $\alpha-$ or β-methyl substituted aldehydes and ketones LVI, LVII [26, 44] (Scheme 15).

Scheme 15



The first step of these reactions is probably the nucleophilic attack of oxygen at the germanium centre while the attack of phosphorus occurs at the carbonyl carbon or β-carbon depending on the substituents at these atoms [26, 44].

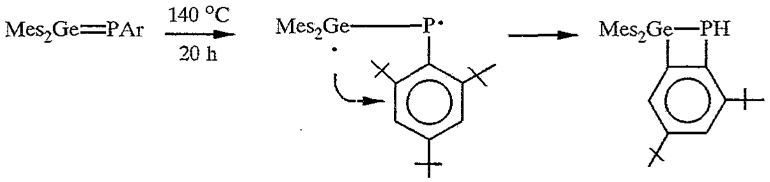
An interesting transformation, which is equivalent to a [2+4] cycloaddilion, has been observed in reaction of ethylene with germaphosphenes obtained by thermolysis of four-membered ring [21, 40] (eq. 24).



(24)

R = Me, Et

Heating dimesityl (tri-*t*-butylphenyl)germaphosphene at 140 °C affords the stable germaphosphetene LVIII probably due to the intramolecular radical aromatic substitution. Although the four-membered ring is highly strained, it is thermally stable. Its structure has been determined by X-ray analysis [21, 45] (eq. 25).



LVIII

(25)

The germaphosphenes isolated in pure crystalline form appears very reactive in spite of the high steric hindrance necessary for its stabilization.

Germanones and germathiones

The chemistry of the species =Ge = Y (Y = O, S) essentialy remains a transient species chemistry. In spite of numerous attempts one metastable germanone and six germanethiones are the only species of this type stable at room temperature [27].

Transient germanones and germathiones are obtained by different ways described in Refs. [2, 4, 5, 9, 12, 13, 18—21, 26, 27].

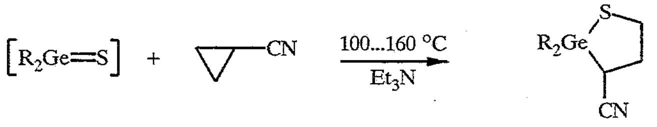
These germanones and germathiones with strongly polarized double bond [46] are highly reactive and may be used in organometallic synthesis in various types of reactions such as:

1) addition reactions to various σ bonds of organometallic and organic compounds,

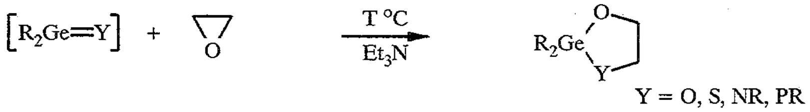
2) insertion reactions with ring expansion of small organic rings,

3) cycloaddition reactions.

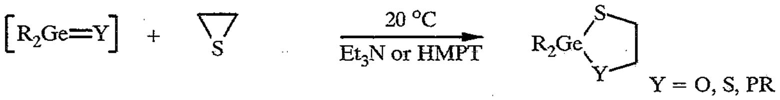
Certain results of insertion reactions with small organic rings [19] are summarized in equations [26—31].



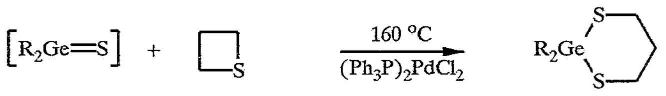
(26)



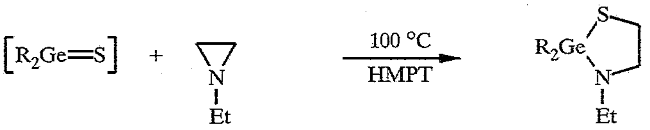
(27)



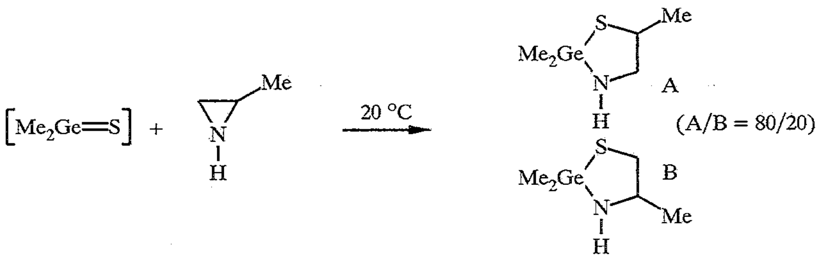
(28)



(29)



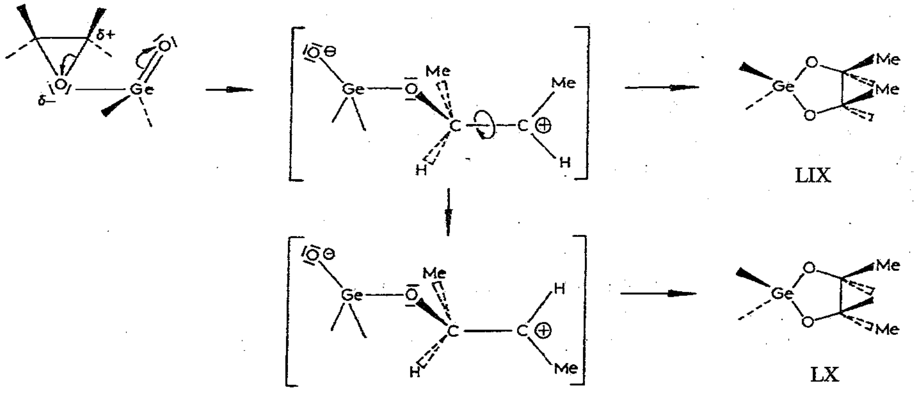
(30)



(31)

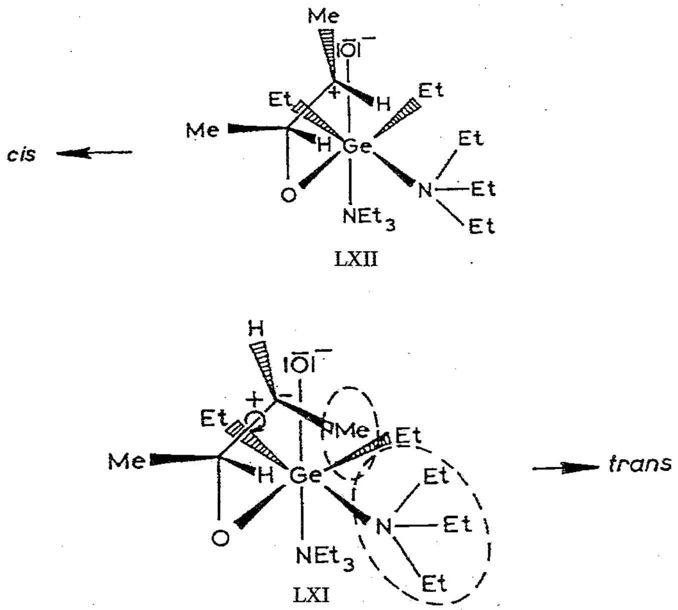
The mechanism and stereochemistry of some of these additions to small ring have been studied [47]. Condensation reactions of germanone with oxirane begin with the nucleophilic attack of oxygen at germanium followed by the ring opening and cyclization. This non-concerted mechanism is supported by the results of condensation of germanone with *cis-* or *trans*-isomers of butene oxide. Each reaction leads to a mixture of *cis-* (LIX) and *trans*-adducts (LX): 45/55 from the *cis*-butene oxide and 52/48 from the *trans*-butene oxide. However, in the presence of triethylamine, the percentage of the *cis*-adduct increases, and with 300% excess of triethylamine, almost exclusive formation of the *cis*-adduct is observed from both *cis-* and *trans*-butene oxide along with a ≤2% of the *trans*-adduct [9, 19, 47] (Scheme 16).

Scheme 16



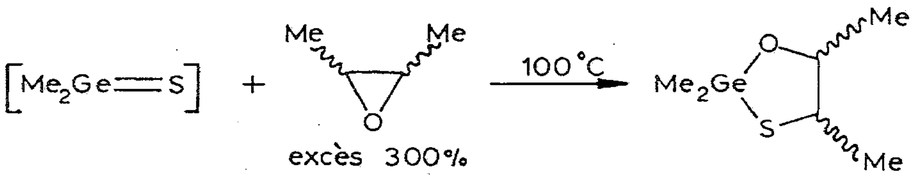
The high stereoselectivity in the presence of triethylamine seems to imply a germanium atom hexacoordinated by two molecules of triethylamine. The study of molecular models shows very strong steric overcrowding of the methyl and triethylamino groups in the equatorial positions of the bipolar intermediate (LXI) during the cyclization process. The steric hindrance diminishes when both methyl groups are in *cis*-position (LXII), which leads to the *cis*-isomer [9, 19, 47] (Scheme 17).

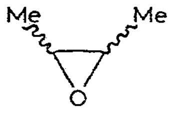
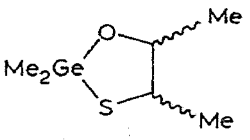
Scheme 17



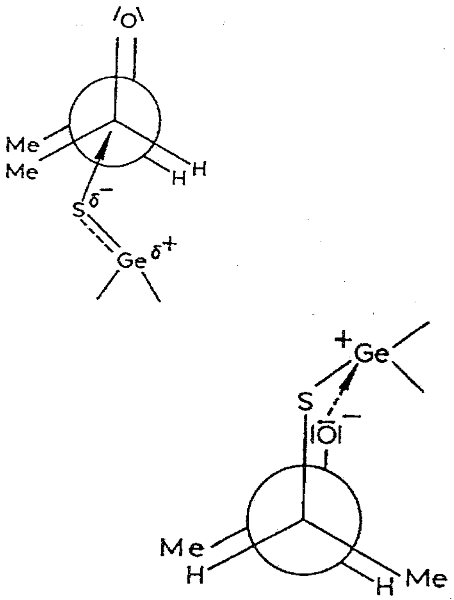
On the other hand, the condensation of germathione with *cis*- or *trans*-butene oxide gives a stereospecific reaction with inversion of configuration: *cis*- and *trans*-butene oxides lead to *trans*- and *cis*-adducts LXIII, respectively, in proportion higher than 95% with or without triethylamine [9, 19, 47] (Scheme 18 and 19).

Scheme 18



			yield (%)
with Et$_3$N	*cis* *trans*	*cis* / *trans* ∿0 / 100 *cis* / *trans* 95/5	85 95
without Et$_3$N	*cis* *trans*	*cis* / *trans* ∿0 / 100 *cis* / *trans* 95 / 5	40−50 15

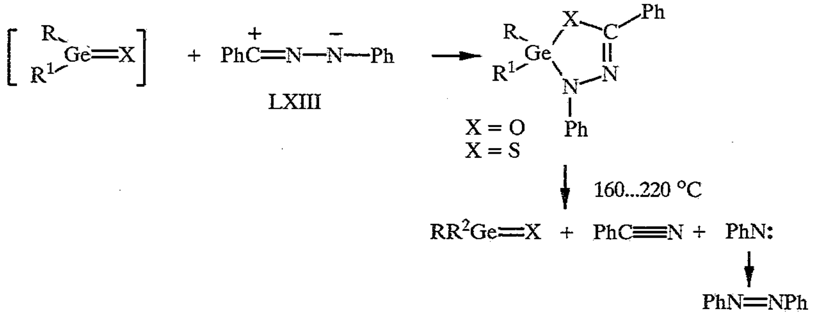
Scheme 19



Cycloaddition reactions with 1,3-dipolar reagents (nitrilimines, nitrones and nitrile oxides) have been observed [2, 18, 19, 48, 49].

The reactions of germanone and germathione with diphenyl-2,5-tetrazole (precursor of nitrilimine LXIII) lead to the regioselective cycloaddition to form germaoxa- or germathiadiazoline LXIV (Scheme 20).

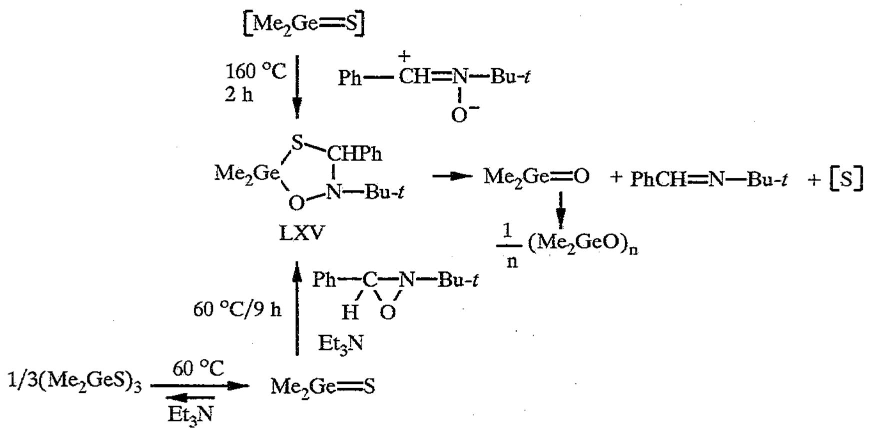
Scheme 20



Dimethylgermathione reacts with the nitrones (diphenylnitrone and phenyl N-*t*-butylnitrone) to give germaoxathiazolidines.

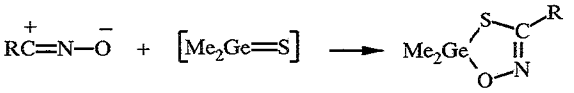
Dimethylgermathione undergoes with *t*-butylphenyloxazirane an insertion reaction in the oxazirane ring form the same germaoxathiazolidine LXV as in the reaction with isomeric phenyl-N-*t*-butylnitrone [2, 18, 19, 48, 49] (Scheme 21).

Scheme 21



LXV

Nitrile oxides give cycloadducts LXVI with germathiones [2, 8, 19, 49] (eq. 32).

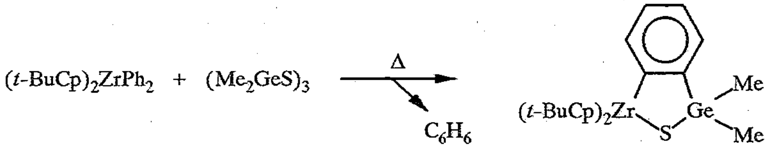


LXVI

R = Ph, Mes

(32)

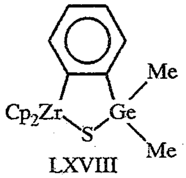
The trimer $(Me_2GeS)_3$ reacts with bis (π^5-*tert*-butylcyclopentadienyl)-diphenylzirconium to give dimetallacycle LXVII in good yield. This complex results from the insertion of the monomer germanethione $Me_2Ge{=}S$ into the Zr—C bond of the transient benzynezirconocene formed from the diphenyl complex. [13, 50] (eq. 33).



LXVII

(33)

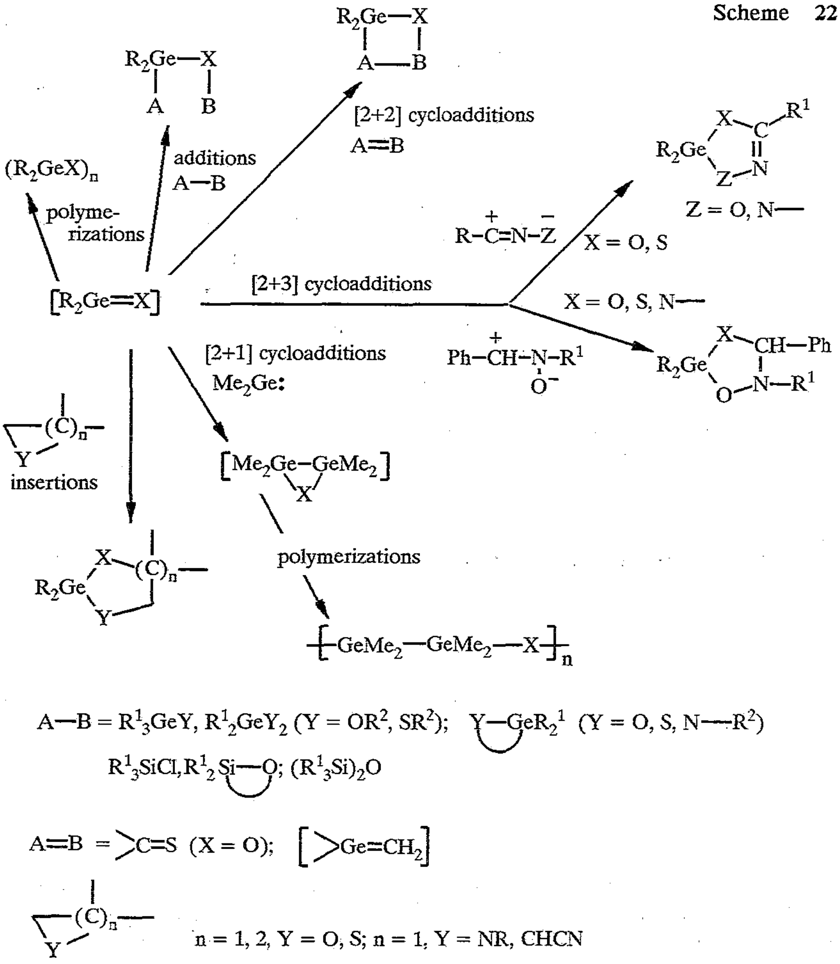
A similar reaction of $(Me_2GeS)_3$ and $Cp_2ZrMePh$ in boiling benzene afforded the complex LXVIII [13, 50].



LXVIII

Scheme 22 summarizes the most important reactions known for germanones and germathiones [20].

Scheme 22



In conclusion, the germylenes and the =Ge= X derivatives appear much more reactive than the corresponding carbon analogs.

Various types of cycloadditions ([2+1], [2+2], [2+3], [2+4]) are possible with these species. The studies of these new «organometallic functions» is now in progress in several groups and appears very promising in organometallic synthesis

The author wishes to express gratitude and thanks to his collaborators largely cited in the Bibliography.

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Received June 18, 1999