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REACTIONS OF GERMYLENES WITH NITROSOBENZENE AND PHENYL-t-BUTYL OXAZIRIDINE AND ITS ISOMERIC NITRONE *

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Summary

The reactions of germylenes with nitrosobenzene lead to nitrene and $>Ge{=}O$ intermediates via the zwitterionic form of the appropriate germaoxa-aziridines Interactions between the germylenes and the nitrene generated in the reactions give new $>Ge{=}N$-intermediates

The formation of germaoxa-azetidine is observed in the insertion reaction of germylene into the oxaziridine ring, in the 1,3-cycloaddition of germylene to the nitrone which is an isomer of the oxaziridine and also in the dehydrochlorination reaction of *C*-germylated hydroxylamines $Cl{-}\overset{|}{\underset{|}{Ge}}{-}CH(Ph){-}NOH(t\text{-}Bu)$

The β-elimination process from germaoxa-azetidines leads to imine and $>Ge{=}O$ intermediates

Introduction

We present some results in the general field of germylenes relating to some aspects of the reactivity of these bivalent species with the 1-2 dipole nitrosobenzene, and also with the 1-3 dipole phenyl-t-butyl nitrone and its isomeric oxaziridine

We propose the formation of transient species such as germaoxa-azetidines or germaoxa-aziridines (probably in zwitterionic form), this is supported by spectroscopic data (NMR and ESR) and independent chemical generation of the species (in the case of germaoxa-azetidines) These transient species produce, through a β-elimination process, new germyl intermediates which contain a doubly bonded germanium, i e., $>Ge{=}N$- and $>Ge{=}O$.

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* Dedicated to Professor Henri Normant on the occasion of this 72nd birthday 25th June 1979

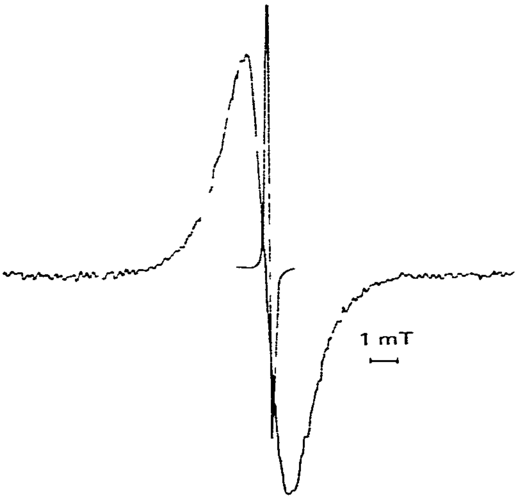


Fig 1 ESR spectrum reaction of F_2Ge and PhNO (dioxane −20°C)

Results and discussion

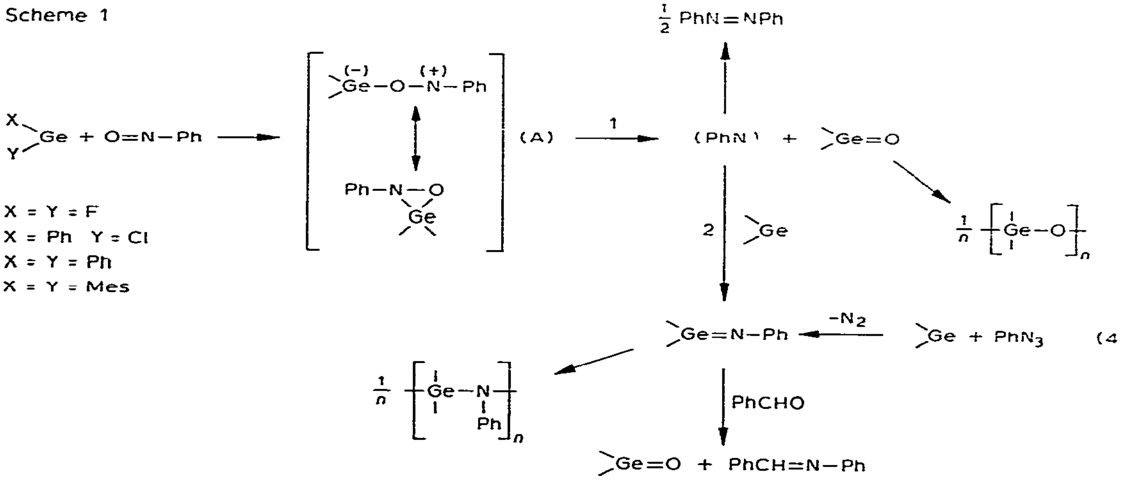
Reaction with nitrosobenzene

The high reactivity of electrophilic germylenes such as F_2Ge or PhGeCl (compared to Ph_2Ge [1]) towards nitrosobenzene in benzene solution [2] suggests an electrophilic attack of the germylene on the nitroso oxygen as the first step of the reaction This leads to the 3-germa-2-oxa-aziridine (A) in either zwitterionic or cyclic form.

The ESR study of this reaction shows a broad, strong signal (singlet 8 m teslas wide, $g = 2.0024$) which may support the postulated transient zwitterionic form (A) (Fig. 1).

The intermediate (A) undergoes decomposition and quickly leads to phenylnitrene, characterized as its dimer, i.e. azobenzene. The observed germoxanes are formed by polycondensation reactions of the doubly bonded $>Ge{=}O$ intermediates [3] (reaction 1, Scheme 1)

Scheme 1



Direct interaction between the germylene and the nitrene generated in the reaction (reaction 2, Scheme 1) leads to a transient germa-imine [4] which polycondenses to the corresponding cyclogermazanes [4] Furthermore, the germa-imine has been characterized by a pseudo-Wittig reaction with benzaldehyde [4] similar to that previously observed in the case of sila-imines [5—7].

Reaction with phenyl N-t-butyloxaziridine and its isomeric nitrone

The reaction of germylenes with oxaziridines could possibly lead, by insertion and ring expansion, to two unstable germaoxa-azetidines isomers (B) and (C) (reaction 1 and reaction 2, Scheme 2)

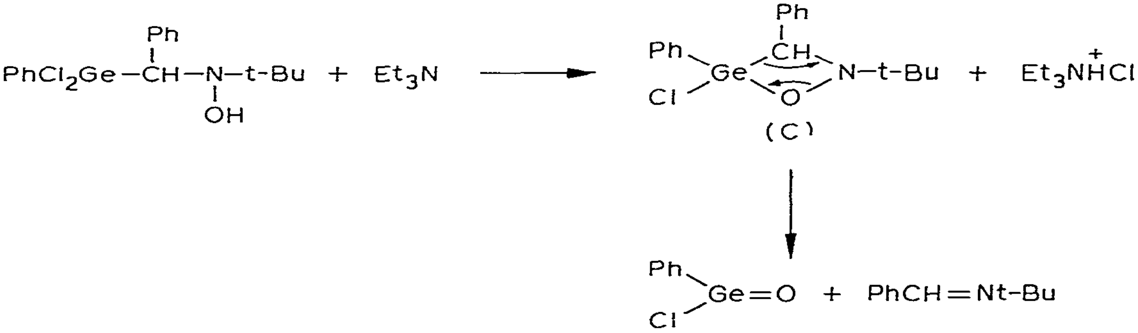
N—O opening in the oxaziridine, more usually considered as a homolytic reaction [8] would lead to an unstable 2-germa-3-oxa-azetidine (B) This same 2-germa-3-oxa-azetidine structure has been obtained in a pseudo-Wittig reaction between the corresponding germa-imine and aldehyde [4]

C—O bond opening in the oxaziridine, usually considered as a heterolytic mechanism [8,9], would lead to the intermediate (C) (C) can also be obtained from 1,3 cycloaddition of germylenes to the isomeric nitrone (reaction 3) The rapid decomposition of (C) gives the corresponding imines and germoxanes (cf. Scheme 2).

These reactions show an increasing germylene reactivity according to their relative electrophilic character. $Ph_2Ge < PhGeCl < F_2Ge$ (1)

Thus, it is possible to postulate an electrophilic attack of germylene on the oxygen of the oxaziridine which leads to a polar C—O cleavage similar to those observed in the protonation reactions of the oxygen in the same compounds [9]

This hypothesis is supported by an NMR study of these reactions We have observed in reactions of germylene, PhCeCl, with both oxaziridine and nitrone the formation of a transient intermediate (C) which has resonances assigned to CH and N-t-Bu (cf experimental section) similar to those of the intermediate which was observed during the dehydrochlorination reaction of the corresponding *C*-germylated hydroxylamines [10].

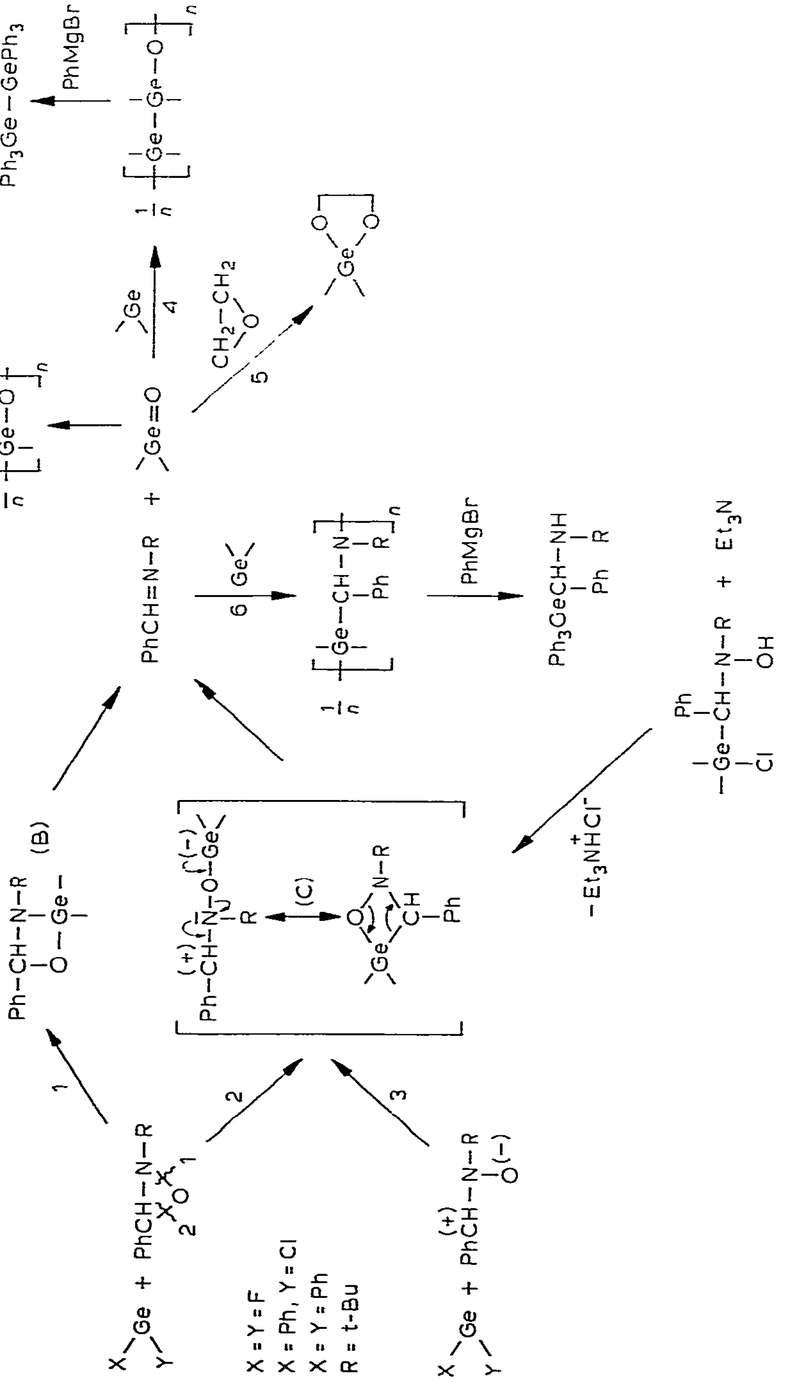


The intermediate (C) (cf. Scheme 2) is common to polar addition of germylenes on both oxaziridine and on its isomeric nitrone.

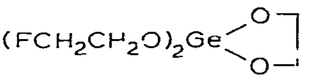
(C) gives rise to two signals in the NMR spectrum in C_6H_6 at δ 0 97 and δ 0 94 ppm (s) (N-t-Bu) which show that the germaoxa-azetidine (X = Ph, Y = Cl, Scheme 2) exists in two diastereoisomeric forms

In these reactions, the transient $>$Ge=O derivatives have been characterized

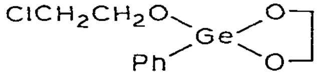
Scheme 2


X = Y = F
X = Ph, Y = Cl
X = Y = Ph
R = t-Bu
PhCH—N—R
(+) PhCH—N—R O(−)
1
2
3
4
5
6
(B)
(C)
PhCH=N—R
Ge=O
Ph3Ge—GePh3
PhMgBr
CH2—CH2 O
1/n
n
Ph3GeCH—NH Ph R
−Et3NHCl−
Et3N
Ph Cl OH

either as their adducts with the starting germylene (digermylated oxide $[-\overset{|}{\underset{|}{Ge}}-\overset{|}{\underset{|}{Ge}}-O-]_n$ which can be arylated to give $Ph_3GeGePh_3$) [11] (reaction 4) or as their insertion products with ethylene oxide (leading to germadioxolane) (reaction 5) [3] This last reaction gives new germadioxolanes,



and



(cf experimental section) These are formed by the insertion of $>Ge{=}O$ into ethylene oxide and ring opening followed by insertion of the oxirane into the germanium—halogen bond [12] However, the ring opening of the oxaziridine by derivatives containing germanium—halogen bonds (F, Cl) has not been observed [13]. The adducts of the initial germylene with the imine which has been generated lead to oligomers previously described [14] (reaction 6).

In summary, the reactions of germylenes with nitrosobenzene lead to $>Ge{=}O$ and $>Ge{=}N-$ intermediates by formal oxidation of germylenes, and secondary interaction of phenylnitrene with these bivalent species The formation of unstable germaoxa-azetidines (new four-membered heterocycles) from germylenes or chlorogermylhydroxylamines is strongly implicated in reactions of this kind, the β-elimination process from these heterocyles is a new route to $>Ge{=}O$ intermediates

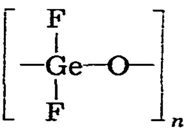
Experimental

The compounds described in this paper were characterized using standard analytical technics GLC (Aerograph 1400, SE 30, DEGS, internal reference Et_4Ge or Bu_4Ge), NMR (EM 360 A and T 60 Varian), IR (Perkin—Elmer 457), liquid film, Nujol mull or solid solution in KBr Elemental analyses were carried out by the "Service Central de microanalyse" of the CNRS and ESR spectra were obtained using a Varian E 104 in Professor Lappert's laboratory, University, of Sussex (U K.).

Reaction of F_2Ge with PhNO

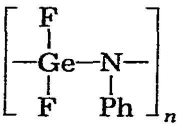
F_2Ge (0 42 g, 0 0036 mol) is added to a green solution of PhNO (0.193 g, 0 0018 mol) in C_6H_6 (1 cm^3) in a Schlenk tube. An exothermic reaction takes place with formation of a transient purple intermediate After 12 h at 20°C, the solvent is removed under vacuum The IR spectrum of the residue shows.

ν(GeOGe) 905 cm^{-1}



$$\left[-\overset{F}{\underset{F}{Ge}}-O-\right]_n \qquad (4)$$

ν(GeNGe) 830 cm^{-1}



$$\left[-\overset{F}{\underset{F}{Ge}}-\underset{Ph}{N}-\right]_n \qquad (4)$$

The ESR study of the reaction shows a broad signal (cf. Discussion).

The great reactivity of F_2Ge with PhN [4] explains why extensive formation of PhN=NPh was not observed in this reaction.

Reaction of PhGeCl with PhNO

In a Carius tube 0.5 cm^3 of a solution of PhGeCl in C_6H_6 (3.3 mol/1) and PhNO (0.175 g, 0.0016 mol) are heated for 5 min at 60°C. An exothermic reaction takes place with a change of coloration from green to purple, and finally to brown.

After 2 h at 60°C, the solvent is removed under vacuum. The residue shows the following bands in the IR spectrum: ν(GeOGe) 895 cm^{-1} (PhClGeO)$_n$ [4], ν(GeNGe) 830 cm^{-1} (PhClGeNPh)$_n$ [4], ν(CN=NC 930 cm^{-1} (PhN=NPh) [15]. GLC analysis shows formation of PhN=NPh (15%).

In a second experiment, a mixture of PhGeCl (0.0032 mol) and PhNO (0.175 g, 0.0016 mol) is allowed to react with C_6H_5CHO (0.175 g, 0.0016 mol) in a Carius tube for 12 h at 60°C. NMR analysis shows the formation of PhCH=NPh (65%), δ CH 8.05 ppm (s) (C_6D_6), and PhCHO (35%), δ CH 9.55 ppm (s) (C_6D_6) (unreacted). IR analysis shows the formation of (PhClGeO)$_n$, ν(GeOGe) 895 cm^{-1} [4] and PhN=NPh, ν(CN=NC) 930 cm^{-1}.

Reaction of Ph$_2$Ge with PhNO

To a suspension of the complex Ph_2Ge NEt_3 (1) (0.0044 mol) in C_6H_6 (5 cm^3) is added PhNO (0.23 g, 0.0022 mol). The mixture is heated for 12 h at 120°C in a Carius tube.

The solvent is removed under vacuum. Analysis of the residue by IR shows the formation of (Ph_2GeO)$_n$, ν(GeOGe) 860 cm^{-1} [16], (Ph_2GeNPh)$_n$, ν(GeNGe) 825 cm^{-1} [4]; PhN=NPh, ν(CN=NC) 930 cm^{-1}. GLC analysis confirms the formation of PhN=NPh.

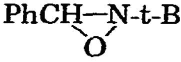
The same reaction carried out in presence of C_6H_5CHO (0.23 g, 0.0022 mol) leads to PhCH=NPh (55% yield) (NMR characterization) and to a residue from which (Ph_2GeO)$_3$ (0.047 g, 23% yield), m.p. 150°C [16] is separated by solvent trituration (C_6H_6, 50% + pentane, 50%) and filtration.

Reaction of Mes$_2$Ge with PhNO

To a suspension of the complex Mes_2Ge NEt_3, prepared from 1.00 g (0.0229 mol) of Mes_2ClGeH and 0.58 g (0.0058 mol) of Et_3N in C_6H_6 (5 cm^3), using the method described in ref. 1, is added PhNO (0.15 g, 0.0014 mol). The mixture is heated for 12 h at 120°C in a Carius tube. IR and NMR analyses of the reaction mixture show the formation of (Mes_2GeO)$_n$, ν(GeOGe) 850 cm^{-1} [4], (Mes_2GeNPh)$_n$, ν(GeNGe) 820 cm^{-1}, PhN=NPh, ν(CN=NC) 930 cm^{-1}.

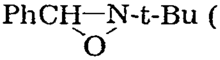
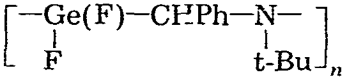
The same reaction carried out in presence of C_6H_5CHO (0.15 g, 0.0014 mol) leads to PhCH=NPh (25—30% yield).

Reaction of F$_2$Ge with N-t-butyloxaziridine

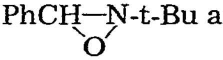
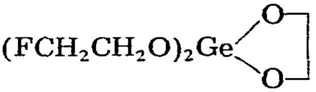
(a)  $PhCH\!-\!N\text{-}t\text{-}Bu$ (ring closed through O) (1.84 g, 0.0070 mol) is added to a solution of F_2Ge (0.77 g, 0.0070 mol) in dioxane (5 cm^3).

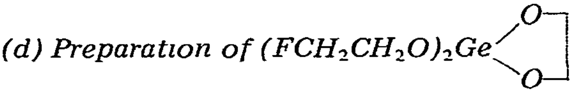
The great reactivity of difluorogermylene with the oxaziridine (or the isomeric nitrone) leads to an exothermic and very fast reaction, even at low temperature, which cannot be followed by NMR The products are $PhCH{=}N\text{-}t\text{-}Bu$, δ CH 8 08 ppm (s), δ t-Bu 1 30 ppm (s), $\nu(C{=}N)$ 1590 cm^{-1} and germyloxide $(F_2GeO)_n$, $\nu(GeOGe)$ 900 cm^{-1}

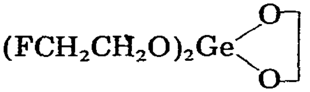
The dioxane is removed under vacuum leading to a residue which, after trituration with (50% ether + 50% pentane) gives $(F_2GeO)_n$ precipitate (0 42 g, 47% yield) IR $\nu(GeOGe)$ 905 cm^{-1} (in KBr) Anal Found F, 29 47. Calcd for GeF_2O F, 30 01%

(b) The same reaction, starting from F_2Ge (0 77 g, 0 0070 mol) and  (0 62 g, 0 0035 mol) leads, after 2 h at 50°C, to the imine $PhCH{=}N\text{-}t\text{-}Bu$ (~60% yield) characterized by NMR and GLC, and to  $\left[\mathrm{-\underset{F}{Ge}(F)-CHPh-\underset{t\text{-}Bu}{N}-}\right]_n$ (~40% yield) characterized from its aryl derivative which is obtained as follows The reaction mixture is arylated by 0 051 mol of PhMgBr in ether After hydrolysis and extraction, the solution obtained is dried over Na_2SO_4 and the solvent removed under vacuum NMR and GLC analysis show the formation of $Ph_3GeCH(Ph)NH\text{-}t\text{-}Bu$ (35% yield), Ph_4Ge (9% yield), $Ph_3GeGePh_3$ (56% yield) (relative %) The digermane is obtained via reaction 4 (see Scheme 2)

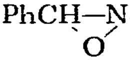
The same germylamine is prepared by arylation of $PhCl_2GeCH(Ph)NH\text{-}t\text{-}Bu$ [17] (0 93 g, 0.0024 mol) with PhMgBr (0 0073 mol) giving $Ph_3GeCH(Ph)NH\text{-}t\text{-}Bu$, 0.68 g (54% yield) B p 180°C/7—10^{-2} mmHg, IR $\nu(NH)$ 3320 cm^{-1}, NMR (C_6D_6), δ t-Bu 0 90 (s), δ CH 4 36 (s) ppm Digermane is prepared according to refs 16 and 18

(c) A solution of 1 95 g (0 0110 mol) of  and 2 50 g (100% excess) of ethylene oxide is added slowly to 1 22 g (0.0110 mol) of F_2Ge in THF (5 cm^3). The reaction is exothermic and, after 12 h at room temperature, distillation gives $PhCH{=}N\text{-}t\text{-}Bu$ (1 01 g), b.p 90°C/10 mmHg (57% yield),  (0.57 g), b p., 160°C/10 mmHg (19% yield) (characterized by comparison with authentic samples), undistillable residue.

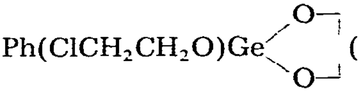
(d) Preparation of 

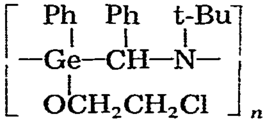
To $Ge(NMe_2)_4$ (0 0065 mol) in THF (2 cm^3) is added, in a Schlenk tube, CH_2OHCH_2OH (0 40 g, 0 0065 mol) After 1 h at room temperature, FCH_2CH_2OH (0 83 g; 0 0130 mol) is added and the mixture heated to 40—50°C for 2 h Distillation leads to pure , 0 73 g (64%). B p. 160°C/10 mmHg, n_D^{20} = 1 4500 NMR δ FCH_2 4.56 ppm (t d), $J(H{-}C{-}F)$ 36 Hz, (CCl_4) δ $FCH_2\underline{CH_2}O$ 3.84 ppm (t d), $J(HC{-}CF)$ 8 Hz, δ OCH_2 3 90 ppm (s), $J(HC{-}CH)$ 5 Hz. Anal.: Found. C, 27.82, H, 4 63, F, 14.67. Calcd. for $C_6H_{12}GeF_2O_4$· C, 26 91, H 4 41, F 15 21%.

Reaction of PhGeCl with phenyl—N-t-butyloxaziridine

(a) PhGeCl (0.0017 mol) in benzene solution (3 mol/l) is added dropwise to a solution of  $PhCH{-}N\text{-}t\text{-}Bu$ (0.29 g, 0.0017 mol) in CCl_4 (10 cm³). The reaction starts at 40—65° C and is followed by NMR. A new and weak signal appears at δ t-Bu 0.95 ppm (broad, s) but disappears after a few minutes as the imine signals appear at δ CH 8.00 ppm (s) and δ t-Bu 1.23 ppm (s).

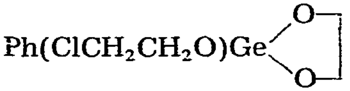
The mixture is then heated for 12 h at 80°C in a Carius tube, NMR analysis shows the formation of PhCH=N-t-Bu in approximately quantitative yield. The solvent is removed under vacuum and the residue, after pentane trituration, gives $(PhClGeO)_n$ precipitate (ν(GeOGe) 895 cm^{-1}).

(b) In the presence of an excess of ethylene oxide (0.5 g, 0.012 mol), the same reaction, carried out at 100° C in a Carius tube, leads to the compounds PhCH=N-t-Bu, $(PhClGeO)_n$, and also  $Ph(ClCH_2CH_2O)Ge$ (characterized by GLC (7% yield)) and to the adduct of the germylene $PhGeOCH_2CH_2Cl$ with imine generated in the reaction



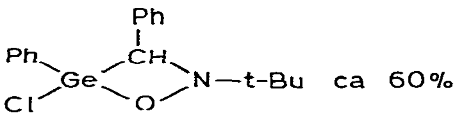
$$\left[-\underset{OCH_2CH_2Cl}{\overset{Ph}{Ge}}-\overset{Ph}{CH}-\overset{t\text{-}Bu}{N}- \right]_n$$

NMR (C_6H_6): δ CH 4.37 ppm (broad, s), δ CH_2 3.00—4.00 ppm (m), δ t-Bu 0.97 ppm (s). This gives, after arylation (PhMgBr), $Ph_3GeCH(Ph)NH$-t-Bu (28% yield) (GLC characterization).

(c) Preparation of  $Ph(ClCH_2CH_2O)Ge$. This compound is prepared from $PhGe(NMe_2)_3$ (2.71 g, 0.0096 mol), $HOCH_2CH_2OH$ (0.60 g, 0.0096 mol) and $ClCH_2CH_2OH$ (0.77 g, 0.0096 mol) following the above method (73% yield). B.p. 140°C/0.7 mmHg; NMR (C_6H_6), δ $ClCH_2$ 3.97 ppm (t), δ $ClCH_2\underline{CH_2}O$ 3.37 ppm (t) (J(HC—CH) 5.5 Hz), δ OCH_2 3.93 ppm (s). Anal. Found C, 41.27, H, 4.48; Cl, 12.41. Calcd. for $C_{10}H_{13}GeClO_3$. C, 41.52, H., 4.53, Cl, 12.25%.

Dehydrochlorination of $PhCl_2GeCHPhNOH$-t-Bu

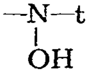
To a solution of 0.40 g (0.0010 mol) of $PhCl_2GeCH(Ph)NOH$-t-Bu [10] in CCl_4 (5 cm³) is added slowly Et_3N (0.10 g, 0.0010 mol). After 5 min at 0° C the Et_3NHCl is filtered off and the filtrate analyzed by NMR (CCl_4) $PhCl_2GeCH(Ph)NOHt$-Bu (ca. 15%): δ CH 5.05 (s), δ t-Bu 1.03 (ms) ppm



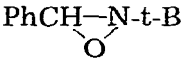
at 0° C. δ CH 4.73 (broad (s), δ t-Bu 0.97 and 0.90 (s) ppm.
at 25—30° C δ CH 4.82 (broad, s), δ t-Bu 0.99 and 0.92 (s) ppm.

PhCH=NtBu (ca. 25%): δ CH 8.00 (s), δ t-Bu 1.26 (s) ppm.

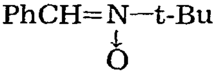
The germaoxa-azetidine decomposes quickly, leading to the imine PhCH=N-t-Bu and the germyloxide $(PhClGeO)_n$ which are characterized by IR spectroscopy (ν(GeOGe) 895 cm^{-1})

Methanolysis of the germaoxa-azetidine leads to Ph(Cl)(MeO)GeCH(Ph)-  $-\underset{\displaystyle OH}{N}-t\text{-}Bu$, characterized by NMR ($CCl_4$) δ OMe 3 68 (s), δ t-Bu 1 06 (s), δ CH 5 00 (s) ppm

Reaction of Ph_2Ge with phenyl-N-t-Butyloxaziridine

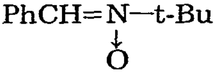
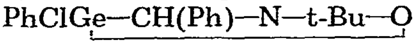
To a suspension of the complex Ph_2Ge NEt_3 [1] (0 16 g, 0 0006 mol) in C_6H_6 (2 cm^3) is added  $\underset{\diagdown O \diagup}{PhCH-N\text{-}t\text{-}Bu}$ (0 11 g, 0 0006 mol). The mixture is heated for 12 h at 120°C in a Carius tube NMR and IR analyses show the formation of PhCH=N-t-Bu (80%) and $(Ph_2GeO)_n$ (ν(GeOGe) 860 cm^{-1})

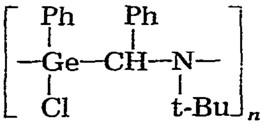
Reaction of F_2Ge with N-t-butyl-α-phenylnitrone

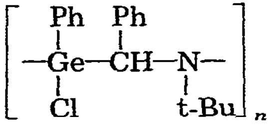
A solution of  $PhCH{=}\underset{\displaystyle \downarrow \atop O}{N}-t\text{-}Bu$ (0 19 g, 0 0011 mol) in C_6D_6 (1 cm^3) is added slowly to F_2Ge (0 18 g, 0 0011 mol) in dioxane (1 cm^3) The exothermic reaction gives PhCH=N-t-Bu (NMR) and a white precipitate of $(F_2GeO)_n$, isolated by filtration m p >350°C (with decomposition), ν(GeOGe) 905 cm^{-1} (KBr))

The reaction is too quick for the observation of intermediates using NMR and only the final products are detected

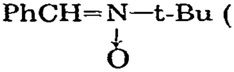
Reaction of PhGeCl with N-t-Butyl-α-phenylnitrone

(a) PhGeCl (0 0017 mol) in benzene solution (3 mol/l) is added dropwise to a solution of  $PhCH{=}\underset{\displaystyle \downarrow \atop O}{N}-t\text{-}Bu$ (0 29 g, 0 0017 mol) in CCl_4 (1 cm^3). The reaction is followed by NMR starting at 40°C with the formation of the transient germaoxa-azetidine  $\underline{PhClGe-CH(Ph)-N-t\text{-}Bu-O}$ δ t-Bu 1 00 ppm (broad s), δ CH 4 97 ppm (broad, s) which disappears after a few minutes The imine signals appear at the same time

(b) In benzene solution at a similar temperature (40—45°C), the transient species shows δ CH 4 52 ppm (broad, s) and two δ t-Bu 0 97 (s) and 0 94 ppm (s) (approximatively 1/1) corresponding to the two diastereoisomeric forms of germaoxa-azetidine The imine signals appear at the same time Two weak signals from the germylene imine adduct generated, i e.  $\left[-\underset{\displaystyle Cl}{\overset{\displaystyle Ph}{Ge}}-\overset{\displaystyle Ph}{CH}-\underset{\displaystyle t\text{-}Bu}{N}-\right]_n$ (δ CH 4.35 ppm (m), δ t-Bu 0.87 ppm (broad, s) also appear during the reaction.

(c) The same reaction carried out in C_6D_6 at 85°C for 3 h in a Carius tube leads to PhCH=N-t-Bu (80% yield; NMR and GLC characterization) and to $(PhClGeO)_n$ (ν(GeOGe) 895 cm^{-1} isolated as a viscous polymer mixed with a small quantity of  $\left[-\underset{\displaystyle Cl}{\overset{\displaystyle Ph}{Ge}}-\overset{\displaystyle Ph}{CH}-\underset{\displaystyle t\text{-}Bu}{N}-\right]_n$ (see above) after evaporation of all volatile products under high vacuum.

Reaction of Ph_2Ge with N-t-butyl α-phenylnitrone

To a suspension of the complex Ph_2Ge, NEt_3 [1] (0 16 g, 0 0006 mol) is added  $PhCH{=}\underset{\downarrow \atop O}{N}{-}t\text{-}Bu$ (0.11 g. 0 0006 mol) in C_6D_6 (1 cm^3) The mixture is heated for 12 h at 100° C in a Carius tube and leads to PhCH=N-t-Bu (14% yield) (NMR characterization) and to germyloxide $(Ph_2GeO)_n$ (ν(GeOGe) 860 cm^{-1}

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