

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 $\geq\text{Ge}=\text{O}$ intermediates via the zwitterionic form of the appropriate germaoxa-aziridines. Interactions between the germylenes and the nitrene generated in the reactions give new $\geq\text{Ge}=\text{N}$ -intermediates.

The formation of germaoxa-azetidines 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 $\text{Cl}-\underset{\text{Ph}}{\underset{\text{NOH}(t\text{-Bu})}{\text{Ge}}}-\text{CH}$

The β -elimination process from germaoxa-azetidines leads to imine and $\geq\text{Ge}=\text{O}$ 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., $\geq\text{Ge}=\text{N}$ - and $\geq\text{Ge}=\text{O}$.

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

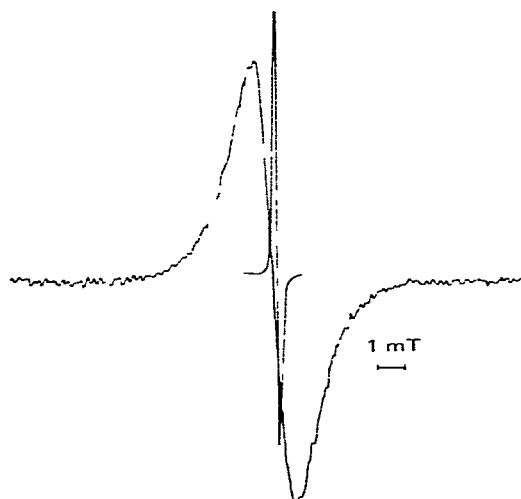


Fig 1 ESR spectrum reaction of F_2Ge and $PhNO$ (max int $-20^\circ C$)

Results and discussion

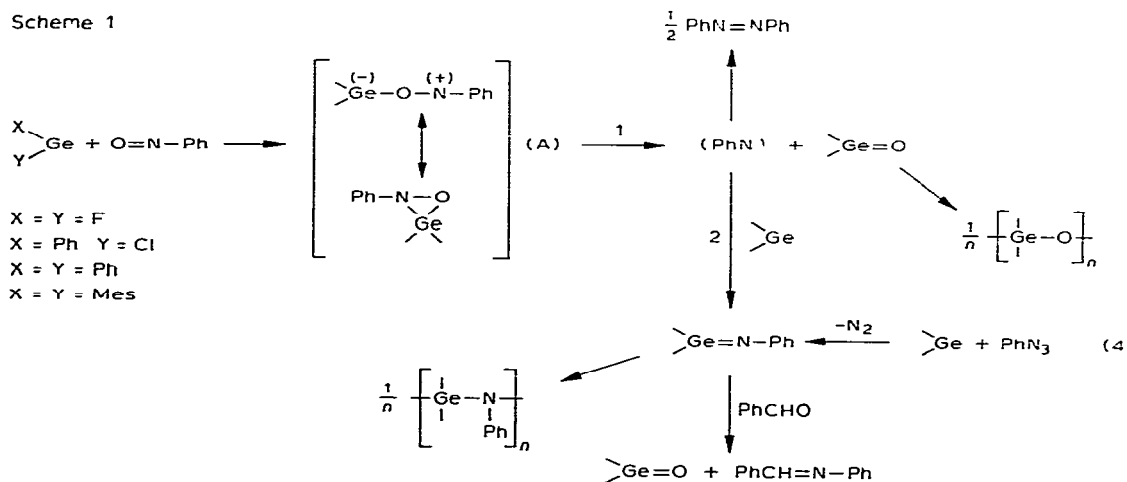
Reaction with nitrosobenzene

The high reactivity of electrophilic germynes 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 phenyl-nitrene, characterized as its dimer, i.e. azobenzene. The observed germoxanes are formed by polycondensation reactions of the doubly bonded $\geq Ge=O$ 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 nitrene

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)

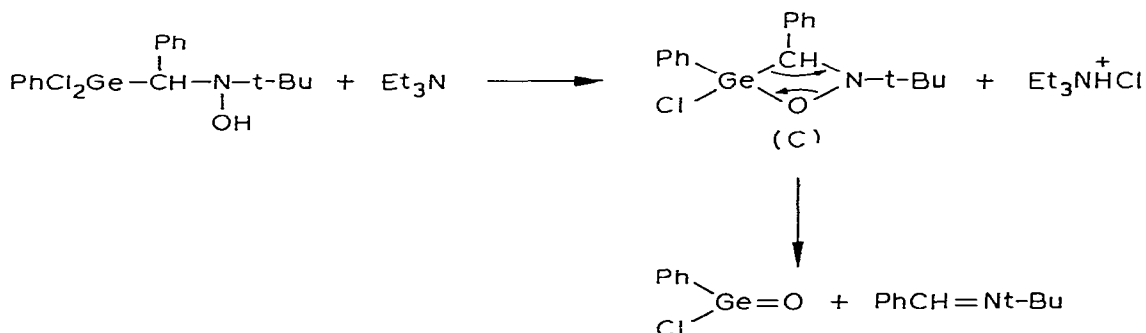
N-O opening in the oxaziridine, more usually considered as a homolytic reaction [8] would lead to an unstable 2-germa-3-oxa-azetidine (B). This same 2-germa-3-oxa-azetidine structure has been obtained in a pseudo-Wittig reaction between the corresponding germa-imine and aldehyde [4].

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 nitrene (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. $\text{Ph}_2\text{Ge} < \text{PhGeCl} < \text{F}_2\text{Ge}$ (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].

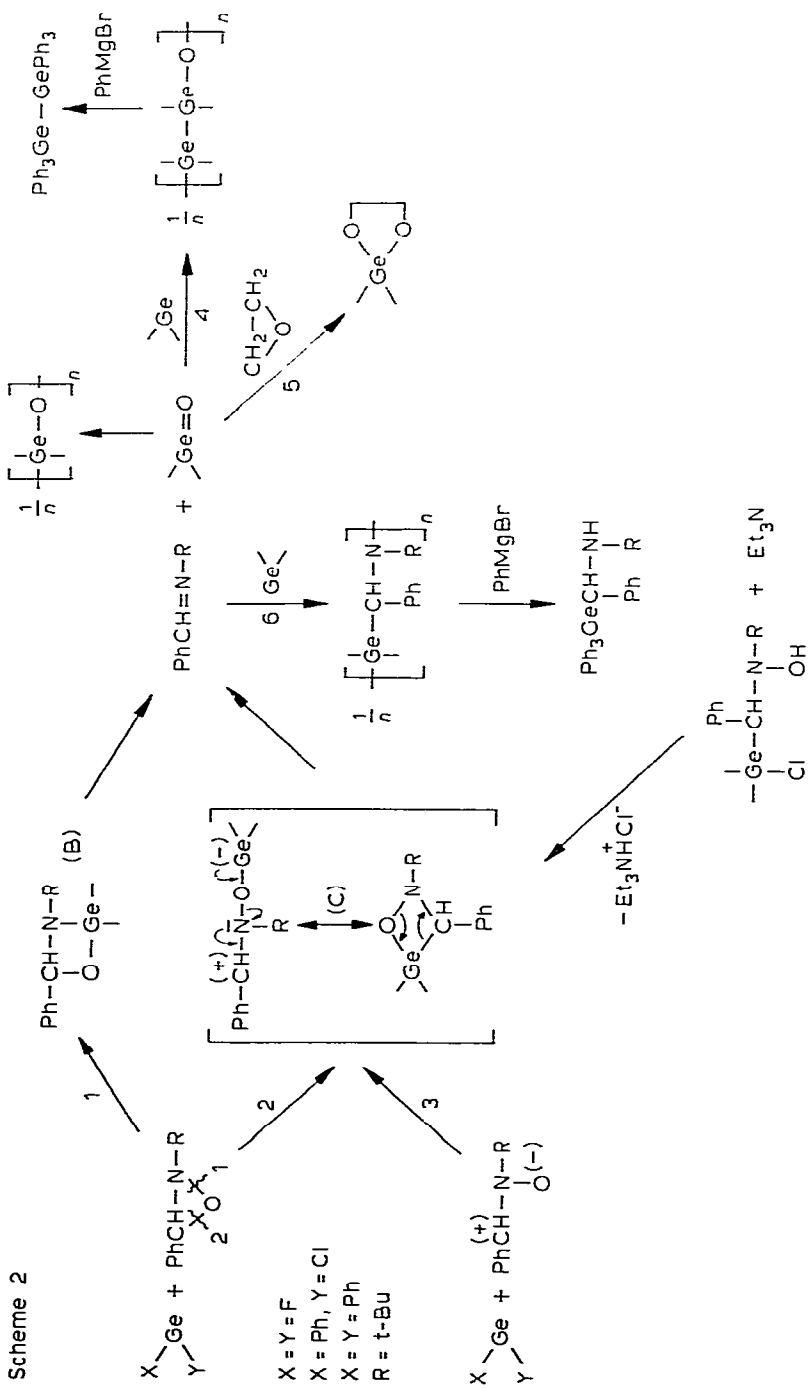
This hypothesis is supported by an NMR study of these reactions. We have observed in reactions of germylene, PhGeCl , with both oxaziridine and nitrene the formation of a transient intermediate (C) which has resonances assigned to CH and N-t-Bu (cf. experimental section) similar to those of the intermediate 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 nitrene.

(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.

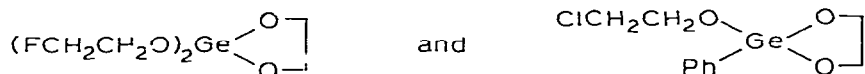
In these reactions, the transient >Ge=O derivatives have been characterized



either as their adducts with the starting germylene (digermylated oxide

$[-\text{Ge} \begin{array}{c} | \\ \text{---} \\ | \end{array} \text{---} \text{Ge} \begin{array}{c} | \\ \text{---} \\ | \end{array} \text{---} \text{O}]_n$ which can be arylated to give $\text{Ph}_3\text{GeGePh}_3$ [11] (reaction 4)

or as their insertion products with ethylene oxide (leading to germadioxolane) (reaction 5) [3]. This last reaction gives new germadioxolanes,



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

Experimental

The compounds described in this paper were characterized using standard analytical techniques: 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.



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 cm³ of a solution of PhGeCl in C₆H₆ (3.3 mol/l) 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: $\nu(GeOGe)$ 895 cm⁻¹ (PhClGeO)_n [4], $\nu(GeNGe)$ 830 cm⁻¹ (PhClGeNPh)_n [4], $\nu(CN=NC)$ 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 C₆H₅CHO (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) (C₆D₆), and PhCHO (35%), δ CH 9.55 ppm (s) (C₆D₆) (unreacted). IR analysis shows the formation of (PhClGeO)_n, $\nu(GeOGe)$ 895 cm⁻¹ [4] and PhN=NPh, $\nu(CN=NC)$ 930 cm⁻¹.

Reaction of Ph₂Ge with PhNO

To a suspension of the complex Ph₂Ge·NEt₃ (1) (0.0044 mol) in C₆H₆ (5 cm³) 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 (Ph₂GeO)_n, $\nu(GeOGe)$ 860 cm⁻¹ [16], (Ph₂GeNPh)_n, $\nu(GeNGe)$ 825 cm⁻¹ [4]; PhN=NPh, $\nu(CN=NC)$ 930 cm⁻¹. GLC analysis confirms the formation of PhN=NPh.

The same reaction carried out in presence of C₆H₅CHO (0.23 g, 0.0022 mol) leads to PhCH=NPh (55% yield) (NMR characterization) and to a residue from which (Ph₂GeO)₃ (0.047 g, 23% yield), m.p. 150°C [16] is separated by solvent trituration (C₆H₆, 50% + pentane, 50%) and filtration.

Reaction of Mes₂Ge with PhNO

To a suspension of the complex Mes₂Ge·NEt₃, prepared from 1.00 g (0.00229 mol) of Mes₂ClGeH and 0.58 g (0.0058 mol) of Et₃N in C₆H₆ (5 cm³), 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 (Mes₂GeO)_n, $\nu(GeOGe)$ 850 cm⁻¹ [4], (Mes₂GeNPh)_n, $\nu(GeNGe)$ 820 cm⁻¹, PhN=NPh, $\nu(CN=NC)$ 930 cm⁻¹.

The same reaction carried out in presence of C₆H₅CHO (0.15 g, 0.0014 mol) leads to PhCH=NPh (25–30% yield).

Reaction of F₂Ge with N-t-butyloxaziridine

(a) $\text{PhCH}-\underset{\text{O}}{\text{N-t-Bu}}$ (1.84 g, 0.0070 mol) is added to a solution of F₂Ge (0.77 g, 0.0070 mol) in dioxane (5 cm³).

The great reactivity of difluorogermylene with the oxaziridine (or the iso-

meric nitron) leads to an exothermic and very fast reaction, even at low temperature, which cannot be followed by NMR. The products are $\text{PhCH}=\text{N}-t\text{-Bu}$, δCH 8.08 ppm (s), $\delta t\text{-Bu}$ 1.30 ppm (s), $\nu(\text{C}=\text{N})$ 1590 cm^{-1} and germyloxide $(\text{F}_2\text{GeO})_n$, $\nu(\text{GeOGe})$ 900 cm^{-1} .

The dioxane is removed under vacuum leading to a residue which, after trituration with (50% ether + 50% pentane) gives $(\text{F}_2\text{GeO})_n$ precipitate (0.42 g, 47% yield). IR $\nu(\text{GeOGe})$ 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 $\text{PhCH}=\text{N}-t\text{-Bu}$ (0.62 g, 0.0035 mol) leads, after 2 h at 50°C, to the imine

$\text{PhCH}=\text{N}-t\text{-Bu}$ (~60% yield) characterized by NMR and GLC, and to

$\left[\begin{array}{c} \text{---Ge(F)---CHPh---N---} \\ | \qquad \qquad \qquad | \\ \text{F} \qquad \qquad \qquad t\text{-Bu} \end{array} \right]_n$ (~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 $\text{Ph}_3\text{GeCH}(\text{Ph})\text{NH}-t\text{-Bu}$ (35% yield), Ph_4Ge (9% yield), $\text{Ph}_3\text{GeGePh}_3$ (56% yield) (relative %). The digermane is obtained via reaction 4 (see Scheme 2).

The same germylamine is prepared by arylation of $\text{PhCl}_2\text{GeCH}(\text{Ph})\text{NH}-t\text{-Bu}$ [17] (0.93 g, 0.0024 mol) with PhMgBr (0.0073 mol) giving $\text{Ph}_3\text{GeCH}(\text{Ph})\text{NH}-t\text{-Bu}$, 0.68 g (54% yield). B.p. 180°C/7–10⁻² mmHg, IR $\nu(\text{NH})$ 3320 cm^{-1} , NMR (C_6D_6), $\delta t\text{-Bu}$ 0.90 (s), δCH 4.36 (s) ppm. Digermane is prepared according to refs. 16 and 18.

(c) A solution of 1.95 g (0.0110 mol) of $\text{PhCH}=\text{N}-t\text{-Bu}$ 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 $\text{PhCH}=\text{N}-t\text{-Bu}$ (1.01 g), b.p. 90°C/10 mmHg (57% yield),

$(\text{FCH}_2\text{CH}_2\text{O})_2\text{Ge} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ (0.57 g), b.p., 160°C/10 mmHg (19% yield) (characterized

by comparison with authentic samples), undistillable residue.

(d) Preparation of $(\text{FCH}_2\text{CH}_2\text{O})_2\text{Ge} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$

To $\text{Ge}(\text{NMe}_2)_4$ (0.0065 mol) in THF (2 cm^3) is added, in a Schlenk tube, $\text{CH}_2\text{OHCH}_2\text{OH}$ (0.40 g, 0.0065 mol). After 1 h at room temperature, $\text{FCH}_2\text{CH}_2\text{OH}$ (0.83 g; 0.0130 mol) is added and the mixture heated to 40–50°C

for 2 h. Distillation leads to pure $(\text{FCH}_2\text{CH}_2\text{O})_2\text{Ge} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$, 0.73 g (64%). B.p. 160°C/

10 mmHg, $n_D^{20} = 1.4500$. NMR: δFCH_2 4.56 ppm (t d), $J(\text{H}-\text{C}-\text{F})$ 36 Hz, (CCl_4) $\delta \text{FCH}_2\text{CH}_2\text{O}$ 3.84 ppm (t d), $J(\text{HC}-\text{CF})$ 8 Hz, δOCH_2 3.90 ppm (s), $J(\text{HC}-\text{CH})$ 5 Hz. Anal.: Found: C, 27.82, H, 4.63, F, 14.67. Calcd. for $\text{C}_6\text{H}_{12}\text{GeF}_2\text{O}_4 \cdot \text{C}$, C, 26.91, H 4.41, F 15.21%.


Reaction of PhGeCl with phenyl-N-t-butyloxazolidine

(a) PhGeCl (0.0017 mol) in benzene solution (3 mol/l) is added dropwise to a solution of PhCH=N-t-Bu (0.29 g, 0.0017 mol) in CCl₄ (10 cm³). The reaction

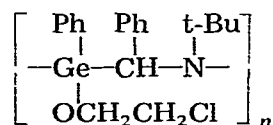
starts at 40–65°C and is followed by NMR. A new and weak signal appears at δ t-Bu 0.95 ppm (broad, s) but disappears after a few minutes as the imine signals appear at δ CH 8.00 ppm (s) and δ t-Bu 1.23 ppm (s).

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(ClCH₂CH₂O)Ge  (characterized by

GLC (7% yield)) and to the adduct of the germylene PhGeOCH₂CH₂Cl with imine generated in the reaction



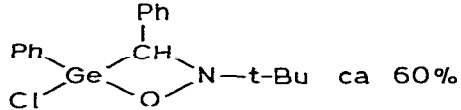
NMR (C₆H₆): δ CH 4.37 ppm (broad, s), δ CH₂ 3.00–4.00 ppm (m), δ t-Bu 0.97 ppm (s). This gives, after arylation (PhMgBr), Ph₃GeCH(Ph)NH-t-Bu (28% yield) (GLC characterization).

(c) Preparation of Ph(ClCH₂CH₂O)Ge  This compound is prepared from

PhGe(NMe₂)₃ (2.71 g, 0.0096 mol), HOCH₂CH₂OH (0.60 g, 0.0096 mol) and ClCH₂CH₂OH (0.77 g, 0.0096 mol) following the above method (73% yield). B.p. 140°C/0.7 mmHg; NMR (C₆H₆), δ ClCH₂ 3.97 ppm (t), δ ClCH₂CH₂O 3.37 ppm (t) (J(HC-CH) 5.5 Hz), δ OCH₂ 3.93 ppm (s). Anal. Found: C, 41.27, H, 4.48; Cl, 12.41. Calcd. for C₁₀H₁₃GeClO₃: C, 41.52, H, 4.53, Cl, 12.25%.

Dehydrochlorination of PhCl₂GeCHPhNOH-t-Bu

To a solution of 0.40 g (0.0010 mol) of PhCl₂GeCH(Ph)NOH-t-Bu [10] in CCl₄ (5 cm³) is added slowly Et₃N (0.10 g, 0.0010 mol). After 5 min at 0°C the Et₃NHCl is filtered off and the filtrate analyzed by NMR (CCl₄) PhCl₂GeCH(Ph)NOH-t-Bu (ca. 15%): δ CH 5.05 (s), δ t-Bu 1.03 (ms) ppm

 ca. 60% 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 germyloxyde (PhClGeO)_n which are characterized by IR

spectroscopy ($\nu(\text{GeOGe})$ 895 cm^{-1})

Methanolysis of the germaoxa-azetidone leads to $\text{Ph}(\text{Cl})(\text{MeO})\text{GeCH}(\text{Ph})\text{-N-t-Bu}$, characterized by NMR (CCl_4) δ OMe 3.68 (s), δ t-Bu 1.06 (s), δ CH

$$\begin{array}{c} \text{OH} \\ | \\ \text{5.00 (s) ppm} \end{array}$$

Reaction of Ph_2Ge with phenyl-*N-t*-Butyloxaziridine

To a suspension of the complex $\text{Ph}_2\text{Ge} \cdot \text{NEt}_3$ [1] (0.16 g, 0.0006 mol) in C_6H_6 (2 cm^3) is added PhCH=N-t-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 $(\text{Ph}_2\text{GeO})_n$ ($\nu(\text{GeOGe})$ 860 cm^{-1})

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

A solution of PhCH=N-t-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 $(\text{F}_2\text{GeO})_n$, isolated by filtration m.p. >350°C (with decomposition), $\nu(\text{GeOGe})$ 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=N-t-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-azetidone $\text{PhClGe-CH(Ph)-N-t-Bu-O}$ 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) (approximately 1/1) corresponding to the two diastereoisomeric forms of germaoxa-azetidone. The imine signals appear at the same time. Two weak signals

from the germylene imine adduct generated, i.e. $\left[\begin{array}{c} \text{Ph} \quad \text{Ph} \\ | \quad | \\ \text{-Ge-CH-N-} \\ | \quad | \\ \text{Cl} \quad \text{t-Bu} \end{array} \right]_n$ (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 $(\text{PhClGeO})_n$ ($\nu(\text{GeOGe})$ 895 cm^{-1}) isolated as a viscous polymer mixed with a

small quantity of $\left[\begin{array}{c} \text{Ph} \quad \text{Ph} \\ | \quad | \\ \text{-Ge-CH-N-} \\ | \quad | \\ \text{Cl} \quad \text{t-Bu} \end{array} \right]_n$ (see above) after evaporation of all volatile products under high vacuum.

Reaction of Ph₂Ge with N-t-butyl α-phenylnitro

To a suspension of the complex Ph₂Ge, NEt₃ [1] (0.16 g, 0.0006 mol) is added PhCH=N-t-Bu (0.11 g, 0.0006 mol) in C₆D₆ (1 cm³). 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 germyloxyde (Ph₂GeO)_n (ν(GeOGe) 860 cm⁻¹)

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