A NEW STEP IN THE UNDERSTANDING OF CYCLOADDITION OF GERMYLENES TO QUINONES

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Abstract

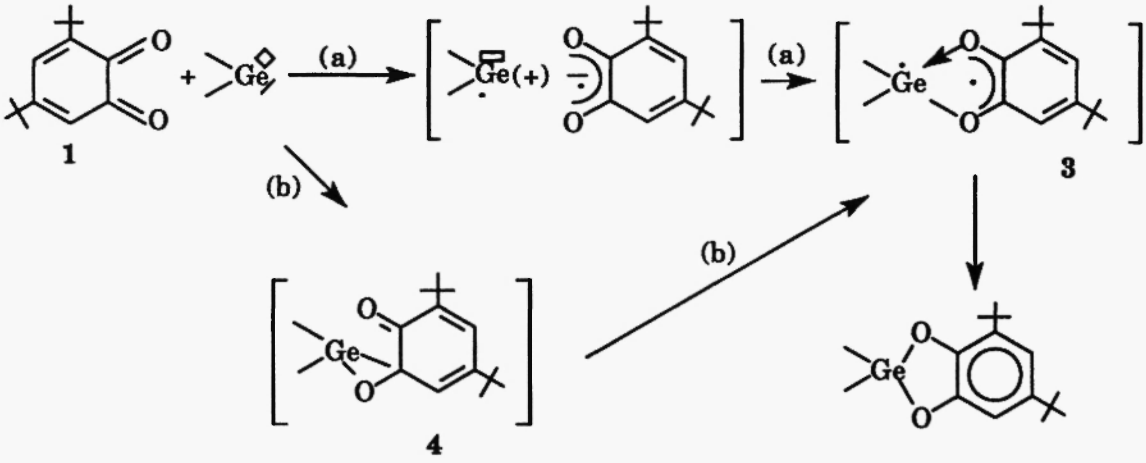
The cycloaddition of Lappert's bulky germylene to 3,5-di-tert-butylorthoquinone gave almost quantitatively the corresponding germadioxolan. The reaction proceeded through a biradical pathway as an o-semiquinonic intermediate was observed by E.S.R. together with the transient germanium centred radical of trapped with 2,4,6-tri-tert-butyl-nitrosobenzene.

A similar reaction with the galvinoxyl radical caused its diamagnetisation although the very bulky germylene was unable to add directly to this quinonic species highly hindered by the tert-butyl groups in α,α'-position to oxygens, showing that the biradical pathway begins by a single electron transfer from germylene to the quinonic species. This last reaction led to polymers the formation of which is discussed.

Introduction

It has been shown that a large number of germylenes undergo cycloaddition with 3,5-di-tert-butylorthoquinone **1** [1] [2]. These additions occur via a monoelectronic transfer processes as the corresponding o-semiquinonic intermediate has been characterized by E.S.R. [3]. These results have been confirmed recently by an important study of the copolymerisation of bulky germylenes (particularly Lappert's germylene **2**) with various paraquinones [4]. Thus Kobayashi et al. have been able to directly observe the formation of not only the transient semi-quinonic radical but also the transient metal-centred radical, demonstrating that a biradical pathway occurs.

Even at this time it is not possible to determine the first step of the monoelectronic processes. Since the direct activation of singlet germylene [5] to triplet germylene in the presence of the quinone is highly improbable, two other possibilities have been proposed [3] [4] : a S.E.T. reaction (scheme I (a)) or a 1-2 addition leading to a transient unstable 1-oxa-2-germacyclo-propane intermediate **4** (scheme I (b)).

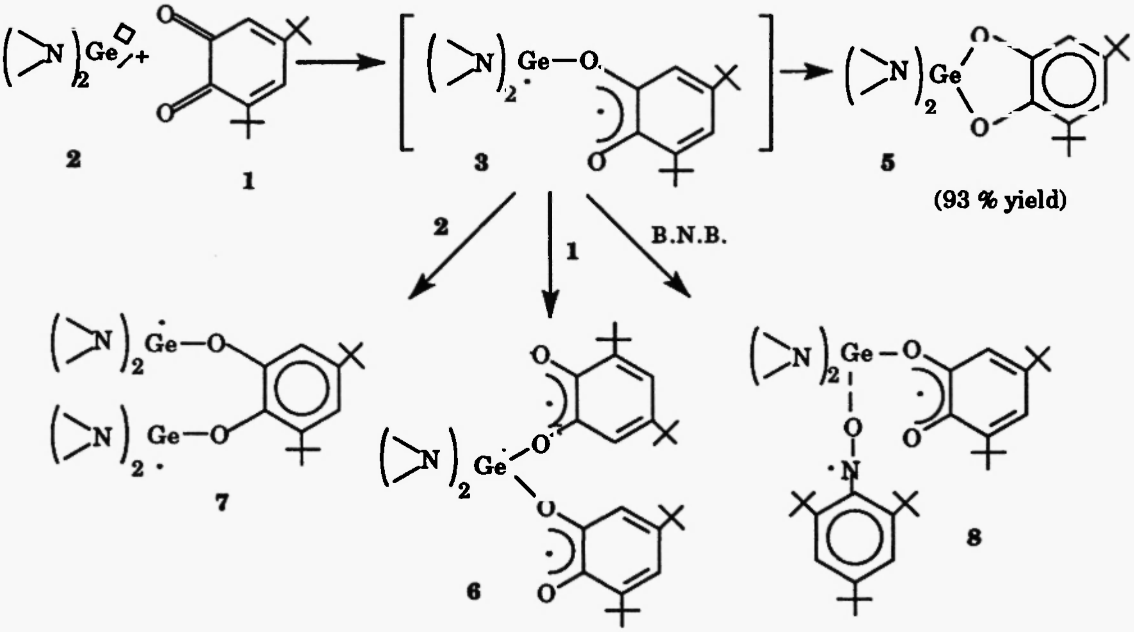


(Scheme I)

The aim of this work is to try to determine the possibility or the impossibility of each route in schema I (a) and (b).

Discussion

First we tried to study the possibility of Lappert's bulky germylene $[(\mathrm{Me_3Si}]_2\mathrm{N}]_2\mathrm{Ge}$ (or (> N)$_2$Ge, **2**) giving cycloaddition to quinones, and to extend this study to other less bulky stable diaminogermylenes. Cycloaddition of **2** to 3,5-di-tert-butylorthoquinone **1** proceeds easily and almost quantitatively (scheme II).

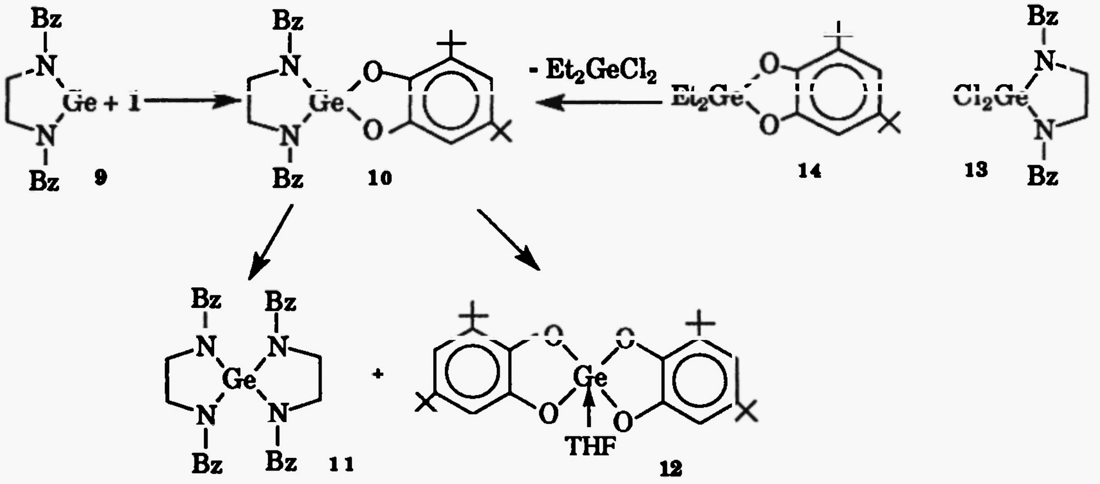


(Scheme II)

An E.S.R. study of the reaction showed two transient but independent paramagnetic species : an o-semiquinonic species **6** and a germanium-centred radical **7**, but **7** was observed only with difficulty when the quinone **1** was added to a suspension of solid germylene in frozen hexane and the temperature rised to -70°C, and it disappeared in solution at -50°C, with only species **6** remaining.

Thus, spectra (Fig. 1) do not constitute a direct observation of intermediate **3**: they reveal only its presence from by-products originating from **6**. **3** gave **6** by reaction with **1** and **7** resulted from the reaction with **2** before its cyclisation (Fig. 2) as observed in [4]. **3** was also characterized using an efficient germanium centred radical spin trap, the **2,4,6-tri-tert-butyl-nitrosobenzene (B.N.B) 8** [4] (Fig. 3) and (scheme II).

An extension of this work to a new, less bulky amino-germylene **9** showed that the cycloadduct obtained became less stable, undergoing symmetrisation (scheme III). It has been also obtained by an exchange reaction (scheme III) but symmetrisation also occured.

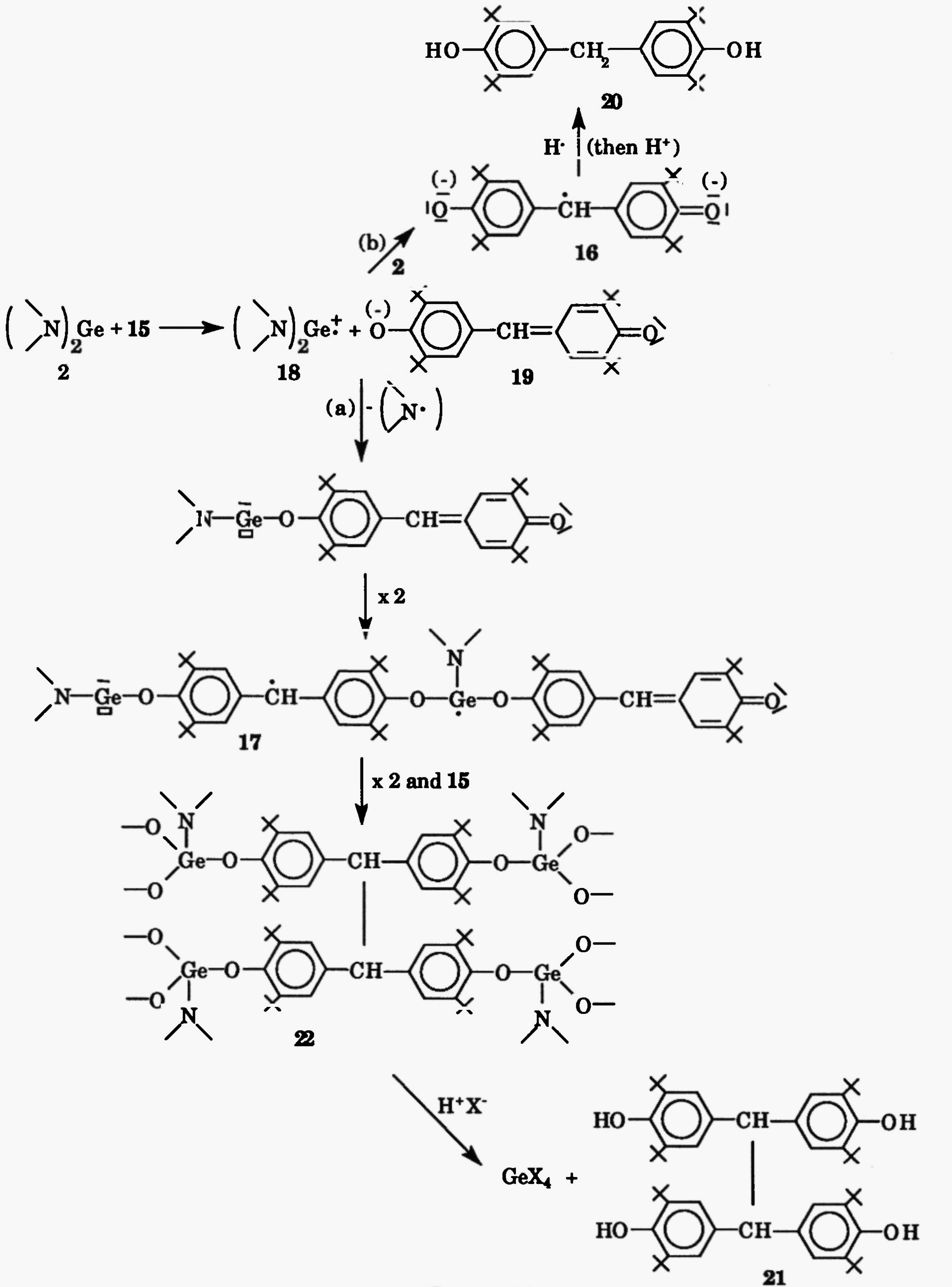


(Scheme III)

Then noting Kobayashi's observation that tert-butyl groups in α,α'-position to the quinone function causes a total inactivation of the compound towards Lappert's germylene **2**, we decided to extend our study to the galvinoxyl radical **15**. **15** presents two inacessible reactive sites towards direct 1,2-addition of the bulky germylene **2**. Thus, in this particular case, route (a) (scheme I) remains possible while route (b) becomes very difficult and hence highly improbable.

We observed that germylene **2** started to react at room temperature with galvinoxyl. Almost stoichiometric 1 to 1 diamagnetisation of **15** was observed by ESR, but we failed to observe directly or clearly detect the transient formation of any germanium centred radical (Fig. 4) like that observed during the reaction of the same germylene **2** with paraquinones [4].

These results demonstrate that even, in the absence of a direct possible 1,2-addition of **2** to **15**, a monoelectronic transfer occurs, which supports the S.E.T. mechanism (scheme I(a)).

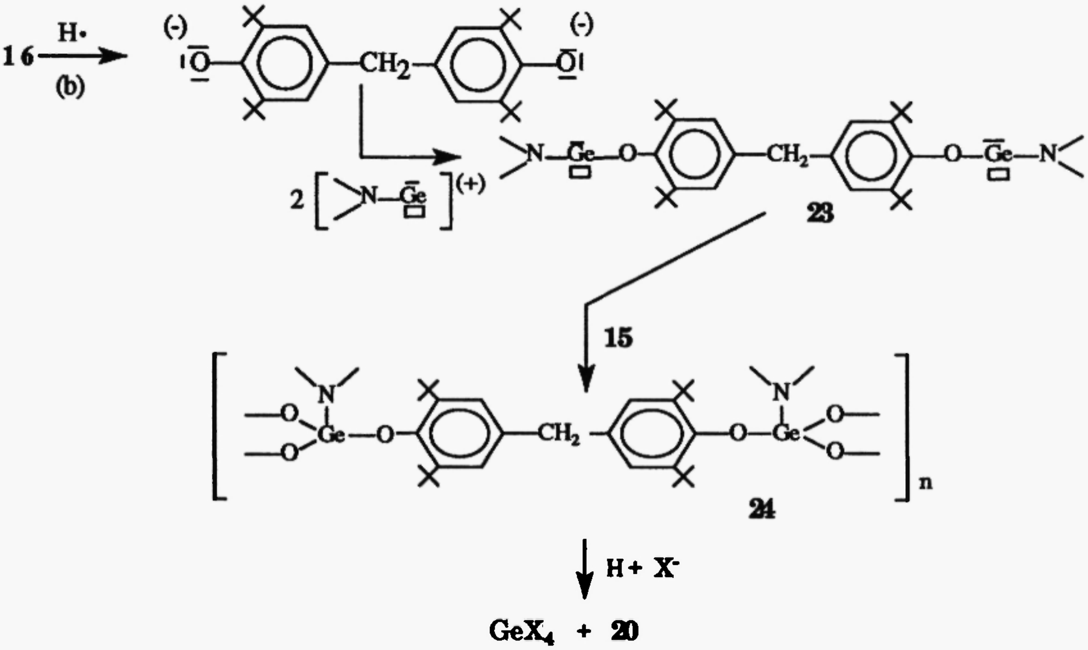

HO
CH2
OH
20
H·
(then H+)
(-)
CH
(-)
16
(b)
2
N
2
Ge + 15
2
Ge·+
18
(-)
O
CH=
19
(a)
N·
N—Ge—O
CH=
x 2
N
N—Ge—O
CH
O—Ge—O
CH=
17
x 2 and 15
N
Ge—O
CH
O—Ge
22
H+X-
GeX4 +
HO
CH
OH
21

(Scheme IV)

The reaction gave polymers the composition of which changed slightly with the reaction conditions (temperature and also the order of addition of the reagents). Two observations we made give an idea of the polymeric structure and of one of the possible polymerisation processes. We observed, particularly when the reaction mixture was heated at 50°C, that an appreciable loss of germylene ligand (about 40 %) occured. Then cleavage reaction of the polymer by protolysis led to dimers of galvinoxyl and also to the 1,1',8-trihydrogalvinoxyl **20** (see experimental part). These results can only be explained by a transient formation of a carbon-centered radical (**16** or **17**) (scheme IV).

The mechanism proposed in (scheme IV), can explain these observations. After an initial monoelectric transfer which causes diamagnetisation of **15**, the germylene cation radical **18**, sterically unable to add to the very bulky galvinoxyl ion **19**, decomposes by valence reduction as previously observed by Lappert in the photolysis of **2** [6]. A less bulky germyne ion is thus formed which is able to undergo copolymerisation with **19** (scheme IV). Successives single electron transfer (route (b) of scheme IV) leading transiently to **16** can also explain the formation of the perhydrogalvinoxyl **20** and the dimer **21** characterized.

Another alternative consists in a diaddition of the transient germyne ion to intermediate **16** leading to a sufficiently stable bis-germylene **23** to be characterized in situ (scheme V).



(Scheme V)

Thus these hypotheses (schemes IV and V) are not exclusive and definitive. It is possible for example that the two mechanisms work simultaneously leading to non homogeneous polymers presenting structures of the type 22 and 24.

In conclusion, this comparaison of the reaction of Lappert's bulky germylene 2 with 3,5-di-tert-butylorthoquinone 1 and galvinoxyl 15 supports, in the context of a monoelectronic pathway, an initial step of single electron transfer. We think that an extension of this work to a study of copolymerisation of difluoro and organofluorogermylenes with 15 with the support of ^{19}F NMR will allow us to better determine the composition of the resulting copolymers.

Experimental section

The compounds described in this paper were characterized by the usual analytical techniques : G.C. : HP 5890 (column SE30, 40°C to 280°C, 20°C mn^{-1}). ^1H NMR : A.C. 80 Bruker ; ^{13}C NMR : A.C. 200 Bruker. IR : Perkin-Elmer 1 600 F.T. E.S.R. : Bruker E.R. 200 with frequency meter E.I.P. Mass spectra : Ribermag R1010H (E.I.) and (D.C.I.CH_4 and NH_3) and H.P. 5989A (G.C./M.S.). Melting points were measured on a Reichert microscope. Elemental analyses were done by the microanalysis center of CNRS and of the Ecole Nationale Supérieure de Chimie de Toulouse.

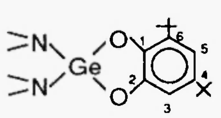
For Lappert's germylene 2, see [6], 3,5-di-tert-butylorthoquinone 1, galvinoxyl 15 and perhydrogalvinoxyl 20 (Aldrich).

Synthesis of N,N'-dibenzyl(1,2-ethylenediamino)germylene 9

To a solution of N,N'-dibenzylethylenediamine (0,48 g, 2 mmole) in 5 mL of hexane and 5 mL of THF, was added dropwise at 0°C a solution of BuLi (4 mmole in hexane). The solution turned yellow. After 2 h at 20°C under stirring, the $GeCl_2$,dioxane complex (0,46 g, 2 mmole) was added at 0°C and the reaction mixture maintained under stirring 14 h at room temperature. Filtration gave a yellow orange solution which gave, after concentration under vacuo, an orange sticky oil (0,52 g) 83 % yield. The crude but almost pure germylene 9 obtained cannot be distilled : it decomposes from 50°C. Residue identified 9 : ^1H NMR ($CDCl_3$, δ ppm) : 7.30 (br.s., C_6H_5) ; 4.12 (s, NCH_2Ph) ; 3.04 (s,NCH_2). M.S (E.I) : 312 [M^+], 221 [M^+-CH_2Ph].

Reaction of bis (bis-trimethylsilyl)aminogermylene 2 with 3,5-di-tert-butylorthoquinone 1

To 2 (0,78 g, 2 mmole) in 3 mL of ether is added dropwise a solution of 1 in 5 mL of THF. The solution turned to green and then to yellow. After 12 h at 20°C under stirring, concentration under vacuo led to a visquous residu identified to almost pure cycloadduct **5** (0,67 g, 93%) which has been completely purified by distillation 0,29 g (40% yield). It crystallised within a few days leading to a pale pink powder. 5 ; m.p. : 85°C. ^1H NMR ($CDCl_3$, δ ppm) : 6.79 (d, 2.3 Hz) and 6.72 (d, 2,3 Hz) (C_6H_2); 1.39 (s) and 1.28 (s) (t-Bu); 0.23 (s, $SiMe_3$).^{13}C NMR ($CDCl_3$, δ ppm) :



4.7 (Me_3Si) ; tBu : 30.0 and 31.8 (CH_3), 34.5 and 34.6 ($C\text{-}CH_3$) ; 109.3 (C_3) and 113 8 (C_5) ; 134 3 (C_6), 142.1 (C_4) ; 143.7 (C_1) ; 148.2 (C_2). M.S (E.I) : 614 [M^+], 599 [$M^+\text{-}CH_3$]. Anal. calc. (found) for $C_{26}H_{56}GeN_2O_2Si_4$: C 50.89 (50.40), H 9.19 (9.27), N 4.56 (4.39).

Reaction of N,N'-dibenzyl(1,2-ethylenediamino)germylene 9 with 1

To a solution of germylene 9 (0,228 g, 0,73 mmole) in 3 mL of THF is added dropwise at -40°C a solution of 1 (0.128 g, 0,584 mmole) in 2 mL of THF. The solution turned to light green and then gradually to brown after 14 h at 20°C. Concentration led to a visquous residue, the analysis of which showed the formation of the cycloadduct **10** : ^1H NMR ($CDCl_3$, δ ppm) : 7.10-7.50 (m, C_6H_5) ; 6.52-6.90 (m, C_6H_2) ; 3.68 (s, NCH_2Ph) ; 2.72 (s, NCH_2) ; 1.25 et 1.32 (s, tBu). M.S (E.I) : 532 [M^+], 517 [$M^+ - CH_3$], 475 [M^+ - tBu], 441 [$M^+ - CH_2Ph$].

This compound was not stable and underwent symmetrisation particularly in solution. Dissolution of the reaction mixture in 5 mL ether caused a gradual precipitation of a white powder identified to the corresponding spirogermoxane 12 [7] : ^1H NMR ($CDCl_3$/DMSO, δ ppm) : 7.15 (br.s, C_6H_5 and C_6H_2) ; 3.58 (m, CH_2O) ; 1.70 and 1.32 (s, tBu) ; 1.30 (m, CH_2). M.S (E.I) : 514 [M^+ - THF] [7]. 10 was also obtained in an other way but its symmetrisation still observed appeared indepen- dent from the used synthetic route.

Synthesis of (dichloro)-N,N'-dibenzyl(1,2-ethylenediamino)germane 13

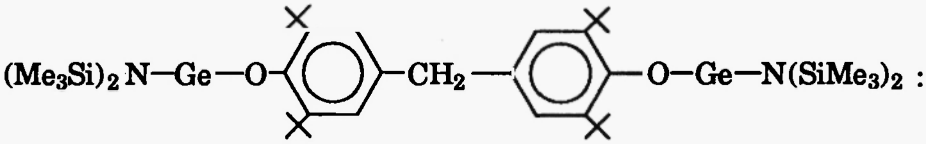
To a solution of N,N'-dibenzylethylenediamine (0,82 g, 3.41 mmole) in 40 mL of pentane was added 1.1 mL of triethylamine (7.83 mmole) and then 0.56 mL of $GeCl_4$ (3.6 mmole). Triethylammonium chloride was separated by filtration and washed with 10 mL of pentane. Concentration of the filtrate led to a white solid recrystallized in pentane 13 (0.664 g) 51 % yield. 13 : m.p : 272-277°C.^1H NMR ($CDCl_3$, δ ppm) : 7.30 (s.l, C_6H_5) ; 4.13 (s, NCH_2Ph) ; 3.06 (s, NCH_2).^{13}C NMR ($CDCl_3$, δ ppm) : 138.5 (C_1) ; 128.8 (C_2,C_6) ; 128.5 (C_3,C_5) ; 127.6 (C_4) ; 53.7 (NCH_2Ph) ; 49.4 (NCH_2). M.S (E.I) : 382 [M^+], 3.47 [M^+ - Cl] 291 [$M^+ - CH_2Ph$]. Anal. calc. (found) for $C_{16}H_{18}Cl_2GeN_2$: C 50.33 (49,75), H 4.75 (5.31), N 7.33 (7.20)

Synthesis of 10 by exchange reaction between (dichloro)-N,N'-dibenzyl(1,2-ethylenediamino) germane 13 and diethylgermanium 3,5-di-tert-butylorthocatecholate 14.

To a solution of 13 (0.236 g, 0.62 mmoles) in 2 mL of THF was added dropwise a solution of **14** (0.217 g, 0.62 mmole) in 2 mL of THF. The reaction mixture was heated up to 40°C and the reaction followed (4 h) by G.C and ^1H NMR. There was formation of **10** followed by its symmetrisation leading to 12 after two days.

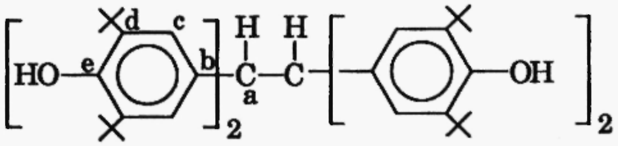
Reaction of bis(bis-trimethylsilyl)aminogermylène 2 with galvinoxyl 15 :

To germylene 2 (0,27 g, 0,69 mmol.) in 2 mL of ether was added at room temperature a solution of 15 in 4 mL of THF. The solution turned to violet and then to red. The reaction mixture was refluxed 3 hours and then maintained under stirring 12 h at room temperature. Concentration under vacuo led to a polymeric residue which was smashed into a dark red powder. Analysis (IR, ^1H and ^{13}C NMR, Mass and G.C/Mass) of this reaction mixture before and after acidic (6N, HCl) hydrolysis allowed the caracterisation of the following compounds or chemical intermediates which give a good idea about the composition of the polymer.



: **23**

Intermediate 23 was detected by ^1H NMR ($CDCl_3$) (δ ppm) : (3,78 (s) CH_2) and M.S (DCI, NH_3) : 906 $[M..H..NH_3]^+$; 674 [906 - $(Me_3Si)_3N$] ; 729 [$(M..H)^+$ - (NH_3 and $(Me_3Si)_2N$)] ; 656 [729 - Me_3Si].



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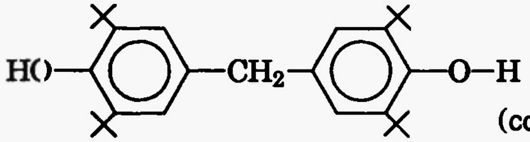
^1H NMR ($CDCl_3$, δ ppm) : 7.24 (s) (C_6H_2), 5.16 (br.s) (OH), 4.48 (s) (CH), 1.44 (s) (tBu). ^{13}C NMR ($CDCl_3$, δ ppm) : 153.1 (C_e), 136.1 (C_d), 126.4 (C_b), 125.9 (C_c), 55.3 (C_a), 34.5 (tBu (C-CH_3)), 30.9 (tBu (CH_3)). M.S (DCI, NH_3) : 864 $[M..H..NH_3]^+$; 846 [864 - H_2O] ; 829 [$M..H^+$ - H_2O].



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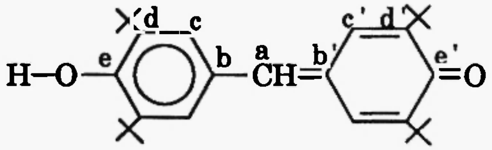
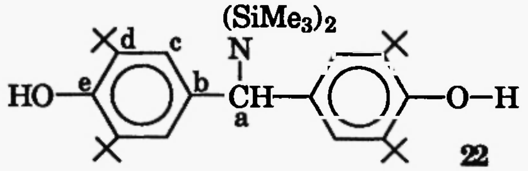
(conform to Aldrich sample characteristics)

M.S (DCI, NH_3) : 442 $[M..H..NH_3]^+$. G.C/M.S (E.I) : 424 $[M^+]$.



conform to [8]

^1H NMR ($CDCl_3$ δppm) : 5.5 (s) (OH) ; 7.34 (s) (CH_d) ; 7.59 and 6.99 (d) ($CH_{c'}$) (J : 2,5 Hz) ; 7.15 : (CH_a) ; 1.47 and 1.32 (s) (tBu). M.S (E.I) : 422 $[M^+]$; 407 [M^+ - CH_3] ; 365 [M^+- tBu].



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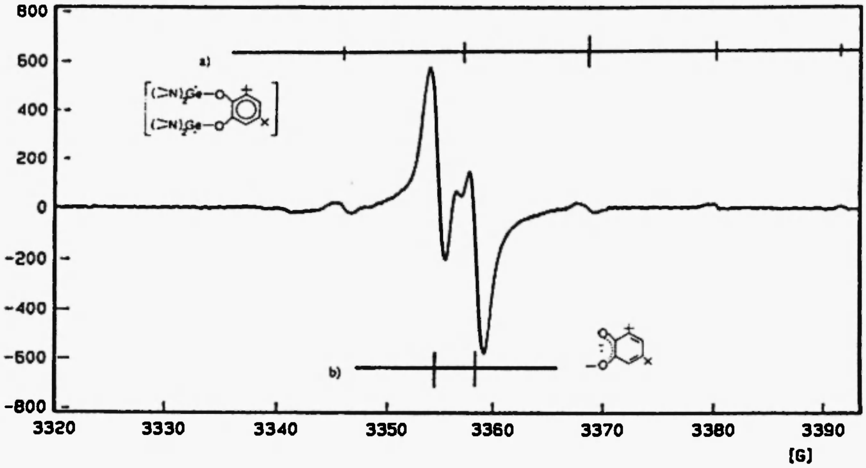
identified in-situ by comparaison with a sample obtained by direct amination of galvinoxyl by $(Me_3Si)_2NLi$ [9].

^1H NMR ($CDCl_3$ δ ppm) : 7.34 (s) (CH_c) ; 5.57 (br.s) (OH) ; 3.92 (s) (CH_a) ; 1.46 (s) (tBu) ; 0.08 (s) (Me_3Si). ^{13}C NMR ($CDCl_3$ δ ppm) : 155.6 (C_e) , 136.5 (C_d) , 135.0 (C_b) , 128.2 (C_c), 77.1 (C_a) , tBu : 35.0 (C-CH_3) and 30.2 (CH_3) , 1.0 (Me_3Si). M.S (E.I) : [M^+ - $(Me_3Si)_2N$]. (DCI, NH_3) : 584 [M - H^+] ; 511 [MH^+-Me_3Si] ; 438 [MH^+ - $2Me_3Si$] ; 423 [MH^+-$(Me_3Si)_2N$] and 527 [MH^+-tBu].

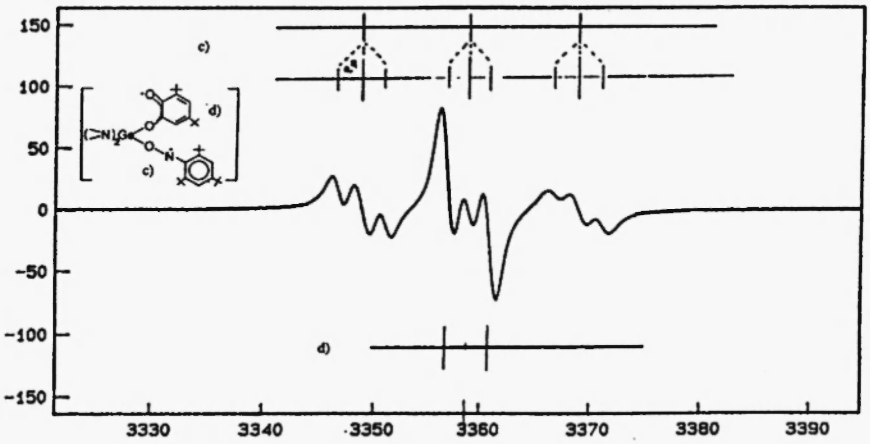
Fig.1 : germylène $[(Me_3Si)_2N]_2Ge$ + **1** (lack) 203°K (Hexane)



a) H = 3366,7
g = 1,9980
a^N = 11,3 G

b) H = 3356,5
g = 2,0039
a^H = 3,8 G

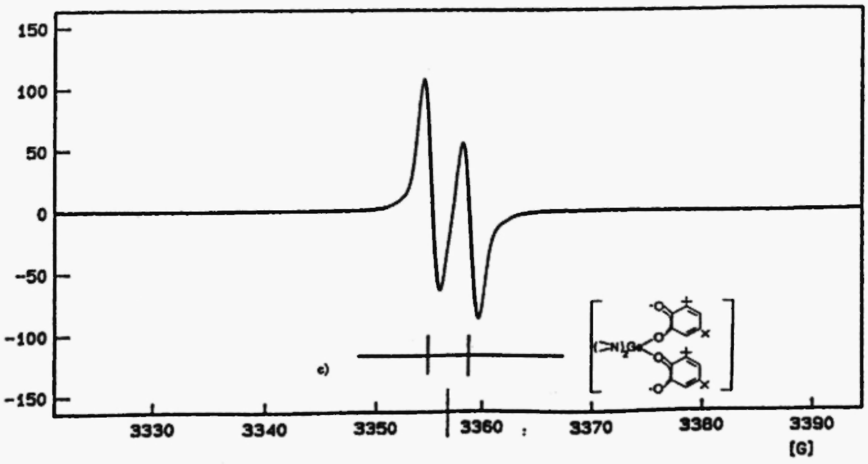
Fig.2 : germylène $[(Me_3Si)_2N]_2Ge$ + **1** + BNB 233°K (Toluène)



c) H = 3358,6
g = 2,0041
a^N = 10,16 G
a^H = 2,16 G

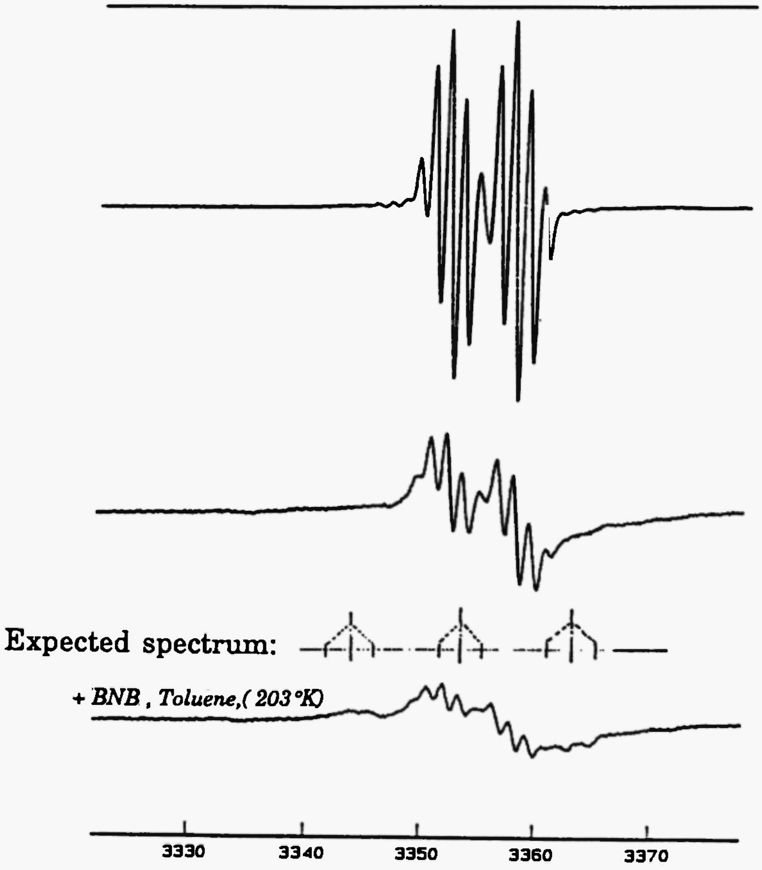
d) H = 3358,6
g = 2,0041
a^H = 3,8 G

Fig.3 : **1** (excès) + germylène $[(Me_3Si)_2N]_2Ge$ 233°K (Toluène)



e) H = 3356,8
g = 2,0042
a^H = 3,8 G

Fig. 4 : Démagnétisation of galvinoxyl in presence of germylene 2



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