

From a germene to a transient germirane

M. Lazraq, J. Escudié, C. Couret, J. Satgé

Laboratoire de Chimie des Organominéraux, URA 477, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex (France)

and M. Soufiaoui

Laboratoire de Cycloadditions, Département de Chimie, Faculté des Sciences, Université Mohammed V, Av. Ibn Batouta, Rabat (Morocco)

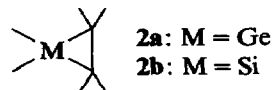
(Received April 5th, 1990)

Abstract

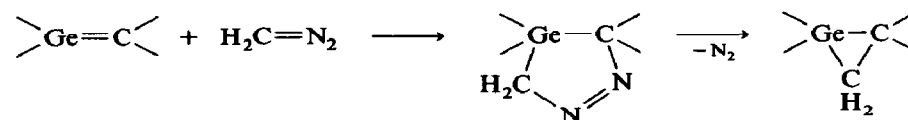
Reaction of dimesityl(fluorenylidene)germene, **1**, with diazomethane leads, depending on the experimental conditions, to the germapyrazoline **3** or **4**. Thermal decomposition of **4** gives an unstable germirane **14**, which was identified from its $[3] \rightarrow [2 + 1]$ decomposition products, viz. 9-methylenefluorene **12** and dimesitylgermylene **15**.

Introduction

Three-membered ring germylated derivatives such as germiranes **2a** are still unknown, in contrast to their silicon analogues **2b** [1].



Because of their very severe internal strain they should be very reactive, and probably behave as valuable synthons in organometallic chemistry. Since dimesityl(fluorenylidene)germene **1**, recently synthesized in our group [2,3], is very active in cycloaddition reactions (we have described its $[2 + 2]$, $[2 + 3]$ and $[2 + 4]$ cycloadditions, respectively, with aldehydes and ketones [4], nitrones [2] and conjugated dienes [2]), its reaction with diazomethane appeared to us likely to be very promising, and to involve initial formation of a five-membered ring germapyrazoline, followed by elimination of nitrogen to give a germirane:

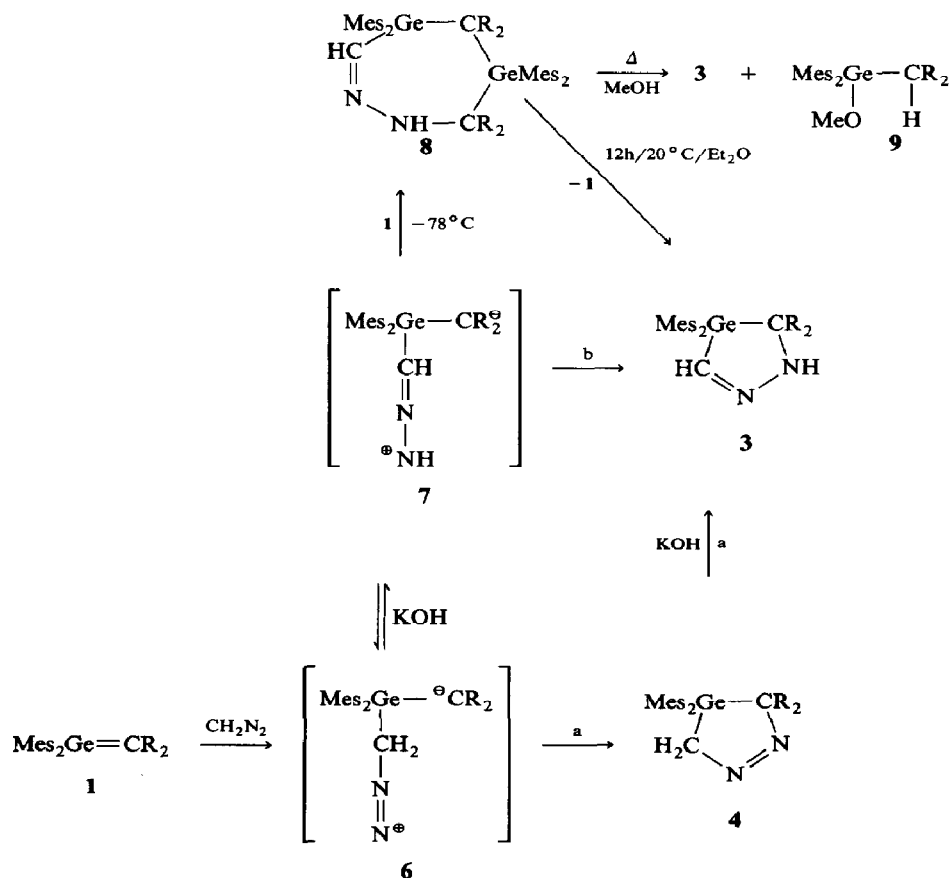


The formation of three-membered rings has been observed in the reaction of diazomethane with other doubly-bonded Main Group elements such as disilenes >Si=Si< [5], digermenes >Ge=Ge< [6], diphosphenes =P=P= [7], and diarsenes =As=As= [8].

Results and discussion

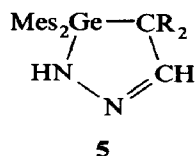
The outcome of the reaction between germene and diazomethane **1** proved to be very dependent on experimental conditions. When a large excess of an ethereal solution of diazomethane, dried over potassium pellets, was added to a solution of **1** in Et_2O at -78°C , the only observable product was the five-membered ring species **3** (Scheme 1). When the reaction was carried out with a solution of distilled diazomethane (thus free of traces of KOH), the 4-germa-1-pyrazoline **4** was obtained.

Compound **3** was identified from its spectral data. Thus its ^1H NMR spectrum exhibits a very low field chemical shift for the CH proton (8.45 ppm), characteristic of an imine function. In the ^{13}C NMR spectrum the signal from the carbon doubly-bonded to nitrogen also appears at low field (154.13 ppm), as a doublet of doublets as a result of $^1J(\text{CH})$ and $^3J(\text{CNNH})$ couplings; addition of D_2O im-



Scheme 1

mediately converts this signal into a simple doublet, confirming unambiguously the existence of coupling between this carbon and the NH. (Such coupling is rarely observed.) Compound **3** is insensitive toward oxygen and moisture; **4** was shown to be identical to the compound obtained by Krebs et al. [9]. Addition of traces of a base (KOH) to **4** immediately generates **3**, owing to a 1,3-migration of hydrogen: such a prototropy is well known and has already been observed in other five-membered rings containing the $\text{CH}_2\text{-N=N}$ linkage [10]. This $4 \rightarrow 3$ rearrangement confirms unambiguously the structure of **3** with the nitrogen bound to the fluorenyl group, and excludes the possibility that reverse addition of diazomethane has given **5**.

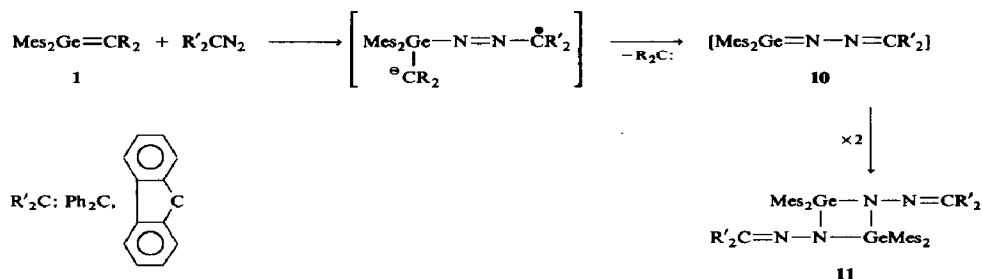


The polarity $\begin{array}{c} \delta^+ \\ \diagup \\ \text{Ge}=\text{C} \\ \diagdown \\ \delta^- \end{array}$ of the germene accounts for this direction of addition of diazomethane.

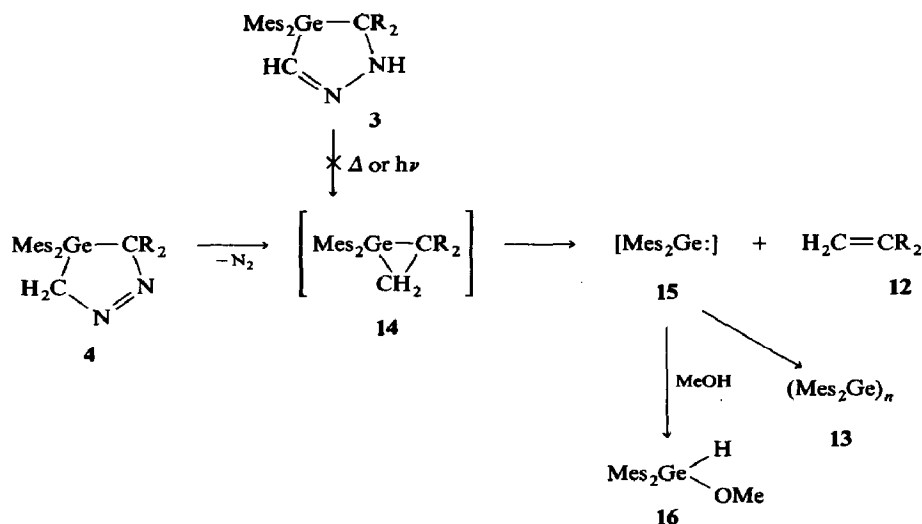
The first step in these reactions is probably the formation of the dipolar intermediate **6**; with distilled diazomethane, cyclisation of **6** leads to the expected **4**. When the diazomethane contains traces of KOH, two pathways are possible: route a, involving preliminary formation of **4** and prototropy, or route b, involving the formation of intermediate **7** followed by its cyclisation.

When diazomethane was added to an excess of germene **1** at -78°C , the formation of the dipolar intermediates **6** or **7** was revealed by trapping with germene **1** itself, leading to the seven-membered ring **8**. Compound **8** is very stable as crystals, but slowly decomposes in solution at room temperature to give germene **1** and germapyrazoline **3** in a $[7] \rightarrow [5 + 2]$ cycloreversion. Thus **8** can be considered as a store for germene **1**. Species **1** was quantitatively trapped by methanol to give **9**.

We note that we have observed a completely different type of reaction between germene **1** and other diazo compounds, such as diphenyldiazomethane and diazofluorene. In these cases we have never obtained a five-membered ring germapyrazoline, but exclusively the four-membered ring cyclodigermazane **11**, probably via a germanimine intermediate **10** [11].



As reported previously [9], thermolysis of **4** (1/2 h at 60°C or ca. 3 days at room temperature in ethereal solution) results in its decomposition with formation of 9-methylenefluorene **12** [12] and $(\text{Mes}_2\text{Ge})_n$ **13**. Formation of **12** and **13** can only be accounted for in terms of the initial formation of germirane **14**, followed by its rapid $[3] \rightarrow [2 + 1]$ decomposition to give **12** and dimesitylgermylene **15** (Scheme 2).



Scheme 2

Similar chemical behaviour is observed for siliranes; for example, hexamethylsilirane gives dimethylsilylene and 2,3-dimethyl-2-butene at 60 °C [1b]. Attempts to trap the three-membered ring derivative 14 with methanol or sulfur were unsuccessful, probably because this germirane has a very short life. In the decomposition reaction in methanol only the germylene trapping derivative 16 was observed, along with alkene 12. In contrast, germapyrazoline 3 is thermally stable, and loss of nitrogen to afford germirane 14 has not been observed. Attempts to stabilize such three-membered ring derivatives sterically by use of suitably-substituted diazo compounds are in progress.

Experimental

General procedures

Since solutions of germene 1 are highly air- and moisture-sensitive, all the experiments were performed under argon or nitrogen with carefully dried and deoxygenated solvents. ^1H NMR spectra were recorded on a Bruker AC 80 at 80 MHz or on a Bruker AM 300 WB at 300.1 MHz, and ^{13}C NMR spectra on a Bruker AC 200 at 50.3 MHz (TMS internal standard). Mass spectra were obtained with a Nermag R10 O1O spectrometer (EI). Melting points were determined with a Reichert apparatus. Elemental analyses were performed by the "Service de micro-analyse de l'Ecole de Chimie", Toulouse (France).

Germene 1 was prepared in near quantitative yield as previously described [2] by addition of an equivalent of *tert*-butyllithium (1.7 *N* in pentane) to a solution of dimesitylfluorenylfluorogermane in Et_2O at -50°C . Crude, orange solutions of germene 1 were used without further purification.

Synthesis of 4-germa-2-pyrazoline, 3

To a solution of 1 (0.90 g, 1.9 mmol) in Et_2O (30 ml) cooled at -78°C was added an ethereal solution of diazomethane (excess) prepared from *N*-methyl-*N*-

nitroso-*N'*-nitroguanidine (1.0 g, 6.8 mmol) and dried over potassium pellets. The initially orange mixture immediately became red, and then turned light yellow at room temperature. After removal of Et₂O under vacuum, 40 ml of pentane were added, and the lithium salt was filtered off. Recrystallization from pentane at -20 °C afforded white crystals of **3** (0.75 g, 76%), mp: 219–220 °C. ¹H NMR (CDCl₃)(300 MHz): 1.86 (s, 12 H, *o*-Me), 2.20 (s, 6H, *p*-Me), 6.43 (s, 1H, NH), 6.70 (s, 4H, arom. Mes), 6.92–7.86 (m, 8H, CR₂), 8.45 (s, 1H, NCH). ¹³C NMR (CDCl₃): 20.95 (*p*-Me), 23.54 (*o*-Me), 74.18 (C₉ (CR₂)), 119.77 (C₄, C₅), 123.66, 127.23, 127.36 (C₁C₂C₃C₆C₇C₈), 129.08 (*m*-C(Mes)), 132.36 (*i*-C(Mes)), 139.15 (*p*-C(Mes)), 139.72 (C₁₂, C₁₃), 143.51 (*m*-C(Mes)), 147.61 (C₁₀, C₁₁), 154.13 (CH=N). Without decoupling of hydrogen, this signal appears as a doublet of doublets: ¹J(CH): 182.5 Hz, ³J(CNNH): 7.9 Hz. MS (EI, 70 eV, ⁷⁴Ge), *m/z*: 491 (Mes₂GeCR₂NH, 40), 312 (Mes₂Ge, 60), 192 (MesGe - 1, 100). IR: ν(NH): 3340 cm⁻¹, ν(C=N): 1605 cm⁻¹.

Synthesis of 4-germa-1-pyrazoline, **4**

To a solution of **1** (0.90 g, 1.9 mmol) in Et₂O (30 ml) cooled at -78 °C was added a distilled solution of diazomethane in Et₂O prepared from *N*-(4-(tolylsulfonyl)-*N*-methylnitrosamide (diazald) (2.15 g, 10.0 mmol). The orange-red mixture was allowed to warm to room temperature, and then treated as previously described [9] to afford pure **4** (yield 70%).

Synthesis of 7-membered ring derivative, **8**

An ethereal solution of diazomethane, prepared from *N*-methyl-*N*-nitroso-*N'*-nitroguanidine (0.50 g, 3.4 mmol) dried over potassium pellets, was slowly added to a solution of **1** (1.80 g, 3.8 mmol) in Et₂O (30 ml) cooled at -78 °C. The mixture was allowed to warm to -10 °C and the solvents and low-boiling compounds were removed under vacuum (10⁻² mmHg) at this temperature. Cold pentane (50 ml) was added and the precipitate of **8** rapidly filtered off. Product **8**, which is only slightly soluble in pentane, was recrystallized from Et₂O at -20 °C: 1.22 g (65%), mp: 154–154 °C. Compound **8** is stable in the solid state (it crystallizes with one molecule of Et₂O), but slowly decomposes in solution.

9 · Et₂O

¹H NMR (CDCl₃): 1.21(t, ³J(HH): 7.0 Hz, 6H, OCH₂CH₃), 1.53 (broad s, 12H, *o*-Me), 1.83 (s, 12H, *o*-Me), 2.03 (s, 6H, *p*-Me), 2.19 (s, 6H, *p*-Me), 3.49 (q, ³J(HH): 7.0 Hz; 4H, OCH₂), 5.42 (s, 1H, NH), 6.16 (s, 4H, arom. Mes), 7.05 (s, 4H, arom. Mes), 7.07–7.92 (m, 16H, CR₂), 8.51 (s, 1H, NCH). MS (DCI/CH₄, ⁷⁴Ge), *m/z*: 393 (*M* + H, 21), 827 (*M* - CR₂ - H, 16), 519, (*M* - Mes₂GeCR₂ + H, 21), 477 (Mes₂Ge=CR₂ + H, 100), 313 (Mes₂Ge + H, 52) IR: ν(NH): 3405 cm⁻¹, ν(C=N): 1602 cm⁻¹.

Reaction of **4** with methanol

A solution of **4** (0.52 g, 1.0 mmol), MeOH (5 g) and THF (15 ml) was kept at 50 °C for 3 h. The ¹H NMR spectrum of the mixture showed the presence of 2-methylenefluorene (identical with an authentic sample prepared as described in ref. 12) and minor quantities of dimesitylmethoxygermane **16**. The yield of **16**, as estimated by NMR spectroscopy was 20%, the most abundant products being the oligomers (Mes₂Ge)_{*n*}. Compound **16** could not be isolated in a pure state from the

reaction mixture, but was unambiguously identified from its ^1H NMR spectrum (by comparison with a pure sample prepared from dimesitylchlorogermane Mes_2GeHCl , methanol, and triethylamine [13]): ^1H NMR (CDCl_3): 2.00 (s, 6H, *p*-Me), 2.35 (s, 12H, *o*-Me), 3.23 (s, 3H, OMe), 6.20 (s, 1H, GeH), 6.52 (s, 4H, arom. Mes).

References

- 1 (a) R.L. Lambert, Jr and D. Seyferth, *J. Am. Chem. Soc.*, 94 (1972) 9246. (b) D. Seyferth, D.C. Annarelli, S.C. Vick and D.P. Duncan, *J. Organomet. Chem.*, 201 (1980) 179. (c) W. Ando and H. Saso, *Tetrahedron Lett.*, 27 (1986) 5625. (d) P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel and K.R. Anderson, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 1355. (e) H. Saso, W. Ando and K. Ueno, *Tetrahedron*, 45 (1989) 1929.
- 2 C. Couret, J. Escudié, J. Satgé and M. Lazraq, *J. Am. Chem. Soc.* 109 (1987) 4411.
- 3 M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Dräger and R. Dammel, *Angew. Chem.* 100 (1988) 885, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 828.
- 4 M. Lazraq, Thesis, Toulouse University, 1988.
- 5 S. Masamune, S. Murakami, H. Tobita and D.J. Williams, *J. Am. Chem. Soc.* 105 (1983) 7776.
- 6 W. Ando, T. Tsumuraya, *Organometallics*, 7 (1988) 1882.
S.A. Batcheller, S. Masamune, *Tetrahedron Lett.*, 29 (1988) 3383.
- 7 J. Bellan, G. Etemad-Moghadam, M. Payard and M. Koenig, *Tetrahedron Lett.* 27 (1986) 1145.
G. Etemad-Moghadam, J. Bellan, C. Tachon and M. Koenig, *Tetrahedron* 43 (1987) 1793.
- 8 L. Weber, U. Sonnenberg, *Chem. Ber.*, 122 (1989) 1809.
- 9 M.P. Egorov, S.P. Kolesnikov, O.M. Nefedov and A. Krebs, *J. Organomet. Chem.* 375 (1989) C5.
- 10 T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis* (1986) 31.
F. Zurmühlen, W. Rösch and M. Regitz, *Z. Naturforsch.* 40b (1985) 1077.
- 11 M. Lazraq, C. Couret, J.P. DeClercq, A. Dubourg, J. Escudié and M. Rivière-Baudet, *Organometallics*, 9 (1990) 845.
- 12 M. Nevenschwander, R. Vögeli, H.P. Fahrni, H. Lehmann and J.P. Ruder, *Helv. Chim. Acta*, 60 (1977) 1073.
- 13 P. Rivière, A. Castel and J. Satgé, unpublished results.