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From a germene to a transient germirane

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Abstract

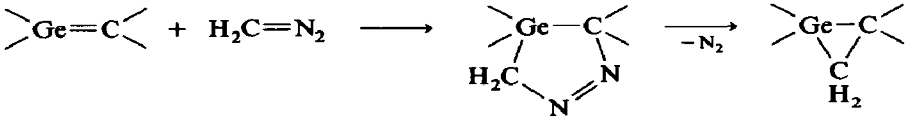
Reaction of dimesityl(fluorenylidene)germene, **1**, with diazomethane leads, depending on the experimental conditions, to the germapyrazoline **3** or **4**. Thermal decomposition of **4** gives an unstable germirane **14**, which was identified from its [3] → [2 + 1] decomposition products, viz. 9-methylenefluorene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

2a: M = Ge
2b: M = Si

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:



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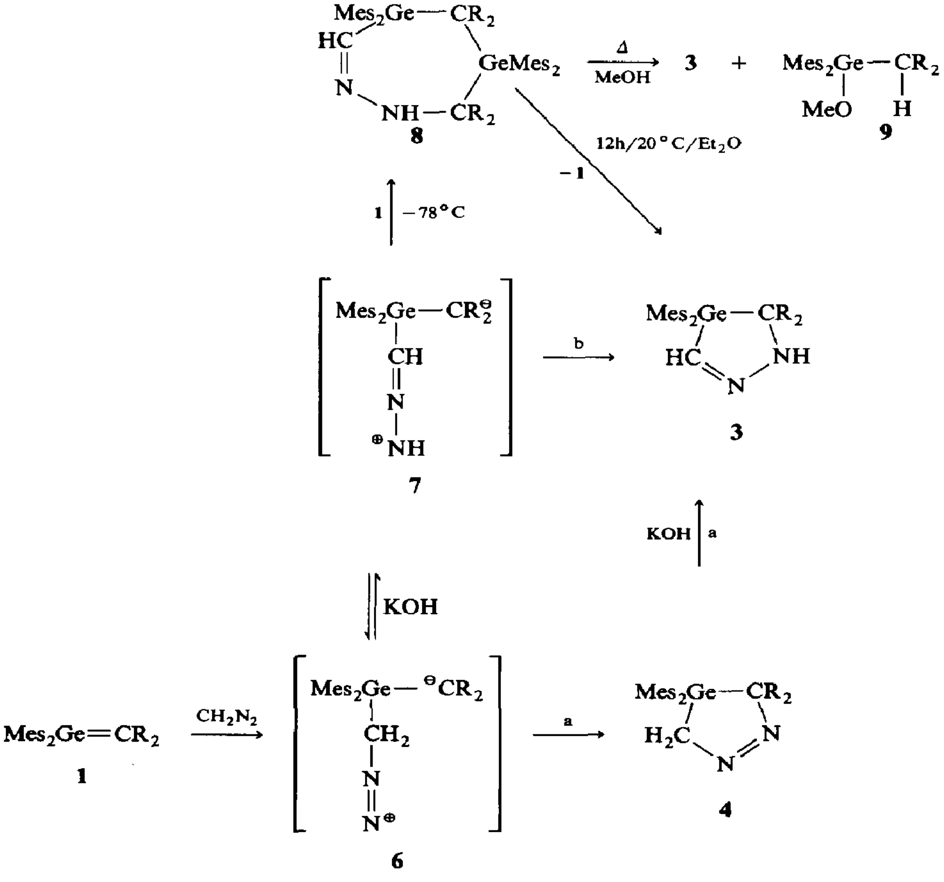
The formation of three-membered rings has been observed in the reaction of diazomethane with other doubly-bonded Main Group elements such as disilenes >Si=Si< [5], digermenes >Ge=Ge< [6], diphosphenes –P=P– [7], and diarsenes –As=As– [8].

Results and discussion

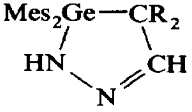
The outcome of the reaction between germene and diazomethane **1** proved to be very dependent on experimental conditions. When a large excess of an ethereal solution of diazomethane, dried over potassium pellets, was added to a solution of **1** in Et_2O at $-78\,^\circ C$, the only observable product 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(CH) and ^3J(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 $CH_2-N=N$ linkage [10]. This **4** → **3** rearrangement confirms unuambiguously the structure of **3** with the nitrogen bound to the fluorenyl group, and excludes the possibility that reverse addition of diazomethane has given **5**.



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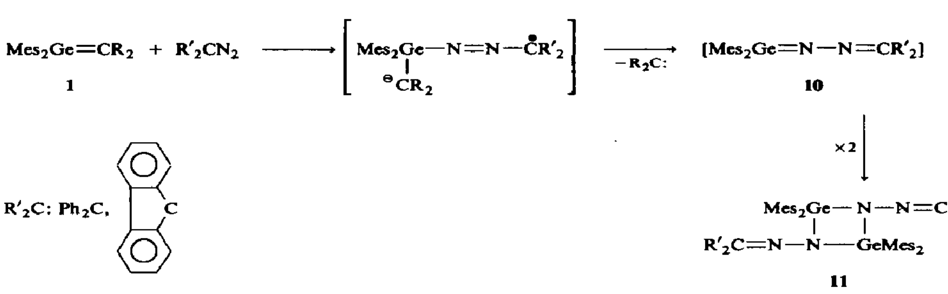
The polarity $>\overset{\delta^+}{\mathrm{Ge}}=\overset{\delta^-}{\mathrm{C}}<$ of the germene accounts for this direction of addition of diazomethane.

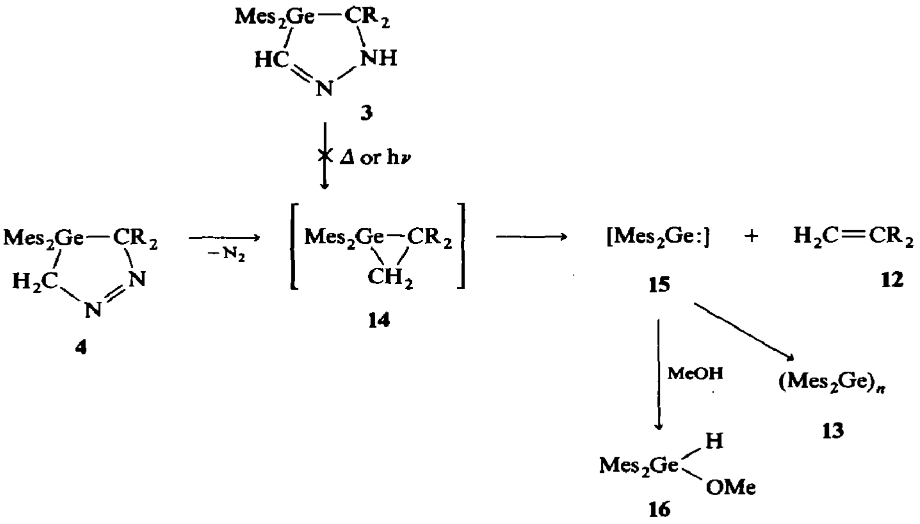
The first step in these reactions is probably the formation of the dipolar intermediate **6**; with distilled diazomethane, cyclisation of **6** leads to the expected **4**. When the diazomethane contains traces of KOH, two pathways are possible: route a, involving preliminary formation of **4** and 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] → [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 $(Mes_2Ge)_n$ **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] → [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. ^{1}H 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 microanalyse 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 Et_2O 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 (CDCl$_3$)(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, CR_2), 8.45 (s, 1H,NCH). ^{13}C NMR ($CDCl_3$): 20.95 (*p*-Me), 23.54 (*o*-Me), 74.18 (C_9 (CR_2)), 119.77 (C_4, C_5), 123.66, 127.23, 127.36 ($C_1C_2C_3C_6C_7C_8$), 129.08 (*m*-C(Mes)), 132.36 (*i*-C(Mes)), 139.15 (*p*-C(Mes)), 139.72 (C_{12}, C_{13}), 143.51 (*m*-C(Mes)), 147.61 (C_{10}, C_{11}), 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, ^{74}Ge), *m/z*: 491 (Mes_2GeCR_2NH, 40), 312 (Mes_2Ge, 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 Et_2O (30 ml) cooled at −78 °C was added a distilled solution of diazomethane in Et_2O 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 Et_2O (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 Et_2O 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 Et_2O), but slowly decomposes in solution.

8 *· Et_2O*

^1H NMR ($CDCl_3$): 1.21(t, ^3J(HH): 7.0 Hz, 6H, OCH$_2$*CH$_3$*), 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, OCH_2), 5.42 (s, 1H, NH), 6.16 (s, 4H, arom. Mes), 7.05 (s, 4H, arom. Mes), 7.07–7.92 (m, 16H, CR_2), 8.51 (s, 1H, NCH). MS (DCl/CH_4, ^{74}Ge), *m/z*: 993 (*M* + H, 21), 827 (*M* − CR_2 − H, 16) 519, (*M* − Mes_2GeCR_2 + H, 21), 477 ($Mes_2Ge{=}CR_2$ + H, 100), 313 (Mes_2Ge + 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 ^1HNMR spectrum of the mixture showed the presence of 9-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 $(Mes_2Ge)_n$. 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).

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