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Preliminary communication

Synthesis of the first germa-1-pyrazoline and its decomposition via a germirane intermediate

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Abstract

The first germapyrazoline, 4-germa-1-pyrazoline (**2**), has been obtained by [2 + 3] cycloaddition of diazomethane to the Ge=C bond of the germene (**1**). Thermal or photochemical decomposition of **2** via a germirane intermediate (**4**) gives 9-methylenefluorene and dimesitylgermylene, which can be trapped by 2,3-dimethylbutadiene.

The synthesis and reactions of small strained heterocycles, especially heterocyclopropanes and heterocyclopropenes, have recently attracted particular interest. One of the methods for the synthesis of heterocyclopropanes, developed in recent years, is based on the reaction between diazo compounds and the stable heteroolefins containing multiple E = X (X = E, C, etc.) bonds. By use of this route some 1-phospha- (X = C, E = P) [1], 1,2-diphospha- (X = E = P) [2], 1,2-disila- (X = E = Si) [3], 1,2-digerma- (X = E = Ge) [4] cyclopropanes have been synthesised.

In continuation of our investigations of germanium-containing heterocycles [5] and aiming at the synthesis of the unknown germacyclopropane system, we have studied the reaction of the stable germene **1** (as a complex with Et_2O) [6,11] with diazomethane. It turned out that this reaction in fact gave a stable primary [2 + 3]-cycloadduct, the 4-germa-1-pyrazoline (**2**), which was isolated from the mixture. The formation of [2 + 3]-cycloadducts as intermediates in the reactions between diazo compounds and heteroolefins E = X has been postulated previously [2,3,7], but adducts were isolated only for phosphenes [8].

An ethereal solution of diazomethane (7 mmol, in 20 ml of Et_2O) carefully dried and degassed (by a freeze-thaw procedure) was transferred under vacuum (10^{-4}

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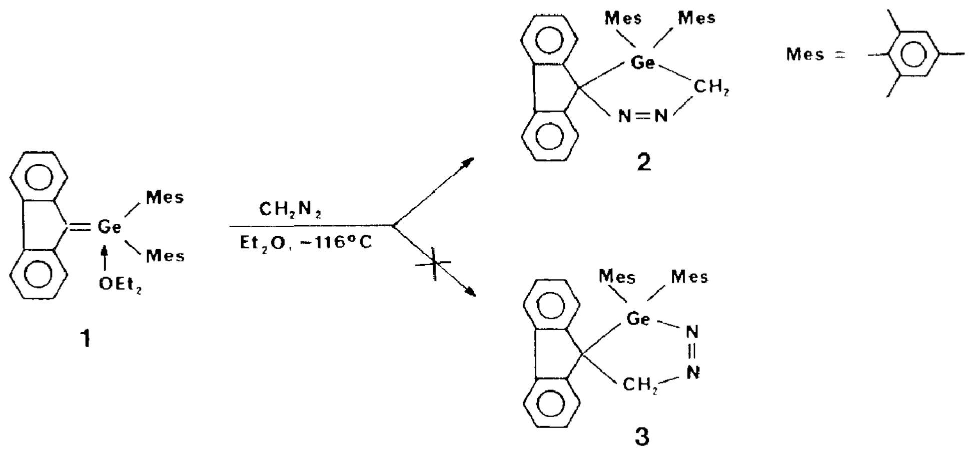
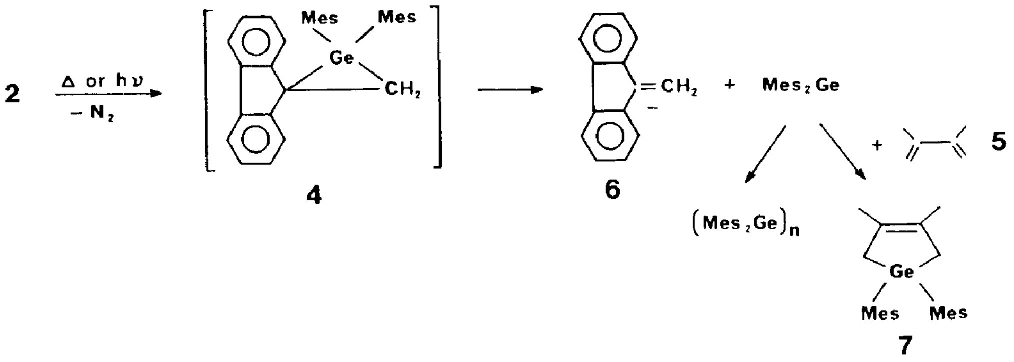


Torr) to a solution of germene **1** (obtained in situ from 0.2 mmol of dimesitylfluorenylfluorogermane and 0.13 ml of 1.6 *N* t-butyllithium in 5 ml of Et_2O [6]) in ether frozen at −196 °C. The reaction was completed within a few minutes as the ether melted. The mixture was then allowed to warm to room temperature and the ether and the excess of CH_2N_2 were removed in vacuum. The solid residue was extracted with benzene (2–3 ml) (to leave behind lithium salts) and the benzene was evaporated off under vacuum at 20 °C and the residual solid was washed with pentane (1–2 ml), to give, as a white powder, the germapyrazoline (**2**) (70% yield, m.p. 104–109 °C, with evolution of N_2). Mass spectra: (FAB) 519 ($M+1$); (EI) 490 ($M-N_2$, 12%), 312 (Mes_2Ge, 52%), 192 (MesGe − H, 77%), 178 (100% 9-methylenefluorene); ^1H NMR (400 MHz, C_6D_6): δ 1.85 (s, 12H, *o*-CH_3), 1.98 (s, 6H, *p*-CH_3), 5.18 (s, 2H, CH_2), 6.53 (s, 4H, $CH_{arom.}$, Mes), 6.7–7.8 (m, 8H, $CH_{arom.}$, R_2C); ^{13}C NMR (100 MHz, C_6D_6, INEPT): δ 20.82 (*p*-CH_3), 24.07 (*o*-CH_3), 72.74 (CH_2), 93.98 (C_q(9) fluor.), 119–146 ($C_{arom.}$ mesit. and fluor.); IR (KBr): ν(N=N) 1524 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ) 315 (2.5×10^3), 300 (5.0×10^3), 265 (1.9×10^4), 205 (1×10^5).

The identification of this substance as a germapyrazoline can be firmly made from its spectral data (mass spectra, ^1H, ^{13}C NMR, UV spectrum). For example, the ^1H chemical shifts (δ 5.18 ppm) and carbon (72.74 ppm) atoms of a CH_2 group have values typical of 1-pyrazolines (4.9–5.14 and 77–84 ppm respectively) [9]. The position of the absorption maximum (315 nm) in the UV spectrum of **2** is also in the range observed for 1-pyrazolines (315–325 nm [10]). The choice between the two possible structures **2** and **3**, favouring **2**, was made on the basis of the low-field ^{13}C chemical shift of the quaternary C_q(9) carbon atom of the fluorenylidene group (93.98) connected to the electron-withdrawing azo group. In other 1-*H*-pyrazolines, for example, in 3,3-dimethyl-4-methylene-1-pyrazoline, the quaternary C_q(3) carbon atom gives a signal at lower field (87.1 ppm) than the secondary C_q(5) carbon atom (79.7 ppm) [9]. In the regioisomer **3** the C_q(9) atom should have a chemical shift at higher field.

Germapyrazoline **2** is kinetically stable in the solid state at room temperature. It is insensitive towards the oxygen and moisture of the air both in solid state and in solution, and does not react with sulphur or methanol (20 °C, C_6H_6). However, in



solution it is readily decomposed thermally (C_6H_6, 60 °C, 20 min or 20 °C, 2–4 days; [**2**] 0.3 *M*) or photochemically (cyclohexane, 20 °C, 30 s, [**2**] 1.3×10^{-4} *M*; quartz cell, low-pressure Hg lamp, 25 W) with quantitative formation of 9-methylenefluorene (isolated by column chromatography (silica gel, CCl_4) and identified by its m.p. (47–50 °C), mass spectra, ^1H NMR and UV spectral data [12]) and Mes_2Ge, which gives oligomers $(Mes_2Ge)_n$. Dimesitylgermylene can be trapped by 2,3-dimethylbutadiene (**5**) ([**2**]/[**5**] 1/30).

The product of the trapping reaction, germacyclopentene (**7**), was isolated in 34% yield by column chromatography and identified by its mass spectrum and ^1H NMR spectra [13].

The formation of 9-methylenefluorene (**6**) from the thermolysis or photolysis of **2** provides strong evidence for the participation of germirane (**4**) as a reactive intermediate in these reactions.

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