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THE FIRST SYNTHESIS OF AZA-GERMACYCLOPENTENES: CYCLOADDITIONS OF 1-AZA- AND 1,4-DIAZABUTADIENES WITH FREE SINGLET DIMETHYL GERMYLENE

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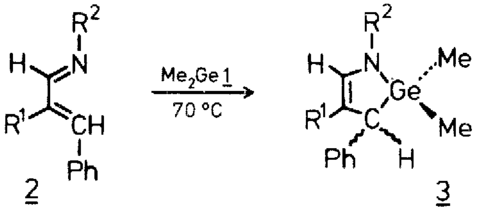
Summary. 1-Aza- and 1,3-diaza-2-germacyclopent-4-enes have been prepared for the first time by cycloaddition of several substituted 1,4-diaryl-1-azabutadienes and 1,4-diaryl or dialkyl 1,4-diazabutadienes with free singlet dimethyl germylene Me_2Ge. Spectroscopic and a number of chemical properties of the new compounds **3**, **5**, and **7** are reported.

Since the singlet and nucleophilic character of dimethyl germylene 1, generated thermally or photolytically from 7-germanorbornadiene[1)], has been demonstrated by reactions with 1,4-disubstituted butadienes[2)], we have used vinyl ketones and vinyl aldehydes as electron-deficient heterodienes[3)]. By this way, 1-oxa-2-germacyclopent-4-enes are accessible easily and in good yields.

This prompted us, since no azagermacyclopentenes are described in the literature to our knowledge[4)], to look for cycloadditions of free germylenes 1 to aza- and diazabutadienes. In the case of Diels-Alder reactions, azabutadienes have been found to be less electron-deficient, hence less reactive than oxabutadienes[5)]. Therefore, the question was, whether the former could react in our case. Moreover, N-Ge bonds (D = 60-70 kcal/mol[6)]) are generally weaker than O-Ge bonds (D = 107 kcal/mol[6)]). Thus, we report here the first synthesis of 1-aza- and 1,3-diaza-2-germacyclopent-4-enes.

Thermal generation of 1 at 70°C in the presence of the 1-azabutadienes **2a-d** yields 85-95% of the substituted 1-aza-2-germacyclopent-4-enes **3a-d**[7)]:

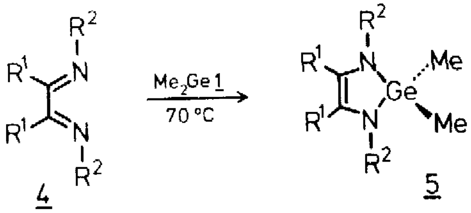


2,3:	R^1	R^2
a	R^1 = Me	R^2 = Ph
b	H	Ph
c	H	p-EtOOC-C_6H_4
d	H	p-MeO-C_6H_4
e	H	NH-C_6H_5

The compounds **2e**, R^1 = H, R^2 = NHPh, and **2f**, 1,4,4-Ph_3-1-azabutadiene, remained unchanged under these conditions, **1** formed $(Me_2Ge)_n$ exclusively.

From competition experiments with mixtures of **2b**+**2c** and **2b**+**2d** a reactivity **2b**:**2c**:**2d** = 3:6:1 results. The sequence **2d** < **2b** < **2c** points to an electrophilic behaviour of the azadiene, and a nucleophilic character of **1** (as usual), in the rate determining step of these cycloadditions. A concerted 1,4-addition like that with dienes, a [4+2] cheletropic reaction with inverse electron demand, is assumed here, but cannot be proved because of the absence of stereospecifity arguments in this system. E. g., a 3,4-addition giving a germirane first which rearranges rapidly giving **3** cannot be excluded. In every case, however, no intermediate could be detected so far, and the rate constants of the product formation and of the spontaneous, first order thermolysis$^{1)}$ are exactly the same.

In a similar way, the 1,4-diazadienes **4a-e** formed the substituted 1,3-diaza-2-germacyclopent-4-enes **5a-e** in yields of 50-85%:



4 **5**

4,**5**:	R^1	R^2
a	R^1 = Me	R^2 = Ph
b	H	tBu
c	H	cyclo-C_6H_{11}
d	H	p-Me-C_6H_4
e	H	2,6-$Me_2C_6H_3$

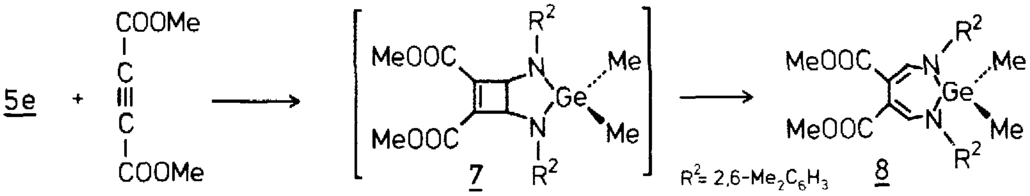
The products are identified in solution unequivocally$^{7)}$, but decompose easily upon heating. They do not survive the usual workup procedures, and are split promptly by air forming the diazadiene **4**$^{8)}$ and $(Me_2GeO)_n$, and by moisture. We assume that water, bound in or at the glass of the reaction flask$^{9)}$ even after heating it twice to ca. 150°C/10^{-3} Torr and filling it with dry argon, prevents quantitative yields. Concerning the mechanism of this cycloaddition forming **5**, the same statements are made as for **3**.

The products **5b**, **e** could be prepared, alternatively, also by lithiation of **4b**, **e** and subsequent reaction with Me_2GeCl_2, in analogy to the corresponding Si compounds$^{10)}$, but the reaction remains incomplete. The analytic data, however, are the same as obtained for the product of the cycloaddition of **1**$^{7)}$, see above.

$$\underline{4b,e} \xrightarrow[2)\ Me_2GeCl_2]{1)\ 2\ Li} \underline{5b,e} + 2\ LiCl$$

When we started from 2,3-diazabutadienes, e. g. the 1,4-Ph_2 derivative, and **1**, no product could be observed. 1-Oxa-4-azabutadienes, however, e. g. the 2,3-Ph_2-4-isopropyl compound, formed very labile 1,4-adducts of the expected 1-oxa-3-aza-2-germacyclopent-4-ene structure **6**$^{11)}$, but decompose spontaneously within one hour.

A [2+2]-cycloaddition of **5e** with acetylenic dicarbonic ester takes place easily even at 20°C forming lastly the new heterocycle, 1,3-diaza-2-germacyclohepta-4,6-diene 8[12], probably via the (non detectable) strained bicyclic adduct 7. This is easily explained by the high electron density of the double bond in 5e.



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3) E. Michels, W. P. Neumann, Tetrahedron Lett. 27, 2455 (1986);
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4) A few 4,5-benzo derivates have been prepared from aromatic 1,2-diamines:
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7) The azabutadienes 2 and diazabutadienes 3 are prepared from cinnamaldehyde, glyoxal (40% aqueous solution) or diacetyl and the respective amines by published procedures[13].

In a typical procedure 2.0 g (3.7 mmol) 7-germanorbornadiene[1] and 3.5 mmol azabutadiene 2 are heated for 1 h without solvent at a temperature which is necessary to get a homogenous melt (90°C for **3a**, 110°C for **3b**). At 120°C the products 3 decay. The pure products are isolated by distillation at 10^{-3} Torr (Kugelrohr). Isolated yields: 45% **3a**, 39% **3b**.

For analytical determinations 54 mg (0.1 mmol) 7-germanorbornadiene and 0.1 mmol azabutadiene 2 (diazabutadiene 3) are heated 4 h at 70°C in 0.4 ml dry C_6D_6. The reaction mixtures are investigated by ^1H- and ^{13}C-NMR as well as mass spectroscopy without further purification.

Some characteristic data of the new compounds are given, the listed yields are found in the crude reaction mixtures (GC, ^1H-NMR).

3a: 85%; bp. 100°C/$5\cdot10^{-3}$ Torr; ^{1}H-NMR: 0.00, 0.37 (s, GeMe), 1.70 (m, Me), 3.08 (m, GeCH); ^{13}C-NMR: -2.41, 0.40 (GeMe), 16.62 (Me), 43.58 (GeCH), 112.80 (C_q), 133.39 (CH); GC-MS (70 eV): m/e = 325 (90%, M^+), 220 (100%).

3b: 90%; bp. 110°C/10^{-3} Torr; ^{1}H-NMR: 0.00, 0.40 (s, GeMe), 3.41 (dd, ^3J = 3.02 Hz, ^4J = 2.20 Hz, GeCH), 5.03 (dd, ^3J = 5.77 Hz, =CH); ^{13}C-NMR: -2.83, 0.34 (GeMe), 39.21 (GeCH), 104.90, 137.35 (CH); GC-MS (70 eV): m/e = 311 (100%, M^+).

3c: 95%; ^{1}H-NMR: -0.04, 0.33 (s, GeMe), 3.23 (dd, GeCH), 5.03 (dd, =CH); ^{13}C-NMR: -2.85, 0.05 (GeMe) 38.95 (GeCH), 107.38, 136.19 (CH); GC-MS (70 eV): m/e = 383 (46%, M^+), 234 (100%).

3d: 85%; ^{1}H-NMR: 0.05, 0.42 (s, GeMe), 3.38 (m, OMe and GeCH), 5.02 (dd, =CH); ^{13}C-NMR: -2.77, 0.35 (GeMe), 39.17 (GeCH), 105.03, 137.38 (CH); GC-MS (70 eV): m/e = 341 (100%, M^+).

5a: 80%; ^{1}H-NMR: 0.37 (s, GeMe), 1.96 (s, Me); ^{13}C-NMR: 1.67 (GeMe), 14.08 (Me), 123.20 (C_q); GC-MS (70 eV): m/e = 340 (31%, M^+), 118 (100%).

5b: 50%; ^{1}H-NMR: 0.62 (s, GeMe), 1.22 (s, tBu), 5.75 (=CH); ^{13}C-NMR: 8.30 (GeMe), 31.37 (tBu), 52.30 (tBu_q), 112.99 (CH); MS (70 eV): m/e = 272 (89%, M^+), 159 (100%).

5c: 65%; ^{1}H-NMR: 0.52 (s, GeMe), 5.69 (s, =CH); ^{13}C-NMR: 6.67 (GeMe), 115.53 (CH); GC-MS (70 eV) : m/e = 324 (100%, M^+).

5d: 75%; ^{1}H-NMR: 0.52 (s, GeMe), 2.17 (s, Me), 6.29 (=CH); ^{13}C-NMR: 1.83 (GeMe), 20.62 (Me), 114.58 (CH); GC-MS (70 eV): m/e = 340 (92%, M^+), 310 (100%).

5e: 85%; ^{1}H-NMR: 0.27 (s, GeMe), 2.29 (s, Me), 5.56 (s, =CH); MS (70 eV): m/e = 368 (39%, M^+), 249 (100%).

8) see 1,3-diaza-2-silacyclopentene: M. Zettlitzer, H. tom Dieck, L. Stamp, Z. Naturforsch. 41b, 1230 (1980).

9) W. P. Neumann, H. Sakurai, G. Billeb, H. Brauer, J. Köcher, S. Viebahn, Angew. Chem. 101, 1074 (1989).

10) Procedure and workup as described for diazasilacyclopentenes: H. tom Dieck, M. Zettlitzer, Chem. Ber. 120, 795 (1987); yields: 25% **5b**; 50% **5e**.

11) **6**: ^{1}H-NMR: 0.54 (s, GeMe), 0.86 (d, Me, ^3J = 6.50 Hz), 3.48 (sept, CH); ^{13}C-NMR: 5.60 (GeMe), 24.95 (Me), 46.07 (CH).

12) A benzene solution of **5e** is treated with an equimolar amount of dimethyl acetylenedicarboxylate at 20°C. To complete the reaction, the mixture is left at room temperature overnight (see[10]).

7: ^{1}H-NMR: 0.20 (s, GeMe), 2.07 (s, Me), 3.56 (s, OMe), 7.66 (s, =CH); ^{13}C-NMR: 0.59 (GeMe), 19.24 (Me), 51.25 (OMe), 107.57 (C_q), 148.09 (CH), 170.19 (C_q); MS (70 eV): m/e = 510 (24%, M^+), 249 (100%).

13) H. v. Pechmann, Ber. dtsch. chem. Ges. 21, 1411 (1888); J. M. Kliegman, R. K. Barnes, Tetrahedron 26, 8555 (1970); H. tom Dieck, I. W. Renk, Chem. Ber. 104, 92 (1971).

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