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INTERACTION OF HETEROATOM-CONTAINING PROPYNALS WITH S-, N-BINUCLEOPHILES

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Reactions of α-silicon- and α-germanium-containing acetylenic aldehydes with 2-aminoethanethiol, ethylenediamine, and 2-amino-1,2,4-triazole proceed chemoselectively at the aldehyde group. The ratio of tautomers, azomethine and 1,3-thiazolidine, on interaction with 2-aminoethanethiol depends significantly on the nature of the heteroatom at the triple bond of the aldehyde, the presence of a catalyst, and the use of microwave activation.

Keywords: bisheteronucleophiles, N^1,N^2-bis(3-triorganyl-2-propynylidene)-1,2-ethanediamines, α-silicon- or α-germanium-containing propynals, 5-(3-triorganyl-2-propynylidene)amino-1H-1,2,4-triazoles, 2-[3-triorganosilyl(germyl)-2-propynyl]-1,3-thiazolidines, heteroatom-containing 1,3-azaenynes, microwave activation.

We have shown previously that the reaction of propynals $R_3MC{\equiv}CCHO$ (M = Si, Ge, C) with primary amines in the absence of catalyst proceeds chemoselectively at the aldehyde group with the formation of the corresponding azomethines [1]. The direction of the interaction with thiols depends on the nature of the heteroatom. On interacting trimethylsilylpropynal and thiols in the absence of solvent and catalyst at room temperature, depending on the reactant ratio, relatively stable acetylenic hemithials or thioacetals are isolated in quantitative yield. In the case of triethylgermylpropynal under comparable conditions (20°C, aldehyde–thiol, 1 : 2) adducts at the triple bond, the corresponding β-thiopropenals, are formed preferably [2]. Recently we discovered unexpectedly that, on interacting trimethylsilylpropynal with nucleophiles in the presence of catalysts, cascade heterocyclization reactions may take place. Under the action of *p*-toluenesulfonic acid trimethylsilylpropynal reacts with 2-aminopyridine on microwave (MW) activation with the formation of N (2'-pyridyl)-2-(trimethylsilylethynyl)-1,2-dihydropyridine-3,5-dicarbaldehyde [3], and under conditions of base catalysis (DABCO) undergoes trimerization into 4-(trimethylsilylethynyl)-4H-pyran-3,5-dicarbaldehyde [4].

The interaction of hetero-containing propynals with bisheteronucleophiles has not been investigated up to the present time. The aim of the present work is the study of the reaction of trimethylsilyl- and triethylgermylpropynal **1a,b** with certain N,N- and N,S-binucleophiles, in particular 2-aminoethanethiol, ethylenediamine, and 3-amino-1,2,4-triazole, and to search for conditions for the selective reaction process. The presence in the 2-aminoethanethiol molecule of two nucleophilic centers *a priori* affords the possibility of forming

* Dedicated to our teacher, Academician of the Russian Academy of Sciences M. G. Voronkov, in connection with his 85th birthday

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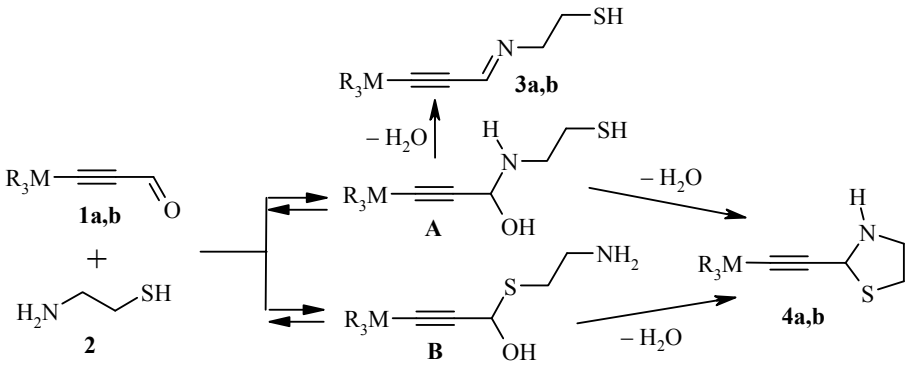
azomethines and/or the corresponding 1,3-thiazolidines, and also in the case of propynal **1b** adducts at the triple bond with the participation of the SH acidic center. The presence of silicon- and germanium-containing groups stabilizes the adducts at the carbonyl center, and subsequent heterolysis of the M-C_{sp} bond enables the preparation of analogs with a terminal triple bond. The introduction of a triple bond and a heteroatom of silicon or germanium also permits enrichment of the synthetic and biological potential of the adducts.

The chemistry of 1,3-thiazolidines has in recent years aroused growing interest, mainly due to the presence of this structural fragment in natural antibiotics [5-8]. 2-Alkyl-substituted thiazolidines possess radioprotective, antimutagenic, and hepatoprotective activity [9-12]. The majority of the known 2-substituted thiazolidines are obtained by condensing 2-aminoethanethiols with aromatic aldehydes or aldoses [13, 14]. Study of the ring–chain equilibrium showed that the ratio of tautomers depends significantly on the nature of the solvent, the reactant ratio, and the pH of the medium [15, 16].

Using the example of the reaction of propynals **1a,b** with 2-aminoethanethiol **2** the chemoselectivity of the process was shown with the participation of the aldehydic center with the formation of the corresponding azomethines **3a,b** or the products of their cyclization, the 2-[3-trimethylsilyl(germyl)-2-propynyl]-1,3-thiazolidines **4a,b**.



1, 3, 4 a $R_3M = Me_3Si$, **b** $R_3M = Et_3Ge$

The significant effect of the reaction conditions on the selectivity of the interaction and the ratio of the open chain and cyclic forms was noted. It was established that in dichloromethane at room temperature after 16 h the reaction of propynals **1a,b** with an equimolar quantity of 2-aminoethanethiol proceeds selectively with the formation of 2-[3-triorganosilyl(germyl)-2-propynyl]-1,3-thiazolidines **4a,b** in 85-87% yield. The isolated 1,3-thiazolidines **4a,b** were oils, decomposing on distillation in vacuum. The IR spectra are characterized by absorption bands for the stretching vibrations of the triple bond at 2170-2180, N-H bonds at 3240-3250, and Si-CH_3 bonds at 1250 cm^{-1}. In the ^1H NMR spectra ($CDCl_3$) of compounds **4a,b** signals were present for the methine proton in position 2 of the thiazolidine ring at 4.51 (**4a**) and 5.02 (**4b**), the methylene protons at 3.05-3.50, the N-H proton at 1.95-1.97, and for the protons of the trimethylsilyl with δ 0.15, and triethylgermyl groups with δ 0.8-1.1 ppm. The ^1H NMR spectrum ($CDCl_3$) of azomethine **3a** was characterized by the presence of signals for the trimethylsilyl group with δ 0.62, the S-H proton with δ 2.06, the methylene protons at 2.85-3.70, and the CH=N proton with δ 7.5 ppm.

It is known that molecular sieves are used as dehydrating agents in reactions of carbonyl compounds with primary amines [17]. We have shown that the use of 4 Å molecular sieves leads to a nonselective course for the process with the formation of a mixture of isomers of **3a,b** and **4a,b** (Table 1).

We have recently developed highly effective methods of solid phase direct conversion of silicon or germanium acetylenic alcohols into the corresponding azomethines by oxidation with activated manganese dioxide in the presence of primary amines on MW irradiation [18, 19]. It is known that MW irradiation may lead to significant shortening of reaction times, increased conversion, and occasionally also affect the selectivity

TABLE 1. Effect of the Reaction Conditions on the Tautomer Ratio of Azomethines **3a,b**/Thiazolidines **4a,b**

Expt.	Reaction conditions*	Time	Ratio	
			3a–4a	**3b–4b**
1**	Room temp.	16 h	1 : 4	0 : 1
2	Room temp.	16 h	2 : 1	
3	MW (140 W)	3 min	1 : 1.3	
4	MW (140 W)	6 min	1 : 1.8	
5	MW (140 W)	10 min	1.5 : 1	
6	MW (140 W)	3 min	1 : 1	
7	MW (140 W)	6 min	1.5 : 1	
8	MW (140 W)	10 min	1.5 : 1	
9	MW (140 W)	12 min	0 : 1	0 : 1

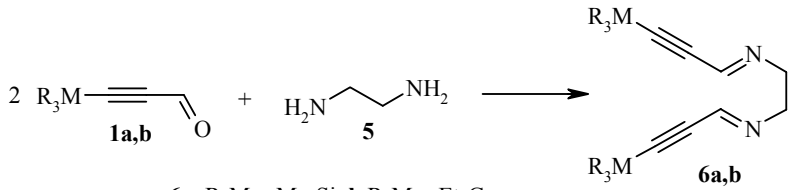
* Dehydrating agent was 4 Å molecular sieves (expt. 2-8).
** In CH_2Cl_2; expt. 2-9 were carried out without solvent.

of the process [20-23]. We have studied the effect of MW irradiation on the efficiency and selectivity of the reaction of propynals **1a,b** with 2-aminoethanethiol in the presence of 4 Å molecular sieves and in their absence without solvent (ampule, unmodified MW oven). According to the data of Table 1 the use of MW irradiation enables significant acceleration of the formation of 1,3-thiazolidines **4a,b**.

In the case of propynal **1a** the content of thiazolidine **4a** was 80% (without solvent, 25°C, 16 h, ^{1}H NMR) and on MW irradiation (power 420 W) the selective formation of 1,3-thiazolidine was observed after 12 min. An analogous result was also obtained for the germyl analog **1b**. A check on the progress of the reaction was effected by TLC and by ^{1}H NMR spectroscopy.

We noted that under all the reaction conditions 100% conversion of propynals **1a,b** was observed according to data of ^{1}H NMR. Study of the dynamics of the reaction of aldehyde **1a** on MW irradiation by ^{1}H NMR clearly shows the presence of ring–chain tautomerism between **3a** and **4a**. The predominance of azomethine **3a** in the reaction mixture in the presence of molecular sieves may be explained by the zeolites acting as a Lewis acids, stabilizing the immonium cation of the azomethine $Me_3SiC{\equiv}CCH{=}N^+(H)CH_2CH_2SH$ [24].

The reaction of propynals **1a,b** with ethylenediamine (**5**) in methylene chloride for 1 h at a temperature from -15 to -20°C, and then 1 h at room temperature, proceeds chemoselectively at the aldehyde center of the propynal with the participation of both amino groups of the binucleophile. In spite of the equimolar ratio of reactants the bis(azomethines) **6a,b** were isolated in 80 and 43% yield respectively. Compounds **6a,b** may be of interest as polydentate ligands in the directed synthesis of mono-, di-, and polynuclear complexes [25, 26].



6 a $R_3M = Me_3Si$, **b** $R_3M = Et_3Ge$

The IR spectra of compounds **6a,b** are characterized by the presence of absorption bands for the stretching vibrations of the triple bond (2170-2180), the C=N bonds (1595-1610) and the Si–CH_3 bond at 1240 cm^{-1}. In the ^{1}H NMR spectra ($CDCl_3$) of compounds **6a,b** in the region of methylene group signals two singlets were observed with δ 3.79 and 3.95 ppm belonging to the *cis,cis* and *trans,trans* isomers. In addition there were two multiplets at 3.81 and 3.91 ppm corresponding to two nonequivalent methylene groups in the *cis,trans* isomer.

In the region for resonance of azomethine groups three signals appeared at 7.52, 7.56, and 7.59 ppm, the first having double intensity. In the ^{13}C NMR spectrum four signals were detected both in the region of methylene (55.85-62.22) and azomethine groups (144.47-147.09 ppm) corresponding to the three isomers indicated (Fig. 1). Elemental analysis confirmed the composition of azomethines **6a,b**.

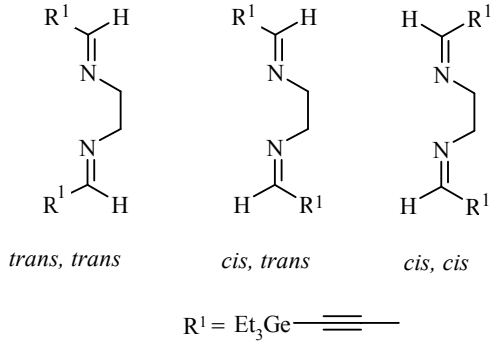
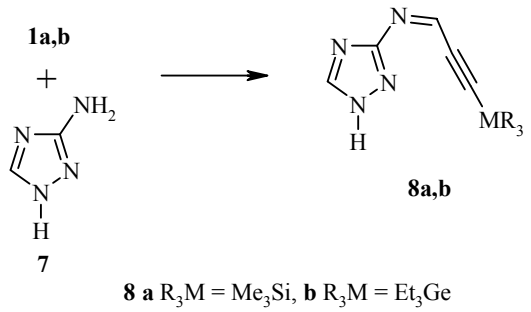


Fig. 1. Isomers of bis(azomethines) **6a,b**.

The interaction of compounds **1a,b** and 3-amino-1,2,4-triazole **7** was effected in THF or acetonitrile at room temperature for 3 h with the formation of the previously unknown aldimines **8a** (88% yield) and **8b** (62% yield). The isolated compounds were colorless crystals, soluble with difficulty in the majority of organic solvents.



The structures of aldimines **8a,b** were demonstrated by IR and NMR (**8b**) spectroscopy, and their compositions were confirmed by elemental analysis. The IR spectra contained absorption bands for the stretching vibrations of the triple bond (2170-2180), the C=N bond of the azomethine group and the ring (1595, 1550 w, 1470), N-H (3240-3250), Si-CH_3 (1240 cm^{-1}). The ^1H NMR ($CDCl_3$) spectrum of compound **8b** was characterized by signals of the Et_3Ge group with δ 0.92-1.09, azomethine protons CH=N at 6.07 and 6.48, ring CH=N at 7.78 and 8,34, and NH group protons with δ 14.12 ppm. Qualitative NMR spectra were not obtained for azomethine **8a** due to the poor solubility in the majority of organic solvents and D_2O.

The resonances of all the carbons in the ^{13}C NMR spectrum of compound **8b** were tripled, which is probably caused by the existence of this compound in solution as three tautomers (Fig. 2).

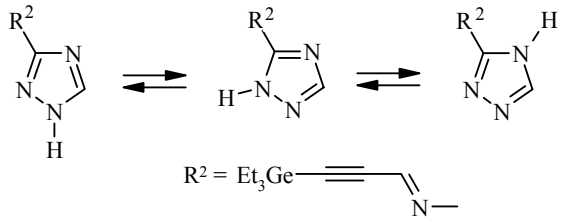


Fig. 2. Possible tautomers of aldimine **8b**.

The reaction of hetero-containing propynals with the studied bis(heteronucleophiles) with an available primary amino group proceeds chemoselectively at the aldehyde group. In the case of ethylenediamine reaction occurs with the participation of both amino groups with the formation of bis(azomethines) irrespective of the reactant ratio. In the case of 2-aminoethanethiol in the absence of catalyst 2-[3-triorganosilyl(germyl)-2-propynyl]-1,3-thiazolidines are formed selectively or preferentially in high yield. The use of MW activation leads to a substantial shortening of the reaction time and the selective formation of the cyclic adduct. In the presence of 4 Å molecular sieves a mixture of azomethine and thiazolidine is formed irrespective of the reaction conditions.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in KBr disks and in a microlayer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 instrument (400, 100, and 80 MHz respectively) in $CDCl_3$, internal standard was HMDS (δ 0.05 ppm). For MW activation an unmodified type LG microwave oven was used, power 700 W, frequency 2450 MHz. A check on the progress of reactions was effected with TLC on Silufol UV-254 plates, eluent was chloroform–acetonitrile, visualizing with iodine vapor in a chamber. 3-Trimethylsilyl-2-propyn-1-al (**1a**) was obtained by the oxidation of 3-trimethylsilyl-2-propyn-1-ol with the γ-modification of neutral manganese dioxide according to the method of [27]. 3-Triethylgermyl-2-propyn-1-al was obtained by the method of [28].

2-(3-Trimethylsilyl-2-propynyl)-1,3-thiazolidine (4a). A. A solution of 2-aminoethanethiol **2** (0.77 g, 10 mmol) in absolute methylene chloride (20 ml) was added dropwise to a solution of propynal **1a** (1.26 g, 10 mmol) in absolute methylene chloride (10 ml). The reaction mixture was stirred at a temperature from -15 to -20°C for 1 h, left overnight at room temperature, then dried over $MgSO_4$. After removing the solvent in vacuum the residue was chromatographed on a column of Al_2O_3 (eluent was chloroform–hexane, 3 : 1). Thiazolidine **4a** (1.6 g, 87%) was obtained as a pink oil. IR spectrum, ν, cm^{-1}: 3350 (N–H), 2170 (C≡C), 1250, 850 (Me_3Si). ^{1}H NMR spectrum, δ, ppm: 0.15 (9H, s, $(CH_3)_3Si$); 1.95 (1H, br. s, N–H); 3.05 (2H, m, CH_2–S); 3.05-3.50 (2H, m, CH_2–N); 4.51 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: -0.60 ($(CH_3)_3Si$); 36.14 CH_2–S); 52.58 (CH_2-N); 58.31 (CH); 90.40 (≡CSi); 102.94 (C≡). ^{29}Si NMR spectrum, δ, ppm: -17.29. Found, %: C 51.52; H 8.25; N 7.70; S 17.33; Si 14.80. $C_8H_{15}NSSi$. Calculated, %: C 51.84; H 8.16; N 7.55; S 17.20; Si 15.15.

B. A mixture of aldehyde **1a** (0.13 g, 1 mmol) and 2-aminoethanethiol (0.08 g, 1 mmol) was sealed in an ampule of volume 10 ml, which was placed in a teflon container with a screw-on cap (the volume of solution must not exceed 10% of the ampule volume!). The reaction mixture was irradiated in the microwave oven for 12 min at 420 W (60% oven power), with exposures of 2 min and subsequent cooling to room temperature. After cooling the ampule was opened, and the residue evacuated. Compound **4a** (0.18 g, 95%) was obtained as a pink oil. The ^{1}H NMR spectrum of the isolated compound was identical to that described above.

C. Aldehyde **1a** (0.14 g, 1.1 mmol) in methylene chloride (2 ml) was added with stirring to a mixture of 2-aminoethanethiol (0.085 g, 1.1 mmol) thoroughly ground with freshly calcined 4 Å molecular sieves (0.8 g). The reaction mixture was stirred for 30 min, the solvent was blown off in a current of air, the residue was divided into four portions, and placed into glass test tubes of volume 10 ml. One of them was maintained at room temperature for 16 h, and three were irradiated at 140 W for 3, 6, and 10 min. Irradiation was carried out with exposures of 3 min and subsequent cooling to room temperature, in the last case for 3+3+4 min. The reaction mixtures were extracted with dichloromethane, and the residue analyzed by ^{1}H NMR. Products isolated were 0.039 g (80%) (at room temperature); 0.036 g (74%) (MW irradiation for 3 min) 0.043 g (87%) (MW irradiation for 6 min); 0.048 g (98%) (MW irradiation for 10 min). According to data of ^{1}H NMR spectra mixtures of tautomers **4a** and **3a** were obtained in the ratios indicated in Table 1.

2-(3-Triethylgermyl-2-propynyl)-1,3-thiazolidine (4b) was obtained analogously to compound **4a** by method A from propyn-1-al **1b** (2.13 g, 10 mmol) and 2-aminoethanethiol (0.77 g, 10 mmol) with a yield of 2.3 g (85%) as an orange oil. IR spectrum, ν, cm^{-1}: 3300 (N–H), 2170 (C≡C). ^1H NMR spectrum, δ, ppm: 0.83-1.10 (15H, m, Et_3Ge); 1.97 (1H, br. s, N–H); 3.08 (2H, m, CH_2–S); 3.49 (2H, m, CH_2–N); 5.02 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 5.82, 8.93 (Et_3Ge); 36.26 (CH_2–S); 52.68 (CH_2–N); 58.73 (CH); 88.73 (≡CGe); 103.61 (C≡). Found, %: C 48.51; H 7.89; Ge 6.69; N 5.30; S 12.10. $C_{11}H_{21}GeNS$. Calculated, %: C 48.58; H 7.79; Ge 26.69; N 5.15; S 11.79.

N^1,N^2-Bis(3-trimethylsilyl-2-propynylidene)-1,2-ethylenediamine (6a). A solution of ethylenediamine (0.3 g, 5 mmol) in absolute methylene chloride (10 ml) was added dropwise to a solution of aldehyde **1a** (1.26 g, 10 mmol) in absolute methylene chloride (10 ml). The reaction mixture was stirred at a temperature of -15 to -20°C for 1 h and then for a further 1 h at room temperature. The mixture was dried over $MgSO_4$, the solvent removed under reduced pressure, and compound **6a** (1.1 g, 80%) was obtained as a yellow powder of mp 65°C. IR spectrum, ν, cm^{-1}: 2170 (C≡C), 1600 (C=N), 1240, 850 (Me_3Si). ^1H NMR spectrum, ν, cm^{-1}: 0.21 (18H, s, $(CH_3)_3Si$); 3.87 (4H, m, CH_2); 7.51 (2H, s, CH=N). ^{13}C NMR spectrum, δ, ppm: 0.20 ($(CH_3)_3Si$); 62.30 (CH_2); 96.46 (≡CSi); 101.42 (C≡). ^{29}Si NMR, δ, ppm: -16.45. Found, %: C 58.73; H 8.15; N 10.23; Si 18.85. $C_{14}H_{24}N_2Si_2$. Calculated, %: C 60.81; H 8.75; N 10.13; Si 20.31.

N^1,N^2-Bis(triethylgermyl-2-propynylidene)-1,2-ethylenediamine (6b) was obtained analogously to compound **6a** from propynal **1b** (2.13 g; 10 mmol) and ethylenediamine (0.3 g, 5 mmol) in a yield of 0.9 g (43%) as an orange oil. IR spectrum, ν, cm^{-1}: 2170 (C≡C), 1595 (C=N). ^1H NMR spectrum, δ, ppm: 0.88-1.25 (30H, m, Et_3Ge); 3.79, 3.95 (4H, s, CH_2, *cis-,cis-* and *trans-,trans*-isomers); 3.81, 3.91 (4H, m, CH_2 nonequivalent methylene groups in *cis-, trans*-isomer); 7.52, 7.56, 7.59 (2H, s, CH=N). ^{13}C NMR spectrum, δ, ppm: 5.68, 9.17 (Et_3Ge); 55.85, 56.32, 61.72, 62.22 (CH_2); 97.99 (≡CGe); 102.58 (C≡); 144.47, 144.75, 146.53, 147.09 (CH=N). Found, %: C 51.00; H 7.53; Ge 34.21; N 6.32. $C_{18}H_{32}Ge_2N_2$. Calculated, %: C 51.25; H 7.69; Ge 34.42; N 6.64.

5-(3-Trimethylsilyl-2-propynylidene)amino-1H-1,2,4-triazole (8a). A solution of aldehyde **1a** (0.88 g, 7 mmol) and 3-amino-1,2,4-triazole (**7**) (0.59 g, 7 mmol) in absolute THF (10 ml) was stirred for 3 h at room temperature. The precipitated white crystalline solid was filtered off, washed with ether, and dried in vacuum. Triazole **8a** (1.19 g, 88%) was obtained with mp 188-190°C. IR spectrum, ν, cm^{-1}: 3250 (N–H), 2180 (C≡C), 1595 (C=N), 1240, 850 (Me_3Si). Found, %: C 49.96; H 6.76; N 28.82; Si 14.44. $C_8H_{12}N_4Si$. Calculated, %: C 49.98; H 6.28; N 29.13; Si 14.61.

5-(3-Triethylgermyl-2-propynylidene)amino-1,2,4-triazole (8b) was obtained analogously to compound **8a** from aldehyde **1b** (1.49 g, 7 mmol) and compound **7** (0.59 g; 7 mmol) in absolute acetonitrile (20 ml) in a yield of 1.2 g (62%). Mp 161°C. IR spectrum, ν, cm^{-1}: 3240 (N–H), 2180 (C≡C), 1595 (C=N). ^1H NMR spectrum, δ, ppm: 0.92-1.09 (15H, m, (Et_3Ge)); 6.07, 6.48 (1H, s, CH=N, *cis, trans*); 7.78, 8.34 (1H, s, N–CH=, triazole); 14.12 (1H, br. s, N–H). ^{13}C NMR spectrum, δ, ppm: 5.92, 9.83 (Et_3Ge); 103.22 (≡CGe); 109.52 (C≡); 142.06-143.13 (CH=N); 150.11 ($C_{(5)}$ triazole); 161.18-161.59 ($C_{(3)}$ triazole). Found, %: C 47.16; H 6.06; Ge 26.03; N 20.08. $C_{11}H_{18}GeN_4$. Calculated, %: C 47.38; H 6.51; Ge 26.03; N 20.08.

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