Russian Journal of Organic Chemistry, Vol. 40, No. 12, 2004, pp. 1804–1809. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 12, 2004, pp. 1852–1857.
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1,3-Dipolar Cycloaddition of Trimethylsilyl Azide to Propynals and Dimerization of 1*H*-1,2,3-Triazole-5-carbaldehydes to Tricyclic Bis-hemiaminals

M. M. Demina[1], P. S. Novopashin[1], G. I. Sarapulova[1], L. I. Larina[1], A. S. Smolin[2], V. S. Fundamenskii[3], A. A. Kashaev[3], and A. S. Medvedeva[1]

[1] *Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,*
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: amedved@irioch.irk.ru

[2] *Institute of the Earth's Crust, Siberian Division, Russian Academy of Sciences,*
ul. Lermontova, 128, Irkutsk, 664033 Russia

[3] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*

Received November 27, 2003

Abstract—Reactions of trimethylsilyl azide with 3-trimethylsilyl-2-propynal and 2-propynal were studied. X-Ray analysis of the molecular structure of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde showed that the carbonyl group appears in the *s-cis* conformation with respect to the double C=C bond in the heteroring. The effect of the temperature and polarity of the medium on the ability of 1*H*-1,2,3-triazole-5-carbaldehyde to undergo dimerization to tricyclic bis-hemiaminals was examined by IR and ^{1}H NMR spectroscopy.

Using a wide series of substituted propynals we previously showed [1–3] that these compounds act as ambident electrophiles toward methyl diazoacetate. Depending on the propynal structure, the reactions with methyl diazoacetate follow 1,3-dipolar cycloaddition pattern with formation of isomeric pyrazoles and products of dimerization of 5-formylpyrazoles to tricyclic bis-hemiaminals or/and aldol-like condensation to give α-diazo-β-hydroxyalkynes (in the absence of initiating species). It was also found that in the absence of a solvent 5-formylpyrazoles exist mainly as the corresponding dimers, 3,8-disubstituted dimethyl 4,9-dihydroxy-4*H*,9*H*-dipyrazolo[1,5-*a*:1',5'-*d*]pyrazine-2,7-dicarboxylates, in a way similar to other fromylazoles (e.g., imidazoles and their fused derivatives and 1,2,4-triazoles) in which the formyl group is attached to a carbon atom neighboring to the endocyclic NH group [4]. It should be noted that methyl 5-formyl-4-phenylpyrazole-3-carboxylate, unlike silicon-, germanium-, and alkyl-containing analogs, does not undergo dimerization under the same conditions [2].

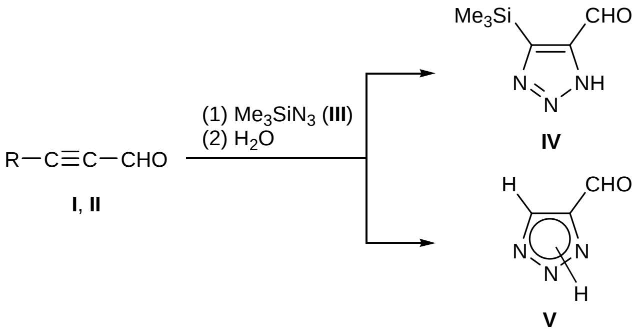
In the present work we examined reactions of 3-trimethylsilyl-2-propynal (**I**) and 2-propynal (**II**) with trimethylsilyl azide (**III**) with a view to elucidate the effect of the propynal structure on the regioselectivity of the addition process, as well as the ability of 5-formyl-substituted 1,2,3-triazoles to undergo dimerization with formation of the corresponding cyclic bis-hemiaminals. There are no published data on dimerization of 1*H*-1,2,3-triazole-5-carbaldehydes. However, this way of formation of tricyclic dihydroxypirazines may underlie an effective method of synthesis of difficultly accessible fused polyaza compounds which attract interest as biologically active compounds [5] and energy-rich substances. Dipyrazolopyrazinediols prepared by us previously showed a high cytostatic and tuberculostatic activity [6].

It is known that the regioselectivity in the 1,3-dipolar cycloaddition of azides to activated acetylenes is determined by the structure of both dipolarophile and 1,3-dipole. As shown in [7], hydrazoic acid reacts with 2-propynal to give 1*H*-1,2,3-triazole-4-carbaldehyde; on the other hand, published data on the addition of HN_3 to 3-trimethylsilyl-2-propynal are contradictory. According to Piterskaya *et al*. [8], the product is 5-trimethylsilyl-1*H*-1,2,3-triazole-4-carbaldehyde, while Huttel [9] identified it as 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde [9]. Reaction of aldehydes **I** and **II** with trimethylsilyl azide (**III**) were not studied previously.

We carried out reactions of propynals **I** and **II** with an equimolar amount of trimethylsilyl azide (**III**) in toluene at 90–95°C (32 h) (compound **I**) and in tetrahydrofuran at –30 to –25°C (7 days) (compound **II**). Mixing of the reactants in the absence of a solvent was accompanied by a strong exothermic effect, and external cooling was necessary. The progress of reactions was monitored by TLC and ^{1}H NMR spectroscopy.

The addition of trimethylsilyl azide (**III**) to aldehyde **I** regioselectively afforded 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**) (Scheme 1) which was isolated in 75% yield as colorless crystals with mp 188°C (from toluene). The structure of **IV** was confirmed by elemental analysis and spectral methods. In the IR spectrum of **IV** we observed absorption bands belonging to stretching vibrations of the carbonyl group (1697 cm^{-1}), NH group (3100 cm^{-1}), and Si–C bond (1250 cm^{-1}). The ^{1}H NMR spectrum of formyltriazole **IV** in $CDCl_3$ contained signals from protons of the trimethylsilyl group and aldehyde proton at δ 0.41 and 10.26 ppm, respectively; no NH proton signal was observed in that solvent. In the spectra recorded from solutions in CD_3CN and DMSO-d_6, the NH signal appeared at δ 13.07 and 15.1 ppm, respectively. The ^{13}C and ^{29}Si NMR spectra were also consistent with the assumed structure.

Scheme 1.



I, R = Me_3Si; **II**, R = H.

Formyltriazole **V** was isolated as a crystalline substance with mp 137–138°C (from benzene–hexane); yield 74% (Scheme 1). The presence of a broadened signal at δ 8.26 ppm in the ^{1}H NMR spectrum of a solution of triazole **V** in CD_3CN and of signals at δ_C 128.72 and 146.25 ppm (C^4, C^5) in the ^{13}C NMR spectrum suggests proton migration between nitrogen atoms in the triazole ring. The NH proton gives rise to a broad singlet at δ 13.4 ppm.

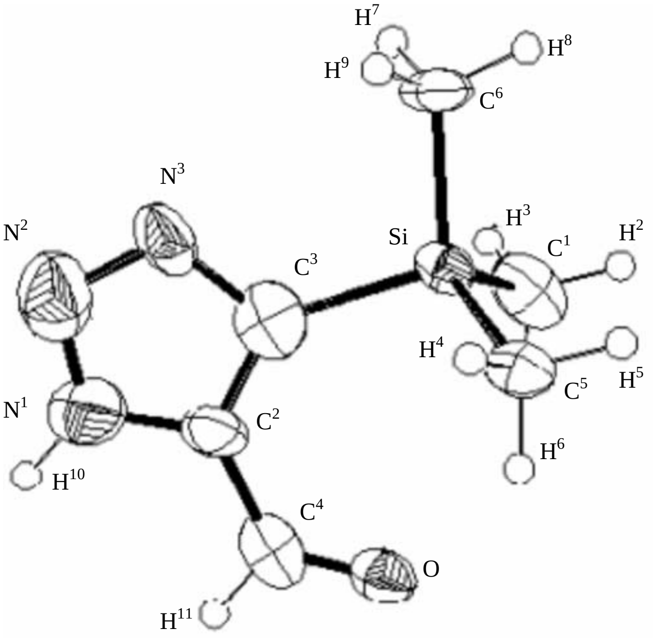


Fig. 1. Structure of the molecule of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**) with atom numbering.

The molecular structure of compound **IV** in crystal was studied by X-ray analysis (Fig. 1). The coordinates of atoms are available from the authors, and the interatomic distances, bond angles, and torsion angles are given in table. The silicon atom in molecule **IV** has a tetrahedral configuration.The Si–C^5 and Si–C^6 bond lengths are very similar, 1.842(7) and 1.840(7) Å, respectively. The distance between the silicon atom and C^3 atom in the triazole ring [1.858(7) Å] is slightly longer than the other bonds formed by the tetrahedral silicon atom. The triazole ring is planar: the N^1, C^2, N^3,

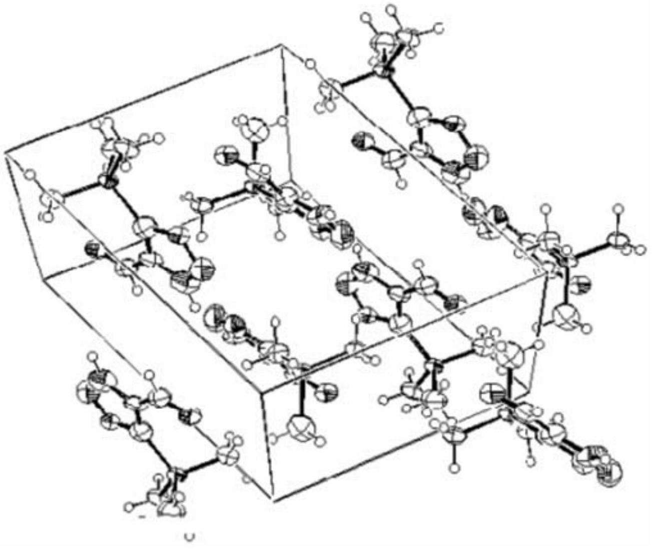


Fig. 2. Packing of molecules of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**) in crystal.

Bond lengths *d*, bond angles ω, and torsion angles φ in the molecule of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**)

Bond	*d*, Å	Bond	*d*, Å
Si–C^1	1.858(7)	N^1–N^2	1.291(6)
Si–C^3	1.889(6)	N^2–N^3	1.352(7)
Si–C^5	1.841(6)	N^3–C^3	1.358(7)
Si–C^6	1.840(7)	C^2–C^4	1.448(8)
C^2–C^3	1.386(7)	C^4–O	1.201(8)
N^1–C^2	1.366(8)		
Angle	ω, deg	Angle	ω, deg
C^1SiC^6	111.2(3)	C^3SiC^5	108.6(3)
C^1SiC^5	111.6(3)	SiC^3N^3	123.3(3)
C^1SiC^3	107.4(3)	$Si^1C^3C^2$	134.3(4)
C^6SiC^3	105.5(3)	$C^3C^2C^4$	130.2(5)
C^6SiC^5	112.1(4)	C^2C^4O	124.4(7)
Angle	φ, deg	Angle	φ, deg
$OC^4C^2C^3$	2.4(3)	$OC^4C^2N^1$	–179.0(3)
$C^4C^2C^3Si$	4.2(3)	$OC^4C^2C^3$	2.4(3)
$N^2N^2N^3C^3$	–0.8(2)	$C^2C^3SiC^6$	174.1(3)
$N^2N^3C^3Si$	176.0(3)		

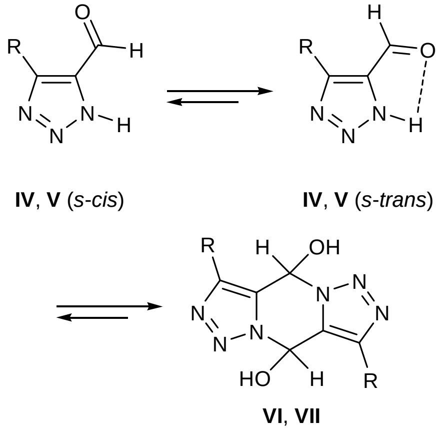
N^2, and C^3 atoms deviate from the mean-square plane by 1.13, 1.11, 0.54, 1.41, and 0.4°, respectively, i.e., by no more than 1.5°. The OC^4H aldehyde group lies in the triazole ring plane. The angle between the normals to the corresponding planes, $N^1N^2N^3C^2C^3$ and C^2C^4O is 1.7°. The torsion angles $OC^4C^2C^3$ and $OC^4C^2N^1$ are 2.4° and 179.0°, respectively, indicating that the aldehyde group is conjugated with the triazole ring. The carbonyl group occurs in an *s-cis* conformation with respect to the double C^2=C^3 bond; rotation of the OC^4H group about the C^2–C^4 bond is restricted by methyl groups of the trimethylsilyl fragment, as in 4-*tert*-butyl-1-(4-nitrophenyl)-1,2,3-triazole-5-carbaldehyde [10]. The carbonyl oxygen atom is located at equal distances to the methyl groups: $O\cdots C^1$ 3.427(6), $O\cdots H^1$ 2.677(5), $O\cdots C^5$ 3.502(7), $O\cdots H^6$ 2.799(6) Å.

Figure 2 shows packing of molecules **IV** in crystal. They give rise to head-to-head and tail-to-tail chains; the heterorings are linked in pairs through the intermolecular contacts $H^{10}(\mathbf{1})\cdots H^3(\mathbf{2})$ and $H^{10}(\mathbf{3})\cdots H^3(\mathbf{4})$ estimated at 1.985(6) Å. Probably, these intermolecular contacts stabilize the crystal packing and determine the molecular conformation.

Taking into account that, unlike many NH-azolecarbaldehydes which exist as dimeric bis-hemiaminals in the absence of a solvent [1–4], compounds **IV** and **V** in crystal retain their formyltriazole structure, we tried to find conditions promoting their dimerization to heterocyclic bis-hemiaminas. For this purpose, we examined the effects of the polarity of the medium and temperature by ^{1}H NMR and IR spectroscopy. We analyzed the IR spectra of both crystalline triazoles **IV** and **V** and their solutions in CCl_4, $CHCl_3$, $C_2H_2Cl_4$, CH_3CN, and octane over a wide temperature range (from 20 to 110°C). The character of variation of the ν(C=O) and ν(NH) absorption patterns in going from the crystalline state to dilute solutions in carbon tetrachloride, as well as typical temperature dependences, suggests that intermolecular hydrogen bonding involves only the NH groups (hydrogen bonds like $NH\cdots N$) and that associates decompose in dilute solutions. The N–H stretching vibration frequency increases from 3230 to 3430 cm^{-1}, while the carbonyl absorption frequency, ν(C=O) 1700 cm^{-1}, does not change over a wide range of concentrations. Absorption bands at 1660, 1540, 1458, 1308, and 1207 cm^{-1} belong to vibrations of the triazole ring.

The spectral parameters of the C=C–C=O fragment are consistent with the *s-cis* orientation of the C=O and C=C groups [12], dtermined by the X-ray diffraction study. In going from solutions of formyltriazole **IV** in carbon tetrachloride to solutions in chloroform and tetrachloroethane, absorption bands assignable to the *s-trans* conformer (which is more favorable for dimerization) appeared in the spectrum [ν(C=O) 1715 cm^{-1}], while the ν(C=C) band at 1660 cm^{-1} decreased in intensity. Simultaneously, a number of new bands appeared, which were displaced to shorter frequencies. This effect became stronger in going to solutions in

Scheme 2.



IV, **VI**, R = Me_3Si; **V**, **VII**, R = H.

acetonitrile and on raising the temperature to 100°C: new absorption bands at 1630, 1520, 1420, 1300, and 1202 cm^{-1} considerably increased in intensity. In addition, an absorption corresponding to free hydroxy groups was observed at 3620 cm^{-1}. This pattern may be interpreted in terms of formation of tricyclic dimer **VI** (Scheme 2).

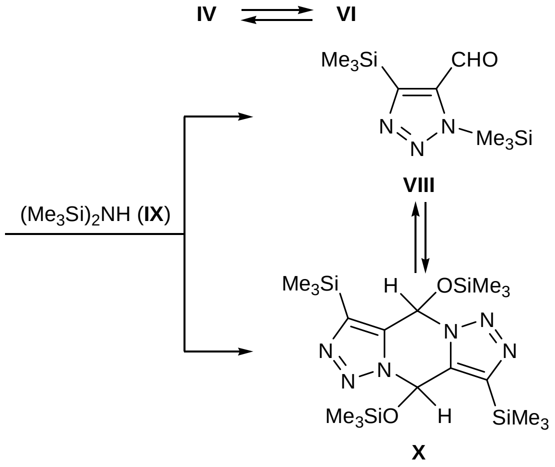
Analogous analysis of the IR spectra of crystalline triazole **V** and its solution led us to conclude that compound **V** exists in two conformations: *s-cis*, ν(C=O) 1700 cm^{-1}, and *s-trans*, ν(C=O) 1690 cm^{-1} [10]. The lower C=O frequency in the *s-trans* isomer is explained by formation of intramolecular hydrogen bond with participation of the carbonyl group (C=O···HN). This follows from the fact that the absorption band at 1690 cm^{-1} disappears from the IR spectrum of **V** in tetrachloroethane with rise in temperature; simultaneously, a band at 1720 cm^{-1} appears due to free carbonyl group in the *s-trans* conformer, and absorption bands belonging to cyclic dimer **VII** arise at 1600, 1520, 1440, and 1200 cm^{-1}. As with compound **IV**, the observed effect is stronger in more polar solvents. Thus formyltriazoles **IV** and **V** in solution undergo dimerization to the corresponding tricyclic bis-hemiaminals **VI** and **VII** according to Scheme 2.

The results of AM1 quantum-chemical calculations showed that structure **V** with intramolecular hydrogen bond is more favorable in the gas phase. The energy of the hydrogen bond is 5.0 kcal/mol, and the distance between the oxygen and NH hydrogen atoms is 2.57 Å. The charges on the oxygen and hydrogen atoms are –0.28 and 0.29 *e*, respectively. Planar arrangement of the triazole ring and aldehyde group favors stronger hydrogen bonding.

The IR spectral data obtained for triazolecarbaldehydes **IV** and **V** were in agreement with their ^1H NMR spectra. The ^1H NMR spectrum (CD_3CN) of the reaction mixture obtained from propynal **I** and trimethylsilyl azide (**III**) contained signals belonging to triazole **IV** and a signal at δ 7.33 ppm (2H, d), which was assigned to CH proton in the pyrazine ring (monomer–dimer ratio 1:1). In keeping with published data, signal from the CH(OH) fragment in cyclic hemiaminals derived from NH-azolecarbaldehydes is observed at δ 6.3–7.5 ppm [4]. Likewise, the ^1H NMR spectrum (CD_3CN) of the reaction mixture obtained from propynal (**II**) and trimethylsilyl azide (**III**) contained signals from protons of triazole **V**, methine proton in the pyrazine ring of tricyclic hemiaminal **VII** at δ 6.46 ppm (2H, d), and methine proton in the triazole ring at δ 8.64 ppm (2H, d), the ratio monomer–dimer being 1:1. In CD_3OD at room temperature, the equilibrium monomer–dimer (ratio 1:3) establishes within 2 h.

We previously showed [1] that treatment of dimethyl 4,9-dihydroxy-3,8-bis(triethylgermyl)-4*H*,9*H*-dipyrazolo[1,5-*a*:1',5'-*d*]pyrazine-2,7-dicarboxylate with hexamethyldisilazane (**IX**) gives the corresponding bis(trimethylsilyl) ether. Assuming that silylation of the dimer should promote displacement of the monomer–dimer equilibrium toward the latter, formyltriazole **IV** was heated in boiling hexamethyldisilazane (**IX**) for 4 h. The residue obtained by removal of excess reagent **IX** showed in the IR spectrum (mineral oil) an absorption band at 1050 cm^{-1} (Si–O–C) [11], while no carbonyl or NH absorption band was present. In the ^1H NMR spectrum of the product in acetone-d_6 we observed a multiplet at δ 6.80 ppm (CH, monomer–dimer ratio 1:11). Splitting of the CH proton signal in the ^1H NMR spectra of dimers derived from some azolecarbaldehydes was explained in [4] by the presence of isomeric structures. Raising the temperature to 50°C changes the intensity ratio of the CHO and CH–O proton signals to 1:140, and this ratio increases to 1:40 on cooling to 28°C (after 24 h). These data indicate that the formation of dimer **X** is favored at elevated temperature, as we already found by IR spectroscopy (Scheme 3).

Scheme 3.



The results of our spectral studies indicate that the dimerization of 5-formyl-1,2,3-triazoles to tricyclic hemiaminals is favored by elevated temperature and increased polarity of the medium. These data contradict those reported by us previously for dimerization of pyrazolecarbaldehydes [1, 2], according to which the equilibrium monomer–dimer shifts toward the monomeric form on raising the temperature or increasing the solvent polarity. The observed inconsistency may be rationalized by formation in solutions of compounds **IV** and **V** of a relatively strong intramolecular hydrogen bond $C=O\cdots H–N$ which is destroyed on heating and in going to more polar solvents.

Thus, unlike most formylazoles in which the aldehyde group is contiguous to the NH moiety, 1,2,3-triazole-5-carbaldehydes obtained by 1,3-dipolar cycloaddition of trimethylsilyl azide to 3-trimethylsilyl-2-propynal and 2-propynal exist mainly in the monomeric form. According to the IR and ^{1}H NMR data, increase in the solvent polarity and temperature, as well as trimethylsilylation, favors dimerization of 1,2,3-triazole-5-carbaldehydes to the corresponding tricyclic bis-hemiaminals.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR instrument from samples prepared as KBr pellets, dispersed in mineral oil, and dissolved in CCl_4, $CHCl_3$, $C_2H_2Cl_4$, CH_3CN, and octane. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker DPX-400 spectrometer using hexamethyldisiloxane as internal reference. The progress of reactions was monitored by TLC on Silufol UV-254 plates using chloroform–methanol (3:1) as eluent. 2-Propynal (**II**) [12], 3-trimethylsilyl-2-propynol [13], 3-trimethylsiloxypropyne [14], and 3-trimethylsilyl-2-propynal [15] were synthesized by known methods.

X-Ray analysis of compound IV. Colorless single crystals of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**) were preliminarily examined by the photo method using RKOP, KFOR, and RRECESSION cameras. The unit cell parameters and space group were thus determined and were refined on a Syntex $P2_1$ four-circle automatic diffractometer (MoK_α radiation, graphite monochromator, ω-scanning).

Single crystals of compound **IV** were grown from a solution in toluene; they are stable on exposure to air. Crystal system monoclinic, space group $P2_1/c$; unit cell parameters: $a = 11.655(4)$, $b = 8.960(3)$, $c = 9.503(3)$ Å; $\beta = 109.90(1)°$; $V = 933$ Å^3; $Z = 4$; $d_{calc} = 1.718(2)$ g/cm^3. Intensities of 1198 reflections with $I > 2\sigma(I)$ were measured. The structure was solved by the direct least-squares procedure in the full-matrix anisotropic approximation for the Si, O, C, and N atoms and isotropic approximation for hydrogen atoms; the final divergence factors were $R = 0.0506$, $wR = 0.060$. The calculations were performed using SHELXTL software package [16].

Reaction of 3-trimethylsilyl-2-propynal (I) with trimethylsilyl azide (III). *a*. A solution of 2.52 g (20 mmol) of 3-trimethylsilyl-2-propynal (**I**) and 2.3 g (20 mmol) of trimethylsilyl azide (**III**) in 40 ml of anhydrous toluene was heated for 16 h at 90–95°C under stirring. The colorless crystals were filtered off, washed with hexane, and dried under reduced pressure. Yield of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**) 0.85 g (25%), mp 189°C. IR spectrum (KBr), ν, cm^{-1}: 3100 (NH), 1697 (C=O), 1251 [$(CH_3)_3Si$]. ^{1}H NMR spectrum ($CDCl_3$-), δ, ppm: 0.40 s [9H, $(CH_3)_3Si$], 10.26 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –2.20 [$(CH_3)_3Si$], 140.13 (C^4), 152.42 (C^5), 186.52 (C=O). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si}: –6.5 ppm [$(CH_3)_3Si$]. Found, %: C 42.58; H 6.76; N 24.71; Si 16.55. $C_6H_{11}N_3OSi$. Calculated, %: C 42.58; H 6.55; N 24.81; Si 16.60. The filtrate was heated for an additional 16 h, the solvent was removed under reduced pressure, 7 ml of methanol was added to the residue, and the mixture was heated for 1 h under reflux. Removal of the solvent left a viscous residue which crystallized on storage. We thus isolated an additional portion of triazole **IV**, 1.7 g; overall yield 75%.

b. A mixture of 3.0 g (24 mmol) of aldehyde **I** and 2.76 g (24 mmol) of trimethylsilyl azide (**III**) was kept for 14 days at room temperature. Mixing of the reactants was accompanied by spontaneous heating to 70°C. The mixture was evacuated, 10 ml of methanol was added to the residue, and the mixture was heated at the boiling point over a period of 1 h. We isolated 2.47 g (62%) of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**IV**) with mp 188–189°C.

Reaction of 2-propynal (II) with trimethylsilyl azide (III). A solution of 1.2 g (22 mmol) of 2-propynal in tetrahydrofuran was cooled to –30°C, and 2.3 g (20 mmol) of trimethylsilylazide (**III**) was added. The mixture was kept for 7 days at room temperature, the solvent was removed under reduced pressure, 5 ml of methanol was added to the residue, and the mixture was heated at the boiling point over a period of 1 h. The red–brown viscous residue was dissolved in benzene, and the product was precipitated with hexane. Yield of 1*H*-1,2,3-triazole-4(5)-carbaldehyde (**V**) 1.44 g (74%); brown crystals, mp 137–138°C. IR spectrum (thin layer), ν, cm^{-1}: 3100 (NH), 1700 (C=O). ^{1}H NMR spectrum (CD_3CN), δ, ppm: 8.26 s (1H, 4-H or 5-H), 10.07 s (1H, CHO), 13.4 s (1H, NH).

^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 128.72 ($C^{4(5)}$), 146.25 ($C^{5(4)}$), 185.60 (CHO). Found, %: C 37.44; H 3.02; N 43.21. $C_3H_3N_3O$. Calculated, %: C 37.13; H 3.12; N 43.27.

Reaction of 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (IV) with hexamethyldisilazane (IX). A mixture of 0.51 g (3 mmol) of triazole **IV** and 5 g (31 mmol) of hexamethyldisilazane (**IX**) was heated for 4 h under reflux. Excess hexamethyldisilazane was removed under reduced pressure to obtain 0.68 g (93%) of 4,9-bis(trimethylsiloxy)-3,8-bis(trimethylsilyl)-4*H*,9*H*-di[1,2,3]triazolo[1,5-*a*:1',5'-*d*]pyrazine (**X**) as a viscous material. IR spectrum (mineral oil), ν, cm^{-1}: 1648, 1462, 1377, 1159, 696 (ring); 1252 [$Si(CH_3)_3$]; 1106 [$OSi(CH_3)_3$]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.13 s [18H, $OSi(CH_3)_3$], 0.43 s [18H, $Si(CH_3)_3$], 6.80 m (2H, CH). ^{13}C NMR spectrum (CD_3COCD_3), δ_C, ppm: –0.11 [$Si(CH_3)_3$], 2.00 [$OSi(CH_3)_3$], 83.58 (CH), 146.70 and 152.62 (triazole). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: –6.80 [$Si(CH_3)_3$], 18.12 [$OSi(CH_3)_3$].

This study was performed under financial support by the European Agency of Aerospace Research.

REFERENCES

1. Medvedeva, A.S., Demina, M.M., Borisova, A.I., Margorskaya, O.I., Kalikhman, I.D., and Vyazankin, N.S., *J. Organomet. Chem.*, 1982, vol. 231, p. 109.
2. Margorskaya, O.I., Medvedeva, A.S., Demina, M.M., Kalikhman, I.D., and Voronkov, M.G., *J. Organomet. Chem.*, 1989, vol. 376, p. 31.
3. Medvedeva, A.S., *Russ. J. Org. Chem.*, 1996, vol. 32, p. 272.
4. Browne, E.J., *Aust. J. Chem.*, 1971, vol. 24, p. 2389.
5. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 4. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1985, vol. 8, pp. 300, 429.
6. Medvedeva, A.S., *Doctoral (Chem.) Dissertation*, Irkutsk, 1988.
7. Birkofer, L. and Richtzenhain, K., *Chem. Ber.*, 1979, vol. 112, p. 2829.
8. Piterskaya, Yu.L., Khramchikhin, A.V., and Stadnichuk, M.D., *Russ. J. Gen. Chem.*, 1994, vol. 64, p. 1614.
9. Huttel, R., *Chem. Ber.*, 1941, vol. 74, p. 1680.
10. Piterskaya, Yu.L., Khramchikhin, A.V., Stadnichuk, M.D., Bel’skii, V.K., and Stash, A.I., *Russ. J. Gen. Chem.*, 1996, vol. 66, p. 1150.
11. Dabrowski, J., *Spectrochim. Acta*, 1963, vol. 19, p. 475.
12. *Organic Syntheses*, Noland, W.E., Ed., New York: Wiley, 1963, collect. vol. 4, p. 813. Translated under the title *Sintezy organicheskikh preparatov*, Moscow: Inostrannaya Literatura, 1958, vol. 8, p. 46.
13. Medvedeva, A.S., Novokshonov, V.V., Demina, M.M., and Voronkov, M.G., *J. Organomet. Chem.*, 1998, vol. 553, p. 481.
14. Demina, M., Velikanov, A., Medvedeva, A., Larina, L., and Voronkov, M., *J. Organomet. Chem.*, 1998, vol. 553, p. 129.
15. Borisova, A.I., Medvedeva, A.S., and Vyazankin, N.S., USSR Inventor's Certificate no. 715580, 1978; *Byull. Izobret.*, 1980, no. 9.
16. Sheldrick, G.M., *SHELXTL, V5, Software Reference Manual*, Madison: Siemens Industrial Automation, 1994.