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Dedicated to the Full Member of the Russian Academy of Sciences I.P. Beletskaya on occasion of her anniversary

Decisive Role of Water in Efficient Noncatalyzed Synthesis of Polyfunctional 1*H*-1,2,3-Triazoles Proceeding from γ-Hydroxypropynals

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Abstract—A highly efficient method was developed for the synthesis of new polyfunctional 1*H*-1,2,3-triazoles by the reaction of γ-hydroxypropynals with trimethylsilyl azide in water at room temperature without catalyst. The addition of trimethylsilyl azide to γ-hydroxypropynals occurs regioselectively: Previously unknown hydroxyalkyl-1*H*-1,2,3-triazolecarbaldehydes have been isolated in 69–96% yields with the prevalence of 1,5-isomers and the content of minor 1,4-isomers equal 9–21%. In the reaction of γ-hydroxypropynals with sodium azide in DMSO the formation of 4-hydroxyalkyl-1*H*-1,2,3-triazole-5-carbaldehydes is accompanied by the dimerization of initial aldehydes into the corresponding 1,3-dioxolanes.

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γ-Hydroxypropynals can be successfully used in the synthesis of heterocyclic compounds: aminodihydrofurans [1], hydroxydiazepines [2], polyfunctional acetylene 1,3-dioxolanes [3], 4-hydroxyalkynyl-substituted 3,4-dihydropyrimidin-2(1*H*)-ones as a result of the mlticomponent Biginelli reaction [4]. The synthesis of γ-hydroxypropynals can be easily performed by the oxidation of the corresponding diols with 2-iodoxybenzoic acid [5]. In continuation of this research we have investigated the synthesis of polyfunctional 1*H*-1,2,3-triazoles underlain by the application of acetylene γ-hydroxyaldehydes and trimethylsilyl azide.

Notwithstanding the absence of 1,2,3-triazoles in nature a wide range of compounds of this series possess a versatile biological activity[6], in particular, against the HIV virus [7], antiepileptic [8] or antimicrobial [9] action.

Diverse approaches to 1,2,3-triazole synthesis are known [10, 11], yet the reaction of ''click chemistry'' between azides and terminal alkynes catalyzed with Cu(I) is now the most practical and efficient procedure of preparation of 1,4-disubstituted 1,2,3-triazoles [12, 13]. The impossibility to use in this reaction of disubstituted alkynes and to synthesize N-unsubstituted triazoles are the limitations of this method.

The «click chemistry» reactions found extensive application in living system, but the toxicity of the catalyst (univalent copper) [14, 15] promotes the development of noncatalyzed methods of triazole synthesis under physiological conditions.

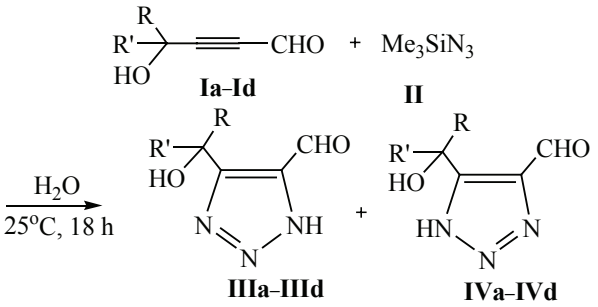
We recently showed the high efficiency of water application as reaction environment in the synthesis of element-containing 1,2,3-triazolecarbaldehydes by the regiospecific 1,3-dipolar cycloaddition of trimethylsilyl azide and benzyl azide to silicon- and germanium-acetylene aldehydes providing a possibility to obtain the corresponding 1,5-triazolecarbaldehydes in nearly

quantitative yield at room temperature within 18 h without catalyst [16]. We obtained previously 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde in classical conditions of Huisgen reaction [17]: by heating the dipolarophile and trimethylsilyl azide in toluene (90–95°C, 32 h) with subsequent hydrolysis with the yield of 75% [18]. The comparison of these processes shows essential advantages of the synthesis of organolelement 1,5-1*H*-1,2,3-triazolecarbaldehydes in water. The high efficiency of water was also observed at the 1,3-dipolar cycloaddition of phosphorylated azides to dimethyl acetylenedicarboxylate or sodium azide to tetramethylacetylenediphosphonate [19]. At the same time the noncatalyzed cycloaddition of aromatic azides to silylalkynes with unactivated triple bond or to esters of trimethylsilylpropiolic acid even at the microwave heating (85–110°C) proceeds rather slow, within 5–70 h, giving 1,5-disubstituted 4-(trimethylsilyl)-1*H*-1,2,3-triazoles [20].

We found in the modern chemical literature only few examples of the application of trimethylsilyl azide in water as a safe source of the hydrazoic acid, for instance, in the synthesis of azidodigermane from digermene [21], and also of 1,2-azidoalcohols at the enantioselective opening of epoxides in the presence of β-cyclodextrin [22]. 1,3-Dipolar cycloaddition of trimethylsilyl azide to triple bond in water was not described prior to our research.

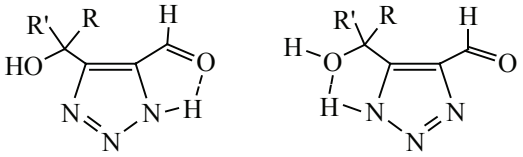
Aiming at the synthesis of previously unknown polyfunctional 4-hydroxyalkyl-1*H*-1,2,3-triazole-5-carbaldehydes we studied the reaction between γ-hydroxypropynals **Ia–Id** with trimethylsilyl azide (**II**) in water under the conditions optimal for the synthesis of 4-trialkylsilyl(germyl)-1*H*-1,2,3-triazole-5-carbaldehydes [16]. It was found that unlike the element-containing propynals the γ-hydroxypropynals added the trimethylsilyl azide under analogous conditions nonregiospecifically, but regioselectively: 4-hydroxyalkyl-1*H*-1,2,3-triazole-5-carbaldehydes **IIIa–IIId** formed in 69–96% yields, the content of minor isomers, 5-hydroxyalkyl-1*H*-1,2,3-triazole-4-carbaldehydes **IVa–IVd** was 9–21% (^{1}H NMR data) (Scheme 1).

Scheme 1.



R = Me, R' = Me (**a**), Et (**b**), Pr (**c**); R,R' = $(CH_2)_5C$ (**d**).

Although it is known that noncatalyzed addition of azides to a triple bond usually proceeds nonregioselectively [17], the formation of 1,4-isomers **IVa–IVd** may be favored by the presence of the intramolecular hydrogen bond HO···H–N. The existence of an intramolecular hydrogen bond CHO···H–N in 1,5-triazolecarbaldehydes of type III (in 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde) [18] was formerly proved by X-ray analysis. The possible formation of the intramolecular H-bond in compounds **IIIa–IIId** and **IVa–IVd** is shown below.



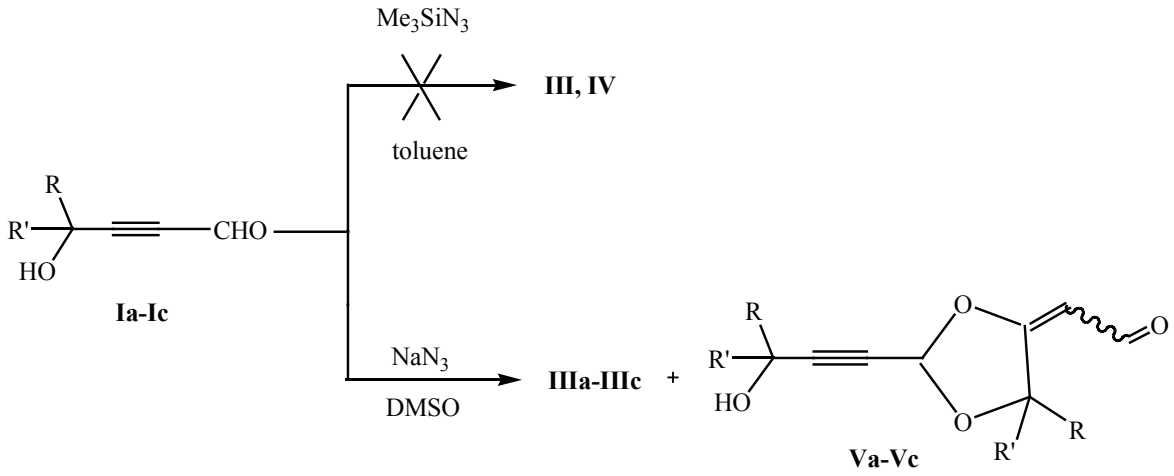
4(5)-Hydroxyalkyl-1*H*-1,2,3-triazole-5(4)-carbaldehydes **IIIa–IIIc** and **IVa–IVc** are light yellow viscous substances unlike 4(5)-(1-hydroxycyclohexyl)-1*H*-1,2,3-triazole-5(4)-carbaldehydes **IIId**, **IVd**. In the case of γ-hydroxypropynal **Id** an individual isomer, 4-(1-hydroxycyclohexyl)-1*H*-1,2,3-triazole-5-carbaldehyde (**IIId**), was isolated from the reaction mixture.

The composition and the structure of 4(5)-hydroxyalkyl-1*H*-1,2,3-triazole-5(4)-carbaldehydes **IIIa–IIId** and **IVa–IVd** were proved by the data of elemental analysis and IR, ^{1}H, ^{13}C NMR spectra.

IR spectrum of compound **IIId** is characterized by the presence of stretching vibrations bands: ν 3437 (OH), 3138 (NH), 1676 (C=O), 1639, 1561 [δ(NH)], 1447, 1325, 1224 (triazole ring) cm^{-1}. IR spectra of individual isomer **IIId** and of the mixture of isomers **IIId**, **IVd** do not significantly differ, the values of the characteristic frequencies differ only by several tenths or hundredths of cm^{-1}.

Our attempts to obtain 1,2,3-triazoles under the traditional conditions, namely, at boiling γ-hydroxypropynals with trimethylsilyl azide in toluene [18] or at the reaction of the substrates with sodium azide in DMSO by the method [23] were unsuccessful. In the first case the aldehydes were recovered intact from the reaction mixture that might be caused by sterical reasons; in the presence of sodium

Scheme 2.



R = Me; R' = Me (**Ia**, **IIIa**, **Va**), Et (**Ib**, **IIIb**, **Vb**), Pr (**Ic**, **IIIc**, **Vc**).

azide in DMSO along with the expected 4-hydroxyalkyl-1*H*-1,2,3-triazole-5-carbaldehydes **III** we isolated dimers of the initial aldehydes, {2-(3-hydroxy-3-alkyl-1-ynyl)-5,5-dialkyl[1,3]dioxolan-4-ylidene}acetaldehydes **V** (Scheme 2). The dimerization of γ-hydroxypropynals into the corresponding 1,3-dioxolanes under catalysis with bases we established before [3].

According to ^{1}H NMR data the ratio of triazoles **IIIa–IIIc** and dimers **Va–Vc** was 77 : 23, 63 : 37, 83 : 17 respectively.

Thus we have shown the decisive importance of water in the efficient synthesis of polyfunctional N-unsubstituted 4-(hydroxyalkyl)-1*H*-1,2,3-triazole-5-carbaldehydes **IIIa–IIId** containing three reaction sites (NH, CHO, OH) by the reaction of the corresponding propynals with trimethylsilyl azide in water at room temperature.

EXPERIMENTAL

IR spectra were registered on a spectrophotometer Bruker Vertex-70. ^{1}H and ^{13}C NMR spectra were taken on a spectrometer Bruker DPX-400 at 400.13 and 101.62 MHz respectively, from solutions in DMSO-d_6, internal reference hexamethyldisiloxane. Elemental analysis was carried out on an analyzer Thermo Finnigan FlashEA 1112. Melting points were measured on an instrument Micro-Hot-Stage PolyTherm A. The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluents chloroform–methanol, 10 : 1, or hexane–ether, 3 : 2. Initial γ-hydroxypropynals were obtained by procedure [5].

4(5)-(1-Hydroxyalkyl)-1*H*-1,2,3-triazole-5(4)-carbaldehydes IIIa–IIId, IVa–IVd. General procedure. A mixture of 1 mmol of γ-hydroxypropynal **Ia–Id**, 1.2 mmol of trimethylsilyl azide, and 2 ml of distilled water was stirred at room temperature for 18 h. The products were extracted into ethyl acetate (3 × 10 ml), the extract was dried with $MgSO_4$. The solvent was distilled off, the residue was analyzed by IR, ^{1}H, ^{13}C NMR spectroscopy and by elemental analysis.

Mixture of compounds **IIIa**, **IVa**, 88 : 12, was obtained from 0.11 g (1 mmol) of 4-hydroxy-4-methyl-2-pentynal (**Ia**) and 0.14 g (1.2 mmol) of trimethylsilyl azide (**II**) in 2 ml of distilled water. Yield 0.11 g (69%), viscous oily substance. IR spectrum ν, cm^{-1}: 3396 (OH), 3219 (NH), 1683 (C=O), 1645, 1557, 1343, 1237 (triazole).

4-(1-Hydroxy-1-methylethyl)-1*H*-1,2,3-triazole-5-carbaldehyde (IIIa). ^{1}H NMR spectrum, δ, ppm: 1.55 s [6H, $(CH_3)_2$], 5.62 br.s (1H, OH), 10.15 s (1H, CHO), 15.40 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 29.97 (CH_3), 69.04 (COH), 140.39 (C=), 159.03 (C=), 186.17 (C=O). Found, %: C 46.32; H 5.47; N 26.94. $C_6H_9N_3O_2$. Calculated, %: C 46.45; H 5.85; N 27.08.

5-(1-Hydroxy-1-methylethyl)-1*H*-1,2,3-triazole-4-carbaldehyde (IVa). ^{1}H NMR spectrum, δ, ppm: 1.37 s [6H, $(CH_3)_2$], 5.74 br.s (1H, OH), 10.25 s (1H, CHO), 15.40 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 30.55 (CH_3), 69.04 (COH), 143.26 (C=), 151.01 (C=), 186.47 (C=O).

Mixture of compounds **IIIb**, **IVb**, 91 : 9, was obtained from 0.13 g (1 mmol) of 4-hydroxy-4-methyl-2-hexynal (**Ib**) and 0.14 g (1.20 mmol) of trimethylsilyl azide (**II**) in 2 ml of distilled water. Yield 0.15 g (88%), viscous oily substance. IR spectrum, ν, cm^{-1}: 3361 (OH), 3174 (NH), 1686 (C=O), 1645, 1559, 1463, 1324, 1235 (triazole).

4-(1-Hydroxy-1-methylpropyl)-1*H*-1,2,3-triazole-5-carbaldehyde (IIIb). ^{1}H NMR spectrum, δ, ppm: 0.72 t (3H, $CH_2\underline{CH_3}$), 1.53 s (3H, CH_3), 1.72–1.89 m (2H, CH_2), 5.45 br.s (1H, OH), 10.13 s (1H, CHO), 15.39 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 8.30 ($CH_2\underline{C}H_3$), 27.81 (CH_3), 34.77 (CH_2), 71.67 (COH), 127.67 (C=), 143.40 (C=), 185.99 (C=O). Found, %: C 49.60; H 6.35; N 24.94. $C_7H_{11}N_3O_2$. Calculated, %: C 49.70; H 6.55; N 24.84.

5-(1-Hydroxy-1-methylpropyl)-1*H*-1,2,3-triazole-4-carbaldehyde (IVb). ^{1}H NMR spectrum, δ, ppm: 0.80 t (3H, $CH_2\underline{CH_3}$), 1.49 s (3H, CH_3), 1.72–1.89 m (2H, CH_2), 5.23 br.s (1H, OH), 10.25 s (1H, CHO), 15.39 br.s (1H, NH). ^{13}C, δ, ppm: 7.86 ($CH_2\underline{C}H_3$), 27.95 (CH_3), 35.74 (CH_2), 71.67 (COH), 186.49 (C=O) [the value of the chemical shift of (C=) were not determined because of the low content of the isomera in the mixture].

Mixture of compounds **IIIc**, **IVc**, 79 : 21, was obtained from 0.12 g (0.86 mmol) of 4-hydroxy-4-methyl-2-heptynal (**Ic**) and 0.12 g (1.04 mmol) of trimethylsilyl-azide (**II**) in 2 ml of distilled water. Yield 0.14 g (89%), viscous oily substance. IR spectrum, ν, cm^{-1}: 3357 (OH), 3178 (NH), 1688 (C=O), 1615, 1562, 1467, 1289, 1244 (triazole).

4-(1-Hydroxy-1-methylbutyl)-1*H*-1,2,3-triazole-5-carbaldehyde (IIIc). ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, $CH_2CH_2\underline{CH_3}$), 1.20–1.32 m (2H, $CH_2\underline{CH_2}CH_3$), 1.54 s (CH_3), 1.68–1.88 m (2H, $\underline{CH_2}CH_2CH_3$), 5.47 br.s (1H, OH), 10.13 s (1H, CHO), 15.38 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 14.54 ($CH_2CH_2\underline{C}H_3$), 17.07 ($CH_2\underline{CH_2}CH_3$), 28.69 (CH_3), 44.44 ($\underline{CH_2}CH_2CH_3$), 71.54 (COH), 140.80 (C=), 158.39 (C=), 186.10 (C=O). Found, %: C 52.32; H 7.25; N 22.75. $C_8H_{13}N_3O_2$. Calculated, %: C 52.45; H 7.15; N 22.94.

5-(1-Hydroxy-1-methylbutyl)-1*H*-1,2,3-triazole-4-carbaldehyde (IVc). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, $CH_2CH_2\underline{CH_3}$), 1.20–1.36 m (2H, $CH_2\underline{CH_2}CH_3$), 1.50 s (CH_3), 1.68–1.85 m (2H, $\underline{CH_2}CH_2CH_3$), 5.75 br.s (1H, OH), 10.25 s (1H, CHO), 15.38 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 14.38 ($CH_2CH_2\underline{C}H_3$), 16.73 ($CH_2\underline{CH_2}CH_3$), 28.29 (CH_3), 45.51 ($\underline{CH_2}CH_2CH_3$), 71.54 (COH), 143.73 (C=), 149.56 (C=), 186.61 (C=O).

Compounds **IIId, IVd** were obtained from 0.18 g (1.18 mmol) of 3-(1-hydroxycyclohexyl)-2-propynal (**Id**) and 0.15 g (1.3 mmol) of trimethylsilyl azide (**II**) in 2 ml of distilled water. The precipitate separated from the reaction mixture was filtered off and dried in a vacuum. According to ^{1}H NMR spectrum the precipitated product was individual isomer **IIId**. Yield 0.04 g (17%), colorless solid substance, mp 143–144°C. After workup of the filtrate we obtained 0.19 g (79%) of viscous product consisting of the mixture of isomers **IIId**, **IVd**, 86 : 14. Overall yield of triazoles **IIId**, **IVd** 96%. IR spectrum (mixture of isomers), ν, cm^{-1}: 3437 (OH), 3138 (NH), 1676 (C=O), 1639, 1561, 1447, 1325, 1224 (triazole).

4-(1-Hydroxycyclohexyl)-1*H*-1,2,3-triazole-5-carbaldehyde (IIId). ^{1}H NMR spectrum, δ, ppm: 1.52–1.98 m [10H, $(CH_2)_5$], 5.28 br.s (1H, OH), 10.16 s (1H, CHO), 15.40 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 21.26, 25.18, 36.42 ($C_{cyclohexyl}$), 69.91 (COH), 141.32 (C=), 155.71 (C=), 186.19 (C=O). Found, %: C 55.26; H 6.85; N 21.47. $C_9H_{13}N_3O_2$. Calculated, %: C 55.37; H 6.71; N 21.52.

5-(1-Hydroxycyclohexyl)-1*H*-1,2,3-triazole-4-carbaldehyde (IVd). ^{1}H NMR spectrum, δ, ppm: 1.52–1.98 m [10H, $(CH_2)_5$], 5.04 br.s (1H, OH), 10.24 s (1H, CHO), 15.38 br.s (1H, NH).

A solution of 0.55 g (5 mmol) of 4-hydroxy-4-methyl-2-pentynal (**Ia**) and 0.58 mg (5 mmol) of trimethylsilyl azide (**II**) in 10 ml of anhydrous toluene was heated at 90–95°C for 35 h under stirring. Toluene was removed at a reduced pressure, the residue (0.54 g), according to ^{1}H NMR data was initial aldehyde **Ia**, bp 56–58°C (2.5 mm Hg), n_D^{20} 1.4708 {bp 57–59°C (2.5 mm Hg), n_D^{20} 1.4688 [24]}.

A solution of 0.30 g (2.7 mmol) of 4-hydroxy-4-methyl-2-pentynal (**Ia**) in 2 ml of DMSO was added at vigorous stirring to a solution of 0.188 g (2.9 mmol) of sodium azide in 6 ml of DMSO. The reaction mixture was stirred at room temperature for 40 min, then it was poured at vigorous stirring into a two-phase liquid obtained from 16 ml of 15% water solution of KH_2PO_4 and 20 ml of ethyl ether. The water phase was extracted with ethyl acetate (3 × 5 ml), the combined organic solutions were washed with 5 ml of water and dried with $MgSO_4$. On removing the solvent we obtained 0.2 g (31%) of yellow semicrystalline residue consisting of a mixture of 1,5- and 1,4-isomers **IIIa, IVa** in the ratio 50:1 (ЯМР ^{1}H). Alongside triazoles **IIIa**, **IVa** we isolated 0.065 g (23%) of the dimer of initial aldehyde, *Z,E*-

{2-(3-hydroxy-3-methylbut-1-ynyl)-5,5-dimethyl[1,3] dioxolan-4-ylidene}-acetaldehyde (**Va**). IR spectrum, ν, cm^{-1}: 3400 (OH), 2240 (C≡C), 1660 (CH=O, C=CH). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *Z*-isomer: 1.43 s and 1.60 s [6H, $(CH_3)_2$], 1.57 s [6H, $(CH_3)_2COH$], 2.60 br.s (1H, OH), 5.10 d (1H, =CH, ^3J 8.0 Hz), 6.10 s (1H, H^2), 9.94 d (1H, CH=O); *E*-isomer: 1.38 s and 1.46 s [6H, $(CH_3)_2$], 1.66 s [6H, $(CH_3)_2COH$], 5.57 d (1H, =CH, ^3J 8.0 Hz), 6.08 s (1H, H^2), 9.74 d (1H, CH=O) [3]. Found, %: C 64.45; H 7.28. $C_{12}H_{16}O_4$. Calculated, %: C 64.27; H 7.19.

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