ISSN 1070-4280, Russian Journal of Organic Chemistry, 2017, Vol. 53, No. 1, pp. 1–5. © Pleiades Publishing, Ltd., 2017. Original Russian Text © A.A. Yarofeeva, O.A. Tsutsura, T.A. Frolenko, E.S. Semichenko, A.A. Kondrasenko, G.A. Suboch, 2017, published in Zhurnal Organicheskoi Khimii, 2017, Vol. 53, No. 1, pp. 9–13.

Reaction of Alkyl- and Arylamines with 2-(Hydroxyimino)-3-oxobutanal

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Received August 31, 2016

Abstract—The condensation of 2-(hydroxyimino)-3-oxobutanal with primary aliphatic amines, cyclohexanamine, and amines containing an adamantane fragment afforded 4-(alkylamino)- and 4-(cyclohexylamino)-3nitrosobut-3-en-2-ones. Analogous reaction with substituted anilines $RC_6H_4NH_2$ (R = H, 4-Me, 4-OMe, 4-NH₂, 4-Br, 4-I, 3-NO₂) led to the formation of 4-aryl-3-hydroxyiminobutan-2-ones.

DOI: 10.1134/S1070428017010018

The direction of reactions of 1,3-dicarbonyl compounds with amines is determined by enolization of one of the carbonyl groups. For example, unsymmetrical fluorinated 1,3-diketones react with alkylamines to give Schiff bases through that carbonyl group which is not linked to fluorinated substituent and is not enolized [1]. Reactions of fluorinated 1,3-diketones with aromatic amines lead to the formation of mixtures of isomeric Schiff bases, in which the fraction of the condensation product through the carbonyl group at the fluorinated substituent is considerably lower [2].

It may be presumed that 3-oxobutanal which is enolized almost completely should react with amines in a way similar to activated β -diketones to form Schiff bases through the ketone carbonyl. However, 3-oxobutanal readily undergoes trimerization; therefore, the corresponding Schiff bases, 4-(alkyl- and dialkylamino)but-3-en-2-ones are synthesized by reaction of amines with 3-oxobutanal dimethyl acetal [3]. If a hydroxyimino group is present in the 2-position of 3-oxobutanal, the reaction with R-benzylamines involves the aldehyde group, and the products are 4-(R-benzylamino)-3-nitrosobut-3-en-2-ones [4].

In this work we studied the reaction of 2-(hydroxyimino)-3-oxobutanal with aliphatic and aromatic amines. An aqueous solution of 2-(hydroxyimino)-3oxobutanal (A) was obtained by nitrosation of 3-oxobutanal which was prepared *in situ* by acid hydrolysis of 4,4-dimethoxybutan-2-one [4, 5]. Amine 1a-1c or





 $R = Bu(a), t-Bu(b), Cy(c), 1-AdCH_2(d), 1-AdCH(Me)(e); Ar = 4-BrC_6H_4(f), 4-IC_6H_4(g), 3-O_2NC_6H_4(h).$

a solution of amine 1d-1g in ethanol was added with stirring to an aqueous solution of A at 0-5°C (Scheme 1). In the reaction with 3-nitroaniline (1h), aldehyde A was preliminarily extracted with diethyl ether, and a solution of amine 1h in diethyl ether was added to the extract. The precipitate of 4-(alkylamino)-3-nitrosobut-3-en-2-one 2a or 2c-2e or 4-(arylimino)-3-(hydroxyimino)butan-2-one 2f-2g was filtered off. Compound 2b was isolated from the reaction mixture by extraction with methylene chloride.

The condensation of substituted anilines **1i–11** with 2-(hydroxyimino)-3-oxobutanal (**A**) was carried out in the presence of acetic acid (Scheme 2); we thus synthesized 4-(arylimino)-3-(hydroxyimino)butan-2-ones **2i–21**. By reaction of 2-(hydroxyimino)-3-oxobutanal (**A**) with 2-aminoethane-1-thiol we obtained 1-(hydroxyimino)-1-(thiazolidin-2-yl)propan-2-one (**3**) (Scheme 2).



The structure of compounds 2a-2l and 3 was confirmed by elemental analyses and UV (2a-2e, 2i-2k) and ¹H and ¹³C NMR spectra. Signals in the NMR spectra of 2a-2l and 3 were assigned using two-dimensional homo- (COSY) and heteronuclear (HSQC, HMBC) shift correlation techniques.

Compounds 2a-2e in chloroform exist as nitroso isomers, as follows from the presence in their electronic spectra of NO absorption band at λ 578–592 nm $(n-\pi^*$ transition). This conclusion is consistent with the spectral parameters of the Schiff base synthesized from 2-(hydroxyimino)-3-oxobutanal and benzylamine according to the procedure described in [4].

The ¹H NMR spectra of **2a–2e** in CDCl₃ characteristically displayed a signal at δ 16.6–16.8 ppm, which was assigned to NH proton of the secondary amino group involved in intramolecular hydrogen bond. In the ¹³C and ¹H NMR spectra of **2a–2e** (CDCl₃), the position of signals of the enamine carbon atom and proton attached thereto depended on the substituent on the nitrogen atom. The signals shifted upfield in going from compound **2a** (R = Bu; δ_C 150.2, δ 8.03 ppm) to **2d** [R = Ad-1-CH(Me); δ_C 148.0, δ 7.92 ppm] and **2b** (R = *t*-Bu; δ_C 144.0, δ 7.91 ppm) possessing bulky substituents on the nitrogen.

The hydroxyimino proton of 2f-2l resonated in the ¹H NMR spectra at δ 18.00–17.35 ppm, indicating formation of intramolecular hydrogen bond with that proton. The ¹³C and ¹H signals of the N=CH group of compounds 2f-2h containing an electron-withdrawing substituent in the *para* position of the benzene ring were located in a stronger field than the corresponding signals of 2g-2l.

EXPERIMENTAL

The electronic absorption spectra were measured on a Helios Omega spectrophotometer from solutions in CHCl₃ with concentrations of 5×10^{-5} (λ 200–500 nm) and 5×10^{-3} M (λ 500–800 nm); cell path length 1 cm. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 600 spectrometer at the Krasnoyarsk Joint Regional Center (Siberian Branch, Russian Academy of Sciences). The progress of reactions was monitored by TLC on Sorbfil PTSKh-AF-V plates (Krasnodar, Russia) with fluorescent indicator using hexane–ethyl acetate (4:1) as eluent. Neutral silica gel L 100/400 (Chemapol) was used for column chromatography.

4-(Butylamino)-3-nitrosobut-3-en-2-one (1a). A mixture of 1.32 g (10 mmol) of 4.4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping for 30 min under reduced pressure (water-jet pump), 0.657 g (9 mmol) of butylamine was added dropwise at 0°C, and the mixture was stirred for 30 min. The light violet crystals were filtered off. Yield 1.18 g (77%), mp 80-82°C. Electronic absorption spectrum, λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹): 259 (8620), 338 (6000), 588 (47). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.95 t (3H, CH₃, J = 7.34 Hz), 1.39 m (2H, CH₂, J = 7.34 Hz), 1.67 g (CH₂, J = 7.52 Hz), 2.61 s (3H, CH₃C=O), 3.52 m (2H, NCH₂, J = 5.87 Hz), 8.03 br.s (1H, =CHN), 16.65 br.s (NH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 13.6 (CH₃), 19.9 (CH₂), 25.1 (CH₃C=O), 31.7 (CH₂), 55.3 (NCH₂), 150.2 (NCH), 151.1 (CNO), 197.1 (C=O). Found, %: C 56.36; H 8.22; N 16.53. C₈H₁₄N₂O₂. Calculated, %: C 56.45; H 8.29; N 16.46.

4-(tert-Butylamino)-3-nitrosobut-3-en-2-one (2b). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min, 0.657 g (9 mmol) of tert-butylamine was added dropwise at 0°C, and the mixture was stirred for 30 min and extracted with 20 mL of methylene chloride. The extract was dried over sodium sulfate and evaporated under reduced pressure with addition of 1 mL of hexane. The oily residue was treated with 2 mL of pentane and kept for 3 days at -18°C, and the dark violet crystals were filtered off. Yield 0.17 g (11%), mp 51°C. Electronic absorption spectrum, λ_{max} , nm (ϵ , \hat{L} mol⁻¹ cm⁻¹): 258 (8120), 336 (5600), 578 (52). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.39 s (9H, *t*-Bu), 2.64 s (3H, CH₃C=O), 7.91 br.s (1H, =CHN), 16.77 br.s (NH). 13 C NMR spectrum (CDCl₃), δ_{C} , ppm: 25.2 (CH₃C=O), 29.0 (CH₃), 144.0 (=CHN), 152.1 (CNO), 197.5 (C=O). Found, %: C 56.37; H 8.12; N 16.52. C₈H₁₄N₂O₂. Calculated, %: C 56.45; H 8.29; N 16.46.

4-(Cyclohexylamino)-3-nitrosobut-3-en-2-one (2c). A mixture of 1.32 g (10 mmol) of 4.4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min, 0.891 g (9 mmol) of cyclohexylamine was added dropwise at 0°C, and the mixture was stirred for 30 min. The precipitate was filtered off. Yield 1.01 g (57%), blue crystals, mp 90°C. Electronic absorption spectrum, λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹): 259 (9060), 338 (5700), 592 (42). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.20–2.00 m (CH₂, C₆H₁₁), 2.64 s (3H, CH₃C=O), 3.31 m (1H, CH, C_6H_{11}), 8.02 d (1H, =CHN, J= 4.80 Hz), 16.61 br.s (1H, NH). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 23.9 (CH₂), 24.8 (CH₂), 25.5 (CH₃C=O), 33.2 (CH₂), 63.1 (NCH), 147.2 (=CHN), 151.4 (CNO), 197.1 (C=O). Found, %: C 61.20; H 8.22; N 14.27. C₁₀H₁₆N₂O₂. Calculated, %: C 61.29; H 7.97; N 14.23.

4-[(Adamantan-1-yl)methylamino]-3-nitrosobut-3-en-2-one (2d). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of

1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min, and a solution of 1.485 g (9 mmol) of (adamantan-1-yl)methanamine in 8 mL of ethanol was added dropwise at 0°C. The mixture was stirred for 30 min, and the precipitate was filtered off. Yield 0.56 g (24%), blue powder, mp 96°C. Electronic absorption spectrum, $\hat{\lambda}_{max}$, nm (ϵ , L mol⁻¹ cm⁻¹): 259 (9200), 339 (6360), 587 (46). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.51 m (6H, CH₂₋, Ad), 1.63-1.74 m (6H, CH₂, Ad), 2.03 m (3H, CH, Ad), 2.66 s (3H, CH₃C=O), 3.16 s (2H, NCH₂), 7.90 d (1H, NCH, J = 7.04 Hz), 16.59 br.s (1H, NH). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 25.2 (CH₃C=O), 28.0 (CH, Ad), 33.9 (Ad), 36.6 (CH₂, Ad), 40.2 (CH₂, Ad), 67.7 (NCH₂), 149.9 (NCH), 151.6 (CNO), 197.1 (C=O). Found, %: C 68.59; H 8.34; N 10.57. C₁₅H₂₂N₂O₂. Calculated, %: C 68.67; H 8.45; N 10.68.

4-[1-(Adamantan-1-yl)ethylamino]-3-nitrosobut-**3-en-2-one (2e).** A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min, and a solution of 1.611 g (9 mmol) of 1-(adamantan-1-yl)ethanamine in 8 mL of ethanol was added dropwise at 0°C. The mixture was stirred for 30 min, and the light violet powder was filtered off. Yield 1.15 g (46%), mp 114°C. Electronic absorption spectrum, λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹): 259 (9120), 338 (6380), 586 (51). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.22 d [3H, CH₃CH(Ad), J = 6.79 Hz], 1.48 m (6H, CH₂), 1.61–1.72 m (6H, CH₂), 2.02 m (3H), 2.64 s (3H, CH₃C=O), 2.94 m (1H, CH), 7.92 d (1H, =CHN, J = 7.20 Hz), 16.62 br.s (1H, NH). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 14.8 (CH₃CH), 25.1 (CH₃C=O), 28.0 (CH^{γ}, Ad), 35.4 (C^{α}, Ad), 36.6 (CH₂, Ad), 38.4 (CH₂, Ad), 71.1 (NCH), 148.0 (=CHN), 151.3 (=CHO), 197.1 (C=O). Found, %: C 69.58; H 8.60; N 10.12. C₁₆H₂₄N₂O₂. Calculated, %: C 69.53; H 8.75; N 10.14.

4-(4-Bromophenylimino)-3-(hydroxyimino)butan-2-one (2f). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min, and a solution of 1.548 g (9 mmol) of 4-bromoaniline in 8 mL of ethanol was added dropwise at 0°C. The mixture was stirred for 30 min, and the precipitate was filtered off and dried in air. Yield 1.712 g (71%), dark green crystals, mp 123–125°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.55 s (3H, CH₃C=O), 7.23 m (2H, *o*-H, *J* = 8.8 Hz), 7.60 m (2H, m-H, J = 8.62 Hz), 8.71 s (1H, =CHN), 17.33 br.s (NH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 24.9 (CH₃C=O), 123.2 (C^o), 123.5 (C^p), 133.0 (C^m), 144.4 (C^{*i*}), 148.0 (C=NOH), 151.1 (CH=N), 196.3 (C=O). Found, %: C 44.59; H 3.29; Br 29.61; N 10.23. C₁₀H₉BrN₂O₂. Calculated, %: C 44.63; H 3.37; Br 29.69; N 10.41.

3-(Hydroxyimino)-4-(4-iodophenylimino)butan-**2-one (2g).** A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min, and a solution of 1.971 g (9 mmol) of 4-iodoaniline in 8 mL of ethanol was added dropwise at 0°C. Yield 1.514 g (53%), light green crystals, mp 134–136°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.55 s (3H, CH₃C=O), 7.06 m (2H, *o*-H, *J* = 8.25 Hz), 7.74 m (2H, m-H, J = 8.07 Hz), 8.72 s (1H, =CHN), 17.27 br.s (NH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 24.6 (CH₃C=O), 94.7 (C^{*p*}), 123.2 (C^{*o*}), 138.9 (C^{*m*}), 144.9 (Cⁱ), 147.9 (C=NOH), 151.0 (CH=N), 196.2 (C=O). Found, %: C 38.07; H 2.82; I 40.08; N 8.79. C₁₀H₉IN₂O₂. Calculated, %: C 38.00; H 2.87; I 40.15; N 8.86.

3-(Hydroxyimino)-4-(3-nitrophenylimino)butan-2-one (2h). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, and the mixture was freed from nitrogen oxides by keeping under reduced pressure (waterjet pump) for 30 min and extracted with 25 mL of diethyl ether. A solution of 1.242 g (9 mmol) of 3-nitroaniline in 26 mL of diethyl ether was added dropwise to the extract under vigorous stirring, and the mixture was stirred for 1 h. The mixture was evaporated, and the solid residue was recrystallized from chloroform. Yield 0.241 g (11%), dark green crystals, mp 182–183°C (from CHCl₃). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.58 s (3H, CH₃C=O), 7.67 m (1H, 6'-H, *J* = 7.89 Hz), 7.70 m (1H, 5'-H, *J* = 7.89 Hz), 8.22 s (1H, 2'-H), 8.28 m (1H, 4'-H, *J* = 7.52 Hz), 8.82 s (1H, =CHN), 16.88 br.s (NH). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 24.9 (CH₃C=O), 116.5 (C^{2'}), 123.5 (C^{4'}), 127.5 (C^{5'}), 130.6 (C^{6'}), 147.1 (C^{1'}), 147.7 (C=NOH), 148.9 (C^{3'}), 153.8 (CH=N), 196.0 (C=O). Found, %: C 50.80, 50.64; H 3.80, 3.77; N 17.71. C₁₀H₉N₃O₄. Calculated, %: C 51.07; H 3.86; N 17.87.

3-(Hydroxyimino)-4-(phenylimino)butan-2-one (2i). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min and cooled to 0°C, and a solution of 0.837 g (9 mmol) of aniline in 0.54 g (9 mmol) of acetic acid and 6 mL of water was added dropwise with stirring. The precipitate was filtered off. Yield 0.826 g (48%), light green crystals, mp 88-90°C. Electronic absorption spectrum, λ_{max} , nm ($\hat{\epsilon}$, L mol⁻¹ cm⁻¹): 244 (9040), 305 (6620). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.57 s (3H, CH₃C=O), 7.36 m (2H, *o*-H, *J* = 7.70 Hz), 7.41 m (1H, p-H, J = 6.42 Hz), 7.48 m (2H, m-H, J = 8.07 Hz), 8.72 s (1H, HC=N), 17.63 br.s (NH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 24.7 (CH₃C=O), 121.4 (C^o), 129.3 (C^{p}), 129.6 (C^{m}), 145.0 (C^{i}), 148.3 (C=NOH), 150.1 (CH=N), 196.5 (C=O). Found, %: C 63.21; H 5.22; N 14.67. C₁₀H₁₀N₂O₂. Calculated, %: C 63.15; H 5.30; N 14.73.

3-(Hydroxyimino)-4-(4-methylphenylimino)butan-2-one (2j). A mixture of 1.32 g (10 mmol) of 4.4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min and cooled to 0°C, and a solution of 0.963 g (9 mmol) of p-toluidine in 5 mL of water and 0.81 g (13.5 mmol) of acetic acid was added with stirring. The mixture was stirred for 30 min, a solution of 0.477 g (4.5 mmol) of sodium carbonate in 5 mL of water was added, and the precipitate was filtered off. Yield 1.195 g (65%), light green crystals, mp 106°C. Electronic absorption spectrum, λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹): 245 (9900), 327 (7340), 600 (9). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.40 s (3H,

CH₃C₆H₄), 2.56 s (3H, CH₃C=O), 7.27 m (4H, H_{arom}), 8.65 s (1H, HC=N), 17.75 br.s (NH). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 21.2 (CH₃C₆H₄), 24.7 (CH₃C=O), 121.3 (C^o), 130.3 (C^m), 139.8 (C^p), 142.1 (Cⁱ), 148.4 (C=NOH), 148.7 (CH=N), 196.6 (C=O). Found, %: C 64.58; H 5.81; N 13.55. C₁₁H₁₂N₂O₂. Calculated, %: C 64.69; H 5.92; N 13.72.

3-(Hydroxyimino)-4-(4-methoxyphenylimino)butan-2-one (2k). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min and cooled to 0°C, and a solution of 1.107 g (9 mmol) of *p*-anisidine in 0.54 g (9 mmol) of acetic acid and 3.6 mL of water was added under vigorous stirring. The precipitate was filtered off. Yield 1.656 g (84%), dark yellow crystals, mp 84–85°C. Electronic absorption spectrum, λ_{max} , nm (ϵ , L× mol⁻¹ cm⁻¹): 243 (2940), 352 (3560). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.55 s (3H, CH₃C=O), 3.84 s $(3H, OCH_3), 6.97 (2H, m-H, J = 9.0 Hz), 7.36 m (2H, M)$ *o*-H, *J* = 9.0 Hz), 8.68 s (1H, CH=N), 17.81 br.s (NH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 24.7 (CH₃C=O), 55.5 (OCH₃), 115.0 (C^m), 123.3 (C^o), 137.7 (Cⁱ), 147.5 (CH=N), 148.5 (C=NOH), 160.9 (C^p), 196.7 (C=O). Found, %: C 55.91; H 5.42; N 12.63. C₁₁H₁₂N₂O₃. Calculated, %: C 59.99; H 5.49; N 12.72.

4-(4-Aminophenylimino)-3-(hydroxyimino)butan-2-one (21). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min and cooled to 0°C, and a solution of 0.972 g (9 mmol) of benzene-1,4-diamine in 8 mL of water and 0.59 g (9 mmol) of acetic acid was added with vigorous stirring. The mixture was stirred for 30 min, and the precipitate was filtered off. Yield 1.22 g (66%). The product was additionally purified by chromatography in a 50×2 -cm column charged with 50 g of silica gel (eluent hexane-ethyl acetate, 5:2). Light brown powder, mp 149–151°C (decomp.). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.55 s (3H,

CH₃C=O), 4.02 br.s (2H, NH₂), 6.71 m (2H, *m*-H, *J* = 7.50 Hz), 7.26 (*o*-H, *J* = 8.07 Hz), 8.65 s (1H, =CHN), 18.00 br.s (NH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 24.9 (CH₃C=O), 115.4 (C^o), 123.5 (C^m), 135.2 (Cⁱ), 145.0 (CH=N), 148.4 (C=NON), 148.7 (C^p), 197.0 (C=O). Found, %: C 58.56; H 5.36; N 20.41. C₁₀H₁₁N₃O₂. Calculated, %: C 58.53; H 5.40; N 20.48.

1-(Hydroxyimino)-1-(thiazolidin-2-yl)propan-2-one (3). A mixture of 1.32 g (10 mmol) of 4,4-dimethoxybutan-2-one and 10 mL (10 mmol) of 1 N aqueous HCl was stirred for 30 min at 20°C. The mixture was cooled to 0°C, a solution of 0.76 g (11 mmol) of sodium nitrite in 4 mL of water was added dropwise, the mixture was freed from nitrogen oxides by keeping under reduced pressure (water-jet pump) for 30 min and cooled to 0°C, and a solution of 0.693 g (9 mmol) of 2-aminoethane-1-thiol was added dropwise with stirring. The precipitate was filtered off. Yield 0.305 g (35%), light yellow powder, mp 109°C (from CH₂Cl₂). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.35 s (3H, $CH_3C=O$), 2.97 d.d.d (1H, CH_2N , J = 12.1, 9.6, 6.2 Hz), 3.05 d.d.d (1H, CH_2S , J = 9.61, 5.72, 6.0 Hz), 3.14 d.d.d (1H, CH_2S , J = 9.8, 6.0, 2.0 Hz), 3.71 d.d.d (1H, CH₂N, J = 12.1, 6.0, 2.3 Hz), 4.28 br.s (1H, NH), 5.75 s (1H, NCHS), 12.88 br.s (NOH). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 26.3 (CH₃C=O), 35.0 (CH₂S), 52.4 (CH₂N), 60.5 (SCHNH), 152.5 (C=NOH), 198.3 (C=O). Found, %: C 41.34; H 5.80; N 16.01. C₆H₁₀N₂O₂S. Calculated, %: C 41.36; H 5.79; N 16.08.

This study was performed under financial support by the Ministry of Education and Science of the Russian Federation in the framework of the base part of state assignment.

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