ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 10, pp. 1421–1425. © Pleiades Publishing, Inc., 2006.
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Synthesis of 2-Ethoxyprop-2-enal Dimethylhydrazone and Its Diels–Alder Reactions

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Received June 30, 2005

Abstract—Conditions were found for the preparation of 2-ethoxyprop-2-enal dimethylhydrazone by reaction of 2-ethoxypropenal with *N*,*N*-dimethylhydrazine. 2-Ethoxyprop-2-enal dimethylhydrazone reacted with methyl vinyl ketone and methyl acrylate according to the [4+2]-cycloaddition pattern with regioselective formation of substituted tetrahydropyridines. The major product in the reaction of 2-ethoxyprop-2-enal dimethylhydrazone with 1,4-benzoquinone was 5-hydroxy-1-benzofuran-2-carbaldehyde dimethylhydrazone formed as a result of [3+2]-cycloaddition; a small amount of the corresponding [4+2]-cycloaddition product was also obtained. Some spontaneous transformations of the primary cycloaddition products were revealed.

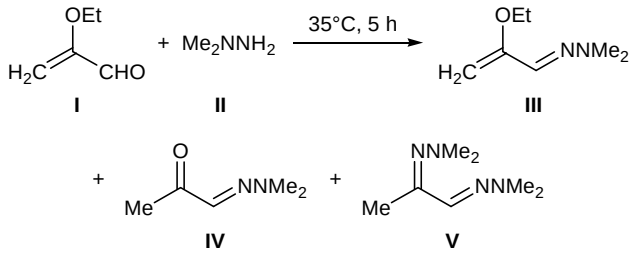
DOI: 10.1134/S1070428006100010

Interest in dimethylhydrazones derived from unsaturated aldehydes originates primarily from their high reactivity in Diels–Alder reactions which could lead to the formation of various heterocyclic compounds [1–3]. α,β-Unsaturated dimethylhydrazones having electron-donor groups ($OSiR_3$, NMe_2, OEt) in the α-position turned out to be even more reactive than their unsubstituted or alkyl-substituted analogs [1–6]. In particular, 2-alkoxybut-2-enal dimethylhydrazones were reported to react with various dienophiles according to the [4+2]-cycloaddition pattern, and the cycloaddition products showed antitumor activity and were used as starting compounds in the synthesis of aromatic alkaloids [2, 7–9]. The initial hydrazones were obtained by conjugate addition of bromine and ethanol [10] or methanol [7] to but-2-enal dimethylhydrazone, followed by dehydrobromination; the yields were 96 and 34%, respectively. However, 2-ethoxypropenal dimethylhydrazone was not reported so far [11].

While continuing our studies on the chemistry of α-functionalized alk-2-enals [12], in the present work we made an attempt to synthesize 2-ethoxyprop-2-enal dimethylhydrazone by direct reaction of the aldehyde with *N*,*N*-dimethylhydrazine, as well as to estimate the reactivity of the product in Diels–Alder reactions with electron-deficient dienophiles and regioselectivity of these reactions.

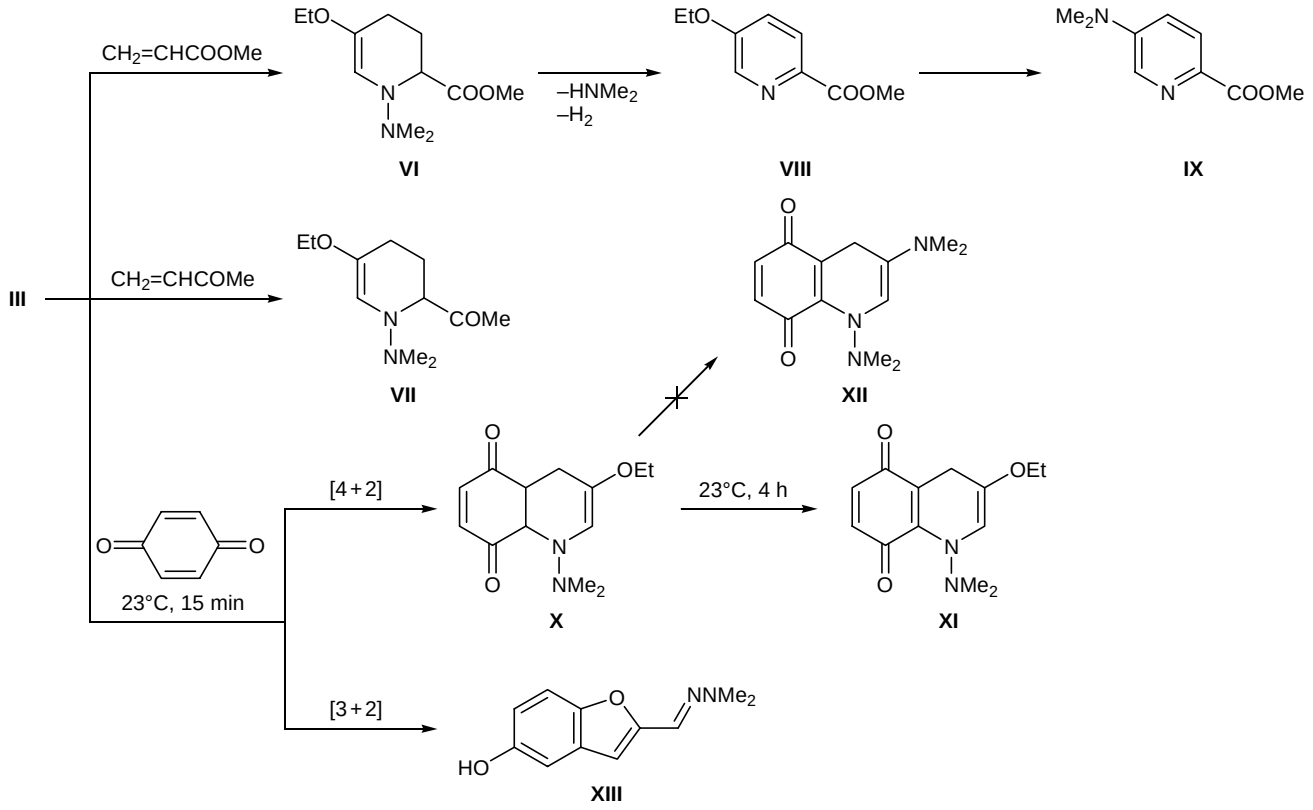
The reaction of 2-ethoxyprop-2-enal (**I**) with *N*,*N*-dimethylhydrazine (**II**) in diethyl ether on heating was complete in 5 h. Apart from the target 2-ethoxyprop-2-enal dimethylhydrazone (**III**), the mixture contained an approximately equal amount of 2-oxopropanal dimethylhydrazone (**IV**) (Scheme 1) which was identified by ^{1}H NMR spectroscopy (by comparing with the spectrum of an authentic sample [11, 13]).

Scheme 1.



In addition, 5–8% of 2-oxopropanal bis(dimethylhydrazone) (**V**) was present in the reaction mixture; compound **V** was identified on the basis of the ^{1}H NMR and GC–MS data (an authentic sample of **V** was obtained from 2-oxopropanal and 2 equiv of dimethylhydrazine). To avoid side formation of compounds **IV** and **V**, the reaction was carried out in the presence of an equimolar amount of potassium carbonate; as

Scheme 2.



a result, we succeeded in raising the yield of hydrazone **III** to 80%.

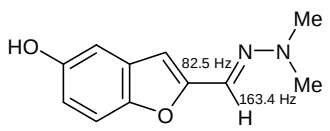
The Diels–Alder reactions of 2-methylpropenal dimethylhydrazone with methyl vinyl ketone and methyl acrylate usually require fairly severe conditions (benzene, sealed ampule, 100°C, 211–264 h [1, 14] or 120°C, 6–8 h [4]), and the yields range from 50 to 80%. Due to the presence of an electron-donor ethoxy group [2, 15], 2-ethoxyprop-2-enal dimethylhydrazone (**III**) reacted with methyl vinyl ketone and methyl acrylate much more readily (100–115°C, 5–6 h); the reactions followed the [2+4]-cycloaddition pattern and led to the formation of substituted tetrahydropyridines **VI** and **VII**, respectively, with high regioselectivity (yield up to 80%, according to the ^{1}H NMR data; Scheme 2).

Tetrahydpropyridine **VI** was found to readily lose dimethylamine molecule and undergo dehydrogenation by the action of atmospheric oxygen on storage or (partially) on heating (e.g., during chromatography or distillation) to give methyl 5-ethoxypyridine-2-carboxylate (**VIII**) (^{1}H NMR and GC–MS data). Analogous processes (i.e., elimination of dimethylamine and aromatization) were observed for other dimethylamino-substituted tetrahydropyridines during their synthesis [2, 9] and chromatographic purification on silica gel [4, 6, 16] or Al_2O_3 [14]. 5-Ethoxypyridine **VIII** is an intermediate product. Upon attempted distillation it was converted into methyl 5-dimethylaminopyridine-2-carboxylate (**IX**) via nucleophilic replacement of the ethoxy group by dimethylamino group. The ratio of substituted pyridines **IX** and **VIII** in different fractions of the distillate and in the still residue varied from 1.4:1 to 4:1. The ^{1}H NMR spectrum of 5-dimethylaminopyridine **IX** was similar to the spectrum of a sample prepared previously from 2-dimethylaminoprop-2-enal dimethylhydrazone [4] (with account taken of different performances of the NMR instruments). When the Diels–Alder reaction of hydrazone **III** with methyl vinyl ketone was performed under microwave irradiation [17], the reaction time shortened to 36 min, and the yield of tetrahydropyridine **VII** attained 97% (^{1}H NMR data).

The cycloaddition of α,β-unsaturated dimethylhydrazones to quinones is known [2, 3] to occur much more readily; sometimes, two regioisomeric Diels–Alder adducts are formed [7]. Thus the reaction of aza diene **III** with benzoquinone was accompanied by appreciable heat evolution, and the primary product (after 15 min, according to the ^{1}H NMR data in $CDCl_3$) was

1-dimethylamino-3-ethoxy-1,4,4a,5,8,8a-hexahydroquinoline-5,8-dione (**X**). It was identified by the ^{1}H NMR spectrum and GC–MS data. Like its 3-methyl-substituted analog [4], compound **X** is unstable on storage and is converted into 1-dimethylamino-3-ethoxy-1,4,5,8-tetrahydroquinoline-5,8-dione (**XI**) in 4 h (^{1}H NMR, $CDCl_3$). Compound **XI** is also unstable, and both **X** and **XI** underwent fast tarring on attempted distillation. One more product quickly deposited as dark violet crystals on the walls of the reaction flask. This product is poorly soluble in $CDCl_3$; presumably this is the reason why it was not detected within the first 15 min of the process, when the conversion of the initial reactants was already complete. The formation of a black crystalline product was observed in the Diels–Alder reaction of benzoquinone with methacrolein dimethylhydrazone [4] (its structure was not analyzed).

The elemental composition and molecular weight (*m*/*z* 204, $[M]^+$) indicated that the isolated compound could be formed via elimination of dimethylamine molecule from compound **X** and subsequent nucleophilic replacent of the ethoxy group by Me_2N, by analogy with published data [6]. In this case, it would have structure **XII**. However, using modern NMR techniques we showed that the product has alternative structure **XIII**. Compound **XIII** could be formed via [3+2]-cycloaddition of 2-ethoxyprop-2-enal dimethylhydrazone (**III**) to benzoquinone. According to the ^{15}N NMR data, one nitrogen atom in molecule **XIII** belongs to a dimethylamino group (δ_N –265.1 ppm), and the other is an imino nitrogen atom (δ_N –17.4 ppm) [18]. The two dimensional (2D) ^{1}H–^{15}N HMBC spectra showed that both nitrogen atoms give cross peaks with methyl protons (δ 2.98 ppm) and CH=N proton (δ 7.17 ppm). These data are consistent with structure **XIII**, and they rule out alternative isomer **XII**. Structure **XIII** is also confirmed by the 2D CH-CORR NMR spectrum. In keeping with the INADEQUATE (^{13}C–^{13}C couplings) and proton-coupled ^{13}C NMR spectra, compound **XIII** is *E* isomer [19].



E-**XIII**

The 2D NOESY spectrum (^{1}H–^{1}H) revealed interaction between the CH=N proton and protons in the *N*-methyl groups, which is also consistent with *E* configuration of molecule **XIII**. The signals from protons on C^4, C^6, and C^7 were assigned on the basis of the two-dimensional ^{1}H–^{13}C HMBC spectra. As noted previously [8, 20], the reactions of 2-ethoxybut-2-enal dimethylhydrazone with quinoline-5,8-diones and 1,4-naphthoquinones can follow both [3+2]- and [4+2]-cycloaddition patterns.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer at 400 and 100.61 MHz, respectively; $CDCl_3$ and $(CD_3)_2CO$ were used as solvents, and HMDS, as internal reference. Gas chromatographic–mass spectrometric analysis was performed on an Hewlett–Packard HP-5890 chromatograph (Ultra-2 column, 5% of phenylmethylsilicone, injector temperature 250°C, oven temperature programming from 70 to 280°C at a rate of 20 deg × min^{-1}) coupled with an HP 5971A mass-selective detector (electron impact, 70 eV). Microwave-assisted reactions were performed in an LG MS-1904H microwave furnace (700 W).

2-Ethoxyprop-2-enal dimethylhydrazone (III). A mixture of 100 ml of anhydrous diethyl ether, 7.27 g (0.121 mol) of *N*,*N*-dimethylhydrazine (**II**), 12.71 g (0.121 mol) of 2-ethoxyprop-2-enal (**I**), and 10.87 g (0.079 mol) of potassium carbonate was heated for 5 h at the boiling point under stirring. The mixture was cooled and filtered from K_2CO_3, the solvent was removed from the filtrate under reduced pressure, and the residue was distilled under reduced pressure to isolate 12.44 g (68.9%) of hydrazone **III** with bp 92°C (12 mm), n_D^{26} = 1.5030. IR spectrum, ν, cm^{-1}: 1645 (C=N), 1520 (C=C), 1250 (COC). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, $CH_2C\mathbf{H}_3$), 2.89 s (6H, NMe_2), 3.87 q (2H, OCH_2, ^3J = 7 Hz), 4.19 d (1H, $=CH_2$, ^2J = 2.1 Hz), 4.26 d (1H, $=CH_2$, ^2J = 2.1 Hz), 6.67 s (1H, CH=N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.38 ($CH_2\mathbf{C}H_3$), 42.61 (NMe_2), 63.17 (OCH_2), 85.63 ($H_2C=$), 129.35 (CH=N), 157.86 (OC=). Mass spectrum, *m*/*z* (I_{rel}, %): 142 (31.2) $[M]^+$, 127 (5.4) $[M - Me]^+$, 113 (31.1) $[M - Et]^+$, 99 (4.1), 98 (4.1) $[M - NMe_2]^+$, 83 (5.0), 71 (10.1) $[CH=NNMe_2]^+$, 58 (100) $[NNMe_2]^+$, 43 (51.6), 42 (60.1) $[CH_2=C=O]^+$. Found, %: C 58.84; H 19.77; N 19.97. $C_7H_{14}N_2O$. Calculated, %: C 59.12; H 9.92; N 19.70.

1-(1-Dimethylamino-5-ethoxy-1,2,3,4-tetrahydropyridin-2-yl)ethanone (VII). *a*. An ampule was charged with a mixture of 0.59 g (0.0041 mol) of

hydrazone **III**, 0.29 g (0.0041 mol) of methyl vinyl ketone, 0.002 g of hydroquinone, and 1 ml of anhydrous benzene. The ampule was sealed, placed into a metal container, and heated for 5 h at 100–115°C. According to the ^{1}H NMR data, the yield of ketone **VII** was 80%.

b. An ampule was charged with a mixture of 1 g (0.07 mol) of hydrazone **III**, 0.49 g (0.07 mol) of methyl vinyl ketone, 1 ml of anhydrous benzene, and 0.002 g of hydroquinone. The ampule was sealed, placed in a Teflon container with a screw cap, and subjected to microwave irradiation (12×3 min) with intermediate cooling after each pulse. The mixture was distilled under reduced pressure. Yield 1.08 g (72.48%), bp 95°C (1.5 mm), n_D^{20} = 1.4885. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 t (3H, $CH_2C\mathbf{H}_3$), J = 7.1 Hz), 1.71 m (1H, 3-H), 1.77 s (3H, $COCH_3$), 1.85 m (1H, 3-H), 1.98 d.d.d (1H, 4-H, J = 1.1, 2.6, 16.2 Hz), 2.17 d.d.d (1H, 4-H, J = 1.1, 2.6, 16.2 Hz), 2.16 m (1H, 3-H), 2.82 s (6H, NMe_2), 3.59 q (2H, OCH_2, ^3J = 7.0 Hz), 4.57 m (1H, 2-H), 6.49 s (1H, 6-H); the signals were assigned on the basis of the two-dimensional CH-CORR spectrum. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.65 ($CH_2\mathbf{C}H_3$), 17.73 (C^3), 19.95 ($\mathbf{C}H_3CO$), 29.73 (C^4), 42.74 (NMe_2), 57.76 (OCH_2), 97.07 (C^2), 98.51 (C^5), 134.06 (C^6), 147.04 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 212 (1) $[M]^+$, 166 (100) $[M - EtOH]^+$, 165 (49.32), 151 (11.3) $[M - EtOH_2 - CH_3]^+$, 123 (38.2), 122 (52.2) $[M - EtOH - NMe_2]^+$, 108 (21.8), 95 (54.7), 94 (36.2), 80 (17.5), 66 (20.5), 55 (13.0), 43 (64.3) $[COCH_3]^+$. Found, %: C 61.50; H 9.72; N 13.87. $C_{11}H_{20}N_2O_2$. Calculated, %: C 62.24; H 9.50; N 13.20.

Reaction of hydrazone III with methyl acrylate. An ampule was charged with a mixture of 1.2 ml of benzene, 0.6 g (0.007 mol) of methyl acrylate, 1 g (0.007 mol) of hydrazone **III**, and 0.002 g of hydroquinone. The ampule was placed into a metal container and heated for 6 h 35 min at 100°C. According to the ^{1}H NMR data, the yield of methyl 1-dimethylamino-5-ethoxy-1,2,3,4-tetrahydropyridine-2-carboxylate (**VI**) was 76%. By vaccum distillation we isolated 0.9 g (56.07%) of **VI** with bp 115–119°C (1 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t (3H, CH_3, ^3J = 7.0 Hz), 2.02 m (2H, CH_2), 2.25 m (2H, CH_2), 3.52 m (1H, NCH), 3.64 m (2H, OCH_2), 5.51 s (1H, CH=). Found, %: C 57.36; H 8.78; N 12.59. $C_{11}H_{20}N_2O_3$. Calculated, %: C 57.87; H 8.83; N 12.27.

After storage of **VI** for 2.5 months at 8°C, distillation gave only 13% of the unchanged compound. The solid still residue contained (according to the ^{1}H NMR data) compounds **IX** and **VIII** at a ratio of 4:1. When the reaction mixture was heated for 3 h, other conditions being equal, the conversion of initial hydrazone **III** was only 34%, and the solid still residue contained 80% of methyl 5-ethoxypyridine-2-carboxylate (**VIII**). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 t (3H, $CH_2C\mathbf{H}_3$, J = 7.0 Hz), 3.97 s (3H, OCH_3), 4.13 q (2H, OCH_2, J = 7.0 Hz), 7.22 d.d (1H, 4-H, ^3J = 8.7, ^4J = 2.8 Hz), 8.09 d (1H, 3-H, ^2J = 8.7 Hz), 8.36 d (1H, 6-H, ^4J = 2.8 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 181 (7.8) $[M]^+$, 151 (10.5) $[M - OCH_2]^+$, 123 (100) $[M - COOCH_2]^+$, 108 (1.4), 95 (57.9) [*M* – hydroxypyridine]$^+$, 76 (8.1), 59 (15.4) $[COOCH_3]^+$, 50 (10.2), 39 (39.0).

Methyl 5-dimethylaminopyridine-2-carboxylate (IX). IR spectrum, ν, cm^{-1}: 1720 (C=O), 1590 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.07 s (6H, NMe_2), 3.93 s (3H, OCH_3), 6.92 d.d (1H, 4-H, ^3J = 8.8, ^4J = 3.6 Hz), 7.96 d (1H, 3-H, ^2J = 8.8 Hz), 8.15 d (1H, 6-H, ^4J = 3.6 Hz) (cf. [4]). Mass spectrum, *m*/*z* (I_{rel}, %): 180 (55.5) $[M]^+$, 149 (13.6) $[M - OCH_3]^+$, 122 (100) $[M - COOCH_2]^+$, 106 (21.6), 94 (13.8), 79 (32.5), 59 (38.1) $[COOCH_3]^+$, 42 (80.1).

Reaction of 2-ethoxyprop-2-enal dimethylhydrazone (III) with benzoquinone. A flask was filled with argon and charged with 30 ml of chloroform, 0.27 g (0.0025 mol) of benzoquinone, and 0.002 g of hydroquinone, and 0.36 g (0.0025 mol) of 2-ethoxyprop-2-enal dimethylhydrazone (**III**) was added dropwise. After 15 min, the mixture contained (^{1}H NMR, $CDCl_3$) the primary [4+2]-cycloaddition product, 1-dimethylamino-3-ethoxy-1,4,4a,5,8,8a-hexahydroquinoline-5,8-dione (**X**). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 t (3H, CH_3, ^3J = 7.0 Hz), 2.26 d.d (1H, CH_2, ^3J = 1.5, ^2J = 17.0 Hz), 2.30 s (6H, CH_3N), 2.71 d.d (1H, CH_2, ^3J = 3.0, ^2J = 17.0 Hz), 3.22 m (1H, 4a-H), 3.60 d.q (1H, OCH_2, J = 7.0 Hz), 3.70 d.q (1H, OCH_2, ^3J = 7.0 Hz), 3.81 d (1H, 8a-H, ^3J = 2.4 Hz), 5.33 s (1H, 2-H), 6.63 d (2H, 6-H, 7-H, J = 2.0 Hz). Adduct **X** was completely converted in 4 h into 1-dimethylamino-3-ethoxy-1,4,5,8-tetrahydroquinoline-5,8-dione (**XI**). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 t (3H, $CH_2C\mathbf{H}_3$), 2.81 s (6H, NMe_2), 3.13 d (1H, 4-H, J = 16.7 Hz), 3.62 q (2H, OCH_2, J = 7.0 Hz), 3.77 d (1H, 4-H, J = 16.7 Hz), 6.56 d and 6.63 d (2H, 6-H, 7-H, ^3J = 8.5 Hz), 6.65 s (1H, 2-H). The black tarry material was removed from the flask to leave dark violet crystalline drusen of 5-hydroxy-1-benzofuran-2-carbaldehyde dimethylhydrazone (**XIII**). Yield 0.6 g (95%), mp 172–174°C. IR spectrum, ν, cm^{-1}: 3120, 1610, 1600, 1520, 1508, 1460, 1350, 1330, 1270,

1190, 1180, 1120, 1030, 970, 850, 800. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 2.98 s (6H, NMe_2), 6.61 s (1H, 3-H), 6.74 d.d (1H, 6-H, J = 8.7, 2.6 Hz), 6.83 d (1H, 4-H, J = 2.5 Hz), 7.17 s (1H, CH=N), 7.24 d (1H, 7-H, J = 8.7 Hz), 8.08 s (1H, OH). ^{13}C NMR spectrum [$(CD_3)_2CO$], δ_C, ppm: 42.52 (CH_3), 102.66 (C^3), 105.97 (C^4), 111.62 (C^7), 113.28 (C^6), 121.86 (C=N), 130.03 (C^9), 149.01 (C^8), 153.53 (C^5), 155.81 (C^2). The ^{15}N, 2D CH-CORR, HMBC-GP ^{1}H–^{13}C, HMBC-GP ^{1}H–^{15}N, and 2D NOESY spectra were recorded from solutions in $(CD_3)_2CO$. Mass spectrum, m/z (I_{rel}, %): 204 (100) $[M]^+$, 189 (1.4) $[M - Me]^+$, 174 (2.8) $[M - 2Me]^+$, 160 (18.6) $[M - NMe_2]^+$, 146 (35.7) $[M - NNMe_2]^+$, 105 (27.1) $[HOC_6H_3CH]^+$, 89 (12.8) $[C_6HO]^+$, 76 (5.7), 63 (5.7), 43 (22.8). Found, %: C 64.58; H 6.22; N 13.50. $C_{11}H_{12}N_2O_2$. Calculated, %: C 64.71; H 5.88; N 13.73.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 03-03-33143).

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