

## Reactions of 1-[Benzoyl(2-heteroyl)]-2,2-dimethylhydrazines with 1,3-Dibromopropyne, 2-Propynyl Bromide, and Allyl Bromide

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**Abstract**—Reactions of 1-[benzoyl(2-heteroyl)]-2,2-dimethylhydrazines with 1,3-dibromopropyne in MeOH at 50°C afforded 2-phenyl(heteryl)-6-bromomethylidene-4,4-dimethyl-5*H*-1,3,4-oxadiazinium bromides. Reactions of 1-[benzoyl(2-heteroyl)]-2,2-dimethylhydrazines with propargyl bromide and allyl bromide gave rise to 1,1-dimethyl-1-(2-propyn-1-yl)- and 1,1-dimethyl-1-(2-propen-1-yl)-2-benzoyl(heteroyl)hydrazinium bromides. On treating these compounds with NaOH solution the corresponding imides were obtained.

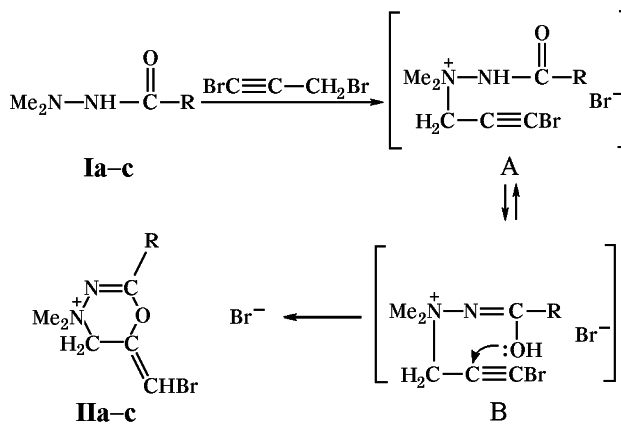
Quaternization of 1,1-dimethylhydrazine and its derivatives with alkynyl and alkenyl halides up till now remains relatively poorly studied.

The known reactions of 1,1-dimethylhydrazine with propargyl bromide [1] and propargyl chloride [2] afford 1,1-dimethyl-1-(2-propynyl)hydrazinium bromide or chloride. Arylolethynyl bromides with 1,1-dimethylhydrazine give rise to 1-(2-arylolethynyl)-1,1-dimethylhydrazinium bromides [3]. In reactions of 1,1-dimethylhydrazones with propargyl bromide and 1,3-dibromopropyne the corresponding bromides of 1,1-dimethyl-1-(2-propynyl)hydrazonium and 1,1-dimethyl-1-(3-bromo-2-propynyl)hydrazonium were obtained in 30–72% yield [4].

We established that reactions of 1-benzoyl-, 1-(2-thienyl)-, and 1-(2-furyl)-2,2-dimethylhydrazines (**Ia–c**) with 1,3-dibromopropyne carried out in anhydrous methanol at 50°C furnished 2-phenyl(heteryl)-6-bromomethylidene-4,4-dimethyl-5*H*-1,3,4-oxadiazinium bromides (**IIa–c**) in 68–87% yield.

In the first stage hydrazines **Ia–c** were alkylated with 1,3-dibromopropyne at the tertiary nitrogen giving 1-benzoyl(heteroyl)-2-(3-bromo-2-propyn-1-yl)-2,2-dimethylhydrazinium bromides (A) which we failed to isolate.

We previously [4] proved in the study of reactions between 1,1-dimethylhydrazones and 1,4-dibromopropyne or propargyl bromide that the tertiary nitrogen atom was alkylated exclusively by the CH<sub>2</sub>Br group.

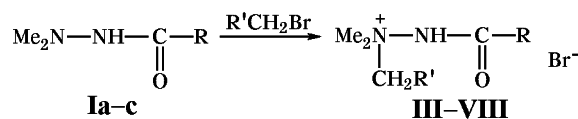


R = Ph (**a**); thienyl-2 (**b**); furyl-1 (**c**).

As a result of amide-imide tautomerism bromides **A** in the methanol solution formed intermediates **B** which under the synthesis conditions readily underwent cyclization into 1,3,4-oxadiazinium bromides **IIa–c**.

The structure of the latter was proved by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra.

1-Benzoyl(heteroyl)-2,2-dimethylhydrazines **Ia–c** also actively reacted with propargyl bromide and allyl



R = Ph, R' = HC≡C (**III**); R = 2-thienyl, R' = HC≡C (**IV**); R = 2-furyl, R' = HC≡C (**V**); R = Ph, R' = CH<sub>2</sub>=CH (**VI**); R = 2-thienyl, R' = CH<sub>2</sub>=CH (**VII**); R = 2-furyl, R' = CH<sub>2</sub>=CH (**VIII**).

bromide in anhydrous MeOH at 50°C affording in good yield (55–72%) bromides **III–VIII**.

In contrast to intermediates B bromides **III–VIII** under the same conditions did not undergo intra molecular cyclization into substituted 1,3,4-oxadiazinium bromides. This fact is apparently due to the lack of polarization of the triple bond in compounds **III–V** and double bond in compounds **VI–VIII** unlike the triple bond in the  $\text{CH}_2\text{-C}\equiv\text{CBr}$  moiety of intermediates B, and the nucleophilic addition of OH group to the  $\text{C}\equiv\text{C}$  and  $\text{C}=\text{C}$  bonds in compounds **III–VIII** failed to occur.

Thus the reaction of 1-[benzoyl(2-heteroyl)]-2,2-dimethylhydrazines (**Ia–c**) with 1,3-dibromopropyne opens up new way to the synthesis of substituted 1,3,4-oxadiazinium bromides **IIa–c**.

## EXPERIMENTAL

Compounds synthesized were studied by the use of multidimensional (1D, 2D) multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ) NMR spectroscopy. The spectra were registered at 20°C from solutions in  $\text{DMSO-}d_6$  on spectrometer Bruker DPX-400 at operating frequencies 400.13 ( $^1\text{H}$ ) and 100.62 ( $^{13}\text{C}$ ) MHz with accuracy of chemical shifts measurements of 0.01 and 0.02 ppm respectively, the coupling constants determined with accuracy of 0.1 Hz. HMDS was used as internal reference. The signals assignment in the spectra was made using two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  spectra (XH-CORR).

IR spectra were recorded on Specord 75IR instrument from samples pelletized with KBr.

**1-Benzoyl-2,2-dimethylhydrazine (Ia)** was prepared by previously described procedure [5] from 3.0 g (0.05 mol) of 1,1-dimethylhydrazine and 7.05 g (0.05 mol) of benzoyl chloride in 30 ml of benzene at 20°C. Yield 2.27 g (28%). Colorless crystals, mp 106–107°C (from  $\text{CCl}_4$ ). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3205 (NH), 1645 (C=O). Found, %: C 65.72; H 7.22; N 17.11.  $\text{C}_9\text{H}_{12}\text{N}_2\text{O}$ . Calculated, %: C 65.83; H 7.37; N 17.06.

**1-(2-Thenoyl)-2,2-dimethylhydrazine (Ib)** was prepared from 4.41 g (0.03 mol) of 2-thenoyl chloride and 3.0 g (0.05 mol) of 1,1-dimethylhydrazine in 30 ml of anhydrous THF at 40°C. Yield of compound **Ib** 4.43 g (87%). Light-yellow crystals, mp 122–123°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3220 (NH), 1655 (C=O), 680 (C–S). Found, %: C 49.35; H 6.06; N 16.41; S 18.70.  $\text{C}_7\text{H}_{10}\text{N}_2\text{OS}$ . Calculated, %: C 49.41; H 5.88; N 16.47; S 18.82.

**1-(2-Furoyl)-2,2-dimethylhydrazine (Ic)** was prepared from 5.24 g (0.04 mol) of 2-furoyl chloride

and 3.0 g (0.05 mol) of 1,1-dimethylhydrazine in 30 ml of anhydrous THF at 40°C. Yield of compound **Ic** 3.7 g (60%). Colorless crystals, mp 110–112°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3230 (NH); 1658 (C=O). Found, %: C 54.66; H 6.35; N 18.46.  $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$ . Calculated, %: C 54.55; H 6.49; N 18.18.

**2-Phenyl-6-bromomethylidene-4,4-dimethyl-5H-1,3,4-oxadiazinium bromide (IIa)**. To a solution of 1.64 g (0.01 mol) of 1-benzoyl-2,2-dimethylhydrazine (**Ia**) in 30 ml of anhydrous methanol was added at stirring a solution of 3.58 g (0.01 mol) of 1,3-dibromopropyne in 20 ml of anhydrous methanol, the mixture was heated to 50°C, and stirred at this temperature for 4 h. On cooling the reaction mixture to 0°C the separated precipitate was filtered off, washed on the filter with cold ether, and dried in a vacuum. Yield of compound **IIa** 3.81 g (73%), colorless crystals, mp 148–149°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2955 ( $\text{CH}_2$ ), 1612 (C=N), 1570 (C=C), 695 (C–Br).  $^1\text{H}$  NMR spectrum ( $\text{DMSO-}d_6$ ),  $\delta$ , ppm: 3.58 s (6H, 2 $\text{CH}_3$ ), 4.95 s (2H,  $\text{CH}_2$ ), 6.82 s (1H, =CHBr), 7.68–8.02 m (5H, Ph).  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO-}d_6$ ),  $\delta$ , ppm: 55.9 ( $\text{CH}_3$ ), 57.4 ( $\text{CH}_2$ ), 94.8 (CHBr), 124.8–134.5 (Ph), 139.4 (C=CHBr), 157.8 (C=N). Found, %: C 39.70; H 3.66; Br 44.38; N 8.12.  $\text{C}_{12}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}$ . Calculated, %: C 39.78; H 3.87; Br 44.20; N 7.93.

**2-(2-Thienyl)-6-bromomethylidene-4,4-dimethyl-5H-1,3,4-oxadiazinium bromide (IIb)** was prepared in the similar way as compound **IIa** from 1.7 g (0.01 mol) of 1-(2-thenoyl)-2,2-dimethylhydrazine (**Ib**) and 3.58 g (0.01 mol) of 1,3-dibromopropyne. Yield of compound **IIb** 3.59 g (68%). Colorless crystals, mp 136–138°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2950 ( $\text{CH}_2$ ), 1600 (C=N), 1565 (C=C), 730 (C–Br), 690 (C–S).  $^1\text{H}$  NMR spectrum ( $\text{DMSO-}d_6$ ),  $\delta$ , ppm: 3.50 s (6H, 2 $\text{CH}_3$ ), 4.89 d (2H,  $\text{CH}_2$ ), 6.78 s (1H, =CHBr), 7.32 d.d (1H,  $\text{H}^3$ ,  $^3J$  5,  $^3J$  3.4 Hz), 7.88 (1H,  $\text{H}^4$ ,  $^3J$  3.4 Hz), 8.09 (1H,  $\text{H}^2$ ,  $^3J$  5 Hz).  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO-}d_6$ ),  $\delta$ , ppm: 56.0 ( $\text{CH}_3$ ), 57.9 ( $\text{CH}_2$ ), 95.05 (=CHBr), 128.66 ( $\text{C}^2$ ), 128.80 ( $\text{C}^5$ ), 133.32 ( $\text{C}^3$ ), 135.04 ( $\text{C}^4$ ), 139.26 (–C=), 154.56 (C=N). Found, %: C 32.35; H 3.15; Br 43.65; N 7.82; S 8.73.  $\text{C}_{10}\text{H}_{12}\text{Br}_2\text{N}_2\text{OS}$ . Calculated, %: C 32.61; H 3.26; Br 43.48; N 7.61; S 8.70.

**2-(2-Furyl)-6-bromomethylidene-4,4-dimethyl-5H-1,3,4-oxadiazinium bromide (IIc)** was prepared in the similar way as compound **IIa** from 1.54 g (0.01 mol) of 1-(2-furoyl)-2,2-dimethylhydrazine (**Ib**) and 3.58 g (0.01 mol) of 1,3-dibromopropyne. Yield of compound **IIc** 4.45 g (87%). Colorless crystals,

mp 141–142°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2920 ( $\text{CH}_2$ ), 1610 ( $\text{C}=\text{N}$ ), 1560 ( $\text{C}=\text{C}$ ), 710 ( $\text{C}-\text{Br}$ ).  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.44 s (6H,  $2\text{CH}_3$ ), 4.84 d (2H,  $\text{CH}_2$ ), 6.77 t (1H, CH), 6.84 d.d (1H,  $\text{H}^4$ ,  $^3J$  3.7,  $^3J$  1.8 Hz), 7.41 d.d (1H,  $\text{H}^3$ ,  $^3J$  3.7,  $^4J$  0.7 Hz), 8.14 d.d (1H,  $\text{H}^5$ ,  $^3J$  1.8,  $^4J$  0.7 Hz).  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 56.09 ( $\text{CH}_3$ ), 58.08 ( $\text{CH}_2$ ), 95.12 (CH), 113.13 ( $\text{C}^3$ ), 118.84 ( $\text{C}^4$ ), 139.00 ( $\text{C}^2$ ), 140.53 ( $-\text{C}=\text{CHBr}$ ), 148.93 ( $\text{C}^5$ ), 150.61 ( $\text{C}=\text{N}$ ). Found, %: C 34.37; H 3.33; Br 45.65; N 8.02.  $\text{C}_{10}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2$ . Calculated, %: C 34.09; H 3.41; Br 45.45; N 7.95.

**1-Benzoyl-2,2-dimethyl-2-(2-propyn-1-yl)-2-hydrazinium bromide (III).** To a solution of 1.64 g (0.01 mol) of 1-benzoyl-2,2-dimethylhydrazine (**Ia**) in 25 ml of anhydrous methanol was slowly added at stirring a solution of 1.99 g (0.01 mol) of propargyl bromide in 15 ml of anhydrous methanol, the mixture was heated to 50°C, and stirred at this temperature for 4 h. The solvent was evaporated in a vacuum, the oily residue was dissolved in a little of methanol and bromide **III** was precipitated from solution by adding cold ethyl ether. The precipitate was filtered off and dried in a vacuum. Yield 2.14 g (59%). Colorless crystals, mp 125–126°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3280 (NH), 2920 ( $\text{N}^+\text{CH}_2$ ), 2140 ( $\text{C}\equiv\text{C}$ ), 1680 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.95 s (6H,  $2\text{CH}_3$ ), 4.04 m (1H,  $\equiv\text{CH}$ ), 5.37 d (2H,  $\text{CH}_2$ ), 7.29–7.52 m (5H,  $\text{C}_6\text{H}_5$ ), 8.13 t (1H, NH). Found, %: C 50.68; H 5.51; Br 28.09; N 9.75.  $\text{C}_{12}\text{H}_{15}\text{BrN}_2\text{O}$ . Calculated, %: C 50.90; H 5.34; Br 28.22; N 9.89.

**1-(2-Thenoyl)-2,2-dimethyl-2-(2-propyn-1-yl)-2-hydrazinium bromide (IV)** was prepared in the same way as compound **III** from 1.7 g (0.01 mol) of 1-(2-thenoyl)-2,2-dimethylhydrazine (**Ib**) and 1.99 g (0.01 mol) of propargyl bromide. Yield of bromide **IV** 2.03 g (55 %). Light-yellow crystals, mp 127–129°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3295 (NH), 2940 ( $\text{CH}_2$ ), 2140 ( $\text{C}\equiv\text{C}$ ), 1680 ( $\text{C}=\text{O}$ ), 685 ( $\text{C}-\text{S}$ ).  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.73 m (6H,  $2\text{CH}_3$ ), 4.09 s (1H,  $\equiv\text{CH}$ ,  $^3J$  2.1 Hz), 5.12 d (2H,  $\text{CH}_2$ ,  $^3J$  2.1 Hz), 7.25 d.d (1H,  $\text{H}^4$ ,  $^3J$  5,  $^3J$  3.2 Hz), 7.94 (1H,  $\text{H}^3$ ,  $^3J$  3.2 Hz), 8.01 d (1H,  $\text{H}^5$ ,  $^3J$  5 Hz).  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 54.95 ( $\text{CH}_3$ ), 57.29 ( $\text{CH}_2$ ), 71.98 ( $\text{CH}_2-\text{C}\equiv$ ), 83.61 ( $\equiv\text{CH}$ ), 128.36 ( $\text{C}^4$ ), 132.56 ( $\text{C}^3$ ), 134.04 ( $\text{C}^2$ ), 134.44 ( $\text{C}^3$ ), 163.45 ( $\text{C}=\text{O}$ ). Found, %: C 41.22; H 5.53; Br 27.79; N 9.88; S 11.32.  $\text{C}_{10}\text{H}_{13}\text{BrN}_2\text{OS}$ . Calculated, %: C 41.52; H 4.50; Br 27.68; N 9.69; S 11.07.

**1-(2-Furoyl)-2,2-dimethyl-2-(2-propyn-1-yl)-2-hydrazinium bromide (V)** was prepared in the same way as compound **III** from 1.54 g (0.01 mol) of 1-(2-furoyl)-2,2-dimethylhydrazine (**Ic**) and 1.99 g (0.01 mol) of propargyl bromide. Yield of bromide **V** 1.98 g (56 %). Colorless crystals, mp 129–130°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3310 (NH), 3020 ( $\text{CH}_2$ ), 2125 ( $\text{C}\equiv\text{C}$ ), 1688 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.71 s (6H,  $2\text{CH}_3$ ), 4.11 t (1H, CH,  $^3J$  2.2 Hz), 5.10 d (2H,  $\text{CH}_2$ ,  $^3J$  2.2 Hz), 6.76 d.d (1H,  $\text{H}^4$ ,  $^3J$  3.5,  $^3J$  1.7 Hz), 7.43 (1H,  $\text{H}^3$ ,  $^3J$  3.5 Hz), 8.05 (1H,  $\text{H}^5$ ,  $^3J$  1.7 Hz).  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 55.04 ( $\text{CH}_3$ ), 57.45 ( $\text{CH}_2$ ), 71.83 ( $\equiv\text{C}-$ ), 83.72 ( $\equiv\text{CH}$ ), 112.56 ( $\text{C}^4$ ), 118.25 ( $\text{C}^3$ ), 143.82 ( $\text{C}^2$ ), 147.66 ( $\text{C}^5$ ), 156.26 ( $\text{C}=\text{O}$ ). Found, %: C 44.15; H 4.55; Br 29.26; N 10.05.  $\text{C}_{10}\text{H}_{13}\text{BrN}_2\text{O}_2$ . Calculated, %: C 43.96; H 4.76; Br 29.30; N 10.26.

**1-Benzoyl-2,2-dimethyl-2-(2-propen-1-yl)-2-hydrazinium bromide (VI)** was prepared in the same way as compound **III** from 1.64 g (0.01 mol) of hydrazine **Ia** and 1.68 g (0.01 mol) of allyl bromide. Yield of bromide **VI** 2.26 g (68 %). Colorless crystals, mp 133–134°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3445 (NH); 3020, 2945 ( $\text{CH}_2$ ), 1684 ( $\text{C}=\text{O}$ ), 1582 ( $\text{C}=\text{C}$ ).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.91 s (6H,  $2\text{CH}_3$ ); 4.97 d (2H,  $\text{CH}_2$ ); 5.74 t (2H,  $=\text{CH}_2$ ); 6.02 m (1H, CH); 7.26–8.05 m (5H,  $\text{C}_6\text{H}_5$ ); 11.82 t (1H, NH). Found, %: C 50.88; H 5.65; Br 28.32; N 10.12.  $\text{C}_{12}\text{H}_{17}\text{BrN}_2\text{O}$ . Calculated, %: C 50.52; H 5.96; Br 28.07; N 9.82.

**1-(2-Thenoyl)-2,2-dimethyl-2-(2-propen-1-yl)-2-hydrazinium bromide (VII)** was prepared in the same way as compound **III** from 1.7 g (0.01 mol) of 1-(2-thenoyl)-2,2-dimethylhydrazine (**Ib**) and 1.68 g (0.01 mol) of propargyl bromide. Yield of bromide **VII** 2.43 g (72 %). Colorless crystals, mp 134–136°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3450 (NH), 3042, 2975 ( $\text{CH}_2$ ), 1670 ( $\text{C}=\text{O}$ ), 1548 ( $\text{C}=\text{C}$ ), 685 ( $\text{C}-\text{S}$ ).  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.68 m (6H,  $2\text{CH}_3$ ), 4.69 s (2H,  $\text{CH}_2$ ,  $J$  7.3 Hz), 5.66 d.d (2H,  $\text{CH}_2$ ,  $^3J$  16.6,  $^3J$  9.9 Hz), 6.03 (1H, CH), 7.25 d.d (1H,  $\text{H}^4$ ,  $^3J$  5,  $^3J$  3.8 Hz), 7.91 d.d (1H,  $\text{H}^3$ ,  $^3J$  3.8,  $^4J$  1 Hz), 8.01 d.d (1H,  $\text{H}^5$ ,  $^3J$  5,  $^4J$  1 Hz).  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 54.75 ( $\text{CH}_3$ ), 68.38 ( $\text{CH}_2$ ), 125.43 (CH), 128.21 ( $=\text{CH}_2$ ), 128.31 ( $\text{C}^4$ ), 132.43 ( $\text{C}^5$ ), 134.16 ( $\text{C}^6$ ), 134.40 ( $\text{C}^2$ ), 160.41 ( $\text{C}=\text{O}$ ). Found, %: C 41.02; H 4.95; Br 27.78; N 9.42; S 11.22.  $\text{C}_{10}\text{H}_{15}\text{BrN}_2\text{OS}$ . Calculated, %: C 41.24; H 5.15; Br 27.49; N 9.62; S 11.00.

**1-(2-Furoyl)-2,2-dimethyl-2-(2-propen-1-yl)-2-hydrazinium bromide (VIII)** was prepared in the same way as compound **III** from 1.54 g (0.01 mol) of 1-(2-furoyl)-2,2-dimethylhydrazine (**Ic**) and 1.68 g (0.01 mol) of allyl bromide. Yield of compound **VIII** 2.29 g (71 %). Colorless crystals, mp 127–128°C (from MeCN). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3448 (NH), 3024, 2980 ( $\text{CH}_2$ ), 1676 (C=O), 1568 (C=C).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 3.71 s (6H, 2 $\text{CH}_3$ ), 4.74 d (2H,  $\text{CH}_2$ ,  $^3J$  7.2 Hz), 5.64 d.d (2H,  $\text{CH}_2$ ,  $^3J$  17,  $^3J$  9.9 Hz), 6.02 m (1H, CH), 6.75 d.d (1H,  $\text{H}^4$ ,  $^3J$  3.7 Hz), 7.46 (1H,  $\text{H}^3$ ,  $^3J$  3.7 Hz), 8.05 (1H,  $\text{H}^5$ ,  $^3J$  3.7 Hz), 11.20 s (1H, NH).  $^{13}\text{C}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 54.77 ( $\text{CH}_3$ ), 68.43 ( $\text{CH}_2$ ), 112.42 ( $\text{C}^4$ ), 117.94 ( $\text{C}^3$ ), 125.33 (=CH), 128.23 (=CH $_2$ ), 143.85 ( $\text{C}^2$ ), 147.41 ( $\text{C}^5$ ), 156.15 (C=O). Found, %: C 43.48; H 5.68; Br 29.31;

N 10.02.  $\text{C}_{10}\text{H}_{15}\text{BrN}_2\text{O}_2$ . Calculated, %: C 43.64; H 5.45; Br 29.09; N 10.18.

## REFERENCES

1. Smith, R.F. and Coffman, K.I., *Synth. Commun.*, 1982, vol. 12, p. 801.
2. Konig, K.H. and Zeeh, B., *Chem. Ber.*, 1970, vol. 103, p. 2052.
3. Elokhina, V.N., Nakhmanovich, A.S., Larina, L.I., Shishkin, O.V., Baumer, V.N., and Lopyrev, V.A., *Izv. Akad. Nauk, Ser. Khim.*, 1999, p. 1536.
4. Elokhina, V.N., Nakhmanovich, A.S., Karnaukhova, R.V., Larina, L.I., and Lopyrev, V.A., *Zh. Org. Khim.*, 2000, vol. 36, p. 502.
5. Hinman, R.L., *J. Am. Chem. Soc.*, 1956, vol. 28, p. 1645.