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# Reactions of *N*- and *C*-Alkenylanilines: VI.* Synthesis of 6-Methyl-2-[(*E* or *Z*)-1-propenyl]anilines and the Corresponding Anilides and Their Reaction with Bromine

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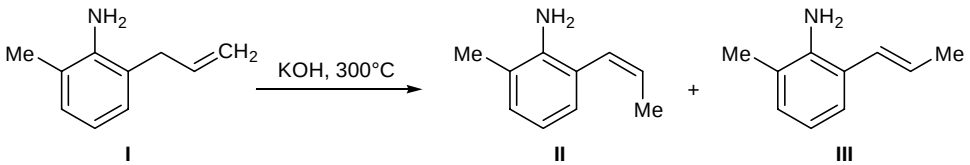
**Abstract**—Isomerization of 2-allyl-6-methylaniline by the action of potassium hydroxide at 300°C afforded *cis* and *trans* isomers of 2-methyl-6-(1-propenyl)aniline which were converted into the corresponding carbamates by treatment with ethyl chloroformate. Ethyl 2-methyl-6-(1-propenyl)phenylcarbamates reacted with bromine to give mixtures of 4-(1-bromoethyl)-8-methyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one and ethyl 2-methyl-6-(1,2-dibromopropyl)phenylcarbamates. Treatment of the same compounds with *N*-bromosuccinimide resulted in formation of 2-ethoxy-4*H*-3,1-benzoxazine derivatives. The reaction of *N*-{6-methyl-2-[(*Z*)-1-propenyl]-phenyl}methanesulfonamide gave a mixture of stereoisomeric *N*-[6-methyl-2-(1,2-dibromopropyl)-phenyl]-methanesulfonamides.

Some benzoxazine derivatives exhibit a high biological activity. In this respect, 3,1-benzoxazin-2-ones [2] and 2-amino-3,1-benzoxazines [3] are the most interesting. These compounds are synthesized from aminobenzyl alcohol derivatives or anthranilic acid. In continuation of our studies [4] on the synthesis of benzoxazinones, in the present work we prepared *cis* and *trans*-*o'*-(1-propenyl) derivatives of *o*-toluidine and examined their reactions with bromine.

Isomerization of 2-allyl-6-methylaniline (**I**) by the action of potassium hydroxide at 300°C afforded *cis* and *trans* isomers of 2-methyl-6-(1-propenyl)aniline **II** and **III** in 17 and 80% yield, respectively (Scheme 1). Compounds **II** and **III** were treated with ethyl chloroformate to obtain N-substituted carbamates **IV** and **V**, respectively. The addition of bromine at the exocyclic double bond in **IV** and **V** was accompanied by intramolecular cyclization with formation of 4*H*-3,1-benzoxazin-2-one derivatives. The cyclization of *trans* isomer **V** was characterized by lower stereoselectivity, as compared to *cis* isomer **IV**. From *cis* isomer **IV**, we obtained a mixture of *threo*-1,2-dibromopropyl derivative **VI** and *threo*-(1-bromoethyl)-8-methyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (**VII**) at a ratio of 5:2 in an overall yield of about 90%. The bromination of *trans* isomer **V** resulted in formation of *erythro*-dibromopropyl derivative **VIII**, *erythro*-(1-bromoethyl)-8-methyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (**VIII**), and benzoxazine **VII** at a ratio of ~12:4:1 (overall yield ~90%) (Scheme 2). *N*-Methylsulfonyl derivative **X** reacted with bromine to give a mixture of stereoisomeric dibromides **XI** and **XII** (Scheme 3); isomer **XI** was isolated in the pure state by recrystal-

**Scheme 1.**




* For communication V, see [1].

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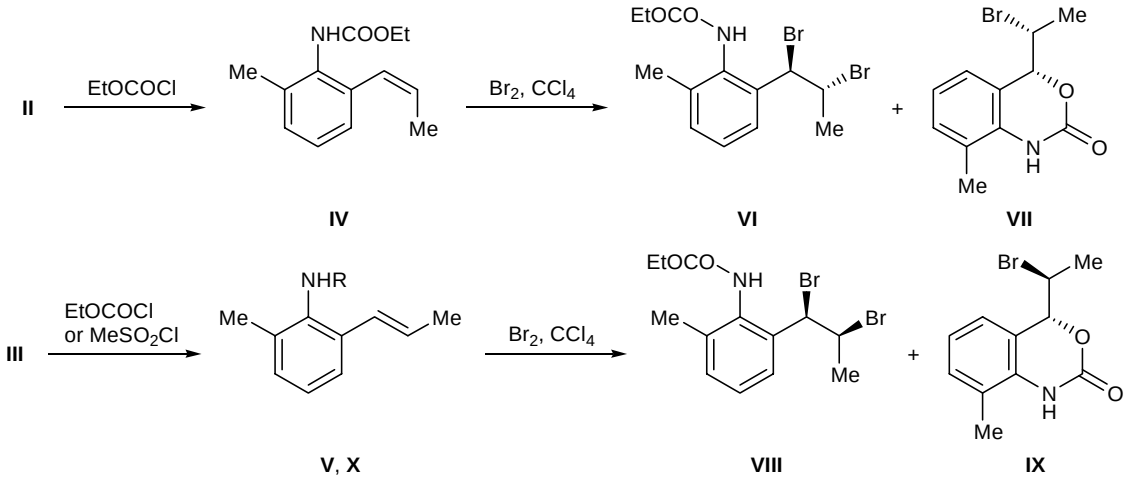
**Scheme 2.**

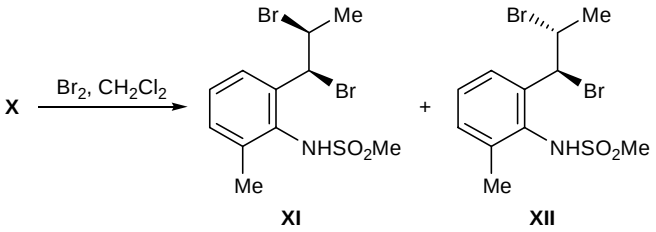



**V**, R = EtOCO; **X**, R = $MeSO_2$.

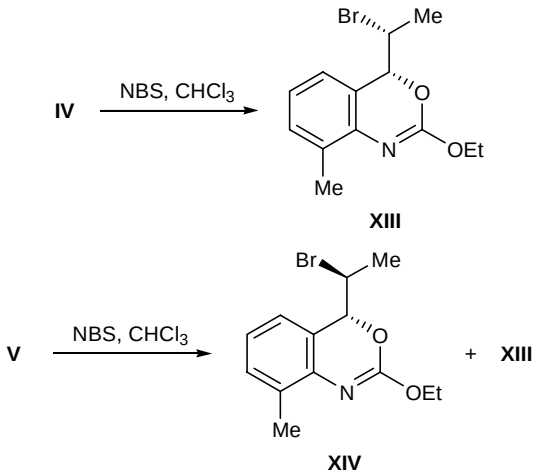
lization from ethanol. The reactions of carbamates **IV** and **V** with *N*-bromosuccinimide in chloroform gave stereoisomeric 4-(1-bromoethyl)-2-ethoxy-8-methyl-4*H*-3,1-benzoxazines **XIII** and **XIV** (Scheme 4). Presumably, the stability of cyclic imidates **XIII** and **XIV** is ensured by weak acidity of succinimide, which makes elimination of the ethyl group impossible [5].

The steric structure of the products was determined by analysis of their $^1$H NMR spectra. The smaller coupling constants between the 4-H and 1'-H protons in benzoxazine **VII** ($J$ = 4.2 Hz) corresponds to its *threo* configuration [6, 7]; the coupling constant between 4-H and 1'-H in *erythro* isomer **IX** is 5.5 Hz. The configuration of compounds **VII** and **IX** is consistent with the *trans*-addition mechanism in halocyclization reactions [8]. Dibromide **VI** obtained from *cis* isomer **IV** also belongs to the *threo* series, for the coupling constant between 1'-H and 2'-H is equal to 6.0 Hz. Correspondingly, compound **VIII** is an *erythro* isomer ($J$ = 10.5 Hz), in keeping with the known mechanism of *trans*-addition of bromine at a double bond [7]. The large 1'-H–2'-H coupling constant in sulfonamide **XI** ($J$ = 10.8 Hz) indicates *erythro* configuration of the 1,2-dibromopropyl group therein.

**Scheme 3.**




**Scheme 4.**




## EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument. The $^1$H and $^{13}$C NMR spectra were obtained on a Bruker AM 300 spectrometer at 300.13 and 75.7 MHz, respectively; the chemical shifts were measured relative to tetramethylsilane as internal reference. The elemental compositions were determined on an M-185B CHN analyzer. The reaction mixtures and products were analyzed by GLC on a Chrom-5 chromatograph equipped with a flame ionization detector; carrier gas helium (flow rate 50 ml/min); stationary phases SE-30 (5%) on Chromaton N-AW DMCS (1200×3-mm column, oven temperature 50–300°C) and PEG-6000 (5%) on Chromaton AW DMCS (2400×3-mm column, oven temperature 50–200°C). Silica gel LS 40/100 μm and Silpearl (Czechia) was used for column chromatography. Qualitative TLC

analysis was performed using Silufol UV-254 and UV-254/366 plates (Czechia); eluent benzene–ethyl acetate (6:1); spots were visualized under UV light (λ 254 nm) and by treatment with iodine vapor.

**Synthesis of anilines II and III**. A mixture of 10 g of 2-allyl-6-methylaniline (**I**) and 10 g of potassium hydroxide was heated for 1 h at 300°C. The mixture was cooled, the liquid phase was separated by decanting, and the isomeric products were separated by fractional distillation under reduced pressure (aniline **III**). The fraction with bp 85–89°C (3 mm) was additionally subjected to column chromatography on silica gel using benzene as eluent to isolate aniline **II**.

**6-Methyl-2-[(*Z*)-1-propenyl]aniline (II).** Yield 1.7 g (17%). bp 85–87°C (3 mm). IR spectrum, ν, $cm^{-1}$: 3350, 3470 ($NH_2$). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.80 d (3H, $CH_3$, $J$ = 6.8 Hz), 2.24 s (3H, $CH_3$), 3.75 br.s (2H, $NH_2$), 5.95 d.q (1H, 2'-H, $J_1$ = 7.0, $J_2$ = 11.2 Hz), 6.38 d (1H, 1'-H, $J$ = 11.2 Hz), 6.75 t (1H, 4-H, $J$ = 7.5 Hz), 7.02 d (1H, 5-H, $J$ = 7.5 Hz), 7.04 d (1H, 3-H, $J$ = 7.5 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 14.5 ($C^{3'}$), 17.7 ($CH_3$), 117.5 ($C^4$), 122.0 ($C^2$), 122.6 ($C^6$), 126.2 ($C^{2'}$), 127.6 ($C^3$), 128.6 ($C^5$), 129.0 ($C^{1'}$), 142.0 ($C^1$). Found, %: C 81.34; H 8.80; N 9.42. $C_{10}H_{13}N$. Calculated, %: C 81.59; H 8.90; N 9.51.

**6-Methyl-2-[(*E*)-1-propenyl]aniline (III).** Yield 8 g (80%). bp 89–91°C (3 mm). IR spectrum, ν, $cm^{-1}$: 3360, 3470 ($NH_2$). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.06 d (3H, $CH_3$, $J$ = 6.6 Hz), 2.26 s (3H, $CH_3$), 3.75 br.s (2H, $NH_2$), 6.19 d.q (1H, 2'-H, $J_1$ = 6.6, $J_2$ = 15.5 Hz), 6.56 d (1H, 1'-H, $J_1$ = 15.5 Hz), 6.80 t (1H, 4-H, $J$ = 7.5 Hz), 7.08 d (1H, 5-H, $J$ = 7.5 Hz), 7.23 d (1H, 3-H, $J$ = 7.5 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 17.5 ($CH_3$), 18.8 ($CH_3$), 118.1 ($C^4$), 122.26 ($C^2$), 124. ($C^6$), 125.3 ($C^5$), 127.0 ($C^{2'}$), 127.7 ($C^3$), 129.0 ($C^{1'}$), 141.5 ($C^1$). Found, %: C 81.30; H 8.72; N 9.40. $C_{10}H_{13}N$. Calculated, %: C 81.59; H 8.90; N 9.51.

**Ethyl 2-methyl-6-(1-propenyl)phenylcarbamates IV and V.** Potassium carbonate, 4 g (30 mmol), was added to a solution of 1.47 g (10 mmol) of aniline **II** or **III** in 20 ml of methylene chloride, and a solution of 1.6 g (15 mmol) of ethyl chloroformate in 15 ml of methylene chloride was added dropwise under stirring at 20°C. The mixture was stirred for 2 h and was left to stand for 18 h at 20°C. The precipitate (inorganic material) was filtered off and washed with methylene chloride (2×10 ml), and the filtrate was washed in succession with a 10% aqueous solution of sodium hydrogen carbonate (until $CO_2$ no longer evolved) and water and dried over magnesium sulfate. The solvent was removed, the residue was treated with hot hexane, and the hexane extract was evaporated to obtain carbamate **IV** or **V**.

**Ethyl 2-methyl-6-[(*Z*)-1-propenyl]phenylcarbamate (IV).** Yield 1.3 g (60%). $R_f$ 0.55. IR spectrum, ν, $cm^{-1}$: 3400 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, $CH_3$, $J$ = 6.2 Hz), 1.77 d (3H, $CH_3$, $J$ = 7.0 Hz), 2.30 s (3H, $CH_3$), 4.19 q (2H, $CH_2O$, $J$ = 6.2 Hz), 5.87 d.q (1H, 2'-H, $J_1$ = 7.0, $J_2$ = 11.4 Hz), 6.31 br.s (1H, NH), 6.44 d (1H, 1'-H, $J$ = 11.4 Hz), 7.10–7.21 m (3H, $H_{arom}$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 14.2 ($C^{3'}$), 14.4 ($CH_3$), 18.2 ($CH_3$), 61.1 ($CH_2$), 126.2 ($C^4$), 126.6 ($C^3$), 127.3 ($C^{2'}$), 128.0 ($C^6$), 129.1 ($C^{1'}$), 133.2 ($C^2$), 134.6 ($C^5$), 135.7 ($C^{1'}$), 155.1 (C=O). Found, %: C 70.93; H 7.68; N 6.17. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39.

**Ethyl 2-methyl-6-[(*E*)-1-propenyl]phenylcarbamate (V).** Yield 1.49 g (68%). $R_f$ 0.58. IR spectrum, ν, $cm^{-1}$: 3390 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.24 t (3H, $CH_3$, $J$ = 6.2 Hz), 1.90 d (3H, $CH_3$, $J$ = 6.5 Hz), 2.26 s (3H, $CH_3$), 4.22 q (2H, $CH_2O$, $J$ = 6.2 Hz), 6.18 d.q (1H, 2'-H, $J_1$ = 15.1, $J_2$ = 6.5 Hz), 6.59 d (1H, 1'-H, $J_1$ = 15.1 Hz), 6.76 br.s (1H, NH), 7.08–7.18 m (2H, 4-H, 5-H), 7.34 d (1H, 3-H, $J$ = 6.6 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 14.3 ($CH_3$), 18.0 ($C^{3'}$), 18.5 ($CH_3$), 60.3 ($CH_2$), 123.4 ($C^4$), 126.7 ($C^3$), 126.9 ($C^{2'}$), 127.5 ($C^6$), 128.7 ($C^{1'}$), 131.9 ($C^2$), 135.6 ($C^5$), 136.0 ($C^1$), 154.58 (C=O). Found, %: C 71.02; H 7.72; N 6.07. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39.

**Reaction of carbamates IV and V with bromine.** A solution of 0.3 g (1.65 mmol) of bromine in 3 ml of carbon tetrachloride was added dropwise under stirring to a solution of 0.36 g (1.63 mmol) of carbamate **IV** or **V**, the mixture was left to stand for 1 h at 20°C and evaporated, and the residue was subjected to column chromatography on silica gel using benzene as eluent.

**Ethyl (1'*RS*,2'*RS*)-2-(1,2-dibromopropyl)-6-methylphenylcarbamate (VI).** Yield 0.37 g (60%). $R_f$ 0.6. IR spectrum, ν, $cm^{-1}$: 3400 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, $CH_3$, $J$ = 6.7 Hz), 1.69 d (3H, $CH_3$, $J$ = 6.8 Hz), 2.27 s (3H, $CH_3$), 4.21 q (2H, $CH_2O$, $J$ = 6.7 Hz), 4.66 d.q (1H, 2'-H, $J_1$ = 6.8, $J_2$ = 6.0 Hz), 5.52 d (1H, 1'-H, $J$ = 6.0 Hz), 6.62 br.s (1H, NH), 7.20–7.30 m (2H, $H_{arom}$), 7.45 d (1H, 3-H, $J$ = 6.4 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 14.5 ($CH_3$), 18.3 ($CH_3$), 23.5 ($C^{3'}$), 53.2 ($C^{2'}$), 54.9 ($C^{1'}$), 61.6 ($CH_2$), 127.3 ($C^4$), 127.4 ($C^5$), 131.1 ($C^3$), 132.6 ($C^6$), 136.0 ($C^2$), 137.2 ($C^1$), 154.3 (C=O). Found, %: C 40.92; H 4.40; Br 41.93; N 3.54. $C_{13}H_{17}Br_2NO_2$. Calculated, %: C 41.19; H 4.52; Br 42.16; N 3.69.

**(4*RS*,1'*RS*)-4-(1-Bromoethyl)-8-methyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (VII).** Yield 0.13 g (30%). mp 127–129°C. $R_f$ 0.4. IR spectrum, ν, $cm^{-1}$: 3410 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.80 d (3H, $CH_3$, $J$ = 6.8 Hz), 2.32 s (3H, $CH_3$), 4.39 d.q (1H, 2'-H, $J_1$ = 4.2, $J_2$ = 6.8 Hz), 5.42 d (1H, 4-H, $J$ = 4.2 Hz), 6.96–7.17 m (3H, $H_{arom}$), 8.57 s (1H, NH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 16.6 ($CH_3$), 21.8 ($C^{2'}$), 51.1 ($C^{1'}$), 82.6 ($C^4$), 117.3 ($C^8$), 122.8 ($C^6$), 123.0 ($C^{4a}$), 123.1 ($C^5$), 131.1 ($C^7$), 133.4 ($C^{8a}$), 151.3 ($C^2$). Found, %: C 48.47; H 4.36; Br 29.34; N 4.94. $C_{11}H_{12}BrNO_2$. Calculated, %: C 48.91; H 4.48; Br 29.58; N 5.19.

**Ethyl (1'*RS*,2'*SR*)-2-(1,2-dibromopropyl)-6-methylphenylcarbamate (VIII).** Yield 0.36 g (60%). mp 93–95°C. $R_f$ 0.67. IR spectrum, ν, $cm^{-1}$: 3380 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.33 t (3H, $CH_3$, $J$ = 7.0 Hz), 2.07 d (3H, $CH_3$, $J$ = 6.4 Hz), 2.30 s (3H, $CH_3$), 4.24 q (2H, $CH_2O$, $J$ = 7.0 Hz), 4.63 d.q (1H, 2'-H, $J_1$ = 10.4, $J_2$ = 6.4 Hz), 5.44 d (1H, 1'-H, $J$ = 10.4 Hz), 6.29 br.s (1H, NH), 7.20–7.30 m (2H, 4-H, 5-H), 7.40 d (1H, 3-H, $J$ = 7.5 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 14.4 ($CH_3$), 18.1 ($CH_3$), 25.2 ($C^{3'}$), 50.2 ($C^{2'}$), 54.1 ($C^{1'}$), 61.3 ($CH_2$), 125.5 ($C^4$), 127.5 ($C^5$), 130.6 ($C^3$), 132.6 ($C^6$), 136.9 ($C^2$), 138.1 ($C^1$), 154.36 (C=O). Found, %: C 41.08; H 4.35; Br 41.87; N 3.46. $C_{13}H_{17}Br_2NO_2$. Calculated, %: C 41.19; H 4.52; Br 42.16; N 3.69.

**(4*RS*,1'*SR*)-4-(1-Bromoethyl)-8-methyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (IX).** Yield 0.11 g (24%). mp 125–127°C. $R_f$ 0.4. -IR spectrum, ν, $cm^{-1}$: 3420 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.78 d (3H, $CH_3$, $J$ = 6.7 Hz), 2.32 s (3H, $CH_3$), 4.38 d.q (1H, 2'-H, $J_1$ = 5.5, $J_2$ = 6.7 Hz), 5.45 d (1H, 4-H, $J$ = 5.5 Hz), 6.96–7.16 m (3H, $H_{arom}$), 8.78 s (1H, NH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 16.7 ($CH_3$), 20.7 ($C^{2'}$), 49.8 ($C^{1'}$), 83.0 ($C^4$), 117.2 ($C^8$), 122.6 ($C^6$), 123.2 ($C^{4a}$), 124.3 ($C^5$), 131 ($C^7$), 133.3 ($C^{8a}$), 154.3 ($C^2$). Found, %: C 48.25; H 4.40; Br 29.34; N 4.94. $C_{11}H_{12}BrNO_2$. Calculated, %: C 48.91; H 4.48; Br 29.58; N 5.19.

***N*-{6-Methyl-2-[(*Z*)-1-propenyl]phenyl}methanesulfonamide (X).** Methanesulfonyl chloride, 2.34 g (20.4 mmol), was added under stirring to a solution of 2 g (13.6 mmol) of compound **III** in 15 ml of pyridine, and the mixture was kept for 24 h at 20°C. The mixture was evaporated under reduced pressure, the residue was dissolved in 100 ml of methylene chloride, the solution was washed in succession with 5% hydrochloric acid (2×25 ml) and a 10% solution of NaOH (2×25 ml) and evaporated, and the residue was recrystallized from ethanol. Yield 2.2 g (72%). mp 103–105°C. IR spectrum, ν, $cm^{-1}$: 3350 (NH). Found, %: C 58.30; H 6.55; N 6.10; S 14.30. $C_{11}H_{15}NO_2S$. Calculated, %: C 58.64; H 6.71; N 6.22; S 14.23.

***N*-[2-(1,2-Dibromopropyl)-6-methylphenyl]methanesulfonamide (XI).** A solution of 0.29 g (1.8 mmol) of bromine in 5 ml of acetonitrile was added dropwise under stirring to a solution of 0.415 g (1.8 mmol) of compound **X** in 20 ml of acetonitrile. The mixture was stirred for 3 h and evaporated under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.32 g (45%). mp 155–157°C. IR spectrum, ν, $cm^{-1}$: 3380 (NH). $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.10 d (3H, $CH_3$, $J$ = 6.4 Hz), 2.49 s (3H, $CH_3$), 3.20 s (3H, $CH_3$), 4.7 d.q (1H, 2'-H, $J_1$ = 10.8, $J_2$ = 6.4 Hz), 5.69 d (1H, 1'-H, $J$ = 10.8 Hz), 6.08 s (1H, NH), 7.27–7.37 m (2H, 4-H, 5-H), 7.50 d.d (1H, 3-H, $J_1$ = 7.6, $J_2$ = 2.2 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 19.5 ($CH_3$), 25.9 ($CH_3$), 42.0 ($CH_3$), 52.0 ($C^{2'}$), 53.4 ($C^{1'}$), 126.4 ($C^4$), 129.0 ($C^3$), 131.2 ($C^2$), 131.6 ($C^5$), 136.4 ($C^1$), 140.5 ($C^6$). Found, %: C 34.10; H 3.59; Br 41.30; N 3.29; S 8.17. $C_{11}H_{15}Br_2NO_2S$. Calculated, %: C 34.31; H 3.93; Br 41.50; N 3.64; S 8.33. Evaporation of the mother liquor gave an additional 0.37 g of a mixture of dibromides **XI** and **XII**.

**Reaction of carbamates IV and V with *N*-bromosuccinimide.** A solution of 0.2 g (0.91 mmol) of compound **IV** or **V** and 0.195 g (1 mmol) of *N*-bromosuccinimide in 20 ml of chloroform was kept for 8 h at room temperature (the progress of the reaction was monitored by TLC). The mixture was evaporated under reduced pressure, the residue was dissolved in 10 ml of carbon tetrachloride, and the mixture was left to stand for 4 h. The undissolved material (succinimide) was filtered off and washed with 3 ml of carbon tetrachloride, and the filtrate was evaporated under reduced pressure.

**(4*RS*,1'*RS*)-4-(1-Bromoethyl)-2-ethoxy-8-methyl-4*H*-3,1-benzoxazine (XIII).** Yield 0.22 g (80%). $R_f$ 0.7. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, $CH_3$, $J$ = 7.1 Hz), 1.70 d (3H, $CH_3$, $J$ = 6.8 Hz), 2.35 s (3H, $CH_3$), 4.28 d.q (1H, 1'-H, $J_1$ = 6.8, $J_2$ = 5.1 Hz), 4.42 q (2H, $CH_2O$, $J$ = 7.1 Hz), 5.34 d (1H, 4-H, $J$ = 5.1 Hz), 6.87 d (1H, 5-H, $J$ = 7.5 Hz), 6.97 t (1H, 6-H, $J$ = 7.5 Hz), 7.29 d (1H, 7-H, $J$ = 7.5 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 14.0 ($CH_3$), 16.6 ($CH_3$), 21.5 ($C^{2'}$), 50.9 ($C^{1'}$), 64.4 ($CH_2O$), 82.1 ($C^4$), 120.1 ($C^8$), 122.3 ($C^5$), 123.3 ($C^6$), 130.5 ($C^7$), 131.7 ($C^{4a}$), 138.8 ($C^{8a}$), 154.1 ($C^2$). Found, %: C 51.41; H 5.24; Br 26.62; N 7.54. $C_{13}H_{16}BrNO_2$. Calculated, %: C 52.37; H 5.41; Br 26.80; N 4.70.

**(4*RS*,1'*SR*)-4-(1-Bromoethyl)-2-ethoxy-8-methyl-4*H*-3,1-benzoxazine (XIV).** Yield 0.14 g (50%). $R_f$ 0.7. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (3H, $CH_3$, $J$ = 7.0 Hz), 1.64 d (3H, $CH_3$, $J$ = 6.7 Hz), 2.30 s (3H, $CH_3$), 4.28 d.q (1H, 1'-H, $J_1$ = 6.7, $J_2$ = 5.5 Hz), 4.39 q (2H, $CH_2O$, $J$ = 7.07 Hz), 5.43 d (1H, 4-H, $J$ = 5.5 Hz), 6.91–7.12 m (2H, 5-H, 6-H), 7.29 d (1H, 7-H, $J$ = 7.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm 14.5 ($CH_3$), 16.6 ($CH_3$), 19.6 ($C^{3'}$), 50.0 ($C^{1'}$), 64.7 ($CH_2O$), 82.6 ($C^4$), 120.2 ($C^8$), 123.4 ($C^5$), 125.7 ($C^6$), 130.7 ($C^7$), 131.2 ($C^{4a}$), 138.2 ($C^{8a}$), 154.5 ($C^2$). Found, %: C 51.54; H 5.20; Br 26.55; N 7.47. $C_{13}H_{16}BrNO_2$. Calculated, %: C 52.37; H 5.41; Br 26.80; N 4.70.

## REFERENCES


1. Gataullin, R.R., Minnigulov, F.F., Spirikhin, L.V., and Abdrakhmanov, I. B., *Russ. J. Org. Chem*., 2004, vol. 40, p. 986.
2. Gûtschow, M., *Sci. Pharm*., 1999, vol. 67, p. 524; *Ref. Zh., Khim*., 2000, no. 19Zh280.
3. Pierce, M.E., Parsons, R.L., Radesca, L.A., Lo, Y.S., Silverman, St., Moore, J.R., Islam, Q., Choudhury, A., Fortunak, J.M.D., Nguyen, D., Luo, C., Morgan, S.G., Davis, W.P., Confalone, P.N., Chen, C., Tillyer, R.D., Frey, L., Tan, L., Xu, F., Zhao, D., Thomson, A.S., Corley, E.G., Grabowski, E.G.G., Robert, R., and Reider, P.P., *J. Org. Chem*., 1998, vol. 63, p. 8536.
4. Gataullin, R.R., Afon'kin, I.S., Fatykhov, A.A., Spirikhin, L.V., and Abdrakhmanov, I.B., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2001, no. 12, p. 2355.
5. Roger, R. and Neilson, D.G., *Chem. Rev*., 1961, vol. 61, p. 179.
6. Potapov, V.M., *Stereokhimiya* (Stereochemistry), Moscow: Khimiya, 1988, p. 175.
7. Faney, R.C. and Schneider, H.-J., *J. Am. Chem. Soc*., 1968, vol. 90, p. 4429.
8. Cardillo, C. and Orena, M., *Tetrahedron*, 1980, vol. 46, p. 3321.