

Synthesis of Substituted N-Alkylamines in Aqueous Media

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ABSTRACT

Synthesis of N-substituted aminopentanes based on the reaction of the amines with 1-bromopentanes (*n*- and *iso*-structure) and amino (bis-amino) hydroxy compounds via opening reaction of epoxides with amines environmentally friendly practices in water medium has been developed. Structure of obtained compounds by elemental analysis and IR-, ¹H and ¹³C NMR-spectroscopy were confirmed.

Keywords: N-Alkylamines; Ionic Liquids; Amino Alcohols; Antibacterial Properties

1. Introduction

Modern direction of chemistry and chemical technology includes the development of new, environmentally safe chemical processes. Currently, the synthesis of nitro compounds containing different functional groups environmentally friendly methods in “green” solvents such as ionic liquids or water has attracted special attention of researchers [1-5]. Water use has several advantages such as simplicity of implementation, low cost, high efficiency in many organic reactions involving water soluble substrates, fire safety. Improvement general methods of synthesis based on the available raw materials in aqueous medium are very relevant [6-8]. Substituted diamines were used for the synthesis of azacrown ethers [9], and polymers for special purposes [10], stable carbenes [11], silylenes [12] and other stable ions. They are used as ligands in asymmetric synthesis of valuable synthetic and natural products [13] and also for the preparation of complexes with metals such as magnesium, copper, silver, palladium and platinum. The antitumor properties of physiologically active complexes of platinum (II) with diamines have been studied in detail and are widely used in medical practice [14].

2. Experimental

IR spectra of the compounds were recorded on a UR-20 spectrometer in the 4000 - 400 cm⁻¹. ¹H and ¹³C NMR recorded on a Bruker-300 (300 MHz), solvent CDCl₃ and D₂O, chemical shifts are given relative to TMS. Mass-spectra were obtained on a mass spectrometer VG-7070E (ionizing voltage 70 eV). Chromatographic analysis of reaction mixtures and determination of purity of

the synthesized compounds was performed on a chromatograph LXM MD-8, a glass column (2000 × 3 mm) (10%-Apiezon on Chromosorb G), carrier gas-helium (40 cm³/min), katarometer, column temperature -150°C, the evaporator -200°C.

N-Pentylamines(III_{a-j}), Common methods of synthesis.

To a solution of 5 mmol of amines (I_{a-c}) in 5 - 7 ml of water was added 1 mmol 1-brom-pentane (II_{a,b}) and stirred at a given temperature (50°C - 90°C) for 6 - 9 h. The mixture was saturated by 10 g dry powder NaOH. The organic layer was separated, the aqueous layer extracted with ether. The organic layers were combined, dried over Na₂CO₃. After distillation of the solvent, the residue was distilled in a vacuum.

β-Aminoalcohols, Bis-aminopropane (VI_{a-c}, VII_{a-c}), General method of synthesis.

To a solution of 1.1 - 5 mmol amines (I_{a-c}) in 5 - 7 ml of water was added 1 mmol of epoxide (II or III) and stirred at a given temperature (50°C - 90°C) for 9 h. The mixture was saturated with 10 g of dry NaOH. The organic layer was separated, the aqueous layer extracted with ether. The organic layers combine, and dried. After distillation of the solvent, the residue was distilled in a vacuum.

N-Pentyl-diethylamin(III_a), IR (ν, cm⁻¹): 2910 (CH₃), 2840 (CH₂), 1230 (CN). ¹H NMR (300 MHz, D₂O) δ: 0.9 - 1.2 d.d (9H, CH₃), 1.4 - 1.6 m (6H, CH₂), 2.45 m (2H, NCH₂), 2.6 q (4H, CH₂N). ¹³C NMR (300 MHz, D₂O) δ: 12 (CH₃), 14 (CH₃), 22 (CH₂), 27 (CH₂), 39 (CH₂), 48 (CH₂N), 56 (NCH₂). Found, %: C 75.82, H 14.51; N 9.50. C₉H₂₁-N. Calculated, %: C 75.54, H 14.67; N 9.78.

N-Pentylpiperidine (III_b). Obtained from 17 g (0.2 mol)

piperidine (1 b) and 6.0 g (0.04 mol) 1-bromopentane (IIa). Yield 4.79 (78%), bp. 65°C in (2 mm Hg), n_D^{20} 1.4221, d_4^{20} 0.8419. IR (ν , cm^{-1}): 2900 (CH₃), 2830 (CH₂), 1230 (CN). ¹H NMR (300 MHz, D₂O) δ : 1.04 mp (CH, CH₃), 1.3 - 1.7 (12H, CH₂), 2.3 m (2H, NCH₂), 2.4 s (4H, CH₂ Pip.). ¹³C NMR (300 MHz, D₂O) δ : 14.4 (CH₃), 22.8 (CH₂), 24.9 (CH₃), 26.0 (CH₂), 26.9 (CH₂ pip.), 30.0 (CH₂ pip.), 54.8 (CH₂N pip.), 59.3 (NCH₂ aliph.). Found, %: C 77.82, H 13.62; N 9.13. C₁₀H₂₁N. Calculated, %: C 77.42, H 13.55; N 9.03. Yield 11 g (77%), bp. 41°C - 42°C (20 mm·Hg), n_D^{20} 1.4109, d_4^{20} 0.7779.

N-Pentylmorpholine (III_c), 0.8957. IR (ν , cm^{-1}): 2910 (CH₃), 2850 (CH₂), 1230 (C-N). ¹H NMR (300 MHz, D₂O) δ : 1.05 m (3H, CH₃), 1.45 - 1.65 m (6H, CH₂), 2.4 m (2H, NCH₂), 2.5 m (4H, CH₂N), 3.65 - 3.75 m (4H, OCH₂). ¹³C NMR (300 MHz, D₂O) δ : 14 (CH₃), 23 (CH₂), 26 (CH₂), 30 (CH₂), 46 (NCH₂), 54 (CH₂N), 59 (CH₂N morph.), 66 (OCH₂ morph.), 67 (OCH₂ morph.). Found, %: C 68.75, H 12.97; N 8.92. C₉H₁₉NO. Calculated, %: C 68.81, H 12.09; N 8.91. Yield 5 g (62%), bp. 60°C (2 mm·Hg), n_D^{20} 1.4111, d_4^{20} .

N-Pentylethanolamine (III_d), IR (ν , cm^{-1}): 3475 (OH), 3400 (NH), 2920 (CH₃), 2820 (CH₂), 1225 (C-N). ¹H NMR (300 MHz, D₂O) δ : 0.87 t (3H, CH₃), 1.25 m (4H, CH₂), 1.45 m (2H, CH₂), 2.5 и 2.65 t (4H, CH₂N), 3.5 - 3.6 t. t (3H, NH, NCH₂), 4.75 s (3H, CH₂OH). ¹³C NMR (300 MHz, D₂O) δ : 13.8 (CH₃), 22.4 (CH₂), 29.0 (CH₂), 29.5 (CH₂), 49.1 (NHC), 50.7 (CHN), 60.0 (C-OH). Mass spectrum (ES), m/z (I, %): 131 [M] + (37) 100 (100), 74 (100), 56 (100). Found, %: C 65.02, H 13.01; N 10.73. C₇H₁₇NO. Calculated, %: C 64.12, H 12.97; N 10.68. Yield 2.98 g (76%), bp. 83°C - 85°C (2 mm·Hg), n_D^{20} 1.4382, d_4^{20} 0.8712.

N-Pentylbenzylamine (III_e), IR (ν , cm^{-1}): 2910 (CH₃), 2850 (CH₂), 1220 (CN). ¹H NMR (300 MHz, D₂O) δ : 0.95 m (3H, CH₃), 1.35 q (2H, CH₂), 1.45 - 1.6 m (7H, NH, CH₂), 2.63 m (2H, NCH₂), 3.8 s (2H, CH₂Ph), 7.15 - 7.4 (4H, H ar). ¹³C NMR (300 MHz, CDCl₃) δ : 54.25 (CH₂Ph), 126.82, 128.12, 128.37, 128.89 (C_{Ar}). Found, %: C 81.51, H 10.61; N 7.99. C₁₂H₁₉N. Calculated, %: C 81.37, H 10.73; N 7.90. Yield 2.97 g (85%), b.p. 112 - 114 (6 mm·Hg), n_D^{20} 1.5073, d_4^{20} 0.9088.

N-(3-methylbutyl)diethylamine (III_f), IR (ν , cm^{-1}): 2940 (CH₃), 2860 (CH₂), 1227 (C-N). ¹H NMR (300 MHz, D₂O) δ : 1.07 d (6H, CH₃), 1.15 m (6H, CH₃), 1.47 (2H, CH₂), 1.79 s (1H, CH), 2.5 q and 2.65 m (6H, CH₂N). ¹³C NMR (300 MHz, D₂O) δ : 14 (CH₃), 17 (CH₃), 23 (CH₃), 26 (CH₃), 27 (CH₂), 36 (CH), 46 (CH₂), 47 (CH₂), 51 (NCH₂). Found, %: C 75.63, H 14.48; N 9.62. C₉H₂₁N. Calculated, %: C 75.54, N 14.67; N 9.78. Yield 8.57 g (60%), bp. 139°C, n_D^{20} 1.4109, d_4^{20} - 0.7779.

N-(3-methylbutyl)piperidine (III_g), IR (ν , cm^{-1}): 2920 (CH₃), 2860 (CH₂), 1230 (C-N). ¹H NMR (300 MHz,

D₂O) δ : 1 d (6H, CH₃), 1.45 s (1H, CH), 1.5 - 1.8 m (6H, CH₂ pip. CH₂ alif.), 2.34 m (2H, NCH₂), 2.4 m (6H, CH₂ pip.). ¹³C NMR (300 MHz, D₂O) δ : 11.8 (CH₃), 18.0 (CH₃), 25.5 (CH₂), 24.5 (CH), 26 (CH₂), 27 (CH₂ pip.), 35 (CH), 54.4 (CH₂N pip.), 55.5 (CH₂N pip.), 57.7 (NCH₂ alif.). Found, %: C 77.73, H 13.45; N 9.10. C₁₀H₂₁N. Calculated, %: C 77.42, N 13.55; N 9.03. Yield 8.13 g (81%), bp. 60°C (2 mm·Hg), n_D^{20} 1.4378, d_4^{20} - 0.8392.

N-(3-methylbutyl)morpholine (III_h), IR (ν , cm^{-1}): 2900 (CH₃), 2850 (CH₂), 1230 (C-N). ¹H NMR (300 MHz, D₂O) δ : 1.05d (6H, CH₃), 1.5 q. (2H, CH₂), 1.8 s (1H, CH), 2.4 m, 2.5 m (6H, CH₂N morph.), 3.17 m (4H, OCH₂ morph.). ¹³C NMR (300 MHz, D₂O) δ : 12 (CH₃), 17.7 (CH₃), 23.3 (CH), 26.6 (CH₂), 35.5 (NCH₂), 53 (NCH₂mor-ph.), 54 (CH₂N morph.), 57 (CH₂O morph.), 67 (CH₂O morph.). Found, %: C 69.01, H 12.34; N 9.02. C₉H₁₉NO. Calculated: C 68.81, H 12.09; N 8.91. Yield 4.42 g (71%), bp. 70°C (10 mm·Hg), n_D^{20} 1.4381, d_4^{20} - 0.8935.

N-(3-methylbutyl)ethanolamine (III_i), IR (ν , cm^{-1}): 3440 (OH), 2910 (CH₃), 2860 (CH₂), 1225 (CN). ¹H NMR (300 MHz, D₂O) δ : 0.9 d (6H, CH₃), 1.3 m (2H, CH₂), 1.5 sep (1H, CH), 2.4 - 2.65 m (3H, CH₂NH), 3.5 t (2H, NCH₂), 4.7 s (3H, CH₂OH). ¹³C NMR (300 MHz, D₂O) δ : 22.55 (CH₃), 22.47 (CH₃), 26.4 (CH), 38.22 (CH₂), 50.95 (CH₂N), 59.94 (CH₂OH). Found, %: C 64.09, H 4.13; N 11.65. C₇H₁₇NO. Calculated, %: C 64.12, H 12.97; N 12.68. Yield 3.84 g (74%), bp. 77°C - 78°C (2 mm·Hg), n_D^{20} 1.4371, d_4^{20} 0.8772.

N-(3-methylbutyl)benzylamine (III_k), IR (ν , cm^{-1}): 2920 (CH₃), 2840 (CH₂), 1225 (C-N). ¹H NMR (300 MHz, CDCl₃) δ : 0.95 t (6H, CH₃), 1.4 kv (2H, CH₂), 1.7 sep (1H, CH), 2.7 tr. (2H, N-CH₂), 3.38 s (2H, PhCH₂), 7.2 - 7.5 m (5H, H Ar). ¹³C NMR (300 MHz, D₂O) δ : 17.7 (CH₃), 22.7 (CH₃), 22.6 (CH₂), 39.27 (CH), 47.7 (N-CH₂), 54.25 (PhCH₂), 126.82, 128.12, 128.37, 128.89 (C Ar). Found, %: C 81.62, H 10.59; N 7.81. C₁₂H₁₉N. Calculated, %: C 81.37, H 10.73; N 7.90. Yield 4.53 g (82%), bp. 78°C - 79°C (2 mm·Hg), n_D^{20} 1.4891, d_4^{20} - 0.8972.

3-(N, N-diethylamino)propan-2-ol (VII_a), IR (ν , cm^{-1}): 3342 (OH), 2970 (CH₃), 2875 (C-N), 1067 (C-O). ¹H NMR (300 MHz, CDCl₃) δ : 0.9 t (3H, CH₃), 1.0 d (6H, 2CH₃), 2.1 t (2H, NCH₂), 2.25 - 2.5 m. (4H, 2CH₂N), 3.6 sep. (1H, CH), 3.7 s. (wide) (1H, OH). ¹³C NMR (300 MHz, CDCl₃) δ : 20.0 (CH₃), 20.3 (CH₃), 21.4 (CH₃), 24.2 (CH₂), 49.5 (NCH₂), 55.8 (C-OH). Found, %: C 64.03, H 16.82; N 13.75. C₇H₁₇NO. Calculated, %: C 64.13, H 17.00; N 14.01. Yield 11.5 g (80%), bp. 64°C - 65°C (15 mm·Hg), n_D^{20} 1.4210

3-Piperidinopropan-2-ol (VII_b), IR (ν , cm^{-1}): 3352 (OH), 2934 (CH₃), 2855 (CN), 1072 (C-O). ¹H NMR (300 MHz, CDCl₃) δ : 1.0 d (3H, CH₃), 1.55 - 1.65 m (6H,

CH₂ pip.), 2.8 - 2.9 m (4HCH₂N), 3.0 d.d (2H, NCH₂), 3.5 sep (1H, -CH), 3.7 s.(waid), (1H, OH). ¹³C NMR (300 MHz, CDCl₃) δ: 24 (CH₃), 24.5 (C pip.), 24.7 (C pip.), 26.6 (C, pip.), 54.1 (NCH₂), 56.8 (C-OH). Found, %: C 67.08, H 11.9; N 9.69. C₈H₁₇NO. Calculated, %: C 67.18, H 11.88; N 9.78. Yield 7.13 g (96%), bp. 75°C -76°C (20 mm·Hg) n_D²⁰ 1.4775.

3-Morpholinopropan-2-ol (VII_c), IR (ν, cm⁻¹): 3441 (OH), 2965 (CH₃), 2854 (CN), 1063 (C-O). ¹H NMR (300 MHz, CDCl₃) δ: 1.0 d (3H, CH₃), 2.17 d.d (2H, NCH₂), 2.4 - 2.5 m (4H, CH₂N morph.), 3.57 m (4H, CH₂O), 3.7 sep. (1H, CH), 3.8 s.(wiat) (1H, OH). ¹³C NMR (300 MHz, CDCl₃) δ: 22.3 (CH₃), 53 (CH₂N morph.), 56 (NCH₂), 56.6 (C-OH), 66 (OCH₂ morph.). Found, %: C 56.96, H 10.14; N 9.55. C₇H₁₅O₂N. Calculated, %: C 57.96, H 10.34; N 9.65. Yield 14.2 g (98%), bp. 70°C -71°C (3 mm·Hg), n_D²⁰ 1.4590.

3-Benzilaminopropan-2-ol (VII_d), IR (ν, cm⁻¹): 3250 (OH), 2980 (CH₃), 2830 (CN), 1058 (C-O). ¹H NMR (300 MHz, CDCl₃) δ: 1.17 d (3H, CH₃), 2.5 - 2.6 t.d (2H, NCH₂), 3.32-3.36 s.(wiat) (2H, NHOH), 3.78 d (2H, PhCH₂), 3.86 sep.(1H, CH), 7.28 - 7.29 m (5H, *n*-C₆H₅). ¹³C NMR (300 MHz, CDCl₃) δ: 22.2 (C¹), 53.3 m (C³), 56.6 m (C²), 65.5 (RhCH₂), 126, 127, 140 (C_{Ar}). Found, %: C 72.67, H 9.15; N 8.54. C₁₀H₁₅ON. Calculated, %: C 72.75, H 9.08; N 8.48. Yield 9.9 g (60%), bp. 126°C -127°C (2 mm·Hg), n_D²⁰ 1.5270.

Bis-1,3-(*N,N*-diethylamino)propan-2-ol (VIII_a), IR (ν, cm⁻¹): 3415 (OH), 2940 (CH₃), 2805 (CN), 1115 (C-O). ¹H NMR (300 MHz, D₂O) δ: 0.95 m (12H, 4CH₃), 2.34 - 2.52 m (12H, 6NCH₂), 3.28 s (1H, -OH), 3.5 sep. (1H, OCH). ¹³C NMR (300 MHz, D₂O) δ: 10 (CH₃), 47.1 m (C3), 57.05 m (NCH₂), 66.49 (C2). Found, %: C 65.42, H 12.97; N 13.93. C₁₁H₂₆N₂O. Calculated, %: C 65.37, H 12.86; N 13.85. Yield 9.1 g (93%), bp. 122°C (10 mm·Hg.) n_D²⁰ 1.4571, d₄²⁰ 0.9101.

Bis-1,3-piperidinopropan-2-ol (VIII_b), IR (ν, cm⁻¹): 3410 (OH), 2980 (CH₃), 2800 (CN), 1125 (C-O). ¹H NMR (300 MHz, CDCl₃, δ): 1.28 - 1.53 m (12H, CH₂N pip. NCH₂aliph.), 2.18 s (OH), 3.75 sept (OCH). ¹³C NMR (300 MHz, D₂O) δ: 24.5 (CH₂ pip.), 26.6 (CH₂ pip.), 54.4 (CH₂N pip.), 63.33 (N-CH₂ alf.), 64.44 (OCH). Found, %: C 66.13, H 11.62; N 12.05. C₁₃H₂₆N₂O. Calculated, %: C 69.03, H 11.49; N 12.38. Yield 12 g (90%), bp. 135°C - 136°C (3 mm·Hg.) n_D²⁰ 1.4955, d₄²⁰ 1.1137.

Bis-1,3-morpholinopropan-2-ol (VIII_c), IR (ν, cm⁻¹): 3422 (OH), 2940 (CH₃), 2805 (CN), 1110 (C-O). ¹H NMR (300 MHz, D₂O) δ: 2.17 d (1H, OH), 2.2 - 2.5 m (8H, CH₂,NCH₂cycl), 3.5 t (4H, OCH₂cycl), 3.7 s (OCH). ¹³C NMR (300 MHz, D₂O) δ: 53 (NCH₂), 62 (CH₂N cycl.), 63 (OCH), 66 (OCH₂). Found, %: C 57.30, H 9.38; N 12.29. C₁₁H₂₂N₂O₃. Calculated, %: C 57.42, H 9.56; N 12.17. Yield 11.6 g (87%), bp. 142°C - 144°C (2 mm·Hg.) n_D²⁰ 1.4358, d₄²⁰ 0.9818.

Bis-1,3-(*N,N*-diethylamino)propane (IX_a), IR (ν, cm⁻¹): 2980 (CH₃), 1275, 865 (CN). ¹H NMR (300 MHz, D₂O) δ: 1.1t (12H, CH₃), 1.6 q. (2H, CH₂), 2.46 - 2.62 sq. (12H, CH₂NCH₂). ¹³C NMR (300 MHz, CDCl₃) δ: 11.4 (CH₃), 25 (CH₂), 47 (CH₂N), 52 (NCH₂). Found, %: C 70.73, 70.79; H 14.26, 14.20; N 15.21, 15.19. C₁₁H₂₆N₂. Calculated, %: C 70.97, H 13.96; N 15.05. Yield 11.7 g (63%), bp. 85°C (20 mm·Hg), n_D²⁰ 1.4295, d₄²⁰ 0.8392.

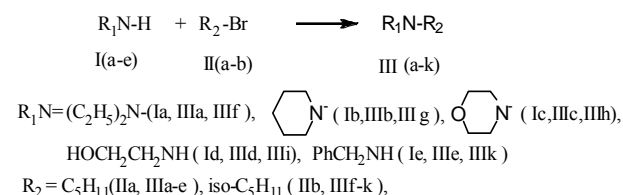
Bis-1,3-piperidinopropan (IX_b), IR (ν, cm⁻¹): 1278, 850 (C-N). ¹H NMR (300 MHz, D₂O) δ: 1.43 - 1.54 m (14H, CH₂), 2.33 - 2.43 m (12H, CH₂NCH₂). ¹³C NMR (300 MHz, D₂O) δ: 22.0, 23.0, 26.0 (CH₂, pip. CH₂ alif.), 54 (CH₂N pip.), 57 (NCH₂ aliph.). Found, %: C 74.49, 74.51; H 12.43, 12.49; N 13.15, 13.21. C₁₃H₂₆N₂. Calculated, %: C 74.29, H 13.37; N 13.33. Yield 8.13 g (66%), bp. 116°C (2 mm·Hg). n_D²⁰ 1.4773, d₄²⁰ 0.9354,

Bis-1,3-morpholinopropane (IX_c), IR (ν, cm⁻¹): 1235, 850 (C-N). ¹H NMR (300 MHz, D₂O) δ: 1.43 - 1.54 and 1.56 - 1.7 m (14H, CH₂), 2.33 - 2.43 m (12H, CH₂ morph., NCH₂ alif.). ¹³C NMR (300 MHz, D₂O) δ: 24.0 (CH₂ alif.), 54.0, 56.0 (CH₂; NCH₂ morph.), 66 (CH₂O morph.). Found, %: C 61.65, 61.58, H 10.13, 10.20; N 13.15, 13.13. C₁₁H₂₂N₂O₂. Calculated, %: C 61.69, H 10.27; N 13.08. Yield 8.12 g (60%), bp. 125°C (1 mm·Hg), n_D²⁰ 1.4781, d₄²⁰ 1.0367.

3. Results and Discussion

We have directed our efforts on the region-selective synthesis of amino- and bis-amino alcohols, which may have antibacterial and anticorrosion properties. Interactions of a number of initial amines (I_{a-e}) with brom-pentanes (II_{a-b}) result in *N*-alkylamines (III_{a-k}) (Scheme 1).

The synthesis of target products (III_{a-m}) was carried out in aqueous medium at 50°C - 90°C for 6 - 9 h. The yields of target products were in the range 60% - 98%. Synthesis of alkyl amines (III_a, III_b, III_f, III_g, IX_a, IX_b) was performed at 50°C for 8 h at a molar ratio of initial components (amines: pentylbromide or dibromopropane) equal to 5:1. The reaction of monoethanolamine (I_d) and morpholine (I_c) with pentylbromides (II_{a,b}) goes at a relatively high temperature of 60°C and long duration (9 h) at optimum component ratio of 5:1. The reaction between benzylamine (I_e) and pentylbromides (II_{a,b}) is better to carry out at the even higher temperature (90°C) for 9 h and the same ratio of reactants. Another possible ap-

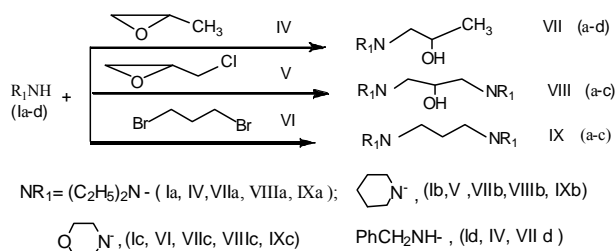


Scheme 1. Synthesis of substituted *N*-alkylamines by the alkylation with brompentanes.

proach has been realized by us in obtaining aminoalcohols VII_(a-d), bis-aminopropane-2-ols VIII_(a-c) and bis-aminopropanes IX_(a-c). We carried out regioselective oxirane ring opening of propylene oxide (IV), epichlorohydrin (V) and 1,3-dibromopropane (VI) as a result of interaction with various amines in aqueous medium according to **Scheme 2**.

The interaction of propylene oxide (IV) and epichlorohydrin (V) with diethylamine (I_a) was carried out with stirring the mixture of reagents in the water by heating at 50°C for 9 hours. The optimum ratio of initial components in this case was as follows: diethylamine/propylene oxide = 1.1:1; diethylamine/epichlorohydrin = 5:1. The reaction of diethylamine with propylene oxide formed secondary amino alcohol (VII_a), while the interaction with epichlorohydrin leads to the formation of bis-amino alcohol (VIII_a), with the yields 80% and 98%, respectively. The reactions of piperidine (I_b), morpholine (I_c) and benzylamine (I_e) with epoxy compounds were carried out at the higher temperature (90°C) for 9 h. The optimal relations between the components of amines (I_b, I_c and I_e) and propylene oxide (IV) were 1.1-1, and in the case of epichlorohydrin 5:1. Yields of the products with in the limits of 60% - 90% were achieved. Earlier aminoalcohols (VII_(a-d) and VIII_(a-c)) were obtained in organic solvents in the presence of catalysts such as salts, metal triflates as complexing agents and others with the yields within 75% - 85% [15-24].

Aminolysis of epoxides could precede regionselectively under (a) or against (b) Krasusky rule [25]. The value of δ protons CH (C²) group in ¹H NMR spectrum of compound (VII_a) is in the range of 3.60 ppm, indicating a shift of the signals in a weak field. This result shows that the OH group is located at the carbon atom C². Proton signals of the methyl group at the atom C¹ are also shifted toward weaker fields under the influence of the electronegative oxygen atom in the possession of the neighboring atom (C²) (1.35 ppm). Similarly, proton signals of CH groups of compounds (VII_(b-d)) and CH₂ groups of compounds (VIII_(a-c)) are shifted downfield in comparison with the reference materials. Good correlation with published data for compounds of similar structure [14,15,17,19] also shows in favor of the structure.



Scheme 2. Regioselective oxirane ring opening with amines and synthesis aminoalcohols and diamines.

Chromatographic analysis showed the presence of only one regioisomer for obtained compounds. Thus, the openings of the epoxy fragments in compounds (IV, V) with amines (I_{a-e}) is in accordance with Krasusky rule and follow the path(a) with the formation of secondary alcohols derivatives region selectively.

Original amines (I_{a-d}) are good or partially soluble in water, with the possible formation of the corresponding unstable hydroxides $[\text{RR}_1\text{NH}_2]^+\text{OH}^-$. It is possible and the formation of quaternary ammonium salts $[\text{RR}_1\text{NH}_2]^+\text{Br}^-$ as a result of interaction between amines (I_{a-d}) and bromopentanes (II_(a,b)) or 1,3 dibromopropane (II_c). Obtained hydroxides and quaternary ammonium salts are readily soluble in water and not on-lyplay the role of phase transfer catalysts in the reaction of the starting amines (I_{a-e}) with bromopentanes (II_(a,b)) and also could perform catalysis for opening oxiranes in aqueous media. Epichlorohydrin and 1,3 dibromo-propane also form quaternary ammonium salts next type $\{[\text{R}_2\text{NHR}]^+\text{Cl}^-\}$, that are phase transfer catalysts. The opening of epoxide ring for propylene oxide and epichlorohydrin under the action of these PTC-catalysts proceeds on well-known scheme [5] for the S_N2 mechanism with the formation of amino and bisaminopropane derivatives.

The obtained hydroxyamino- and bis-amino-compounds are promising for use as an anti-bacterial and antirust agent for oil production.

4. Conclusion

An operationally simple and environmentally benign protocol for the ring opening of epoxides with aliphatic amines has been developed. The reactions proceeded smoothly under mild conditions in water to afford *a*-amino alcohols in high yields with excellent regioselectivities. Also substituted amines were also obtained in environmentally acceptable conditions in the water by the alkylation with bromopentanes.

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