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Synthesis of Pyrrole *N*-Derivatives from Oxazolidines

E. Kh. Sadykov, V. K. Stankevich, N. A. Lobanova, and G. R. Klimenko

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk,664033 Russia
e-mail: irk_inst_chem@irioch.irk.ru

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Abstract—Transformations of oxazolidine derivatives synthesized from industrially produced amino alcohols, aldehydes, and ketones under basic or acidic catalysis lead to the formation of *N*-alkyl- and *N*-(hydroxyalkyl)-substituted pyrroles in 19–81% yields.

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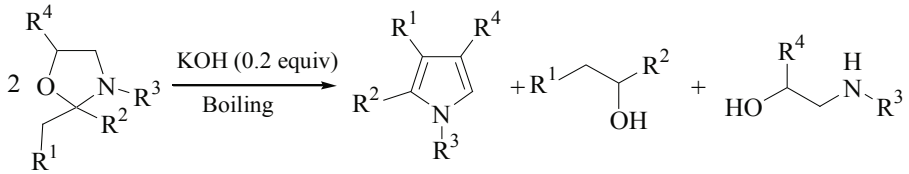
Pyrrole ring is the most important part of a large group of compounds playing the principal role in vital processes of various organisms. Pyrrole and its derivatives are utilized as intermediates in the synthesis of drugs, biologically active substances, optoelectronic materials, conductive polymers, sensors, solar cells, etc. [1]. In this connection a close attention of researchers is attracted to the search for new methods of synthesis of pyrrole derivatives [2]. Among these methods the catalytic conversions of easily synthesized 1,3-oxazolidine derivatives can be cited, which result in the formation of *N*-substituted pyrrole derivatives [3, 4]. For instance, the cleavage of cyclohexanespiro-2-oxazolidines treated with bases affords *N*-substituted 4,5,6,7-tetrahydroindole derivatives [3].

Aiming at the extension of the synthetic potential of oxazolidine series compounds, the investigation of the preparative opportunities and applicability limits of this approach to the pyrrole derivatives preparation we tested a wider set of oxazolidine derivatives. The reaction was carried out by refluxing compounds **Ia–Ik** in the presence of 0.2 equiv of potassium hydroxide. Substituted pyrroles **IIa–IIk** were obtained in 20–81% yields (Scheme 1). In all events the formation of alcohols **IIIa–IIIi** and amino alcohols **IVa–IVd** was observed.

When the oxazolidine contains in the position *2* two different substituents including methylene groups, e.g., 2-butyl-2-methyl-3-(2-hydroxyethyl)oxazolidine (**II**), (Scheme 2) a possibility arises of an alternative closure

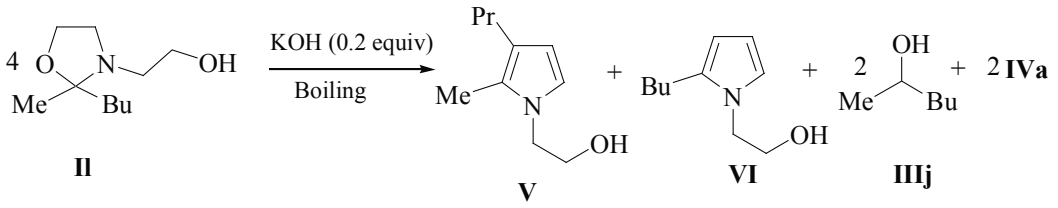
Scheme 1.



Ia–Ik **IIa–IIk** **IIIa–IIIi** **IVa–IVd**

I, II, $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = CH_2CH_2OH$ (**a**); $R^1 = Me$, $R^2 = Et$, $R^3 = CH_2CH_2OH$, $R^4 = H$ (**b**); $R^1 = i$-Pr, $R^2 = R^4 = H$, $R^3 = CH_2CH_2OH$ (**c**); $R^1 = Et$, $R^2 = Pr$, $R^3 = CH_2CH_2OH$, $R^4 = H$ (**d**); $R^1 = Pr$, $R^2 = Bu$, $R^3 = CH_2CH_2OH$, $R^4 = H$ (**e**); $R^1 = C_8H_{17}$, $R^2 = R^4 = H$, $R^3 = CH_2CH_2OH$ (**f**); $R^1 + R^2 = (CH_2)_5$, $R^3 = CH_2CH_2OH$, $R^4 = H$ (**g**); $R^1 = R^4 = H$, $R^2 = Ph$, $R^3 = CH_2CH_2OH$ (**h**); $R^1 = Et$, $R^2 = R^4 = H$, $R^3 =$ cyclo-C_6H_{11} (**i**); $R^1 = i$-Pr, $R^2 = R^4 = H$, $R^3 = Bu$ (**j**); $R^1 = H$, $R^2 = Ph$, $R^3 = CH_2CH(OH)Me$, $R^4 = Me$ (**k**); **III**, $R^1 = H$, $R^2 = Me$ (**a**); $R^1 = Me$, $R^2 = Et$ (**b**); $R^1 = i$-Pr, $R^2 = H$ (**c**); $R^1 = Et$, $R^2 = Pr$ (**d**); $R^1 = Pr$, $R^2 = Bu$ (**e**); $R^1 = C_8H_{17}$, $R^2 = H$ (**f**); $R^1 + R^2 = (CH_2)_5$ (**g**); $R^1 = H$, $R^2 = Ph$ (**h**); $R^1 = Et$, $R^2 = H$ (**i**); **IV**, $R^3 = CH_2CH_2OH$, $R^4 = H$ (**a**); $R^3 =$ cyclo-C_6H_{11}, $R^4 = H$ (**b**); $R^3 = Bu$, $R^4 = H$ (**c**); $R^3 = CH_2CH(OH)Me$, $R^4 = Me$ (**d**).

Scheme 2.



of the pyrrole ring resulting in the formation of equimolar amounts of isomeric compounds **V** and **VI** (according to ^{1}H NMR data) in an overall yield 61%.

The presumable scheme of the pyrrole ring formation may be described as follows: In the presence of bases a part of the substituted oxazolidine is hydrolyzed by traces of moisture into a carbonyl compound and amino alcohol, and the other part reacts with the base to give a salt of enaminoalcohol **A** (Scheme 3). Further a redox reaction proceeds between the carbonyl compound and intermediate **A** that results in the formation of an alcohol and enaminaldehyde **B** similarly to the process occurring in Oppenauer oxidation in the presence of *t*-BuOK as catalyst [5]. Further due to the intramolecular condensation of enaminaldehyde **B** (aldol condesation type) with water liberation followed by prototropic rearrangement in the condensation product **C** pyrrole is formed.

This mechanism is supported by the fact that the reaction with carbonyl compounds under the conditions of alkaline catalysis leads to the oxidation of oxazolidine derivatives with the formation of pyrrole ring and to the reduction of ketones and aldehydes into the corresponding alcohols [6]. However this synthetic procedure for pyrrole series compounds is less attractive from the preparative viewpoint since due to the autocondensation of some ketones an intractable mixture of substances is obtained.

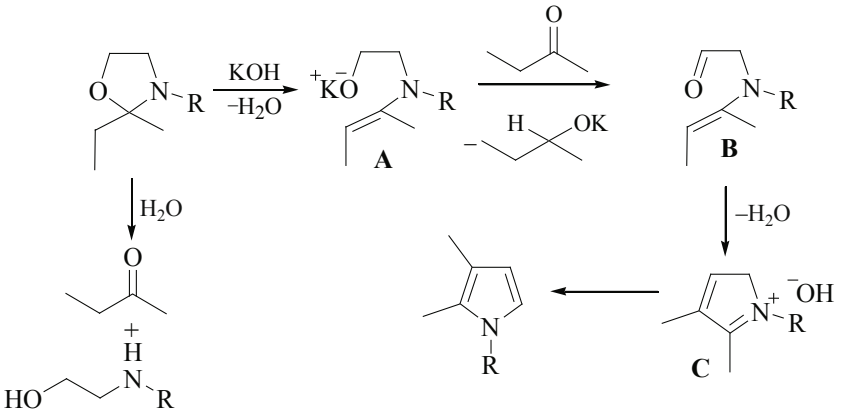
However it is not excluded that the process results in the total hydrolysis of the oxazolidine derivatives into ketone and amino alcohol, subsequent Oppenauer oxidation of amino alcohol to aminoaldehyde and the condensation of the latter with ketone, like in the Knorr synthesis of pyrrole compounds in Piloty version [7]. This assumption is confirmed by the formation of 1-(hydroxyethyl)-4,5,6,7-tetrahydroindole in the reaction of 2,2'-iminodiethanol with cyclohexanone in the presence of KOH [8].

The attempts to synthesize pyrrole derivatives from *N*-unsubstituted oxazolidines **VIIa, VIIb** were unsuccessful. In all cases compounds **VIIa, VIIb** suffered complete decomposition giving 2-aminoethanol (**VIII**) and alcohol **IIIh, IIIk**, the reduction product of the intermediate carbonyl compounds, but instead of pyrrole derivatives only tar was obtained (Scheme 4).

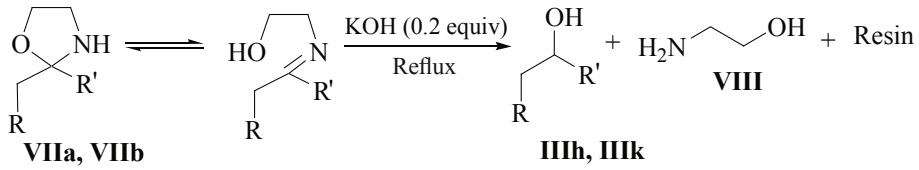
Evidently this reaction route is due to the existence of *N*-unsubstituted oxazolidine in a tautomeric equilibrium with iminoalcohols [9], and just the latter undergo the oxidation followed by condensation into tar.

Yet it was reported that the acid-catalyzed cleavage of cyclohexanespiro-2-oxazolidine (**VIIa**) led to the formation in a low yield (5.2%) of 1-(2-hydroxyethyl)-

Scheme 3.

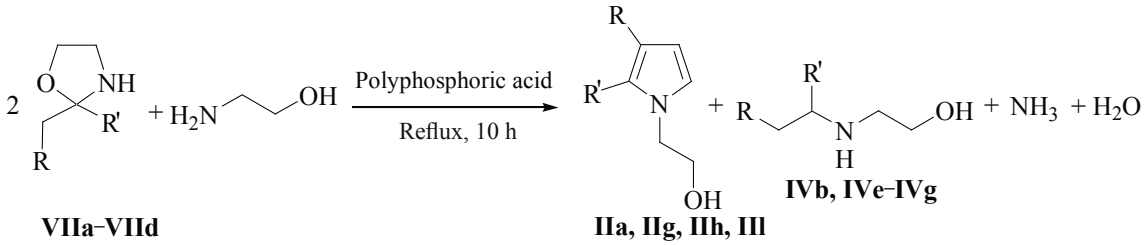


Scheme 4.



R + R' = $(CH_2)_4$ (**VIIa, IIIk**); R = H, R' = Ph (**VIIb, IIIh**).

Scheme 5.



R + R' = $(CH_2)_4$ (**VIIa, III, IVb**); R = H, R' = Ph (**VIIb, IIh, IVe**); R + R' = $(CH_2)_5$ (**VIIc, IIg, IVf**); R = H, R' = Me (**VIId, IIa, IVg**).

4,5,6,7-tetrahydroindole (**III**) and a complex mixture of unidentified substances [4].

In continuation of the study of this reaction we found that in 2-aminoethanole it proceeded more selectively forming prevailingly tetrahydroindole **III**, *N*-(2-hydroxyethyl)cyclohexylamine (**IVb**), ammonia, and water. The lack of other reaction products (besides tars) makes it possible to describe this process with a stoichiometric equation (Scheme 5).

By extension of this approach to other *N*-unsubstituted oxazolidines **VIIb–VIId** obtained from the corresponding ketones and 2-aminoethanol we demonstrated that the reaction possessed a general character and afforded a series of 1-(2-hydroxyethyl)pyrroles **IIa, IIg, IIh** and *N*-substituted amino alcohols **IVe–IVg** (Scheme 5). Yields of compounds **IIa, IIg, IIh, III** were 19–46%, of **IVb, IVe–IVg**, 18–48%.

The structure of compounds **IIa–III, V, VI** is confirmed by the IR and ^{1}H NMR spectra. Their IR spectra contain absorption bands in the region 1372–1670 and 3092–3118 cm^{-1} corresponding to the vibrations of the pyrrole skeleton and to the stretching vibrations of the C–H bond of the pyrrole ring. The wide absorption band in the region 3391–3453 cm^{-1} in the spectra of a number of *N*-(hydroxyalkyl)pyrroles **IIa–IIh, IIk, III, V, VI** originates from the stretching vibrations of the O–H bond.

In the ^{1}H NMR spectra of compounds **IIa–III, V, VI** signals appear belonging to the protons of the pyrrole ring with the chemical shifts 6.23–6.45 (H^2), 5.77–6.19 (H^3), 5.75–6.19 (H^4), and 6.26–6.77 ppm (H^5). In the ^{1}H NMR spectrum of the mixture of isomers **V, VI** two doublets are present at 5.91 and 6.50 ppm (*J* 2.7 Hz) belonging to the pyrrole ring protons of compound **V** in the positions *4* and *5*, a triplet at 6.02 ppm (*J* 3.1 Hz), and two multiplets with the chemical shifts 5.84 and 6.56 ppm, corresponding to the pyrrole ring protons of compound **VI** in the positions *4*, *3*, and *5* respectively. The integral intensities of the pyrrole ring protons of compounds **V, VI** show that the isomers are formed in equimolar ratio.

The comparison of yields of pyrrole series compounds obtained from the corresponding oxazolidine derivatives under basic and acidic catalysis conditions shows the preparative advantage of the basic catalysis. Thus while the yields of 1-(hydroxyethyl)-2-methylpyrrole (**IIa**) in both conditions are comparable, the yields of compounds **IIg, IIh, III** at the use of acid catalysis are 1.5–2.5 times smaller. Besides the necessity to use a large excess of 2-aminoethanol also should be regarded as a disadvantage of the acid catalysis.

It should also be noted that the aminoalcohols and alcohols formed as a result of the basic catalysis can be used again in the synthesis of oxazolidine after simple oxidation of the alcohols into carbonyl compounds. The isolation of the products from the reaction mixture is es-

sentially simplified by extraction of aminoalcohols with water, and the remaining alcohols and pyrrole derivatives are easily separated by distillation due to a large difference in the boiling points.

Although the yields of the pyrrole derivatives are relatively low (10–41% with respect to oxazolidine or 20–81% taking into account the stoichiometry of the equation cited in Scheme 1), the preparation of *N*-unsubstituted pyrroles is impossible, and the reaction conditions are severe (large concn. of potassium hydroxide and high temperature), the main advantage of this method is the simple procedure of the preparation of initial compounds of oxazolidine series by condensation of carbonyl compounds with amino alcohols which in their turn are available commercial products. Hence assembling of the pyrrole ring and the synthesis of *N*-alkyl- and *N*-(hydroxyalkyl)pyrrole derivatives is performed from simple readily available material.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker DPX-400 (400.13 MHz) in $CDCl_3$ at 26°C, internal reference HMDS. IR spectra were recorded on a Bruker Vertex-70 from thin films. GLC analysis was carried out on a chromatograph LKhM-80, detector catharometer, carrier gas helium, steel column (3000 × 3 mm), stationary phase 3% OV-17 on Inerton Super (0.160–0.200 mm).

Oxazolidine derivatives Ia–Il, VIIa–VIId were obtained by condensation of carbonyl compounds with amino alcohols by methods [10]. All initial compounds were purchased from Aldrich and Alfa Aesar and were used without additional purification.

Cleavage of oxazolidine derivatives Ia–Il, VIIa,VIIb in the presence of alkaline. *a.* A mixture of 0.2 mol of compound **Ia–Il, VIIa, VIIb** and 0.04 mol of powdered KOH was refluxed at stirring till complete conversion of initial oxazolidine (GLC monitoring). Then the cooled reaction mixture was dissolved in 100 mL of benzene, washed with water (3 × 50 mL). The benzene layer was dried with K_2CO_3 and distilled in a vacuum to isolate alcohols **IIIa–IIIk** and compounds of pyrrole series **IIa–IIk, V**, **VI**. The distillation of water layer provided the corresponding amino alcohols **IVa–IVd, VIII**.

Cleavage of oxazolidine derivatives VIIa–IVd in the presence of acid in the solution of 2-aminoethanol. *b.* A mixture of 0.2 mol of compound **VIIa–VIId**, 1 mol of 2-aminoethanol, and 1.0 g of polyphosphoric acid was refluxed for 10 h. Then the cooled reaction mixture was diluted with 100 mL of benzene, washed with water (3 × 100 mL). The benzene layer was dried with K_2CO_3 and distilled in a vacuum to isolate pyrrole derivatives **IIa, IIg, IIh, III**. The distillation of water layer provided the aminoalcohols **IVb**, **IVe–IVg**.

1-(2-Hydroxyethyl)-2-methylpyrrole (IIa). Yield 2.50 g (20%) (*a*), 2.37 g (19%) (*b*), bp 95–96°C (4 mm Hg), d_4^{20} 1.0378, n_D^{20} 1.5171 {bp 43–45°C (0.8 mm Hg) [11]}. IR spectrum, ν, cm^{-1}: 3420 (OH), 3105 (=CH), 1550, 1502, 1460 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.10 s (3H, Me), 3.20 br.s (1H, OH), 3.56 t (2H, NCH_2, ^3J 5.5 Hz), 3.77 t (2H, CH_2O, ^3J 5.5 Hz), 5.77 m (1H, H^3), 5.90 m (1H, H^4), 6.59 m (1H, H^5). Found, %: C 67.31; H 8.79; N 11.03. $C_7H_{11}NO$. Calculated, %: C 67.17; H 8.86; N 11.19.

1-(2-Hydroxyethyl)-2-ethyl-3-methylpyrrole (IIb). Yield 12.41 g (81%) (*a*), bp 106–107°C (3 mm Hg), d_4^{20} 0.9982, n_D^{20} 1.5101. IR spectrum, ν, cm^{-1}: 3450 (OH), 3100 (=CH), 1670, 1495 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.00 t (3H, MeCH_2, ^3J 7.6 Hz), 1.93 s (3H, C^{3}Me), 2.47 q (2H, MeCH_2, ^3J 7.6 Hz), 3.14 br.s (1H, OH), 3.71 t (2H, NCH_2, ^3J 5.5 Hz), 3.83 t (2H, CH_2O, ^3J 5.5 Hz), 5.68 d (1H, H^4, ^3J 2.5 Hz), 6.26 d (1H, H^5, ^3J 2.5 Hz). Found, %: C 70.31; H 9.92; N 9.22. $C_9H_{15}NO$. Calculated, %: C 70.55; H 9.87; N 9.14.

1-(2-Hydroxyethyl)-3-isopropylpyrrole (IIc). Yield 4.60 g (30%) (*a*), bp 115–116°C (5 mm Hg), d_4^{20} 0.9755, n_D^{20} 1.4988. IR spectrum, ν, cm^{-1}: 3445 (OH), 3100 (=CH), 1650, 1500 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.18 d (6H, 2Me, ^3J 6.9 Hz), 2.24 br.s (1H, OH), 2.79 m (1H, CH), 3.79 t (2H, NCH_2, ^3J 5.5 Hz), 3.91 t (2H, CH_2O, ^3J 5.5 Hz), 6.02 m (1H, H^4), 6.45 s (1H, H^2), 6.58 m (1H, H^5). Found, %: C 70.41; H 9.93; N 9.10. $C_9H_{15}NO$. Calculated, %: C 70.55; H 9.87; N 9.14.

1-(2-Hydroxyethyl)-2-propyl-3-ethylpyrrole (IId). Yield 11.60 g (64%) (*a*), bp 106–109°C (2 mm Hg), d_4^{20} 0.9678, n_D^{20} 1.5040 {bp 109–111°C (2.7 mm Hg), d_4^{20} 0.9676, n_D^{20} 1.5038 [6]}. IR spectrum, ν, cm^{-1}: 3443 (OH), 3094 (=CH), 1651, 1489, 1463, 1375 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, CH_2CH_2Me, ^3J 7.4 Hz), 1.14 t (3H, CH_2Me, ^3J 7.6 Hz), 1.47 m (2H, CH_2CH_2Me), 2.39 q (2H, CH_2Me, ^3J 7.6 Hz), 2.48 t (2H, CH_2CH_2Me, ^3J 7.4 Hz), 2.60 br.s (1H, OH), 3.71 t (2H, NCH_2, ^3J 5.5 Hz), 3.86 t (2H, CH_2O, ^3J 5.5 Hz), 5.97 d (1H, H^4, ^3J 2.5 Hz), 6.52 d (1H, H^5, ^3J 2.5 Hz). Found,

%: C 72.97; H 10.51; N 7.66. $C_{11}H_{19}NO$. Calculated, %: C 72.88; H 10.56; N 7.73.

2-Butyl-1-(2-hydroxyethyl)-3-propylpyrrole (IIe). Yield 11.09 g (53%) (*a*), bp 125–127°C (2 mm Hg), d_4^{20} 0.9479, n_D^{20} 1.4965. IR spectrum, ν, cm^{-1}: 3441 (OH), 3093 (=CH), 1657, 1490, 1465, 1377 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, $CH_2CH_2CH_2\underline{Me}$, ^3J 7.2 Hz), 0.94 t (3H, $CH_2CH_2\underline{Me}$, ^3J 7.4 Hz), 1.32–1.56 m (6H, $CH_2C\underline{H}_2Me$, $CH_2C\underline{H}_2C\underline{H}_2Me$), 2.02 br.s (1H, OH), 2.32 t (2H, $C\underline{H}_2CH_2Me$, ^3J 7.7 Hz), 2.50 t (2H, $C\underline{H}_2CH_2CH_2Me$, ^3J 7.5 Hz), 3.76 t (2H, NCH_2, ^3J 5.5 Hz), 3.90 t (2H, CH_2O, ^3J 5.5 Hz), 5.96 d (1H, H^4, ^3J 2.6 Hz), 6.53 d (1H, H^5, ^3J 2.6 Hz). Found, %: C 74.46; H 11.15; N 6.54. $C_{13}H_{23}NO$. Calculated, %: C 74.59; H 11.07; N 6.69.

1-(2-Hydroxyethyl)-3-octylpyrrole (IIf). Yield 11.84 g (53%) (*a*), bp 99–101°C (3 mm Hg), d_4^{20} 0.9380, n_D^{20} 1.5050. IR spectrum, ν, cm^{-1}: 3400 (OH), 3110 (=CH), 1650, 1494 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.84 t (3H, Me, ^3J 6.0 Hz), 1.21–1.38 m [12H, $(CH_2)_6$], 2.35 t (2H, C^3CH_2, ^3J 7.0 Hz), 3.20 br.s (1H, OH), 3.79 t (2H, NCH_2, ^3J 5.5 Hz), 3.91 t (2H, CH_2O, ^3J 5.5 Hz), 5.79 m (1H, H^4), 6.26 s (1H, H^2), 6.36 m (1H, H^5). Found, %: C 75.33; H 11.37; N 6.20. $C_{14}H_{25}NO$. Calculated, %: C75.28; H 11.28; N 6.27.

1-(2-Hydroxyethyl)-5,6,7,8-tetrahydrocyclohepta(*b*)pyrrole (IIg). **Yield** 13.62 g (76%) (*a*), 8.25 g (46%) (*b*), bp 140–142°C (3 mm Hg), d_4^{20} 1.0651, n_D^{20} 1.5410 {bp 138–140°C (4 mm Hg), d_4^{20} 1.0652, n_D^{20} 1.5408 [5]}. IR spectrum, ν, cm^{-1}: 3436 (OH), 3118 (=CH), 1486, 1443, 1372 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.72–1.74 m (4H, C^5H_2, C^6H_2), 1.85–1.88 m (2H, C^7H_2), 2.61–2.64 m (2H, C^8H_2), 2.68–2.74 m (3H, OH, C^4H_2), 3.73 t (2H, NCH_2, ^3J 5.5 Hz), 3.96 t (2H, CH_2O, ^3J 5.5 Hz), 5.94 d (1H, H^3, ^3J 2.4 Hz), 6.48 d (1H, H^2, ^3J 2.4 Hz). Found, %: C 73.61; H 9.60; N 7.76. $C_{11}H_{17}NO$. Calculated, %: C 73.70; H 9.56; N 7.81.

1-(2-Hydroxyethyl)-2-phenylpyrrole (IIh). Yield 6.37 g (34%) (*a*), 4.11 g (22%) (*b*), bp 142–143°C (2 mm Hg), d_4^{20} 1.1129, n_D^{20} 1.6021. IR spectrum, ν, cm^{-1}: 3391 (OH), 3101, 3060, 3028 (=CH), 1651, 1602, 1493, 1472 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.13 br.s (1H, OH), 3.61 t (2H, NCH_2, ^3J 5.5 Hz), 3.99 t (2H, CH_2O, ^3J 5.5 Hz), 6.16–6.19 m (2H, H^3, H^4), 6.77 m (1H, H^5), 7.24–7.35 m (5H, Ph). Found, %: C 77.00; H 6.95; N 7.34. $C_{12}H_{13}NO$. Calculated, %: C 76.98; H 7.00; N 7.48

1-Cyclohexyl-3-ethylpyrrole (IIi). Yield 10.64 g (60%) (*a*), bp 156–157°C (2 mm Hg), d_4^{20} 0.9282, n_D^{20} 1.4869. IR spectrum, ν, cm^{-1}: 3110, 3090 (=CH), 1650, 1500 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.13 t (3H, Me, ^3J 6.0 Hz), 1.30–1.95 m [10H, $(CH_2)_5$], 2.42 q (2H, $MeC\underline{H}_2$, ^3J 6.0 Hz), 3.60 m (1H, NCH), 5.75 m (1H, H^4), 6.30 s (1H, H^2), 6.42 m (1H, H^5). Found, %: C 81.20; H 10.96; N 7.78. $C_{12}H_{19}N$. Calculated, %: C 81.30; H 10.80; N 7.90.

1-Butyl-3-isopropylpyrrole (IIj). Yield 12.06 g (73%) (*a*), bp 68–70°C (3 mm Hg), d_4^{20} 0.8642, n_D^{20} 1.4705 {bp 66–68°C (2.7 mm Hg), d_4^{20} 0.8639, n_D^{20} 1.4701 [5]}. IR spectrum, ν, cm^{-1}: 3120 (OH), 3110 (=CH), 1650, 1500 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, Me, ^3J 7.0 Hz), 0.96–1.59 m (4H, $C\underline{H}_2C\underline{H}_2Me$), 1.14 d (6H, $CH\underline{Me}_2$, ^3J 6.9 Hz), 2.67 m (1H, $C\underline{H}Me_2$), 3.65 t (2H, NCH_2, ^3J 7.0 Hz), 5.80 m (1H, H^4), 6.23 s (1H, H^2), 6.31 m (1H, H^5). Found, %: C 80.07; H 11.43; N 8.34. $C_{11}H_{19}N$. Calculated, %: C 79.94; H 11.59; N 8.47.

1-(2-Hydroxypropyl)-4-methyl-2-phenylpyrrole (IIk). Yield 7.10 g (33%) (*a*), bp 163–165°C (5 mm Hg), d_4^{20} 1.0421, n_D^{20} 1.5731. IR spectrum, ν, cm^{-1}: 3410 (OH), 3105 (=CH), 1660, 1585, 1490 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.20 d (3H, Me, ^3J 5.4 Hz), 2.03 s (3H, C^4Me), 3.57–3.74 m (2H, $NC\underline{H}_2CHOH$), 3.96 m (2H, $NCH_2C\underline{H}O\underline{H}$), 6.03 s (1H, H^3), 6.57 m (1H, H^5), 7.26–7.34 m (5H, Ph). Found, %: C 78.23; H 8.06; N 6.60. $C_{14}H_{17}NO$. Calculated, %: C 78.10; H 7.96; N 6.51.

1-(2-Hydroxyethyl)-4,5,6,7-tetrahydroindole (III). Yield 7.27 g (44%) (*b*), bp 134–136°C (3 mm Hg), d_4^{20} 1.0803, n_D^{20} 1.5418. {bp 136–138°C (4 mm Hg), d_4^{20} 1.0800, n_D^{20} 1.5400 [8]}. IR spectrum, ν, cm^{-1}: 3433 (OH), 3092 (=CH), 1576, 1487, 1367 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.73–1.79 m (2H, C^5H_2), 1.83–1.89 m (2H, C^6H_2), 2.09 br.s (1H, OH), 2.55 m (4H, C^4H_2, C^7H_2), 3.79 t (2H, NCH_2, ^3J 5.5 Hz), 3.91 t (2H, CH_2O, ^3J 5.5 Hz), 5.98 d (1H, H^3, ^3J 2.7 Hz), 6.59 d (1H, H^2, ^3J 2.7 Hz). Found, %: C 72.63; H 9.20; N 8.42. $C_{10}H_{15}NO$. Calculated, %: C 72.69; H 9.15; N 8.48.

1-(2-Hydroxyethyl)-2-methyl-3-propylpyrrole (**V**) and **2-butyl-1-(2-hydroxyethyl)pyrrole** (**VI**). Yield 10.20 g (61%) (*a*), bp 117–119°C (4 mm Hg), d_4^{20} 0.9685, n_D^{20} 1.5016. IR spectrum, ν, cm^{-1}: 3450 (OH), 3100 (=CH), 1670, 1495 (=CH). ^{1}H NMR spectrum, δ, ppm: 0.92–0.99 m (3H, $2\underline{Me}CH_2$), 1.41–1.68 m [3H, $Me(C\underline{H}_2)_2CH_2$, $MeC\underline{H}_2CH_2$], 2.15 s (1.5H, MeC^2), 2.37 t (1H, $MeCH_2C\underline{H}_2$, ^3J 7.8 Hz), 2.58 t [1H, $Me(CH_2)_2C\underline{H}_2$, ^3J 7.6 Hz], 3.21 br.s (1H, OH), 3.76–3.81 m (2H, CH_2O), 3.92–3.98 m (2H, NCH_2) 5.84 m [0.5H, H^3 (**VI**)], 5.91 d [0.5H, H^4 (**V**), ^3J 2.7 Hz], 6.02 t [0.5H, H^4 (**VI**), ^3J 3.1 Hz], 6.50 d [0.5H, H^5 (**V**), ^3J 2.7 Hz], 6.56 m [0.5H,

H[5] (VI)]. Found, %: C 71.68; H 10.38; N 8.22. $C_{10}H_{17}NO$. Calculated, %: C 71.81; H 10.25; N 8.37.

2-(Cyclohexylamino)ethanol (IVb). Yield 6.30 g (44%), bp 122–126°C (12 mm Hg), mp 48°C {bp 123–127°C (14 mm Hg), mp 50°C [12]}.

2-[(1-Phenylethyl)amino]ethanol (IVe). Yield 2.97 g (18%), bp 140–143°C (12 mm Hg), d_4^{20} 1.0319, n_D^{20} 1.5349 {bp 139–140°C (9 mm Hg), d_4^{25} 1.0311, n_D^{25} 1.5326 [13]}.

2-(Cycloheptylamino)ethanol (IVf). Yield 7.55 g (48%), bp 126–128°C (5 mm Hg), d_4^{20} 0.9717, n_D^{20} 1.4931. IR spectrum, cm^{-1}: 3367, 3294, 2924, 2854, 1460, 1356, 1207, 1116, 1058, 929, 851, 784, 756. ^1H NMR spectrum, δ, ppm: 1.38–1.84 m [12H, $(CH_2)_6$], 2.59–2.64 m (3H, CHN, NH, OH), 2.72 t (2H, NCH_2, ^3J 5.3 Hz), 3.61 t (2H, CH_2O, ^3J 5.3 Hz). Found, %: C 68.91; H 12.04; N 8.78. $C_9H_{19}NO$. Calculated, %: C 68.74; H 12.18; N 8.91.

2-(Isopropylamino)ethanol (IVg). Yield 3.51 g (34%), bp 77–79°C (12 mm Hg), d_4^{20} 0.9055, n_D^{20} 1.4402 {bp 76–77°C (15 mm Hg), d_4^{25} 0.8977, n_D^{25} 1.4390 [13]}.

REFERENCES

1. Gossauer, A., *Die Chemie der Pyrrole*, Berlin: Springer-Verlag, 1974; Jones R.A.and Bean, G.P., *The Chemistry of Pyrroles*, New York: Academic Press, 1977; Trofimov, B.A., *The Chemistry of Heterocyclic Compounds. Part 2,* Jones*,* R.A.*,* New York: Wiley, 1992, vol. 48, p. 131; Trofimov, B.A., Mikhaleva, A.I., Schmidt, E.Yu., Sobenina, L.N., *Adv. Heterocycl. Chem*. 2010, vol. 99, p. 209; Baumann, M., Baxendale, I.R., Ley, S.V. and Nikbin, N. *Beilst.,* 2011, vol. 7, p. 442; Trofimov, B.A., Mikhaleva, A.I., Shmidt, E.Yu., and Sobenina, L.N., *Khimiya pirola. Novye stranitsy* (Chemistry of Pyrrole. New Trends), Novosibirsk: Nauka, 2012; Song, S., Ko, S.-J., Shin, H., Jin, Y., Kim, I., Kim, J.Y., and Suh, H., *Sol. Energy Mater. Sol. Cell,* 2013, vol. 112, p. 120; Ates, M., *Mater. Sci. Eng. C,* 2013, vol. 33*,* no. 4*,* p. 1853.
2. Ono, N. *Heterocycles,* 2008, vol. 75, p. 243; Estevez, V., Villacampa, M., and Menendez, J.C.*, Chem. Soc. Rev*., 2010, vol. 39, p. 4402; Bergman, J. and Janosik, T., *Mod. Heterocycl. Chem. Sh. 4*, Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2011, p. 269; Sakhuja, R., Panda, S. S., and Bajaj, K., *Curr. Org. Chem*. 2012, vol. 16, p. 789.
3. Kukharev B.F., Stankevich V.K., and Kukhareva V.A., *Chem. Heterocycl. Comp*, 1986, no. 4, p. 440.
4. Kukharev, B.F., *Russ. Chem. Bull.,* 1997, vol. 46, p. 1482.
5. Woodward, R.B., Wendler, N.L., and Brutschu, F.J., *J. Am. Chem. Soc*. 1945, vol. 67, p. 1425.
6. Kukharev, B.F., Stankevich, V.K., and Kukhareva, V.A., *Khim. Geterotsikl. Soedin*., 1984, vol. 5, p. 700.
7. Piloty, O. and Hirsch, P., *Lieb. Ann. Chem*., 1913, vol. 395, p. 63.
8. Kukharev, B.F. and Atavin, A.S., *Zh. Org. Khim*., 1974, vol. 10, p. 670.
9. Bergman, E.D., *Chem. Rev.,* 1953, vol. 53, p. 309.
10. Cope, A.C. and Hancock, E.M., *J. Am. Chem. Soc.* 1944, vol. 66, p. 1453; Bergmann, E.D., Gil-Av, E., and Pinchas, S., *J. Am. Chem. Soc.,* 1953, vol. 75, p. 358; Neelakantan, L., *J. Org. Chem.,* 1971, vol. 36, p. 2256; Saavedra, J.E., *J. Org. Chem*., 1985, vol. 50, p. 2379.
11. Amarnath, V., Amarnath, K., Amarnath, K., Davies, S., and Roberts, L., *J. Chem. Res. Toxicol.,* 2004, vol. 17, no. 3*,* p. 410.
12. Malinovskii, M.S., *Okisi olefinov i ikh proizvodnye* (Olefin Oxides, and Their Derivatives), Moscow: GKhI, 1961, p. 263.
13. Cope, A.C. and Hancock, E.M., *J. Am. Chem. Soc.,* 1942, vol. 64, p. 1503.