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SELECTIVE MONOALKYLATION AND DITHIOCARBONYLATION OF ETHYLENEDIAMINE

Abstract. Selective monoalkylation and one-pot monoalkylation-dithiocarbonylation reactions of ethylenediamine were carried out in good and high yields (60-78%). The structures of the obtaining products – N-alkylethane-1,2-diamines and sodium 2-(alkylamino)ethyl dithiocarbamates were confirmed by IR, ^{1}H NMR and ^{13}C spectra.

Key words: ethylenediamine, alkylation, alkyl bromide, dithiocarbonylation, sodium 2- (alkylamino)ethylcarbamodithioates.

Introduction. Before we in [1, 2] have got excellent results with sodium N-(3-phenylprop-2-yn-1-yl)-N-butyldithiocarbamate (AN-16) as rooting accelerator on cuttings of blackcurrant, exceeding over 10 % results obtained with the help of a known rooting agent - indolylacetic acid (IAA) [3]. At the same time, its working concentration was as10 times lower as than the working concentration of IAA. This compound proved highly effective in stimulating the laying of generative buds of fruit trees, which makes it promising for use in innovative technologies for producing fast-growing seedlings [4], and it is also of practical interest in the cultivation of wild medicinal plants, for example, *Serratula coronata*, increasing threefold the germination of seeds [5].

In this regard, the search of highly effective plant growth regulators among the new sodium dithiocarbamates of alkylated diamines can be fruitful.

EXPERIMENTAL PART

The spectra of NMR were recorded on a JNN-ECA 400 spectrometer from Jeol (Japan). The working frequency of the spectrometer is 400 MHz on the ^{1}H and 100 MHz on ^{13}C nuclear cores, respectively. The survey was carried out at room temperature in a solvent of DMSO. Chemical shifts are measured relative to signals of residual protons or carbon atoms of a deuterated solvent.

The melting points of the obtained substances were determined on a Boetius heating table. The IR spectra are recorded on a Nicolet 5700 spectrometer in KBr tablets. The course of the reaction and the purity of the products were monitored by thin-layer chromatography on plates of "Silufol UV-254", eluent - benzene: ethanol, 1:3 with the appearance of spots of substances with iodine vapor.

N-butylethane-1,2-diamine 1. A 3-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel was charged with 5 ml (0.075 mol) of ethylenediamine, 20 ml of ethanol and 7.3 g (0.074 mol) of acetate potassium were added. At a temperature of 50 °C 7.9 ml (0.075 mol) of freshly distilled butyl bromide in 10 ml of ethanol was added dropwise over a period of 30 minutes. The reaction was monitored by thin layer chromatography. After a two-day stirring, TLC showed the completion of the reaction to the disappearance of the octyl bromide and ethylenediamine spots. After removal of the precipitate and ethanol, an oily substance was obtained. As a result, 5.7 g (a yield 66%) of N-butylethane-1,2-diamine **1** was obtained.

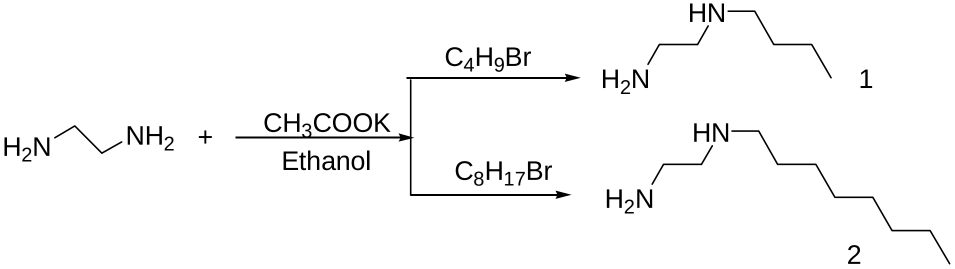
N-octylethane-1,2-diamine 2. A 3-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel was charged with 5 ml (0.075 mol) of ethylenediamine, solute in 20 ml of ethanol and 7.3 g (0.074 mol) of potassium acetate. At a temperature of 50 °C, 16 ml (0.09 mole) of freshly distilled octyl bromide solute in 20 ml of ethanol was added dropwise to the reaction flask over a period of 30 minutes. The reaction was monitored by thin layer chromatography. After a two-day stirring, TLC showed the completion of the reaction to the disappearance of the octyl bromide and ethylenediamine spots. After removal of the precipitate and ethanol, an oily substance was obtained. As a result, 10.1 g of N-octylethane-1,2-diamine **2** was obtained in a yield of 78%.

Sodium 2-(heptylamino)ethyl-dithiocarbamate 3. 10 ml (0.15 mol) of ethylenediamine solute in 20 ml of ethanol were introduced into a three-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. 12 ml (0.076 mole) of heptyl bromide was added dropwise to the reaction flask within 30 minutes. At a temperature of 50-60 °C the reaction mixture was stirred for 4 hours. The reaction was monitored by thin layer chromatography (silufol, eluent benzene: alcohol, 1:3). After the disappearance of the spots of heptyl bromide and ethylenediamine, the reaction temperature was lowered to -5 °C. 3.27 g (0.082 mol) of sodium hydroxide dissolved in water and 4.9 ml (0.079 mol) of carbon disulphide were introduced into the flask. After completion of the reaction, the mass was filtered off, ethanol was removed. The combined crystalline mass was washed with acetonitrile. As a result, 23 g of the sodium 2-(heptylamino)ethyldithiocarbamate **3**, mp 120-122 °C was obtained in a yield of 60%.

Sodium 2-(octylamino)ethyl-dithiocarbamate 4. 10 ml (0.15 mol) of ethylenediamine solute in 20 ml of ethanol were introduced into a three-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. 13 ml (0.075 mole) octyl bromide was added dropwise to the reaction flask within 30 minutes. At a temperature of 50-60 °C, the reaction mixture was stirred for 4 hours. The reaction was monitored by thin layer chromatography. After the disappearance of the octyl bromide and ethylenediamine stains, the reaction temperature was lowered to -5 °C. 2.99 g (0.074 mol) of sodium hydroxide dissolved in water and 5.1 ml (0.08 mol) of carbon disulphide were introduced into the flask. After completion of the reaction, the crystalline mass was filtered off, ethanol was removed. The combined crystalline mass was washed with acetonitrile. As a result, 12.75 g (63% yield) of the sodium 2-(octylamino)ethyl-dithiocarbamate, mp 133 °C were obtained.

RESULTS AND DISCUSSION

In order to synthesize the new hetero-organic compounds and study their chemical, physico-chemical and biological properties, in particular physiological and surface activity, we carried out the selective monoalkylation of ethylenediamine by the method we used earlier for the N-alkylation of monoethanolamine [6]. Alkylation of ethylenediamine was carried out with alkyl bromide in an ethanol medium at the presence of potassium acetate on equimolar ratio of the reagents at the reaction temperature about 50-55 °C. After the usual procedure of isolation the product, N-butylethane-1,2-diamine **1**was obtaind in an individual form by yield of 66% and N-octylethane-1,2-diamine **2** by yield of 78%.

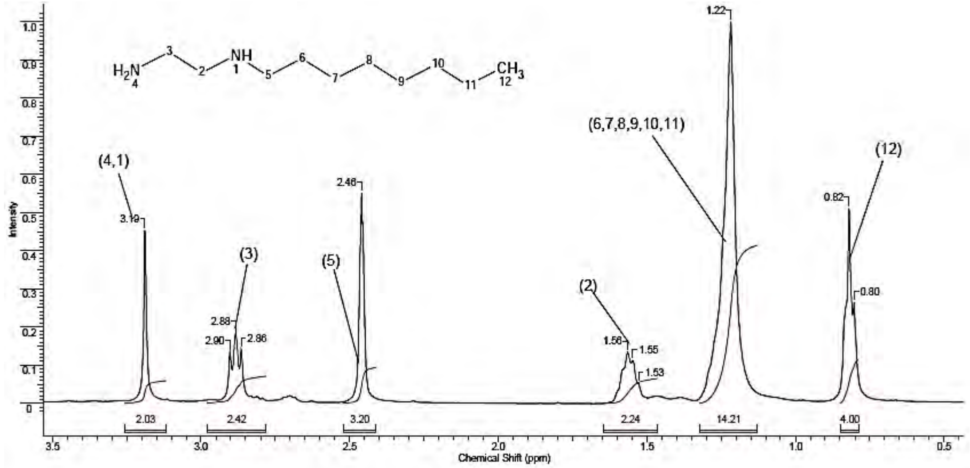


The structures of the synthesized compounds were proved by the methods of IR, ^{1}H NMR and ^{13}C spectroscopy (the spectra of the synthesized N-octylethane-1.2-diamine **2** are shown in figures 1–5).

In the IR spectra of amines **1** and **2**, absorption bands at 3479 cm^{-1}, 3412 cm^{-1} and 1671 cm^{-1}, characteristic for the NH_2 group, are observed. In the regions 2955 cm^{-1}, 2887 and 2935 cm^{-1}, intensive bands of stretching vibrations of C-H bonds characteristic for saturated hydrocarbon substituents are observed.

In the PMR spectrum of N-butyl ethane-1,2-diamine **1**, there is a broadened singlet of CH_3 protons at 0.98 ppm, proton’s signals of $(CH_2)_3$-methylene groups appear in the range of 1.0-2.65 ppm. Protons of NH-$\underline{CH_2}$ groups of the ethylene bridge resonate at 3.4-3.5 ppm. as a multiplet, NH-protons of amine groups are resonated at 3.0-3.10 ppm. In the PMR spectrum of N-octylethane-1,2-diamine **2**, (Figure 1), the signal of the terminal methyl group (H-12) appears as a weakly ordered triplet at 0.82 ppm. Resonance signals of methylene (H-6 - H-11) groups of the octyl fragment are observed as a highly intense broad singlet at 1.22 ppm. The protons of N$\underline{CH_2}$ group (H-5) under the influence of the neighboring nitrogen heteroatom resonate at a region of 2.46 ppm. The protons of the CH_2-groups of the ethylene bridge give signals at a frequency of 1.56 and 2.88 ppm. The highest-frequency signal (3.19 ppm) belongs to the protons of the amino groups.

Figures 2 and 3 show the COSY spectrum and COSY correlations for N-octyl ethane-1,2-diamine **2**, which indicate groups of protons interacting with each other. These data confirm the assignment of signals of the PMR spectrum and the structure of N-octylethane-1,2-diamine **2**.



No.	(ppm)	(Hz)	Height
1	0.80	321.0	0.2646
2	0.82	327.9	0.5108
3	1.22	486.8	1.0000
4	1.53	610.9	0.0529
5	1.55	618.7	0.1119
6	1.56	625.5	0.1336
7	2.46	983.2	0.5511
8	2.86	1145.3	0.1416
9	2.88	1152.6	0.1857
10	2.90	1160.4	0.1344
11	3.19	1274.9	0.4533

No.	(ppm)	Value	Absolute Value
1	[0.79 .. 0.85]	4.000	3.58646e+1
2	[1.13 .. 1.32]	14.207	1.27382e+2
3	[1.46 .. 1.65]	2.238	2.00667e+1
4	[2.41 .. 2.52]	3.201	2.87001e+1
5	[2.78 .. 2.98]	2.425	2.17400e+1
6	[3.12 .. 3.26]	2.025	1.81585e+1

Figure 1 – PMR spectrum of N-octylethane-1,2-diamine **2**

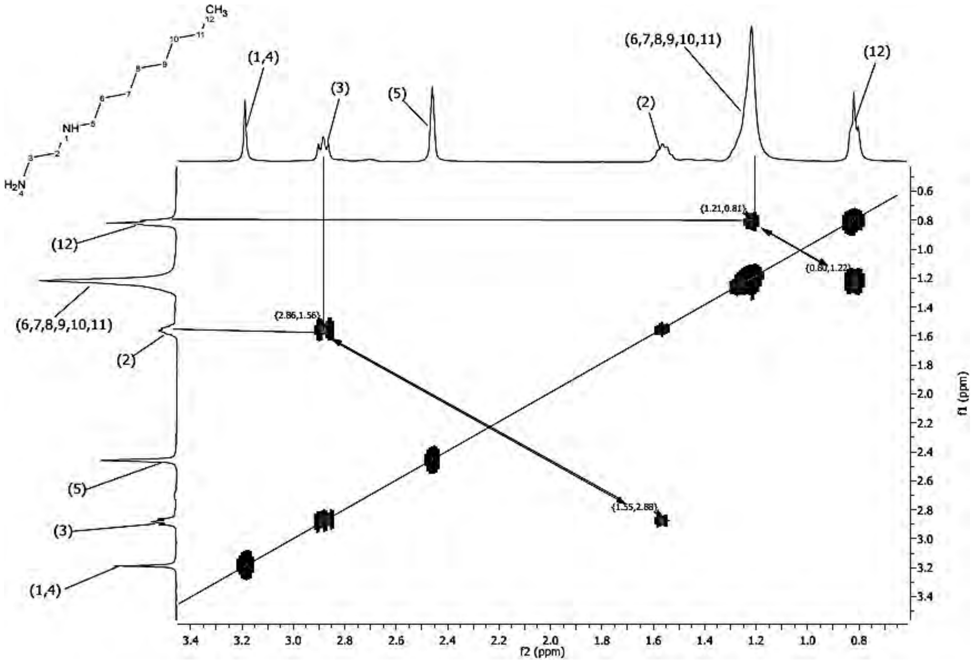


Figure 2 – COSY spectrum of N-octylethane-1,2-diamine **2**

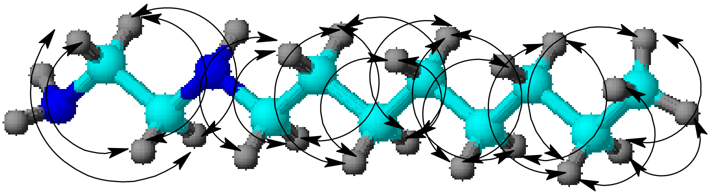
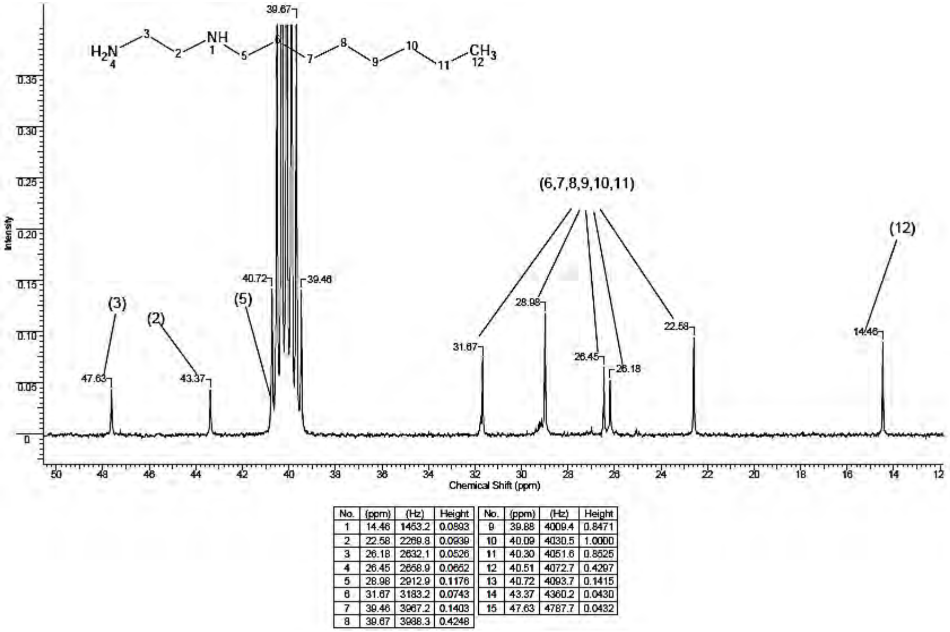


Figure 3 – COSY Correlations for N-octylethane-1,2-diamine **2**

In the carbon spectrum of N-octylethane-1,2-diamine **2** shown in figure 4, the signal of the terminal methyl group of the octyl fragment is observed at 14.46 ppm. The signals of the carbon atoms of C-6 − C-11 methylene groups in the range from 22.58 to 31.67 ppm are observed. Signal of the N-CH_2 group of the octyl substituent is manifested at 40.72 ppm. Signals at 43.37 and 47.63 ppm. can be attributed to the carbon atoms of the ethylene chain C-2 and C-3, respectively.



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	14.46	1453.2	0.0893	9	39.88	4009.4	0.8471
2	22.58	2269.8	0.0939	10	40.09	4030.5	1.0000
3	26.18	2632.1	0.0526	11	40.30	4051.6	0.8525
4	26.45	2658.9	0.0662	12	40.51	4072.7	0.4297
5	28.98	2912.9	0.1176	13	40.72	4093.7	0.1415
6	31.67	3183.2	0.0743	14	43.37	4360.2	0.0430
7	39.46	3967.2	0.1403	15	47.63	4787.7	0.0432
8	39.67	3988.3	0.4248				

Figure 4 – NMR ^{13}C spectrum of N-octylethane-1,2-diamine **2**

The NMR ^{13}C spectrum of N-butylethane-1,2-diamine **1** also shows a signal at 14.0 ppm corresponding to the carbon atom of the terminal CH_3 group, signals at 25.1; 32.0 and 42.2 ppm. are referred to the carbon atoms of the butyl group, the signals at 49.3 and 54.4 ppm. can be attributed to the carbon atoms of the group NH_2-CH_2-CH_2-NH.

Figures 5 and 6 show the HMQC spectrum and HMQC correlations for N-octylethane-1,2-diamine **2**, indicating which carbon atoms interact with certain

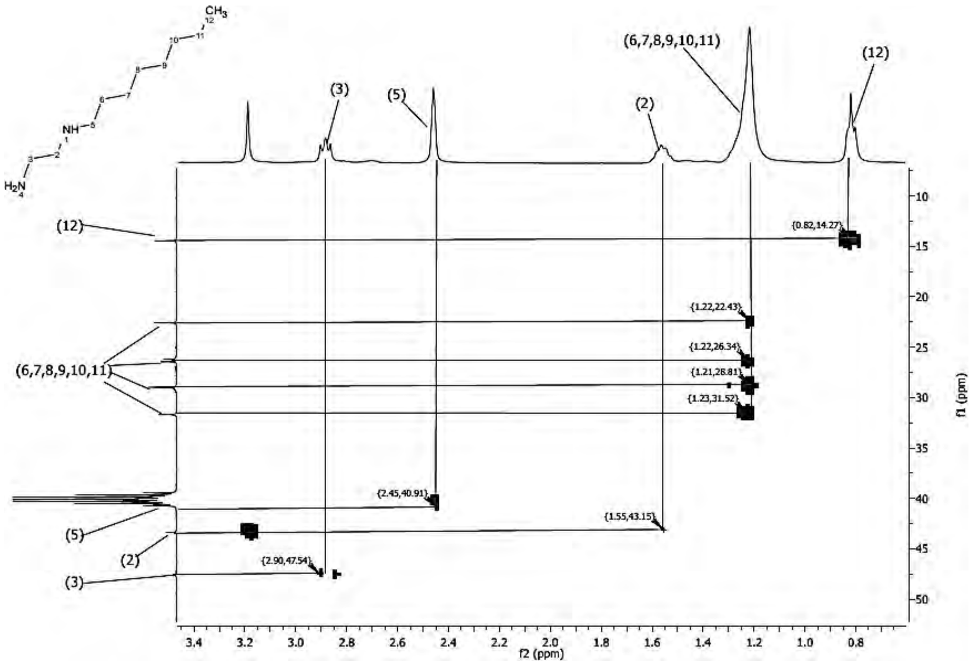


Figure 5 – HMQC spectrum of N-octylethane-1,2-diamine **2**

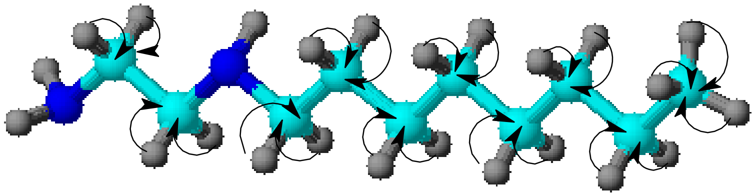
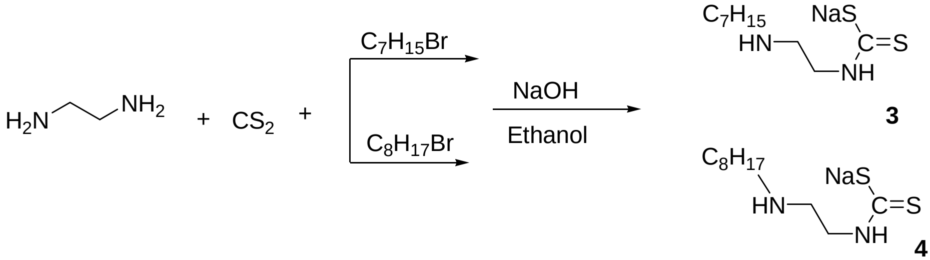


Figure 6 – Correlation of the HMQC compound of N-octylethane-1,2-diamine **2**

proton groups. These data confirm the assignment of the signals from NMR ^{13}C and PMR spectra and the structure of N-octylethane-1,2-diamine **2**.

The sodium dithiocarbamates **3** and **4** were obtained by successive interaction of equimolar amounts of ethylenediamine with alkyl bromide at the temperature 50-60 °C and then with carbon disulphide in the presence of sodium hydroxide at 0-5 °C in an ethyl alcohol medium.



3

4

Dithiocarbamates **3**, **4** settled out of the reaction solution as white crystalline substances with R_f 0.26 and R_f 0.29 (silufol, benzene: alcohol, 1:3), which after reaction finishing are filtered off and washed with acetonitrile. The yields of the sodium salts of 2-(heptylamino)ethyl-dithiocarbamate **3** and 2-(octylamino)ethyl-dithiocarbamate **4** are 60% and 63%, melting points 120-122 °C and 133 °C, respectively.

In the IR spectra of synthesized new dithiocarbamates **3**, **4**, there are absorption bands of C=S bond stretching vibrations in the region of 1420-1460 cm^{-1} and C-S bond in the region of 638-735 cm^{-1}. Absorption bands in the region of 3300-3500 cm^{-1} characteristic for NH groups are also observed. In the region of 2887-2935 cm^{-1} intense bands of stretching vibrations of C-H bonds characteristic for saturated hydrocarbon substituents are observed.

Compounds **3** and **4** are characterized by PMR spectroscopy. A broaden singlet of CH_3 protons is observed in the spectrum at 0.96 - 0.98 ppm. The protons of the $(CH_2)_n$-methylene groups in the region of 1.1-2.6 ppm in the form of multiplets are observed. The protons of the NCH_2 group are resonated in the region of 3.60-3.80 ppm as the multiplets. The protons of the amine group are resonated in the region of 3.0-3.30 ppm.

In the PMR spectrum of the sodium 2-(octylamino) ethyl-dithiocarbamate **4**, a singlet of CH_3-group protons is observed at 0.96. Protons $(CH_2)_n$-methylene groups in the region and 1.1-2.6 ppm in the form of multiplets are observed. The protons of NH-CH_2 groups at 3.73 and 3.60 ppm. in the form of multiplets are resonated, the NH protons of the amine and amide groups are resonated at 3.0 and 3.20 ppm.

Conclusion. Thus, as a result of our studies, the conditions for the selective monoalkylation of ethylenediamine have been experimentally established. For the first time, a one-pot synthesis of sodium 2-(alkylamino)ethyl-dithiocarbamates was carried out. The structure of synthesized compounds is confirmed by physicochemical methods of investigation.

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Резюме

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ЭТИЛЕНДИАМИНДІ СЕЛЕКТИВТІ N-МОНОАЛКИЛДЕУ ЖӘНЕ ДИТИОКАРБОНИЛДЕУ

Этилендиминді бромды алкилдермен этанолды ортада ацетат калий қатысында реагенттердің эквимольді қатынасында 50-55 °С температурада моноалкилдеу нәтижесінде 66% шығыммен N-бутилэтан-1,2-диамин және 78% шығыммен N-октилэтан-1,2-диамин синтезделінді. Әрекеттесудің жалғасы ретінде бір реакциялық колбада эквимольді мөлшерде этиленаминнің алкил броммен 50-60 °С температурада және содан кейін күкіртті көміртекпен натрий гидроксиді қатысында 0-5 °С температурада этил спирті ортасында натрий дитиокарбаматтары алынды. 2-(гептиламино)этилдитиокарбаматтың және 2-(октиламино)этилдитиокарбаматтың шығымдары 60 және 63%, сәйкесінше балқу температуралары 120-122 °С және 133 °С тең. N-алкилэтан-1,2-диаминдер және натрий 2-(алкиламино)этилдитиокарбаматтарының құрылысы ИК, ЯМР ^{1}Н және ^{13}С-спектрлерінің көмегімен дәлелденді. N-октилэтан-1,2-диаминнің COSY және HMQC спектрлері, корреляциясы келтірілген.

Түйін сөздер: этилендиамин, алкилдеу, бромды алкилдер, дитиокарбонилдеу, натрий 2-(алкиламино)этилкарбамодитиоаты.

Резюме

И. Н. Ануарбекова, Н. О. Акимбаева, С. А. Визер, К. Б. Ержанов

СЕЛЕКТИВНОЕ МОНОАЛКИЛИРОВАНИЕ И ДИТИОКАРБОНИЛИРОВАНИЕ ЭТИЛЕНДИАМИНА

Путем селективного моноалкилирования этилендиамина бромистыми алкилами в этанольной среде в присутствии ацетата калия при эквимольном соотношении реагентов и температуре реакции 50-55 °С синтезированы N-бутилэтан-1,2-диамин с выходом 66% и N-октилэтан-1,2-диамин с выходом 78%. Последовательным взаимодействием в одной реакционной колбе эквимолярных количеств этилендиамина с алкилбромидом при температуре 50-60 °С и затем с сероуглеродом в присутствии гидроксида натрия при температуре 0-5 °С в среде этилового спирта получены соответствующие дитиокарбаматы натрия. Выходы натриевых солей 2-(гептиламино)этилдитиокарбамата и 2-(октиламино)этилдитиокарбамата составляют 60 и 63%, температуры плавления 120-122 и 133 °С соответственно. Строение N-алкил-этан-1,2-диаминов и 2-(алкиламино) этилдитиокарбаматов натрия подтверждено данными ИК-, ЯМР ^{1}Н- и ^{13}С-спектров. Приведены COSY и HMQC спектры и соответствующие корреляции N-октилэтан-1,2-диамина.

Ключевые слова: этилендиамин, алкилирование, бромистые алкилы, дитиокарбонилирование, натрий 2-(алкиламино)этилкарбамодитиоаты.