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ALKYLATION OF SODIUM ETHANE-1,2-DIYLDICARBAMODITHIOATE

Abstract. Ssodium ethane-1,2-diyldicarbamodithioate was obtained by the dithiocarbonylation reaction of ethane-1,2-diamine. Then dialkyl ethane-1,2-diyldicarbamodithioates were synthesized by dialkylation of sodium ethane-1,2-diyldicarbamodithioate with 1-bromine(C_7, C_8, C_9, C_{10} and C_{12})alkanes in the good and high yields (63-84%). The structure of the reaction products are confirmed by IR, ^{1}H and ^{13}C NMR spectra data.

Keywords: ethane-1,2-diamine, dithiocarbonylation, alkylation, 1-bromoalkanes, dialkyl ethane-1,2- diyldicarbamodithioates.

Before in [1, 2] we found, that sodium N-(3-phenylprop-2-yn-1-yl)-N-butyldithiocarbamate (AN-16) significantly accelerates root formation on black currant cuttings, exceeding the results obtained with known rooting agent - indolylacetic acid (IAA) [3]. At the same time, its working concentration was an order of magnitude lower than the working concentration of IAA. This compound is highly effective for stimulating the bookmarking of generative buds of fruit trees, which makes it promising in innovative technologies for the production of fast-growing seedlings [4], and it is also of practical interest for cultivation of wild medicinal plants, increasing seed germination by three times [5].

In this regard, the search for highly effective plant growth regulators among the new sodium dithiocarbamates of alkylated diamines can let to useful results.

In order to synthesize new hetero-organic compounds and to study their chemical, physico-chemical and biological properties, in particular physiological activity, we carried out the reaction of ethylenediamine with carbon disulphide, which scheme is shown in figure 1. Reactions of ethylenediamine (EDA) with carbon disulphide were carried out in 96% ethanol medium at room temperature and a molar relation of reagents EDA : CS_2: NaOH = 1:1,4:1,5.

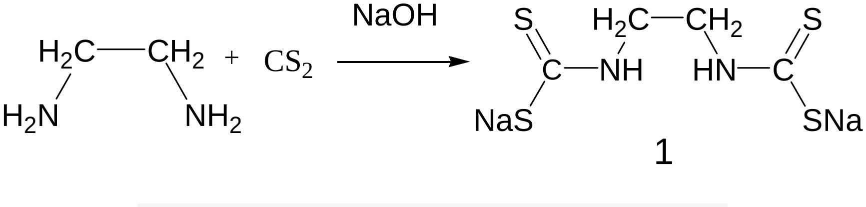


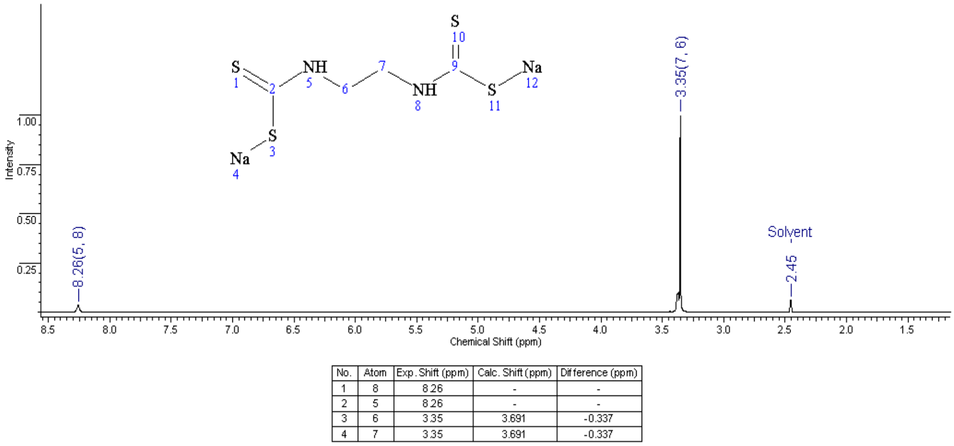
Figure 1 – Reaction of ethylenediamine with carbon disulfide

As a result of the reaction, sodium ethane-1,2-diyldicarbamodithioate **1** was obtained in 90% yield, in the form of a pink crystalline substance with Tm = 72-73 °C. The individuality and composition of the synthesized ethane-1,2-dioldicarbamodithioate of sodium **1** are confirmed by thin-layer chromatography and other physicochemical methods. The structure of the compound was established on the basis of IR spectroscopy and ^{1}H and ^{13}C NMR spectroscopy.

The structure of the synthesized compounds was 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, 2 - 4, 5).

In the IR spectrum of sodium bisdithiocarbamate **1**, bands of characteristic stretching vibrations of the C-H bonds of methylene groups are in the range 2887 ± 2975 cm^{-1}, stretching vibrations of the NH groups are at 3291, 3401 cm^{-1}, intense absorption bands of the thioamide group NC = S are at 1430 cm^{-1} and 1046 cm^{-1}. Oscillations involving the C-S bond are manifested at 627 cm^{-1}.

In the ^{1}H NMR spectrum of compound **1**, shown in Fig. 2, the resonance signals of the protons of NCH_2 groups appear at 3.35 ppm, the signal of protons of NH - at 8.26 ppm.

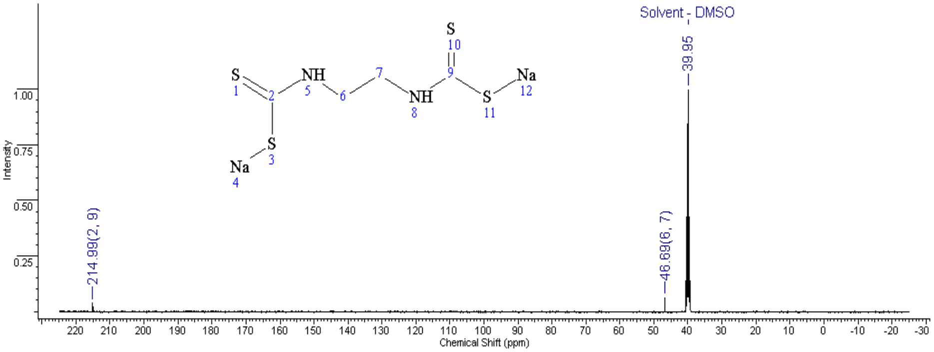


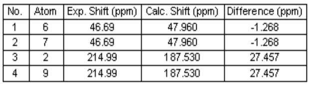
No.	Atom	Exp. Shift (ppm)	Calc. Shift (ppm)	Difference (ppm)
1	8	8.26	-	-
2	5	8.26	-	-
3	6	3.35	3.691	-0.337
4	7	3.35	3.691	-0.337

Figure 2 – NMR ^{1}H spectrum of ethane-1,2-diyldicarbamodithioate sodium **1**

In the ^{13}C NMR spectrum of sodium ethane-1,2-dioldicarbamodithioate **1** obtained which are shown in figure 3, there are resonant signals of carbon atoms of C = S groups at 215.0 ppm, confirming the introduction of dithiocarbamate groups into the molecule of a new compound, and the signal of NCH_2 methylene groups at 46.7 ppm.

In order to synthesize and study the properties of the new bisdithiocarbamate derivatives, we investigated the alkylation reaction of bisdithiocarbamate **1** with 1-bromoalkanes (BA) (bromheptane, bromoclotane, bromonanane, bromodecane, bromododecane). The reaction was carried out by interaction of bisdithiocar-

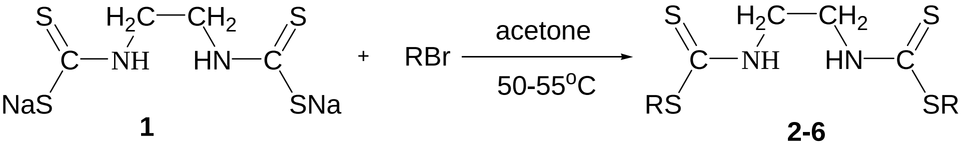




No.	Atom	Exp. Shift (ppm)	Calc. Shift (ppm)	Difference (ppm)
1	6	46.69	47.960	-1.268
2	7	46.69	47.960	-1.268
3	2	214.99	187.530	27.457
4	9	214.99	187.530	27.457

Figure 3 – NMR ^{13}C spectrum of sodium ethane-1,2-diyldicarbamodithioate **1**

bamate **1** with 1-bromoalkanes at a temperature of 50-55 °C in acetone medium, at molar ratios of reagents **1**: BA = 1: 1, 1: 2 and 1: 3.



R = **2** C_7H_{15}, **3** C_8H_{17}, **4** C_9H_{19}, **5** $C_{10}H_{21}$, **6** $C_{12}H_{25}$

Figure 4 – Scheme of alkylation of sodium ethane-1,2-diyldicarbamodithioate **1**

After appropriate treatment of the reaction mixtures diheptyl, dioctyl, dinonyl, didecyl and dododecyl thiodiesters of ethane-1,2-diyldicarbamodithioic acid 2-6 were isolated in individual yields of 31%, 23%, 17%, 31% and 46% respectively, if the initial reagents were taken in the ratio **1**: BA = 1: 1. As we see, the yields of thiodiesters **2-6** are quite low, so we carried out this reaction at other molar ratios of the reagents. At a molar ratio of reagents **1**: BA = 1:2, the yield of thiodiesters **2-6** increases correspondingly to 50%, 35%, 39%, 36% and 62%, respectively. At a molar ratio of reagents **1**:BA = 1:3, the yield of thiodiesters **2-6** increases to 73%, 78%, 63%, 69% and 84%, respectively.

The composition and individuality of the synthesized compounds **2-6** are confirmed by thin-layer chromatography and other physicochemical methods. The structure of the compounds was established on the basis of IR, ^{1}H and ^{13}C NMR spectroscopy.

In the infrared spectra of synthesized compounds **2-6**, intense absorption bands are observed in the region of 2959-2810 cm^{-1}, corresponding to the vibrations of methyl and methylene groups of alkyl substituents; in the region of 3200-

3400 cm^{-1}, broad absorption bands are observed that correspond for valence vibrations of amide NH groups. The presence of the C=S group is confirmed by the very strong absorption bands in the spectra region of ~ 1061-1072 cm^{-1}, the weak bands in the 646-663 cm^{-1} region correspond to the C-S bond vibrations, and the presence of an absorption band, characteristic for NH groups, indicates that the reaction was on the C-S group.

Table 1 – Physicochemical characteristics of bisdithiocarbamate **1** and thiodiesters **2-6**

Comp.	Yield, % (**1**:BA = 1:1)	Yield, % (**1**:BA = 1:2)	Yield, % (**1**:BA = 1:3)	mp, °C	IR spectra, ν, cm^{-1}			
					NH	CH_3, CH_2	C=S	C-S
1	60	–	–	72-73	3400 3290	2810-2985	–	–
2	31	50	73	96-97	3237	2581-2951	1061	646
3	23	35	78	78-84	3370	2921	1072	654
4	17	39	63	80-84	3235	2851-2952	1061	646
5	31	36	69	63-65	3212	2850-2952	1059	663
6	46	62	84	96-97	3214	2850-2954	1061	659

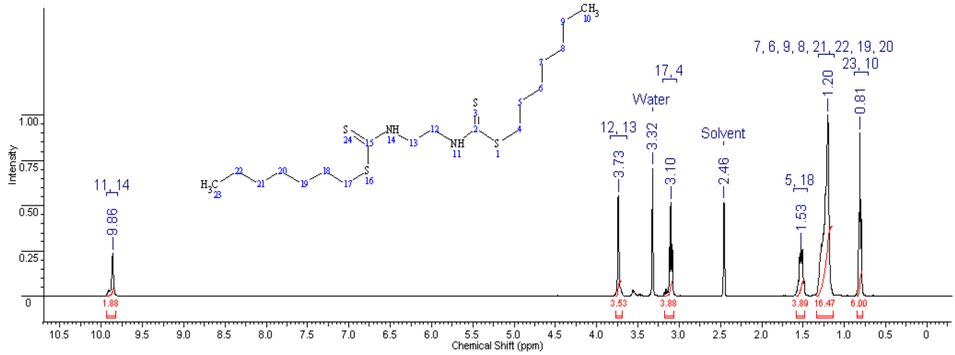
The resonance signals from the alkyl substituents are observed in the ^{1}H NMR spectra of ethane-1,2-diyldicarbamodithioic acid **2-6**: it is a triplet from the protons of the methyl group in the range δ 0.79-0.81, there are the multiplets from the protons of the methylene groups $(CH_2)_{n-1}$ in the 1.18-3.11 ppm region. The protons of the NCH_2 group resonate at 3.49-3.75 ppm. in the form of a triplet, the proton of the thioamide group resonates at 9.84-9.87 ppm. in the form of a broadened singlet.

In the ^{13}C NMR spectra of alkyl thiodiesters **2-6**, signals in the regions 14.48-14.51 and 22.58-34.54 ppm, corresponding to carbon atoms of CH_3 and $(CH_2)_n$ groups, are observed. Signal at 197.71-202.36 ppm corresponds carbon atom of C=S group. Signals in the region of 44.57-44.98 ppm belong to the CH_2N groups.

Table 2 – Data of ^{1}H and ^{13}C NMR spectra for compounds **1-6**

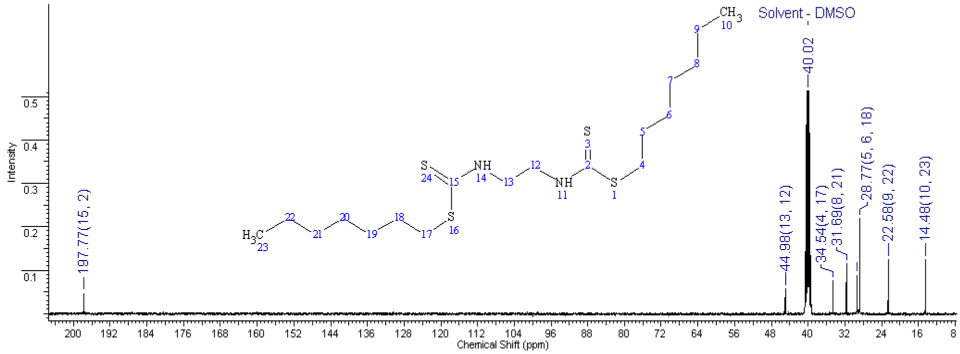
Comp.	NMR ^{1}H, δ				NMR ^{13}C, δ			
	NH	NCH_2	$(CH_2)_n$	CH_3	NCH_2	C=S	CH_3	$(CH_2)_n$
1	8,26	3,35	–	–	47,96	187,53	–	–
2	9,86	3,73	1,20-3,10	0,81	44,98	197,77	14,48	22,58-34,54
3	9,86	3,73; 3,75	1,20-3,10	0,81	44,96	197,74	14,51	22,65-34,52
4	9,87	3,73	1,20-3,11	0,81	44,97	197,76	14,50	22,62-34,52
5	9,85	3,72	1,18-3,07	0,79	44,96	197,71	14,50	22,67-34,51
6	9,84	3,49; 3,74	1,19-3,11	0,81	44,57	202,36	14,50	22,64-33,11

As an example of the experimental NMR spectra, the proton and carbon spectra of diheptyl ethane-1,2-diyldicarbamodithioate **2** are shown in the Figures 5 and 6. In the figures 7 and 8 the two-dimensional HMQC and COSY spectra of the same compound confirming the assignment of the signals in ^{1}H and ^{13}C NMR spectra are shown.



No.	Atom	Exp. Shift (ppm)	Calc. Shift (ppm)	Difference (ppm)	No.	Atom	Exp. Shift (ppm)	Calc. Shift (ppm)	Difference (ppm)
1	14	[9.80 .. 9.93]	-	-	10	20	[1.12 .. 1.31]	1.376	-0.158
2	11	[9.80 .. 9.93]	-	-	11	19	[1.12 .. 1.31]	1.468	-0.250
3	10	[0.71 .. 0.88]	0.877	-0.082	12	6	[1.12 .. 1.31]	1.468	-0.250
4	23	[0.71 .. 0.88]	0.877	-0.082	13	18	[1.45 .. 1.61]	1.735	-0.204
5	21	[1.12 .. 1.31]	1.242	-0.024	14	5	[1.45 .. 1.61]	1.735	-0.204
6	8	[1.12 .. 1.31]	1.242	-0.024	15	17	[3.03 .. 3.20]	3.038	0.074
7	9	[1.12 .. 1.31]	1.333	-0.114	16	4	[3.03 .. 3.20]	3.038	0.074
8	22	[1.12 .. 1.31]	1.333	-0.114	17	13	[3.63 .. 3.83]	3.746	-0.016
9	7	[1.12 .. 1.31]	1.376	-0.158	18	12	[3.63 .. 3.83]	3.746	-0.016

Figure 5 – ^{1}H NMR spectrum of diheptyl ethane-1,2-diyldicarbamodithioate **2**



No.	Atom	Exp. Shift (ppm)	Calc. Shift (ppm)	Difference (ppm)	No.	Atom	Exp. Shift (ppm)	Calc. Shift (ppm)	Difference (ppm)
1	10	14.48	14.070	0.414	10	7	29.34	28.570	0.769
2	23	14.48	14.070	0.414	11	8	31.69	30.960	0.734
3	9	22.58	21.950	0.629	12	21	31.69	30.960	0.734
4	22	22.58	21.950	0.629	13	4	34.54	36.290	-1.754
5	5	28.77	27.070	1.697	14	17	34.54	36.290	-1.754
6	18	28.77	27.070	1.697	15	13	44.98	49.580	-4.604
7	6	28.77	28.540	0.227	16	12	44.98	49.580	-4.604
8	19	29.34	28.540	0.799	17	15	197.77	206.990	-9.222
9	20	29.34	28.570	0.769	18	2	197.77	208.480	-10.712

Figure 6 – ^{13}C NMR spectrum of diheptyl ethane-1,2-diyldicarbamodithioate **2**

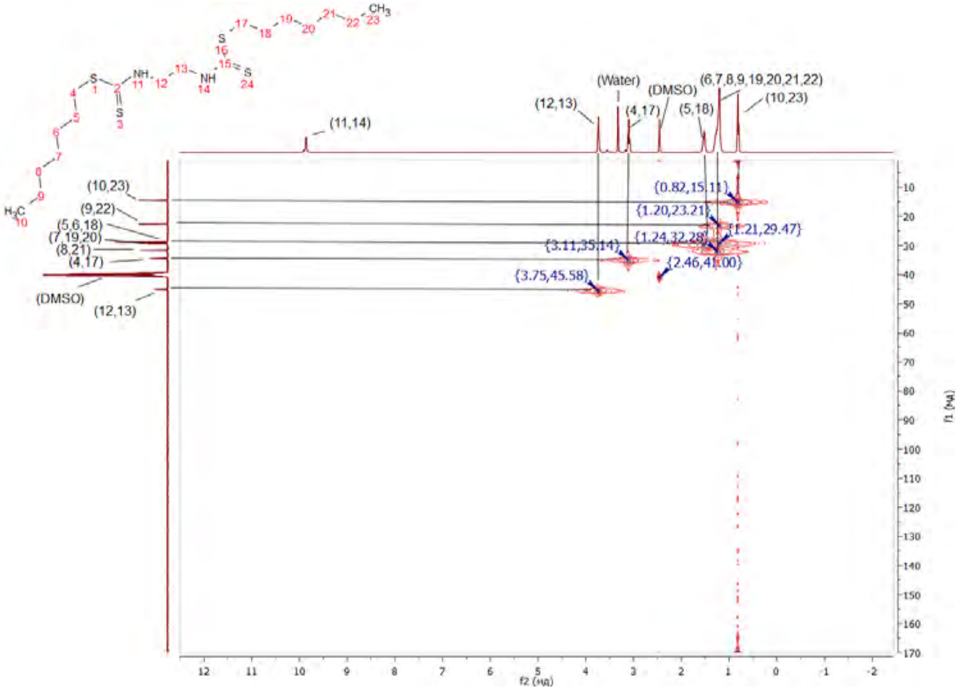


Figure 7 – HMQC NMR spectrum of diheptyl ethane-1,2-diyldicarbamodithioate **2**

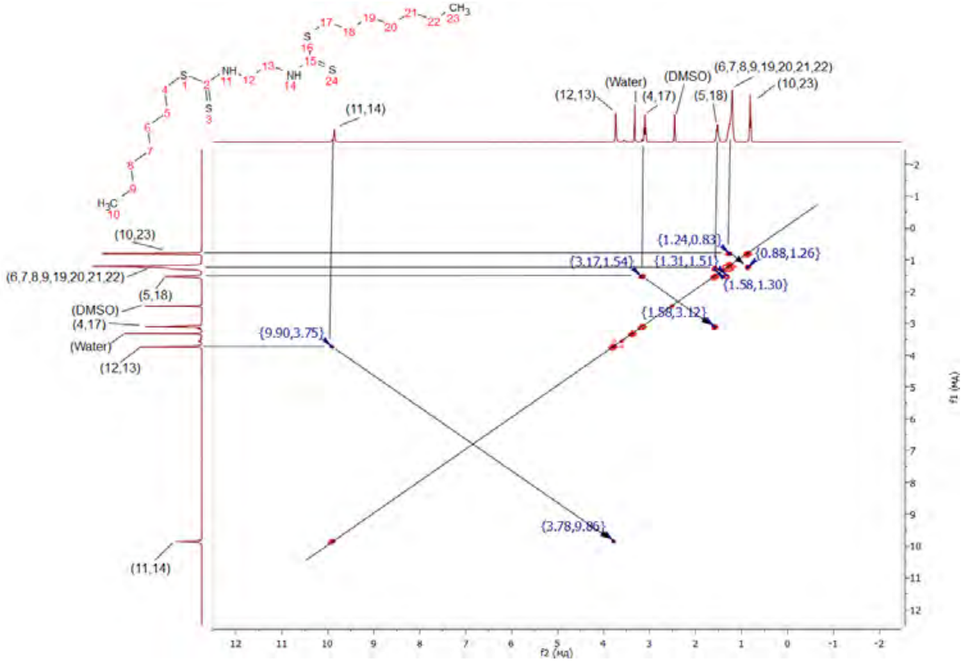


Figure 8 – COSY NMR spectrum of diheptyl ethane-1,2-diyldicarbamodithioate **2**

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 ^1H 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.

Sodium ethane-1,2-diyldicarbamodithioate 1. A solution of 10 ml (8.8 g, 0.15 mol) of ethylenediamine in 10 ml of 90% alcohol was introduced into a three-necked flask. The temperature of the reaction mixture was lowered to -5 °C. and 8.7 g (0.22 mol) of sodium hydroxide dissolved in 2 ml of distilled water was added. After 10 to 15 minutes of stirring, 12.66 ml (15.95 g, 0.21 mol) of carbon disulfide were added dropwise to the reaction flask and stirred at room temperature for 1 hour. Then, alcohol was distilled from the reaction mixture, the remaining precipitate was washed with acetonitrile. As a result, sodium ethane-1,2-diyldicarbamodithioate **1** was obtained as crystals $R_f = 0.04$, mp = 72-73 °C. Yield 22.8 g (0.09 mole) (90%).

Diheptyl ethane-1,2-diyldicarbamodithioate 2. A solution of 1 g (0.004 mol) of sodium ethane-1,2-diydicarbamodithioate **1** in 10 ml of acetone was introduced into a three-necked flask. The temperature of the reaction mixture was raised to 50 °C and 2.15 g (0.012 mol) of heptyl bromide in 10 ml of acetone was added. After the addition of the total amount of heptyl bromide, the reaction mixture was stirred for 2 hours at 50 °C. The reaction was monitored by thin layer chromatography. Then acetone was distilled from the reaction mixture, the remaining precipitate was washed with acetonitrile. As a result, 1.2 g (73%) of diheptyl ethane-1,2-diyldicarbamodithioate **2** with $R_f = 0.04$ was obtained as crystals, mp 96-97 °C.

According to the developed procedure, 1.36 g (78%) of dioctyl ethane-1,2-diyldicarbamodithioate **3**, mp 78-84 °C was obtained from 1 g (0.004 mole) of sodium ethane-1,2-diyldicarbamodithioate **1**, 2.32 g (0.012 mole) of octyl bromide.

According to the developed procedure, 1.17 g (63%) of dinonyl ethane-1,2-diyldicarbamodithioate **4**, mp 80-84 °C was obtained from 1 g (0.004 mol) of sodium ethane-1,2-diyldicarbamodithioate **1** and 2.49 g (0.012 mol) of nonyl bromide,.

According to the developed procedure, 1.36 g (69%) of didecyl ethane-1,2-diyldicarbamodithioate **5**, mp 63-65 °C was obtained from 1 g (0.004 mol) of sodium ethane-1,2-diyldicarbamodithioate **1** and 2.65 g (0.012 mol) of decyl bromide.

According to the developed procedure, 1.75 g (84%) of diododecyl ethane-1,2-diyldicarbamodithioate **6**, mp 96-97 °C were obtained from 1 g (0.004 mol) of sodium ethane-1,2-diyldicarbamodithioate **1** and 2.99 g (0.012 mol) dodecyl bromide.

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Резюме

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ЭТАН-1,2-ДИИЛДИКАРБАМОДИТИОАТ НАТРИЙДІ АЛКИЛДЕУ

Этан-1,2-диаминнің күкіртті көміртекпен әрекеттесуін этанол ортасындағы бөлме температурасында, реагенттердің ЭДА:CS_2:NaOH = 1:1,4:1,5 мольдік қатынасында жүргізген реакцияның нәтижесінде 90% шығыммен балқу температурасы $T_{балку}$ = 72-73 °С, қызғылт кристалды зат түрінде этан-1,2-диилдикарбамодитиоат натрий (НЭД) алынған. Оны 1-бром(C_7, C_8, C_9, C_{10} және C_{12})алкандармен 50-55 °С температурада ацетон ортасында, реагенттердің НЭД: БА = 1:1, 1:2, 1:3 мольдік қатынасында диалкилдеу жолы арқылы жүргізгенде жоғары шығыммен (63-84 %) сәйкес диалкилденген этан-1,2-диилдикарбамодитиоаттар синтезделген. Реакция өнімдерінің құрылысы ИҚ, ЯМР ^{1}Н және ^{13}С спектрлердің мәліметтерімен дәлелденген

Түйін сөздер: этан-1,2-диамин, дитиокарбонилдеу, алкилдеу, бромды алкилдер, диалкил этан-1,2-диилдикарбамодитиоаты.

Резюме

Н. О. Акимбаева, С. А. Визер, Т. М. Сейлханов, К. Б. Ержанов

АЛКИЛИРОВАНИЕ ЭТАН-1,2-ДИИЛДИКАРБАМОДИТИОАТА НАТРИЯ

В результате реакции взаимодействия этан-1,2-диамина (ЭДА) с сероуглеродом, проведенной в среде 96% этанола при комнатной температуре, при мольном соотношении реагентов ЭДА: CS_2: NaOH = 1:1,4:1,5, получен этан-1,2-диилдикарбамодитиоат натрия (НЭД) с выходом 90 %, в виде розового кристаллического вещества с $T_{пл}$ = 72-73 ^oC. Путем его диалкилирования 1-бром(C_7, C_8, C_9, C_{10} и C_{12}) алканами (БА) при температуре 50-55 °С в среде ацетона, при мольных соотношениях реагентов НЭД: БА = 1:1, 1:2 и 1:3 синтезированы соответствующие диалкилированные этан-1,2-диилдикарбамодитиоаты с хорошими и высокими выходами (63-84%). Строение продуктов реакций подтверждено данными ИК, ЯМР ^1H и ^{13}C спектров.

Ключевые слова: этан-1,2-диамин, дитиокарбонилирование, алкилирование, 1-бромалканы, диалкил этан-1,2-диилдикарбамодитиоаты.