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SYNTHESIS OF (3-MORPHOLYL)PROPYLDITHIOCARBAMIC ACID ALKYL ESTERS

Abstract. The alkylation of potassium (3-morpholyl)propyldithiocarbamate with haloalkylswas studied. Conditions for the synthesis of new alkyl esters of (3-morpholyl)-propyldithiocarbamic acid were developed. Hexyl, heptyl, octyl, nonyl, decyl and dodecyl esters of (3-morpholyl)propyldithiocarbamic acid were synthesized in67, 68, 91, 81, 67 and 87 % yield. Structure of alkyl esters of (3-morpholyl)propyldithiocarbamic acid was established based on IR and ^{13}C NMR spectroscopic data.

Keywords: alkylation reaction, potassium (3-morpholyl)propyldithiocarbamate, alkyl esters of (3-morpholyl)propyldithiocarbamic acid.

The chemistry of sulfur compounds is an important and intensively developing field of organic synthesis. Most of the reactions involving sulfur are associated with the use of various sulfurizing reagents. So, a special place in the synthesis of organic sulfur compounds is occupied by carbon disulfide, which is a sulfurizing reagent in the synthesis of dithiocarbamates and dithiocarbamic acids. Dithiocarbamates are widely used in various fields of practice: chemistry and chemical technology, mineral processing, agriculture, medicine and technology.

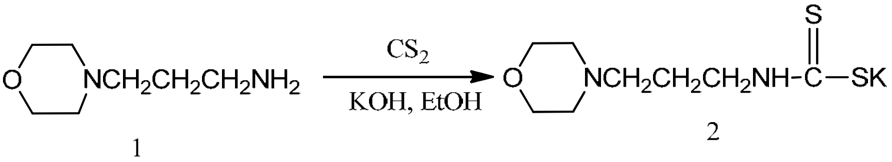
Dithiocarbamatesare used in analytical chemistry to detect p- and d-elements having affinity to sulfur, as well as for separation, masking and extraction photometric determination of many metals, for example, Cu, Ag, Bi, Cd, Co, As (III), for gravimetric definition of In, titrimetric – Hg, Pb, Pt, Te. Thus, morpholindithiocarbamateis used for the photometric determination of Cu, Co, and Ni in an aqueous methanol medium. Diethanoldithiocarbamateis used for photometric determination of Cu, Co and Ni or pairs of elements Cu and Ni, Cu and Coin aqueous solutions, for the determination of Cu in lubricating oils, alloys, steels and aluminum alloys [1].

Derivatives of thio- and dithiocarbamic acids are widely used as herbicides and fungicides.By the transition from the derivatives of thiocarbamic acid to the derivatives of dithiocarbamic acid decreases herbicidal activity, whereas fungicidal and bactericidal activity increases.Salts of dithiocarbamic acids with different metals have the practical importance, which are used as fungicides for combating plants diseases [2].Many derivatives of dithiocarbamic acids are usedalso as flotation reagents in the flotation of polymetallicsulphide ores [3].

The diverse activity of the dithiocarbamates and their derivatives, the increased stability of many of them to the action of radiation, as well as the use in mineral processing, agriculture and medicine, all contribute to the urgency of our studies on the synthesis of new dithiocarbamic acid derivatives.

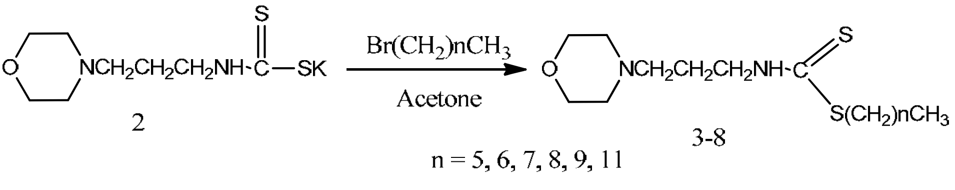
With a view to the synthesis of new derivatives of alkyl esters of dithiocarbamic acids containing in their structure the saturated hydrocarbonic chain was taken (3-morpholyl)propylditiocarbamate potassium as the starting substrate.

Potassium (3-morpholyl)propyldithiocarbamate was synthesized by the interaction of equimolar amounts of 4- (3-aminopropyl)morpholine**1** with carbon disulfide at a temperature of 0-5 °C in the presence of potassium hydroxide in ethyl alcohol. Potassium dithiocarbamate**2**was formed as a white crystalline substance, which was isolated by filtration from the reaction mixture and washed with methylene chloride. The potassium (3-morpholyl)propyldithiocarbamate **2** was synthesized in 96% yield.



The composition and structure of the potassium dithiocarbamate**2**were established bythe elemental analysis and IR spectroscopy. The physicochemical characteristics of the compound **2** are shown in the table 1. An absorption band of the valence vibrations of the NH group is presentin the IR spectrum in the region of 3299 cm^{-1}. The absorption bands in the region 2962, 2918, 1241-1448 cm^{-1} refer to the valence vibrations of the CH_2 groups. The valence vibrations C = S correspond to absorption in the region of 1027 cm^{-1}. In the region of 816 cm^{-1}appears an absorption band of the C-S bond.

Conditions of alkylation of potassium (3-morpholyl)propyldithiocarbamate were studied and new alkyl esters of (3-morpholyl)propyldithiocarbamic acid were synthesized. The alkylation reaction of potassium (3-morpholyl)propyldithiocarbamate**2** with saturated haloalkylswas carried out at room temperature in acetone.



As a result of isolation from reaction mixtures were obtained in the individual form hexyl, heptyl, octyl, nonyl, decyl and dodecyl esters of (3-morpholyl)propyldithiocarbamic acid **3-8**in 67, 68, 91, 81, 67, 87 % yield, respectively.

The elemental analysis, TLC and IR spectral data confirm composition and individuality of the synthesized compounds. The yield and physicochemical constants are presented in table 1. Structure of the synthesized alkyl esters of (3-morpholyl)propyldithiocarbamic acid **3-8** is established based on the ^{13}C NMR spectra, thespectral data of which are presented in table 2.

Table1 – Physicochemical constants for compounds **2-8**

№	Yield, %	m.p., °C	R_f acetone : hexane (1:7)	ИК-spectra, υ, cm^{-1}		
				NH	C=S	C-S
1	**2**	**3**	**4**	**5**	**6**	**7**
2	96	193-195	0.14	3299	1027	816
3	67	Oil	0.86	3234	1117	939
4	68	Oil	0.85	3234	1120	936
5	91	Oil	0.83	3240	1115	868
6	81	34-36	0.82	3234	1120	936
7	67	oil	0.81	3236	1115	869
8	87	38-40	0.79	3238	1115	998

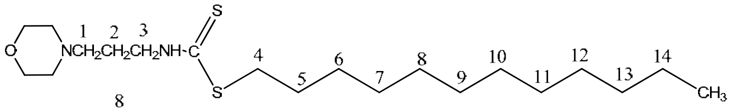
Continious of the table 1

№	Found, %				Formula	Calculated, %			
	C	H	N	S		C	H	N	S
1	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
2	37.30	5.57	10.62	25.03	$C_8H_{15}KN_2OS_2$	37.18	5.85	10.84	24.81
3	55.45	9.03	9.50	21.36	$C_{14}H_{28}N_2OS_2$	55.22	9.27	9.20	21.06
4	56.32	9.27	8.55	20.31	$C_{15}H_{30}N_2OS_2$	56.56	9.49	8.79	20.13
5	57.57	9.50	8.20	19.05	$C_{16}H_{32}N_2OS_2$	57.78	9.70	8.42	19.28
6	58.75	9.68	8.31	18.29	$C_{17}H_{34}N_2OS_2$	58.91	9.89	8.08	18.50
7	59.80	10.28	7.53	17.53	$C_{18}H_{36}N_2OS_2$	59.95	10.06	7.77	17.78
8	61.37	10.25	4.04	19.13	$C_{19}H_{38}N_2OS_2$	61.58	10.03	4.22	19.34

In the IR spectra of compounds **3-8** in the region of3234 $cm^{-1}$is found an absorption band of the stretching vibrations of the NH group. An absorption band of the valence vibrations of the C = S group is present in the region of 1115-1120 cm^{-1}. The absorption band of the C-S bond is present in the region of 543-669 cm^{-1}.

Analysis of the^{13}C NMR spectra (table 2) of the compounds **3-8** confirms their structure. In the ^{13}C NMR spectrum, the signal of the carbon atom of the methyl group is manifested in the strong-field spectral region δ 14.11-14.24 ppm. Chemical shifts of carbon atoms of methylene groups of the alkane chain appear in the range of δ 22.55-58.60 ppm. The carbon atoms of morpholine are resonated in the range of δ 53.40-53.60 ppm. (-N (CH2) 2) and δ 66.54-67.04 ppm. (O (CH2) 2). The carbon atom of the C = S group resonates in the weak-field region δ 197.43-197.77 ppm.

Table 2 – ^{13}C NMR(δ, ppm) spectraldataforcompounds **3-8**

Carbon atom						
	3	**4**	**5**	**6**	**7**	**8**
$O(CH_2)_2$-	67,02	66,61	66,54	66,85	67,04	66,71
$N(CH_2)_2$-	53,60	53,42	53,40	53,53	53,60	53,47
-C=S	197,43	197,73	197,77	19762	197,44	197,73
C^1H_2	58,57	58,17	58,12	58,46	58,60	58,30
C^2H_2	22,67	22,68	22,72	22,77	22,77	22,79
C^3H_2	48,50	47,84	47,75	48,27	48,55	48,01
C^4H_2	35,23	35,24	35,24	35,27	35,24	35,27
C^5H_2	29,34	29,34	29,32	29,56	29,00	29,75
C^6H_2	28,63	28,94	28,98	29,00	29,28	29,01
C^7H_2	31,43	28,94	29,22	29,29	29,40	29,37
C^8H_2	22,60	31,78	29,22	29,36	29,63	29,73
C^9H_2	–	22,55	31,88	29,38	29,60	29,70
$C^{10}H_2$	–	–	22,55	31,96	29,40	29,62
$C^{11}H_2$	–	–	–	22,55	31,97	29,44
$C^{12}H_2$	–	–	–	–	22,64	29,30
$C^{13}H_2$	–	–	–	–	–	32,09
$C^{14}H_2$	–	–	–	–	–	22,54
CH_3	14,11	14,19	14,20	14,23	14,22	14,24

Experiment

Control of the reaction was carried out by TLCon Silufol UV-254 plates, eluent acetone-hexane (1: 7). IR spectra of synthesized compounds are recorded on a Nicolet 5700 device in tablets with KBr, with 0.25% and in a thin layer. NMR spectra were obtained on a JNM-ECA 400 (JEOL) spectrometer.

Potassium (3-morpholyl)propyldithiocarbamate 2. Solution of potassium hydroxide (8.4 g, 0.15 mol) in water (5 ml) was addedto the mixture of of 4-(3-aminopropyl) morpholine1 (21.63 g, 0.15 mol) in 50 ml of alcohol. Then a solution of carbon disulfide (12.16 g, 0.16 mole) in alcohol (10 ml) was added-dropwise at 0-5 ° C with stirring. The reaction mixture was stirredat 0-5° C for 3 hours. The resulting white crystals were filtered on a Shott funnel and washed with methylene chloride. Potassium (3-morpholyl)propyldithiocarbamate was obtained in 35 g (96%) yield.

Hexyl(3-morpholynolpropyl)carbamodithioate 3. Solution of 1-Bromohexane (4.95 g, 0.03 mol)in acetone (5 ml)was added dropwiseto the mixture of Potassium (3-morpholyl)propyldithiocarbamate 2in acetone (25 ml)with stirring. The reaction mixture was stirred at room temperature for 16 hours. The precipitate formed was filtered out, the solvent was distilled off in a vacuum of the water jet pump.The resulting mass as an oil was dried in a vacuum of the oil pump. Product was obtained in6.12 g (67%) yield.

Heptyl(3-morpholynolpropyl)carbamodithioate 4 was synthesized by the similar procedure. The yield was 6.5 g (68%).

Octyl(3-morpholynolpropyl)carbamodithioate 5 was synthesizedby the similar procedure. The yield was 9.11 g (91%).

Nonyl(3-morpholynolpropyl)carbamodithioate6 was synthesized by the similar procedure. The yield was 7.02 g (81%).

Decyl(3-morpholynolpropyl)carbamodithioate7 was synthesized by the similar procedure. The yield was7.19 g (67%).

Dodecyl(3-morpholynolpropyl)carbamodithioate 8 was synthesized by the similar procedure. The yield was 10.17 g (87%).

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REFERENCES

[1] Byrko V.M. Dithiocarbamates. M.: Nauka, 1984. 342 p.

[2] Melnikov N.N. Pesticides. Chemistry, technology and application. M.: Chemistry, 1987. 710 p.

[3] Shubov L.Ya., Ivankov S.I., Scheglova N.K. Flotation reagents in the processes of mineral processing. M.: Nedra, 1990. Prince. 1. 400 p.

Резюме

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(3-МОРФОЛИЛ)ПРОПИЛДИТИОКАРБАМИН ҚЫШҚЫЛЫНЫҢ АЛКИЛ ЭФИРЛЕРІНІҢСИНТЕЗДЕУ

Калий (3-морфолил)пропилдитиокарбаматын галогеналкилдермен алкилдеу зерттелінді. (3-морфолил)пропилдитиокарбамин қышқылының жаңа алкил эфирлері синтезінің жағдайлары жасалынды. (3-морфолил)пропилдитиокарбамин қышқылының гексил, гептил, октил, нонил, децил және додецил эфирлері сәйкесінше 67, 68, 91, 81, 67, 87% шығыммен синтезделінді. ИҚ-спектроскопиясы және ЯМР 13С спектроскопия әдістері арқылы (3-морфолил)пропилдитиокарбамин қышқылының алкил эфирлерінің құрылысы анықталынды.

Түйін сөздер: алкилдеу реакциясы, калий (3-морфолил)пропилдитиокарбаматтар, (3-морфолил)пропилдитиокарбамин қышқылының алкил эфирлері.

Резюме

М. С. Муканова

СИНТЕЗ АЛКИЛОВЫХ ЭФИРОВ (3-МОФОЛИЛ)ПРОПИЛДИТИОКАРБАМИНОВОЙ КИСЛОТЫ

Изучено алкилирование(3-морфолил)пропилдитиокарбамата калиягалогеналкилами. Разработаны условия синтеза новых алкиловыхэфиров (3-морфолил)пропилдитиокарбаминовой кислоты. Синтезированы гексиловый, гептиловый, октиловый, нониловый, дециловый и додециловый эфиры (3-морфолил)пропилдитиокарбаминовой кислоты с выходами 67,68, 91, 81, 67, 87%, соответственно.Методами ИК-спектроскопии и спектроскопии ЯМР ^{13}С установлена структура алкиловых эфиров (3-морфолил)пропилдитиокарбаминовой кислоты.

Ключевые слова: реакция алкилирования, (3-морфолил)пропилдитиокарбамат калия, алкиловые эфиры(3-морфолил)пропилдитиокарбаминовой кислоты.