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CHEMISTRY

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Abstract

Full Text

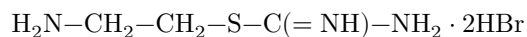
CHEMISTRY

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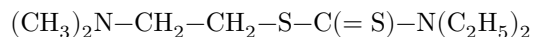
NEW ESTERS OF DITHIOCARBAMIC ACIDS

(Presented by Academician B. A. Kazanskii, 17 I 1960)

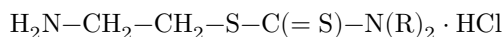
In connection with the appearance in the literature of data on the protective properties of β -aminoethylisothiuronium bromide (I) (Antiradon, AET) against the action of ionizing radiation (^{1,2}), it was of interest to synthesize compounds of related structure, namely β -aminoethyl dithiocarbamates (II).



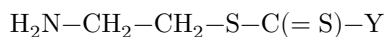
(I)



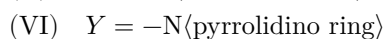
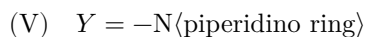
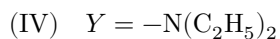
(III)



(II)



(IV-VI)



In the patent literature one compound of this structure has been described— β -dimethylaminoethyl ester of diethyldithiocarbamic acid (III) (3). We have obtained new carbamates with an unsubstituted amino group (IV, V, VI). These substances are formed by the interaction of β -chloroethylamine with the sodium salts of the corresponding dithiocarbamic acids (sodium diethyldithiocarbamate, sodium tetramethylenedithiocarbamate, and sodium pentamethylenedithiocarbamate). The products were isolated in the form of well-crystallizing hydrochlorides (Table 1).

Table 1

β -Aminoethyl dithiocarbamates

Compound No.	Y	Substance	Solvent for crystallization	M.p., °C	Yield, %	Empirical				
						for- mula	N, % found	N, % calcd.	S, % found	S, % calcd.
IV	(C ₂ H ₅) ₂ N-	Ethyl Aminoethyl di-ethylthio- carbamate (hydrochloride)	Ethyl	122-124	61	C ₇ H ₁₆ N ₂ S ₂ ·HCl	25.00	21.25	27.91	28.08
V	piperidino- N-	Ethyl Aminoethyl pentamethylenedithio- carbamate (hydrochloride)	Ethyl	187-189	59	C ₈ H ₁₆ N ₂ S ₂ ·HCl	25.00	21.43	26.40	26.66

Compound No.	Y	Substance	Solvent for crystallization	M.p., °C	Yield, %	Empirical formula			
						N, % found	N, % calcd.	S, % found	S, % calcd.
VI		pyrrolidino- N- Aminoethyl tetramethylenedithiocarbamate (hydrochloride)	Alcohol	184-186	60	C ₇ H ₁₄ N ₂ S ₂ ·HCl	23.36	28.10	28.25

Table 2

Products of the interaction of β -aminoethyl dithiocarbamates with quinones

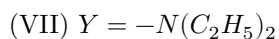
Compound No.	X	Y	Name of substance	Appearance of crystals under solvent	M.p., °C	Yield, %	Molecular weight	N, % found	N, % calcd.	S, % found	S, % calcd.
VIII	H	piperidino-	bis[β -fine (pentamethylenedithiocarbamino)-ethylamino]-benzoquinone	Very fine Dimethylformamide	225	51	C ₂₂ H ₃₂ O ₂ N ₄ S ₄	19.95	25.03	25.00	

Compound No.	X	Y	Name of substance	Appearance of crystals under for	Solvent	M.p., °C	Yield, %	Molecular formula	Nr, %	N, %	S, %	S, %
IX	H		pyrrolidino- N-bis[β-tetrahydro- ethylamino]- benzoquinone	Very fine	Dimethylformamide	226-228	53	C ₂₀ H ₂₈ N ₄ S ₂	41.51	26.40	26.44	
X	H		(C ₂ H ₅) ₂ N- [β-(diethyldithiocarbamino)- ethylamino]- naphthoquinone- 1,4	Orange-red	Dimethylformamide	113-115	59	C ₁₇ H ₂₀ N ₂ S ₂	55.04	18.80	18.39	
XI	Cl		(C ₂ H ₅) ₂ N- [β-(diethyldithiocarbamino)- ethylamino]- 3-chloronaphthoquinone- 1,4	Red	Ethylalcohol	135-137	57	C ₁₇ H ₁₉ ClN ₂ S ₂	53.21	16.96	16.73	
XII	H		piperidino- N-[β-(pentamethylenedithiocarbamino)- ethylamino]- naphthoquinone- 1,4	Red	Dimethylformamide	176-177	51	C ₁₈ H ₂₀ N ₂ S ₂	57.8	18.02	17.77	
XIII	Cl		piperidino- N-[β-(pentamethylenedithiocarbamino)- ethylamino]- 3-chloronaphthoquinone- 1,4	Red	Dimethylformamide	172-173	50	C ₁₇ H ₁₈ ClN ₂ S ₂	59.01	18.89	18.50	

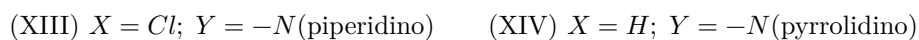
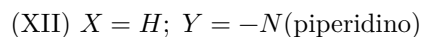
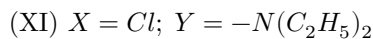
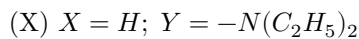
Compound No.	X	Y	Name of substance	Appearance of crystals under for	Solvent	M.p., °C	Yield, %	Molecular formula found	N, % calc.	S, % found	S, % calc.
XIV	H		pyrrolidino-Orange dimethylformamide N-[β-(tetramethylenedithiocarbamino)ethylamino]-naphthoquinone-1,4	Orange crystals		146	53	C ₁₈ H ₁₉ O ₂ N ₂ S ₂ Cl	16.99	16.22	

Using the known reaction of amines with quinones, we carried out the synthesis of new derivatives of benzo- and naphthoquinone (VII–XIV).

(VII–XI)



(X–XIV)



Interest in compounds of this type arose in connection with the fact that recently new physiologically active quinones have become known ⁴⁻⁶, as well as new synthetic medicinal preparations containing the quinone nucleus (for example, antibacterial substances ⁷, ethylenimine derivatives with antitumor properties ^{7,8}).

Benzoquinone derivatives (VII-IX) and naphthoquinone derivatives (X-XIV), containing β -aminoethyl dithiocarbamate residues, are formed smoothly upon interaction of the free amines (IV, V, VI) with quinones in ether solution and are well-crystallizing, sparingly soluble substances of red color (Table 2).

Experimental Part

Preparation of dithiocarbamates. Sodium pentamethylene- and tetramethylenedithiocarbamates were obtained by interaction of the corresponding amines (piperidine and pyrrolidine) with carbon disulfide in benzene solution in the presence of sodium hydroxide. The dithiocarbamates were characterized in the form of carboxymethyl derivatives, which are formed upon interaction of the sodium salts of dithiocarbamic acids with monochloroacetic

Table 3

Carboxymethyl dithiocarbamates ($Y-C-S-CH_2COOH$)

§

Y	Substance	M.p., °C	Yield, %	Empirical formula	N, % found	N, % calc.	S, % found	S, % calc.
(C_2H_5) ₂ N-	Carboxymethyl-diethyl-dithiocarbamate	82-84	82	$C_7H_{13}O_2N_2S_2$	7.95	6.76	31.60	30.91
piperidine-N-	Carboxymethyl-pentamethylenedithiocarbamate	139-141	81	$C_{13}H_{23}O_2N_2S_2$	6.69	6.39	29.60	29.22
pyrrolidine-N-	Carboxymethyl-tetramethylenedithiocarbamate	143	80	$C_{11}H_{19}O_2N_2S_2$	7.54	6.83	30.82	31.22

acid. The carboxymethyl derivatives are colorless products that crystallize well from water and have relatively low melting points (Table 3).

β -Aminoethyl dithiocarbamates. 0.01 g-mol of the corresponding sodium dithiocarbamate was dissolved in the cold in a minimum amount of water; 0.01 g-mol of β -chloroethylamine hydrochloride was likewise dissolved in a small amount of water, and the solution was made strongly alkaline with solid caustic soda. The two solutions were combined, and the reaction mixture was left to stand at room temperature for 24 hours. The separated oil was extracted with ether. The dried ethereal extract was saturated with dry hydrogen chloride; a precipitate of β -aminoethyl dithiocarbamate hydrochloride formed, which was filtered off and washed with ether.

Reaction of aminoethyl esters of dithiocarbamic acids with quinones.

To an ethereal solution of quinone (0.01 g-mol) was added an ethereal solution of the β -aminoethyl ester of the corresponding dithiocarbamic acid, in an amount of 0.01 g-mol for naphthoquinone and 0.02 g-mol for benzoquinone. On standing, shiny red-orange crystals precipitated from the solution.

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Note: Figure translations are in progress. See original paper for figures.

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