ml 4% sodium hydroxide solution (in a few portions). The alkaline solution was energetically stirred and cooled, and dilute (1: 1) hydrochloric acid added until it was acid to congo red. The precipitate was filtered off, washed with water, and dried in air. Yield of II 3. 4 g (31. 4%), mp 161-163°. After recrystallizing from 50% ethanol it formed pale yellow plates, mp 175-176°. Found: N 6. 38, 6. 42%. Calculated for $C_8H_7NS_3$: N 6. 56%.

2-Methylthieno(2, 3-b)thieno(2, 3-d)thiazole (I). 21. 3 g II was dissolved at 45° in 450 ml 2% aqueous sodium hydroxide, the solution energetically stirred, and a solution of 60 g potassium ferricyanide in 540 ml water dropped in at 1°. The mixture was stirred for a further 2 hr, then left overnight. The precipitate was filtered off, the mother liquor extracted with several portions of ether, 3000 ml in all, the ether distilled off, and the residue, plus the precipitate filtered off, were steam distilled. The distillate was extracted with ether, the extract dried over potassium carbonate, and the ether distilled off. On cooling, the residue solidified to a colorless crystalline mass. Yield of I 2. 7 g (12. 6%), mp 79-81°. After recrystallizing from petroleum ether it formed colorless plates, mp 88-89°. Found: N 6. 52, 6. 61%. Calculated for $C_8H_7NS_3$: N 6. 56%. Picrate: yellowish plates mp 146-147° (from ethanol). Found: N 12. 54, 12. 60%. Calculated for $C_8H_5NS_3 \cdot C_6H_3N_3O_7$: N 12. 66%. Methiodide: pale yellow plates mp 217-218° (from ethanol). Found: N 3. 67, 3. 70%. Calculated for $C_{10}H_{10}JNS_3$: N 3. 79%.

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PYRIDYLETHYLATION OF SOME HETEROCYCLIC THIOAMIDES AND POTENTIAL MERCAPTANS

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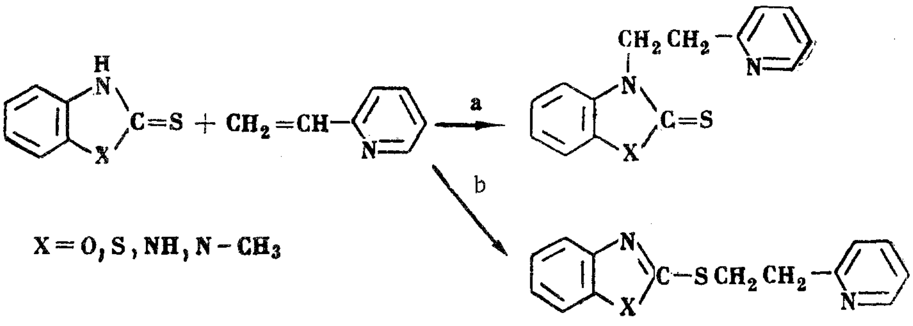
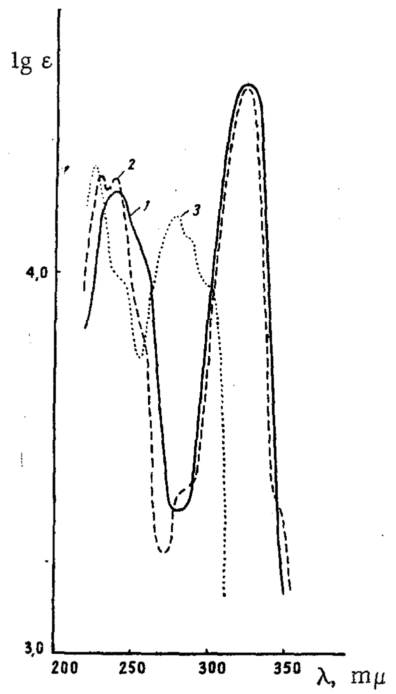
2-Pyridylethylation of benzazothiones-2 which are potential mercapto compounds (benzothiazolethione-2, benzoxazolethione-2, 1-methylbenzoimidazolethione-2, benzoimidazolethione-2, 5, 6-dimethylbenzoimidazolethione-2), is described, as well as preparation of 5, 6-dimethylbenzoimidazolethione-2 by direct oxidation of 5, 6-dimethylbenzoimidazole.

Continuing previous work on pyridylethylation of cyclic thioamides [1], 2-vinylpyridine has been reacted with benzothiazolethione-2 (I), benzoxazolethione-2 (II), 1-methylbenzoimidazolethione-2 (III), benzoimidazolethione-2 (IV), and 5, 6-dimethylbenzoimidazolethione-2 (V). These compounds are distinguished by a dual functionality, for they can react at the nitrogen atom of the thioamide group, or at its sulfur atom as mercaptans. Hence thioamides can react with 2-vinylpyridine in two ways



The reaction was effected by heating the thiones with the 2-vinylpyridine in glacial acetic acid at 110-115°. 30-90% yields of crystalline compounds were obtained, these giving picrates and water-soluble hydrochlorides.



UV spectra (in alcohol, SF-4 instrument, concentration 10^{-3} M): 1) Benzothiazolethione-2; 2) 3-2-(α-pyridylethyl)benzothiazolethione-2; 3) 2-methylmercaptobenzothiazole.

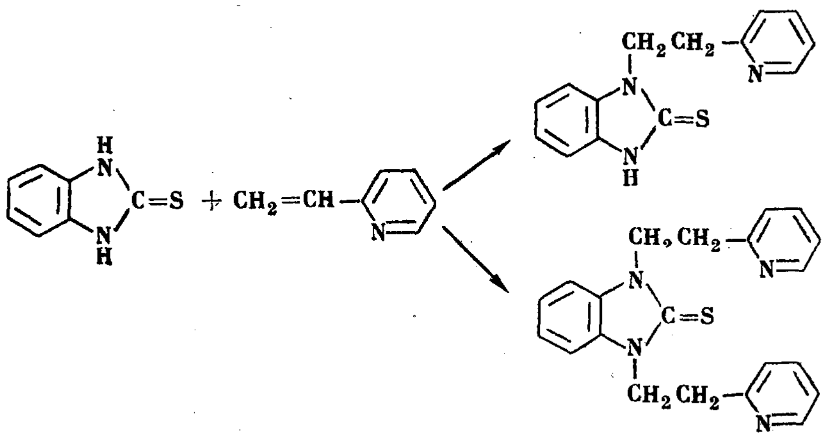
To determine the structures of the reaction products, the UV spectra of the starting thiones were observed, as well as those of compounds, 2-butylmercaptobenzoimidazole and 2-methylmercaptobenzothiazole, known to have a sulfide structure, and those of the pyridylethylation products obtained in the present work. From comparison of spectra it could be concluded that the vinylpyridine portion adds at the nitrogen atom of the thioamide group, and not at the sulfur atom (see equations).

In the case of compound IV two compounds would be expected to be formed, containing one and two vinylpyridine moieties, respectively.

If reaction is carried out using 1 mole thione to 2 moles vinylpyridine, the latter adds at two nitrogen atoms. If however 1 mole of thione is used with 1 mole of vinylpyridine, then, while the main product is the disubstituted one, it is accompanied by a small amount of monosubstituted derivative. The mono-derivative can be separated from the di- one by fractional crystallization. When 5, 6-dimethylbenzoimidazolethione-2 is pyridylethylated, a disubstituted product is also obtained if the reaction is carried out with 1 mole thione and 2 moles 2-vinylpyridine.

5, 6-Dimethylbenzoimidazolethione-2 is not described in the literature, and here it was prepared by a new method, direction sulfurizing of 5, 6-dimethylbenzoimidazole, analogous to the method used for preparing benzoimidazolethione-2 [2].

The hydrochlorides of the pyridylethylation products prepared here do not exhibit any significant antitubercular activity.



Experimental

The starting thiones I-IV were prepared by known methods [3, 4].

5, 6-Dimethylbenzoimidazolethione-2 (V). 6 g (0. 04 mole) 5, 6-dimethylbenzoimidazole and 4 g (0. 12 mole) sulfur were melted together at 210-215°, to give a solid mass (10-15 min). After cooling, the melt was dissolved in 2 N NaOH, filtered to remove excess sulfur, and the filtrate made acid with acetic acid. The precipitate of thione formed was filtered off, washed with water, and dried. Yield 7. 2 g (98%). It was twice recrystallized from alcohol, using activated carbon. Glistening needles mp >280°. A solution in alcohol had a marked violet fluorescence. Found: N 15. 75; S 17. 64%. Calculated for $C_9H_{10}N_2S$: N 15. 72; S 17. 97%.

3-[2-(α-Pyridylethyl)]benzazolethiones-2. The thione (0. 01 mole), 2-vinylpyridine (0. 011 mole) and glacial acetic acid (0. 01 mole) were heated together at 110-115°, in the case of compound I for 3 hr, for compound II and III 4 hr, for compound IV 6 hr, and for compound V 8 hr. (With compounds IV and V, 0. 022 mole 2-vinylpyridine was used.) The melt obtained was warmed to 30-40° with 2 N NaOH to remove unreacted starting thione. The residual precipitate was filtered off, washed with water, and dried. To obtain the hydrochlorides, a small amount of concentrated hydrochloric acid was added to this precipitate. The hydrochlorides were filtered off, crystallized from alcohol, then dissolved in water, and soda solution added to the latter. The precipitate of base was filtered off, dried, and recrystallized from the appropriate solvent. The final products were characterized as their picrates.

Products Obtained by Pyridylethylation of Benzazolethiones-2

Compound	Mp, °C	Picrate, mp, °C	Formula	Found, %		Calc., %	Yield, %
3-[2-(α-Pyridylethyl)]-benzothiazolethione-2	92—94[a]	200—202	$C_{14}H_{12}N_2S_2$	C H N S	61.82 4.42 10.41 23,32	61.76 4.44 10.28 23.52	85
3-[2-(α-Pyridylethyl)]-benzoxazolethione-2	65—67[b]	204—205	$C_{14}H_{12}N_2OS$	C H N S	65.48 4.85 11.03 12.54	65.62 4.72 10.93 12.50	87
1-Methyl-3-[2-(α-pyridylethyl)]-benzoimidazolethione-2	106—107[b]	211—212	$C_{15}H_{15}N_3S$	C H N S	66.79 5.60 75 11.92	66.91 5.61 15.61 11.88	60
1, 3-Di[2-(α-pyridylethyl)]-benzoimidazolethione-2	122—124[c]	230—231	$C_{21}H_{20}N_4S$	C H N S	70.22 5.73 15.44 9.34	69.98 5.59 15.55 8.88	45
3-[2-(α-Pyridylethyl)]-benzoimidazolethione-2	142—144[d]	207—210	$C_{14}H_{13}N_3S$	C H N S	66.27 5.29 16.45 12.29	65.87 5.13 16.47 12.55	*
5, 6-Dimethyl-1, 3-di[2-(α-pyridylethyl)]benzoimidazolethione-2	105—107[d]	228—230	$C_{23}H_{24}N_4S$	N S	14.08 8.20	14.43 8.24	30

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*A by-product of the preparation of the compound mp 122-124°.

a) From petroleum ether and benzene.

b) From petroleum ether.

c) From ether.

d) From methanol.

The Table gives data for the compounds prepared.

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A NEW METHOD OF PREPARING 1, 2, 4-TRIAZOLE CARBOXYLIC-3 ACIDS

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A new convenient method of preparing 1, 2, 4-triazole carboxylic acids-3 is worked out. Aminoguanidine bicarbonate and oxalic acid give 5-amino-1, 2, 4-triazole carboxylic acid-3, and this is converted, via the diazotriazole carboxylic acid and treatment of the latter with methanol, to 1, 2, 4-triazole carboxylic-acid-3.