SYNTHESIS OF DERIVATIVES OF THIENO[2,3-c]PYRAZOLE AND THIENO[2,3-d]THIAZOLINE

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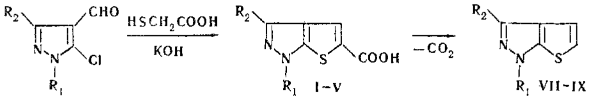
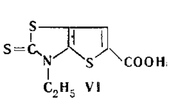
Studying the properties of the chloroaldehydes of heterocyclic compounds that we had synthesized [1], we found that in their reaction with thioglycolic acid in aqueous ethanolic alkali the chlorine atom was replaced by a thioglycolic acid residue and intramolecular condensation took place with the formation of 1,3-substituted thieno[2,3-c]pyrazole-5-carboxylic acids (I–V), not previously described in the literature.



Analogously, from 4-chloro-3-ethyl-5-formylthiazoline-2-thione we obtained 3-ethyl-2-thioxothieno[2,3-d]thiazoline-5-carboxylic acid (VI).



The decarboxylation of the carboxylic acids gave derivatives of new heterocyclic systems—1,3-substituted derivatives of thieno[2,3-c]-pyrazole (VII–IX) and 3-ethylthieno[2,3-d]thiazoline-2-thione (X), and the reactivities of these compounds have been studied. Some of them were subjected to electrophilic substitution reactions: nitration, chloromethylation, formylation. The corresponding substituents apparently enter in position 5 of the thieno[2,3-c]pyrazole ring. Thus, the formylation of **VII** led to 3-methyl-1-phenylthieno[2,3-c]pyrazole-5-aldehyde (XI), the oxidation of which gave an acid identical with **I**.

From the carboxylic acids the corresponding esters, amides, and other derivatives were obtained. More detailed information will be given in subsequent papers.

3-Methyl-1-phenylthieno[2,3-c]pyrazole-5-carboxylic acid (I). To a solution of 13.44 g of caustic potash and 8.28 g of thioglycolic acid in 100 ml of 80% aqueous methanol was added 13.3 g of finely ground 5-chloro-4-formyl-3-methyl-1-phenylpyrazole, and the mixture was boiled for 4 hr. After the solvent had been driven off, the residue was dissolved in water, and the aqueous solution was filtered, cooled, and acidified. The precipitate that deposited was filtered off, washed with water, and dried, giving 10.8 g (80%) of I, mp 235–236° C (ethanol). Found, %: N 10.76; S 12.43. Calculated for $C_{13}H_{10}N_2O_2S$, %: N 10.85; S 12.40. Compounds **II–V** were obtained similarly (table).

Decarboxylation was carried out by heating compounds I–V above the melting point for 10–30 min.

3-Ethyl-2-thioxothieno[2,3-d]thiazoline-5-carboxylic acid (VI). This was obtained in a similar manner to I. Mp 246–248° C (reprecipitation from alkaline solution). Yield 59%. Found, %: S 39.17. Calculated for $C_8H_7NO_3S_2$, %: S 39.20.

3-Ethylthieno[2,3-d]thiazoline-2-thione (X). This was obtained by the decarboxylation of VI. Mp 76–78° C (aqueous ethanol). Found, %: N 6.87; S 47.77. Calculated for $C_7H_7NS_3$, %: N 6.96; S 47.78.

REFERENCE

1. I. Ya. Kvitko and B. A. Porai-Koshits, ZhOrKh, 2, 169, 1966.

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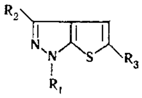

Compound*	R1	R2	Mp, °C	Solvent for crystallization	Empirical formula	Found, %		Calculated, %		Yield, %
						N	S	N	S	
II	C_6H_5	C_6H_5	282—283	Acetic acid	$C_{18}H_{12}N_2O_2S$	8.80	10.08	8.75	10.0	77.3
III	p-$C_6H_4NO_2$	CH_3	294—295	Acetic acid	$C_{13}H_9N_3O_4S$	13.76	10.44	13.86	10.56	57.7
IV	CH_3	CH_3	316—317	Benzene	$C_8H_8N_2O_2S$	—	16.05	—	16.33	81.6
V	CH_3	C_6H_5	249—250	Acetic acid —water	$C_{13}H_{10}N_2O_2S$	—	12.50	—	12.40	56.3
VII	C_6H_5	CH_3	53	Aqueous dioxane	$C_{12}H_{10}N_2S$	13.17	—	13.08	—	94.0
VIII	C_6H_5	C_6H_5	135—136	Acetic acid	$C_{17}H_{12}N_2S$	10.18	11.66	10.01	11.56	81.0
IX	p-$C_6H_4NO_2$	CH_3	210—212	Acetic acid	$C_{12}H_9N_3O_2S$	16.38	12.30	16.21	12.35	85.1
XI	C_6H_5	CH_3	141.5	Aqueous dioxane	$C_{13}H_{10}N_2OS$	11.17	13.26	11.56	13.22	85.9

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* For **II–V**, R_3 = COOH; for **VII–IX**, R_3 = CHO.