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	61.82	61.76	85
				H	4.42	4.44	
				N	10.41	10.28	
				S	23.32	23.52	
3-[2-(α-Pyridylethyl)]-benzoxazolethione-2	65—67^{b}	204—205	$C_{14}H_{12}N_2OS$	C	65.48	65.62	87
				H	4.85	4.72	
				N	11.03	10.93	
				S	12.54	12.50	
1-Methyl-3-[2-(α-pyridylethyl)]-benzoimidazolethione-2	106—107^{b}	211—212	$C_{15}H_{15}N_3S$	C	66.79	66.91	60
				H	5.60	5.61	
				N	75	15.61	
				S	11.92	11.88	
1, 3-Di[2-(α-pyridylethyl)]-benzoimidazolethione-2	122—124^{c}	230—231	$C_{21}H_{20}N_4S$	C	70.22	69.98	45
				H	5.73	5.59	
				N	15.44	15.55	
				S	9.34	8.88	
3-[2-(α-Pyridylethyl)]-benzoimidazolethione-2	142—144^{d}	207—210	$C_{14}H_{13}N_3S$	C	66.27	65.87	*
				H	5.29	5.13	
				N	16.45	16.47	
				S	12.29	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	14.08	14.43	30
				S	8.20	8.24	

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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.

REFERENCES

1. I. Ya. Postovskii and V. L. Nirenburg, KhGS, 309, 1965.
2. W. Treibs, Naturwiss., 49, 13, 1962.
3. Organic Syntheses [Russian translation], IL, Moscow, 4, 295, 1953.
4. German Patent 557138, 1931; C. A., 27, 1233, 1933.

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

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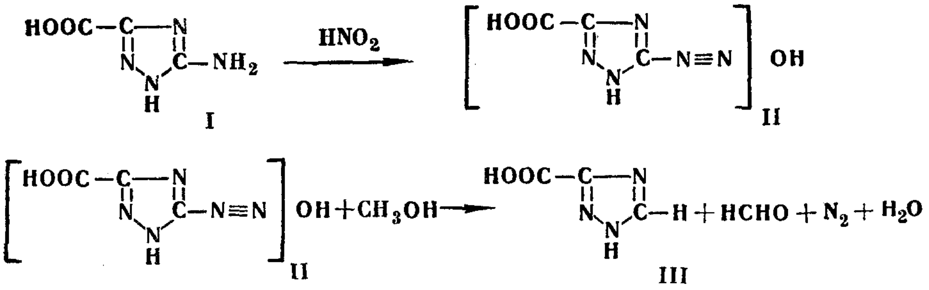
A new convenient method of preparing 1, 2, 4-triazole carboxylic acids-3 is worked out. Aminoguanidine bicarbonate and oxalic acid give 5-amino-1, 2, 4-triazole carboxylic acid-3, and this is converted, via the diazotriazole carboxylic acid and treatment of the latter with methanol, to 1, 2, 4-triazole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

1, 2, 4-Triazole carboxylic acid-3 is widely used for preparing antihypertensive agents, compounds with a histamine-like action, but also antagonists to histamine [1]. Hitherto 1, 2, 4-triazole carboxylic acid-3 has been obtained only by oxidizing alkyl or aryl substituted 1, 2, 4-triazoles [1-4], which in their turn must be prepared by multistage synthesis.

The method offered here for preparing 1, 2, 4-triazole carboxylic acid-3 (III) is



The aminotriazole carboxylic acid I required for the reaction can be obtained directly, in 80% yield, from aminoguanidine bicarbonate and oxalic acid [5, 6]. Acid I is suspended in water, hydrochloric acid added, and diazotization effected by adding an aqueous solution of sodium nitrite. The diazotriazole carboxylic acid (II) which separates in the precipitate is filtered off, and without drying (the dry diazotriazole carboxylic acid is liable to explode) reduced with methanol. For the latter purpose the diazotriazole carboxylic acid is suspended in methanol, and warmed to 45-50°; the exothermic reduction reaction starts at that temperature. When the reaction is finished, the acid III in the precipitate is filtered off, and dried in air. Yield, based on acid I, 60-70%.

As the triazole carboxylic acid is unstable (decarboxylation), in synthetic work use is made of its esters, obtained by esterifying the acid at room temperature with the appropriate alcohol and hydrogen chloride. The hitherto unknown methyl 1, 2, 4-triazole carboxylate-3 has now been prepared.

Experimental

1, 2, 4-Triazole carboxylic-3 acid (III). 78 g (0. 6 mole) aminotriazole carboxylic acid I was suspended in 500 ml water, 180 ml concentrated hydrochloric acid added, and the mixture heated until solution took place. It was then cooled to room temperature, 300 g ice added (partial separation of finely-divided crystalline aminotriazole carboxylic acid was observed), the whole stirred, and a solution of 83 g (1. 2 mole) sodium nitrate in 200 ml water added over a few minutes, after which stirring was continued for half an hour more.

The diazotriazole carboxylic acid II which separated in the precipitate was filtered off, squeezed as dry as possible on the filter, then transferred to a 2-*l* three-necked flask fitted with a triple condenser with internal coils. 300 ml methanol was put in the flask, which was heated on a water bath. At 45-50° exothermic reaction of decomposition of the diazotriazole carboxylic acid set in, and the water bath was replaced by an ice one. When reaction was complete (2-3 min), the reaction products were cooled to room temperature, the triazole carboxylic acid III, which separated in the precipitate was filtered off and dried in air. Yield 38-46 g (60-70%), mp 127-130° (decomp.), after recrystallizing from water mp 135-137° (decomp.) (137° [3]).

Recrystallization involved a large loss of product through decarboxylation. Impure acid was used for preparing the methyl ester.

Methyl 1, 2, 4-triazole carboxylate-3. 70 g (0. 6 mole) triazole carboxylic acid was suspended in 500 ml methanol, which was then saturated with hydrogen chloride. After 72 hr the precipitated methyl ester hydrochloride was filtered off and dried in air. Yield 6. 15 g (61%). Recrystallized from water (hydrolysis) gave the free base, mp 198° (decomp.). Found: N 33. 21%. Calculated for $C_4H_5N_3O_2$: N 33. 05%.

REFERENCES

1. G. Ainsworth and R. G. Jones, U. S. Patent 2719849; C. A., 50, 12115, 1956.
2. J. A. Bladin, Ber., 25, 744, 1892.
3. A. Andreocco, Atti. Linc., 7, 2, 462, 1898.
4. G. Ainsworth and R. G. Jones, J. Am. Chem. Soc., 77, 1538, 1955.
5. G. I. Chipen and V. Ya. Grinshtein, Izv. AN LatvSSR, ser. khim., 204, 1965.
6. Preparative Organic Chemistry [in Russian], Gos. nauchn.-tekhn. izd-vo khim. lit., Moscow, 764, 1959.

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