SYNTHESIS AND TRANSFORMATION OF ACIDS OF THE 1,2,4-TRIAZOLE SERIES

III.* PREPARATION AND REACTIONS OF 3-METHYL-1,2,4-TRIAZOLE-5-CARBOXYLIC ACID

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It is shown that a mixture of 1,2,4-triazole-3,5-dicarboxylic acid and 3-methyl-1,2,4-triazole-5-carboxylic acid is formed by oxidation of 3,5-dimethyl-1,2,4-triazole with insufficient oxidizing agent. Some derivatives of 3-methyl-1,2,4-triazole-5-carboxylic acid were obtained.

Acids of the 1,2,4-triazole series are obtained by the oxidation of the corresponding alkyltriazoles [3] of from 3-amino-1,2,4-triazole-5-carboxylic acid by diazotization and subsequent replacement of the diazo group [1,2,4].

We have shown that 1,2,4-triazole-3,5-dicarboxylic acid is formed by oxidation of 3,5-dimethyl-1,2,4-triazole with potassium permanganate and that a mixture of 1,2,4-triazole-3,5-dicarboxylic acid and 3-methyl-1,2,4-triazole-5-carboxylic acid is formed when smaller amounts of oxidizing agent are used. 3-Methyl-1,2,4-triazole-5-carboxylic acid is readily decarboxylated to 3-methyl-1,2,4-triazole even on attempts to recrystallize it. A number of derivatives of this acid were obtained. All of the synthesized compounds have acid properties due to the labile ring hydrogen atom.

The analytical data and several constants of the compounds obtained are presented in Table 1.

EXPERIMENTAL

Oxidation of 3,5-Dimethyl-1,2,4-triazole. Potassium permanganate [94.8 (0.6 mole)] was added to a warm solution of 29.1 g (0.3 mole) of 3,5-dimethyl-1,2,4-triazole in 250 ml of water. The mixture was kept on a boiling-water bath for 12 h. The precipitated manganese dioxide was filtered and washed with water. The filtrate and wash waters were evaporated to dryness on a water bath. The residue was dissolved in 100 ml of water and acidified to pH 1 with 10% hydrochloric acid. After 30 min, the resulting monocalcium salt of 1,2,4-triazole-3,5-dicarboxylic acid was filtered to give 18.8 g (32%) of product.

After 24 h, 7.7 g (20%) of 3-methyl-1,2,4-triazole-5-carboxylic acid (I) precipitated from the filtrate and was purified by dissolving in 10% alkali and precipitation with 10% hydrochloric acid with cooling.

3-Methyl-1,2,4-triazole (II). Compound I (1 g) was heated in 10 ml of boiling water, during which a gas was evolved in great quantities. The solution was evaporated to dryness. Recrystallization of the residue from benzene gave 0.6 g (95%) of 3-methyl-1,2,4-triazole with mp 94-95 deg [5].

3-Methyl-1,2,4-Triazole-5-carboxylic Acid Methyl Ester (III). A. I [3 g (0.023 mole)] was added to 45 ml of methanol saturated with hydrogen chloride. After 72 h, 1.7 g (50%) of III precipitated. A sample for analysis was recrystallized from water.

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*See [1,2] for Communication II.

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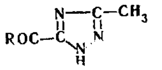
TABLE 1. Characteristics of the Compounds Obtained



Compound	R	Equivalent wt.		Mp (dec)	pK_{a_1}	pK_{a_2}	$\nu_{C=O}$, cm^{-1}	Empirical formula	Found, %			Calc., %		
		Potentiometric titration	calc.						C	H	N	C	H	N
I	OH	133	127	114—115	3,57	10,73	1715	$C_4H_5N_3O_2$	37,50	3,91	32,80	37,79	3,94	33,07
III	OCH_3	137,5	141	204—206	8,46	—	1730	$C_5H_7N_3O_2$	42,25	4,96	29,43	42,55	4,96	29,79
IV	NH_2	122,5	126	214—216	8,94	—	1695	$C_4H_6N_4O$	37,92	4,57	44,32	38,10	4,76	44,44
V	$NHNH_2$	145	141	211—213	8,94	—	1690	$C_4H_7N_5O$	33,69	5,06	49,43	34,04	4,96	49,65

B. Dry hydrogen chloride was passed through a suspension of 0.6 g (0.003 mole) of 3-methyl-1,2,4-triazole-5-carboxylic acid hydrazide (V) in 50 ml of methanol until it is dissolved, after which dry chlorine was passed through the solution for 2 h. The solution was evaporated to dryness, and the residue was recrystallized from water to give 0.36 g (60%) of a product with mp 204-205 deg, which did not depress the melting point of a sample obtained via method A.

3-Methyl-1,2,4-triazole-5-carboxamine (IV). Compound III [3.6 g (0.02 mole)] was dissolved in 50 ml of ammonium hydroxide. The solution was heated for 4 h to give a quantitative yield of IV. A sample for analysis was recrystallized from water.

3-Methyl-1,2,4-triazole-5-carboxylic acid Hydrazide (V). Compound III [3.6 g (0.02 mole)] was heated with 6 ml of 98% hydrazine hydrate. The solution was then refluxed for 30 min. The resulting precipitate was recrystallized from aqueous methanol to give 2.7 g (75%) of product.

The potentiometric titration was carried out with an LP-60 potentiometer with glass and calomel electrodes. The pK_a was claculated via the method in [6]. The IR spectra of films or mineral oil suspensions of the compounds were obtained with a UR-10 spectrometer.

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