B) A solution of 5 mmole of 1-heptyl-4,5-dihydroxymethyl-1,2,3-triazole in 5 ml of dioxane containing 0.01 g of sodium was added to a solution of 1.3 g (0.01 mole) of benzoylacetylene in 5 ml of dioxane, and the mixture was heated with stirring for 1 h. It was then worked up as in method A to give 1.22 g (68%) of acetal VIII with mp 68-69°C.

c) A solution of 1.3 g (0.01 mole) of benzoylacetylene, 0.9 g (0.01 mole) of 2-hydroxymethyl-1,2,3-triazole (IVa), and one to two drops of triethylamine in 5 ml of dioxane was heated for 3 h, after which the solution was concentrated, and the precipitated crystals of triazolyl vinyl ketone VIIIa were removed by filtration to give 0.6 g (30%) of a product with mp 130-131°C [1]. The evaporated mother liquor was chromatographed with a column filled with aluminum oxide, and the eluent was removed to give 0.2 g (10%) of VIIIa and 0.4 g (20%) of VIIIb with mp 92-93°C. The PMR spectra of triazolyl vinyl ketones VIIIa,b contain signals of protons of the triazole ring (8.81 and 8.04 ppm for VIIIa and 8.07 ppm for VIIb) and protons of a double bond (7.80, 8.45, 7.90, and 8.40 ppm). The IR spectra contain a band at 1680 cm⁻¹, which is characteristic for a carbonyl group, and a band at 1620 cm⁻¹, which is characteristic for a conjugated double bond. The principal constants of the compounds obtained are presented in Table I.

**LITERATURE CITED**


**TETRAZOLES.**

13. * PROTONATION OF TETRAZOLYLACETIC ACIDS*

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and G. I. Koldobskii

The protonation of isomeric 1H-, 2H-, and 5H-tetrazolylacetic acids, as well as a series of 5-aryl-1H- and 5-aryl-2H-tetrazolylacetic acids, in aqueous sulfuric acid solutions was studied by IR, UV, and PMR spectroscopy. It is shown that all of the investigated tetrazolylacetic acids are protonated in the tetrazole ring at sulfuric acid concentrations up to 96%; the proton adds to the nitrogen atom in the 4 position.

The acid-base properties of tetrazolylacetic acids have not been adequately studied [2]. It is known that these compounds are stronger acids than acetic acid [3]. No information regarding the basicities of tetrazolylacetic acids is available. At the same time, such data are necessary in the investigation of the kinetics and mechanism of acid-catalyzed reactions of these compounds. In this connection we studied the protonation of isomeric 1H-, 2H-, and 5H-acids.

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*See [1] for communication 12.*

TABLE 1. Chemical Shifts of the Methylenne Protons and Frequencies of the Stretching Vibrations of the Carbonyl Group of Tetrazolylacetic Acids in Aqueous H₂SO₄ Solutions at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>H₂SO₄ concn., %</th>
<th>δCH₂, ppm</th>
<th>νC=O, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30.2</td>
<td>76.4</td>
<td>96.5</td>
</tr>
<tr>
<td>Ia</td>
<td>5.55</td>
<td>5.82</td>
<td>5.82</td>
</tr>
<tr>
<td>IIa</td>
<td>5.78</td>
<td>6.10</td>
<td>6.10</td>
</tr>
<tr>
<td>III</td>
<td>4.30</td>
<td>4.75</td>
<td>4.75</td>
</tr>
</tbody>
</table>

TABLE 2. Protonation of Tetrazolylacetic Acids in Aqueous H₂SO₄ Solutions at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>m</th>
<th>−pK⁺BH⁺</th>
<th>−pK⁺BH⁺</th>
<th>r</th>
<th>n</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>1.02±0.01</td>
<td>3.72±0.07</td>
<td>3.65; 3.65*</td>
<td>0.98</td>
<td>9</td>
<td>0.21</td>
</tr>
<tr>
<td>IIa</td>
<td>0.90±0.05</td>
<td>4.08±0.21</td>
<td>4.53; 4.32*</td>
<td>0.99</td>
<td>8</td>
<td>0.08</td>
</tr>
<tr>
<td>III</td>
<td>0.91±0.04</td>
<td>2.72±0.11</td>
<td>2.99; 2.92*</td>
<td>0.99</td>
<td>9</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*Calculated from Eq. (2)

Fig. 1. UV spectra of 5-(m-methylphenyl)-2H-tetrazolylacetic acid in aqueous sulfuric acid solutions, %: 1) 39.0; 2) 45.0; 3) 60.8; 4) 65.4; 5) 69.9.

2H-, and 5H-tetrazolylacetic acids (Ia, IIa, and III), as well as two series of 5-aryl-1H- and 5-aryl-2H-tetrazolylacetic acids (Ib-i, IIb-i), in aqueous sulfuric acid solutions by IR, UV, and PMR spectroscopy.

On the basis of the available information on the basicities of substituted tetrazoles [4] and carboxylic acids [5] it may be assumed that in aqueous sulfuric acid solutions with moderate concentrations tetrazolylacetic acids are protonated in the tetrazole ring; protonation at the carboxy group is also possible when the sulfuric acid concentration is increased.

This fact must be taken into account in the quantitative evaluation of the basicities of tetrazolylacetic acids.