SYNTHESIS OF AZO COMPOUNDS CONTAINING TRIAZOLE AND TETRAZOLE RESIDUES

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Triazole- and tetrazolediazonium sulfates were coupled with aromatic azo components. The effect of the structure and medium on the chromaticity of the azo compounds was studied.

The ability of many heterocyclic diazonium salts to undergo coupling reactions is well known [1, 2]. Heterylhydroxyazo and heterylaminoazo compounds have been obtained as a result of coupling. There have been studies devoted to the investigation of the tautomerism and electronic structures of heterylazo compounds [3, 4], but the problem of the effect of the nature of the heterocycle on their structures, chromaticity, and complexing ability has not yet received adequate study.

It seemed of interest to accomplish the synthesis of aminoazo and hydroxyazo compounds that contain triazole and tetrazole residues. For this, we carried out the coupling of 1,2,4-triazole-3-diazonium



Fig. 1. Absorption spectra in ethanol (1-3) and alcoholic alkali (1a-3a): 1 and 1a) tetrazolylazophenol; 2 and 2a) 4-tetrazolylazo-1-naphthol; 3 and 3a) 9-tetrazolylazo-10hydroxyanthracene. and tetrazolediazonium sulfates with various aromatic azo components, as a result of which we obtained a series of azo compounds in good yields (Table 1). These compounds are slightly soluble in water but soluble in organic solvents.

Compound IX was also obtained by alternative synthesis by reaction of 5-hydrazinotetrazole with p-benzoquinone. The compounds synthesized by the two methods proved to be identical with respect to melting points and absorption spectra.

The spectra of hydroxyazo compounds I, IV, V, VI, XII, XIII, and XIV in the visible region contain two absorption maxima; this is apparently due to the presence of a tautomeric equilibrium between the oxoid (A) and quinoid (B) forms (Fig. 1).

It is interesting to note that in conformity with [4], the presence of the greater electron-acceptor tetrazole ring generally causes a bathochromic change in the color as compared with the corresponding triazolylazo compounds. A bathochromic shift in the absorption maximum, which is associated with transition to the ionic state with a delocalized negative charge, is observed during the action of alkali on the hydroxyazo compound.

The color of 4-(1,2,4-triazolyl-3-azo)dimethylaniline (VIII) and 4-tetrazolylazodimethylaniline (XVI)

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Com- pound	z	R	mp, °C*	Empírical formula	N, %		λ _{max} , nm		%
					found	calc.	in ethanol	in al- coholic alkali	Yield,
I II	CH CH	p-HOC ₆ H 2,4-Dihydroxy- phenyl	205206 280282	$\begin{array}{c} C_8H_7N_5O\cdot H_2O\\ C_8H_7N_5O_2\end{array}$	33,4 34,4	33,8 34,1	402; 450 408	453 456	77 99
Ш	ĊH	4-Hydroxy-3-carboxy-	258259	$C_9H_7N_5O_3$	29,5	30,0	402	430	48
IV	СН	4-Hydroxy-α-naph-	253255	$C_{12}H_9N_5O$	28,7	29,3	446; 536	514	59
V	СН	2-Hydroxy-α-naph- thyl	237238	C12H9N5O	28,9	29,3	402; 460	490	90
VI VII	CH CH	10-Hydroxyl-9- anthryl 2-Hydroxy-5-methyl-	254-256 255-257	C ₁₆ H ₁₁ N5O C9H9N5O	23,8 35,1	24,2 34,8	404; 556 406	565 484	55 74
VIII	СН	phenyl p-Dimethylamino-	205208	C10H12N67	39,2	38,9	485	-	13
IX	N	p-HOC ₆ H ₅	134-135	C7H6N6O	43,8	44,0	406	454	54
X	IN N	2,4-Dinydroxy- phenyl	178—17 9	$C_7H_6N_6O_2\cdot H_2O$	37,9	37,5	412	488	99
XI	N	phenyl	266-268	$C_8H_6N_6O_3$	28,6	28,1	406	422	89
XII	N	4-Hydroxy-α-naph- thyl	242-243	C11HaNaO	35.5	35.0	410: 536	516	98
XIII	N	2-Hydroxy-α-naph- thyl	184-185	CuH _n N _n O	35.3	35.0	418 458	490	80
XIV	N	10-Hydroxyl-9-anthryl	239-240	$C_{15}H_{10}N_{6}O$	28,4	28,9	416; 535	565	45
· XV	ĩN	2-Hydroxy-5-methyl- phenyl	142-143	C ₈ H ₈ N ₆ O	41,8	41,6	410	496	44
XVI	N	p-Dimethylamino- phenyl	145146	C ₉ H ₁₁ N ₇	47,7	45,6	491‡		44

* The compounds were purified for analysis by crystallization: I, IV, V, VI, IX, XIII, XIV, XV, and XVI from ethanol, VII from aqueous acetone, XII from aqueous pyridine, and II, III, VIII, X, and XI from water.

 \dagger In acidic media, λ_{\max} 543 nm, compared with 462 nm in concentrated acid.

 \ddagger In acidic media, λ_{max} 515 nm, compared with 444 nm in concentrated acid.

undergoes a bathochromic change when acid is added; this is associated with the formation of a cation bearing a delocalized positive charge (C). While XVI has a deeper color than triazolylazo compound VIII



due to the better delocalization of the free pair of electrons of the dimethylamino group in the electronacceptor tetrazole ring, in the case of cation form C the tetrazole ring hinders redistribution of the positive charge, and the cation of XVI is less deeply colored.

The addition of concentrated sulfuric acid to amines VIII and XVI, on the other hand, causes a hypsochromic shift of the absorption maximum, which is associated with the formation of a dication (D).



EXPERIMENTAL

1,2,4-Triazolyl-3-azosalicylic Acid (III). A total of 7 ml of a 1% sodium nitrite solution was added at 0° to a solution of 0.84 g (0.01 mole) of 3-amino-1,2,4-triazole in 25 ml of 30% sulfuric acid, after which the mixture was allowed to stand for 15 min. A solution of 1.38 g (0.01 mole) of salicylic acid in 40 ml of ethanol was then added to the diazonium salt solution, and the mixture was neutralized to pH 3-4 by the addition of sodium acetate. The mixture was then allowed to stand in the cold for 24 h, and the precipitated III was removed by filtration and washed with water. A similar method was used to obtain II, X, and XI.

Compounds I, IV, VII, and XV were obtained by the method described above, but without neutralization of the reaction mixture with sodium acetate (Table 1).

<u>1,2,4-Triazolyl-3-azodimethylaniline (VIII)</u>. A 0.84 g (0.01 mole) sample of 3-amino-1,2,4-triazole in 25 ml of 30% sulfuric acid was diazotized at 0° with 7 ml of a 1% solution of sodium nitrite. The diazonium salt solution was then added to a solution of 1.3 ml (0.01 mole) of dimethylaniline in 40 ml of ethanol and 17 ml of pyridine at 0°, and the mixture was allowed to stand at 0° for 24 h. The dark-red precipitate was then removed by filtration and washed with water. Compounds VI, IX, XIV, and XVI were similarly obtained.

Tetrazolylazophenol (IX). A 0.85 g (0.01 mole) sample of 5-aminotetrazole was diazotized in 25 ml of 30% sulfuric acid at 0° with 7 ml of 1% sodium nitrite solution, and the resulting diazonium salt was reduced at 0-3° with a solution of 3.8 g (0.02 mole) of ShCl_2 in 8 ml of concentrated HCl. A 1.1 g (0.01 mole) sample of benzoquinone was added to the solution, and the mixture was heated for 1 h on a water bath. It was then cooled, and the precipitated IX was removed by filtration and crystallized from aqueous ethanol to give 1.47 g (77%) of a product with mp 134-135°. No melting-point depression was observed for a mixture of this product with a sample of IX obtained via the preceding method.

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