HETERYLARYL N-HYDROXYTRIAZENES

I. SYNTHESIS OF N-HYDROXYTRIAZENES, QUATERNARY SALTS, AND CYANINE DYES WITH HYDROXYTRIAZENE GROUPS

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N-Hydroxytriazenes were obtained by the coupling of phenylhydroxylamine with diazotized 5(6)-amino-2-methylbenzothiazole, 1-phenyl-2-methyl-5-aminobenzimidazole, and 3-aminopyridine. Quaternary salts, which were used for the synthesis of cyanine dyes, were synthesized by alkylation of the N-hydroxytriazenes with methyl and ethyl iodides.

Very little study has been devoted to heterylaryl N-hydroxytriazenes. Only aliphatic aromatic, aromatic, and several heteroaromatic N-hydroxytriazenes – 2-benzothiazolylhydroxylamine derivatives – have been described [1,2]. In recent years N-hydroxytriazenes have been attracting the attention of researchers owing to their complexing ability. Several alkylaryl and diaryl N-hydroxytriazenes have been proposed as analytical reagents for metal cations [3].

One method for the preparation of N-hydroxytriazenes is coupling of diazonium salts with hydroxylamine derivatives in the presence of sodium acetate or a mineral acid. We used this method to synthesize heteroaromatic N-hydroxytriazenes (I-IV) from phenylhydroxylamine and diazotized 5(6)-amino-2-methylbenzothiazole, 1-phenyl-2-methyl-5-aminobenzimidazole, and 3-aminopyridine (Table 1). The N-hydroxytriazenes are yellow substances that are soluble in organic solvents and almost insoluble in water; they also have all of the properties characteristic for alkylaryl and diaryl N-hydroxytriazenes. Blue, black, and green colorations appear when a drop of aqueous $FeCl_3$ solution is added to an alcohol solution of the hydroxytriazene. The N-hydroxytriazenes are decomposed by mineral acids and melt with decomposition.

Like aromatic hydroxytriazenes, the UV spectra of alcohol solutions of the investigated hydroxytriazenes have two sharply expressed absorption maxima at 260 and 360 nm, as well as a small inflection at 320-350 nm. The long-wave maximum corresponds to the absorption of the hydroxytriazene group and is bathochromically shifted for hydroxytriazenes I and II as compared with 1,3-diphenyl-3-hydroxytriazene (348 nm). The position of the hydroxytriazene group in the benzothiazole ring affects the intensity of the hydroxytriazene maximum. A hydroxytriazene group in the 6 position of the benzothiazole ring is in conjugation with the heterocyclic nitrogen atom, which leads to an increase in the absorption intensity. This sort of conjugation is absent in the 5 position.

The previously undescribed quaternary salts of N-hydroxytriazenes (V-VIII) were obtained by the reaction of N-hydroxytriazenes with alkylating agents (methyl and ethyl iodides). The quaternary salts of N-hydroxytriazenes are colorless or slightly yellowish, crystalline substances that are soluble in alcohol and almost insoluble in organic solvents (Table 1).

The presence of an active methyl group in the 2 position of the quaternary salts made it possible to synthesize the previously unreported cyanine dyes with hydroxytriazene groups (Table 2) by known methods [4,5]. From a comparison of the absorption maxima of the cyanine dyes that we obtained with the absorption maxima of the corresponding dyes that do not contain hydroxytriazene groups, it can be concluded that the introduction of a hydroxytriazene group into the benzothiazole and benzimidazole rings of the cyanine dyes leads to a slight bathochromic shift of the absorption maximum. A comparison of the absorption max-

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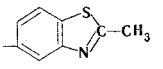
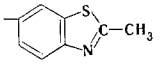
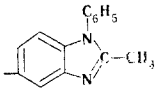
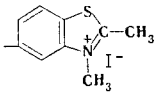
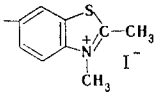
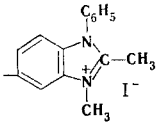
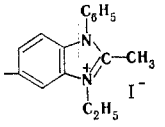
TABLE 1

$C_6H_5N-N=N-R$
|
OH

Compound	R	Mp, °C (dec., alcohol)	Empirical formula	Found, % N	Found, % S	Calc., % N	Calc., % S	λ_{max}, nm (lg ε)	Yield, %
I		144	$C_{14}H_{12}N_4OS$	19,7	11,1	19,7	11,3	250 (4,38); 360 (4,39)	72
II		148	$C_{14}H_{12}N_4OS$	19,7	11,6	19,7	11,3	258 (4,19); 365 (4,49)	77
III		141	$C_{20}H_{17}N_5O$	20,3	—	20,1	—	252 (4,38); 360 (4,35)	48
IV	β-Pyridyl	135	$C_{11}H_{10}N_4O$	26,2	—	26,2	—	235 (4,13); 345 (4,42)	76
V		205	$C_{15}H_{15}IN_4OS$	13,0	7,4	13,1	7,5	355 (4,32)	63
VI		182	$C_{15}H_{15}IN_4OS$	13,0	7,6	13,1	7,5	364 (4,57)	67
VII		179	$C_{21}H_{20}IN_5O$	14,3	—	14,4	—	357 (4,58)	65
VIII		186	$C_{22}H_{22}IN_5O$	14,1	—	14,0	—	355 (4,61)	60

ima of dyes with hydroxytriazene groups with the maxima of unsubstituted dyes and dyes that have electron-donor and electron-acceptor groups confirms the electron-donor character of the hydroxytriazene group.

EXPERIMENTAL

Heteroaromatic N-Hydroxytriazenes (I-IV). A solution of a diazonium salt, obtained by diazotization of 0.018 mole of the appropriate amino derivative of benzothiazole, benzimidazole, or pyridine by the usual method, was added to 2 g (0.018 mole) of phenylhydroxylamine dissolved in 200 ml of water acidifed with 40 ml of concentrated HCl. The mixture was cooled with ice. The viscous, amorphous precipitate that formed after 0.5 h was removed by filtration, washed with ice water, dried in a vacuum desiccator, and washed with benzene and ether (Table 1).

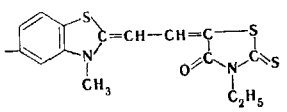
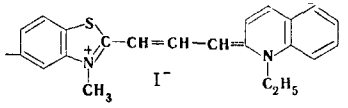
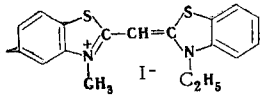
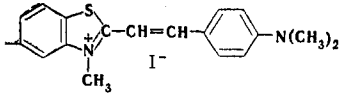
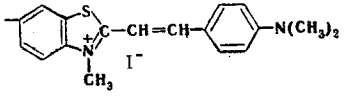
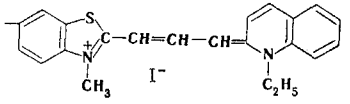
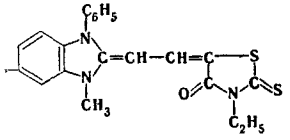
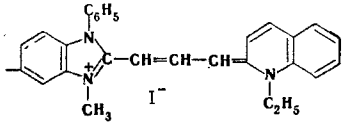
Quaternary Salts of N-Hydroxytriazenes (V-VIII). A mixture of 0.01 mole of the hydroxytriazene and 0.5 mole of alkyl halide was heated in a sealed ampul at 55-60° for 20 h. The ampul was cooled and opened, and the residue was extracted and washed with hot benzene (Table 1).

3-Ethyl-5-[3-methyl-5-(3-phenyl-3-hydroxy-1-triazeno)benzothiazolinylidene-2-ethylidene]thiazolidine-2-thion-4-one (IX). A mixture of 0.001 mole of 1-(2-methyl-6-benzothiazolyl)-3-phenyl-3-hydroxytriazene, 0.001 mole of 5-acetanilidomethylidyne-3-ethylrhodanine, 0.001 mole of triethylamine, and 5 ml of ethanol was heated on a water bath for 0.5 h. The mixture was cooled, and the precipitated product was removed by filtration and washed with water, alcohol, and ether (Table 2). Compound XV (Table 2) was similarly obtained.

[1-Phenyl-3-methyl-5-(3-phenyl-3-hydroxy-1-triazeno)-2-benzimidazolyl]-[1-ethyl-2-quinolinyl]trimethylidynecyanine Iodide (XVI). A mixture of 0.001 mole of 1-(1-phenyl-2-methyl-5-benzimidazolyl)-3-

TABLE 2

$C_6H_5N-N=N-R$
|
OH

Compound	R	Mp, °C (dec. from alcohol)	Empirical formula	Found, %		Calc., %		λ_{max}, nm (lg ε)	Bathochromic shift, nm	Yield, %
				N	S	N	S			
IX		218	$C_{21}H_{19}N_5O_2S_3$	14,7	20,5	14,9	20,5	535 (4,87)	5	58
X		223	$C_{28}H_{26}IN_5OS$	11,4	5,3	11,5	5,3	585 (4,81)	5	47
XI		215	$C_{24}H_{22}IN_5OS_2$	11,7	10,9	11,9	10,9	445 (4,44)	23	43
XII		220	$C_{24}H_{24}IN_5OS$	12,5	6,0	12,6	5,7	540 (4,63)	10	62
XIII		198	$C_{24}H_{24}IN_5OS$	12,5	5,6	12,6	5,7	535 (4,44)	7	65
XIV		200	$C_{28}H_{26}IN_5OS$	11,5	5,4	11,5	5,3	583 (4,71)	3	48
XV		201	$C_{27}H_{24}N_6O_2S_2$	15,7	12,2	15,9	12,1	525 (4,80)	6	46
XVI		212	$C_{34}H_{31}IN_6O$	12,5	—	12,6	—	580 (4,82)	6	45

phenyl-3-hydroxytriazene, 0.001 mole of 2-ω-acetanilidovinylquinoline ethiodide, and 0.001 mole of triethylamine in 5 ml of acetic anhydride was heated for 30 min. The mixture was cooled, and the precipitated dye was removed by filtration and washed with alcohol and ether (Table 2). Compounds X and XIV (Table 2) were similarly obtained.

[3-Methyl-5-(3-phenyl-3-hydroxy-1-triazeno)-2-benzothiazolyl]-[3-ethyl-2-benzothiazolyl]monomethyldynecyanine Iodide (XI). A mixture of 0.001 mole of 1-(2-methyl-5-benzothiazolyl)-3-phenyl-3-hydroxytriazene, 0.001 mole of 2-methylmercaptobenzothiazole methiodide, and 0.001 mole of triethylamine in 5 ml of absolute ethanol was heated on a water bath for 1 h and cooled, and the resulting precipitate was removed by filtration and washed with alcohol and ether (Table 2).

2-(p-Dimethylaminostyryl)-1-(2-methyl-5-benzothiazolyl)-3-phenyl-3-hydroxytriazene Methiodide (XII). A mixture of 0.001 mole of 1-(2-methyl-5-benzothiazolyl)-3-phenyl-3-hydroxytriazene methiodide and 0.001 mole of p-dimethylaminobenzaldehyde in 5 ml of acetic anhydride was heated for 0.5 h and cooled, and the resulting precipitate was removed by filtration and washed with water, alcohol, and ether (Table 2). Compound XIII (Table 2) was similarly obtained.

The UV spectra of alcohol solutions were recorded with an SF-4A spectrophotometer. The absorption spectra in the visible region were recorded with an SF-10 spectrophotometer.

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