SYNTHESIS OF THIAZOLE DERIVATIVES

XXIV. 5- and 6-Vinyl-2methylbenzothiazoles and Cyanine Dyes Derived from Them*

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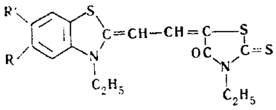
5- and 6-Vinyl-2-methylbenzothiazoles were synthesized. Thiacyanine dyes with vinyl groups attached to the heterocyclic residues were obtained from the quaternary salts of the new bases. The main absorption maxima of the dyes were determined.

2-Vinylbenzothiazole is reported in the literature [2–4]. Other vinyl-substituted benzothiazoles, in particular, 2-methylbenzothiazoles with a vinyl group attached to the benzene ring, have hitherto remained unknown. Thiacyanine dyes with vinyl groups as substituents can be synthesized from the latter compounds. The influence of vinyl groups on the color and sensitizing properties of the thiacyanines has not been studied.

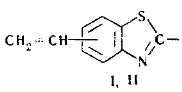
Table 1

Vinylthiadimethinemerocyanines Derived from 3-Ethylrhodanine.



Dye	R	R'	λ_{max}, nm	$\Delta\lambda$, nm
III	$CH_2{=}CH$	H	528	4
IV	H	$CH_2{=}CH$	534	10
V	H	H	524	—

We have synthesized 5- and 6-vinyl-2-methylbenzothiazoles (I) and (II) from the previously-reported [5] 5- and 6-(β-hydroxyethyl)-2-methylbenzo-thiazoles, which were converted into the corresponding chlorides, the latter then being treated with a hot KOH solution.



I, II

Vinyl groups located in the benzene ring of the benzothiazoles are not as active in addition reactions with nucleophilic reagents as the vinyl group in 2-vinylbenzothiazole. Therefore, boiling chloroethylmethylbenzothiazoles with alcoholic alkali is not accompanied by addition of the alcohol during the formation of the vinyl-2-methylbenzothiazoles, and yields of 75–77% are achieved. The vinylmethylbenzothiazoles, I and II, may be vacuum-distilled, after which they crystallize. The purified bases do not polymerize, even after standing for several days. They form dibromides by the addition of bromine to the double bonds of the vinyl groups; haloalkylates are obtained from quaternization of the nitrogen in the thiazole ring. In obtaining the thiacyanine dyes from the quaternary salts of the bases I and II, the vinyl group is not affected, and remains unchanged on prolonged storage of the dye. Thiamethinemerocyanines with 3-ethylrhodanine residues (III, IV), unsymmetrical thiacyanines (VII, VIII) and thiacarbocyanines (X, XI), and symmetrical thiacarbo-, thiadicarbo- and thiatricarbocyanines (XII, XIII, XV, XVI, XVIII, XIX) were synthesized.

The absorption maxima of the vinylthiacyanines and the corresponding unsubstituted thiacyanines are given in Tables 1 and 2. The differences (Δλ) between the former and the latter were calculated. The main absorption maxima (λ_{max}) of the vinylthiacyanines dissolved in ethanol were determined on SF-10 and SF-4 spectrophotometers, while the λ_{max} figures for the unsubstituted thiacyanine dyes V, VI, IX, XIV, and XVII are taken from the literature. From the data presented in Tables 1 and 2, it may be seen that the introduction into the symmetrical monomethine- and trimethinethiacyanines of one vinyl group at position 5 results in a shift in the absorption maximum of the dyes to longer wavelengths of 4–6 nm, and substitution at position 6 gives a shift of 10 nm. Analogous changes may be observed in the spectra of the vinylthiadimethinemerocyanines, derived from 3-ethylrhodanine (III and IV). The presence of two vinyl groups in the symmetrical monocarbo-, dicarbo- and tricarbothiacyanines at the 5,5' or 6,6' positions gave bathochromic shifts in the maxima, in the first cases of 11–14 nm and in the second cases of 21–24 nm.

EXPERIMENTAL

2-Methyl-5-(β-chloroethyl)benzothiazole. To a mixture of 9.2 g (0.044 mole) phosphorus pentachloride and 50 ml of anhydrous toluene was added, with stirring, 7.7 g (0.04 mole) of 2-methyl-5-(β-hydroxyethyl)benzothiazole [5]. When the temperature caused by the spontaneous reaction started to drop, the mixture was heated for 15 min at 110° C (in an oil bath). After heating was discontinued, stirring was continued for 30 min., 100 g of ice and 130 ml of a 20% aqueous solution of Na_2CO_3 were added, and the reaction product was extracted with toluene. The extract was dried over Na_2SO_4 and decolorized with charcoal. The toluene was removed under a vacuum at 60° C giving 8.1 g (95.2%) of yellowish crystalline product, suitable without further purification for the subsequent work. After crystallization, colorless crystals mp 49° C (from hexane). Found, %: Cl 16.64, 16.85. Calculated for $C_{10}H_{10}ClNS$: Cl 16.79.

2-Methyl-6-(β-chloroethyl)benzothiazole. Obtained as in the previous example from 7.7 g of 2-methyl-6-(β-hydroxyethyl)benzothiazole [5]. Yield of product distilling at 122–123° C (1 mm), 6.5 g

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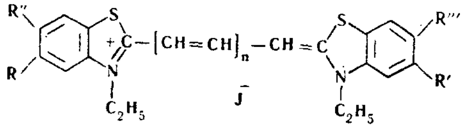
*For part XXIII, see [1].

Table 2

Vinylthiacyanines and Unsubstituted Thiacyanines and Their Absorption Maxima



Dye	R	R′	R″	R‴	*n*	λ_{max}, nm	Δλ, nm
VI	H	H	H	H	0	425	—
VII	$CH_2{=}CH$	H	H	H	0	429	4
VIII	H	H	$CH_2{=}CH$	H	0	435	10
IX	H	H	H	H	1	558	—
X	$CH_2{=}CH$	H	H	H	1	564	6
XI	H	H	$CH_2{=}CH$	H	1	568	10
XII	$CH_2{=}CH$	$CH_2{=}CH$	H	H	1	569	11
XIII	H	H	$CH_2{=}CH$	$CH_2{=}CH$	1	580	22
XIV	H	H	H	H	2	651	—
XV	$CH_2{=}CH$	$CH_2{=}CH$	H	H	2	665	14
XVI	H	H	$CH_2{=}CH$	$CH_2{=}CH$	2	675	24
XVII	H	H	H	H	3	762	—
XVIII	$CH_2{=}CH$	$CH_2{=}CH$	H	H	3	773	11
XIX	H	H	$CH_2{=}CH$	$CH_2{=}CH$	3	783	21

Table 3

Melting Points, Analytical Data, and Yields of Thiacyanine Dyes Containing Vinyl Groups

Dye	Mp, °C	Empirical formula	Found, %	Calc., %	Yield, %
III	212—216	$C_{18}H_{18}N_2OS_3$	S 25.59 25.54	S 25.68	40
IV	235	$C_{18}H_{18}N_2OS_3$	N 7.21 7.17	N 7.49	37
VII	261 (decomp.)	$C_{21}H_{21}IN_2S_2$	I 25.73 25.80	I 25.81	20
VIII	259 (decomp.)	$C_{21}H_{21}IN_2S_2$	I 25.68 25.89	I 25.81	54
X	236 (decomp.)	$C_{23}H_{23}IN_2S_2$	I 24.49 24.52	I 24.05	20
XI	230 (decomp.)	$C_{23}H_{23}IN_2S_2$	I 23.81 23.46	I 24.05	21
XII	Carbonizes without melting	$C_{25}H_{25}IN_2S_2$	I 23.16 22.97	I 23.34	55
XIII	Carbonizes without melting	$C_{25}H_{25}IN_2S_2$	S 11.50 11.44	S 11.76	55
XV	170 (decomp.)	$C_{27}H_{27}IN_2S_2$	I 21.96 21.93	I 22.28	36
XVI	195 (decomp.)	$C_{27}H_{27}IN_2S_2$	I 22.60	I 22.28	33
XVIII	235	$C_{29}H_{29}IN_2S_2$	I 21.10 21.07	I 21.30	48
XIX	175 (decomp.)	$C_{29}H_{29}IN_2S_2$	I 21.53 21.63	I 21.30	47

(76.2%). Found, %: Cl 16.59, 16.58. Calculated for $C_{10}H_{10}ClNS$: Cl 16.79.

2-Methyl-5-vinylbenzothiazole. (I). A mixture of 11.7 g (0.05 mole) 5-(β-chloroethyl)-2-methylbenzothiazole dissolved in 20 ml of ethanol and 6.2 g (0.11 mole) KOH in 60 ml of the same solvent was boiled for 40 min. After the KCl had been filtered off, the liquid was treated with 220 ml of water and extracted several times with benzene. After the extract had been dried with Na_2SO_4, the solvent was evaporated under vacuum, and the residual liquid was treated with 0.01 g of tert-butylpyrocatechol or hydroquinone and vacuum-distilled, the fraction boiling at 88–90° C (1 mm) being collected. Yield, 7.6 g (78.4%), of a dense, colorless, highly refractive liquid with a distinctive odor, resembling that of the 2-alkylbenzothiazoles. After a second distillation in the presence of hydroquinone (bp 91–92° C at 1 mm) the product slowly solidified. The crystals, pressed out on a porous plate, melted at 34–35° C. Found, %: S 18.02, 17.98. Calculated for $C_{10}H_9NS$, %: S 18.28.

To a solution of 0.6 g of the base I in 4 ml chloroform was slowly added a solution of 0.43 g of bromine in 4 ml chloroform. After 1 hr the solvent was evaporated and the residue recrystallized from methanol after decolorization with charcoal. The 2-methyl-5-(α, β-dibromoethyl)benzothiazole formed yellowish-white needles mp 96–100° C. Found, %: Br 48.04, 48.15. Calculated for $C_{10}H_9Br_2NS$: Br 47.76.

The methiodine was obtained by heating the base I for 1 hr at 100° C with a tenfold excess of methyl iodide. The crude salt was washed with acetone. Yield 73.5%, colorless crystals, mp 234–236° C (decomp. from alcohol). Found, %: I 40.08, 40.19. Calculated for $C_{11}H_{12}INS$, %: I 40.06.

The ethriodide of the base I was obtained in a similar manner to the previous salt, but the starting materials were heated to 115° C for 3 hr. Yield after washing with acetone 50–52%. Yellowish-white micro-crystalline powder, mp 214° C (from water). Found, %: I 38.23, 38.17. Calculated for $C_{12}H_{14}INS$, %: I 38.36.

2-Methyl-6-vinylbenzothiazole (II). Obtained from 2-methyl-6-(β-chloroethyl)benzothiazole in a similar manner to the preparation of base I. Yield of vacuum-distilled base II 75–77%, bp 83–85° C (1–1.5 mm). On cooling, it crystallized to yellowish white crystals; after pressing on a porous plate, mp 26° C. Found, %: S 18.22, 18.36. Calculated for $C_{10}H_9NS$, %: S 18.28.

Dibromide, small colorless needles mp 86–89° C (from methanol). Found, %; Br 48.19, 48.16. Calculated for $C_{10}H_9Br_2NS$, %: Br 47.76.

Methiodide of base II, yellowish-white crystals, mp 232° C, (decomp., from alcohol). Yield 80–82%. Found, %: I 40.09, 40.19. Calculated for $C_{11}H_{12}INS$, %: 40.06.

Methiodide of base II, colorless crystals, mp 192–194° C. (from water). Yield 51–52%. Found, %: I 38.35, 38.29. Calculated for $C_{12}H_{14}INS$, %: I 38.37.

Cyanine Dyes (Tables 1–3). Synthesized from the ethiodides of 5- and 6-vinyl-2-methylbenzothiazole by standard methods. The dimethinemerocyanines III and IV and the unsymmetrical thiacyanines VII and VIII were obtained by heating the above-mentioned quaternary salts with ethyl-2-methylmercaptobenzothiazole tosylate or 3-ethyl-5-acetanilidomethylenerhodanine in anhydrous ethanol in the presence of triethylamine. The unsymmetrical thiacarbocyanines X and XI were obtained from the initial ethiodides and the ethiodide of 2-(β-acetanilidovinyl)-benzothiazole in a mixture of pyridine and acetic anhydride (5:1). The symmetrical thiacarbocyanines XII and XIII and the thiadicarbocyanines XI and XVI were synthesized by heating the corresponding quaternary salts with orthoformic ester or with tetraethoxypropane in pyridine; and the symmetrical thiacarbocyanines by heating the intial salts with the hydrochloride of the anilide of glutaconic aldehyde in anhydrous ethanol in the presence of piperidine. The dyes X and XI were purified chromatographically in chloroform solution on alumina, while the others were crystallized from alcohol or pyridine, or boiled with alcohol, taking less than the amount necessary for solution.

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