SYNTHESIS OF THIAZOLE DERIVATIVES

XXV.* ANALOGS OF MALACHITE GREEN CONTAINING A BENZOTHIAZOLE NUCLEUS

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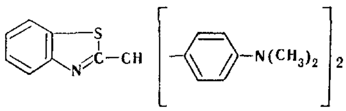
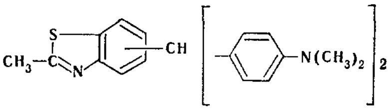
By condensing aldehydes of the benzothiazole series with dimethylaniline, leuco-bases of dyes of the type of Malachite Green have been synthesized. The oxidation of these bases has given new analogs of Malachite Green containing benzothiazole nuclei; the main absorption maxima of the dyes have been determined.

Dyes of the triphenylmethane type derived from hetaryldiphenyl-, dihetarylphenyl-, and trihetarylmethanes with residues of nitrogenous heterocycles have been little studied. Compounds containing benzothiadiazole nuclei have recently been described [2]. We have performed the condensation with dimethylaniline of aldehydes of the benzothiazole series with the aldehyde group in position 2, 5, or 6 of this heterocycle. The condensation was performed in the presence of acidic catalysts. The condensation products (I, II, and III) – analogs of the leuco-base of Malachite Green – are oxidized with lead peroxide in an acid medium to the dyes (IV-VI) of the Malachite Green type, which were isolated in the pure state in the form of salts (iodides or perchlorates).

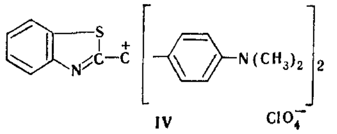
The dyes (V and VI), which are derivatives of benzothiazol-5-yl- and benzothiazol-6-yldiphenylmethanes, are obviously closer analogs of Malachite Green than the dye (IV). The latter is more deeply colored than the dyes (V) and (VI) and more deeply than Malachite Green. The light-absorption curves of the dye (IV) in ethanolic solution are characterized in the visible region by two maxima, at 450 and 666 nm, while in the spectrum of Malachite Green the two maxima are located at 430 and 620 nm.



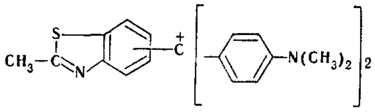
I



II, III



IV ClO_4^-



V, VI X^-

The spectrum of the dye (V) containing a 2-methylbenzothiazol-5-yl residue is characterized by maxima at 444 and 622 nm. Thus, in the dyes (V and VI) the differences from Malachite Green and from one another in the position of the long-wave and short-wave maxima are relatively small, while in the dye (IV) both maxima are shifted towards the long-wave region of the spectrum as compared with Malachite Green. The relatively deep coloration of the dye (IV) is explained, in agreement with the known rule of the influence of substituents present in a chromophore on the coloration of polymethine dyes [3], by the strong electronegative properties of a benzothiazol-2-yl residue introduced into an even-numbered position of a polymethine chromophore. The closeness of the optical properties of the dyes (V and VI) and Malachite

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Green is due to the closeness of the structures of these three dyes: the electronic influences of phenyl- and of 2-methylbenzothiazol-5-yl and -6-yl groups on the color of the dye obviously differ little, if at all.

When the dyes (V) and (VI), the molecules of which each contain an active methyl group in the benzothiazole nucleus, were heated with methyl iodide, methiodides were formed, salt formation taking place at the nitrogen atom of the benzothiazole nucleus, as is shown by the capacity of the methiodides obtained for taking part in the cyanine condensation with ethyl orthoformate.

EXPERIMENTAL

The main absorption maxima of the dyes (IV-VI) were determined in ethanolic solution on an SF-10 spectrophotometer.

Condensation of Benzothiazolecarbaldehydes with Dimethylaniline [preparation of the leuco-bases (I-III)]. In the case of benzothiazole-2-carbaldehyde, a mixture of 1.63 g (0.01 mole) of this aldehyde [4], 3.6 g (0.03 mole) of freshly distilled dimethylaniline, and 2.4 g of 30% hydrochloric acid was heated at 150°C for 13 h. In the case of 2-methylbenzothiazole-5- and -6-carbaldehydes, a mixture of 1.77 g (0.01 mole) of one of these aldehydes [5], 2.7 g (0.022 mole) of dimethylaniline, 25 ml of isopropanol, and 8.6 g (0.05 mole) of p-toluenesulfonic acid was boiled for 23 h. The subsequent working up of the reaction mixture was the same in each case: to it was added 1.2 g of anhydrous sodium acetate, and the unchanged dimethylaniline and the solvent were distilled off with steam; the residue of the leuco-base was filtered off, washed with water, and dried in the air. For analysis it was crystallized from acetone.

Benzothiazol-2-ylbis(p-dimethylaminophenyl)methane (I). Lustrous yellow crystals with mp 147-149°C; on storage they acquired a greenish tinge. Yield 77.5%. Found,%: S 8.2. $C_{24}H_{25}N_3S$. Calculated,%: S 8.3.

Bis(p-dimethylaminophenyl)(2-methylbenzothiazol-2-yl)methane (II). Colorless crystals with mp 195°C. Yield 94%. Found, %: S 8.2. $C_{25}H_{27}N_3S$. Calculated, %: S 8.0.

Bis(p-Dimethylaminophenyl)(2-methylbenzothiazol-6-yl)methane (III). Lustrous yellow crystals with mp 150-152°C. On storage in the air, they acquired a greenish tinge. Yield 90%. Found, %: S 7.9. $C_{25}H_{27}N_3S$. Calculated, %: S 8.0.

Bis(p-dimethylaminophenyl) (benzothiazol-2yl)methylium Perchlorate (IV). With heating, 3 g (7.7 moles) of the leuco-base (I) was dissolved in 48 ml of water and 3.5 ml of concentrated hydrochloric acid. The filtered solution, cooled to 0°C, was treated with 2 g of an aqueous slurry of freshly prepared lead dioxide. The mixture was stirred for half an hour, a solution of 2.2 g of sodium sulfate in 10 ml of water was added, and after 10 min the precipitate of lead sulfate was filtered off. The filtrate was mixed with a solution of 5 g zinc chloride in 5 ml of water. The zinc salt of the dye was precipitated with a saturated solution of sodium chloride and was filtered off and dried. Yield 1.65 g (22.5% calculated on the initial aldehyde). It was dissolved in acetic acid and the dye was precipitated in the form of the perchlorate by the addition of an aqueous solution of sodium perchlorate. Dark-green powder with mp 180°C (decomp.), λ_{max} 450 and 666 nm. Found, %: N 8.3. $C_{24}H_{24}ClN_3O_4S$. Calculated, %: N 8.6.

Bis(p-dimethylaminophenyl)(2-methylbenzothiazol-5-yl)methylium Iodide (V). To a solution of 2 g (5 mmoles) of the crude leuco-base (II) in a mixture of 4 ml of 5 N hydrochloric acid and 250 ml of 10% acetic acid cooled to 0°C was added 1.2 g of a freshly prepared paste of lead dioxide, and the mixture was stirred for half an hour. Then a solution of 0.7 g of sodium sulfate in a small amount of water was added, and the precipitate of lead sulfate was filtered off. The filtrate was treated with an aqueous solution of 3 g of sodium iodide. The precipitate of (V) was washed repeatedly with hot water; yield 2.2 g (78%). Dark powder with mp 191°C (decomp.), λ_{max} 444 and 622 nm. Found, %: I 24.3. $C_{25}H_{26}IN_3S$. Calculated, %: I 24.1.

When (V) was heated with an excess of methyl iodide in a sealed tube at 100°C for 1 h, the methiodide was formed, and this was easily freed from the initial dye by washing with acetone and chloroform. The methiodide of (V) reacts under the conditions of the cyanine condensation with ethyl orthoformate forming a cyanine dye with λ_{max} 572 and 618 nm.

Bis(p-dimethylaminophenyl)(2-methylbenzothiazol-6-yl)methylium Perchlorate (VI). This was synthesized from the leuco-base (III) in a similar way to (V), but it was isolated in the form of the perchlorate. Yield 1.7 g (60%). Dark green powder with mp 195°C (decomp.), λ_{max} 450 and 624 nm. Found, %: S 6.5. $C_{25}H_{26}ClN_3O_4S$. Calculated, %: S 6.4.

The dye (VI) reacts with methyl iodide in the same way as dye (V).

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