SOME REACTIONS OF 2-METHYL-3-ETHOXYCARBONYL-1,4,5,6-TETRAHYDROPYRIDINE-6-THIONE

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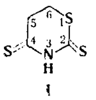
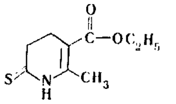
2-Methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydropyridine-6-thione was synthesized, and its reactions at the methylene and thioketo groups were investigated. The absorption spectra in the visible region were obtained for the dyes thus synthesized.

We have previously described some reactions of thiopropiorhodanine (I) at the methylene group in the 5-position [1] and at the 4-thioketo group [2].



I

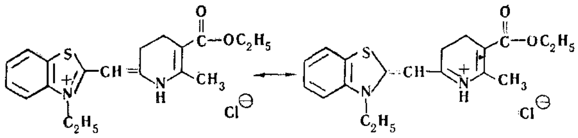


II

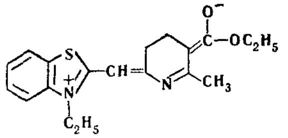
The presence of a sulfur atom in the 2-position has a definite effect on the reactivity of I. Compound II also has an acceptor group (ethoxycarbonyl), and it was therefore of interest to compare both the chemical behavior of I and II and the colors of the dyes obtained from them.

Condensations of II at the methylene group with the quaternary salt of 2-methylmercaptobenzothiazole and 1,3,3-trimethyl-2-formylmethyleneindoline lead to dyes III and IV.

The activity of the thioketo sulfur in II toward reactions with nucleophilic reagents (quaternary salt of 2-methylbenzothiazole, 3-ethylrhodanine, and aniline) was also investigated; and V, VI, and VII were obtained. Deepening of the color by 30 nm occurs when acid is added to an alcohol solution of V. This is apparently explained by the fact that, in the cationoid dye (VIII) thus formed, structures with charges on the nitrogen atoms are closer to equivalency than in the starting compound, whose polar limiting structure (Va) has a negative charge on the carbonyl oxygen atom:



VIII VIIIa



Va

The structural formulas and spectroscopic data for the dyes (III-VI) synthesized from II and, for comparison, the absorption maxima of the corresponding dyes (IX-XII) from I [1, 2] are presented in Table 1. As seen from Table 1, the absorption maxima of the dyes obtained from II are shifted to the short-wave region as compared with the analogous dyes from I. The extinction of the dyes from II with respect to the methylene group is considerably lower than the extinction of the dyes obtained via the thione group.

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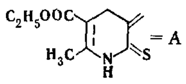
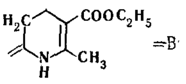
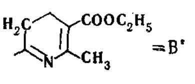
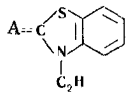
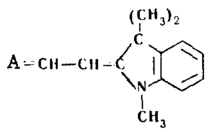
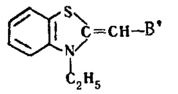
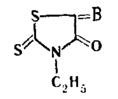
TABLE 1

Compound	Formula	λ_{max}, nm	lg ε	Compound	λ_{max} of the dyes from the salt I, nm
III		453	4,20	IX	468
IV		536	4,20	X	569
V		421	4,96	XI	475
VI		426	5,25	XII	426

EXPERIMENTAL

2-Methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydropyridine-6-thione (II). Phosphorus pentasulfide (3.2 g) was added to a solution of 2 g of 2-methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydropyridin-6-one in 26 ml of pyridine, and the mixture was refluxed for 1 h and poured into water. The resulting yellow crystals were filtered to give 1.47 g (73%) of a product with mp 109-111 deg (from alcohol). Found %: S 16.2. $C_9H_{13}NO_2S$. Calc. %: S 16.1.

2-(2-Methyl-3-ethoxycarbonyl-6-thioketo-1,4,5,6-tetrahydro-5-pyridylidene)-3-ethylbenzothiazole (III). A mixture of 0.19 g (0.001 mole) of II and 0.38 g (0.001 mole) of 2-methylmercapto-3-ethylbenzothiazolium p-toluenesulfonate was dissolved with slight heating in 1 ml of absolute alcohol. Triethylamine [0.1 g (0.001 mole)] was added to the solution; and the mixture was refluxed for 30 min, cooled, and treated with dilute (50%) alcohol. The semisolid product was separated to give 9% of long, bright-orange prisms with mp 124-126 deg (from alcohol). Found %: S 17.6. $C_{18}H_{20}N_2O_2S_2$. Calc. %: S 17.8.

2-[(2-Methyl-3-ethoxycarbonyl-6-thioketo-1,4,5,6-tetrahydro-5-pyridylidene)ethylidene]-1,3,3-trimethylindoline (IV). A mixture of 0.19 g (0.001 mole) of II and 0.19 g (0.001 mole) of 1,3,3-trimethyl-2-formylindoline was triturated in 1 ml of acetic anhydride and heated at 100 deg for 2 min. Cooling gave 0.07 g (19%) of red crystals with a metallic luster and mp 190 deg (from alcohol). Found %: S 8.2; N 7.2. $C_{22}H_{26}N_2O_2S \cdot H_2O$. Calc. %: S 8.2; N 7.1.

2-(2-Methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydro-2-pyridylidene)-3-ethylbenzothiazole (V). A mixture of 0.68 g (0.002 mole) of 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate and 0.38 g (0.002 mole) of II was dissolved with slight heating in 2 ml of absolute alcohol, and 0.2 g (0.002 mole) of triethylamine was added. An intense yellow color appeared immediately. The solution was refluxed for 5 min and worked up as in the preparation of III to give 0.1 g (16%) of lemon-yellow needles with mp 135 deg (from alcohol). Found %: S 9.3. $C_{19}H_{22}N_2O_2S$. Calc. %: S 9.4.

2-Methyl-3-ethoxycarbonyl-5-(3-ethyl-2-thioketo-4-oxo-2-thiazolinylidene)-1,4,5,6-tetrahydropyridine (VI). A mixture of 0.38 g (0.002 mole) of II and 0.32 g (0.002 mole) of 3-ethylrhodanine was dissolved with slight heating in 2.5 ml of anhydrous alcohol, and 0.2 g (0.002 mole) of triethylamine was added. The solution was refluxed for 1 h, and the precipitate was filtered to give 0.16 g (25%) of lemon-yellow needles with mp 127 deg (from alcohol). Found %: S 19.5. $C_{14}H_{17}N_2O_3S_2$. Calc. %: S 19.7.

2-Phenylamino-5-ethoxycarbonyl-6-methyl-1,4,5,6-tetrahydropyridine (VII). Compound II [0.19 g (0.001 mole)] was dissolved in 5 ml of methanol, 0.1 g (0.0011 mole) of aniline was added; and the mixture was refluxed on a water bath for 2 h. Hydrogen sulfide evolution was observed. After 3 days, the precipitate was filtered to give 0.63 g (26%) of colorless crystals with mp 143-145 deg [from alcohol–dichloroethane (3:1)]. Found %: N 10.7. $C_{15}H_{18}N_2O_2$. Calc. %: N 10.8.

LITERATURE CITED

1. E. D. Sych and I. V. Fesenko, Khim. Geterotsikl. Soedin., No. 3 (1971, in press).
2. E. D. Sych and I. V. Fesenko, Khim. Geterotsikl. Soedin., No. 2, 228 (1971).