SYNTHESIS OF NEW SPIROPYRANS FROM 2,5-DIMETHYL-1,3-BENZODITHIOLIUM SALTS

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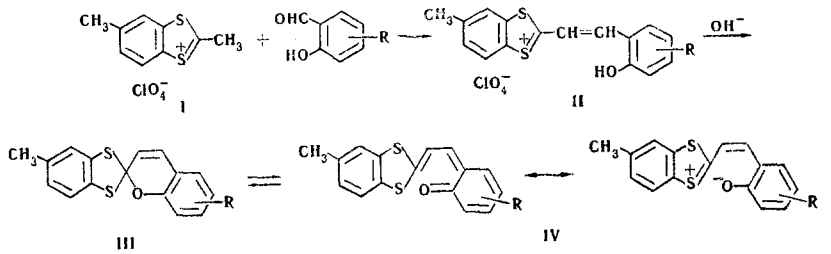
New spiropyrans that have thermochromic properties were obtained by the condensation of 2,5-dimethyl-1,3-benzodithiolium perchlorate with o-hydroxy aromatic aldehydes and subsequent treatment of the resulting 2-styryl derivatives with ammonia in ether.

Spiropyrans based on 1,3-benzodithiolium salts (I) have not been previously synthesized and studied. In the present communication, we describe the synthesis of the first representatives of this series:



a R = 5,6 = benzo; b R = 5 = NO_2

In the solid state and in solutions at low temperatures, IIIa, b exist as weakly colored cyclic forms (III). When solutions of spiropyran IIIa are heated, it undergoes a reversible transition to the intensely colored valence-tautomeric form IV, which is facilitated by an increase in the solvent polarity. The thermochromic behavior of IIIa in isoamyl alcohol is illustrated in Fig. 1. The reversible increase in the intensity

TABLE 1. 2-Styryl-5-methyl-1,3-benzodithiolium Perchlorates

Compound	Mp, °C*	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	S	C	H	S	
2-[2-(2-Hydroxy-1-naphthyl)-vinyl]-5-methyl-1,3-benzodithiolium perchlorate	201—202	$C_{20}H_{15}ClO_5S_2$	55,0	3,7	14,5	55,3	3,5	14,7	80
2-(2-Hydroxystyryl)-5-methyl-1,3-benzodithiolium perchlor.	215—216	$C_{16}H_{13}ClO_5S_2$	49,6	3,5	16,5	49,9	3,4	16,7	70
2-(2-Hydroxy-5-nitrostyryl)-5-methyl-1,3-benzodithiolium perchlorate	208—210	$C_{16}H_{12}ClNO_7S_2$	44,4	3,0	14,5	44,7	2,8	14,9	85
2-(4-Hydroxystyryl)-5-methyl-1,3-benzodithiolium perchlorate	218—219	$C_{16}H_{13}ClO_5S_2$	49,8	3,4	16,5	49,9	3,4	16,7	75

*From acetic acid.

Rostov-on-Don State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 318-320, March, 1972. Original article submitted April 27, 1971.

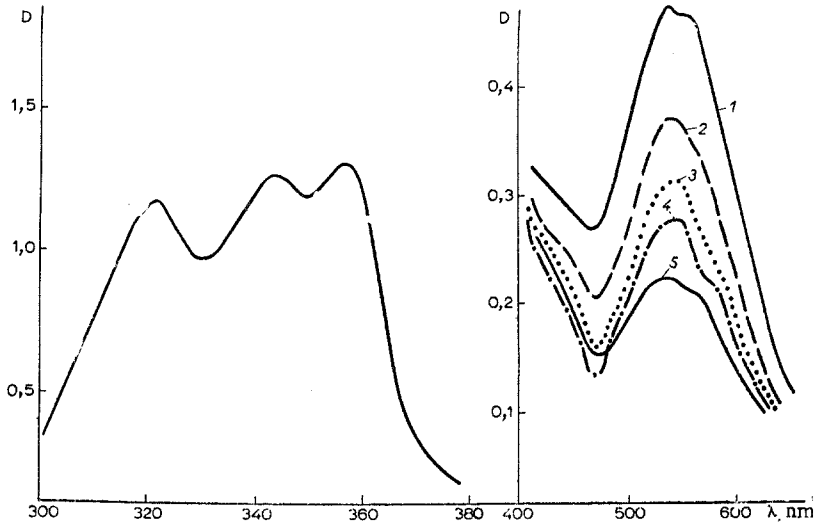


Fig. 1. Absorption spectra of IIIa in isoamyl alcohol (c $4.22 \cdot 10^{-4}$ M at 300-400 nm, $4.22 \cdot 10^{-3}$ M at 400-600 nm): 1) 70°C; 2) 60°C; 3) 50°C; 4) 40°C; 5) 30°C.

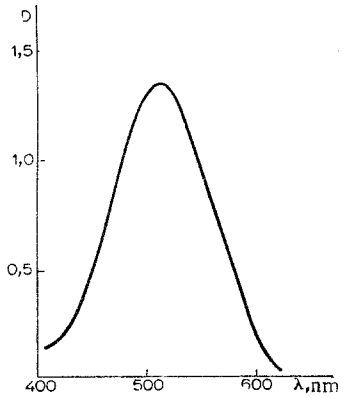
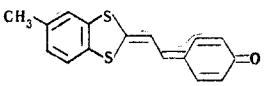


Fig. 2. Absorption spectrum of V in dimethyl sulfoxide (c $9.7 \cdot 10^{-4}$ M).

of the long-wave band (λ_{max} 540-550 nm) is explained by the buildup of the IV form. The analogy between the spectrum of spiropyran IIIa (Fig. 1)



V

and the spectrum of the synthesized p-quinoid compound V (Fig. 2) is a confirmation of the assignment of the band at 545 nm to the absorption of structure IV.

EXPERIMENTAL

2-Styryl-5-methyl-1,3-benzodithiolium Perchlorates (II). These salts were synthesized by refluxing 0.01 mole of the salt obtained in [1] with excess aldehyde in glacial acetic acid in the presence of 0.1 ml of perchloric acid for 10-15 min. The characteristics of the products are presented in Table 1.

Spiropyrans IIIa and IIIb. These compounds were obtained by treatment of the styryl derivatives (II) with ammonia in dry ether with subsequent removal of the ether by distillation. Compound IIIa was obtained in 65% yield as light-yellow crystals with mp 152-153°C (from propyl alcohol). Electronic spectra, λ_{max}, nm (D): in dimethyl sulfoxide (c $3.27 \cdot 10^{-5}$ M, cuvette thickness 1 mm) 321 (0.627), 343 (0.502), 349 (0.470); c $3.27\ 10^{-3}$ M) 560 (0.109 at 30°C, 0.2 at 70°C); in dibutyl ether (c $3.2 \cdot 10^{-4}$ M, cuvette thickness 1 mm) 321 (0.672), 343 (0.674), 349 (0.701); (c $1.6 \cdot 10^{-2}$ M) 520 (0.22 at 30°C, 0.35 at 70°C). Found: C 72.0; H 4.2; S 18.7%. $C_{20}H_{14}OS_2$. Calculated: C 71.8; H 4.2; S 19.2%. Compound IIIb was obtained in 70% yield and had mp 176-177°C (from petroleum ether–ether). Electronic spectra, λ_{max}, nm (D): in dimethyl sulfoxide (c $7.53 \cdot 10^{-5}$ M) 435 (0.77); in isoamyl alcohol (c $2.89 \cdot 10^{-3}$ M) 365 (1.5); in dibutyl ether (c $2.8 \cdot 10^{-3}$ M) 350 (1.4). Found: C 59.1; H 3.3; S 19.0%. $C_{16}H_{11}NO_3S_2$. Calculated: C 59.0; H 3.3; S 19.4%.

The spectra of the compounds were recorded with a VSU-2 spectrophotometer with a thermostat adapter.

LITERATURE CITED

1. L. Soder and R. Wizinger, Helv. Chim. Acta, 42, 1733 (1959).