PRODUCTS OF THE CONDENSATION OF 1,2,3-TRIMETHYLBENZIMIDAZOLIUM SALTS WITH o-HYDROXY ALDEHYDES

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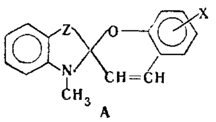
The neutralized products of the condensation of 1,2-dimethylbenzoxazolium salts [1] and 1,2-dimethylbenzothiazolium salts [2] with o-hydroxyaldehydes exist in the form of colorless spiropyranes (A, Z = O, S) which are converted into labile colored forms (B, Z = O, S) merely on heating or by the action of light.


A

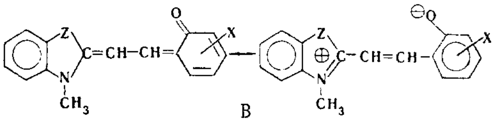
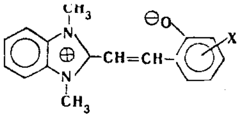
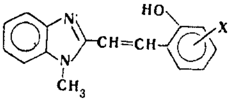

B

TABLE 1



Compound	X	mp, °C (decomp)	Empirical formula	N, % found	N, % calc.	UV Spectra λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)	UV Spectra $c \cdot 10^5 M$	Yield, %
I	H	144—147 (water)	$C_{17}H_{16}N_2O$	10,6	10,6	320 (1,6); 455 (0,48)	6,4	62
II	5-NO_2	291—296 (ethanol)	$C_{17}H_{15}N_3O_3$	13,4	13,6	260 (1,08); 300 (1,31); 420 (1,96)	4,8	83
III	3,5-Br_2	293—295 (ethanol)	$C_{17}H_{14}Br_2N_2O$	6,6	6,6	248 (1,89); 320 (1,57); 450 (1,28)	4,4	79
IV	5, 6-Benzo	290 (benzene)	$C_{21}H_{18}N_2O$	8,8	8,9	248 (3,04); 283 (1,85); 347 (1,08); 490 (1,68)	6,5	77

TABLE 2



Compound	X	mp, °C (decomp.)	Empirical formula	N, % found	N, % calc.	Yield, %
V	H	239 (ethanol)	$C_{16}H_{14}N_2O$	11,2	11,2	82
VI	5-NO_2	240 (50% ethanol)	$C_{16}H_{13}N_3O_3$	14,4	14,2	98
VII	3,5-Br_2	304 (ethanol)	$C_{16}H_{12}Br_2N_2O$	7,1	6,8	87

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In contrast to this, the stable form of the analogous 1,2,3-trimethylbenzimidazolium derivatives that we have obtained (I-IV) is the colored open structure (B, Z = N$-$CH$_3$), which cannot be converted into the colorless form A. We explain this difference by the low electrophilicity of position 2 of the imidazole ring. Since the IR spectra of I-IV (in KBr) lack absorption in the 1650-1690 cm^{-1} region, it may be assumed that the structure of these compounds largely corresponds to the bipolar limiting structure (B).

1,3-Dimethyl-2-(2-oxidoarylvinyl)benzimidazolium (I) and Its Derivatives (II-IV). These were obtained by the brief heating of equimolar amounts of 1,2,3-trimethylbenzimidazolium methosulfate and the corresponding o-hydroxyaldehydes in ethanol in the presence of piperidine (Table 1).

To confirm their structure, compounds I-III were also obtained by the action of ammonia on the methosulfates of the corresponding 1,3-dimethyl-2-(2-hydroxy-X-styryl)benzimidazoles, obtained in their turn by the quaternization of 1-methyl-2-(2-hydroxy-X-styryl)benzimidazoles (V-VII), which were prepared by Horwitz's method [3] (Table 2). The C and H contents of IV and V and the Br contents of III and VII were determined; the experimental results agreed with the calculated figures.

LITERATURE CITED

1. Australian Patent No. 62,296 (1960); British Patent No. 889,186 (1962).
2. R. Guglielmetti, E. Pretelli, and E. J. Metzger, Bull. Soc. Chim. France, 1967, 2824.
3. L. Horwitz, J. Am. Chem. Soc., 77, 1687 (1955).