CONDENSATION OF 2,3,3-TRIMETHYLINDOLENINE WITH SALICYLALDEHYDES

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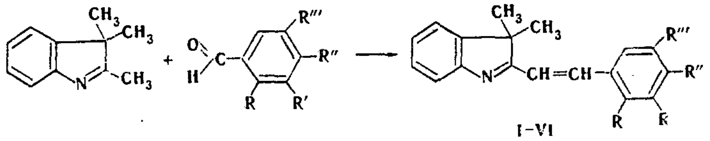
2,3,3-Trimethylindolenine undergoes condensation with aromatic aldehydes to give the corresponding 2-styrylindolenines. It is shown by means of spectroscopic data that hydroxystyrylindolenines rather than the corresponding merocyanines or spiropyrans are formed in the reaction with salicylaldehydes.

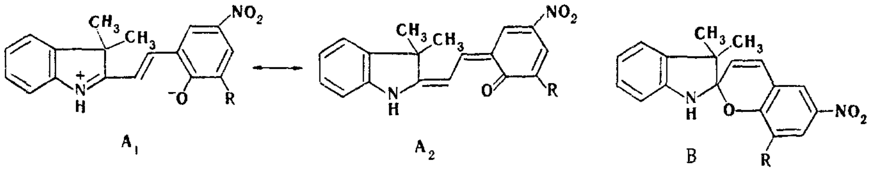
The condensation of salicylaldehydes with quaternary salts of nitrogen-containing heterocyclic compounds with labile methyl groups in the ortho position relative to the heterocyclic nitrogen atom proceeds smoothly to give the corresponding o-hydroxystyryl-substituted salts [1]. It was recently shown that the reaction of 2,3,3,-trimethylindolenine hydrobromide with aromatic aldehydes proceeds similarly to give the corresponding nitrogen-unsubstituted dyes – styryls [2].

In the present research we have established that the 2,3,3-trimethylindolenine free base also undergoes smooth condensation with aromatic aldehydes, particularly salicylaldehydes, to give the corresponding 3,3-dimethyl-2-styrylindolenines (I-VI):



I-VI

In addition to o-hydroxystyrylindolenine structures, merocyanine (intermediate between the A_1 dipolar structure and the A_2 quinoid structure) or spiropyran (B) structures can be proposed for III-VI (R=OH):



The 2-(m-nitrostyryl)-3,3-dimethylindolenine (I) structure is determined unambiguously by the method of synthesis. We made our choice in favor of the hydroxystyrylindolenine structure for II-VI on the basis of an analysis of their UV, NMR, and mass spectra. These compounds do not have an appreciable solvatochromic effect [3], and this makes the assumption of a merocyanine structure for them unlikely. The similarity between the UV spectra of II-IV and the spectrum of model compound I (Fig. 1) and the spectra of azomethines with isoelectronic structures [4] and the position of the maximum of the absorption band of II-IV at 340-360 nm (the bases obtained from 3,3-dimethyl-2-styrylindoleninium salts are characterized by λ_{max} 355-420 nm [2]) constitute evidence in favor of a hydroxystyrylindolenine structure for the investigated substances and exclude the corresponding merocyanine form, for which absorption at 500-600 nm is characteristic [5]. In view of the absence of photochromic properties and the intense absorption at 250-300 nm that is characteristic for spiropyrans of the indoline series [6], spiran structure B is also unlikely for III-VI.

The signal of the protons of the methyl groups in the 3 position in the NMR spectra of III-VI has the form of a singlet at δ 1.1-1.6 ppm. The absence of the splitting of this

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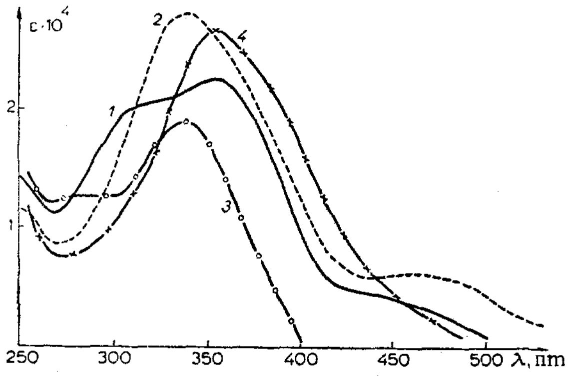

Fig. 1. Spectra of ethanol solutions of: 1) III; 2) IV; 3) I; 4) II.

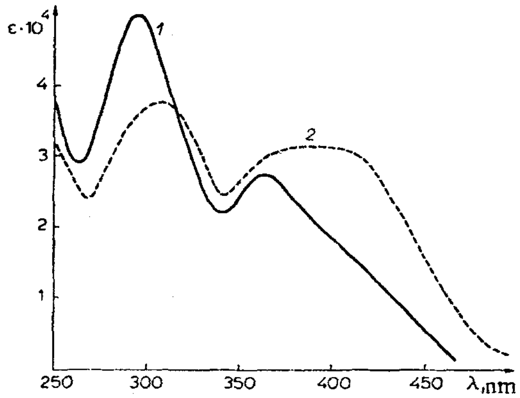

Fig. 2. Spectra of hydrogen chloride-saturated ethanol solutions of 1,3,3-trimethyl-6'-nitroindoline-2-spiro-2'-2H-chromene (1) and III (2).

TABLE 1. 3,3-Dimethyl-2-styrylindolenines (I-VI)

Compound	R*	R'	R'''	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
I	H	NO_2	H	131	73,9	5,7	9,4	$C_{18}H_{16}N_2O_2$	74,0	5,5	9,6	67,5
II	H	NO_2	H	136	69,8	5,2	8,8	$C_{18}H_{16}N_2O_3$	70,1	5,2	9,1	23,0
III	OH	H	NO_2	233—236	69,9	5,2	9.0	$C_{18}H_{16}N_2O_3$	70,1	5,2	9,1	46,0
IV	OH	OCH_3	NO_2	235—238	67,5	5,4	8,2	$C_{19}H_{18}N_2O_4$	67,3	5,4	8,3	68,0
V	OH	NO_2	NO_2	278—280	61,2	4,0	11,6	$C_{18}H_{15}N_3O_5$	61,2	4,3	11,9	90,6
VI	OH	Br	NO_2	250	55,5	3,4	7,4	$C_{18}H_{15}BrN_2O_3$	55,8	3,9	7,2	73,4

*R'' = H, except for II, for which R'' = OH.

signal that is characteristic for nonequivalent methyl groups of 3,3-dimethyl-substituted indoline spiropyrans [7] also excludes structure B for III-VI.

One of the most intense peaks in the mass spectra of III-VI is the peak of the fragment formed by detachment of a hydroxy group from the molecular ion, and this also constitutes evidence in favor of the o-hydroxystyrylindolenine structure. An intense peak at m/e 145, which evidently corresponds to a 3,3-dimethylindoleninium fragment, is also observed in the mass spectra of III-VI.

In the case of reaction with hydrogen chloride any of the forms under consideration should form the same 2-hydroxystyrylindoleninium chloride. The extremely similar spectral curves for the products of the reaction of III and 1,3,3-trimethyl-6'-nitroindoline-2-spiro-2'-2H-chromene [8] with hydrogen chloride are presented in Fig. 2. The long-wave absorption band of the N-methyl-substituted compound is shifted 28 nm hypsochromically as compared with the unsubstituted compound. Hypsochromic shifts of this sort have been previously observed [2] in the case of analogous structural changes.

In addition to II, in the reaction of 2,3,3-trimethylindolenine with 3-nitro-4-hydroxybenzaldehyde we also isolated (in low yield) the product of condensation of two molecules of the indolenine with one molecule of the aldehyde; in analogy with the products of the analogous reaction of 1,3,3-trimethyl-2-methylindoline [9], we assigned the 1,3-bis(3,3-dimethyl-3H-indol-2-yl)-2-(3-nitro-4-hydroxyphenyl)propane structure to this product.

EXPERIMENTAL

The UV spectra of the compounds were recorded with a Unicam SP-8000 spectrophotometer. The mass spectra were obtained with an MKh-1303 mass spectrometer. The NMR spectra of deuterodimethyl sulfoxide solutions of the compounds were recorded with a Tesla BS-467 spectrometer.

3,3-Dimethyl-2-styrylindolenines (I, III-VI). A solution of 1.59 g (0.01 mole) of freshly distilled 2,3,3-trimethylindolenine [10] and 0.01 mole of the aldehyde in 15-25 ml of ethanol was refluxed for 1.5-4 h, after which it was cooled, and the precipitate was separated and crystallized from ethanol (I, III, and IV) or tetrahydrofuran (V) or washed with boiling ethanol (VI). The properties of the compounds obtained are presented in Table 1.

3,3-Dimethyl-2-(3-nitro-4-hydroxystyryl)indolenine (II). A solution of 1.59 g (0.01 mole) of 2,3,3-trimethylindolenine and 1.67 g (0.01 mole) of 3-nitro-4-hydroxybenzaldehyde [11] in 20 ml of benzene was refluxed for 6.5 h, after which it was evaporated to a small volume and chromatographed with a column filled with L 40/100μ silica gel; successive elution with 100 ml of benzene and 100 ml of a mixture of benzene and ethyl acetate (9:1) gave indolenine II, which was crystallized from hexane. Indolenine II had R_f 0.33 (on Silufol in benzene—ethyl acetate). Workup of the subsequent fractions gave 0.2 g (4.3%) of 1,3-bis(3,3-dimethyl-3H-indol-2-yl)-2-(3-nitro-4-hydroxyphenyl)propane with mp 196°C (from isopropyl alcohol) R_f 0.45 (on Silufol in a benzene—ethyl acetate system), and a molecular weight of 467 (by mass spectrometry). Found: C 74.7, H 6.3, N 8.9%. $C_{29}H_{29}N_3O_3$. Calculated: C 74.5, H 6.3, N 9.0%.

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