

SYNTHESIS OF 1,3-DIMETHYL-3-PHENYLSPIRO[INDOLINE-2,2'-(2'H-1-BENZOPYRAN)]S AND AN INVESTIGATION OF THE ELECTRONIC ABSORPTION SPECTRA OF THEIR MEROCYANINE FORMS

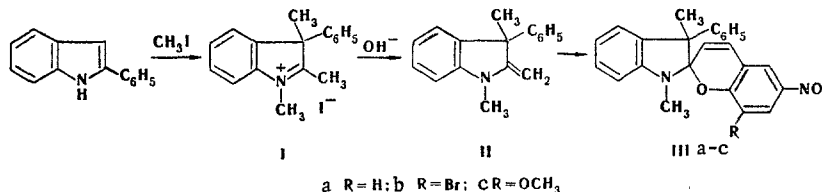
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UDC 541.145:547.752'814.1

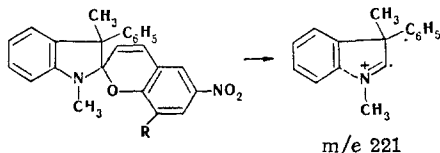
The synthesis of photochromic indoline spiropyrans containing a phenyl substituent in position 3 has been effected. The electronic absorption spectra of the colored forms of the spiropyrans obtained reveal the properties typical for merocyanine dyes.

The investigation of the photochromism of 1,3-dimethyl-3-phenyl-substituted indoline spiropyrans in comparison with the behavior of the widely known 1,3,3-trimethyl-substituted compounds may provide the possibility of drawing a conclusion concerning the influence of a substituent in position 3 of the molecule of the spiropyran on its photochromic properties. In view of this, we have performed the synthesis of a number of 1,3-dimethyl-3-phenylspiro[indoline-2,2'-(2'H-1-benzopyran)]s. The key compound for obtaining substances of this type is 1,3-dimethyl-2-methylene-3-phenylindoline (II). Making use of Plancher's procedure [1], we obtained 1,2,3-trimethyl-3-phenylindoleninium iodide (I), the treatment of which with alkali formed the methyleneindoline (II). Without isolating compound (II) in the pure state, we brought it into reaction with 5-nitro-, 3-bromo-5-nitro-, and 3-methoxy-5-nitrosalicylaldehydes and obtained the corresponding spiropyrans (IIIa-c) with satisfactory yields.

We also obtained the 1,3-dimethyl-2-methylene-3-phenylindoline (II) by the Fischer reaction of the methylphenylhydrazone of 3-phenylbutanone with anhydrous zinc chloride and then converted it into the spiropyran (IIIa). The spiropyrans synthesized by the two methods proved to be identical.



We confirmed the structure of the compounds obtained by mass spectrometry. In the mass spectra of the spiropyrans (IIIa,c) molecular peaks were found at  $m/e$  384 and 414, respectively. For the spiropyran (IIIb) the presence of two molecular peaks of approximately equal intensities at  $m/e$  464 and 462, corresponding to the molecules with the isotopes  $^{81}\text{Br}$  and  $^{79}\text{Br}$ , is characteristic. The spectra also show the peaks corresponding to the fragments formed in the splitting off from the molecular ion of one or two methyl groups. The strongest peak in the mass spectra of all the spiropyrans studied is that with  $m/e$  221, apparently corresponding to the most probable fragmentation pathway.



Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 9, pp. 1209-1211, September, 1973. Original article submitted August 28, 1972.

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TABLE 1. Characteristics of the Electronic Absorption Spectra of the Merocyanine Forms of the Spiropyrans (IIIa-c)

Comp.	Solvent	1st band			2nd band		
		$\lambda_{max}, nm$	$\epsilon_{max}$	$f$	$\lambda_{max}, nm$	$\epsilon_{max}$	$f$
IIIa	Ethanol	540	48600	0,66	369	21900	0,46
IIIa	Dioxane	582	35300	0,44	374	16200	0,27
IIIa	Toluene	593	72700	0,91	375	29500	0,50
IIIb	Ethanol	529	46300	0,66	368	28500	0,56
IIIb	Dioxane	587	19200	0,25	372	14600	0,31
IIIb	Toluene	601	90000	1,20	381	44900	0,74
IIIc	Ethanol	565	40100	0,59	392	34000	0,63
IIIc	Dioxane	602	65900	0,95	402	51900	0,78
IIIc	Toluene	603	60700	0,91	402	39300	0,59

The further decomposition of this fragment apparently takes place with the splitting off of the phenyl group, since in the spectra of the spiropyrans (IIIa-c) a peak is found at  $m/e$  144, and also with the splitting off of a methyl group and of the  $CH_3NC$  fragment (peak at  $m/e$  156). The results obtained agree well with those of French authors [2].

The spiropyrans (IIIa-c) possess photochromic properties at room temperature: on irradiation with UV light, colorless solutions in toluene and dioxane acquire a blue color which gradually disappears after the cessation of the irradiation. Solutions of the spiropyrans (IIIa-c) in ethanol are red-violet; the intensity of the coloration increases when the solutions are irradiated with UV light and decreases on irradiation with the total light of an incandescent lamp. By using a procedure developed previously [3], we determined the absorption spectra of the merocyanine forms of the spiropyrans (IIIa-c) in ethanol, dioxane, and toluene. The spectral parameters obtained after the approximation of the experimental results to Gaussian curves are given in Table 1.

It may be concluded from the results obtained that the electronic absorption spectra of the colored forms of the spiropyrans obey the laws characteristic for merocyanine dyes. In the 320-700 nm region they are represented by two nonoverlapping symmetrical bands. In the spectra of ethanolic solutions, the maximum of the first band is in the 530-565 nm region, and on passing to dioxane and toluene it shifts bathochromically by 40-70 nm. The absorption maxima of the second band, which is in the 370-390 nm region for ethanolic solutions, undergoes a bathochromic shift of 10-15 nm on passing to dioxane and toluene.

Thus, the phenomenon of negative solvatochromy is extremely characteristic for the colored forms of the spiropyrans under investigation. A comparison of the positions of the maxima of the absorption bands of the spiropyrans (IIIa-c) in the same solvents permits the conclusion that the introduction of a methoxy group into position 8' of the spiropyrans of the type studied causes a considerable bathochromic shift of both bands. The replacement of a methyl substituent (results from our previous paper [3]) by a phenyl radical in position 3 leads to a very slight bathochromic shift of the long-wave absorption band.

## EXPERIMENTAL

The measurement of the absorption spectra of the initial solutions of the spiropyrans and of solutions of the spiropyrans in the photostationary state, the calculation of the extinction coefficients of the colorless and colored forms of the spiropyrans at various wavelengths, and also the approximation of the results obtained to Gaussian curves with the aid of an M-220 computer were performed as described previously [3]. The mass spectra were obtained on an MKh-1303 instrument at an ionization potential of 40 eV.\*

**1,2,3-Trimethyl-3-phenylindoleninium Iodide (I).** A mixture of 10 g (52 mmoles) of 2-phenylindole, 10 g of methanol, and 25 g (170 mmoles) of methyl iodide was heated in an autoclave at 120°C for 3 h; the pressure reached 15-20 atm. The autoclave was cooled, and the precipitate was separated off, washed with ethyl acetate, and crystallized from methanol. This gave 5 g (27%) of (I) with mp 226-227°C [1].

**8'-R-1,3-Dimethyl-6'-nitro-3-phenylspiro[indoline-2,2'-2'H-1-benzopyran]s (IIIa-c).** A mixture of 3.4 g (9.4 mmoles) of (I) and an excess of a 10% solution of caustic soda was shaken and was then extracted with ether, and the ether was distilled off from the extract. The residue was treated with a solution of 9.6 mmoles of the corresponding salicylaldehyde derivative in 10 ml of ethanol and was boiled under reflux for 2 h. After the reaction mixture had been cooled, the precipitate was separated off and crystallized from ethanol.

\*We express our deep gratitude to A.D. Vasil'eva and I.A. Rotérmel' for measuring the mass spectra.

Compound (IIIa) (R = H) was obtained with a yield of 73%, mp 196°C. Mass spectrum, m/e (I/I<sub>max</sub>, %): 384 (37), 369 (6), 354 (5), 337 (4), 322 (4), 221 (100), 165 (4), 144 (4). Found, %: C 74.8; H 5.2; N 7.2. C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: C 75.0; H 5.2; N 7.3.

Compound (IIIb) (R = Br) was obtained with a yield of 64%, mp 264-265°C. Mass spectrum, m/e (I/I<sub>max</sub>, %): 464 (12), 462 (13), 434 (8), 432 (4), 221 (100), 165 (10), 144 (15). Found, %: C 62.4; H 4.3; Br 17.2; N 6.1. C<sub>24</sub>H<sub>19</sub>BrN<sub>2</sub>O<sub>3</sub>. Calculated, %: C 62.2; H 4.1; Br 17.3; N 6.1.

Compound (IIIc) (R = CH<sub>3</sub>O) was obtained with a yield of 45%, mp 160-161°C. Mass spectrum, m/e (I/I<sub>max</sub>, %): 414 (24), 384 (4), 221 (100), 165 (4), 144 (8). Found, %: C 72.3; H 5.4; N 6.6. C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 72.5; H 5.5; N 6.8.

Preparation of (IIIa) by the Fischer Reaction. A mixture of 7.7 g (52 mmoles) of 3-phenylbutanone [5] and 6.2 g (51 mmoles) of N-methyl-N-phenylhydrazine was heated at 95-100°C for 2 h and cooled, and then 68.1 g of fused zinc chloride and 50 ml of absolute ethanol were added and the mixture was boiled under reflux for 2 h. Then it was cooled, poured into 75 ml of a 30% solution of caustic soda, and extracted with ether, the extract was dried over caustic potash, the ether was evaporated off, and the residue was distilled in vacuum to give 5.44 g (45%) of 1,3-dimethyl-2-methylene-3-phenylindole (II) in the form of a yellow oil with mp 130°C (0.08 mm), which rapidly oxidized on storage. As described above, 1.5 g of (II) and 1.05 g of 5-nitrosalicylaldehyde gave (IIIa) with a yield of 61%, mp 196°C (from ethanol).

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