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3-NITRO-5-CHLOROMETHYLSALICYLALDEHYDE IN THE SYNTHESIS OF PHOTOCHROMIC SPIROCHROMENES OF THE INDOLINE SERIES

E. V. Braude and M. A. Gal'bershtam

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The nitration of 5-chloromethylsalicylaldehyde leads to 3-nitro-5-chloromethylsalicylaldehyde, the chlorine atom in which is smoothly replaced by a hydroxy or acetoxy group. The salicylaldehydes obtained condense with 1,3,3-trimethyl-2-methyleneindoline to give the corresponding photochromic indolinespirochromenes. The spectral-kinetics of the photochromic transformations of the spirochromenes are discussed.

The introduction of a chloromethyl group in the 3 position of 5-nitrosalicylaldehyde has made it possible to carry out the synthesis of a number of interesting indolinespirochromenes that have photochromic properties [1]; other chloromethylnitrosalicylaldehydes have not been described in the literature.

In an attempt to carry out the nitration of 5-chloromethylsalicylaldehyde (I)[2] by the action of nitric acid in glacial acetic acid or acetic anhydride or by means of copper nitrate in acetic anhydride under conditions of treatment of the reaction mixture that permit contact with water, instead of the expected 3-nitro-5-chloromethylsalicylaldehyde (II) we isolated its hydrolysis product — 3-nitro-5-hydroxymethylsalicylaldehyde (III); aldehyde II was isolated in satisfactory yield when treatment with water was excluded. The reaction of 3-nitro-5-hydroxymethylsalicylaldehyde III with thionyl chloride in the presence of dimethylaniline in chloroform also led to aldehyde II.

The lability of the halogen atom in the chloromethylnitrosalicylaldehyde (II) molecule is illustrated by its easy replacement by an acetoxy group on reaction with anhydrous sodium acetate in acetic acid, which leads to 3-nitro-5-acetoxymethylsalicylaldehyde (IV).

Aldehydes III and IV react with 1,3,3-trimethyl-2-methyleneindoline to give the corresponding indolinespirochromenes Va,b. We were unable to obtain a spirochromene from aldehyde II via a similar reaction; only pronounced resinification of the reaction mixture was observed.

For comparison, by reaction of 1,3,3-trimethyl-2-methyleneindoline with 3-nitro-5-methylsalicylaldehyde [3] we obtained the corresponding methyl-substituted spirochromene Vc.

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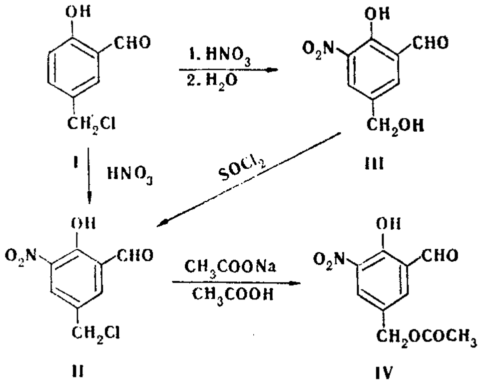

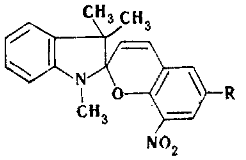

Va-c

Va R=CH$_2$OH; b R=CH$_2$OCOCH$_3$; c R=CH$_3$

Solutions of the spirochromenes have photochromic properties at room temperature: When colorless solutions of these compounds in toluene and dioxane are irradiated with UV light, they take on a blue coloration due to conversion of the spirochromene to the open merocyanine form; the blue coloration vanishes after irradiation is discontinued.

We measured the rate constants (k) of dark decolorization and the spectral properties of the compounds by the methods described in [4, 5]. The results of the studies and analogous data for spirochromenes V (R = H, C_6H_5) [7] are presented in Table 1.

The introduction of a methyl or substituted methyl group in the 6 position increases the stability of the merocyanine form in dioxane slightly; the transition to toluene increases the rate of the dark reaction. The kinetic data obtained do not make it possible to establish the relationship between the electronic or steric effect of the substituent in the 6 position and the rate constant of the dark decolorization reaction; this is in agreement with the results obtained in [4].

The spectra of the colored forms of spirochromenes V are characterized by the negative solvatochromism that is typical for merocyanine dyes [9]: The transition from toluene to alcohol gives rise to a 40-50 nm hypsochromic shift of the long-wave absorption band.

The position of the long-wave absorption band changes substantially when the substituent in the 6 position of the spirochromene molecule is changed; one should note the 20-30 nm bathochromic shift caused by the introduction of a methyl group. This fact is particularly interesting if one considers that the introduction of a methyl group in the 8 position of the 6-nitro-substituted spirochromene causes a bathochromic shift of only 3 nm [10].

Thus the introduction of substituents in the 6 position of 8-nitro-substituted indoline-spirochromene makes it possible, without changing the stability of the photomerocyanine appreciably, to substantially alter its spectral properties. This result can be used in research involving the specific creation of photochromic materials with desirable properties.

EXPERIMENTAL

The measurement of the absorption spectra of solutions of the spirochromenes in the photoelectric steady state and the approximation of the data by Gaussian curves by means of a computer were accomplished as described in [5]. The purification of the solvents, the preparation of the solutions, and the measurement of the rate constants of the dark decolorization of the photomerocyanines were accomplished as described in [4]. The samples of the compounds were purified by chromatography with 120-mm long columns with a diameter of 25 mm and L-100/250 silica gel.

TABLE 1. Parameters of the Photochromic Transformations of Spirochromenes V

R	$k \cdot 10^2$, sec^{-1}, at 20°C		Spectrum of the merocyanine form		
	toluene	dioxane	λ_{max}, nm		position of the center of the band in toluene, nm
			toluene	alcohol	
CH_2OH	2,80	2,30	590	540	585
CH_2OCOCH_3	4,10	2,36	600	555	591
CH_3	5,60	2,59	625	575	612
H	3,89[a]	3,49[a]	602[b]	542[c]	598[c]
C_6H_5	4,14[a]	4,58[a]	—	578[c]	631[c]

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[a] According to the data in [6]. [b] According to the data in [8]. [c] According to the data in [7].

TABLE 2. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, % (method)
		C	H	N		C	H	N	
II	68	44,6	2,8	6,5	$C_8H_6ClNO_4$	44,6	2,8	6,5	43 (A) 43 (B)
III	116,5—118	48,8	3,4	7,1	$C_8H_7NO_5$	48,7	3,6	7,1	61 (A) 56 (B) 50 (C)
IV	81—82	50,4	4,0	5,7	$C_{10}H_9NO_6$	50,2	3,8	5,9	42
Va	168—169	68,4	6,1	7,6	$C_{20}H_{20}N_2O_4$	68,2	5,7	8,0	22
Vb	122	67,1	5,8	7,2	$C_{22}H_{22}N_2O_5$	67,0	5,6	7,1	15
Vc	159—161	71,5	6,2	8,0	$C_{20}H_{20}N_2O_3$	71,4	6,0	8,3	21

3-Nitro-5-chloromethylsalicylaldehyde (II). A) A 50-g (0.29 mole) sample of 5-chloromethylsalicylaldehyde I [2] was dissolved by heating to 40°C in 50 ml of glacial acetic acid, and a solution of 12.5 ml (0.3 mole) of nitric acid (sp. gr. 1.51) in 20 ml of acetic acid was added dropwise at this temperature in the course of 30 min. The mixture was then stirred at 35°C for 2 h, after which it was cooled to ~20°C. Benzene (30 ml) was added, and the resulting precipitate was separated and dissolved in the minimum amount of chloroform. The solution was chromatographed on silica gel (elution with 800 ml of benzene), the eluate was evaporated, and the residue was crystallized twice from benzene.

B) A 0.79-g (4 mmole) sample of 5-hydroxymethyl-3-nitrosalicylaldehyde (III) was dissolved in 15 ml of dry chloroform, a solution of 2 g of dimethyl aniline in 5 ml of chloroform was added, and the mixture was cooled to 5-10°C. A solution of 2 g (16 mmole) of thionyl chloride in 15 ml of chloroform was added to the mixture at the same temperature in the course of 1 h, after which the mixture was stirred at 10°C for 1 h. It was then refluxed for 3 h, after which the solvent was evaporated, and the residue was dissolved in the minimum amount of chloroform. The solution was chromatographed on silica gel (elution with 100 ml of benzene), the eluate was evaporated, and the residue was crystallized twice from benzene. The product had R_f 0.2 (on Silufol, elution with benzene).

5-Hydroxymethyl-3-nitrosalicylaldehyde (III). A) A 1.7-g (0.01 mole) sample of 5-chloromethylsalicylaldehyde (I) was dissolved in 20 ml of glacial acetic acid, a solution of 0.63 g (0.01 mole) of nitric acid (sp. gr. 1.49) in 10 ml of glacial acetic acid was added in the course of 30 min at 30°C, and the mixture was stirred at 30°C for 2 h. It was then poured over ice, and the precipitate was removed by filtration and crystallized from 50 ml of alcohol to give 1.5 g of crude product. For its final purification, the product was dissolved in 50 ml of chloroform, the solution was chromatographed on silica gel (elution with 500 ml of chloroform), the eluate was evaporated, and the residue was subjected to vacuum sublimation (1 mm). The product had R_f 0.2 (on Silufol, elution with chloroform).

B) A solution of 0.63 g (0.01 mole) of nitric acid (sp. gr. 1.49) in 10 ml of acetic anhydride was added to a solution of 1.7 g (0.01 mole) of aldehyde I in 20 ml of acetic anhydride, and the mixture was stirred at 35°C for 2 h. It was then poured into a mixture of 300 ml of ice water and 2 ml of concentrated sulfuric acid, and the mixture was stirred for 4 h. The precipitate was separated and purified as described in method A.

C) A 1.1-g (5.3 mmole) sample of copper nitrate was added at 35°C in the course of 30 min to a solution of 1.7 g (0.01 mole) of aldehyde I in 20 ml of acetic anhydride, and the mixture was stirred at 35°C for 2 h. It was then evaporated to half its original volume, and a mixture of 5 ml of concentrated H_2SO_4 and 50 ml of water was added to the residue. The resulting oily precipitate was separated and dissolved in 50 ml of benzene, and the solution was chromatographed on silica gel (elution with 150 ml of benzene). The eluate was evaporated to give a product with R_f 0.15 (on Silufol, elution with benzene).

3-Nitro-5-acetoxymethylsalicylaldehyde (IV). A 2.2-g (0.01 mole) sample of 3-nitro-5-chloromethylsalicylaldehyde (II) was added to a solution of 1.2 g (0.015 mole) of calcined sodium acetate in 20 ml of acetic acid, and the mixture was refluxed for 7 h. It was then cooled and treated with 50 ml of cold water, and the mixture was extracted with chloroform. The extract was dried with anhydrous magnesium sulfate and evaporated, and the residue was triturated with hexane and crystallized twice from alcohol and a mixture of petroleum ether and carbon tetrachloride (1:1).

Spirochromenes Va-c. These compounds were obtained in accordance with the method in [11].

The properties of the compounds obtained in this research are presented in Table 2.

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