ACYLATION OF 1-(β-HYDROXYETHYL)-3,3-DIMETHYL-6'-NITROSPIRO(INDOLINE-2,2'[2H-1]BENZOPYRAN)

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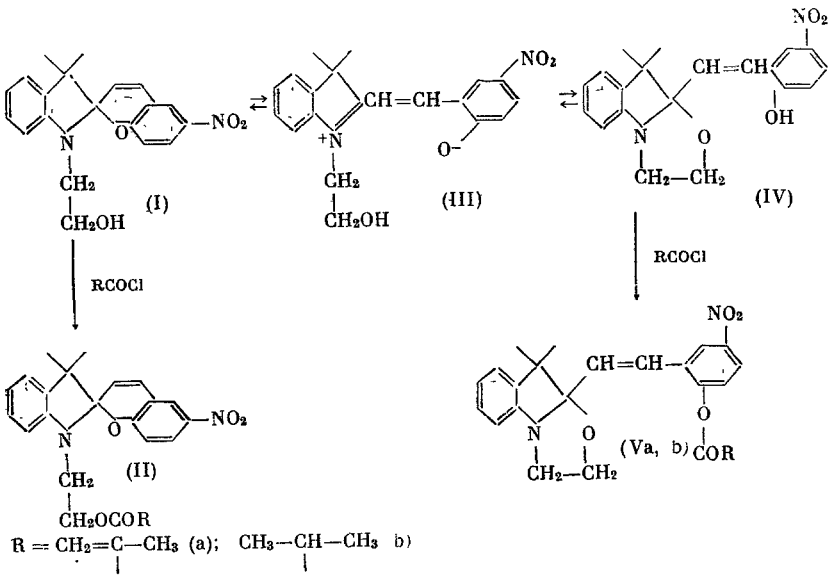
In the synthesis of 1-(β-methacryloyloxyethyl)-3,3-dimethyl-6'-nitrospiro(indoline-2,2'[2H-1]benzopyran) (IIa) the acylation of 1-(β-hydroxyethyl)-3,3-dimethyl-6'-nitrospiro(indoline-2,2'[2H-1]benzopyran) (I) with methacryloyl chloride was run by the Einchorn method in pyridine (E_t = 40.2)* and by the Schotten–Baumann method in acetone (E_t = 42.2) in the presence of NaOH [2, 3].

We found that a mixture of (IIa) and 4,4-dimethyl-3a-(2-methacryloyloxy-5-nitrostyryl)oxazolidino-[3,2-a]indoline (Va) is formed under these conditions, in which connection the yield of (IIa) does not exceed 10%. This is associated with the fact that when (I) is acylated an equilibrium is established between the colorless spiropyran (I) and colored merocyanine (III) forms. The formation of these two forms in ethanol (E_t = 51.9) is confirmed by the appearance, together with bands at 268 and 342 nm of form (I), of the absorption band of the open form (III) at 543 nm in the electronic absorption spectrum of the solution. The equilibrium constant of (I) ⇌ (III), determined from [4], and the position of the maxima of the absorption band of (III) both depend on the polarity of the solvent (Table 1).

A decrease in the equilibrium constant and a bathochromic shift of the maximum of the absorption band of (III) when the polarity of the solvent decreases are explained by the solvation effect. An abnormally high bathochromic shift of the maximum of (III) in pyridine is probably associated with the formation of the complex between the merocyanine form and the solvent. The high values of the equilibrium constants of (I) ⇌ (III) (for 1,3,3-trimethyl-6'-nitrospiro(indoline-2,2'[2H-1]benzopyran) in benzene at 25°, K_p = (0.410 ± 0.131)·10^{-4} [4]), and also the reverse photochromy observed for (I) [5] confirm the stabilization of the merocyanine form due to the formation of 4,4-dimethyl-3a-(2-hydroxy-3-nitrostyryl)oxazolidino[3,2-a]indoline (IV). As a result, the mechanism of the acylation can be depicted by the following scheme. A decrease in the polarity of the solvent shifts



*E_t is the Dimroth polarity of the solvent [1].

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TABLE 1. Value of Equilibrium Constant of (I) ⇌ (III) at 25°C and Position of Maximum of Absorption Band of (III)

Sovent	E_t, kcal/mole	K_p 10^4	λ_{max}, nm
Ethanol	51,9	513±154	543
Pyridine	40,2	23,1±6,9	584
THF	37,4	11,3±3,4	559
Benzene	34,5	2,25±0,68	573

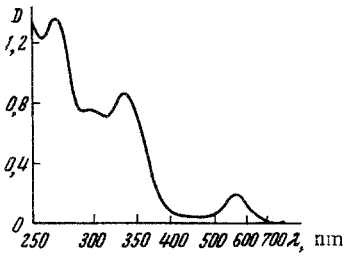

Fig. 1. Absorption spectrum of 1-(β-hydroxyethyl)-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) in ethanol, $C = 1.34 \cdot 10^{-4}$ M, $l = 1$ cm.

the equilibrium toward the closed spiropyran form (I) and creates conditions for the acylation to proceed predominantly toward the formation of (II). A decrease in the temperature exerts a similar effect [6]. The acylation of (I) in THF, in the presence of Et_3N, at −24° gave (IIa, b) in 50-60% yield. In addition, the use of THF instead of pyridine [2, 3] makes it possible to simplify the isolation of (II) substantially.

EXPERIMENTAL METHOD

The UV spectra were taken on a Specord spectrophotometer. The IR spectra were recorded on a UR-20 spectrometer.

1-(β-Methacryloyloxyethyl)-3,3-dimethyl-6'-nitrospiro(indoline-2,2'[2H-1]benzopyran) (IIa). A solution of (I) was prepared by dissolving 6 g (17 mmoles) of (I), synthesized as described in [2], in 80 ml of THF and 21.6 ml (154 mmoles) of Et_3N. With stirring and cooling (−24°), to the reaction mixture was added 5 ml (52 mmoles) of methacryloyl chloride in 1 h. When the temperature of the mixture had reached room temperature the solvent was distilled off, and the residue was extracted with a 1:10 benzene–hexane mixture. The solvent was removed, the residual yellowish crystals were recrystallized from a 1:10 benzene–hexane mixture, dissolved in benzene, and chromatographed on a column packed with silica gel (40-100 μ). The yield of (IIa) was 4.3 g (60%); white crystals with mp 111-112°. Infrared spectrum: 959 and 1720 cm^{-1}. Found: C 68.3; H 5.5; N 6.5%. $C_{24}H_{24}N_2O_5$. Calculated: C 68.6; H 5.7; N 6.7%. The compound is photochromatic at 20°. Ultraviolet spectrum of the colorless form [ethanol, λ_{max}, nm (log ε)]: 269 (4.18) and 336 (3.96). Ultraviolet spectrum of the colored form (benzene, λ_{max}, nm): 612.

1-(β-Isobutyroyloxyethyl)-3,3-dimethyl-5'-nitrospiro(indoline-2,2'[2H-1]benzopyran) (IIb). In a similar manner, we obtained (IIb) in 50% yield as slightly yellow crystals with mp 112-113° (from 1:10 benzene–hexane), and R_f 0.96, as an orange spot using 7:3 benzene–ether (Silufol UV_{254}, and using UV light for detection). Ultraviolet spectrum [ethanol, λ_{max}, nm (log ε)]: 266 (4,14) and 334 (3.86). Infrared spectrum (ν, cm^{-1}): 959, 1726. Found: C 67.9; H 6.0; N 6.5%. $C_{24}H_{26}N_2O_5$. Calculated: C 68.3; H 6.2; N 6.6%.

CONCLUSIONS

1. 1-(β-Hydroxyethyl)-3,3-dimethyl-6'-nitrospiro(indoline-2,2'[2H-1]benzopyran) (I) exists in solution as two isomeric forms. The value of the equilibrium constant varies as a function of the solvent polarity and is $(513 \pm 154) \cdot 10^{-4}$ for the ethanol solution.

2. The mechanism proposed for the acylation of compound (I) includes the reaction of the acid chloride with both isomeric forms.

3. Based on the obtained data, the method for the synthesis of 1-(β-methacryloyloxyethyl)-3,3-dimethyl-6'-nitrospiro(indoline-2,2'[2H-1]benzopyran) was improved, which made it possible to increase the yield of the product up to 60%.

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