3-(α-Hydroxy-α-methoxycarbonyltrifluoroethyl)indoles (Va-d). To a solution of 50 mmole of the appropriate indole in 80 ml of dry chloroform was added dropwise at 0°C with stirring 8.1 g (52 mmole) of methyl trifluoropyruvate. The cooling was removed, and the mixture stirred for 1 h at 20°C, the solvent removed under reduced pressure, and the residue crystallized from $CCl_4$ (Table 1).

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# THERMAL AND PHOTOSTABILITY OF 5',7'-DIALKOXY-5,6'-DINITRO-1,3,3-TRIMETHYLSPIRO(INDOLIN-2,2'-[2H]CHROMENES)

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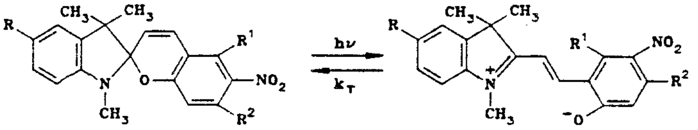
Some photochromic indoline spiropyrans have been synthesized and their thermal and photostability examined in films and in solution. Introduction of the $NO_2$ group into the indoline moiety of the molecule stabilizes the spiropyran form in solution and in films, but blocking the $NO_2$ group in the pyran moiety by adjacent alkoxy groups enhances the light stability of the compounds.

The photochromism of spiropyrans, consisting of reversible changes in color on exposure to light as a result of the conversion of the colorless spiropyran form (A) to the colored merocyanine form (B) is of interest in view of possible practical applications [1].



I-VA I-VB

I $R=NO_2$, $R^1=R^2=OCH_3$; II $R=NO_2$, $R^1=R^2=OC_2H_5$; III $R=H$, $R^1=R^2=OCH_3$; IV $R=NO_2$, $R^1=R^2=H$; V $R=R^1=R^2=H$

In most of the known spiropyrans, the merocyanine forms absorb at 560-630 nm, only a few photomerocyanines absorbing at shorter wavelengths [2, 3]. The latter compounds include 5',7'-dialkoxy-6'-nitro-1,3,3-trimethylspiropyrans, which are deeply colored under normal conditions as a result of the existence of a thermodynamic equilibrium between forms A and B. Continuing earlier investigations [3, 4], we have examined the possibility of stabilizing form A in 5',7'-dialkoxy-6'nitro-1,3,3-trimethylspiropyrans by introducing the electron-acceptor nitro-group into the indoline moiety of the molecule, and also the light stability of such pyrans.

The compounds chosen for study were the spiropyrans (I) and (II). They were obtained in the usual way, by condensing the methylene bases with the appropriately substituted salicyladehydes. The properties of the spiropyrans (I) and (II) were compared with those of the known compounds (III-V). For solutions and films at 20°C there were obtained, as

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described in [4], the photoinduced spectra, the intensity of absorption of form B at the spectral maximum ($\varepsilon_{ef}$ = D/cl), the kinetics of thermal decolorization as measured by the rate constant ($k_t$) or the half-decolorization time ($\tau_{0.5}{}^t$), and the kinetics of photodecomposition, measured by the half-decomposition time ($\tau_{0.5}{}^d$), i.e., the duration of irradiation required for the maximum photoinduced density to decrease by half. The rates of thermal decolorization of polymer films was given by the half-decolorization time $\tau_{0.5}{}^t$ rather than $k_t$, since unlike in solution the thermal reaction in the solid matrix diverges markedly from first-order kinetics. The $\tau_{0.5}{}^t$ values for films were measured after irradiating with UV for one minute. Table 1 shows the results of the examination of (I) and (II) in comparison with the model compounds (III-V), which do not contain nitro and/or alkoxy groups. In the strongly polar methanol, the spiropyran (III) exists solely in the mercocyanine form, and displays the opposite photochromic properties.

Introduction of a nitro group into the 5-position of the spiropyran (III), as shown by comparison of the intensities of long-wavelength absorption ($\varepsilon_{ef}{}^0$) of solutions of compounds (I-III), results in considerably stabilization of the spiropyran form A in solution and in films. In solution, the effect of the nitro group in (I) and (II) as compared with (III) is also apparent in somewhat greater efficiency of photocoloration ($\varepsilon_{ef}{}^{phot}$), increases in the rate constant for thermal decolorization ($k_t$), by a factor of approximately 2 in toluene and 40 in methanol, a reduction of the light stability $\tau_{0.5}{}^d$ by a factor of approximately 30 in toluene, 5-10 in acetone, and 1.2 in methanol, and a shift of up to 10 nm to longer wavelengths in the photoinduced spectrum. During the photocoloration—thermal decolorization photochromic reaction of (I) and (II), a new absorption band appeared with a maximum at around 430-450 nm. Such behavior in spiropyrans (I) and (II), apart from the stabilization of the spiropyran form A, has been observed previously in 5-nitrospirans of other series, and is due to association of forms A and B [4-6].

The observed stabilization of the spiropyran forms of (I) and (II) in solution, as would be expected [4], and in the AS copolymer (butyl methacrylate and methacrylamide) at high concentrations of the spiropyran (0.1 mole/liter) cannot be rationalized by association of form A in the initial, non-irradiated system. It appears that stabilization occurs by means of strengthening of the $C_{spiro}$—O bond in the benzopyran moiety of the molecule as a result of the electron-acceptor influence of the nitro-group in the indoline moeity of the molecule as a result of the electron-acceptor influence of the nitro-group in the indoline moiety of the molecule. Also, the formation of associates of forms A and B during the photochromic reaction, which is responsible for photodecomposition, may be associated with the enhanced light stability of the spiropyran (II) as compared with (I). In the spiropyran (II), the ethoxy-group screens the 6'-nitro group more effectively, preventing the occurrence of bimolecular reactions giving rise to decomposition products. In order of increasing protection of the active groups, primarily the nitro group, the spiropyrans are arranged in the sequence (IV), (I), (II), (V), (III). The spiropyrans are also arranged in the same sequence in respect of their light stability in toluene solution.

In the AS copolymer, the high viscosity of the glassy polymeric matrix limits the mobility of molecules A and B, thus preventing them from reacting. Consequently, the light stability of (I) and (II) in the polymer is much greater than that in solution, becoming similar to that of the spiropyran (III). When the matrix is converted into a highly elastic state by the addition of 20% of dibutyl phthalate (DBP), the light stability of the spiropyrans decreases considerably, thus confirming the significance of bimolecular reactions in the photodecomposition reaction. The difference in the light stability of spiropyrans (I) and (IV) in the glassy AS matrix appears to be due to the existence of segregates of form A with differing degrees of association, formed at the moment of preparation of the film from the highly-concentrated solution (0.1 mole/liter). Photocoloration, the formation of associates of forms A and B, and their subsequent photodecomposition take place within the boundaries of the individual segregates as a result of hindrance to their diffusion, in contrast to solutions, in which the aggregated particles interact. The extent of association is important for the light stability of the spiropyrans, and in the AS copolymer it decreases in the sequence (IV), (I), (II), (III), the same as for solutions. The model spiropyran (IV), with open, reactive nitro groups, has the lowest stability to light of any of these spiropyrans.

Hence, a nitro group in the 5 position of the indole moiety of the molecule increases the thermal stability of the colorless spiropyran form, and alkoxy groups in the benzopyran

TABLE 1. Photochemical Parameters of Spiropyrans in Solution and Films

| Compound | $\lambda_{max}$ phot, nm | $\varepsilon_{ef}^0 \cdot 10^3$, cm²/mmole | $\varepsilon_{ef}$phot $\cdot 10^{-3}$, cm²/mmole | $k_t$, sec$^{-1}$(20°C) | $\tau_{0.5}$d, min |
|---|---|---|---|---|---|
| | | | Toluene | | |
| I | 555 | 0,0 | 7,4 | 0,28 | 2 |
| II | 555 | 0,0 | 8,1 | 0,37 | 3 |
| III | 550 | 0,0 | 4,6 | 0,16 | 100 |
| IV | 630 | 0,0 | 12,4 | 0,28 | 0,6 |
| V | 600 | 0,0 | 35,3 | 0,037 | 12 |
| | | | Acetone | | |
| I | 550 | 0,0 | 6,0 | 0,46 | 6 |
| II | 560 | 0,0 | 7,9 | 0,15 | 16 |
| III | 540 | 1,8 | 5,3 | 0,039 | 82 |
| | | | Methanol | | |
| I | 530 | 0,3 | 1,2 | 0,64 | — |
| II | 530 | 0,3 | 1,3 | 0,54 | 37 |
| III | 520 | 35,4 | 1,2 | 0,012 | 50 |
| | | | Copolymer AS* | | |
| I | 550 | 0,0 | 4,0 | 60 | 60 |
| I+DBP | 550 | 0,0 | 4,3 | 3 | 2,5 |
| II | 550 | 0,0 | 4,7 | 140 | 100 |
| II+DBP | 550 | 0,0 | 7,5 | 6 | 3,5 |
| III | 540 | 1,2 | 6,0 | 30 | 110 |
| III+DBP | 540 | 1,9 | 10,0 | 10 | 40 |
| IV | 600 | 0,0 | 7,0 | 70 | 20 |

*In place of $k_t$, the value of $\tau_{0.5}{}^t$, sec is given.

moiety adjacent to the nitro group in position 6' increase the light stability of indoline spirobenzopyrans.

## EXPERIMENTAL

Spectral kinetic data for solutions of spiropyrans (I-V) at concentrations of $(2\text{-}5)\cdot 10^{-5}$ mole/liter (Table 1) were obtained by measurement in a cell of thickness 1 cm, and for the polymer films in a thickness of 10 µm, as described in [4]. Photoirradiation was carried out with a DPSh-500 lamp fitted with a UFS-6 light filter (light intensity 4.4 W/cm²). PMR spectra were obtained in $CDCl_3$ on a Varian CFT-20 spectrometer (80 MHz) relative to TMS as internal standard. The course of the reactions and the purity of the products were followed by TLC on Silufol UV-254 plates. Polymeric films of thickness 10 µm were obtained by casting a 10% solution of copolymer AS in toluene, containing 2% of the spirochromene and, if required, 20% of DBP on the weight of polymer, on a glass support, followed by drying in air for five days.

4,6-Dimethoxy- and 4,6-diethoxy-5-nitrosalicylaldehydes were obtained by alkylating phloroglucinol with the appropriate alcohols in the presence of sulfuric acid, followed by formylation and nitration of the products [3, 7, 8].

1,3,3-Trimethyl-5-nitro-2-methyleneindoline was obtained in several steps from 4-nitrophenylhydrazine and methyl isopropyl ketone, as described in [9].

5',7'-Dimethoxy-5,6'-dinitro-1,3,3-trimethylspiro(indolin-2,2'-[2H]-chromene) (I). To a boiling solution of 0.45 g (2 mmole) of 4,6-dimethoxy-5-nitrosalicylaldehyde in 70 ml of ethanol was added with stirring 0.4 g (1.8 mmole) of 1,3,3-trimethyl-5-nitro-2-methyleneindoline in 30 ml of ethanol, and the mixture boiled for 12 h. On cooling, a solid separated which was chromatographed on a column of silica gel (100/250 µm, $\ell$ = 65 cm, diameter = 0.4 cm), eluent benzene—ethyl acetate (9:1), $R_f$ 0.56. Yield 0.2 g (25%) of (I), mp 185-187°C. Found: C 59.2; H 5.1; N 9.4%. $C_{21}H_{21}N_3O_7$. Calculated: C 59.0; H 4.9; N 9.8%. PMR spectrum: 1.84 and 1.37 [each 3H, s, 3,3-$(CH_3)_2$], 2.87 (3H, s, 1-$CH_3$), 3.90 (3H, s, 5'-$OCH_3$), 3.88 (3H, s, 7'-$OCH_3$), 5.54 (1H, d, 3'-H), 7.18 (1H, 4'-H, $J_{3',4'}$ = 10.5 Hz), 6.48-8.10 (3H, m, Ar—H).

5',7'-Diethoxy-5,6'-dinitro-1,3,3-trimethylspiro(indolin-2,2'-[2H]-chromene) (II) was obtained by condensing the methylene base with 4,6-diethoxy-5-nitrosalicyaldehyde, as for (I). Yield 0.3 g (40%) of (II), mp 189-190°C. Found: C 60.0; H 5.6; N 9.0%. $C_{23}H_{25}N_3O_7$.

Calculated: C 60.6; H 5.5; N 9.2%. PMR spectrum: 1.17 and 1.37 [each 3H, s, 3,3-$(CH_3)_2$], 2.83 (3H, s, 1-$CH_3$), 5.52 (1H, d, 3'-H), 7.18 (1H, d, 4'-H, $J_{3',4'}$ = 10.5 Hz), 4.09 (4H, q, J = 7.0 Hz, 5'-, 7'-$OCH_2$), 1.49 and 1.39 [each 3H, t, 5'- and 7'-$OCH_2C\underline{H_2}$], 6.47-8.15 (3H, m, Ar—H).

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# NITROGENOUS HETEROCYCLES.

# 6.* REACTIONS OF ORGANOMAGNESIUM DERIVATIVES OF 7-AZA- AND BENZOINDOLES WITH DIETHYL OXALATE AND THE REACTIVITY OF ETHOXALYLINDOLES

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The reactions of organomagnesium derivatives of 2-methyl- or 2,3-dimethyl-7-azaindoles and 2,3-dimethylbenz[4,5]- or -[6,7]indoles with diethyl oxalate, and the reactivity of the resulting ethoxalylindoles towards phenylmagnesium bromide, have been examined. It has been shown that the course of the reaction is dependent on the solvent and the structures of the starting materials.

Previous studies of the reactions of 2-substituted N-indolylmagnesium bromides with dialkyl oxalates have shown [1-3] that when the reaction is carried out in ether, depending on the nature of the substituent in the heteronucleus either 3- or 1-derivatives of indole are obtained. The 1-alkoxalylindoles have been used [4, 5] for the synthesis of substituted benzopyrrolizines [6, 7]. Continuing these studies, we have examined the reactions of the organomagnesium derivatives of 2-methyl- and 2,3-dimethyl-7-azaindoles (Ia, b) and of 2,3-dimethylbenzo[4,5]- or -[6,7]indoles (Ic, d) with diethyl oxalate, and have shown that when the reaction is carried out in ether substituted 1-ethoxalylindoles are invariably obtained, i.e., no transfer of the reaction center takes place in (Ia).

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*No footnote given in Russian original — Publisher.

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