SYNTHESIS AND PHOTOCHEMICAL PROPERTIES OF THE INDOLINE SERIES FULGIDES

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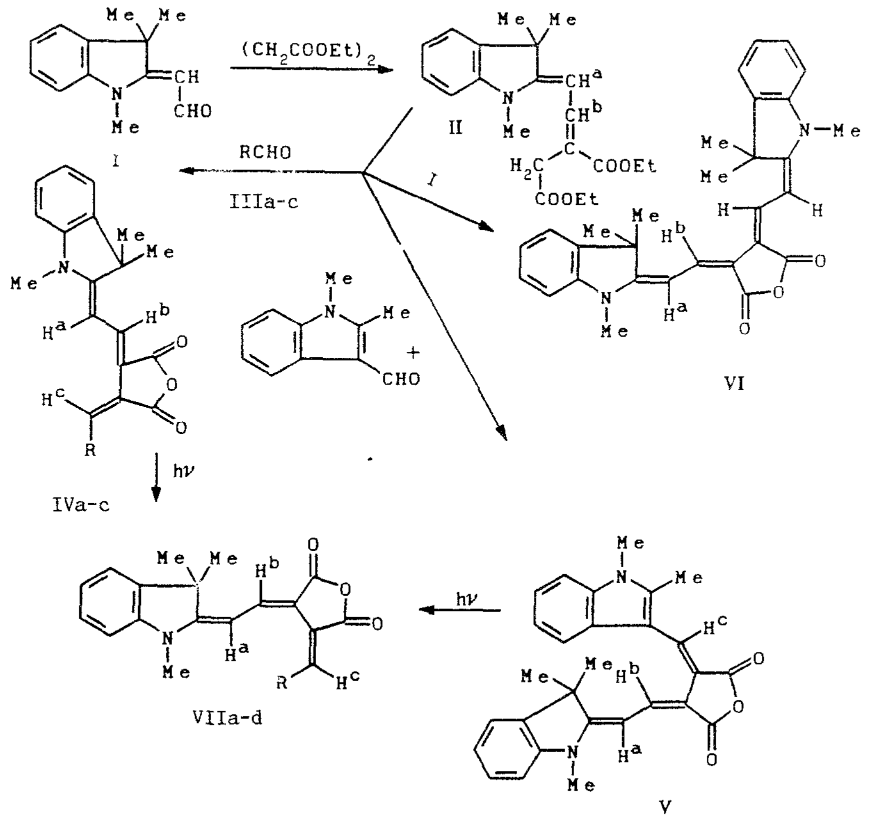
Using the Stobbe condensation fulgides that undergo E, Z-isomerization on exposure to UV radiation are obtained from diethyl [2-(1,3,3-trimethyindoline-2-ilidene)ethylidene]succinate, and benzaldehyde and its derivatives; and from 1,2-dimethyl-3-formylindole and ω-formyl-1,3,3-trimethyl-2-methyleneindoline. The structure and photochemical changes of the fulgides were investigated by means of PMR.

Continuing the search for new photochromic compounds, we have synthesized indoline series fulgides IV—VI using the Stobbe method (see scheme). Diethyl succinate II was obtained by reacting diethyl succinate with ω-formyl-1,3,3-trimethyl-2-methyleneindoline (I, Fischer aldehyde) in the presence of potassium tert-butylate, with subsequent esterification in ethanol saturated with hydrogen chloride. Compounds IV—VI were synthesized by condensing diethyl succinate II with benzaldehyde (IIIa) and its 4-fluoro (IIIb) and 4-ethoxy (IIIc) derivatives, and 1,2-dimethyl-3-formylindole; and with aldehyde I by successive hydrolysis and cyclization of the intermediate dicarbonic acids by acetic anhydride. The composition and structure of the compounds obtained were corroborated by data from elemental analysis, electronic absorption spectra, and PMR spectra (see Experimental and Tables 1 and 2).

In the PMR spectra of diethyl succinate II and fulgides IVa-c the H^a and H^b protons appear as two doublets with $J_{a,b}$ ~ 13-14 Hz, which points to the butadiene fragment having an s-*trans* conformation.



III, VIIa R = C_6H_5, b R = 4-C_6H_4F, c R = $C_6H_4OC_2H_5$; VII d R = 1,2-dimethyl-3-indolyl

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TABLE 1. Properties of Synthesized Compounds II, IVa-c, V, and VI

Compound	Mp, °C	M*	Absorption spectrum: λ_{max} nm, (lgε)	Yield, %
II	104...105**	357	286 (3,1), 325 (3,8), 379 (4,6)	44
IVa	186...188	371	322 (4,1), 367 (3,6), 499 (4,5)	42
IVb	176...178	389	332 (4,1), 366 (3,7), 500 (4,6)	24
IVc	189...190	415	348 (4,5), 503 (4,6)	22
V	214...216	438	371 (4,4), 512 (4,4), 533 (4,4)	24
VI	315...316	467	388 (4,6), 539 (4,5), 579 (4,6)	31

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*By mass spectrometry.

**Compound II recrystallized from 1:2 ethanol—water mixture.

TABLE 2. PMR Spectra of Fulgides IVa-c, V, VI, and VIIa-d

Compound	Configuration	Solvent	δ, ppm						Coupling constant $J_{a,b}$, Hz
			H^a, d	H^b, d	H^c, d	N-CH_3, s	3-$(CH_3)_2$, s	other protons	
IVa	E, E, Z	$CDCl_3$	6,97	7,87	7,41	3,38	1,24	—	13,67
		Acetone-D_6	6,98	7,96	7,31	3,45	1,29	—	13,67
VIIa	E, E, E	$CDCl_3$	4,47	7,80	~7,5*	2,44	1,66	—	13,92
		Acetone-D_6	4,50	7,88	~7,5*	2,58	1,67	—	13,91
IVb	E, E, Z	$CDCl_3$	6,99	7,84	7,33	3,39	1,29	—	13,68
VIIb	E, E, E		4,42	7,89	7,49	2,55	1,67	—	14,03
IVc**	E, E, Z	$CDCl_3$	7,00	8,07	7,35	3,38	1,37	4,11 q (CH_2) 1,48 t (CH_3)	13,68
VIIc**	E, E, Z		4,58	7,83	7,51	2,53	1,66	4,02 q (CH_2) 1,39 t (CH_3)	13,91
V	E, Z, E	$CDCl_3$	~7,1*	~7,3*	7,61	3,30	0,65 (уш.)	3,79 s (N'-CH_3) 2,53 s (2'-CH_3)	—
		Acetone-D_6	6,90	7,19	7,54	3,34	0,65 (уш.)	3,90 s (N'-CH_3) 2,57 s (2'-CH_3)	13,67
VIId	E, E, E	$CDCl_3$	4,77	7,83	7,85	2,08	1,58 1,51	3,66 s (N'-CH_3) 2,31 s (2'-CH_3)	13,91
		Acetone-D_6	4,82	7,82	7,85	2,25	1,59 1,48	3,80 s (N'-CH_3) 2,47 s (2'-CH_3)	13,91
VI	E, Z, Z, E	$CDCl_3$	6,91	7,40	—	3,34	1,72	—	13,06

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*Exact determination of chemical shift and coupling constant was complicated by overlapping of signals.

$**J_{CH_2,CH_3}$ = 7.08 Hz.

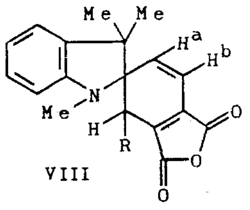
$***J_{CH_2,CH_3}$ = 6.84 Hz.

H^b protons for compounds IVa-c are observed in the 7.87-8.07 ppm region. The chemical shift of these protons suggests that they have a *cis*-arrangement (E-configuration) with respect to the nearest carbonyl group, which has a deshielding effect. Similar deshielding has been observed for E-(1,2-dimethyl-3-indolylmethylene)isopropylidene succinic anhydride [1]. The configuration of the (1,3,3-trimethylindoline-2-ilidene)methyl fragment of compounds IVa-c was determined using the intramolecular Overhauser Nuclear Effect (ONE). In the case of fulgide IVa in $CDCl_3$, for example, the superposition of an exciting field with the same resonant frequency as protons having chemical shift of 3.38 (N—CH_3) and 1.24 ppm [3-$(CH_3)_2$] produces a clear increase (by a factor of 1.6 and 1.3, respectively) in the signal intensity of protons with chemical shift 6.97 (H^a) and 7.87 ppm (H^b). This suggests that the H^a proton and N-methyl group have a *cis*-configuration and confirms that the butadiene fragment has an s-*trans*-conformation, since this is the only geometry that allows spatial interaction between the H^b proton and the protons of the equivalent indoline ring *gem*-methyl groups. The chemical shift for the H^c vinyl proton of the fulgide IV arylidene fragment (7.31 ppm in $CDCl_3$ or 7.41 ppm in acetone-D_6, Table 2) is typical of the Z-isomers of the aryl fulgides [2] and indicates that the H^b proton has a *trans*-configuration with respect to the C=O group (Z-configuration). Compound IIIa, therefore, has an E, E, Z-configuration. Using correlation of PMR spectral data as a basis, a similar structure can be ascribed to fulgides IVb and IVc (Table 2).

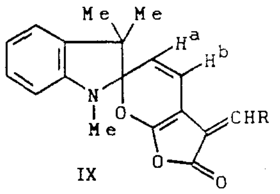
Despite the transoid structure of the butadiene fragment ($J_{a,b}$ = 13.67 Hz) fulgide V has a different molecular geometry to compounds IVa-c. The strong field shift of the H^b proton for compound V (7.19 ppm) compared to the signal for compounds IVa-c (7.87-8.07 ppm) indicates that this proton is separated from the carbonyl group and that the latter has a *cis*-configuration with respect to the (1,3,3-trimethylindoline-2-ilidene) methyl fragment. The quenching of the signal for the indoline ring N-methyl group (3.34 ppm) increases by a factor of 1.5 the signal intensity of the H^a proton having chemical shift of 6.90 ppm, which is similar in value to the chemical shifts for the H^a protons of fulgides IVa-c (6.97-7.00 ppm). This points to the fact that the H^a proton and N-methyl group have a *cis*-configuration. The *gem*-methyl group signal for fulgide V (0.65 ppm) is shifted into a strong-field region compared to the signals for the analogous protons of fulgides IVa-c (1.24-1.37 ppm). This can be explained by the fact that the groups in question are shielded by the indole ring, which is situated in the *trans*-position with respect to the neighboring carbonyl group and in a conformation that has the H^c proton and the indole ring 2-methyl group adjacent to each other. This was confirmed by the ONE method. Thus, with irradiation at the resonant frequency of the particular methyl group referred to (2.57 ppm in acetone-D_6) the signal intensity of the H^c proton is seen to increase by a factor of 1.4. Fulgide V, therefore, has an E, Z, E-configuration.

The signals for the aromatic protons of both indoline rings of anhydride VI overlap with each other, as do those for the *gem*- and N-methyl group protons with the H^a and H^b butadiene fragment protons. This implies that fulgide VI has a symmetrical structure. The similar chemical shift values for the H^a and H^b protons recorded in the case of compounds V and VI point to the fact that the H^a proton and indoline ring N-methyl group have a *cis*-configuration and the H^b proton occupies the *trans*-position with respect to the neighboring carbonyl group. The butadiene fragments, therefore, have an E, Z-configuration. The coupling constant value $J_{a,b}$ = 13.06 Hz accords with a transoid arrangement for the H^a and H^b protons.

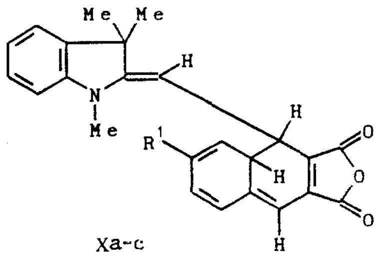
It was supposed that the deep-colored fulgides IV-VI, which show intense absorption in the 322-371 nm region (Table 1), would be converted on exposure to UV radiation into the slightly-colored spiro compounds VIII and IX, or into the naphthalene and carbazole dihydro derivatives X and XI, i.e., they would display reversible photochromism.



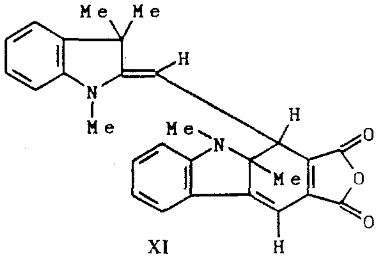
VIII



IX



Xa-c



XI

Xa R' = H, bR' = F, c R' = OEt

However when toluene solutions of fulgides IVa-c, V, and VI were exposed to UV light for 90 sec (T = 293 K), no new photoinduced bands were observed in the electronic absorption spectra, the only change being in the band intensity of the starting, rather than the irradiated form. This suggests that no significant structural changes occurred in the molecule.

PMR was used to show that when compounds IVa-c and V are exposed to UV radiation for the same length of time in deutero-chloroform, the outcome is E, Z-isomerization of the arylidene and (1,3,3-trimethylindoline-2-ilidene)ethylidene fragments, respectively; as a result these substances are partially converted into the structural isomers VIIa-d. The ratios of compounds IVa-c:VIIa-c and V:VIId are 3:2 and 4:1, respectively (from the ratio of integral intensities of methyl group signals). When fulgide IVa is irradiated in acetone-D_6, the ratio of IVa to VIIa is 2:1. Under similar conditions compound V yields a complex mixture of substances which, as PMR showed, contains fulgide VIId (see Table 2). Complete identification of all the substances formed was complicated in the latter case. An even more complex mixture was obtained when a solution of fulgide VI in $CDCl_3$ was irradiated (or heated to 50°C). Compounds VIIa-d, which are formed on exposure to UV light, have a transoid arrangement of the H^a and H^b butadiene fragment protons ($J_{a,b}$ = 13.91-14.03 Hz) and an E, E, E-configuration. Thus, the position of the

H^b doublet in the 7.80-7.89 ppm region points to the fact that the carbonyl group and (1,3,3-trimethylindoline-2-ilidene)methyl fragment have a *trans*-position. The signal for the H^c vinyl proton of compounds VIIa-d is seen in a weaker field (~0.2 ppm) than for fulgides IVa-c and V. For compounds VIIa-c this shift is caused by the isomerization of the arylidene fragment and the deshielding effect of the carbonyl group; for compound VIId it results from the fact that the H^c proton comes near to the neighboring carbonyl group as the molecule's geometry is distorted due to repulsion between the indole and indoline rings. The appreciable displacement of signals for the H^a and N-methyl group protons of fulgides VIIa-d into the strong field region compared to the signals for the analogous protons of fulgides IVa-c and V (by 2.07-2.57 ppm and 0.84-1.22 ppm, respectively) stems from the effective shielding of these protons, which are situated in close proximity to the aromatic ring. The simultaneous shielding of the H^a and indoline N-methyl group protons indicates that they have a *cis*-configuration, which was established using ONE for fulgide VIIa. Thus, when the N-methyl group signal (2.44 ppm) is quenched in $CDCl_3$, the signal intensity of the H^a proton having chemical shift of 4.47 ppm is seen to increase by a factor of 1.3.

Compound VIId is characterized by severe steric complication of the molecule, as indicated by the fact that the equivalence of the indoline ring *gem*-methyl groups is disturbed. Unlike the other indoline series fulgides the signal for these groups appears as two singlets (Table 2), which is more typical of the indoline spiropyrans as a result of the orthogonality of the indoline and pyran rings [3].

PMR with stationary photolysis failed to detect the presence of compounds VIII and IX in solutions of fulgides IVa-c and V; the former two compounds should have a *cis*-coupling constant that is typical of the closed form of spiropyrans, equal to ~ 10 Hz [3]. Neither was the formation of 1,8*a*-dihydronaphthalene (Xa-c) or 1,9*a*-dihydrocarbazole (XI) derivatives confirmed by PMR.

Thus, under fixed experimental conditions with UV radiation of short duration (up to 90 sec) and weak intensity (see Experimental) the indoline series fulgides undergo only E, Z-isomerization, which does not involve the significant change in their electronic absorption spectra that is typical of fulgide cyclization reactions [4]. The structural changes that occur in molecules of the indoline series fulgides exposed to high-intensity radiation will be described in a later work.

EXPERIMENTAL

PMR spectra were recorded on a Bruker-200-SY high-resolution spectrometer with superconducting magnet; internal standard TMS. Electronic absorption spectra were taken on a Hitachi EPS-3T spectrophotometer (in toluene). Molecular weights were determined by means of mass spectrometry on an MX-1303.

An SVD-120 lamp with UFS 5 light filter (λ_{em} 250-400 nm) was used as the source of UV radiation for studying the photochemical properties of the fulgides. The power of the luminous flux falling on the cuvette was 0.5 mW/cm^2 (measurement was made using a PP-2 cavity-type receiver). Thickness of the irradiated layer was 1 cm, area ~3 cm^2.

Elemental analysis data on C, H, and N (and F in the case of fulgide IV) were in line with calculated values for all the compounds synthesized.

1,3,3-Trimethyl-2-formylmethyleneindoline (I) was obtained as in [5]. Mp 114-116°C; yield 41.1%. Data in [5] give mp 116°C and yield 38.5%.

Diethyl [2-(1,3,3-trimethylindoline-2-ilidene)ethylidene] Succinate (II, $C_{21}H_{27}NO_4$). A sample of 0.7 g (17.1 mmoles) of potassium metal was dissolved in 15 ml of dry *tert*-butyl alcohol; to this was added 3.1 g (15.4 mmoles) of Fischer aldehyde (I) and 3.3 g (19.2 mmoles) of diethyl succinate. The mixture was boiled for 40 min. The solvent was driven off in vacuum and the residue dissolved in 100 ml of water; the solution was acidified with acetic acid to pH 6.5 and the resultant oil extracted with ethyl ether (3 × 150 ml). The ethereal solution was dried with Na_2SO_4 and evaporated. The compound obtained was dissolved in 70 ml of absolute alcohol; this solution was saturated with gaseous hydrogen chloride (5 wt. %) and kept for 56 h at 20°C. The solvent was driven off in vacuum; the residue was dissolved in 150 ml of ether, and washed with 50 ml of water, then with 50 ml of a 10% sodium bicarbonate solution and once again with 50 ml of water. The ethereal solution was dried with Na_2SO_4 and the solvent evaporated off. The resulting oil was smoothed out with petroleum ether. The yellow precipitate obtained was filtered off and crystallized from a 1:2 ethanol—water mixture. PMR spectra ($CDCl_3$): 8.09 (1H, d, $J_{a,b}$ = 13.16 Hz, H^b), 7.2-6.7 (4H, m, C_6H_4), 5.32 (1H, d, H^a), 4.23 (2H, q, J_{CH_2,CH_3} = 6.95 Hz, CH_2), 4.16 (2H, q, J_{CH_2,CH_3} =6.95 Hz, CH_2), 3.45 (2H, s, CH_2), 3.18 (3H, s, N—CH_3), 1.62 [6H, s, 3-$(CH_3)_2$], 1.31 (3H, t, CH_3), 1.25 ppm (3H, t, CH_3). Yield 2.4 g.

E,E-[2-(1,3,3-Trimethylindoline-2-ilidene)ethylidene]-Z-benzylidene Succinic Anhydride (IVa, $C_{24}H_{21}NO_3$). To a solution of 0.11 g (2.8 mmoles) of potassium metal in 10 ml of *tert*-butyl ether was added dropwise a mixture of 0.39 g (1.1 mmoles) of diethyl succinate II and 0.21 g (2.0 mmoles) of benzaldehyde (IIIa) in 18 ml of *tert*-butanol. The mixture was boiled for 40 min and the solvent driven off in vacuum. The residue was then dissolved in 100 ml of water and the solution acidified with acetic acid to pH 6.5. The resultant yellow precipitate was extracted with ether (3 × 150 ml) and dried with Na_2SO_4, then the solvent was evaporated. The oil obtained was boiled for 1 h in 50 ml of 10% alcoholic potassium hydroxide, then the solvent was driven off in vacuum. The residue was dissolved in 100 ml of water, then the solution was filtered and acidified with acetic acid to pH 6.5. The resulting precipitate was extracted with ether (3 × 150 ml). The ethereal solution was dried with Na_2SO_4, treated with 7.5 g (74 mmoles) of acetic anhydride, and kept for 24 h at 20°C. The resulting red-colored solution was washed in turn with 100 ml of water, 150 ml of 5% NaOH solution, and 100 ml of water; it was then dried with Na_2SO_4 and the solvent driven off in vacuum. The residue was crystallized from ethanol. A yield of 0.17 g of lustrous, dark-red, flaky crystals was obtained.

E,E-[2-(1,3,3-Trimethylindoline-2-ilidene)ethylidene]-Z-(4-fluorobenzylidene) succinic anhydride (IVb, $C_{24}H_{20}FNO_3$) was obtained in a similar manner to compound IVa from 0.39 g (1.1 mmoles) of diethyl succinate II and 0.25 g (2.0 mmoles) of 4-fluorobenzaldehyde (IIIb) in the form of dark-red, lustrous crystals in 0.1 g yield. **E,E-[2-(1,3,3-Trimethylindoline-2-ilidene)ethylidene]-Z-(4-ethoxybenzylidene)succinic anhydride (IVc, $C_{26}H_{25}NO_4$)** was obtained in a similar way to fulgide IV from 0.39 g (1.1 mmoles) of diethyl succinate II and 0.3 g (2.0 mmoles) of 4-ethoxybenzaldehyde (IIIc) in the form of dark-brown, lustrous crystals in 0.1 g yield.

E,Z-[2-(1,3,3-Trimethylindoline-2-ilidene)ethylidene]-E-(1,2-dimethyl-3-indolylmethylene) Succinic Anhydride (V, $C_{28}H_{26}N_2O_3$). To 0.3 g (11.0 mmoles) of sodium hydride in 15 ml of dry toluene were added 0.5 g (2.8 mmoles) of 1,2-dimethyl-3-formylindole [6] and 1.0 g (2.8 mmoles) of diethyl succinate II. The reaction mixture was stirred for 4 h at 20°C and poured into 100 g of crushed ice; the aqueous layer was then separated and acidified with acetic acid to pH 6.5. The resultant yellow precipitate was extracted with ether (3 × 150 ml); the ethereal solution was then dried with Na_2SO_4 and evaporated. The residue was boiled with 30 ml of 10% alcoholic KOH solution. The solvent was driven off in vacuum; the residue was dissolved in 100 ml of water, and the solution was then filtered and acidified with acetic acid to pH 6.5. The resulting precipitate was extracted with ether (3 × 150 ml). After drying with Na_2SO_4 16.2 g (159 mmoles) of acetic anhydride were added to the ethereal solution and the mixture kept at 20°C for 24 h. The resultant dark-red solution was washed with 150 ml of water, 150 ml of a 10% aqueous sodium bicarbonate solution, and a further 150 ml of water; it was then dried with Na_2SO_4 and the solvent driven off in vacuum. The residue was crystallized from ethanol. A yield of 0.3 g of dark-red crystals was obtained.

Bis-E,Z-[2-(1,3,3-trimethylindoline-2-ilidene)ethylidene]succinic anhydride (VI, $C_{30}H_{30}N_2O_3$) was obtained in a similar manner to fulgide V from 1.61 g (4.5 mmoles) of diethyl succinate II and 0.84 g (4.2 mmoles) of Fischer aldehyde I in the form of dark-violet crystals in 0.6 g yield.

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