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PHOTOCHROMIC FULGIDES BASED ON 1-METHYL-2-FORMYLINDOLE

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The reactions of 1-methyl-2-formylindole with the diethyl esters of alkyl- and phenylmethylene-substituted itaconic acids led to the production of photochromic fulgides, which formed deeply colored 5,8b-dihydrocarbazole derivatives during UV irradiation. It was found by PMR that the fulgides also undergo E,Z isomerization during UV irradiation.

As reported in [1], heterocyclic fulgides (Ia-d), obtained from 1,2-dimethyl-3-formylindole, do not exhibit photochromic characteristics resulting from the formation of the more deeply colored 8,8a-dihydrocarbazole derivatives (IIIa-e) during UV irradiation but only undergo E,Z-isomerization with the formation of compounds (IIa-e). At the same time fulgides based on 1-methyl-3-formyl- and 1-methyl-3-acetylindole exhibit photochromism [2]. The absence of photochromic characteristics in compounds (Ia-e) is evidently due to steric hindrances created by the methyl group at position 2 of the indole ring [1] and also

TABLE 1. The Synthesized Compounds

Compound	Molecular formula	Color of crystals	T_{mp}, °C*	λ_{max}, nm	log ε	M** found	M calc.	Yield,*** %
IIf	$C_{17}H_{15}NO_3$	Yellow	171...172	414	4,1	281	281	63
Ig	$C_{18}H_{17}NO_3$	Bright-yellow	205...207	418	4,1	295	295	68
Ih	$C_{27}H_{19}NO_3$	Orange	241...242	480	4,1	405	405	3
IIh	$C_{27}H_{19}NO_3$	Dark-red	181...183	484	4,2	405	405	25
VII	$C_{20}H_{19}NO_3$	Light-yellow	132...134	330	3,7	321	321	23

*Compounds (IIf, h, Ig, VII) were crystallized from ethanol, (Ih) from isopropanol.
**Measured by mass spectrometry on a Varian MAT-311A instrument.
***Calculated on the initial 1-,ethyl-2-formylindole.

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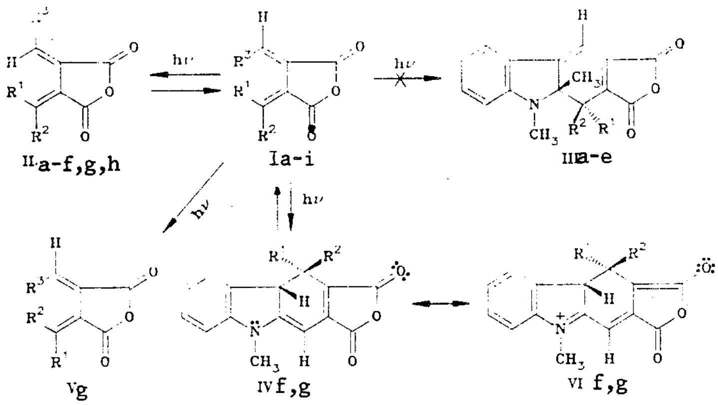
TABLE 2. The Chemical Shifts of the Protons in the Fulgides (I, II, V)

Compound	Configuration	δ, ppm				
		R^1	R^2	$N-CH_3$	β-H	HC=C
If	E	2,41	2,59	3,82	7,1*	8,16
IIf	Z	1,75	2,50	3,85	6,50	7,69
Ig	E, Z	2,39	1,21 t (CH_3); 3,00 q (CH_2)	3,82	7,31	8,15
Vg	E, E	2,53	1,37 t (CH_3); 2,66 q (CH_2)	3,82	7,31	8,15
Ih	E		7,3 . . . 7,5	3,08	7,03	8,40
IIh	Z		6,7 . . . 7,0	3,54	6,03	7,57

*Overlap with the signals for the protons of the benzene part of the indole ring.

by the unfavorable π-electron density distribution for electrocyclic ring closure in the molecule [3]. In this connection we decided to realize the synthesis of fulgides with structures (If-i) from 1-methyl-2-formylindole and the diethyl esters of methyl-substituted itaconic acids, supposing that cyclization should take place more readily at the β-carbon atom of the indole ring than at the α position in compounds (Ia-e) [3].



a, f $R^1=R^2=CH_3$; b, g $R^1=CH_3$, $R^2=C_2H_5$; c, h $R^1=R^2=C_6H_5$; d, i $R^1+R^2=(CH_2)_5$; e $R^1=$ 1,2-dimethyl-3-indolyl, $R^2=H$; a–e $R^3=$1,2-dimethyl-3-indolyl, f-i, $R^3=$1-methyl-2-indolyl

During the synthesis of the fulgide (I) ($R^1 = R^2 = C_6H_5$) the Z isomer (IIh) was formed in addition to the E isomer (Ih), but only the Z isomer (IIf) was obtained when $R^1 = R^2 = CH_3$. The composition and structure of the synthesized compounds were confirmed by the data from elemental analysis, the mass spectra, and the PMR spectra (Tables 1 and 2).

In the PMR spectrum of the fulgide (Ih) compared with the spectrum of the Z isomer (IIh) the signal of the vinyl proton is shifted significantly downfield (Table 2). This is evidently explained by the descreening effect of the cis-located carbonyl group. The similar values of the chemical shifts for the vinyl protons of compounds (IIh) and (IIf) shows that the fulgide (IIf) has the Z configuration. It was established by PMR that in deuterochloroform solution compound (IIf) is partly converted into the E isomer (If) during UV irradiation. [The intensity ratio of the signals of (IIf) and (If) amounts to 5:1.] Here another signal for the vinyl proton appears in the downfield region. The signal for the trans-located methyl group R^1 in relation to carbonyl in compound (If) compared with the analogous group in the Z isomer (IIf) is also observed in the downfield region as a result of the diamagnetic anisotropy of the indole ring, which in the present case has a descreening action, although screening has been observed for fulgides of the 1,2-dimethyl-3-formylindole series [1].

The fulgide (Ig) has the E,Z configuration, i.e., the heterocyclic fragment is in the trans position, while the ethyl group (R^2) is in the cis position in relation to the neighboring carbonyl. This is demonstrated by the position of the signal for the vinyl proton and by the similar values of the chemical shifts for the trans-CH_3 groups (R^1) in compounds (Ig) and (If). During UV irradiation in deuterochloroform solution the fulgide (Ig) undergoes E,Z isomerization and is converted into the E,E isomer with the structure (Vg). [The ratio

TABLE 3. The Photochromic Characteristics of the Fulgides (IIf, Ig)

Compound	Solvent	λ_{max}, nm*		$\tau_{1/2}$, sec
		A	B	
IIf	Toluene	414	510	30
	Ethanol	410	512	200
	Acetonitrile	404	515	600
Ig	Toluene	418	510	55
	Ethanol	416	515	210
	Acetonitrile	412	520	600

*A) Initial form; B) photoinduced form.

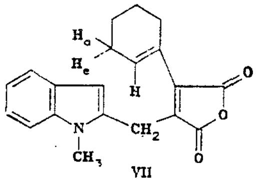
of (Ig) to (Vg) amounts to 1:1.] The signal for the proton of the methyl group R^1 in compound (Vg) is observed in the downfield region compared with the E,Z isomer (Ig), while the signal for the methylene group of the ethyl (R^2) is in the upfield region. Such a shift of the signals is explained by the presence or absence respectively of a descreening effect from the carbonyl group. The chemical shifts of the vinyl protons and $N-CH_3$ groups in the isomers (Ig) and (Vg) coincide (Table 2).

Analysis of the PMR spectra of the synthesized compounds shows that the position of the signal for the β-hydrogen atom of the indole ring also depends on the configuration of the fulgide. Thus, for the E isomers compared with the Z isomers there is a downfield shift of the β-H signal as a result of the diamagnetic anisotropy of the double bond in the butadiene fragment (Table 2).

During UV irradiation the fulgides (IIf) and (Ig) not only undergo E,Z isomerization but also undergo cyclization with the formation of more deeply colored 5,8b-dihydrocarbazole derivatives (IVf, g), and here the photocyclization of (IIf) is preceded by its transformation into the E isomer (If). Solutions of the fulgides (IIf) and (Ig) in toluene, ethanol, or acetonitrile have a yellowish color (λ_{max} 404-414 nm). During irradiation with UV light from an SVD-120 lamp or from a flash lamp in the region of 250-400 nm the solutions acquire a red color, and new photoinduced bands with λ_{max} 510-520 nm (Table 3), characteristic of the compounds (IV) formed as a result of closure of the hexatriene system [4], appear in the electronic absorption spectra. After irradiation the reverse (dark) reaction occurs. The change in color can be repeated many times both in solution and on Silufol plates. The life time $\tau_{1/2}$ of the 5,8b-dihydrocarbazole derivatives (IV) was investigated by flash photolysis at the maximum of the absorption band of the photoinduced form (Table 3). It was determined from the kinetic curve for the disappearance of the photoinduced form with a decrease of half in the optical density at the measurement wavelength. The observed similarity of form between the variation of the polarity of the solvent and the life time is evidently explained by the fact that the photoinduced form (IV) has appreciable polarity, i.e., has partly merocyanine character [structure (VI)] [5]. It should be noted that the stabilization of the dihydrocarbazole derivatives (IV), due to the presence of mesomerism, is absent in the case of compounds (III).

In spite of the visually observed change in color during irradiation of the fulgides (particularly in polar solvents), we were unable to record the presence of compounds (IV) in the solutions by the PMR method on account, evidently, of the low quantum yields of photocyclization. Substitution of the alkyl substituents by phenyl ($R^1 = R^2 = C_6H_5$) in the case of compound (Ih) leads to a loss of the photochromic characteristics on account, evidently, of the appearance of steric hindrances for electrocyclic closure.

We were unable to synthesize the fulgide (Ii) with the cycloalkyl substituent ($R^1 + R^2 = (CH_2)_5$) by the reaction of 1-methyl-2-formylindole with diethyl cyclohexylidenesuccinate [6]. The anhydride (VII), which results from the 1,5-shift of hydrogen in the intermediate fulgide (Ii), is formed in the reaction.



VII

The structure of (VII) was confirmed by the data from PMR spectroscopy (see the experimental section). The singlet with a chemical shift of 4.14 ppm (the integral intensity corresponds to two protons) indicates the presence of an isolated methylene group. According to [7], the multiplicity of the signal for the hydrogen with a chemical shift of 6.47 ppm and spin–spin coupling constants $^3J_{H,Ha} = 5.86$, $^3J_{He,He} = 4.14$ and $^4J = 1.71$ Hz (with one of the distant protons) is typical of cyclohexene systems.

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WP-200-SY ($CDCl_3$) spectrometer in deuterochloroform with TMS as internal standard. The electronic absorption spectra were recorded on toluene on a Hitachi EPS-3T spectrophotometer. The R_f values were determined on Silufol UV-254 plates. For column chromatography we used silica gel L40/100.

The data from the elemental analyses of compounds (Ig, h, IIf, g, VII) for C, H, and N correspond to the calculated data.

1-Methyl-2-formylindole. A 13.7-g sample (85.0 mmole) of 1-methyl-2-hydroxymethylindole [8] was boiled for 5 h with 38.0 g (437.0 mmole) of activated manganese dioxide [9] in 800 ml of benzene. The manganese dioxide was filtered off, the mother solution was dried with calcium chloride, and the solvent was evaporated. The residue was chromatographed on a column of silica gel with carbon tetrachloride as eluant. The fraction containing 1-methyl-2-formylindole (R_f 0.08) was collected. The product was recrystallized from a 2:1 mixture of ethanol and water. It formed fine crystals, and the yield was 7.8 g (58%); mp 82-83°C. Published data [10]: mp 82-84°C.

Z-(1-Methyl-2-indolylmethylene)isopropylidenesuccinic Anhydride (IIf), E-(1-Methyl-2-indolylmethylene)-Z-(2-butylidene)succinic Anhydride (Ig), E-(1-Methyl-2-indolylmethylene)-diphenylmethylenesuccinic Anhydride (Ih), Z-(1-Methyl-2-indolylmethylene)diphenylmethylenesuccinic Anhydride (IIh), and (1-Methyl-2-indolylmethyl)-1-cyclohexenylmaleic Anhydride (VII). The compounds were obtained similarly to the fulgides (Ia-e) [1] from 1-methyl-2-formylindole and the diethyl esters of the substituted itaconic acids. Compounds (Ih) and (IIh), which are formed in the mixture, were separated by column chromatography. The eluant was chloroform (R_f 0.45 and 0.30 respectively). PMR spectrum of (VII) (acetone-d_6): 7.0-7.5 (4H, m, C_6H_4); 6.47 (1H, m, HC=C); 6.28 (1H, d, $J_{3,7} = 1.10$ Hz, 3-H); 4.14 (2H, s, CH_2); 3.80 (3H, s, $N-CH_3$); 2.37 (2H, m, CH_2); 1.57 ppm [4H, m, $(CH_2)_2$].

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