

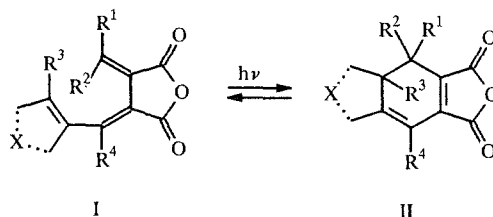
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INDOLE FULGIDES

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 and N. M. Przhivalgovskaya

The syntheses and photochemical properties of fulgides derived from indole and indoline are reviewed.

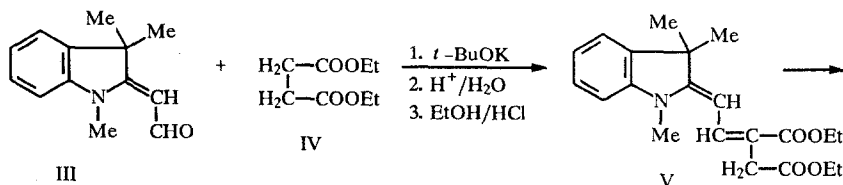
Aryl and heteryl derivatives of bismethylenesuccinic anhydride with the general formula I were first synthesized at the beginning of the present century by the German chemist, Stobbe [1]. These crystals were termed fulgides in light of their appearance from the Latin root *fulgere* meaning "shining, sparkling." Fulgides have photochromic properties, that is, are capable of reversibly altering their color upon the action of light due to an electrocyclic conrotatory closure of the hexatriene ring and formation of deeply colored products II [2].

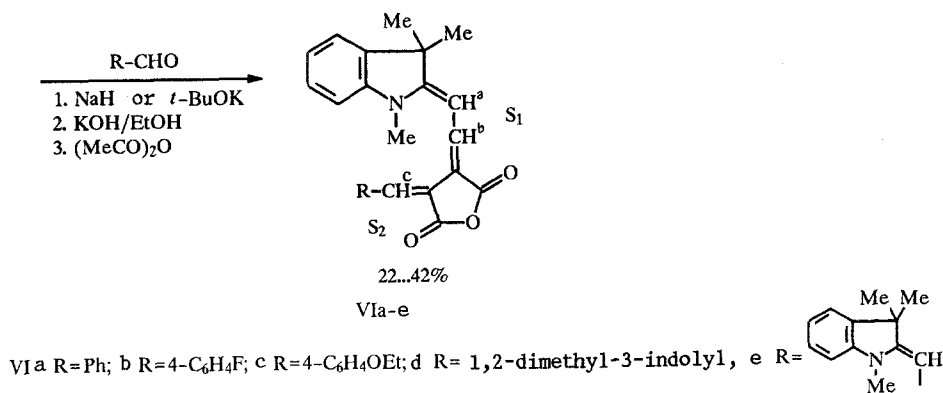


Photochromic compounds have found use for the storage and treatment of optical information, in laser technology, and light filters with variable optical density [3]. Fulgides, in contrast to many other photochromic compounds such as spiropyrans [4], have high photochromic stability, which permits their use in durable photochromic materials [2]. Special interest is found in fulgides with heteryl fragments. Thus, derivatives of bismethylenesuccinic anhydride containing thiophene, furan, or pyrrole rings have been reported [2]. In recent years, we have synthesized and studied fulgide derivatives of indole and indoline. The results of these studies are summarized in this review.

1. INDOLINE FULGIDES

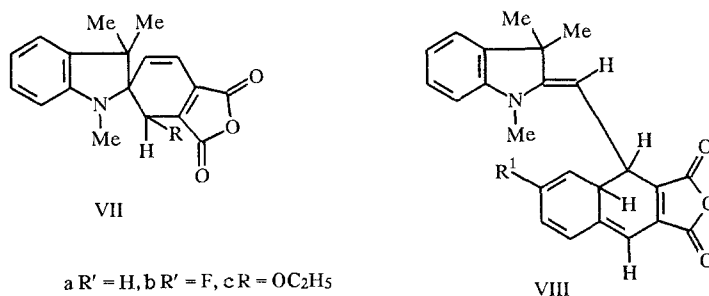
Indoline fulgides with the general formula VI were obtained in a search for new photochromic compounds in our previous work [5, 6] according to Stobbe's method. Diethyl succinate IV was condensed with Fischer's aldehyde III in the presence of potassium tert-butyrate with subsequent esterification in ethanol saturated with hydrogen chloride. Diester V was used in reactions with carbonyl compounds such as benzaldehyde, 4-fluorobenzaldehyde, 4-ethoxybenzaldehyde, 1,2-dimethyl-3-formylindole, and Fischer's aldehyde.



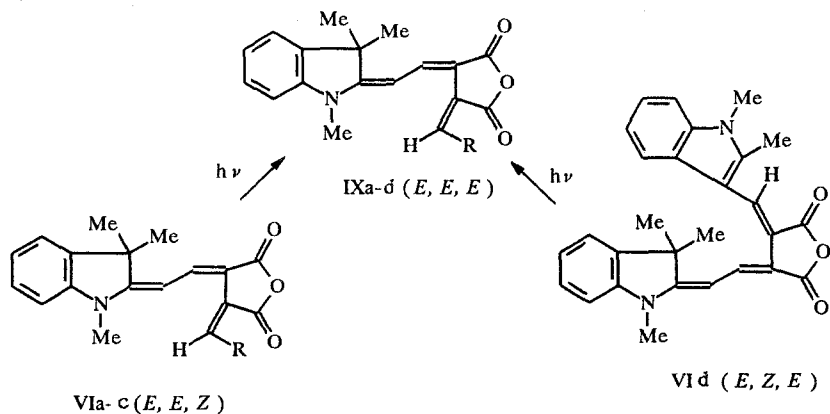


PMR spectroscopy was used to establish that VIa-c have E,E,Z configuration, fulgide VI d has E,Z,E configuration and *s*-trans arrangement of the double bonds relative to the S₁ and S₂ single bonds, while diindoline fulgide VIe has symmetrical structure and E,Z configuration of the butadiene fragments. The assignment of structures to these fulgides was accomplished using the nuclear Overhauser effect relative to the coupling constants of H^a and H^b as well as the chemical shifts of vinyl protons, H^b and H^c, which differ for E and Z isomers due to the presence or absence of the deshielding effect of the carbonyl group.

In previous work [5, 6], we assumed that deeply colored fulgides VI, which have strong absorption at 533-579 nm (in toluene), will be converted upon UV irradiation into weakly colored spiro compounds VII or dihydronaphthalene derivatives VIII, that is, reverse photochromism will be observed. Such reactions are theoretically possible due to the presence of the additional exocyclic double bond in VI.



However, photochemical studies have shown that UV irradiation of these compounds in toluene for 90 sec at 293°K does not lead to the appearance of new photoinduced bands in the electronic spectra related to significant structural changes in the molecule. PMR spectroscopy showed that UV irradiation of VIa-VI d for the same period in deuteriochloroform leads to geometrical E,Z isomerization of the arylidene fragment for fulgides VIa-VI c and (1,3,3-trimethylindolin-2-ylidene)ethylidene fragment for VI d and partial conversion of these compounds into the E,E,E isomers, IXa-IX d.

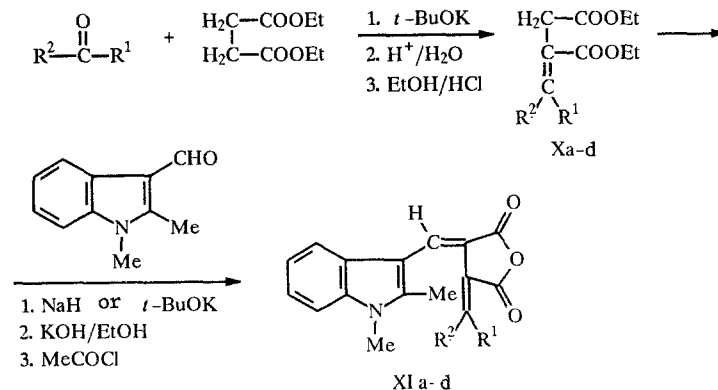


VI, IX a R=Ph, b R=4-C₆H₄F, c R=4-C₆H₄OEt, d R= 1,2-dimethyl-3-indolyl

Thus, fulgides VI do not display photochromic properties, while they undergo only E,Z isomerization upon the action of light. No formation of VII or VIII was detected by PMR spectroscopy upon the stationary photolysis of solutions of fulgides VIa-VIc. An increase in the length of the polyene chain apparently is not conducive to the electrocyclic reaction [5].

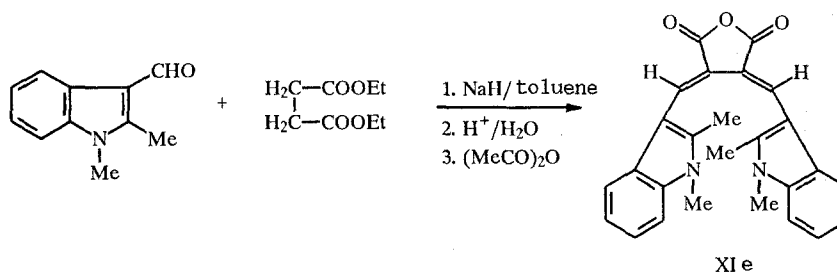
2. SYNTHESIS AND PHOTOCHEMICAL PROPERTIES OF FULGIDES DERIVED FROM 1,2-DIMETHYL-FORMYLINDOLE

Since indoline fulgides do not possess photochromic properties, we synthesized and studied fulgides XI with a classical heterene system obtained using 1,2-dimethyl-3-formylindole [7, 9]. In contrast to the synthesis of fulgides VI, the preparation of XI requires the reverse order of introducing the unsaturated fragments into the succinic anhydride molecule. Thus, we initially obtained the diethyl



X, XI a $\text{R}^1=\text{R}^2=\text{Me}$, b $\text{R}^1=\text{Et}$, $\text{R}^2=\text{Me}$, c $\text{R}^1+\text{R}^2=(\text{CH}_2)_5$, d $\text{R}^1=\text{R}^2=\text{Ph}$

esters of arylidenesuccinic or alkylidenesuccinic acids Xa-Xd by the reaction of diethyl succinate with acetone, 2-butanone, cyclohexanone, and benzophenone, which were then converted to fulgides XIa-XId. The yields of XI were 43-50% relative to 1,2-dimethyl-3-formylindole [8].

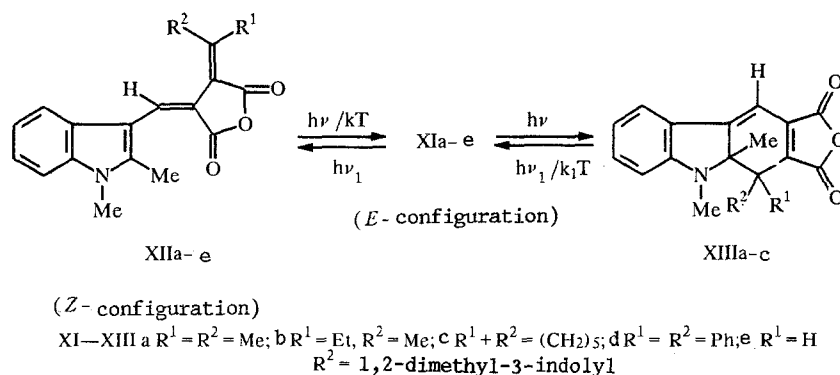


Diindole fulgide XIe was obtained in 9% yield by the direct condensation of 1,2-dimethyl-3-formylindole and diethyl succinate with subsequent hydrolysis of the intermediate half-ester and treatment of the diacid formed with acetic anhydride [8].

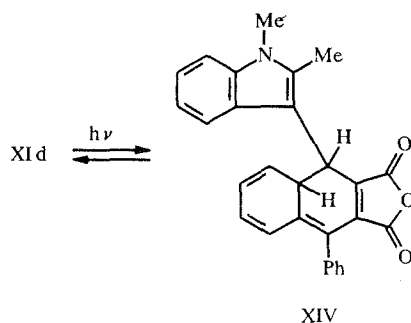
^1H and ^{13}C NMR spectroscopy indicated that the heterocycle in fulgides XIa-XIe is in the trans position relative to the carbonyl group (E configuration). Diindole fulgide XIe has symmetrical structure and E,E-configuration. The structure and E configuration of fulgide XIa was further indicated by x-ray diffraction structural analysis. This molecule was found to have nonplanar structure. The dihedral angle between the virtually coplanar anhydride and indole fragments was 36.7° [10].

A photochemical study showed that fulgides XIa-XIe undergo E,Z isomerization upon stationary UV irradiation. This isomerization may also be induced thermally and gives XIIa-XIIe [7-9]. (See scheme on following page.)

The most marked spectral changes due to the E,Z photoisomerization (shift in λ_{max} in toluene from 434 to 492 nm) were detected for fulgide XIe. The formation of asymmetrical E,Z isomer XIIe was demonstrated by PMR spectroscopy [11]. Flash excitation of fulgides XIa-XIc at 293°K in toluene (λ_{max} 408-435 nm) led to an electrocyclic reaction and formation of more deeply colored 1,9a-dihydrocarbazole derivatives XIIIa-XIIIc (λ_{max} 555-560 nm) [9, 12]. However, products XIIIa-XIIIc have low thermal stability and are readily reconverted to starting form XI with half-life from 450 to 600 msec.



The capacity of XI to undergo photocyclization at C² of the indole system disappears upon replacing alkyl substituents by phenyl groups. Thus, fulgide XI d, which contains phenyl substituents (R¹ = R² = Ph), undergoes photocyclization upon flash photolysis only at the phenyl ring with the formation of 1,8a-dihydronaphthalene derivative XIV [11].



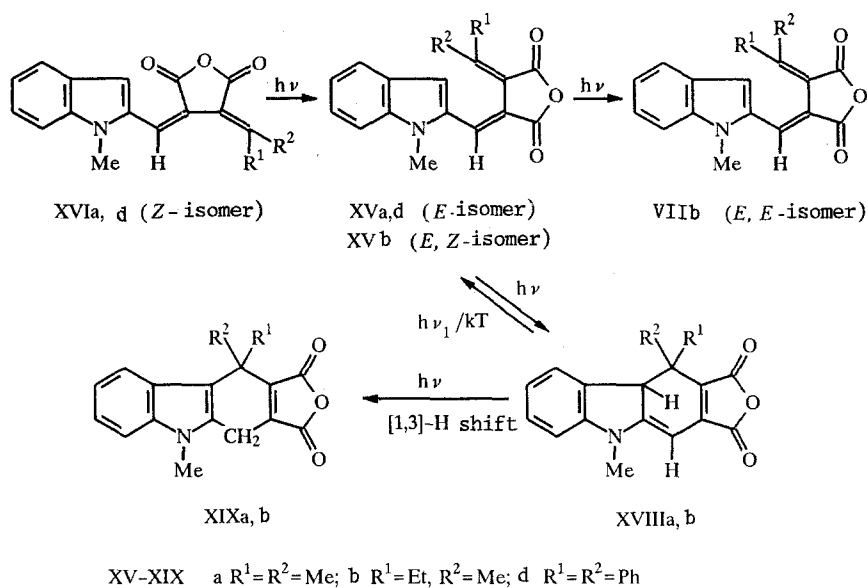
Thus, 3-indolylfulgides XI, in contrast to indoline fulgides VI [5], have photochromic properties. However, the electrocyclic reaction occurring at C² of the indoline ring does not proceed efficiently. This finding is attributed to the unfavorable electron density distribution in XI since the indole α-carbon atom and the attached carbon atom of the alkylidene or arylidene fragment bear partial positive charge [7, 10].

3. PHOTOCROMIC 1-METHYL-2-FORMYLINDOLE FULGIDES

The C³ atom is the most electronegative in indole. Thus, in previous work [7], we predicted that the photocyclization of 2-indolylfulgides involving the β-carbon atom of the indole ring should be more efficient than the corresponding cyclization of 1,2-dimethyl-3-formylindole fulgides XI. 2-Indolylfulgides XVb, XVd, XVIa, and XVI d were obtained by the condensation of 1-methyl-2-formylindole and diesters X by analogy to the synthesis of XI [13]. Fulgide XVIa was obtained in 68% yield and found to have Z configuration. Fulgide XVb was obtained in 63% yield and found to have trans arrangement of the heterocycle and adjacent carbonyl group (E configuration) and Z configuration of the alkylidene fragment (R¹ = Et, R² = Me). Products XVd and XVI d (R¹ = R² = Ph), which are E and Z isomers, are formed in a mixture and separated by column chromatography in 3 and 25% yield, respectively.

PMR spectroscopy indicated that fulgides XVIa and XVI d undergo E,Z isomerization upon UV irradiation at 250-400 nm over 1.5 min in deuteriochloroform to give E isomers XVa and XVd. The XVIa/XVa ratio was 5:1, while the XVI d/XVd ratio was 17:1 (from the integral intensities of the methyl group signals). The reverse conversion of the E isomer XVd to the Z isomer XVI d was not observed upon irradiation under these conditions. E,Z isomerization of the alkyl fragment occurs under analogous conditions upon the irradiation of E,Z isomer XVb to give E,E isomer XVIIb; the XVb/XVIIb ratio was 1:1 [13].

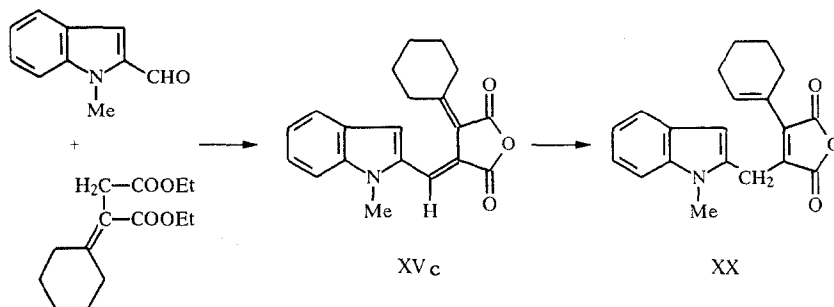
Stationary UV irradiation of fulgides XVIa and XVb (λ_{max} 520-520 nm), as in the case of flash photolysis, leads not only to E,Z isomerization but also to cyclization, giving more deeply colored 4,4a-dihydrocarbazole derivatives XVIIIa and XVIIIb (λ_{max} 510-520 nm). In this case, the photocyclization of Z isomer XVIa is preceded by its conversion to E isomer XVa [9, 13-15]. The half-life (τ_{1/2}) of 4,4a-dihydrocarbazole derivatives XVIIIa and XVIIIb was determined by flash photolysis at the absorption maximum and found to be 40 or 600 sec, respectively, for toluene and acetonitrile. The increase in the half-life with increasing solvent polarity is explained partially by the merocyanine nature of photoinduced form XVIII [13].



PMR spectroscopy showed that dihydrocarbazole derivatives XIXa and XIXb are formed upon the irradiation of solutions of XVIa and XVb in CD₃CN due to a photochemically allowed suprafacial [1,3]-hydrogen shift in photoinduced form XVIII [11, 14, 15]. The conversion of fulgide XVa to colorless derivative XIXa proceeds quantitatively. The photochemical [1,3]-hydrogen shift has not been described for fulgides [14].

Replacement of alkyl substituents by phenyl substituents in the case of XVd (R¹ = R² = Ph) leads to the loss of photochemical properties apparently due to the steric hindrance to electrocyclic closure involving the indole ring [13].

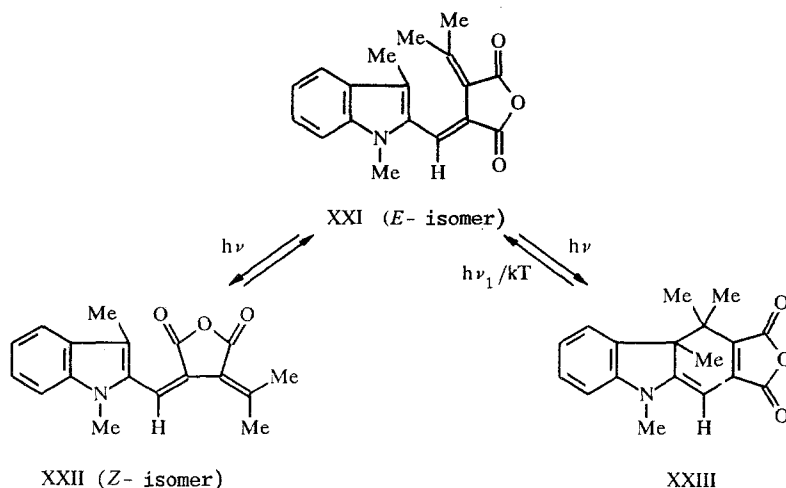
In previous work [13], we attempted to synthesize a fulgide with cycloalkenyl substituent XVc. However, XX, which is formed as the result of a [1,5]-hydrogen shift in intermediate fulgide XVc, was obtained in 23%.



Thus, 1-methyl-2-formylindole fulgides XVIa and XVb have pronounced photochromic properties. Colored 4,4a-dihydrocarbazole derivatives XVIIIa and XVIIIb are thermally stable. However, the lack of a substituent at C³ in the indole system leads to the loss of photochromism due to a nonreversible [1,3]-hydrogen shift in the photoinduced form.

4. 1,3-DIMETHYL-2-FORMYLINDOLE FULGIDES

In order to exclude the undesirable [1,3]-hydrogen shift, we synthesized fulgides starting with 1,2-dimethyl-2-formylindole [9, 11, 17]. The condensation of this aldehyde with diethyl ester of isopropylidenesuccinic acid Xa, by analogy to XI, gave fulgides XXI and XXII. The yields of *E* isomer XXI and *Z* isomer XXII relative to the starting aldehyde were 29 and 6%, respectively. The configurations of these fulgides were determined using PMR spectroscopy. The structure and configuration of *E* isomer XXI were also confirmed by x-ray diffraction structural analysis [11].



PMR and electronic absorption spectroscopy showed that, upon UV irradiation, fulgides XXI and XXII undergo both reversible *E,Z* isomerization and photochemical conrotatory closure of the hexatriene system [14, 15, 17]. The XXI/XXII and XXII/XXI ratios upon the irradiation of fulgides XXI and XXII at 250-400 nm in CDCl_3 were 15:1 and 10:1, respectively (from the ratio of the integral intensities of the methyl group signals). The ratio of the starting fulgide and *Z* isomer XXII and 4,4a-dihydrocarbazole derivative XXIII upon irradiation of *E* isomer XXI in CD_3CN was 8:2.5:1. The observed bathochromic shift of the long-wavelength band upon the UV irradiation of solutions of fulgide XXI (λ_{max} 400-408 nm) corresponds to formation of *Z* isomer XXII. The new long-wavelength band with maximum at 515-518 nm corresponds to photoinduced cyclic form XXIII, whose lifetime (τ) determined by flash photolysis was not less than 10^4 sec for acetonitrile or toluene at 295°K. The reversible conversion of XXIII to starting form XXI may be initiated either photochemically (λ 400-700 nm) or thermally (heating at 353°K) [11]. Irreversible thermal or photochemical reactions were not observed under these conditions [11, 14].

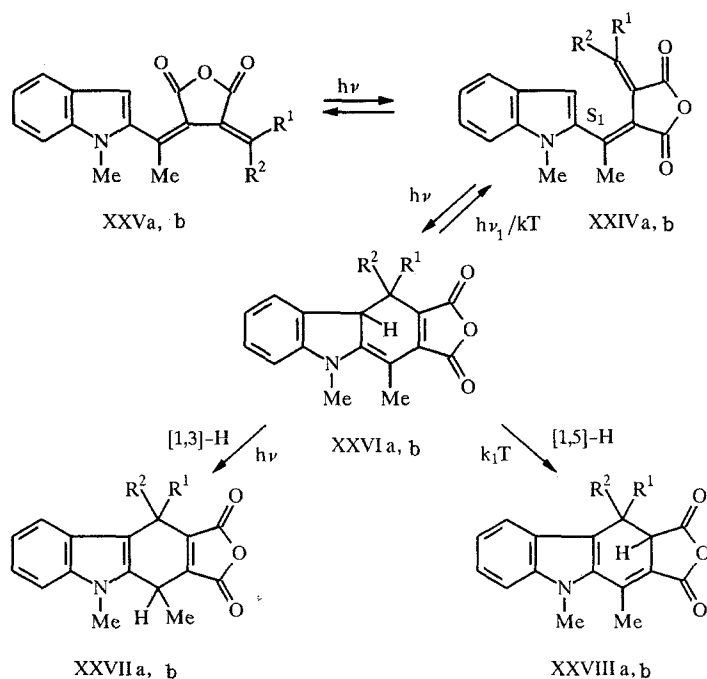
Thus, the introduction of a methyl group at C^3 of the indole system led to elimination of the undesirable [1,3]-hydrogen shift observed for 1-methyl-2-formylindole fulgides and to a significant increase in the stability of the photoinduced colored form. This behavior is attributed to steric hindrance between the 4- and 4a-methyl groups in the thermal disrotatory opening of the cyclohexadiene ring of 4,4a-dihydrocarbazole derivative XXIII [11, 14].

5. STRUCTURE AND PHOTOCHROMIC PROPERTIES OF 1-METHYL- AND 1,3-DIMETHYL-2-ACETYLINDOLE FULGIDES

In previous work [9, 16-18], we synthesized photochromic fulgides from 1-methyl- and 1,3-dimethyl-2-acetylindoles. We assumed that replacement of the vinyl proton in fulgides XV and XXI by the more bulky methyl substituent would lead to an enhanced quantum yield for cyclization.

Fulgides XXIVa, XXVa, and XXVb were obtained from 1-methyl-2-acetylindole by the Stobbe condensation [16]. Fulgide XXVb, which has *Z,Z* configuration, was obtained in 36% yield. Fulgides XXIVa and XXVa, which are formed in a mixture, were separated by fractional crystallization from ethanol. *Z* isomer XXVa was the major product obtained in 36% yield. The yield of *E* isomer XXIVa was 7%. The structures and configurations of isomers XXIVa and XXVa were confirmed by x-ray diffraction structural analysis, which indicated that the dihedral angles between the anhydride and indole fragments are 70.0° and 51.7°, respectively [11]. In the crystalline state, *E* isomer XXIVa exists as a mixture of *s*-cis and *s*-trans conformers, which differ in the orientation of the double bonds relative to the S_1 single bond. The ratio of the *s*-trans and *s*-cis conformers was 63:35 (from the ratio of occupancies of the N-methyl group carbon atom) [11]. (See scheme on following page.)

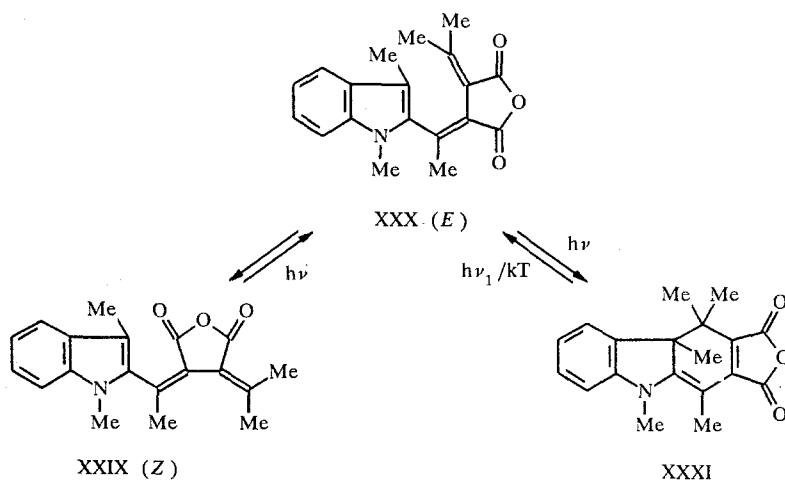
Photochemical studies have shown that fulgides XXIVa, XXVa, and XXVb ($\lambda_{\text{max}} \sim 385$ nm, in acetonitrile) upon UV irradiation undergo reversible *E,Z* isomerization and photocyclization [16-18]. These reactions were demonstrated by PMR and electronic absorption spectroscopy. The formation of colored 4,4a-dihydrocarbazole derivatives XXVIa and XXVIb ($\lambda_{\text{max}} \sim 550$ nm, in acetonitrile) occurs both upon flash and stationary irradiation.



XIV—XVIII a $R^1 = R^2 = \text{Me}$, b $R^1 = \text{Et}$, $R^2 = \text{Me}$

The half-life of photoinduced forms XXVIa and XXVIb ($\tau_{1/2} \sim 900$ sec, in acetonitrile) is 1.5 times greater than the corresponding value for 4,4a-dihydrocarbazole derivatives XXVIIIa and XXVIIIb and indicates that the replacement of the vinyl proton in fulgides XVIa and XVb by a methyl group leads to stabilization of the colored form. Furthermore, this replacement leads to a bathochromic shift of the long-wavelength band of 4,4a-dihydrocarbazole derivatives XXVIa and XXVIb relative to XXVIIIa and XXVIIIb by about 30 nm.

Fulgides XXIVa, XXVa, and XXVb obtained from 1-methyl-2-acetylindole have pronounced photochromic properties, a large difference between the maxima of the long-wavelength bands of the starting and photoinduced form (~ 165 nm), and high thermal stability [16, 18]. However, PMR spectroscopy showed that these compounds gradually lose their photochromic properties as a consequence of a photochemical [1,3]-hydrogen shift to give XXVIIa and XXVIIb and thermal [1,5]-hydrogen shift to give XXVIIIa [14, 15]. In order to avoid these undesirable sigmatropic reactions, we synthesized fulgide XXIX containing a methyl group at C³ in the indole system from 1,3-dimethyl-2-acetylindole according to Stobbe's method [18].



PMR spectroscopy has shown that E,Z isomerization leading to the formation of E isomer XXX is observed upon UV irradiation of fulgide XXIX in CD_3CN ($\lambda_{\text{max}} = 385$ nm) for 1.5 min. The XXIX/XXX isomer ratio was 20:1 [17].

Photochemical E,Z isomerization precedes the photochemical conrotatory closure of the hexatriene system of fulgide XXIX, leading to deeply colored 4,4a-dihydroxycarbazole derivative XXXI ($\lambda_{\text{max}} = 550$ nm) [9, 14, 17]. The reverse

transformation occurs upon irradiation with visible light. PMR and electronic absorption spectroscopy did not reveal any irreversible photochemical and thermal reactions, leading to the loss of photochromic properties [14, 17].

Thus, these recent studies have established that indoline fulgides obtained from the Fischer aldehyde do not possess photochromic properties and UV irradiation leads only to E,Z isomerization. 1,2-Dimethyl-3-formyldinole fulgides upon stationary UV irradiation undergo reversible E,Z isomerization, while flash photolysis leads to deeply colored dihydrocarbazole compounds having low thermal stability. This latter finding is attributed to the unfavorable electron density distribution for the electrocyclic reaction. 1-Methyl-2-formyl- and 1-methyl-2-acetyldinole fulgides give a more stable photoinduced form but lose their photochromic properties due to irreversible [1,3]- and [1,5]-hydrogen shifts. This difficulty may be eliminated by the synthesis of fulgides starting with 1,3-dimethyl-2-formyl- and 1,3-dimethyl-2-acetyldinole. These fulgides not only have pronounced photochromism but also do not display irreversible thermal and photochemical reactions, leading to the loss of photochemical properties.

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