LETTERS TO THE EDITOR

FULGIDES BASED ON 1,3-DIMETHYL-2-FORMYLINDOLE AND 1,3-DIMETHYL-2-ACETYLINDOLE

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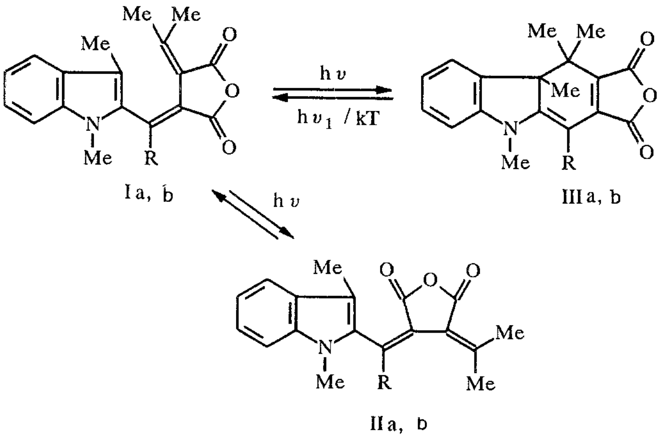
We recently reported the synthesis of photochromic fulgides based on 1-methyl-2-formylindole and 1-methyl-2-acetylindole [1,2] which lose their photochromic properties as a result of irreversible [1,3]- and [1,5]-shifts of the hydrogens in position 3 of the indole ring [3].

To exclude these undesirable side reactions we have prepared fulgides Ia and IIa, b having a methyl group in position 3 of the indole ring. The preparation was effected by condensation of 1,3-dimethyl-2-formyl- and 1,3-dimethyl-2-acetylindole with the diethyl ester of isopropylidenesuccinic acid in toluene in the presence of sodium hydride. Fulgides I and II have E and Z configuration, respectively, as shown by a comparison of their PMR spectra with the spectra of related arylfulgides [4]. The structure and configuration of the E isomer Ia is further confirmed by the results of x-ray analysis.



From the results of NMR and electronic spectroscopy we found that on UV irradiation fulgides I and II undergo a reversible E,Z isomerization and the E isomer is converted by photocyclization into the deeply colored 4,4*a*-dihydrocarbazole derivative III. Thus, on irradiation of fulgides Ia and IIa in the 250-400 nm region for 1.5 min in $CDCl_3$ a mixture of E and Z isomers was obtained, the ratios of Ia:IIa and IIa:Ia being 15:1 and 10:1, respectively (from the relative integral intensities of the methyl group signals). On irradiation of the E isomer Ia in CD_3CN under similar conditions the ratio of the initial fulgide and the newly formed Z isomer IIa and 4,4*a*-dihydrocarbazole derivative IIIa amounted to 8:2.5:1. The bathochromic shift of 20-30 nm in the long-wave absorption band observed on UV irradiation of solutions of compound Ia in toluene or acetonitrile (λ_{max} = 400-408 nm) corresponded to the formation of the Z isomer IIa. A new long-wave band with a maximum at 515-518 nm was assigned to the photoinduced form IIIa, the lifetime of which (τ) was not less than 10^4 sec at 295 K. UV irradiation of compound IIb (in acetonitrile, λ_{max} 385 nm) in the 250-400 nm region for 1.5 min resulted in the formation of the E isomer Ib, the ratio IIb:Ib being 20:1 from PMR results. As a result of photocyclization the E isomer Ib was converted into 4,4*a*-dihydrocarbazole derivative IIIb (λ_{max} = 550 nm) with a half-life ($\tau_{1/2}$) of 415 sec at 295 K (in acetone). Conversion of the compounds III into the initial fulgides was initiated both photochemically (λ = 400-700 nm) and thermally (by heating up to 353 K). Irreversible thermal or photochemical reactions leading to loss of photochromic properties were not observed. From this one can conclude that it is possible to create photochromic systems with considerable potential on the basis of compounds I and II.

E-(1,3-Dimethyl-2-indolylmethylene)isopropylidenesuccinic Anhydride (Ia, $C_{18}H_{17}NO_3$). R_f 0.39 ($CHCl_3$). Mp 198-200°C. PMR spectrum ($CDCl_3$, δ, ppm): 7.79 (1H, s, C=CH), 3.76 (3H, s, N—CH_3), 2.53 (3H, s, cis-CH_3), 1.95 (3H, s, 3-CH_3), 1.33 (3H, s, trans-CH_3). Mass spectrum. m/z: 295 $[M]^+$. Yield 29%.

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Z-(1,3-Dimethyl-2-indolylmethylene)isopropylidenesuccinic Anhydride (IIa, $C_{18}H_{17}NO_3$). R_f 0.20 ($CHCl_3$). Mp 190-191°C. PMR spectrum ($CDCl_3$, δ, ppm): 7.36 (1H, s, C=CH), 3.70 (3H, s, N—CH_3), 2.60 (3H, s, cis-CH_3), 2.38 (3H, s, trans-CH_3), 2.30 ppm (3H, s, 3-CH_3). Mass spectrum m/z: 295 $[M]^+$. Yield 6%.

Z-(1,3-Dimethyl-2-indolylethylidine)isopropylidenesuccinic Anhydride (IIb, $C_{19}H_{19}NO_3$). Mp 210-212°C. PMR spectrum (CD_3CN, δ, ppm): 2.11 (3H, s, trans-CH_3), 2.21 (3H, s, trans-CH_3), 2.23 (3H, s, 3-CH_3), 2.44 (3H, s, cis-CH_3), 3.58 (3H, s, N-CH_3), 7.1-7.5 (4H, m, C_6H_4). Mass spectrum, m/z: 309 $[M]^+$. Yield 2%.

E-(1,3-Dimethyl-2-indolylethylidene)isopropylidenesuccinic Anhydride (Ib). PMR spectrum (CD_3CN, δ, ppm): 1.00 (3H, s, trans-CH_3), 2.04 (3H, s, 3-CH_3), 2.60 (3H, s, cis-CH_3); 3.67 (3H, s, N—CH_3).

Anhydride of 4,4*a*-Dihydro-4,4,4*a*,9-tetramethylcarbazole-2,3-dicarboxylic Acid (IIIa). PMR spectrum (CD_3CN, δ, ppm): 5.35 (1H, s, 1-H), 3.29 (3H, s, N—CH_3), 1.79 (3H, s, 4-CH_3), 1.40 (3H, s, 4*a*-CH_3), 0.98 (3H, s, 4-CH_3).

Isomers I and II were separated by column chromatography. Compounds Ia and IIa, b were recrystallized from ethanol. Elemental analyses were in agreement with the calculated.

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