PHOTOCHROMIC FULGIDES BASED ON 2-ACETYL-1-METHYLINDOLE

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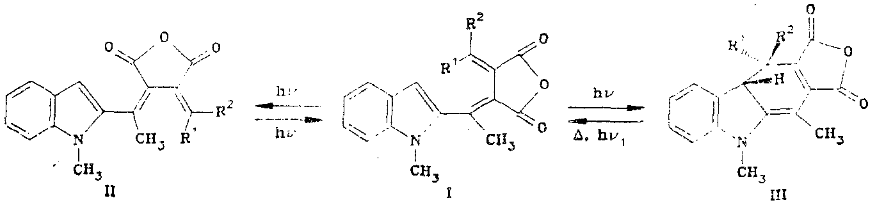
Photochromic fulgides Ia and IIa, b, which have E and Z configurations, respectively, were obtained by the reaction of diethyl isopropylidene- and isobutylidenesuccinate with 2-acetyl-1-methylindole in the presence of sodium hydride in toluene.



I—III a $R^1=R^2=CH_3$; b $R^1=CH_3$, $R^2=C_2H_5$

An intense absorption band with λ_{max} ~550 nm, which corresponds to the more deeply colored III form, which is converted to I by the action of visible light, develops on UV irradiation of solutions of these fulgides in acetonitrile (λ_{max}~385 nm). The lifetime $\tau_{\frac{1}{2}}$ of the photoinduced form changes symbatically with respect to the polarity of the solvent and at 295°K is 40 sec for toluene, 10 min for acetone, and 15 min for acetonitrile.

It was established by PMR spectroscopy that the formation of Z isomer IIa occurs in addition to photocyclization of fulgide Ia on irradiation in CD_3CN. The Ia:IIa:IIIa ratio was 15:3:1. Only E,Z isomerization (Ia:IIa = 8:1, IIa:Ia = 20:1, IIb:Ib = 12:1) was observed on UV irradiation of fulgides Ia, IIa, and IIb under similar conditions in solution $CDCl_3$.

Compounds I differ from the recently described fulgide obtained from 3-acetyl-1-methylindole [1] with respect to the higher photocyclization yield, evidently as a consequence of the more favorable (for the formation of the cyclic form) distribution of the π-electron density in the molecule.

(E-1-Methyl-2-indolylethylidene)isopropylidenesuccinic Anhydride (Ia). This compound was obtained in 7% yield and had mp 150-152°C. PMR spectrum ($CDCl_3$): 7.1-7.6 (4H, m, C_6H_4), 6.64 (1H, s, 3-H), 3.60 (3H, s, N—CH_3), 2.74 (3H, s, cis-CH_3), 2,26 (3H, s, cis-CH_3), 1.14 ppm (3H, s, trans-CH_3). Mass spectrum, m/z: 295 $[M]^+$.

(Z-1-Methyl-2-indolylethylidene)isopropylidenesuccinic Anhydride (IIa). This compound was obtained in 36% yield and had mp 195-197°C. PMR spectrum ($CDCl_3$): 7.1-7.6 (4H, m, C_6H_4), 6.73 (1H, s, 3-H), 3.67 (3H, s, N—CH_3), 2.50 (3H, s, cis-CH_3), 2.31 (3H, s, trans-CH_3), 2.10 ppm (3H, s, trans-CH_3). Mass spectrum, m/z: 295 $[M]^+$.

(Z-1-Methyl-2-indolylethylidene)(Z-2-butylidene)succinic Anhydride (IIb). This compound was obtained in 36% yield and had mp 163-165°C. PMR spectrum ($CDCl_3$): 7.1-7.6 (4H, m, C_6H_4), 6.74 (1H, s, 3-H), 3.68 (3H, s, N—CH_3), 2.93 (2H, q, J = 7.6 Hz, CH_2), 2.30 (3H, s, trans-CH_3), 2.08 (3H, s, trans-CH_3), 1.22 ppm (3H, t, J = 7.6 Hz, CH_2). Mass spectrum , m/z: 309 $[M]^+$.

(E-1-Methyl-2-indolylethylidene)(Z-2-butylidene)succinic Anhydride (Ib). PMR spectrum ($CDCl_3$): 7.1-7.6 (4H, m, C_6H_4), 6.66 (1H, s, 3-H), 3.57 (3H, s, N—CH_3), 2.75 (3H, s, Cis-CH_3), 2.67 (2H, q, J = 7.6 Hz, CH_2), 1.10 (3H, s, trans-CH_3), 0.99 ppm (3H, t, J = 7.6 Hz, CH_3).

4,4-Dihydro-1,4,4,9-tetramethylcarbazole-2,3-dicarboxylic Acid Anhydride (IIIa). PMR spectrum (CD_3CN): 7.0-7.6 (4H, m, C_6H_4), 4.29 (1H, s, 4a-H), 2.38 (3H, s, N—CH_3), 1.88 (3H, s, 1-CH_3), 0.87 ppm (6H, s, 4-CH_3).

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Isomers Ia and IIa were separated by crystallization. The yields of the fulgides were based on 2-acetyl-1-methylindole. All of the compounds were recrystallized from ethanol. The results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

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