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NEW DERIVATIVES OF INDOLE.
SYNTHESIS OF PHOTOCHROMIC
2-ARYLINDOLE SYSTEMS

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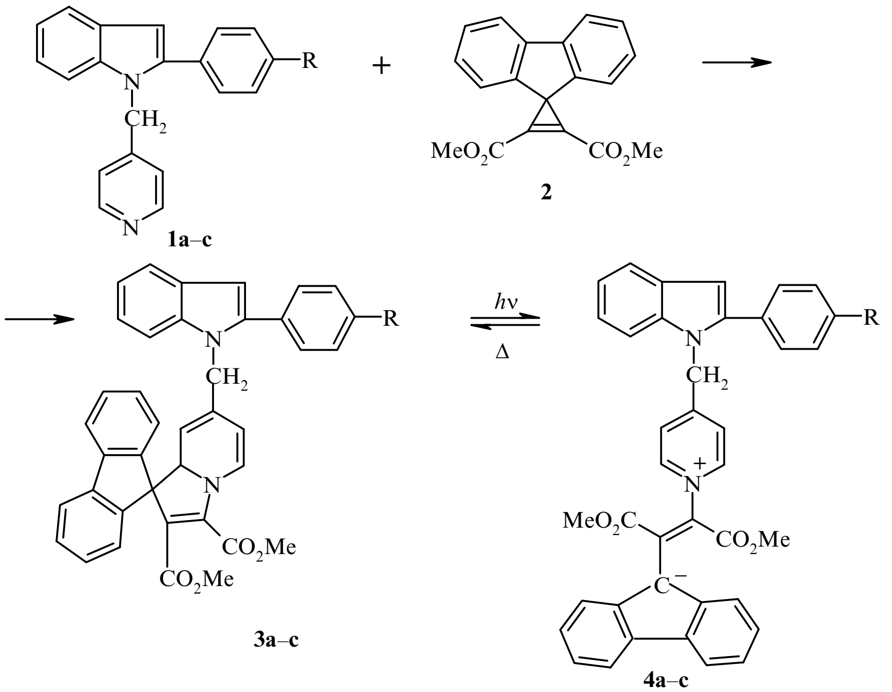
In view of the increasing interest in photochromic compounds, spirodihydroindolizines in particular [1], we have synthesized some light-sensitive systems in which 2-arylindole and spirodihydroindolizine fragments are coupled.



1, 3, 4 a R = H, **b** R = NO_2, **c** R = Br

1-(γ-Pyridylmethyl)-2-arylindoles **1a-c** required for the photochromic compounds were obtained by interphase alkylation of the corresponding 2-arylindoles [2]. Pyridylmethylation was carried out with 4-(chloromethyl)pyridinium chloride by boiling in a two-phase system of 50% aqueous KOH–benzene in the presence of Bu_4NBr.

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Compounds **1a-c** reacted with 2',3'-dimethoxycarbonylspirofluorenylcyclopropene (**2**) [3] in the dark at room temperature [4]. The compounds formed, **3a-c**, are reversibly photochromic. The colorless (**3a,c**) or light yellow (**3b**) solutions in CH_2Cl_2 became deep green on irradition with UV light because of formation of betaines **4a-c**. On cessation of irradiation the solutions slowly returned to their original colors as a result of thermal 1,5-electrocyclization of betaines **4a-c** with half-lives ($\tau_{1/2}$) of 55, 44, and 32 s respectively. The absorption maxima of betaines lie in the long wave region at 600-610 nm while those of the dihydrospiroindolizines occur at 380-430 nm.

2',3'-Dimethoxycarbonyl-7'-[1-methyl-2-phenylindolyl]spiro[fluoren-9,1'-1H-indolizine] (3a). Yield 44%; mp 104-105°C, R_f 0.30 (Silufol UV-254, benzene). UV-vis (CH_2Cl_2), λ_{max} (log ε): 384 nm (4.44). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, J (Hz): 3.18 (3H, s, 2'-$COOCH_3$); 3.91 (3H, s, 3'-$COOCH_3$); 3.98 (1H, s, 8'a-H); 4.50 (2H, br. s, CH_2); 4.91 (1H, dd, $J_{8'6'}$ = 1.36, $J_{8'8'a}$ = 7.48, 8'-H); 5.45 (1H, br. s, 6'-H); 6.43 (1H, br. s, 5'-H); 6.67 (1H, d, J_o = 7.52, H_{arom}); 6.91 (1H, d, J_o = 7.52, H_{arom}); 7.00-7.04 (2H, td, J_m = 1.32, J_o = 7.04, H_{arom}); 7.24-7.45 (11H, m, H_{arom}); 7.58 (1H, d, J_o = 7.52, H_{arom}); 7.75 (2H, t, J_o = 7.52, H_{arom}). Found, %: C 79.52; H 5.40; N 4.48; *m/z* 590 [M^+]. $C_{39}H_{30}N_2O_4$. Calculated, %: C 79.30; H 5.12; N 4.74; M = 590.

2',3'-Dimethoxycarbonyl-7'-[1-methyl-2-(*p*-nitrophenyl)indolyl]spiro[fluoren-9,1'-1H-indolizine] (3b). Yield 53%; mp 135-136°C, R_f 0.26 (Silufol UV-254, benzene). UV-vis (CH_2Cl_2), λ_{max} (log ε): 428 nm (4.40). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, J (Hz): 3.18 (3H, s, 2'-$COOCH_3$); 3.91 (3H, s, 3'-$COOCH_3$); 3.93 (1H, s, 8'a-H); 4.58 (1H, d, J_{gem} = 17.24, CH_2); 4.63 (1H, d, J_{gem} = 17.68, CH_2); 4.88 (1H, dd, $J_{8'6'}$ = 1.32, $J_{8'8'a}$ = 7.52); 5.40 (1H, d, $J_{6'8'}$ = 1.32, 6'-H); 6.68 (2H, t, $J_{5'6'}$ = 7.52, 5'-H, 3-H); 7.02-7.19 (3H, m, H_{arom}); 7.23-7.38 (5H, m, H_{arom}); 7.51-7.56 (4H, m, H_{arom}); 7.72-7.75 (2H, m, J_m = 1.32, J_o = 7.52); 8.32 (2H, dd, J_o = 7.68, H_{arom}). Found, %: C 73.75; H 4.31; N 6.50; *m/z* 635 [M^+]. $C_{39}H_{29}N_3O_6$. Calculated, %: C 73.69; H 4.60; N 6.61; M = 635.

7'-[2-(*p*-Bromophenyl)-1-methylindolyl]-2',3'-dimethoxycarbonylspiro[fluoren-9,1'-1H-indolizine] (3c). Yield 45%; mp 162-163°C, R_f 0.37 (Silufol UV-254, benzene). UV-vis (CH_2Cl_2), λ_{max} (log ε): 388 nm (4.13). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, J (Hz): 3.18 (3H, s, 2'-$COOCH_3$); 3.92 (3H, s, 3'-$COOCH_3$); 3.97 (1H, s, 8'a-H); 4.50 (2H, br. s, CH_2); 4.90 (1H, d, $J_{8'8'a}$ = 7.52, 8'-H); 5.45 (1H, br. s, 6'-H); 6.47 (1H, br. s, 5'-H); 6.93 (1H, d, J_o = 7.52, H_{arom}); 6.98-7.06 (2H, m, H_{arom}); 7.18 (1H, d, J_o = 8.40, H_{arom}); 7.25-7.41 (6H, m, H_{arom}); 7.47 (1H, d, J_o = 7.04, H_{arom}); 7.57 (1H, d, J_o = 7.52, H_{arom}); 7.61 (2H, d, J_o = 8.40, Ar-H); 7.77 (2H, t, J_o = 7.12, H_{arom}). Found, %: C 70.17; H 4.60; N 3.91; *m/z* 669 [M^+]. $C_{39}H_{29}BrN_2O_4$. Calculated, %: C 69.96; H 4.37; N 4.18; M = 669.

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