Chemistry of Heterocyclic Compounds, Vol. 37, No. 10, 2001

BISINDOLES. SYNTHESIS OF A NEW SPIROCYCLIC PHOTOCHROMIC SYSTEM

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Keywords: betaine, bispyrrolizidine, indolinoindoline, spirocyclopropene, photochromes.

The reaction of 1,1,2,9,10,10-hexamethylindolenino[4,5-*e*]indolenine (**1**) with two equivalents of 2',3'-dimethoxycarbonylspirofluorenecyclopropene (**2**) gives a new spirocyclic system, namely, bis[2',3'-dimethoxycarbonyl-5',6',6'-trimethylspirofluoren-9,4'-(1'-aza-2'-cyclopenten)[1',5'-*a*]indolino[4,5-*e*]indoline (**3**) in 81% yield. The starting compound, indolenino[4,5-*e*]indolenine **1**, was obtained in 35% yield from 2,7-naphthalenedihydrazine in the Fischer reaction.

Product **3** is a bispyrrolizidine derivative, which forms an unstable colored betaine form **3b** upon the action of light. A study of the electronic spectra revealed bands for colored betaine form **3b** at 325 and 550 nm. The half-life for colored form **3b** $\tau_{1/2} = 1.402$ sec. Hence, **3** is a rapidly converting photochromic compound.

The mechanism for the formation of the betaine form is given in the Scheme 1. The rings in **3b** presumably open in the following sequence: **3** → **3a** → **3b**.

The structures of **1** and **3** were supported by IR, UV, and ^{1}H NMR spectroscopy and mass spectrometry.

1,1,2,9,10,10-Hexamethylindolenino[4,5-*e*]indolenine (1). A sample of methyl isopropyl ketone (1 ml, 9 mmol) was added to a solution of 2,7-naphthalenedihydrazine (0.5 g, 2.7 mmol) in acetic acid and heated at reflux for 2 h. The product was purified on a silica gel column using ether as the eluent to give 0.30 g (35%) **1**; mp 160-161°C, R_f 0.25 (ether). UV spectrum in ethanol, λ_{max} (log ε): 287 (4.42), 291 nm (4.18). IR spectrum in vaseline mull, ν, cm^{-1}: 1690, 1670, 1500, 1410, 1360, 1250, 1200, 1165, 1095, 1080. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 1.61 (6H, s, 1-CH_3); 2.37 (3H, s, 2-CH_3); 7.74 (1H, d, J_{54} = 8.40, 5-H); 7.94 (1H, d, J_{45} = 8.40, 4-H). Found, %: C 82.77; H 6.93; N 9.81. *m/z* (%): 290 [M^+], 289 (25.1), 275 (96.3), 260 (24.9), 234 (28.1), 218 (17.6), 204 (9.0), 189 (8.8), 178 (13.7), 165 (16.3), 152 (13.0). $C_{20}H_{22}N_2$. Calculated, %: C 82.76; H 7.58; N 9.65; M = 290.

Bis[2',3'-dimethoxycarbonyl-5',6',6'-trimethylspirofluoren-9,4'-(1'-aza-2'-cyclopenten)[1',5'-*a*]-indolino[4,5-*e*]indoline (3). A sample of **1** (0.1 g, 0.3 mmol) was added to a solution of 2',3-dimethoxycarbonylspirocyclopropane (0.2 g, 0.7 mmol) in absolute ether (30 ml) and stirred in the dark for 24 h at room temperature. The product was purified on a silica gel column using benzene as the eluent to give 0.25 g (81%) **3**; mp 178-180°C, R_f 0.65 (benzene). UV spectrum in ethanol, λ_{max} (log ε): 296 (4.53), 361 nm (4.06). IR spectrum in vaseline mull, ν, cm^{-1}: 1720, 1670, 1600, 1495, 1400, 1370, 1305, 1265, 1220, 1160, 1100, 1075, 985. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 0.81 (3H, s, 6'-H); 1.03 (3H, s, 6'-CH_3); 1.58 (3H, s, 5'-CH_3); 3.58 (3H, s, CO_2CH_3); 3.88 (3H, s, CO_2CH_3); 6.33 (1H, d, J_o = 7.60, Ar–H); 6.64 (1H, t, Ar–H); 6.89 (1H, d, $J_{8'7'}$ = 8.80, 8'-H); 7.08 (1H, d, $J_{7'8'}$ = 8.80, 7'-H); 7.16 (1H, d, J_o = 7.50, Ar–H); 7.21 (1H, t, Ar–H);

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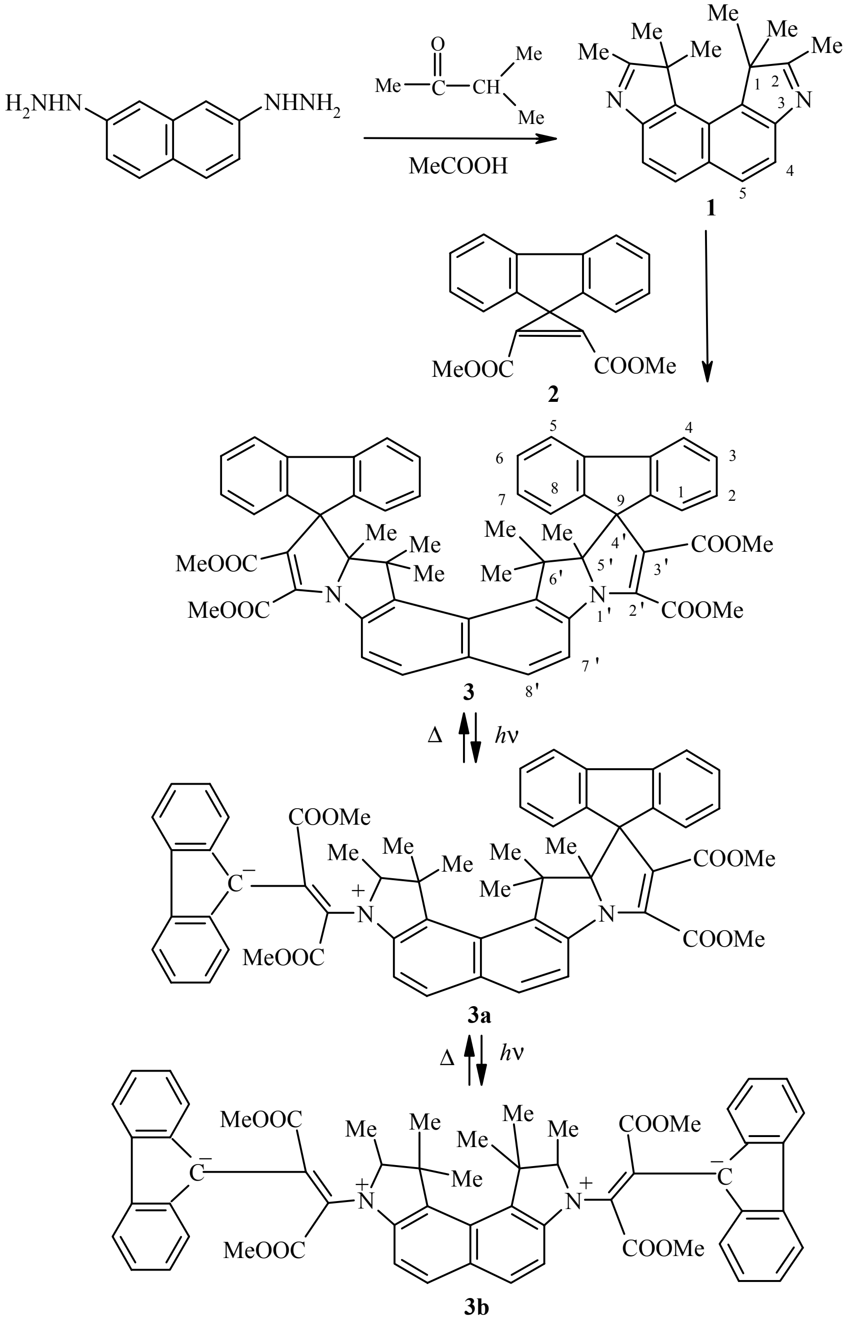
Scheme 1



7.23-7.82 (4H, m, Ar–H). Found, %: C 66.81; H 5.88; N 3.21. *m/z* (%): 902 [M^+] (4.0), 752 (2.8), 736 (10.4), 706 (6.5), 612 (14.0), 606 (21.8), 596 (27.3), 594 (41.7), 580 (34.5), 566 (29.4), 506 (21.5), 445 (14.2), 418 (12.7), 308 (45.2), 276 (53.9), 249 (44.0), 203 (48.0), 189 (70.2), 165 (100.0). $C_{58}H_{50}N_2O_8$. Calculated, %: C 77.16; H 5.54; N 3.10; M = 902.

This work was carried out with the financial support of the Deutsche Forschungsgemeinschaft, Project 436 GEO 113/3/0 R/S and the Fond der Chemische Industrie.