4,8-DIOXO-6,7,8,9-TETRAHYDRO-4H-[1,4]DIAZEPINO[3,2,1-*hi*]PYRIDO[4,3,2-*cd*]-INDOLE – A NEW HETEROCYCLIC SYSTEM

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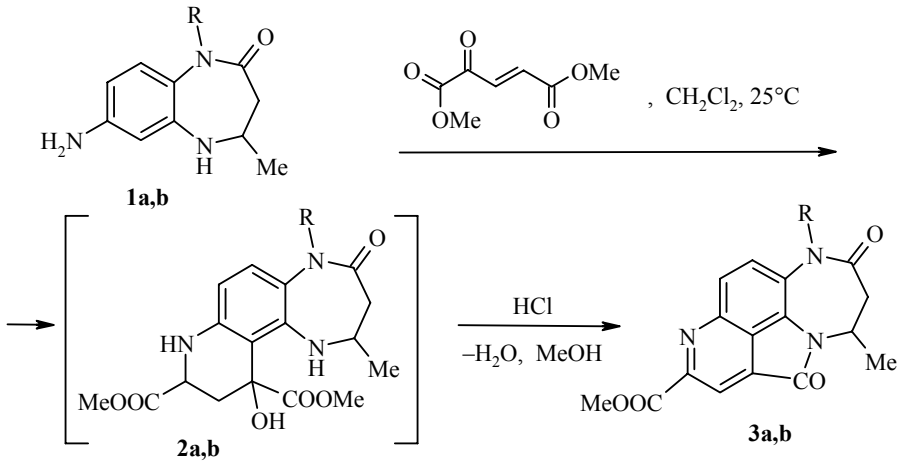
The reaction of dimethyl 2-oxoglutaconate with aromatic amines leads to derivatives containing a 2,4-disubstituted quinoline fragment through a Doebner-Miller reaction [1-3].

We studied the cyclocondensation of 7-amino-4-methyl- (**1a**) and 7-amino-1,4-dimethyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-ones (**1b**) and dimethyl 2-oxoglutaconate in order to establish the direction of the reaction since the addition of a new ring is possible at $C_{(6)}$ and $C_{(8)}$ of the benzene ring. We have found that the condensation proceeds at $C_{(6)}$ of the aromatic ring to give intermediate piperidinol **2a**,**b**. Dehydration and aromatization of this intermediate is accompanied by acylation of the amino group at $N_{(5)}$ of the diazepine ring to give derivatives of a new condensed heterocyclic system, namely, 4,8-dioxo-6,7,8,9-tetrahydro-4H-[1,4]diazepino[3,2,1-*hi*]pyrido[4,3,2-*cd*]indole **3a**,**b**. The structure of these products was supported by their spectral data.



1–3 **a** R = H, **b** R = Me

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The IR spectra were taken on a Perkin-Elmer Spectrum GX FT-IR spectrometer for KBr pellets. The ^{1}H NMR spectra were taken on a Varian Unity Inova 300 spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal standard.

Methyl Ester of 6-Methyl-4,8-dioxo-6,7,8,9-tetrahydro-4H-[1,4]diazepino[3,2,1-*hi*]pyrido-[4,3,2-*cd*]indole-2-carboxylic Acid (3a). Yield 34%; mp 297-299°C (chloroform). IR spectrum, ν, cm^{-1}: 3295, 3210 (NH), 1718, 1666, 1646 (CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.74 (1H, s, H-3); 8.47 (1H, br. s, NH); 7.97 (1H, d, *J* = 9.1, H-11); 7.33 (1H, d, *J* = 9.1, H-10); 4.99 (1H, m, CH); 4.13 (3H, s, OCH_3); 3.18 (1H, ddd, *J* = 1.3, *J* = 5.3, *J* = 14.8, CH_2); 3.07 (1H, dd, *J* = 2.3, *J* = 14.8, CH_2); 1.52 (3H, d, *J* = 6.6, CH_3). Found, %: C 61.68; H 4.29; N 13.45. $C_{16}H_{13}N_3O_4$. Calculated, %: C 61.73; H 4.21; N 13.50.

Methyl Ester of 6,9-Dimethyl-4,8-dioxo-6,7,8,9-tetrahydro-4H-[1,4]diazepino[3,2,1-*hi*]pyrido-[4,3,2-*cd*]indole-2-carboxylic Acid (3b). Yield 36% ; mp 229-231°C (ethyl acetate). IR spectrum, ν, cm^{-1}: 1724, 1701, 1671 (CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.72 (1H, s, H-3); 8.01 (1H, d, *J* = 9.3, H-11); 7.48 (1H, d, *J* = 9.3, H-10); 4.90 (1H, m, CH); 4.13 (3H, s, OCH_3); 3.59 (3H, s, NCH_3); 3.18 (1H, dd, *J* = 5.4, *J* = 14.3, CH_2); 3.00 (1H, dd, *J* = 2.1, *J* = 14.2, CH_2); 1.49 (3H, d, *J* = 6.7, CH_3). Found, %: C 62.66; H 4.71; N 12.83. $C_{17}H_{15}N_3O_4$. Calculated, %: C 62.76; H 4.65; N 12.92.

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