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SHORT COMMUNICATIONS

Spiro Heterocyclization of Hetareno[*a*]pyrrole-2,3-diones in Reactions with *N*-Alkylanilines

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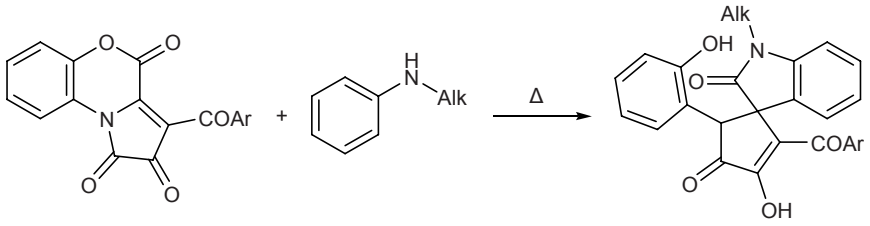
Reactions of hetareno[*a*]pyrrole-2,3-diones with *N*-alkylanilines were not reported previously. We have found that 3-aroyl-2,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]-benzoxazine-1,2,4-triones **Ia** and **Ib** react with *N*-methyl- and *N*-ethylanilines **IIa** and **IIb** at a ratio of 1:1 on heating in boiling toluene (reaction time 0.5–2 h) to give substituted 1-alkyl-3′-aroyl-1′-(2-hydroxyphenyl)-4′-hydroxyspiro[indole-3,2′-pyrrole]-2,5′(1*H*,1′*H*)-diones **IIIa** and **IIIb**.

Presumably, the process involves initial electrophilic attack by the C^{3a} atom of pyrrolobenzoxazinetrione **I** at the activated *ortho*-position in aniline **II**, followed by closure of indole ring via intramolecular attack by the secondary amino group on the lactone carbonyl carbon atom in the 1,4-oxazine ring and cleavage of the latter at the C^4–O^5 bond. The transformation sequence is similar to that proposed previously for the reactions of pyrrolobenzoxazinetriones **I** with 3-amino-5,5-dimethylcyclohex-2-en-1-ones, leading to substituted 3′-aroyl-4′-hydroxy-1′-(*o*-hydroxyphenyl)-6,6-dimethyl-6,7-dihydrospiro[indole-3,2′-pyrrole]-2,4,5′(1*H*,1′*H*,5*H*)-triones whose structure was proved by X-ray analysis [1].

The described reaction is a rare example of selective synthesis of difficultly accessible spiro[indole-3,2′-pyrrole] system containing various substituents in several positions of both heterocyclic fragments.

3′-Benzoyl-1′-(2-hydroxyphenyl)-4′-hydroxy-1-methylspiro[indole-3,2′-pyrrole]-2,5′(1*H*,1′*H*)-dione (IIIa). A solution of 0.002 mol of compound **Ia** and 0.002 mol of *N*-methylaniline (**IIa**) in 10 ml of anhydrous toluene was heated for 2 h under reflux (until it became colorless). The mixture was cooled, and the precipitate was filtered off. Yield 77%, mp 268–270°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3244 br (OH), 1707 (C=O), 1621 (PhC=O). ^{1}H NMR spectrum, δ, ppm: 3.19 s (3H, CH_3N), 6.65–7.72 m (13H, H_{arom}), 9.59 s (1H, 2″-OH), 12.48 br.s (1H, 4′-OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 26.78 (CH_3N), 70.04 (C_{spiro}), 108.56–153.72 (C_{arom}, $C^{3'}$, $C^{4'}$), 165.28 ($C^{5'}$), 172.92 (C^2), 188.53 (**C**OPh). Found, %: C 70.40; H 4.27; N 6.54. $C_{25}H_{18}N_2O_5$. Calculated, %: C 70.42; H 4.25; N 6.57.

3′-(4-Ethoxybenzoyl)-1-ethyl-1′-(2-hydroxyphenyl)-4′-hydroxyspiro[indole-3,2′-pyrrole]-2,5′(1*H*,1′*H*)-dione (IIIb). Yield 85%, mp 265–267°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3237 br (OH), 1707 (C=O), 1626 (ArC=O). ^{1}H NMR spectrum, δ, ppm: 1.14 t (3H, C**H**$_3$CH$_2$N, J = 7.2 Hz), 1.34 t (3H, C**H**$_3$CH$_2$O, J = 7.1 Hz), 3.70 q and 3.80 q (1H each,



Ia, **Ib** **IIa**, **IIb** **IIIa**, **IIIb**

Ar = Ph (**a**), 4-EtOC$_6$H$_4$ (**b**); Alk = Me (**a**), Et (**b**).

CH_2N, J = 7.2 Hz), 4.11 q (2H, CH_2O, J = 7.1 Hz), 6.64–7.73 m (12H, H_{arom}), 9.54 s (1H, 2″-OH), 12.24 br.s (1H, 4′-OH). ^{13}C NMR spectrum, δ_C, ppm: 11.82 (**C**H_3CH_2N), 14.41 (**C**H_3CH_2O), 56.90 (CH_2N), 63.40 (CH_2O), 70.12 (C_{spiro}), 108.58–153.76 (C_{arom}, $C^{3'}$, $C^{4'}$), 162.24 ($C^{5'}$), 172.48 (C^2), 187.00 (3′-C=O). Found, %: C 69.38; H 5.06; N 5.71. $C_{28}H_{24}N_2O_6$. Calculated, %: C 69.41; H 4.99; N 5.78.

The IR spectra were measured from samples dispersed in mineral oil on an FMS-1201 spectrometer. The ^1H and ^{13}C NMR spectra were recorded from solutions in DMSO-d_6 on a Bruker WP-400 instrument using tetramethylsilane as internal reference. The purity of the products was checked by TLC on Silufol plates using ethyl acetate as eluent; spots were detected by treatment with iodine vapor.

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