

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-aryl-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 **Ila** and **Ilb** at a ratio of 1:1 on heating in boiling toluene (reaction time 0.5–2 h) to give substituted 1-alkyl-3'-aryl-1'-(2-hydroxyphenyl)-4'-hydroxyspiro[indole-3,2'-pyrrole]-2,5'(1*H*,1'*H*)-diones **IIla** and **IIlb**.

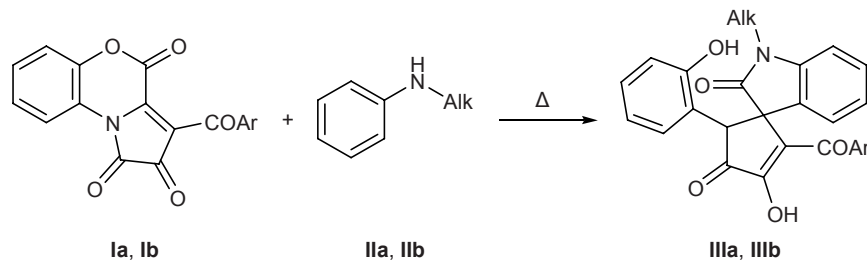
Presumably, the process involves initial electrophilic attack by the C^{3a} atom of pyrrolobenzoxazine-trione **I** at the activated *ortho*-position in aniline **II**, followed by closure of indole ring via intramolecular attack by the secondary amino group on the lactone carbonyl carbon atom in the 1,4-oxazine ring and cleavage of the latter at the C⁴–O⁵ bond. The transformation sequence is similar to that proposed previously for the reactions of pyrrolobenzoxazine-triones **I** with 3-amino-5,5-dimethylcyclohex-2-en-1-ones, leading to substituted 3'-aryl-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 (IIla). A solution of 0.002 mol of compound **Ia** and 0.002 mol of *N*-methylaniline (**Ila**) 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). ¹H NMR spectrum, δ , ppm: 3.19 s (3H, CH₃N), 6.65–7.72 m (13H, H_{arom}), 9.59 s (1H, 2''-OH), 12.48 br.s (1H, 4'-OH). ¹³C NMR spectrum (DMSO-*d*₆), δ _C, ppm: 26.78 (CH₃N), 70.04 (C_{spiro}), 108.56–153.72 (C_{arom}, C^{3'}, C^{4'}), 165.28 (C^{5'}), 172.92 (C^{2'}), 188.53 (COPh). Found, %: C 70.40; H 4.27; N 6.54. C₂₅H₁₈N₂O₅. 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 (IIlb). Yield 85%, mp 265–267°C (from ethyl acetate). IR spectrum, ν , cm⁻¹: 3237 br (OH), 1707 (C=O), 1626 (ArC=O). ¹H NMR spectrum, δ , ppm: 1.14 t (3H, CH₃CH₂N, *J* = 7.2 Hz), 1.34 t (3H, CH₃CH₂O, *J* = 7.1 Hz), 3.70 q and 3.80 q (1H each,



Ar = Ph (**a**), 4-EtOC₆H₄ (**b**); Alk = Me (**a**), Et (**b**).

CH₂N, $J = 7.2$ Hz), 4.11 q (2H, CH₂O, $J = 7.1$ Hz), 6.64–7.73 m (12H, H_{arom}), 9.54 s (1H, 2''-OH), 12.24 br.s (1H, 4'-OH). ¹³C NMR spectrum, δ_C , ppm: 11.82 (CH₃CH₂N), 14.41 (CH₃CH₂O), 56.90 (CH₂N), 63.40 (CH₂O), 70.12 (C_{spiro}), 108.58–153.76 (C_{arom}, C^{3'}, C^{4'}), 162.24 (C^{5'}), 172.48 (C²), 187.00 (3'-C=O). Found, %: C 69.38; H 5.06; N 5.71. C₂₈H₂₄N₂O₆. 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 ¹³C 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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REFERENCE

1. Racheva, N.L., Shurov, S.N., Aliev, Z.G., and Maslivos, A.N., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 108.