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NITROSYLATION OF 3a-SUBSTITUTED 2,3,3a,4-TETRAHYDRO-1H-BENZO[*d*]-PYRROLO[1,2-*a*]IMIDAZOL-1-ONES

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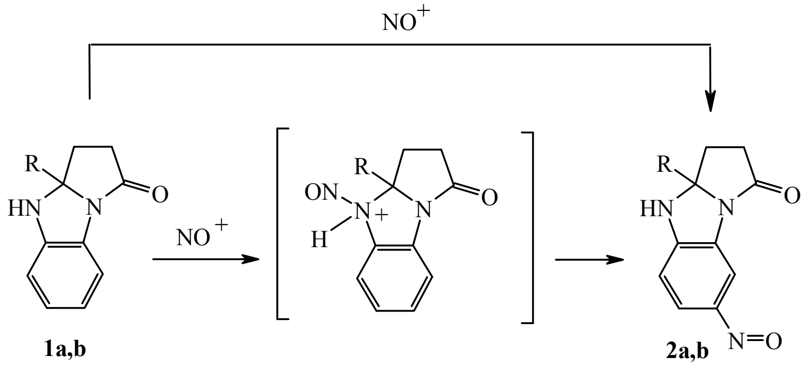
We report the nitrosylation of previously synthesized 3a-substituted 2,3,3a,4-tetrahydro-1H-benzo[*d*]-pyrrolo[1,2-*a*]imidazol-1-ones **1a,b** in the reaction of 5R-3H-furan-2-ones with 1,2-diaminobenzene [1]. The nitrosylation reaction was carried out at 0–5°C in aqueous acetonitrile. Nitrous acid was generated *in situ* and introduced directly to react with the substrate. The crystalline products have a color characteristic for nitroso compounds.



1, **2** **a** R = Ph, **b** R = $4\text{-}MeC_6H_4$

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Since imidazolones **1a,b** possess two reaction sites capable of reacting with electrophilic reagents, we could expect the formation of products of N-nitrosylation and/or C-nitrosylation.

The nitrosonium cation is a weak electrophile and, thus, attack at the secondary amino group in imidazolones **1a,b** is more likely and would obey kinetic control. However, the NMR spectral data indicate the formation of compounds **2a,b**, which were identified as 7-nitroso-3a-R-2,3,3a,4-tetrahydro-1H-benzo[*d*]pyrrolo[1,2-*a*]imidazol-1-ones. The formation of these nitroso products is possible through a Fischer-Hepp rearrangement, which proceeds under acid catalysis conditions as an intramolecular migration of the NO^+ cation, leading to the thermodynamically more stable C-nitrosylation products **2a,b**.

The ^1H NMR spectra were taken on a Varian-400 spectrometer at 400 MHz at 20–25°C in $CDCl_3$ with TMS as internal standard.

7-Nitroso-3a-phenyl-2,3,3a,4-tetrahydro-1H-benzo[*d*]pyrrolo[1,2-*a*]imidazol-1-one (2a). Excess concentrated sulfuric acid was added to a solution of $NaNO_2$ (0.07 g, 1 mmol) in cold water (3–5 ml), followed by a solution of compound **1a** (0.25 g, 1 mmol) in 4:1 acetonitrile-water (10 ml) and then water (50 ml). The mixture was stirred for 2 h at room temperature. The precipitate was filtered off and washed with water to give 0.21 g (75%) pale-yellow crystalline nitroso derivative **2a**; mp 96–98°C. ^1H NMR spectrum, δ, ppm (J, Hz): 1.62 (1H, br.s, NH); 3.61 (2H, t, $J = 6.2$, H-2); 3.88 (2H, t, $J = 6.2$, H-3); 7.47 (1H, d, $J = 2.0$, H-8); 7.49–7.65 (5H, m, C_6H_5); 8.12 (1H, d, $J = 8.0$, H-6); 8.25 (1H, d, $J = 8.0$, H-5). Found, %: C 69.00; H 5.15; N 15.23. $C_{16}H_{13}N_3O_2$ .Calculated, %: C 68.81; H 4.69; N 15.05.

3a-(4-Methylphenyl)-7-nitroso-2,3,3a,4-tetrahydro-1H-benzo[*d*]pyrrolo[1,2-*a*]imidazol-1-one (2b) was obtained in 73% yield analogously from compound **1b** (0.26 g, 1 mmol) and $NaNO_2$ (0.07 g, 1 mmol); mp 120–122°C. ^1H NMR spectrum, δ, ppm (J, Hz): 1.68 (1H, br.s, NH); 2.26 (3H, s, CH_3); 3.24 (2H, t, $J = 6.0$, H-2); 3.44 (2H, t, $J = 6.2$, H-3); 7.21, 7.39 (4H, d, $J = 8.0$, *p*-Tol); 7.47 (1H, d, $J = 2.0$, H-8); 8.12 (1H, d, $J = 8.0$, H-6); 8.25 (1H, d, $J = 8.0$, H-5). Found, %: C 69.49; H 5.06; N 14.69. $C_{17}H_{15}N_3O_2$. Calculated, %: C 69.61; H 5.15; N 14.33.

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REFERENCES

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