

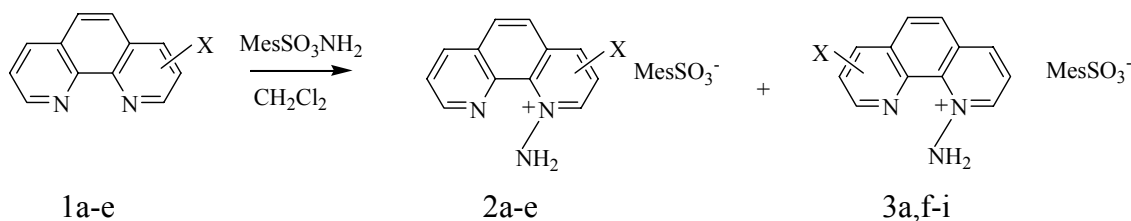
Regioselectivity in Amination of Azines: Interaction of X-1,10-Phenanthrolines with O-Mesitylsulfonylhydroxylamine

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N-Amine salts of azines were shown to be of great utility in synthesis of heterocyclic compounds (see, for example, refs. 1 and 2). When these salts are prepared by amination reaction, regioselectivity is a crucial point in the synthetic procedure.

In order to obtain information on electronic effects of substituents governing selectivity of the amination reaction we have studied the interaction of X-1,10-phenanthrolines with O-mesitylsulfonylhydroxylamine.



X = H(a), 4-Me(b), 5-Me(c), 3-Br(d), 5-NO₂(e), 7-Me(f), 6-Me(g), 8-Br(h), 6-NO₂(i)

Structures of isomeric cations formed in this reaction were determined by ¹H and ¹³C NMR. The ratio of cations **2** and **3** depends on electronic character of the substituent X [ratio **2/3**, X = 4-Me (60:40), 5-Me (44:56), 3-Br (15:85), 5-NO₂ (58:42)], being independent of difference in charges on the respective N-atoms. Interestingly, *ab initio* B3LYP/ 6-31G(dp) calculations of the relative stabilities of isomeric ions **2** and **3** (ΔE) prove to be in agreement with the experimental data:

$$\log ([\mathbf{2}]/[\mathbf{3}]) = (0.030 \pm 0.056) - (0.065 \pm 0.010) \Delta E, r -0.964, s \ 0.11$$

This is apparently due to the late transition state of the reaction. The work aimed at evaluation of generality of this conclusion is in progress.

1. N. Abe, K. Odagiri, M. Otani, E. Fujinaga, H. Fujii, and A. Kakehi, *J. Chem. Soc. Perkin Trans. I*, **1999**, 1339.
2. R.V. Andreev and G.I. Borodkin, *Abstracts of Papers of the Conference "Organic Synthesis in the New Century"*, Saint-Petersburg, **2002**, 64.

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