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SHORT COMMUNICATIONS

Regioselectivity in the Amination of Azines. Reaction of 1,10-Phenanthroline Derivatives with *O*-Mesitylsulfonylhydroxylamine

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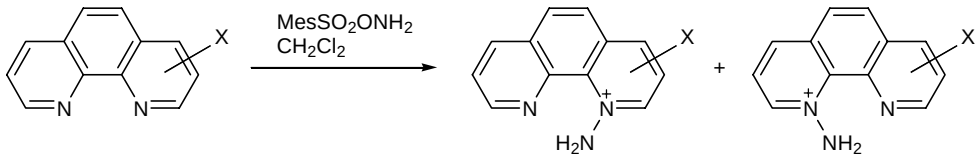
N-Amino-substituted azinium salts are widely used as reagents for amination of arenes [1–5] and synthesis of imines [6–8] and various heterocyclic and other compounds [6–10]. In the synthesis of *N*-amino derivatives of azines having several heteroatoms, the problem arises as to whether the amination will occur at one or another nitrogen atom [11]. 1,10-Phenanthroline derivatives are among promising models for studying regioselectivity in the amination of azines. As shown previously, the reaction of *O*-mesitylsulfonylhydroxylamine with 1,10-phenanthroline gives 1-amino-1,10-phenanthrolinium mesitylenesulfonate [3, 12]. The structure of this salt was proved by the ^{1}H and ^{13}C NMR spectra [3, 12], as well as by the X-ray diffraction data [12]. 1-Amino-1,10-phenanthrolinum cation shows no dynamic properties (on the NMR time scale) up to 100°C, i.e., neither intramolecular nor intermolecular transfer of the amino group occurs. Moreover, even on heating for 1 h at 150°C in dimethyl sulfoxide in the presence of 4-methyl-1,10-phenanthroline, the amino group in 1-amino-1,10-phenanthrolinium mesitylenesulfonate is not transferred to the former [12]. Therefore, such processes should not complicate studies of regioselectivity in the amination of phenanthroline derivatives.

The goal of the present work was to elucidate electronic factors determining regioselectivity in the amination of 1,10-phenanthroline derivatives with *O*-mesitylsulfonylhydroxylamine. The latter was selected as the aminating agent due to its wide application in the synthesis of N-amino salts [11]. The reaction of *O*-mesitylsulfonylhydroxylamine with substituted 1,10-phenanthrolines **Ia**–**Id** in methylene chloride afforded the corresponding cations **IIa**–**IId** and **IIIa**, **IIIe**–**IIIg** with $MesSO_3^-$ as counterion (Mes stands for 2,4,6-C_6H_2). Their structure was confirmed by the ^{1}H NMR spectra (see table). The signals were assigned using various proton–proton shift correlation techniques, in particular ^{1}H-2D NOE spectroscopy (NOESY) and two-dimensional proton–proton spin correlation spectroscopy (COSY). The NOESY spectra of cations **IIb**, **IIc**, **IIIe**, **IIIf** showed NOE for spatially close protons of the NH_2 group and 2-H, whereas cations **IId** and **IIIg** were characterized by NOE between 6-H and 7-H or 4-H and 5-H, respectively. In the case of cations **IId** and **IIIg**, we took into account that the corresponding $J_{8,9}$ values should be lesser than $J_{2,3}$ [12].

The ratio of isomeric cations **II** and **III** strongly depends on the nature of the X substituent. Donor



Ia–**Id** **IIa**–**IId** **IIIa**, **IIIe**–**IIIg**

X = H (**a**), 4-Me (**b**), 3-Br (**c**), 5-NO_2 (**d**), 7-Me (**e**), 8-Br (**f**), 6-NO_2 (**g**).

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^{1}H NMR spectra of ions **II** and **III** in DMSO-d_6 at ~20°C

Comp. no.	Chemical shifts δ,[a] ppm (*J*, Hz)								
	2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	NH_2[b]
IIa[c]	9.20 d.d (6.3, 1.3)	8.25 d.d (8.2, 6.3)	8.92 d.d (8.2, 1.3)	8.35[d] (8.9)	8.30[d] (8.9)	8.83 d.d (8.2, 1.7)	8.11 d.d (8.2, 4.5)	9.25 d.d (4.5, 1.7)	11.3
IIb	9.07 d (6.4)	8.11 d (6.4)	–	8.31[d,e] (9.2)	8.33[d,e] (9.2)	8.81 d.d (8.2, 1.8)	8.08 d.d (8.2, 4.4)	9.21 d.d (4.4, 1.8)	11.1
IIc	9.47 d (1.8)	–	9.26 d (1.8)	8.18[d,e] (9.0)	8.35[d,e] (9.0)	8.81 d.d (8.3, 1.8)	8.10 d.d (8.2, 4.5)	9.23 d.d (4.5, 1.8)	11.4
IId	9.34 d.d (6.4, 1.3)	8.39 d.d (8.2, 6.4)	9.12 d.d (8.2, 1.3)	–	9.29 s	9.12 d.d (8.6, 1.7)	8.27 d.d (8.6, 4.5)	9.39 d.d (4.5, 1.7)	11.4
IIIe	9.18 d.d (6.3, 1.3)	8.22 d.d (8.2, 6.3)	8.89 d.d (8.2, 1.3)	8.41[d,e] (9.2)	8.27[d,e] (9.2)	–	7.92 d (4.6)	9.04 d (4.6)	11.4
IIIf	9.22 d.d (6.3, 1.2)	8.30 d.d (8.2, 6.3)	8.95 d.d (8.3, 1.2)	8.37[d,e] (9.0)	8.32[d,e] (9.0)	9.20 d (2.3)	–	9.28 d (2.3)	11.0
IIIg	9.32 d.d (6.3, 1.2)	8.38 d.d (8.7, 6.3)	9.10 d.d (8.7, 1.2)	9.32 s	–	9.07 d.d (8.2, 1.8)	8.26 d.d (8.2, 4.5)	9.43 d.d (4.5, 1.8)	11.4

[a] The chemical shifts are given relative to TMS (δ_{DMSO} 2.50 ppm).
[b] Broadened signal.
[c] Data of [12].
[d] *AB* pattern.
[e] Alternative assignment is possible.

substituents increase the electron density on the neighboring nitrogen atom in the same ring and favor addition of amino group at that nitrogen atom; therefore, the fraction of the corresponding isomer is larger. However, we have found no quantitative correlation between the ratio of isomers **II** and **III** and the difference in the charges on the N^1 and N^{10} atoms in the initial azine, calculated by the AM1 method. This may be interpreted in terms of the nitrenium–ionic mechanism with a late transition state, according to which the ratio of isomeric ions is determined by their relative stabilities. Thus we observed a linear relation between the logarithms of the ratio of ions **II** and **III** ([**IIa**]/[**IIIa**] = 1, [**IIb**]/[**IIIe**] = 1.5, [**IIc**]/[**IIIf**] = 1.176, [**IId**]/[**IIIg**] = 1.381) and the difference in the enthalpies of formation of these ions ($\Delta\Delta H_f$ = 0, –4.7, 7, and –2.1 kJ/mol, respectively; AM1):

$$\log([\mathbf{II}]/[\mathbf{III}]) = (-0.11 \pm 0.06) - (0.084 \pm 0.015)\Delta\Delta H_f;$$
$$r = -0.971,\ s = 0.13.$$

We can conclude that the direction of amination of substituted 1,10-phenanthrolines strongly depends on the relative stability of the resulting cation, which is determined in turn by the substituent nature.

Amination of 1,10-phenanthroline derivatives (cf. [3, 12]). A solution of 0.57 mmol of *O*-mesitylsulfonylhydroxylamine in 1.5 ml of methylene chloride was added under stirring to a solution of 0.54 mmol of 1,10-phenanthroline **Ia**–**Id** in 1 ml of the same sovent. The mixture was stirred for 0.5 h, the resulting salt was precipitated by adding diethyl ether at ~5°C, and the oily residue was washed with diethyl ether and dried under reduced pressure. In the reaction with compounds **Ic** [13] and **Id**, 2 equiv of *O*-mesitylsulfonylhydroxylamine was added; the amination of 1,10-phenanthroline **Id** was initially performed at ~5°C (1 h), the mixture was then allowed to gradually warm up to ~20°C and was stirred for 2 h at that temperature. The isomer ratio was determined by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectra were recorded from solutions in DMSO-d_6 using a Bruker DRX-500 spectrometer (500 MHz); the chemical shifts were measured relative to signal from the residual protons in the solvent (δ 2.50 ppm).

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