

SHORT
COMMUNICATIONS

Oxidative Cyclization of *N*-*p*-Tolyl-2,5-bis(*p*-tolylamino)-1,4-Benzoquinone Imine

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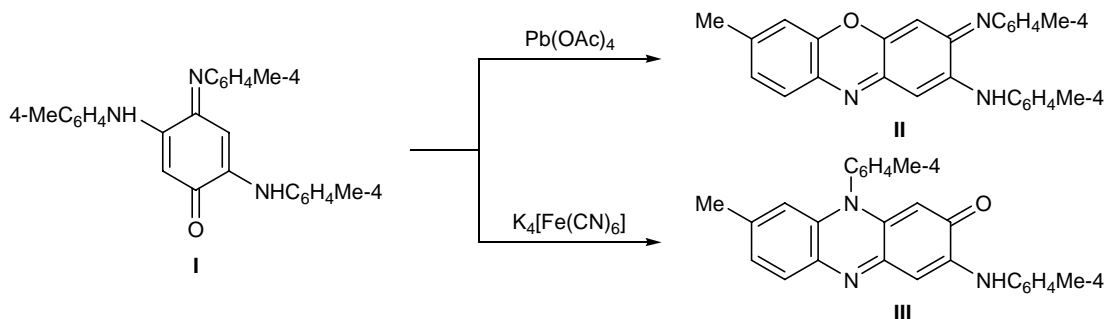
We previously showed [1, 2] that *N*-aryl-2,5-bis(arylamino)-1,4-benzoquinone imines undergo condensation with *N*-aryl-1,4-benzoquinone imines and 4-(arylamino)phenols to give, respectively, substituted carbazole- and dibenzofuranquinone imines. However, apart from these products, the reaction mixtures always contained small amounts of unidentified red substances (according to the TLC data). We presumed that the unidentified compound formed in the condensation with *N*-(*p*-tolyl)-2,5-bis(*p*-tolylamino)-1,4-benzoquinone imine (**I**) is a product of its oxidative cyclization by the action of *N*-aryl-1,4-benzoquinone imines (redox potentials of the latter in acetic acid range from 0.553 to 0.736 V [3]). In the present work we made an attempt to confirm this assumption by studying oxidation of benzoquinone imine **I** with lead tetraacetate.

By oxidation of **I** with Pb(OAc)₄ in benzene at 55–60°C we obtained 8-methyl-2-(*p*-tolylamino)-3-(*p*-tolylimino)phenoxazine (**II**) in a moderate yield. According to the TLC data, compound **II** was identical to the by-product formed in the reaction of **I** with *N*-(*p*-tolyl)-1,4-benzoquinone imine [1, 2]. Thus, the oxidation of benzoquinone imine **I** with lead tetraacetate is accompanied by cyclization involving the *p*-tolylamino group located in position 2 rather than 5

of the quinoid ring, as in the oxidation of *N*-phenyl-2,5-diarylamino-1,4-benzoquinone imines with potassium hexacyanoferrate(II) in boiling DMF or on prolonged heating at 250°C on exposure to air [4]. In our case, the latter reaction should give 2-(*p*-tolylamino)-5-(*p*-tolyl)phenazin-3-one (**III**). The oxidation of **I** with Pb(OAc)₄ in acetic acid also afforded compound **II**; however, this product was not formed in the oxidation with lead dioxide in benzene or with sodium dichromate in acetic acid.

The structure of compound **II** was proved by comparison of its ¹H NMR spectrum with the spectrum of phenazinone **III** synthesized by the procedure described in [4]. The spectra of compounds **II** and **III** contain equal numbers of signals with similar multiplicities, but signals from protons in the quinoid ring of compound **II** (δ 6.18 and 6.50 ppm) appear in a weaker field than the corresponding signals of **III** (δ 5.29 and 5.72 ppm). The NH signals are located at δ 8.66 (**II**) and 8.52 ppm (**III**). These data, in combination with the data of elemental analysis and mass spectrum, unambiguously indicate that compound **II** has the structure of 8-methyl-2-(*p*-tolylamino)-3-(*p*-tolylimino)phenoxazine.

2,5-Bis(*p*-tolylamino)-4-(*p*-tolylimino)-2,5-cyclohexadienone (**I**) was synthesized as described in [2].



5-(*p*-Tolyl)-2-(*p*-tolylamino)phenazin-3-one (III) was prepared by the procedure reported in [4]. Yield 12%, mp >250°C (with decomposition; from benzene–ethyl acetate, 1:1 by volume). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 2.32 s (9H, CH₃), 5.29 s and 5.72 s (1H each, 1-H, 4-H), 7.08 s (1H, H_{arom}), 7.23 d (2H, H_{arom}, *J* = 8.40 Hz), 7.27 d (2H, H_{arom}, *J* = 7.2 Hz), 7.35 d (2H, H_{arom}, *J* = 8.40 Hz), 7.42 d (2H, H_{arom}, *J* = 8.40 Hz), 7.61 d (2H, H_{arom}, *J* = 8.40 Hz), 7.82 d (2H, H_{arom}, *J* = 7.2 Hz), 8.52 s (1H, NH).

8-Methyl-2-(*p*-tolylamino)-3-(*p*-tolylimino)phenoxazine (II). *a.* Lead tetraacetate, 2.22 g (0.005 mol), was added to a solution of 2.03 g (0.005 mol) of quinone imine **I** in 50 ml of benzene, and the mixture was stirred for 3 min at 55–60°C. One drop of ethylene glycol was added, the mixture was washed with 50 ml of water, and the benzene layer was separated, dried over sodium sulfate, and evaporated to a volume of 15 ml. The product was isolated by column chromatography on Kieselgel G-40 (Merck) using benzene as eluent. Yield 0.9 g (44%), mp >250°C (with decomposition, from benzene).

b. Lead tetraacetate, 2.22 g (0.005 mol), was added to a solution of 2.03 g (0.005 mol) of quinone imine **I** in 50 ml of acetic acid, and the mixture was stirred for 15–20 min at room temperature. One drop of ethylene glycol, 50 ml of benzene, and 200 ml of water were added, and the benzene layer was separated, washed with 50 ml of water, 50 ml of a 5% solution of sodium hydrogen carbonate, and 50 ml of water again, dried over sodium sulfate, and evaporated to a volume of 15 ml. The product was isolated by column chroma-

tography as described above in *a.* Yield 1 g (49%). Electron absorption spectrum (methanol), λ_{max}, nm (log ε): 207 (4.25), 269 (4.06), 458 (3.2). IR spectrum, ν, cm⁻¹: 3266 (NH). ¹H NMR spectrum, δ, ppm: 2.33 s (3H, CH₃), 2.35 s (6H, CH₃), 6.18 s and 6.50 s (1H each, 1-H, 4-H), 6.90 d (2H, H_{arom}, *J* = 8.10 Hz), 8.66 s (1H, NH). Found, %: C 79.94; H 5.67; N 10.39. *M*⁺ 405. C₂₇H₂₃N₃O. Calculated, %: C 80.00; H 5.58; N 10.44. *M* 405.

The IR spectrum was recorded in KBr on a Specord IR75 spectrometer. The ¹H NMR spectra were obtained on a Varian VXR-300 spectrometer (300 MHz) from solutions in DMSO-*d*₆ using tetramethylsilane as internal reference. The mass spectrum (electron impact, 70 eV) was obtained on a Varian MAT-312 instrument. The electron absorption spectrum was recorded on a Shimadzu UV-160 spectrophotometer. The purity of compounds **II** and **III** was checked by TLC on Kieselgel 60 F₂₅₄ plates (Merck) using benzene as eluent; spots were visualized under UV light.

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