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Unusual Addition of Hydrogen Chloride to N-Substituted Quinone Imines

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Addition of hydrogen chloride to quinones and N-substituted quinone imines follows 1,4- [1] or 6,3-addition pattern [2], leading to aromatization of the quinoid ring with introduction of chlorine into the aromatic ring. We found that 4-[2-(4-nitrobenzylidene)hydrazono]cyclohexa-2,5-dien-1-one (**I**) reacts with hydrogen chloride to give 4-[2-(α -chloro-4-nitrobenzylidene)hydrazino]phenol (**II**). This reaction is unusual, for no chlorine atom is introduced into the aromatic ring, but highly reactive imidoyl chloride **II** is obtained.

The structure of addition product **II** follows from its ¹H NMR spectrum and elemental composition. In the ¹H NMR spectrum of **I**, protons in the quinoid ring give rise to two AB systems due to restricted Z-E isomerization, whereas compound **II** displays signals from pseudo-AB systems in two para-substituted benzene rings. In addition, the spectrum of **II** lacks N=CH proton signal.

4-[2-(4-Nitrobenzylidene)hydrazono]cyclohexa-2,5-dien-1-one (I) was synthesized according to the procedure reported in [3], mp 139–141°C. ¹H NMR spectrum, δ , ppm: 8.56 s (1H, CH=N), 8.37–8.09 d.d (4H, C₆H₄, J = 8.9 Hz), 7.99–7.95 d.d (1H, 2-H, J = 10.2 Hz), 7.40–7.37 d.d (1H, 5-H, J = 9.5 Hz), 6.69–6.66 d.d (1H, 3-H, J = 9.5 Hz), 6.59–6.56 d.d (1H, 6-H, J = 10.2 Hz).

4-[2-(α -Chloro-4-nitrobenzylidene)hydrazino]-phenol (II). Concentrated hydrochloric acid, 5 ml, was added to a solution of 1.0 g (4 mmol) of compound **I** in 100 ml of glacial acetic acid, the mixture was stirred for 45 min, 100 ml of methylene chloride and 150 ml of water were added, the mixture was shaken for 10 min, and the organic phase was separated, washed with a 5% solution of sodium carbonate and water, and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure, and the brown precipitate was washed with several portions of hexane. Yield 0.81 g (70%), mp 159–162°C. ¹H NMR spectrum, δ , ppm: 10.12 s (1H, NH), 9.11 s (1H, OH), 8.28–8.04 d.d (4H, O₂NC₆H₄, J = 8.9 Hz), 7.24 d (2H, 2-H, 6-H, J = 8.7 Hz), 6.74 d (2H, 3-H, 5-H, J = 8.7 Hz). Found, %: C 53.38; H 4.76; Cl 12.06; N 14.35. C₁₃H₁₀ClN₃O₃. Calculated, %: C 53.42; H 4.79; Cl 12.12; N 14.38.

The ¹H NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz). The purity of compounds **I** and **II** was checked by TLC on Kieselgel 60 F₂₅₄ plates (Merck) using chloroform–acetone (9:1) as eluent.

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