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> SHORT COMMUNICATIONS

Unusual Reaction of 4-[2-(4-Nitrobenzylidene)hydrazinylidene]cyclohexa-2,5-dienone with Propan-1-amine

B. V. Murashevich, K. A. Shreiber, N. V. Toropin, and K. S. Burmistrov

Ukrainian State University of Chemical Technology, pr. Gagarina 8, Dnepropetrovsk, 49005 Ukraine e-mail: murashevich@yahoo.com

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We previously reported that, unlike other quinone imines, 4-(2-benzylidenehydrazinylidene)cyclohexa-2,5-dienones react with nucleophiles according to the 1,8-addition pattern. This reaction path was observed in their reactions with hydrogen halides [1] and secondary aliphatic [2] and primary aromatic amines [3].

We have found that 4-[2-(4-nitrobenzylidene)hydrazinylidene]cyclohexa-2,5-dienone (I) reacts with propan-1-amine to give 4-[5-ethyl-3-(4-nitrophenyl)-1H-1,2,4-triazol-1-yl]phenol (II). This reaction is unusual since the triazole ring is formed via oxidation of the α -methylene group of propylamine under very mild conditions. Obviously, the process involves intermediate formation of amidrazone A (1.8-addition product in the quinoid form) which was detected in the reaction mixture by TLC. However, all attempts to isolate it resulted in its oxidative cyclization to triazole II. The structure of II was proved by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

4-[2-(4-Nitrobenzylidene)hydrazinylidene]cyclohexa-2,5-dienone I was synthesized according to the procedure described in [4]; its melting point coincided with that given in [4] (mp $139-141^{\circ}C$).

4-[5-Ethyl-3-(4-nitrophenyl)-1H-1,2,4-triazol-1yllphenol (II). Propan-1-amine, 2 mL (33 mmol), was added to a solution of 2 g (7.9 mmol) of compound I in 200 mL of propan-2-ol, and the mixture was stirred for 45 min and left to stand for 3 days. The mixture was then treated with 100 mL of dichloroethane and 200 mL of water and vigorously shaken, and the organic phase was separated, washed with dilute acetic acid and several portions of water, and evaporated under reduced pressure to a small volume. The residue was evaporated at room temperature, and the precipitate was filtered off, washed several times with warm hexane, and dried. Yield 1.71 g (71%), mp 180-182°C. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.26 t (3H, CH₃), 2.78 q (2H, CH₂), 6.92 d and 7.39 d (2H each, $NO_2C_6H_4$, J = 8.6 Hz), 8.27 d and 8.33 d (2H each, HOC_6H_4 , J = 8.8 Hz), 10.00 s (1H, OH). ¹³C NMR spectrum (DMSO-*d*₆), δ_C, ppm: 11.51 (CH₃), 19.34 (CH₂); 115.6 (2C), 123.9 (2C), 128.46 (C) (HOC₆H₄);



126.5 (2C), 128.0 (2C), 136.7 (C) (NO₂C₆H₄); 147.3 (COH), 157.7 (C⁵), 157.9 (C³), 158.3 (CNO₂). Mass spectrum, m/z (I_{rel} , %): 310 [M]⁺ (10), 107 (100), 79 (20). Found, %: C 61.94; H 4.57; N 18.03. C₁₆H₁₄N₄O₃. Calculated, %: C 61.93; H 4.55; N 18.05.

The NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz for ¹H). The mass spectrum (electron impact, 70 eV) was obtained on an MKh-1321 mass spectrometer with direct sample admission into the ion source.

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