

SHORT
COMMUNICATIONS

Syntheses of Isonitroso- β -naphthoylacetone and Nitrosopyrazole Based Thereon

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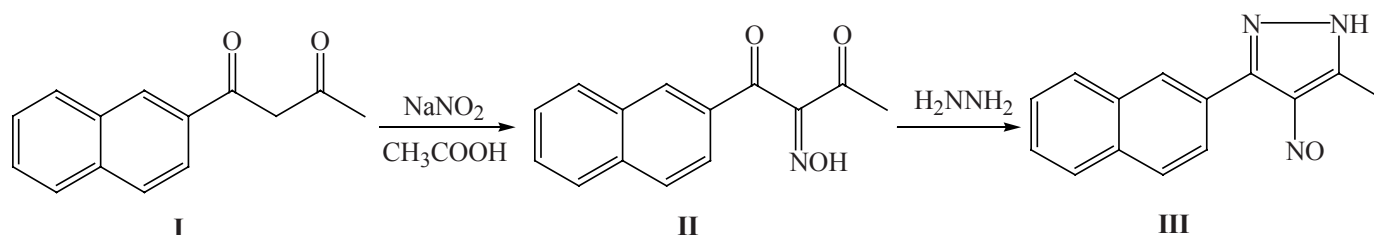
Lately an interest grew to new pyrazole derivatives. For instance, recently naphthyl-substituted pyrazoles were obtained by a condensation of naphthyl-substituted β -diketones with hydrazine [1]. However the attempt to introduce a nitroso group in these pyrazoles failed. The nitroso group is easily reduced to amino group thus opening a way to the synthesis of new aminopyrazoles possessing a biological activity [2]. Therefore we decided to introduce a nitroso group into the initial β -diketone in order to prepare nitroso-substituted naphthylpyrazole.

To this end we synthesized β -naphthoylacetone (**I**) by condensation of β -acetone naphthone with ethyl acetate effected by sodium in anhydrous ethyl ether [3] and then we carried out its nitrosation to obtain for the first time 1-(2-naphthyl)butane-1,2,3-trione 2-oxime (**II**) that by reaction with hydrazine yielded previously unknown 5-methyl-4-nitroso-3-(2-naphthyl)-1*H*-pyrazole (**III**).

1-(2-Naphthyl)butane-1,2,3-trione 2-oxime (II). To a solution of 4.2 g (20.2 mmol) of β -naphthoylacetone (**I**) in 20.2 ml of glacial acetic acid was added within 15 min while cooling and stirring 1.52 g (22 mmol) of dry sodium nitrite maintaining the temperature of the reaction mixture below 15°C. After completion of addition

of the sodium nitrite the reaction mixture was stirred for 3 h at 25°C. The mixture turned thick and became light yellow. Then it was poured in 200 ml of ice water. The separated precipitate was filtered off and recrystallized from water. Yield 2.8 g (57%), colorless needle crystals, mp 173–174°C. IR spectrum, ν , cm⁻¹: 1645 (CH₃C=O), 1679 (C=O naphthyl), 3180 (OH), 998 (NO). ¹H NMR spectrum, δ , ppm: 2.54 s (CH₃), 7.6–8.4 m (naphthyl). Found, %: C 69.9; H 4.6; N 5.8. C₁₄H₁₁NO₃. Calculated, %: C 69.7; H 4.6; N 5.81.

5-Methyl-4-nitroso-3-(2-naphthyl)-1*H*-pyrazole (III). To a solution of 0.34 g (3.2 mmol) of Na₂CO₃ in 2.28 ml of water was added at stirring 0.37 g (2.9 mmol) of hydrazine sulfate. Then within 15 min at 20°C was added 0.7 g (2.9 mmol) of compound **II**. After heating at 80°C for 2.5 h the mixture became bright green. The separated precipitate was filtered off and recrystallized from ethanol. Yield 0.57 g (81%), green crystals, mp 170°C. UV spectrum, λ_{\max} , nm (ϵ): 710 (49.8). IR spectrum, ν , cm⁻¹: 1563 (N=O), 1515 (NH), 1263–1291 (CN). ¹H NMR spectrum, δ , ppm: 2.29 s (CH₃), 7.5–8.8 m (naphthyl). Found, %: C 70.12; H 4.62; N 16.86. C₁₄H₁₁N₃O. Calculated, %: C 70.87; H 4.67; N 17.81.



UV spectra were recorded on a spectrophotometer SF-26 in quartz cells 1 cm thick at concentration 1×10^{-2} mol/l in DMF. IR spectra were registered from KBr pellets of a Fourier spectrometer Infracal ST-801, ^1H NMR spectra from solutions in $\text{DMSO-}d_6$ on a Bruker Avance-200 instrument at the Krasnoyarsk Regional Center of joint instruments utilization, Siberian Division, Russian Academy of Sciences.

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