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THE SYNTHESIS OF 3-NITROSO-4-R-FURAZANES

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The oxidation of 3-amino-4-R-furazanes (AF) by peroxide reagents may give the corresponding azo, azoxy, and nitro derivatives. There is no information in the literature on the possibility of the preparation and isolation of nitrosofurazanes (NSF) although these compounds have been proposed as intermediates [1, 2]. This circumstance is probably a result of the low reactivity of AF due to the strong electron-withdrawing effect of the furazane ring, which requires the use of strong oxidizing mixtures. The isolation of NSF is difficult due to the tendency of these compounds to undergo oxidation under these conditions to 3-nitro-4-R-furazanes (NF).

We have found a range of conditions for the selective oxidation of AF to NSF. The oxidation could be stopped precisely at the stage of the nitroso derivative by proper selection of the temperature, reaction time, and medium acidity. Small amounts of NF and azoxyfurazane were formed as impurities in NSF.



Protonation of the NSF formed, which hinders further oxidation, probably occurs in this range of conditions. A nitroso derivative could not be obtained from 3-amino-4-nitrofurazane.

A sample of 2 g (0.02 mole) 3-amino-4-methylfurazane was added with stirring to a solution of 114 g (0.5 mole) $(NH_4)_2S_2O_8$ in a mixture of 89 ml (1.6 moles) concentrated sulfuric acid and 150 ml water at from -15 to -5°C and maintained for 15 h. The reaction mixture was diluted with 150 ml water and extracted with four 50-ml portions of CH₂Cl₂. The combined extracts were washed with water and dried over anhydrous MgSO₄. The yield was 85% as indicated by NMR spectroscopy. The product was isolated by standard methods, bp 25-28°C (2 mm Hg). Mass spectrum, m/z: 113 (M⁺⁺), 83 (M⁺⁺ – NO), 53 (M⁺⁺ – 2NO). PMR spectrum at 80 MHz in CDCl₃ (δ , ppm): 2.30. UV spectrum in CCl₄ (λ , nm): 755.

The other NSF were obtained by analogy. All the NSF synthesized have very high volatility.

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