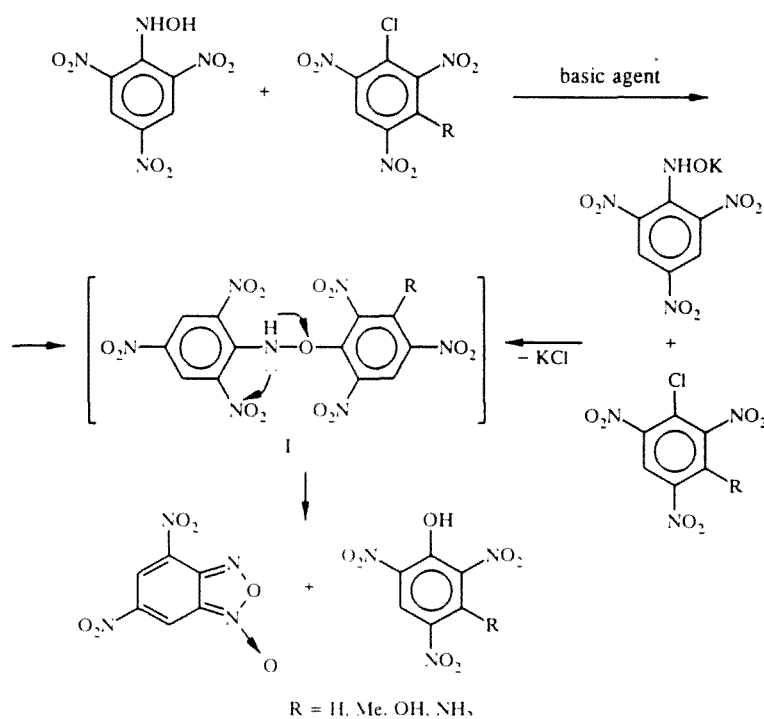


MECHANISM OF FORMATION OF THE FUROXAN RING IN THE NIETZKI-DIETSCHY REACTION

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Up to the present time, the discovery by Nietzki and Dietschy [1] of the formation of a furoxan ring in the reaction of sodium acetate with an equimolar mixture of picryl chloride and hydroxylamine hydrochloride has not found a theoretical explanation [2].

We have found that the reaction of picryl hydroxylamine with picryl chloride or its derivatives in the presence of a base (sodium acetate or bicarbonate, potassium or sodium hydroxide, triethanolamine) gives 4,6-dinitrobenzofuroxan and the corresponding picric acid derivative.



Similarly, the reaction of the potassium salt of picryl hydroxylamine with picryl chloride or its derivatives also gives 4,6-dinitrobenzofuroxan and the corresponding picric acids. Hence, the present reactions confirm picryl hydroxylamine as the intermediate in the Nietzki-Dietschy reaction.

Evidently, the preparation of the furoxan ring occurs via the formation of an unstable ether of hydroxylamine I, simultaneous decomposition of which leads finally to 4,6-dinitrobenzofuroxan and picric acid or its derivative.

4,6-Dinitrobenzofuroxan is obtained by reaction of picryl chloride (4.95 g, 0.02 mole) with the potassium salt of picryl hydroxylamine (6.2 g, 0.022 mole) in methanol (30 ml) at 45-50°C for 1.5 h. Yield 4.4 g (94%). Mp 174°C (from methanol). Using the 3-R-picryl chloride derivatives, the yields of 4,6-dinitrobenzofuroxans are 91% (R = CH₃), 54% (R = OH), or 51% (R = NH₂).

REFERENCES

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2. L. I. Khmel'nitskii, S. S. Novikov, and T. I. Godovikova, *The Chemistry of Furoxans. Structure and Synthesis* [in Russian], Nauka, Moscow (1976), p. 301.