

Reaktionen von Isochinolinium-Salzen mit Hydroxylamin-Derivaten,

3. Mitteilung. Mechanismus der Aminoxid-Bildung

Reactions of Isoquinolinium Salts with Hydroxylamine Derivatives,
3rd Communication. Mechanism of Amine Oxide Generation

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Amidine, Nitron, N-Hydroxyaminal, E/Z-Enamine, *o*-(Enamino)-benzaldehyde-oxime

2-Methylpapaverinium iodide (**1**) reacted with hydroxylamine to papaverine-N-oxide (**2**), but without a detectable intermediate and only in moderate yield, caused by the steric hindrance of the 1-substituent. The ring opened product of 2-dinitrophenylisoquinolinium salt with hydroxylamine, the enamine-oxime **3b** gave rise to a 3-substituted cyclic nitron (**6**), when heated with triethylamine. This alkali-stable compound was transformed with acid quantitatively to isoquinoline-N-oxide (**4**). The enamionitrile **9c**, treated with triethylamine showed cyclization to the iminoisoquinoline **10**, which by loss of nitrous acid produced the tetracyclic azaindole **11**. The 2-methoxyisoquinolinium salt **16** was cleaved with O-methylhydroxylamine to the resistant di(O-methyloximes) (**20a/b**), unable to form the amine oxide **4**. From these and former results, a mechanism for the ring opening of cycliminium salts and the recyclization to amine oxides was proposed.