Hydroxylamin-Funktion als Nachbargruppe bei Dehydrierungen
Hydroxylamine Function as Neighboring Group with Dehydrogenations

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The β-amino-hydroxylamines 5a–d are prepared of the α-amino-oximes 1a–d with borane-dimethylsulfide. With mercury-EDTA, 5a–d react to (E/Z)-oxime-lactams 3a–d and benzaldoxime 7. Additionally 5b,c give the bicyclic amidine-N-oxides 8b,c, which slowly hydrolyze to the hydroxylamine-lactams 9b,c. These are easily oxidized to (E/Z)-3b,c. Postulated as intermediates in the mercury-assisted reduction of 5, the cyclic hydroxylamines 10a–d are available from the nitrones 4a–d with LiAlH4. From 10a–d with mercury-EDTA the same products are obtained as from 5a–d but without 7. Only the pyrrolidine 10a forms besides (E/Z)-3a the nitrone 4a. Thin-layer chromatography shows that the pure isomers of 3a–d in solution isomerize, contrary to the amine-oximes 1a–d. The configuration of the oxime-lactams depends on the manner of preparation. With mercury-EDTA, 1b,c yield 3b,c with retention of the configuration, while the oximation of phenacyl-lactams 13b,c give rise to (E/Z)-mixtures of 3b,c. The condensed imidazoles 12 result from the nitrones 4a–d and the dihydrooxadiazines 2a,d on treatment with hydrogen chloride.

Key words: Mercury-EDTA Dehydrogenation, Nitrone, 1,2,5-Oxadiazine, Lactam