Hydroxylamin-Funktion als Nachbargruppe bei Dehydrierungen

Hydroxylamine Function as Neighboring Group with Dehydrogenations

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Z. Naturforsch. **60b,** 688 – 700 (2005); eingegangen am 7. Februar 2005

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 $LiAlH_4$. 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