

Bromocyclization of Unsaturated Oximes.

Synthesis of Five-Membered Cyclic Nitrones (Pyrroline *N*-Oxides)* [1]

Mahendra Gulla, Lars Bierer, Stefan Schmidt, Leo Redcliffe, and Volker Jäger

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany

Reprint requests to Prof. Dr. V. Jäger. Fax: +49 (0) 711-6854321.

E-mail: jager.ioc@po.uni-stuttgart.de

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Dedicated to Professor Dieter Enders on the occasion of his 60th birthday

The cyclization of a ribose-derived pentenose oxime with various halogen electrophiles showed bromine to be the most effective reagent, leading to 80% of L-*lyxo*/D-*ribo*-pyrroline *N*-oxides in an 84:16 diastereomeric ratio. In order to explore the scope of this facile process, several other γ,δ -unsaturated oximes were submitted to this reaction. Depending on the substitution pattern, 23 – 87%, yields of pyrroline *N*-oxides were registered. With α -allyl- β -ketoester oximes the alkoxycarbonyl group proved a similar (ethoxy) or even better (*t*-butoxy) trapping nucleophile, leading preferentially to the corresponding bromolactone oxime. – With 2,2-dimethyl-3-butene aldoxime, the corresponding 3-bromopyrroline *N*-oxide was formed, due to a formal, unusual *N-endo* cyclization to the chain terminus. This was exploited for a new access to six-membered nitrones from a γ,δ -pentene aldoxime, with addition of Br/OH to the C=C of the 4-pentenal first, and oximation/cyclization following then.

Key words: Unsaturated Oximes, Bromocyclization, Cyclic Nitrones, *endo/exo*-Cyclization, Bromolactonization