

Regiochemistry and mechanism of oxidation of N-benzyl-N-alkylhydroxylamines to nitrones.

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ABSTRACT

The oxidn. of various N-(o-, m-, p-substituted benzyl)-N-alkylhydroxylamines and their dideuteriobenzyl (PhCD₂) counterparts was carried out using mercury(II) oxide and p-benzoquinone (p-BQ) as oxidants. An overwhelming preference for the formation of conjugated nitrones is obsd. in the oxidn. of N-benzyl-N-isopropylhydroxylamines. Considerable intra- and intermol. kinetic isotope effects and neg. ρ values in the Hammett plots point towards a mechanistic pathway that involves electron transfer from nitrogen to the oxidant followed by hydrogen abstraction. The conformation of unstable (E)-nitrones, which readily isomerize to the more stable (Z)-nitrones, is deduced from ¹H NMR data. The E \rightarrow Z isomerization was found to be a bimol. process.