**Stereospecific Radical Bromination of β-Aryl Alcohols with Thiourea Additives**

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Halogen-containing organic molecules have received significant attention as important intermediates in the chemical and pharmaceutical industries. Many halogenated natural products exhibit unique bioactivity and show promise as potential drug candidates. Consequently, stereocontrolled halogenation of drug leads has emerged as a valuable strategy for generating natural products with enhanced bioactivity and target specificity.[1] This has created strong interest in developing new protocols for stereospecific and stereoselective halogenation reactions under mild conditions.

In our previous work,[2] we demonstrated a method for directly converting a broad range of alcohols to alkyl bromides and chlorides. This transformation uses substoichiometric amounts of thioureas and *N*-halosuccinimides (NXS, where X = Br or Cl) as halogen sources in a single step. Notably, when conducting bromination of chiral secondary alcohols in apolar solvents, we observed unexpected stereochemical preservation rather than racemization. This observation prompted us to investigate the stereochemical aspects of this important halogenation reaction in detail. In order to facilitate the characterization of the products we decided to work with compounds containing an additional asymmetric center to obtain diastereomers. To our great surprise, bromination of (±)-*threo*- or (±)-*erythro*-3-phenyl-2-butanols revealed *exclusively* a single diastereomeric brominated product with retention of configuration. The scope of these reactions was expanded on several -aryl alcohols. During these studies an unexpected stereospecific 1,2-migration of the phenyl group was discovered.[3]The proposed mechanism of the extraordinary 1,2-phenyl migration involves the formation of a spiro[2,5]octadienyl radical, which is then attacked by a bromide radical at any of the two cyclopropyl positions anti to the phenyl position, leading to products that retain the stereoisomeric configuration of the starting material.



**References.**

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