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Enantioselective Halocyclization of Polyprenoids Induced by Nucleophilic Phosphoramidites
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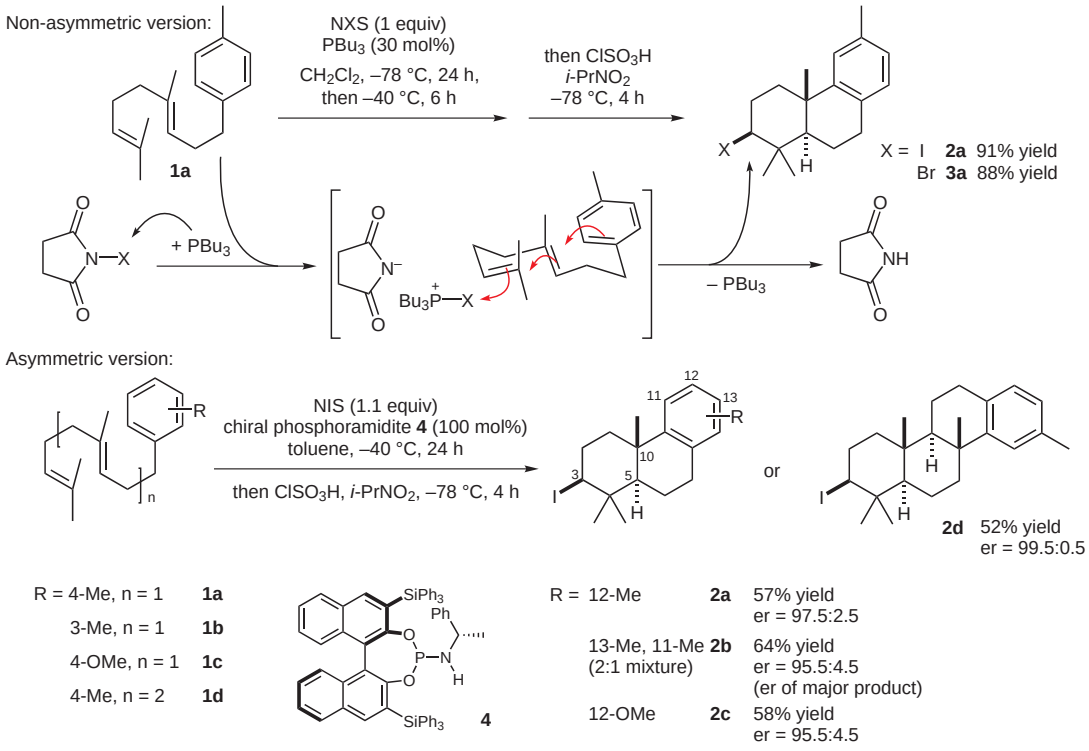
Halocyclization by a 'Chiral Iodine Atom'



Significance: A method for the enantioselective halocyclization of homo(polyprenyl)arenes (**1a**–**d**) induced by chiral phosphoramidite **4** as nucleophilic promoter has been developed. As shown by the authors, various simple P-nucleophiles can also be used catalytically (30 mol%) in a non-asymmetric variant of the described transformation. However, enantiomeric excess is only achieved by using the chiral phosphoramidite in stoichiometric amount. The use of NBS instead of NIS results in both decreased yield and decreased enantioselectivity. Furthermore, the strong solvent effect (no chiral induction in CH_2Cl_2) is discussed and a reaction mechanism to rationalize the observed stereochemical outcome is proposed.

Comment: Since the biosynthesis of halogenated polycyclic terpenoids appears to proceed via similar enzyme-catalyzed halocyclization pathways, the described method represents a close mimic of nature. The relatively simple chiral phosphoramidite **4** does not only activate NIS, but also creates a chiral environment for the active iodine species. However, by now the first enantioselective halocyclization is still limited by the use of one molar equivalent of the chiral P-nucleophile and the restriction of the method to NIS. The authors evade the latter problem by demonstrating that trans-halogenation of **2a** to the bromine and chlorine derivatives can be carried out stereospecifically.

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Organo- and Biocatalysis

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