



Digest Paper

Asymmetric isomerization of allylic alcohols

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ABSTRACT

In this digest, we report the recent advances in asymmetric isomerization of allylic alcohols. We present the different aspects of this asymmetric transformation that include the diastereo-, and enantioselective isomerizations and the kinetic resolution. In addition, we described also our contribution involving fluorinated enantiopure allylic alcohol with achiral catalyst by the enantiospecific approach. Finally, the description of tandem reactions involving such an asymmetric isomerization of allylic alcohols is presented as a perspective.

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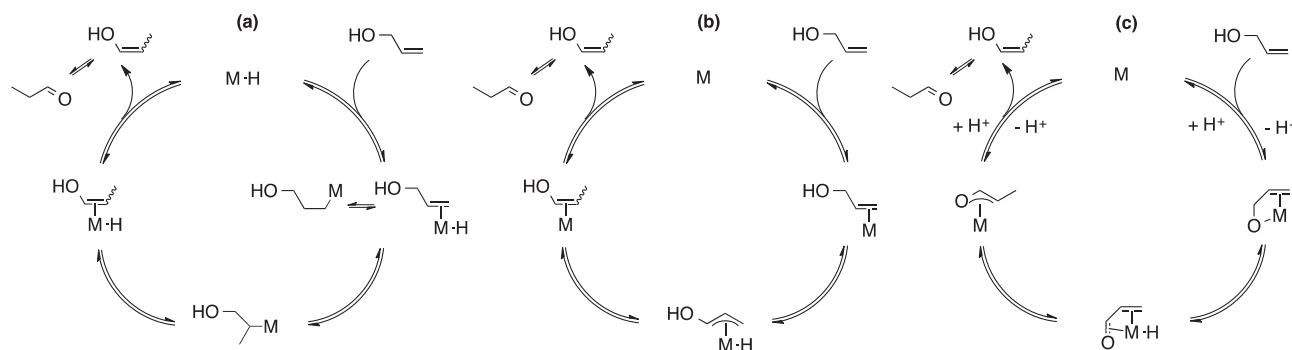
Introduction

The development of new chemical reactions with a low environmental impact is a major concern for the chemists. Efficiency of a process can be defined in terms of complexity, selectivity, and atom economy. Catalysis meets all these criteria and is a key

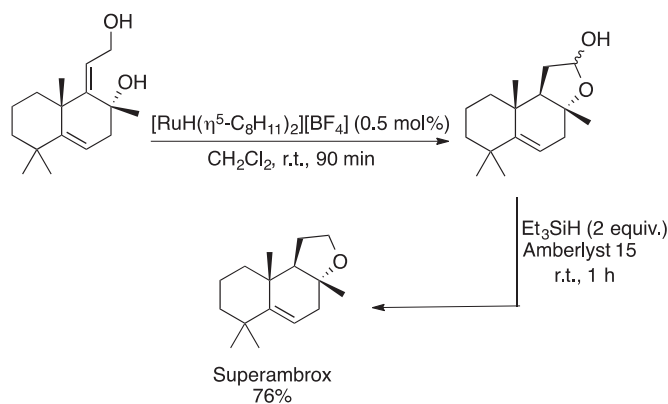
technology for green chemistry.¹ The isomerization of allylic alcohols into the corresponding saturated carbonyl compounds is a catalytic process that is 100% atoms efficient.² In this method, a transition metal assists the migration of the carbon–carbon double bond into an enolate or enol, which tautomerizes to the carbonyl compound. It is a conceptually attractive approach, which compares favorably with the more conventional sequential two-step oxidation and reduction reactions or vice versa. Many transition metals have been employed in the isomerization of allylic alcohols, but ruthenium, rhodium, and iridium complexes dominate the field of the asymmetric versions.²

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Scheme 1. Three possible mechanisms for the isomerization of allylic alcohols.

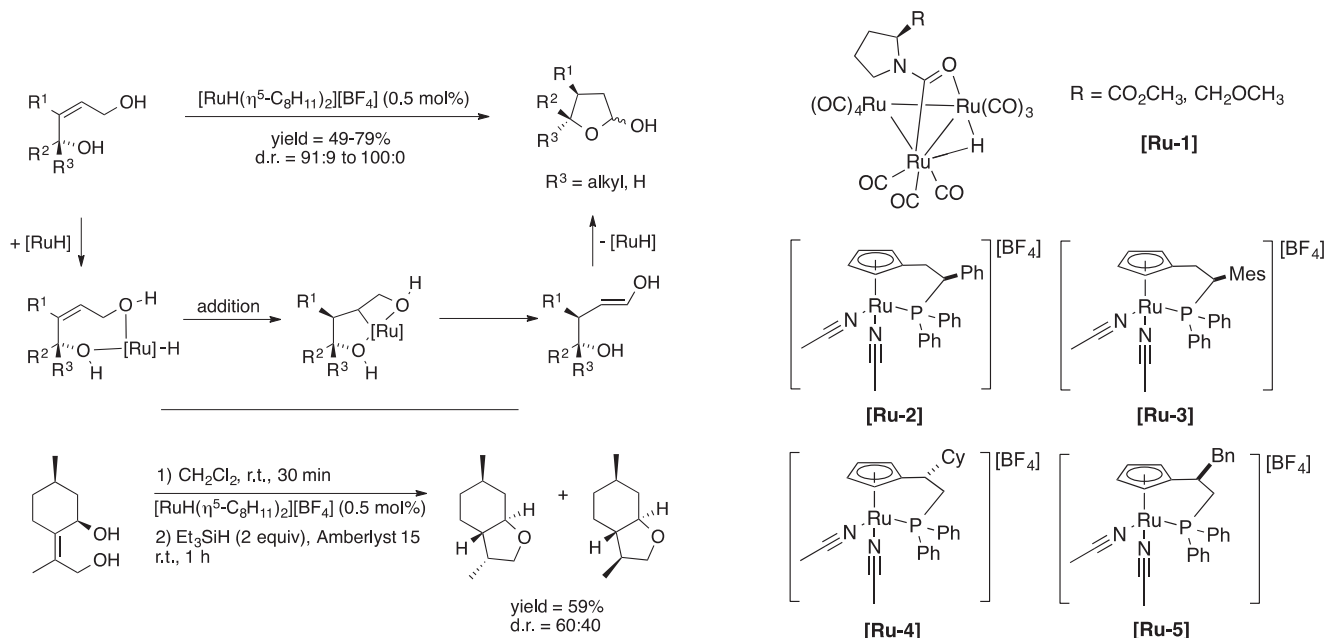


Scheme 2. Diastereoselective synthesis of 'Superambrox'.

While the related asymmetric isomerization of allylic amines has already found application in industry, the asymmetric isomerization of allylic alcohols is still a challenge in organic chemistry even if great progresses have been made in the last decade. In this digest, every aspects of asymmetric isomerization of allylic alcohols will be presented, including our own efforts devoted to the synthesis of chiral fluorinated compounds, as well as tandem asymmetric reactions.

Diastereoselective isomerization

In the course of synthesizing 'Superambrox', Fehr and Farris did not observed any hydrogenation of the highly substituted C=C double bond in the presence of Crabtree or Chaudret catalyst, but



Scheme 3. Synthesis of furan derivatives and proposed mechanism.

Essentially three different mechanisms have been proposed for this reaction, which strongly depend upon the nature of the catalyst, the reaction conditions and involve either a metal hydride addition–elimination mechanism (Scheme 1a), a π -allyl metal hydride mechanism (Scheme 1b), or a mechanism involving a metal alkoxide (Scheme 1c).¹ The mechanism (a) occurs usually in acidic medium, (b) in neutral conditions with low valent metal complexes, whereas mechanism (c) occurs in basic medium.

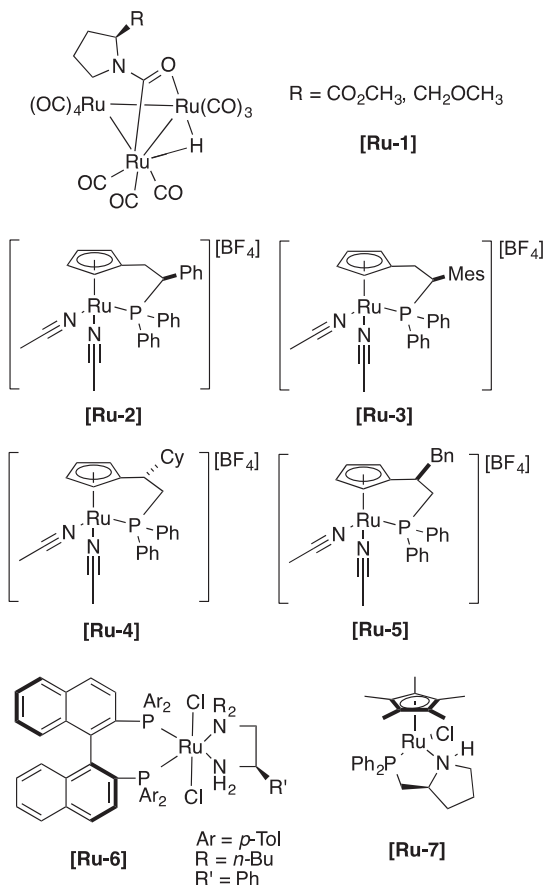


Figure 1. Chiral ruthenium complexes used in enantioselective isomerization of allylic alcohols.

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