

Review

Racemization catalysts for the dynamic kinetic resolution of alcohols and amines

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Abstract

Metal–enzyme bicalyases for the dynamic kinetic resolution (DKR) of alcohols and amines are summarized emphasizing the features of racemization catalysis. A metal complex catalyzes the racemization of alcohols and amines, and an enzyme catalyzes asymmetric acylation in the presence of acyl donor in organic solvent to produce the corresponding optically active acetates and amides, respectively. A few related reactions involving metal-catalyzed racemization, such as the transformations of ketones, enol acetates, ketoximes, and allylic acetates, are also described. The majority of racemization catalysts suitable for the DKR of alcohols are ruthenium complexes, while there are rhodium, palladium, aluminum, and vanadium catalysts effective for limited substrates. Some ruthenium catalysts are active even at room temperature and enable the use of thermally labile enzymes to give (*R*)-ester or (*S*)-esters from racemic alcohols. The DKR of amine is less developed than that of alcohols. Palladium on charcoal is the first example for the racemization catalyst in amine DKR. Improved activities are observed in the amine DKR using palladium on

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basic salts such as CaCO_3 and BaCO_3 . Palladium nanoparticles dispersed in aluminum oxyhydroxide are effective for the DKR of aliphatic amines as well as for that of benzylic ones. The Shvo's complex is the sole example of homogeneous catalyst in the DKR of amines.

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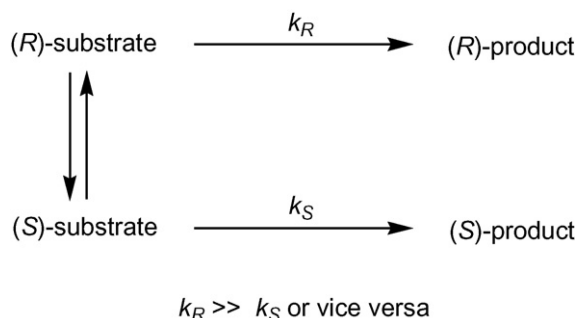
Keywords: Racemization catalyst; Enzyme; Dynamic kinetic resolution; Alcohol; Amine; Allyl acetate

1. Introduction

Though kinetic resolution (KR) is a useful method for the preparation of optically active compounds, it has a limitation in that the yield of one isomer cannot exceed 50%. In conventional methods to improve the yield, the undesired isomer should be isolated from the reaction mixture and recycled for the kinetic resolution. The dynamic kinetic resolution (DKR) [1] is a promising route to overcome the limitation of KR for the synthesis of optically pure compounds, especially alcohols and amines, from racemic mixtures without separating the undesired enantiomer after the reaction. For the successful and efficient DKR, continuous racemization of the less reactive enantiomer is required during the KR process (Scheme 1). The racemization can occur through various pathways [2], however, it should be possible for a wide range of substrates, compatible with resolving process, and not cause side reactions for successful DKR. These requirements have stimulated the development of transition metal catalysts active for the racemization of alcohols and amines [3].

The DKR of alcohols and amines by metal-catalyzed racemization combined with enzymatic kinetic resolution has attracted increasing interest [4], because the optically pure alcohols and amines are important chiral building blocks in fine chemical industries such as pharmaceutical, agrochemical, cosmetics, or food additive industry. Because the enzyme and the metal complex are in one vessel, the metal catalyst should be active under the conditions required for the enzymatic reactions.

For the last 10 years, significant advances have been made for the DKR by metal–enzyme bicatalysis. In this review, the transition metal complexes used as racemization catalysts for the DKR of alcohols, allyl acetates, and amines are summarized.



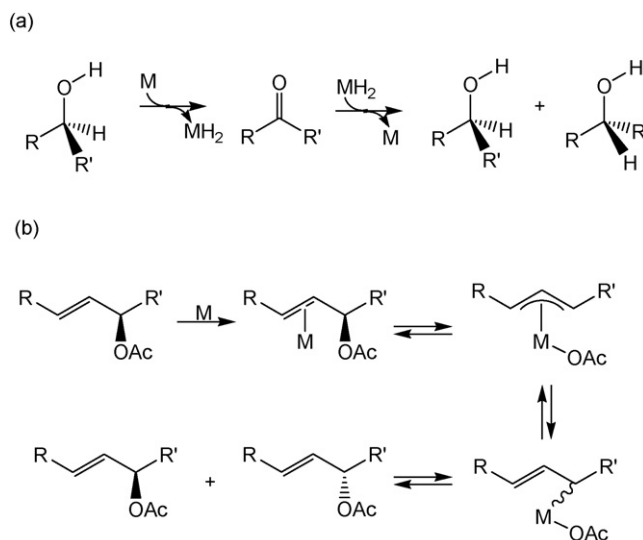
Scheme 1. Dynamic kinetic resolution.

2. Racemization catalysts for the DKR of alcohols and allyl acetates

Reversible hydrogen transfer reactions are typical pathways for alcohol racemization by transition metal catalysts [5] (Scheme 2). For allyl esters, rearrangement reactions are suggested for the racemization through reversible transformation between η^1 - and η^3 -allyl palladium complexes [6]. The allylic alcohol racemization catalyzed by $\text{VO}(\text{OR})_3$ occurs through the formation of allyl vanadate intermediates [7]. In hydrogen transfer reactions, the α -hydrogen of secondary alcohol is transferred to the metal center of the racemization catalyst to give the corresponding ketone and metal hydride complex. Then, ketones are hydrogenated into a mixture of racemic alcohols by the metal hydride complex. In the rearrangement reactions, chiral allyl esters are coordinated to metal center to form η^2 -ene complexes, which are transformed to η^3 -allyl complexes. The η^3 -allyl complexes are in equilibrium with the η^1 -allyl complexes, from which the racemic mixture of allyl esters is given through reductive elimination.

2.1. Rhodium catalysts

In the first alcohol DKR by metal–enzyme bicatalysis, various rhodium, iridium, ruthenium, and aluminum complexes were tested [8]. Among the racemization catalysts, only $\text{Rh}_2(\text{OAc})_4$ and $[\text{Rh}(\text{cod})\text{Cl}]_2$ showed reasonable activity in the



Scheme 2. Racemizations of alcohol and allyl acetates: (a) hydrogen transfer reaction and (b) π -allyl complex formation.

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