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Digest paper

Recent advances on nonenzymatic catalytic kinetic resolution of diols

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ABSTRACT

As one of the most efficient and straight-forward strategies for obtaining optically pure compounds, catalytic kinetic resolution has been widely used in laboratory and industry. Although nonenzymatic catalytic kinetic resolution of secondary alcohol has been well developed, it still remains a formidable challenge for kinetic resolution of diols which play a significant role in natural products synthesis. The purpose of this digest is to present the recent progress on nonenzymatic catalytic kinetic resolution of representative diols.

Contents

Introduction

Among a large number of strategies for preparation of enantiopure compounds, kinetic resolution (KR) represents one of the most efficient and practical approaches. The first KR phenomenon was observed by Pasteur[1] and it has been successfully used in many cases. Since Sharpless and coworkers reported a highly efficient KR of racemic allylic alcohols catalyzed by their titanium alkoxide tartrate epoxidation catalyst,[2] efforts on development of catalytic nonenzymatic KR has been made.[3] Special KRs including dynamic kinetic resolution (DKR)[4] and divergent reactions on racemic mixtures (divergent RRM)[5] have been developed later.

As we all know, diols frameworks are widely found in many natural products and biologically active molecules.[6] A large number of nonenzymatic KRs of secondary alcohols has been well established by synthetic chemists through different processes.[7] Due to the difficulty in manipulating the site-selectivity of two hydroxyl groups and recognition of chiral center, nonenzymatic KRs of unprotected diols are still limited. To the best of our knowledge, KR of four kinds of diols including 1,2-diols, 1,3-diols, 1,4-diols and 1,5-diols has been reported. And examples of KR of diols are included in following concepts, for C_2-symmetric diols: (1) KR via mono-functionalization of one hydroxyl group affording product $\mathbf{B_1}$ and recovered diol $\mathbf{A_1}$; (2) KR via difunctionalization of two hydroxyl groups affording product $\mathbf{D_1}$ and recovered diol $\mathbf{A_1}$; for non-C_2-symmetric diols: (1) KR via mono-functionalization of less hindered hydroxyl group affording product $\mathbf{B_2}$ and recovered

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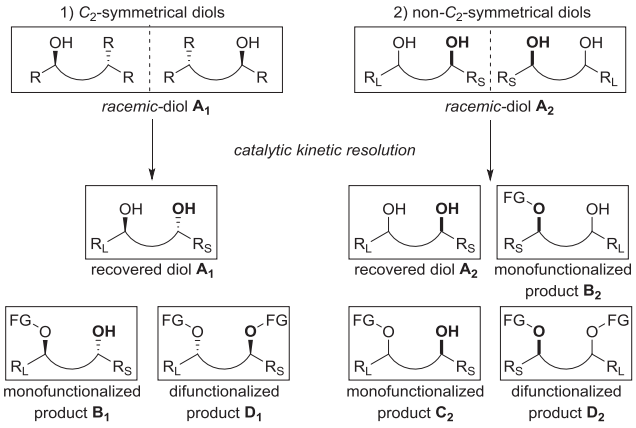


Scheme 1. Overview of kinetic resolution of diols via functionalization of hydroxyl groups.

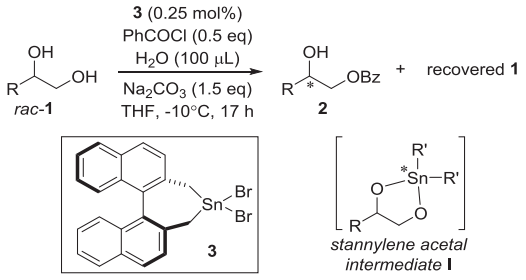
diol $\mathbf{A_2}$; (2) KR via difunctionalization of two hydroxyl groups affording product $\mathbf{D_2}$ and recovered diol $\mathbf{A_2}$; (3) regio-divergent resolution of the racemic mixture (RRRM) via functionalization of each enantioisomers on different sites affording two regioisomers $\mathbf{B_2}$ and $\mathbf{C_2}$ (Scheme 1). It should be noted that transformation of hydroxyl group to other functional group such as ketone and ether is also thought to be functionalization procedure here. In this review, recent representative examples on KR of diols including 1,2-diols, 1,3-diols, 1,4-diols and 1,5-diols are presented.

Kinetic resolution of 1, 2-diols

Kinetic resolution of terminal 1, 2-diols

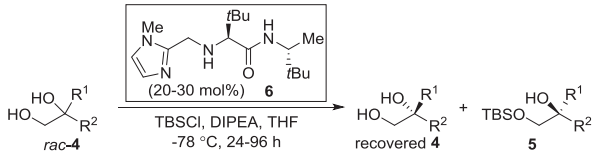
Terminal 1,2-diols are one of the most valuable building blocks in synthetic chemistry. Obtaining enantiopure terminal 1,2-diols are mostly relying on the method of hydrolytic kinetic resolution of epoxides[8] and dihydroxylation of terminal olefins.[9] KR of terminal 1,2-diols through selective protection has been reported recently. Because of the primary alcohol usually reacts faster than adjacent secondary or tertiary carbinol with electrophile in KR process, the long distance between reaction site and chiral center leads to the poor stereoselectivity. Therefore, it remains a challenging task to realize KR of terminal 1,2-diols in high enantioselectivity and few examples have been reported in literature.

Table 1
Organotin catalyzed KR of terminal 1,2-diols.



Entry	R	*ee* of **2** (%)	Yield of **2** (%)	*s*
1	C_6H_5	86	38	22.4
2	2-Naphth	64	25	5.6
3	1-Naphth	72	41	10.0
4	$CH_3(CH_2)_9$	59	35	5.2
5	C_2H_5	44	35	3.2

Table 2
Amino acid based chiral imidazole catalyzed KR of terminal 1,2-diols.



Entry	R^1, R^2	**4** yield (%), *ee* (%)	**5** yield (%), *ee* (%)	*s*
1	H, CH_2OtBu	38, 74	46, 57	8
2	H, $CH_2(OEt)_2$	25, 84	55, 68	14
3	H, *t*Bu	42, >98	44, 76	>50
4	Me, *n*pent	42, 94	50, 58	12
5	Me, *i*Pr	44, >98	52, 84	>50
6	Me, *t*Bu	45, >98	49, 91	>50

Earlier nonenzymatic catalytic KR of terminal 1,2-diols was reported by Matsumura and coworkers in 1999,[10] 1,2-diol **1** was treated with benzoyl chloride in the presence of chiral organotin catalyst which was first synthesized by P. Curran et al.,[11] affording primary alcohol benzoylated ester product **2** with high regioselectivity and moderate enantioselectivity (for most substrates with *s* factors of below 10) (Table 1). The reaction was supposed to react via a stannylene acetal intermediate **I**, followed by acylation process to afford benzoate ester **2**. Since the second step could easily take place even without base, the first step, forming of **I** by mixing diol substrate **1** and catalyst **3** in the presence of sodium carbonate was postulated as the enantioselectivity determination step. It should be pointed out that a small amount of water and inorganic base were essential to the stereocontrol. To explain this phenomenon, a hypothesis was proposed that the discriminating of catalyst **3** to diol **2** took place on a thin aqueous phase formed on the surface of sodium carbonate.

In 2007, Snapper and coworkers developed organocatalytic KR of terminal 1,2-diols through silylation of primary alcohols,[12] In this case, amino acid based imidazole catalyst **6** was proved to be the best catalyst and TBSCl as silylation reagent. Silyl ether products and recovered diols were both obtained in high yields and enantioselectivities (*s* factors up to >50) in the case of diols bearing sterically hindered substituents (Table 2, entry 3, 5, 6), though moderate *s* factor was afforded when the substituted group was smaller.

Later, Tan and coworkers developed a remarkable regiodivergent resolution of terminal 1,2-diols using chiral imidazole catalyst previously used for the desymmetrization of 1,2-diols.[13] Different with traditional kinetic resolution, more than one equivalent electrophile was used in this process, affording regioisomeric products in high enantioselectivity without recovering starting materials. As shown in Table 3 (conditions A), mixed racemic diol **7** with 1.2 to 1.4 equivalent triethylsily chloride (TESCl) under 0 °C in *t*-AmOH in the presence of catalyst **10**, giving product **9** in high enantioselectivity and product **8** in a bit lower enantioselectivity respectively (Table 3). Reversible covalent bonding between catalyst and substrate was responsible for good regioselectivity of this reaction, as well as the enantioselectivity (intermediate **II** and **III**). This protocol of regiodivergent reactions on racemic mixtures (RRRM) provides an efficient and straightforward way to site-selective protection of vicinal functional groups, which is important in natural product synthesis.

As a follow-up to their RRRM of 1,2-diols and in order to get high *ee* of product **8**, the amount of TESCl could be reduced to 0.5–0.7 equivalent.[14] Good enantioselectivities were achieved for most substrates and even methyl substituted silyl ether could be