Zinc-Mediated Hydroxyallylation of Aldehydes with Cyclopropanols: Direct Access to Vicinal *anti-sec,tert*-Diols via Enolized Homoenolate

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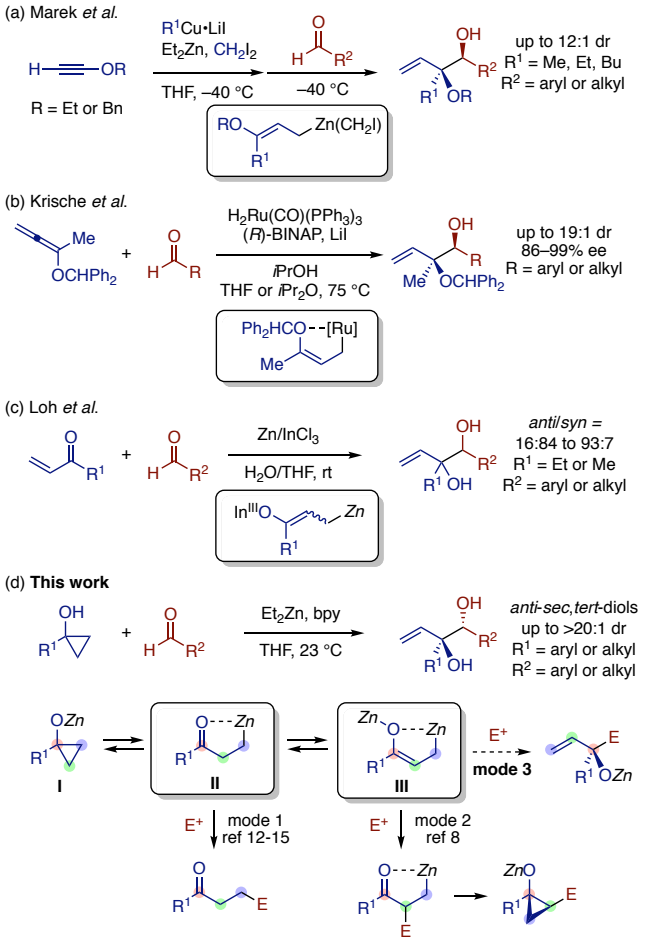
ABSTRACT: Direct and diastereoselective synthesis of vicinal *anti-sec,tert*-diols has been achieved by zinc-mediated α-hydroxyallylation of aldehydes with cyclopropanols. The reaction features the action of zinc enolized homoenolate, formed via ring opening of zinc cyclopropoxide and enolization of the resulting homoenolate, as γ-oxyallyl nucleophile toward the carbonyl electrophile, which stands in contrast to the previously described enolate mode of the same species. A bicyclic chairlike transition state wherein the aldehyde substituent favorably occupies the psuedoaxial position is proposed to account for the *anti* selectivity.

The vicinal diol motif is prevalent in biologically active natural products and synthetically valuable intermediates, and hence its stereoselective construction represents a long-standing challenge in synthetic organic chemistry. Among various approaches to vicinal diols, the addition of γ-alkoxyallylmetal species to aldehydes (α-alkoxyallylation) has received considerable attention, as it provides diols bearing a synthetically versatile olefin moiety.[1] However, despite the advancement in this reaction manifold through continuous development of new approaches to the requisite alkoxyallylmetal nucleophile,[2] α-alkoxylallylation reactions that allow for the diastereocontrolled synthesis of sterically congested, *sec*,*tert*-diols remain scarce.[3] Marek reported carbocupration/zinc homologation of ynol ethers as a means to generate (*E*)-configured α-alkoxyallylzinc species, which reacted with aldehydes to afford *syn-sec*,*tert*-diols (Scheme 1a).[4] More recently, Krische disclosed an enantioselective ruthenium-catalyzed reductive coupling of alkoxyallene and aldehyde via (*Z*)-configured α-alkoxyallylruthenium species, which also afforded *syn*-diol products (Scheme 1b).[5] Besides the need for deprotection of the alkoxy groups, a common limitation in these reactions concerns the scope of the α-substituent in the allylmetal species. Marek's approach was limited by the scope of organocopper reagents capable of carbocupration (R = primary alkyl), whereas Krische's method employed only α-methylalkoxyallene due to the difficulty in the preparation of differently substituted alkoxyallenes. In terms of direct access to unprotected diols, another notable approach is the pinacol-type reductive coupling between enone and aldehyde. Following the seminal report by Takai on a Cr(II)/Me_3SiCl-mediated process,[6] Loh described a Zn/$InCl_3$-mediated coupling in an aqueous media, where the enone was supposed to be converted to α-oxyallylzinc species bearing indium(III) (Scheme 1c).[7] However, the reaction displayed significantly varying and often moderate diastereoselectivity and was again limited in the scope of the α-substituent (Et or Me).

Herein, we disclose a direct and diastereoselective synthesis of *anti-sec*,*tert*-diols via zinc-mediated hydroxylallylation of aldehydes with cyclopropanols (Scheme 1d). The reaction is promoted using the combination of Et_2Zn and 2,2'-bipyridine (bpy) at room temperature, engaging a variety of 1-substituted cyclopropanols and bicyclic cyclopropanols as well as aromatic and aliphatic aldehydes. The present reaction features the action of enolized homoenolate,[8-11] formed through Et_2Zn-mediated ring-opening of cyclopropanol and subsequent enolization of the resulting homoenolate, as a stereodefined α-oxyallylzinc nucleophile toward the aldehyde. The complementary *anti*-selectivity of the reaction was ascribed to a bicyclic chairlike transition state of allylation, where the aldehyde substituent prefers to occupy the pseudoaxial position.

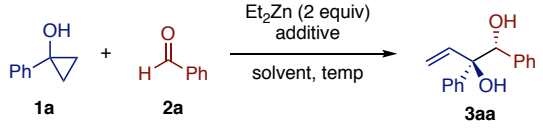
Since the seminal report of Cha and coworkers,[12] zinc homoenolate (**II**) generated by ring opening of zinc cyclopropoxide (**I**) has proved to serve as a β-carbonyl nucleophile in allylation,[12] acylation,[13] alkynylation,[14] and conjugate addition (Scheme 1d, mode 1).[15-18] Recently, we reported a zinc-catalyzed β-functionalization of cyclopropanols with Morita–Baylis–Hillman carbonates, which involves enolization of **II** into enolized homoenolate **III**, its reaction as enolate toward the electrophile, and ring closure of the homoenolate to cyclopropoxide (mode 2).[8] Following this finding, we became interested in the potential reactivity of **III** as an α-oxyallyl nucleophile (mode 3). Prompted by this conjecture and the aforementioned importance of vicinal diols, we set out to explore the reaction of 1-phenylcyclopropanol (**1a**) and benzaldehyde (**2a**).

Scheme 1. Aldehyde Allylation Approaches to Vicinal *sec*,*tert*-Diols



The reaction between **1a** and **2a** in the presence of Et_2Zn (2 equiv) proceeded smoothly in DMSO at 80 °C in 1 h, affording the *anti*-diol **3aa** in 73% yield with diastereoselectivity of 3:1 (Table 1, entry 1). Notably, we did not observe alternative coupling products arising from the mode 1 and mode 2 reactivities. The relative configuration of **3aa** was confirmed by comparison with the opposite diastereomer obtained by the addition of vinyl Grignard reagent to α-hydroxyketone.[19] Unlike our previous reports on catalytic zinc homoenolate and enolized homoenolate reactions,[8,15] the reaction was also feasible in less-coordinating THF, furnishing **3aa** with improved diastereoselectivity (entry 2), while noncoordinating toluene completely shut down the reaction (entry 3). Although the reaction in THF failed at 23 °C (entry 4), the addition of coordinating nitrogen additives (2 equiv) was found to restore the reactivity, among which bpy gave the best results in terms of the yield and the diastereoselectivity (entries 5-8). The amount of bpy could be reduced to 1 equiv without problem (entry 9), while further reduction led to a more sluggish reaction (entry 10). Lowering the amount of Et_2Zn resulted in a decrease in the diastereoselectivity (entry 11).

Table 1. Et_2Zn-Mediated Hydroxyallylation of Benzaldehyde (2a) with 1-Phenylcyclopropanol (1a)[a]

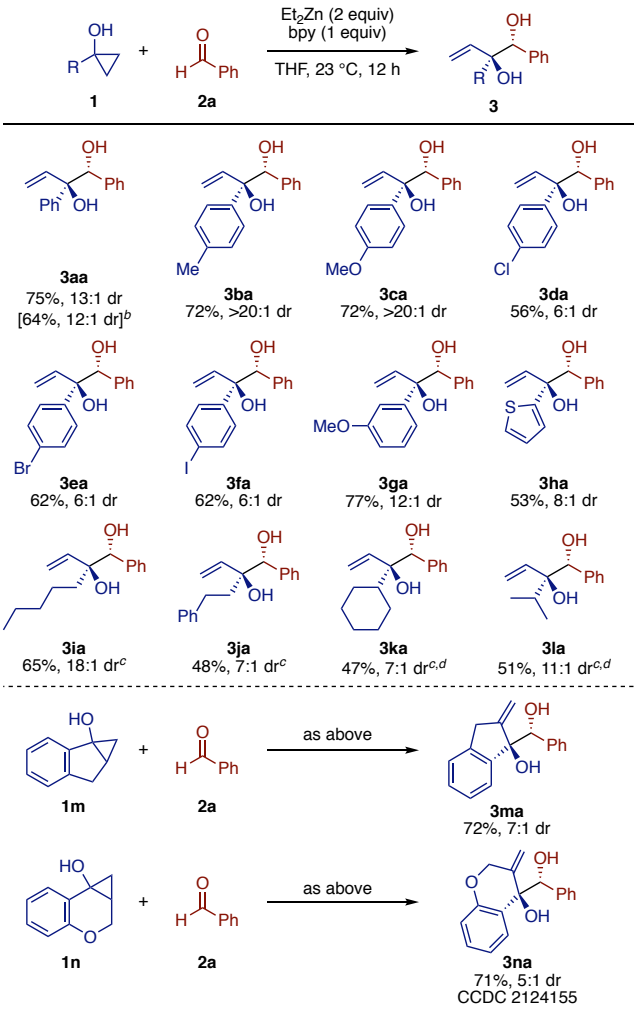


entry	additive (equiv)	solvent	*T* (°C)	yield (%)[b]	dr[c]
1	-	DMSO	80	73	3:1
2	-	THF	80	66	8:1
3	-	toluene	80	0	-
4	-	THF	23	0	-
5	bpy (2)	THF	23	73	11:1
6	pyridine (2)	THF	23	17	7:1
7	TMEDA (2)	THF	23	64	7:1
8	DABCO (2)	THF	23	79	3:1
9	bpy (1)	THF	23	71	11:1
10	bpy (0.5)	THF	23	53	16:1
11[d]	bpy (1)	THF	23	64	4:1

[a]The reaction was performed using 0.05 mmol of **1a** and 0.075 mmol of **2a** in solvent (0.33 M). The reaction time was 1 h (entries 1-3) or 12 h (entries 4-11). [b]Determined by GC using mesitylene as an internal standard. [c]Determined by ^1H NMR of the crude mixture. [d]1 equiv of Et_2Zn was used.

With the optimized conditions (Table 1, entry 9) in hand, we first explored the reaction of various cyclopropanols with **2a** (Scheme 2). A series of 1-(hetero)arylcyclopropanols participated in the hydroxyallylation to afford the corresponding *anti*-diols **3aa**–**3ha** in moderate to good yields with tolerance to electron-donating and -withdrawing substituents and thienyl group. As a general trend, higher diastereoselectivities were observed with electron-rich aryl groups (>20:1, see **3ba** and **3ca**) than with electron-deficient aryl groups (6:1, see **3da**–**3fa**). The model reaction could be performed on a 6 mmol scale, affording **3aa** in 64% yield with 12:1 dr. 1-Alkylcyclopropanols bearing a primary or secondary alkyl group also reacted with **2a** at an elevated temperature (80 °C) to afford the corresponding diols **3ia**–**3la** in moderate yields with good to high diastereoselectivities. Bicyclic cyclopropanols **1m** and **1n** also successfully participated in the reaction to afford the diols **3ma** and **3na**. The structure of the latter was confirmed by X-ray crystallographic analysis.

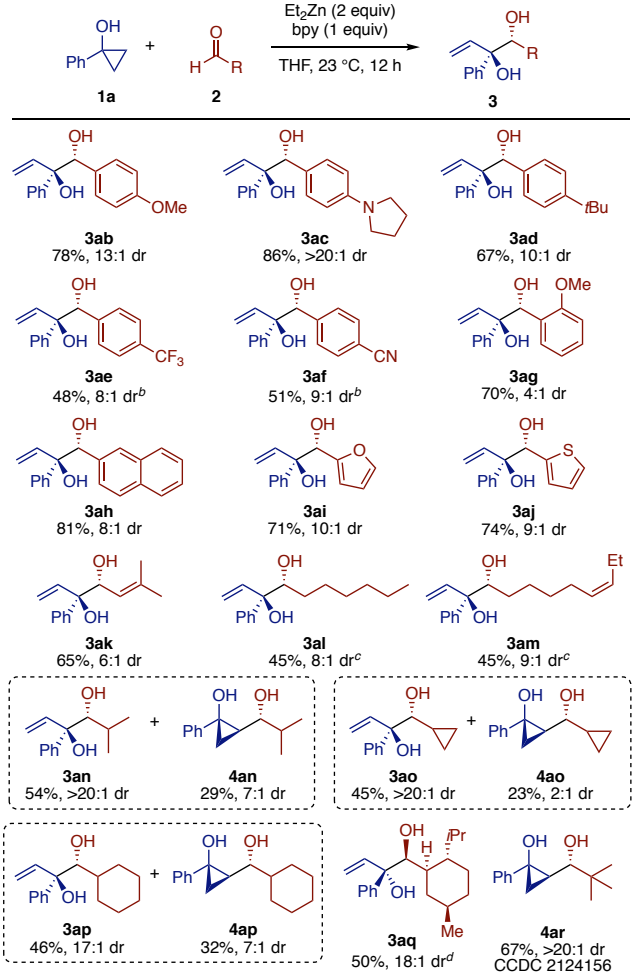
Scheme 2. Hydroxyallylation of Benzaldehyde (2a) with Various Cyclopropanols[a]



[a]The reaction was performed on a 0.3 mmol scale. [b]The yield of a 6 mmol scale reaction is shown in the parentheses. [c]The reaction was performed at 80 °C for 1 h. [d]The reaction was performed in DMSO in the absence of bpy.

We next explored the reaction of **1a** with various aldehydes (Scheme 3). A series of (hetero)aryl aldehydes proved to be good substrates, affording the corresponding products **3ab**–**3aj** in moderate to good yields with moderate to high diastereoselectivities. Electron-rich aldehydes reacted smoothly under the standard conditions with high diastereoselectivities (see **3ab**–**3ad**). On the other hand, the reactions of electron-deficient aldehydes had to be carried out at 0 °C to ensure good diastereoselectivity (see **3ae** and **3af**). The reaction of 3-methyl-2-butenal afforded the desired 1,2-addition product **3ak**. Primary alkyl aldehydes also participated in the reaction at 80 °C to give the diols **3al** and **3am** with good diastereoselectivity. Interestingly, the reactions of secondary alkyl aldehydes produced the desired vicinal diols **3an**–**3ap** as the major products with excellent diastereoselectivity, which were accompanied by 2-(1-hydroxyalkyl)-1-phenylcyclopropanols **4an**–**4ap**, as a result of β-functionalization of **1a** (i.e., mode 2 reactivity). Likewise, the reaction of nonracemic (-)-menthyl 3-carboxaldehyde afforded the adduct **3aq** as the dominant isomer in 50% yield,[20] while the corresponding cyclopropanol-type product was also obtained in 34% yield as a mixture of more than three isomers (data not shown). Pivalaldehyde afforded the cyclopropanol **4ar** as the exclusive product, whose relative configuration was determined by X-ray crystallographic analysis. It should be noted that Matsubara reported diastereoselective synthesis of 2-(1-hydroxyalkyl)-1-alkylcyclopropanols from α,β-epoxyketones and bis(iodozincio)methane[21] as well as their zincate-mediated rearrangement into vicinal diols.[22] The mechanistic connection between the latter and the present reactions remains to be seen.

Scheme 3. Hydroxyallylation of Various Aldehydes with 1-Phenylcyclopropanol (1a)[a]

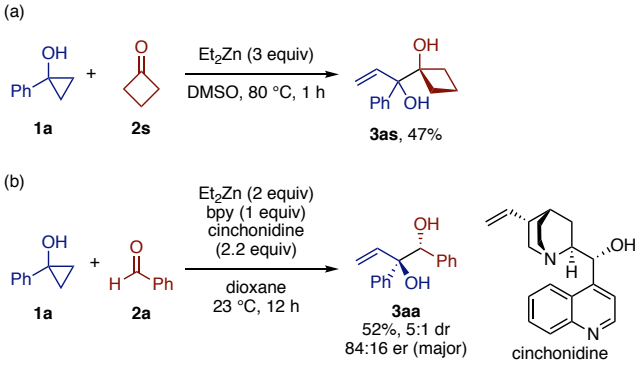


[a]The reaction was performed on a 0.3 mmol scale. [b]The reaction was performed at 0 °C for 24 h. [c]The reaction was performed at 80 °C using 0.1 equiv of bpy. [d]The ratio of the major diastereomer and the rest indicated from ^{1}H NMR analysis of the crude product. The cyclopropanol-type product such as **4ap** was also obtained as a mixture of diastereomers (34% yield).

Having explored the scope and limitation of the present hydroxyallylation of aldehydes, we briefly probed the possibility of its extension to a ketone electrophile and an enantioselective variant. First, the Et_2Zn-mediated reaction between **1a** and highly strained cyclobutanone (**2s**) was found to proceed in DMSO at 80 °C, affording the *tert*,*tert*-diol **3as** in 47% yield (Scheme 4a). Meanwhile, an attempted reaction of **1a** with less strained cyclopentanone resulted in a complex mixture. Next, the model reaction between **1a** and **2a** in the presence of cinchonidine using dioxane as the solvent took place with moderate enantioselectivity of 84:16 er (Scheme 5b). Other chiral additives such as amino alcohol and bisoxazoline

derivatives tested thus far induced lower enantioselectivities (see Scheme S1).

Scheme 4. (a) Addition to Cyclobutanone and (b) Preliminary Enantioselective Variant



Showing consistently good *anti*-selectivity, the present reaction complements the previously reported *syn*-selective alkoxyallylations (Scheme 1a, b). To probe the origin of this diastereoselectivity, we performed DFT calculations on model reactions between enolized homoenolates and aldehydes (Figure 1a).[23] First, (*Z*)-configured enolized homoenolate (*Z*)-**CP**, which is derived from **1a** and features chelation between the enolate oxygen and homoenolate zinc, was calculated to be far more stable ($\Delta\Delta G$ = 7.4 kcal mol^{-1}) than its (*E*)-counterpart ((*E*)-**CP**). Despite the strong chelation, boat-like transition states for the addition of (*Z*)-**CP** to **2a** were not located. Instead, it was found to form bicyclic chairlike transition states *anti*-**TS1** and *syn*-**TS1**, where the aldehyde oxygen was coordinated not only by the homoenolate zinc but also by the enolate zinc. With the aldehyde phenyl group at the psuedoaxial position, *anti*-**TS1** was lower in energy than *syn*-**TS1** by 1.0 kcal mol^{-1}, which was qualitatively in line with the observed selectivity toward *anti*-**3aa**. The same trend was also found with other TSs that modelled substrate combinations such as **1a**/acetaldehyde and 1-methylcyclopropanol/**2a** (see Figure S6 and S7). Thus, we suggest that unfavorable two gauche interactions encountered with psudoequatorial placement of the aldehyde substituent, as described by Marek,[24] account for the generally observed *anti* selectivity of the present reaction.

Besides the diastereoselectivity in hydroxyallylation, we also probed the origin of the diastereoselectivity in the formation of the 1,3-diol such as **4ar** (Figure 1b). Notably, in the aldol reaction step, the bulky *tert*-butyl group displayed preference for occupying the pseudoaxial position in the chairlike TS (*anti*-**TS2**) to avoid the gauche interaction with the zinciomethyl group in the alternative TS (*syn*-**TS2**). Following this aldol step, the subsequent ring closure would occur while avoiding the steric clash between the phenyl group and the alkoxide moiety, thus setting the relative configuration of the cyclopropane substituents. Compared with a related synthesis of 2-(1-hydroxyalkyl)-1-alkylcyclopropanol via Cr(II)-mediated coupling of enone and aldehyde by Takai,[25] which also involves aldol and cyclopropanation steps but with moderate diastereoselectivity with respect to the former, the high diastereoselectivity may be ascribed to the fixed (*Z*)-configuration of enolized homoenolate.

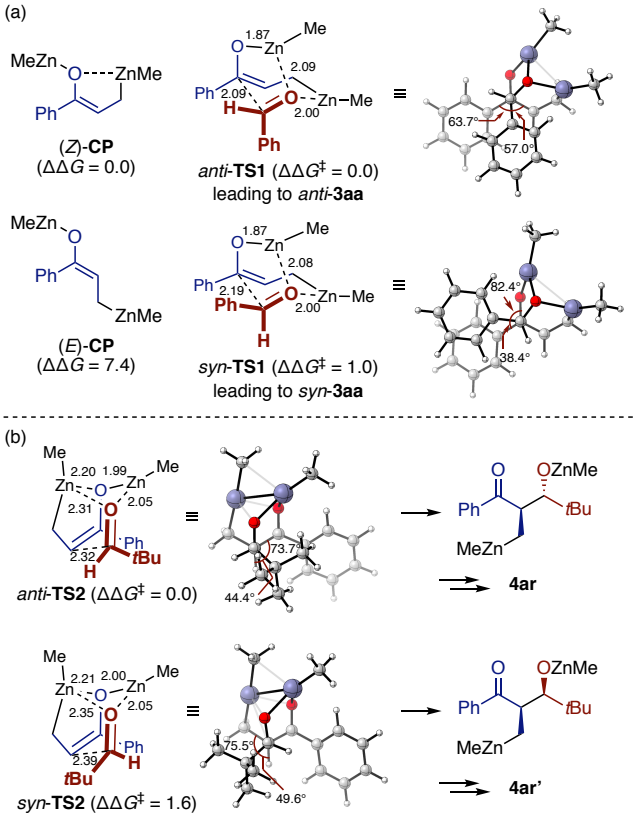


Figure 1. Results of DFT calculations (M062X-SMD(THF)/6-31+G(d,p)//M062X/6-31G(d)): (a) Comparision of (*Z*)- and (*E*)-configured enolized homoenolate and transition states of hydroxyallylation leading to the major and minor diastereomers of **3aa**. (b) Transition states of aldol reaction leading to the major and minor diastereomers of **4ar**.

In summary, we have developed a zinc-mediated hydroxyallylation of aldehydes with cyclopropanols for the synthesis of vicinal *anti*-*sec*,*tert*-diols under operationally simple and mild conditions, which complements the existing alkoxyallylation reactions. Featuring the reaction mode of enolized homoenolate as γ-oxyallyl nucleophile, the present hydroxyallylation further expands the utility of cyclopropanols beyond well-explored homoenolate and β-keto radical transformations.[18] The overall transformation (i.e., cyclopropanol and aldehyde into vicinal diol) is thermodynamically favorable and hence, in theory, could be made catalytic and enantioselective. Further investigations into the reaction chemistry of homoenolate and enolized homoenolate are currently underway in our laboratory.[26]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization data for all the new products (PDF).

Accession Codes

CCDC 2124155-2124156 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB1, 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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