

Regiospecific Ring-Opening of Unsymmetrical Epoxides to the Corresponding Less Substituted Alcohols by Newly-Devised Meerwein-Ponndorf-Verley Type Reagents

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Abstract

A newly-devised Meerwein-Ponndorf-Verley (MPV) reagents, such as diisobutylacetoxyalanes and diisobutylmethanesulfonylalanes, achieved a clean conversion of unsymmetrical epoxides to the corresponding less substituted alcohols. This review covers the recent developments for such a regiospecific ring-opening reaction of epoxides.

Key word : Ring-opening, Epoxide, Meerwein-ponndorf-verley, Alcohol

1. Introduction

The Meerwein-Ponndorf-Verley (MPV) reaction has been known as a mild and specific method of reducing carbonyl compounds since 1925. However, the discovery of sodium borohydride^[1] in 1942 and of lithium aluminum hydride^[2] in 1945 brought about a revolutionary change in procedures for the reduction of functional groups in organic molecules. Today, for instance, in dealing with the problem of reducing an aldehyde or ketone function, the synthetic organic chemist will rarely undertake to use such a conventional technique. Moreover, the advent of a variety of modified metal hydride reagents possessing a high degree of selectivity has made it possible to have a broad spectrum of reagents for selective reductions. However, recent developments in the design of new type of MPV reagent and in its application for the reduction of organic functional groups such as epoxy compounds led us to reassess its applicability and selectivity in organic synthesis. Consequently, it appears of interest to review the regiospecific reaction of epoxides by the newly-developed MPV reactions.

2. Mechanistic Consideration of the MPV Reactions

2.1. Aluminum Reagents

The MPV reaction with aluminum isopropoxide is reversible, but the equilibrium can be shifted to the point of complete reduction by removal of the acetone with a stream of dry nitrogen or by slow distillation. The equilibrium proceeds by an oxidation – reduction reaction of a carbinol – carbonyl pair accelerated by aluminum alkoxide.

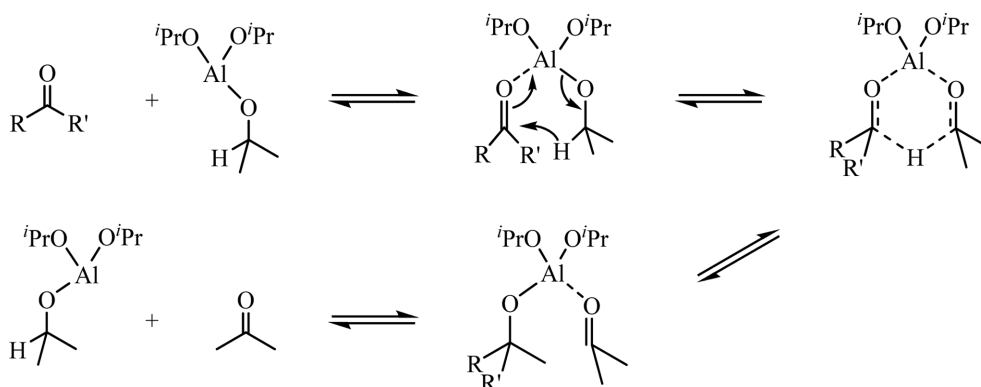
The generally accepted mechanism for MPV reactions proceeds *via* a complex in which both the carbonyl compound and the reducing alcohol are bound to the metal ion as shown in Scheme 1 for the reaction of aluminum isopropoxide. The carbonyl is then activated upon coordination to Al (III), followed by a hydride transfer from the alcoholate to the carbonyl group *via* a six-membered transition state. Likewise, the mechanism of the reaction of carbonyl compounds with triisobutylaluminum (TIBA) involves hydride shift from the β -carbon atom and thus proves to be very similar to the MPV reduction process (Scheme 2).

2.2. Boron Reagents

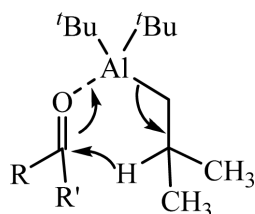
As in the report by Mikhailov^[3] on the reaction of trialkylboranes with benzaldehyde at elevated temperatures, the rate of the elimination of an olefin from a

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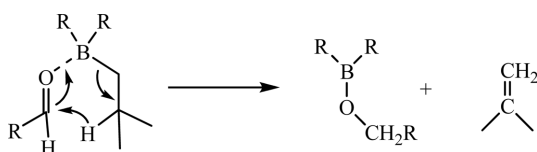
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Scheme 1



Scheme 2



Scheme 3

trialkylborane increases with increase in the number of methyl groups on the β -carbon atom, which indicates reaction with elimination of a hydride ion *via* a cyclic electron transfer (Scheme 3).

2.3. Appearance of New MPV Type Reagents

We usually say that **MPV** reduction is performed with aluminum isopropoxide as a catalyst and isopropyl alcohol as a hydride source. From the mechanistic point of view as depicted in Scheme 19, however, there are two points to be considered. One is that the actual reduction takes place by virtue of the β -hydrogen transfer from isopropoxy group attached to Al atom of catalyst. This means that isopropyl alcohol does not participate at the key step of reduction: isopropyl alcohol acts as an isopropoxy group source which substantially provides a hydride. The other is that **MPV**

reaction is reversible: acetone formed accelerates the reversible reaction.

Practically, there have encountered some problems in this reaction: the reduction usually proceeds sluggishly even with an excess catalyst and requires the removal of acetone in order to shift the equilibrium in the desired direction. Therefore, efforts to devise new catalysts and reagents to overcome such limitations have been continuously devoted.

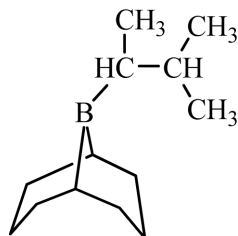
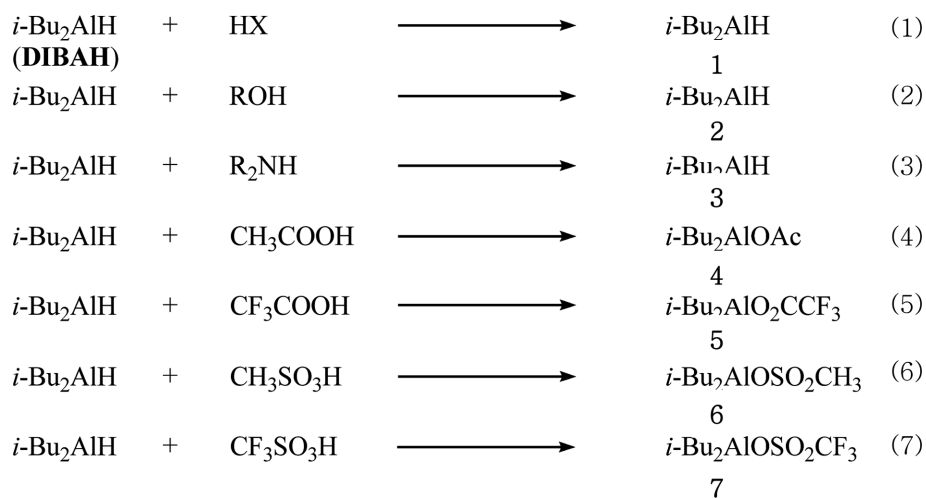
2.4. Aluminum – Containing Reagents

Recently, there have appeared a series of diisobutylaluminum derivatives, such as diisobutylhaloalanes (**1**),^[7-11] diisobutylalkoxyalanes (**2**),^[11-14] diisobutylaminoalanes (**3**),^[15-17] diisobutylacetoxyalanes (**4** and **5**),^[49] and diisobutylmethanesulfonylalanes (**6** and **7**),^[18-22] which were prepared by simple reaction of diisobutylaluminum hydride (**DIBAH**) with the corresponding hydrogen halides, alcohols, amines, acetic acids, and methanesulfonic acids, respectively (Eq. 1-7). These diisobutylaluminum derivatives have achieved a very high chemo-, regio- and stereoselectivity in the reduction of aldehydes and ketones.

2.5. Boron – Containing Reagents

Generally, trialkylboranes are known to be tolerant to a wide variety of functional groups,^[23] but certain **B-R-9-BBN**, especially **B-Sia-9-BBN** (**8**) is a mild chemoselective reducing agent for aldehydes.^[4,5]

However, the first report on trialkylborane being capable of reducing both aldehydes and ketones under mild conditions appeared in 1985.²⁴ Professor Brown and his coworkers devised diisopinocampheylchlorob-



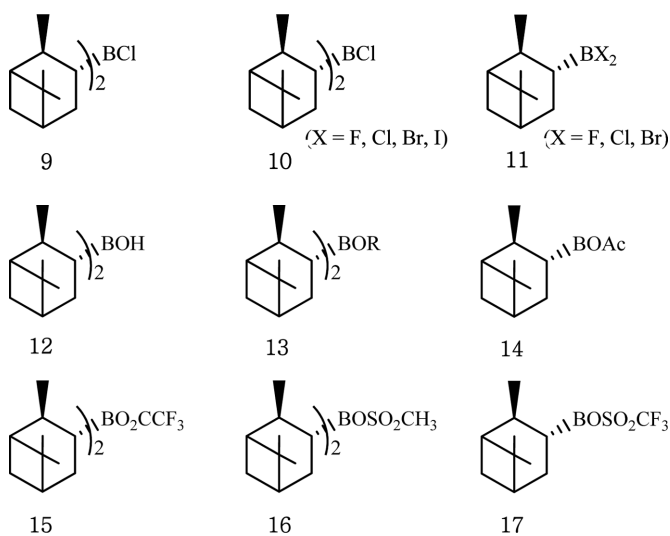
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orane (**Ipc₂BCl**) (**9**), which is the outcome from a strategic modification of the electronic and steric environments of the boron in trialkylboranes can reduce

a variety of ketones as well as aldehydes to the corresponding alcohols even at -25°C . Soon other mono- and diisopinocampheylhaloboranes (**10** and **11**), were also prepared.^[25-29] Furthermore, hydroxy-, alkoxy-, acetoxy- and methanesulfonyl-incorporated diisopinocampheylborane derivatives (**12-17**) were prepared and their applicability in **MPV** type reduction was explored.^[30-36]

2.6. Application for Organic Synthesis

The **MPV** reduction is a classical but still widely used method for organic synthesis, because of high selectivity, relatively mild reaction conditions, simple and safe operations, and the low cost. In general, **MPV** reduction is performed with various catalyst and isopro-



pyl alcohol as a hydride source; the mechanism can be described by the activation of the carbonyl group through its coordination to Lewis acidic metal site followed by reversible hydride transfer from alcoholate to the carbonyl acceptor *via* six-membered cyclic transition state as shown in Scheme 18 to 20. In this mechanistic point of view, the key step of this reaction must be the coordination of carbonyl oxygen to Lewis acidic metal site: without coordination of the substrate, no reduction takes place. Another characteristic feature of this reaction to be considered is the hydride-transfer pathway in which the reduction proceeds through the six-membered transition state. These combined characteristic features seem to play a major role performing an excellent selectivity in the MPV reductions, such as the following chemo, regio, and stereoselective reductions of carbonyl and epoxy compounds.

2.7. General Reducing Characteristics of Diisobutylaluminum and Diisopinocampheylboron Derivatives Toward Common Organic Functional Groups

Recently, the general reducing characteristics of diisobutylaluminum derivatives, such as *i*-Bu₂AlX (1), *i*-Bu₂AlOR (2), *i*-Bu₂AlNR₂ (3), *i*-Bu₂AlOAc (4), *i*-Bu₂AlO₂CCF₃ (5), *i*-Bu₂AlOSO₂CH₃ (6), *i*-Bu₂AlOSO₂CF₃ (7), and diisopinocampheylboron derivatives, such as Ipc₂BX (10), Ipc₂BOR (12 and 13), Ipc₂BOAc (14), Ipc₂BO₂CCF₃ (15), Ipc₂AlOSO₂CH₃ (16), and Ipc₂AlOSO₂CF₃ (17), have been examined systematically. After a broad examination and comparison, some conclusions on the general reducing action of these derivatives toward organic functional groups have been drawn as follows:

(i) the relative reactivities of Ipc₂BX series toward carbonyl compounds are in sequence of Ipc₂BCl >

Ipc₂BF ≫ Ipc₂BBr > Ipc₂BI,

(ii) the reactivity of Ipc₂BOR (12 and 13) is much weaker than Ipc₂BX (10),

(iii) Ipc₂BOR (12 and 13) can reduce aldehydes, but can not attack ketones,

(iv) the relative reactivities of *i*-Bu₂Al-series are *i*-Bu₂AlX > *i*-Bu₂AlOR > *i*-Bu₂AlNR₂,

(v) the relative reactivities of *i*-Bu₂AlOR (2) series are *i*-Bu₂AlOH > *i*-Bu₂AlOEt > *i*-Bu₂AlO^{*i*}Pr > *i*-Bu₂AlO^{*t*}Bu,

(vi) the reactivity of Ipc₂BO₂CCF₃ (15), a fluorinated acetate derivative, is much higher than that of acetate derivative itself, Ipc₂BOAc (14),

(vii) the reactivity of Ipc₂AlOSO₂CF₃ (17), a fluorinated sulfonated derivative, is much higher than that of sulfonate derivative itself, Ipc₂AlOSO₂CH₃ (16).

As a result, the reactivity depends on what kind of moiety being attached to diisobutylaluminum or diisopinocampheylboron. Such reactivity difference may be attributed to the steric and electronic effects of the substituent. A relative reactivity toward organic functional groups is summarized in the Table 1.

Most derivatives are reactive toward aldehydes and ketones, but quite inert to other functional groups including even acid chlorides. Especially noteworthy is that Ipc₂BOH appears the mildest one among the derivatives, exhibiting absolutely no reactivity toward every organic functional groups except aldehyde.

2.8. Regioselective Ring-opening of Epoxide

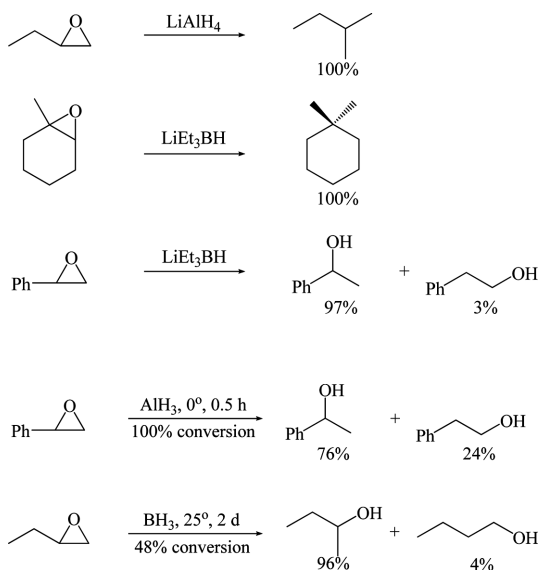
As expected for S_N2 processes, nucleophilic hydride transferring reagents, such as LiAlH₄^[37] and LiEt₃BH^[38] attack epoxides at the less substituted site to afford the more highly substituted alcohol.

On the other hand, with electrophilic hydride reagents such as BH₃^[39] and AlH₃^[40] reverse opening is often observed to produce the less substituted alcohol, but

Table 1. Comparison in Reactivity of Diisopinocampheylboron and Diisobutylaluminum Derivatives toward Common Organic Functional Groups^a

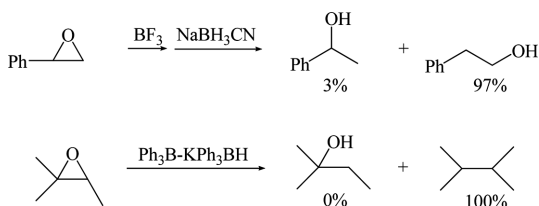
Reagent type	Organic functional groups					
	aldehyde	ketone	ester	acid chloride	nitrile	epoxide
Ipc ₂ BX	+++	++	-	-	+	+
Ipc ₂ BOR	++	-	-	-	-	-
<i>i</i> -Bu ₂ AlX	+++	+++	-	-	+	++
<i>i</i> -Bu ₂ AlOR	++	+	-	-	-	-
<i>i</i> -Bu ₂ AlNR ₂	++	+	-	-	-	-

^a+ Designates 'reactive', whereas designates 'inert'.

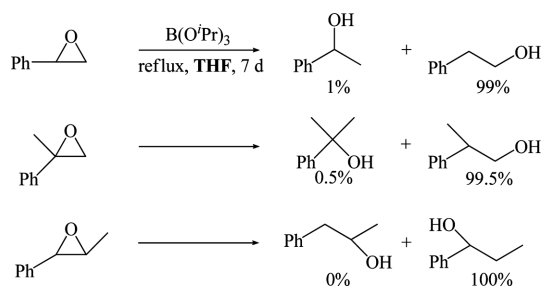
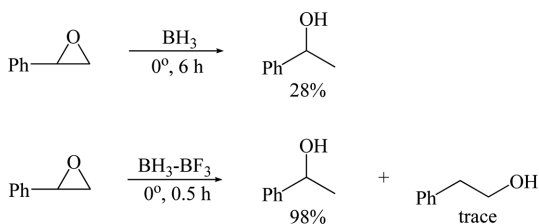


mixtures usually result.

However, activation of epoxide by complexation with a Lewis acid, and followed by nucleophilic attack with conventional mild metal hydrides has been demonstrated to be the most convenient and reliable process for producing predominately the less substituted alcohols.^[41,42] The addition of a Lewis acid not only accelerates the rate but also changes the products drastically. BF_3 and Ph_3B are utilized as an efficient Lewis acid for such activation.



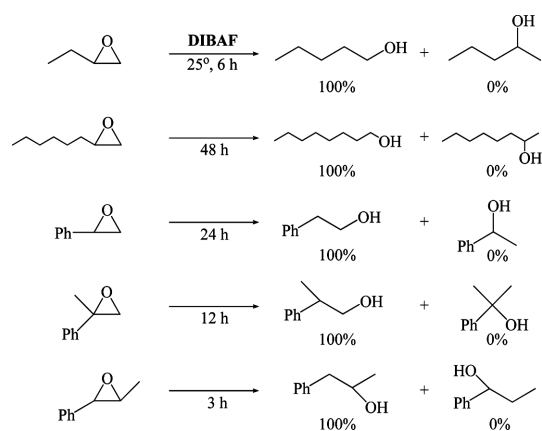
The BF_3 effect on the rate enhancement and hence the clean product formation has also been observed in the reduction of epoxides with BH_3 .^[43] Thus, the reduction



of styrene oxide with BH_3 alone provides only 28% of the expected 2-phenylethanol at 0°C in 6 h.^[39] However, the presence of BF_3 completely reduces styrene oxide at 0°C in less than 0.5 h to give a clean product.

The first report on the **MPV** type reduction of epoxides seems to be the communication which describes the reaction of epoxides with boron isopropoxide.^[44] The reagent is absolutely inert toward aliphatic epoxides such as 1,2-epoxybutane, 1,2-epoxyoctane and 1,2-epoxycyclohexane even in refluxing **THF** for 7 days. On the other hand, the reaction of aromatic epoxides proceeds slowly in refluxing **THF** to produce exclusively the less substituted alcohols. In general, the reactivity of boron triisopropoxide is much milder than that of aluminum triisopropoxide: the reagent can reduce only aliphatic aldehydes and ketones. However, dichloroisopropoxyborane, a chlorine-incorporated boron alkoxide, shows a higher reactivity than that of boron triisopropoxide.^[45]

The fluorine-incorporated diisobutylalane (**DIBAF**), one of the diisobutylhaloalane derivatives (**1**), exhibits a high reactivity toward various epoxides to complete the reduction in less than 24 h at 25°C . Furthermore,



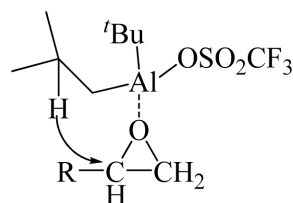
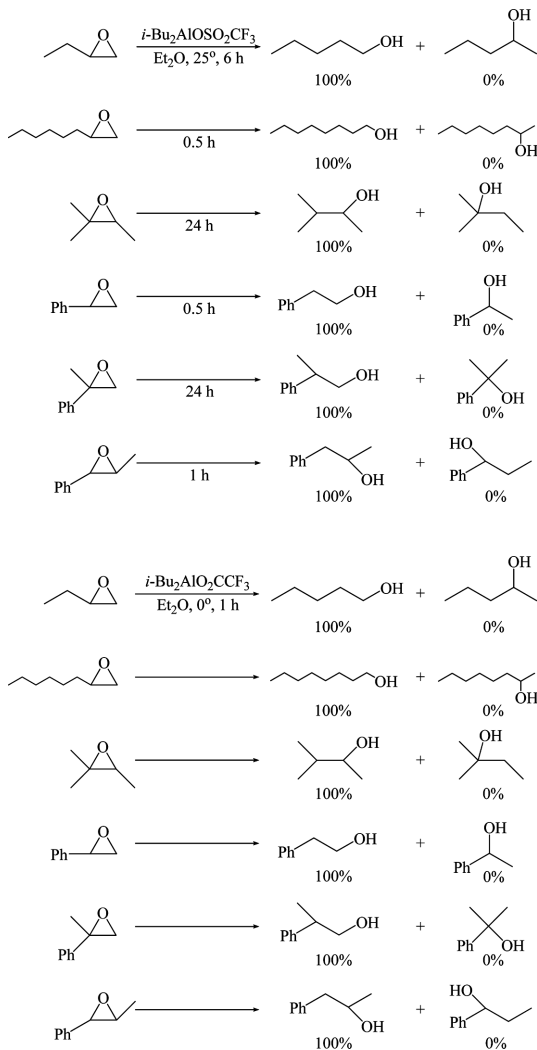
DIBAF achieves the regioselective cleavage of phenyl- or alkyl-substituted epoxides to the less substituted alcohols resulting from anti ring opening. Especially, the reagent attacks only at the phenyl-substituted site where both phenyl and alkyl groups are attached separately at each carbon site of epoxy ring.^[46]

Similarly, the newly-devised acetoxy- and methanesulfonyl-substituted diisobutylalane derivatives, such as *Al*-acetoxydiisobutylalane (**DIBAOAc**, **4**), *Al*-trifluoroacetoxydiisobutylalane (**DIBAO₂CCF₃**, **5**), *Al*-methanesulfonyldiisobutylalane (**DIBAOSO₂CH₃**, **6**), and *Al*-trifluoromethanesulfonyldiisobutylalane (**DIBAOSO₂CF₃**, **7**), achieve the regioselective ring opening of epoxides. In general, the reactivity of fluorine-substi-

tuted derivatives are much higher than that of the parent unsubstituted derivatives. For example, **DIBAOSO₂CF₃** (**7**) can reduce a variety of aliphatic and aromatic epoxides readily at 25°C to the ring-opened alcohol products.^[47,48] In this reaction, the less substituted alcohols are produced as a sole product.

Especially noteworthy is that the results achieved by **DIBAO₂CCF₃** (**5**)^[49]: the ring-opening reaction is completed in less than 1 h at 0°C.

It must be concluded that such a perfect regioselective ring-opening arises from the β-hydrogen transfer from the reagent only to the more positive carbon of the coordinated epoxy ring (Scheme 4).



Scheme 4

3. Concluding Remarks

The regiospecific ring-opening of unsymmetrical epoxides to the corresponding less substituted alcohols are of highly effective synthetic utility. Consequently, this review should provide a useful tool for organic chemists for such a purpose.

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