Asymmetric Baeyer—Villiger oxidation: control of stereoelectronic demand*

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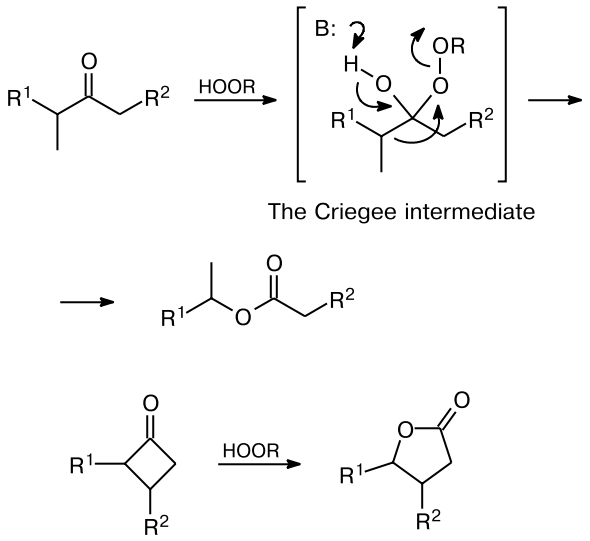
The recent development of asymmetric Baeyer—Villiger oxidation of prochiral and racemic ketones is briefly summarized, focusing on the regio- and stereocontrol of the oxidation attained by regulating the stereoelectronic demand in the step of rearrangement of the Criegee intermediate.

Key words: asymmetric catalysis, Baeyer—Villiger oxidation, hydrogen peroxide, zirconium(salen) complexes, *cis*-β, regiodivergent parallel kinetic resolution.

Baeyer—Villiger (BV) oxidation discovered more than a hundred years ago is the most convenient method for converting carbonyl compounds into esters or lactones.[1] Various peroxy compounds such as peroxy acids, hydrogen peroxide, and alkyl hydroperoxides can be used as the oxidants in the BV oxidation. Later, Criegee proposed a two-step mechanism that included an intermediate, now called the Criegee intermediate, in which an alkyl substituent at the carbonyl carbon atom migrates nucleophilically to a peroxide oxygen atom, resulting in an ester or a lactone (Scheme 1).[2] Thus, the migratory aptitude of the alkyl substituent varies in the following sequence: secondary alkyl groups (containing methine) > primary alkyl groups (containing methylene) > methyl. If the migrating group is chiral ($R^1 \neq H$), its migration proceeds with retention of the configuration. It is noteworthy that, for stereoelectronic reasons, the O—H bond (or a nonbonding electron pair on oxygen) and the peroxy O—O bond in the Criegee intermediate must occur in the antiperiplanar position to the C—C bond of the migrating carbon atom (R_L) (Fig. 1).[1]

Scheme 1



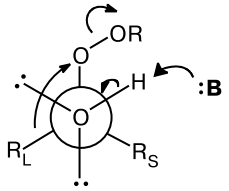


Fig. 1. Desired conformation of the Criegee intermediate for migration of the R_L group.

Biological Baeyer—Villiger oxidation, its characteristics

Baeyer—Villiger oxidation is promoted by acids, bases, or enzymes.[1] The enzymatic catalysis of BV oxidation shows a unique pattern inconsistent with the above description of the migratory aptitude.[3] The strict stereo- and regiocontrol by an enzyme overcomes the features related to nucleophilicity of the migrating alkyl group. For example, BV oxidation of racemic bicyclo[3.2.0]hept-2-en-6-one catalyzed by *Acinetobacter* TD63 affords (1*S*,5*R*)-2-oxabicyclo[3.3.0]oct-6-en-3-one (*ee* >97%) and (1*R*,5*S*)-3-oxabicyclo[3.3.0]oct-6-en-2-one

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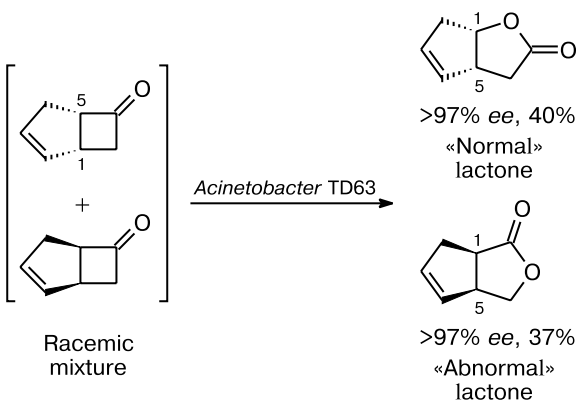
Scheme 2



(*ee* >97%) in 40% and 37% yields, respectively (Scheme 2).[4] The reaction of one enantiomer matches with the migratory aptitude and gives a normal lactone. On the other hand, the reaction of the other enantiomer mismatches with the aptitude, providing exclusively an abnormal lactone. Thus, the reaction is stereospecific and regioselective. This type of reaction is called regiodivergent parallel kinetic resolution (RPKR).[5] The stereo- and regioselectivities of biological reactions are often dependent on the substrate used, which is described in terms of the key-and-lock model. Some examples of biological BV oxidation show a lower level of RPKR.

Enzymes that catalyze the BV oxidation mostly bear a FAD prosthetic group and utilize NADPH as the reductant. The reduced FAD-H_2 reacts with oxygen to give 4a-hydroperoxyflavin, which reacts with a carbonyl compound to give the corresponding Criegee intermediate. It has been considered that the conformation of the intermediate is adjusted to meet the stereoelectronic requirements of the asymmetric reaction site of the enzyme to allow enantioselective alkyl migration (Scheme 3). Presumably,[3c] the Criegee intermediate is further converted into a cyclic peroxy intermediate **A**, which allows enantioselective σ—σ* interaction.

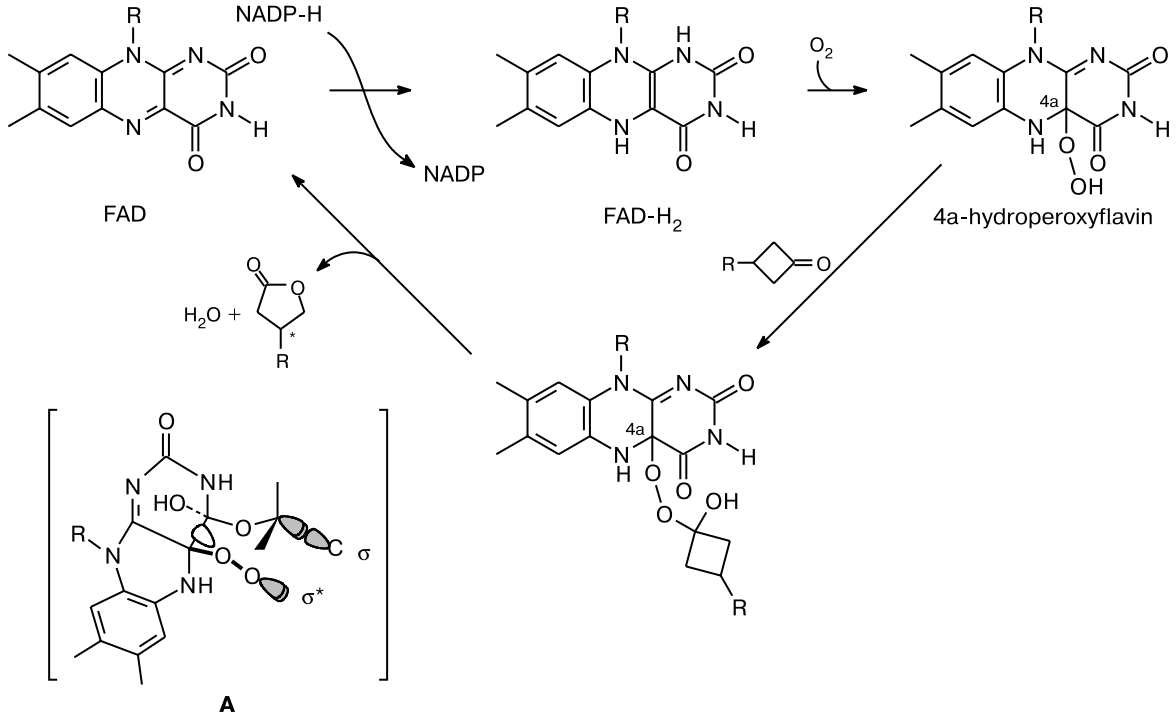
Recently, asymmetric BV oxidation catalyzed by an enzyme-mimicking planar-chiral bisflavin has been reported (Scheme 4).[6]

Chemical asymmetric Baeyer—Villiger oxidation

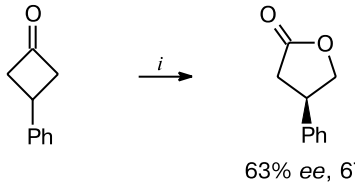
Despite the long history of the Baeyer—Villiger oxidation, study of its asymmetric version was begun only a decade ago. In 1994, Bolm *et al.*[7] reported enantiomer-differentiating BV oxidation of racemic 2-arylcyclohexanones using a combination of molecular oxygen and aldehyde (Mukaiyama conditions) in the presence of chiral copper(II)bis(oxazoline) complex **1** as the catalyst. In the same year, Strukul *et al.*[8] reported independently the enantiomer-differentiating reaction of racemic 2-substituted cyclohexanones with hydrogen peroxide catalyzed by chiral Pt^{II}BINAP complex **2** (Scheme 5).

Later, the BV oxidation of racemic ketones (Scheme 6) with complex **1** was shown to be the RPKR, although of a

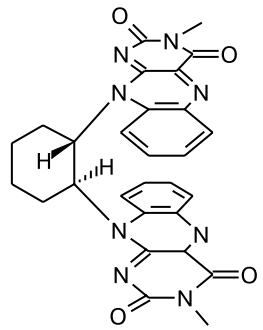
Scheme 3



Scheme 4



63% *ee*, 67%



Bisflavin

i. Bisflavin, H_2O_2, CF_3CH_2OH, MeOH, H_2O (6 : 3 : 1), –30 °C, 6 days

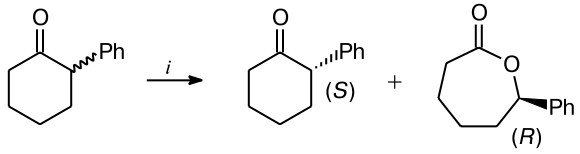
moderate level. This demonstrated once again that the regioselection due to the molecular catalyst can override the migratory aptitude sequence.[9]

Besides the oxidation of racemic ketones, oxidation of prochiral ketones to optically active lactones is an important aspect in the study of asymmetric BV oxidation. As in the case of oxidation of racemic ketones, the oxidation of prochiral ketones with biocatalysts proceeds with high, mostly complete enantiotopos selectivity.[3] In contrast to the biological BV oxidation, only modest enantioselectivity had been achieved in the oxidation of prochiral ketones with molecular catalysts until a few years ago.[10] The BV oxidation of Kelly´s tricyclic ketone was an exception (Scheme 7).[10c]

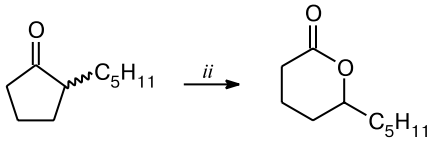
In 2001, three research groups reported independently the following important results on asymmetric BV oxidation. The BV oxidation of 3-phenylcyclobutanone using a magnesium—BINOL complex as the catalyst in the presence of cumene hydroperoxide showed *ee* 65%.[11] Subsequently, the same researchers reported that the use of the aluminum—6,6´-dibromobinaphthol complex further improved the enantioselectivity up to *ee* 77% (Scheme 8),[12] though the mechanism of this reaction has not been discussed.

Seebach *et al.*[13] reported a good level of RPKR attained in the BV oxidation of racemic bicyclobutanones using TADOOH as a chiral oxidant taken in a stoichiometric amount (Schemes 9 and 10). The high enantiotopos selectivity of the reaction has been attributed to the control of the transition state conformation in the rearrangement of the Criegee intermediate. In the BV oxidation of

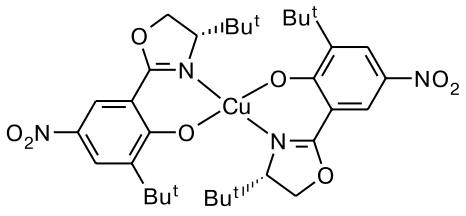
Scheme 5



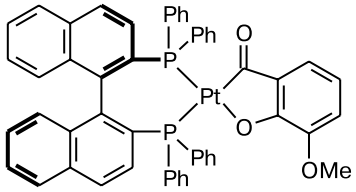
69% *ee*, 41%



58% *ee*, 4%



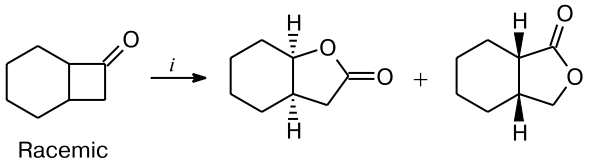
1



2

i. O_2(1 atm), Bu^tCHO, **1** (1 mol.%)
ii. 35%-H_2O_2, 0 °C, $HClO_4$ (1 mol.%), **2** (1 mol.%)

Scheme 6



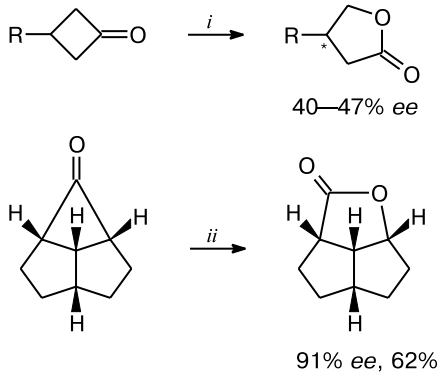
Racemic mixture (*R*,*R*) 67% *ee* (*S*,*R*) 92% *ee*

61% (3 : 1)

i. O_2 (1 atm), Bu^tCHO (0.5 equiv.), **1** (1 mol.%)

bicyclo[3.2.0]heptan-6-one, of the two transition states (**B** and **C**) corresponding to migration of substituents in the Criegee intermediate, transition state **B** corresponding to the fast-isomer is 2.3 kcal mol^{-1} more stable than **C**, as shown by the Dewar semiempirical AM1 method. The

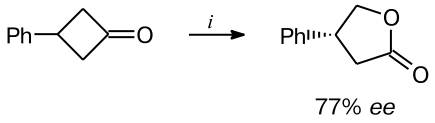
Scheme 7



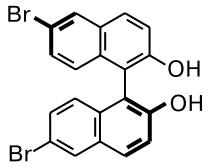
R = Ph, CH_2OH, 4-$MeOC_6H_4$, Bu^t

i. Catalyst, oxidant. *ii*. **1** (1 mol.%), O_2, Bu^tCHO

Scheme 8



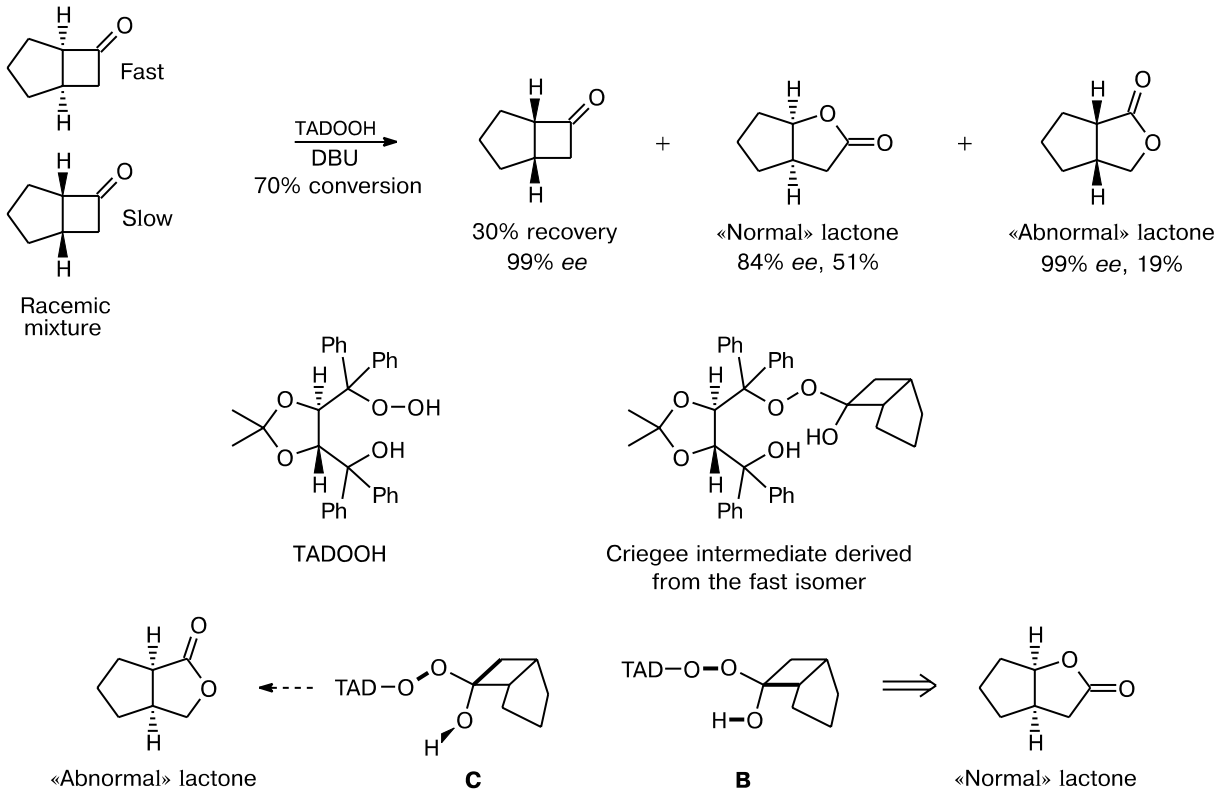
i. Me_2AlCl-6,6′-Br_2BINOL (50 mol.%), cumene hydroperoxide, –25 °C



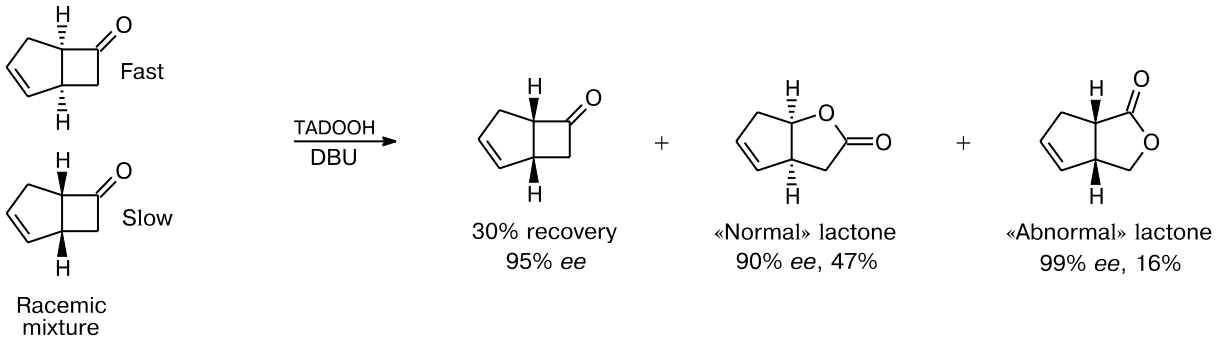
fast-isomer reacts about 15 times faster than the slow-isomer.

Although both the Co^{III}—Schiff base complexes (**3—5**) and cationic *trans*-Co^{III}(salen) complexes (**6**, **7**) catalyze the Baeyer—Villiger oxidation of 3-phenylcyclobutanone, only the former showed enantioselectivity albeit moderate (Scheme 11).[14] A metal complex containing a binaphthyl-derived Schiff base ligand has been reported to adopt a *cis*-β-configuration[15] in which the divalent ligand is expected to chelate the metal center. The Criegee intermediate (R = H) is a sort of divalent ligand (see Scheme 1). Thus, the intermediate has been proposed to form a chelate with the *cis*-β-complex, while the chelate formation is impossible when the *trans*-complex is used as the catalyst (Scheme 12). Thus, the conformation of the chelate is possibly determined by the chiral ligand, which allows the enantiotopos-selective σ—σ*-interaction.[14] It is noteworthy that the oxidation with *tert*-butyl hydroperoxide in the presence of the *cis*-β complex does not show any

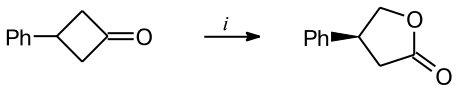
Scheme 9



Scheme 10



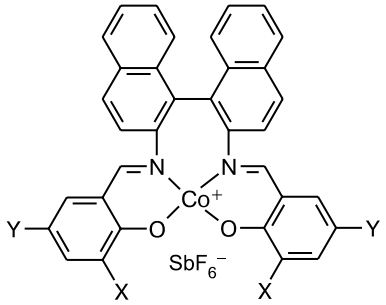
Scheme 11



i. Co^{III} complex (5 mol.%), oxidant ~20 °C, CH_2Cl_2

Catalyst*	Yield (%)	*ee* (%)
3—UHP	53	31
3—TBHP	0	27
4—UHP	57	30
5—UHP	55	10
4—H_2O_2 (aq.)*	77	72
6 or **7** H_2O_2 (aq.)	—	0

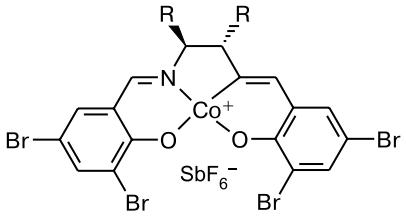
* UHP is the urea adduct with hydrogen peroxide
TBHP is *tert*-butyl hydroperoxide.
** At –20 °C in ethanol.



3—5

cis-β-configuration

X = Y = Br (**3**), X = Y = F (**4**), X = Y = H (**5**)



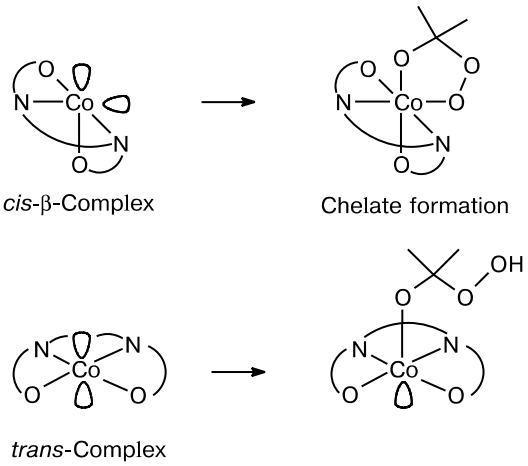
6, **7**

trans-configuration

R = Ph (**6**), $(CH_2)_4$ (**7**)

enantioselectivity, probably because the resulting Criegee intermediate cannot chelate the cobalt ion owing to the presence of the *tert*-butyl group. After the optimization of the reaction conditions, the enantioselectivity has been improved to *ee* 77% (see Scheme 11).

Scheme 12



The BV oxidation with the Pt(BINAP)—hydrogen peroxide system has also been proposed to proceed through a five-membered chelate;[16] the reaction stereochemistry has been explained by steric interaction in the chelate (Fig. 2).

As discussed above, most M-salen complexes usually exist in the *trans*-configuration but some of them acquire the *cis*-β-configuration in the presence of a divalent ligand such as oxalate or acetylacetonate.[17] Belokon´ *et al.*[18]

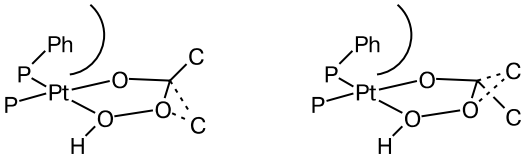
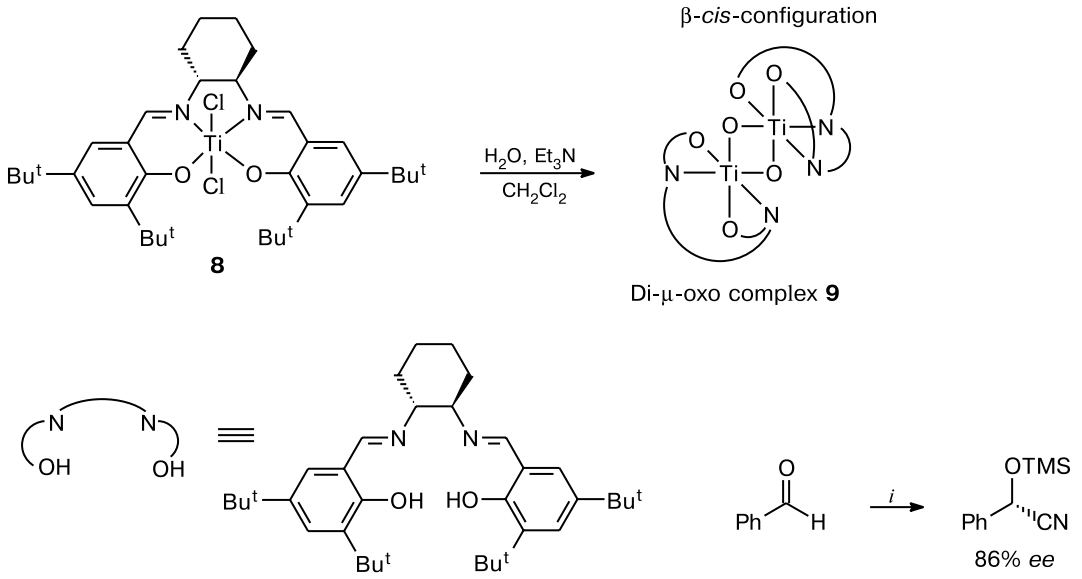


Fig. 2. Presumable transition state models for the Pt(BINAP)-catalyzed BV oxidation.

Scheme 13



i. TMSCN, **9** (0.5 mol.%), CH_2Cl_2, ~20 °C, 24 h

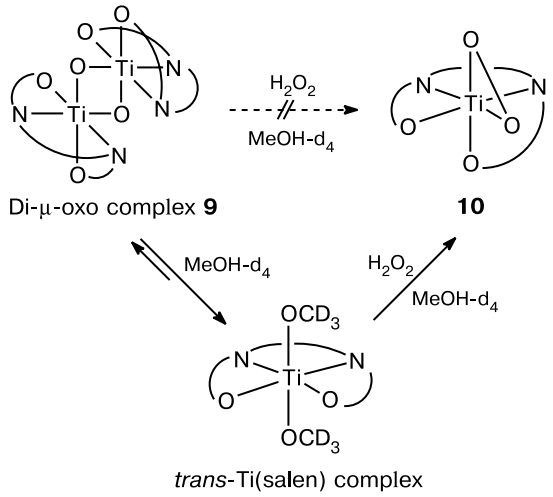
have recently reported that treatment of Ti(salen)Cl_2 (**8**) with water in the presence of triethylamine gives the corresponding di-μ-oxo Ti(salen) complex **9** in which the salen ligands have the *cis*-β-configuration (Scheme 13). This complex is an efficient catalyst for asymmetric cyanation. For example, the cyanation of benzaldehyde proceeds with high enantioselectivity of *ee* 86% even at room temperature.

It is well known that alkoxide exchange in titanium ion is very rapid. Therefore, it was expected that di-μ-oxo Ti(salen) complex **9** would be converted into the corresponding peroxo complex **10** in the presence of hydrogen peroxide, while complex **10** would perform enantioselective oxidation of sulfides (Scheme 14).[19]

Indeed, highly enantioselective oxidation of a wide range of sulfides has been achieved by using di-μ-oxo Ti(salen) complex **12** prepared from Ti(salen) complex **11** according to Belokon´s procedure as the catalyst (Scheme 15).[19a] Later, it has been disclosed that the active peoxo species is not generated directly from the di-μ-oxo complex but *via* a *trans*-Ti(salen) complex (see Scheme 14).[19b]

Peroxo species **10** is expected to promote the BV oxidation if it is equilibrated with the ring-opened peroxide species **13** (Scheme 16). However, complex **12** did not catalyze the desired BV oxidation of 3-phenylcyclobutanone in the presence of the urea—hydrogen peroxide adduct. Taking into account this fact, together with the fact that complex **10** is detected as the sole isomer when complex **12** and the urea—hydrogen peroxide adduct are mixed in methanol-d_4 (^{1}H NMR data),[19b] it is likely that

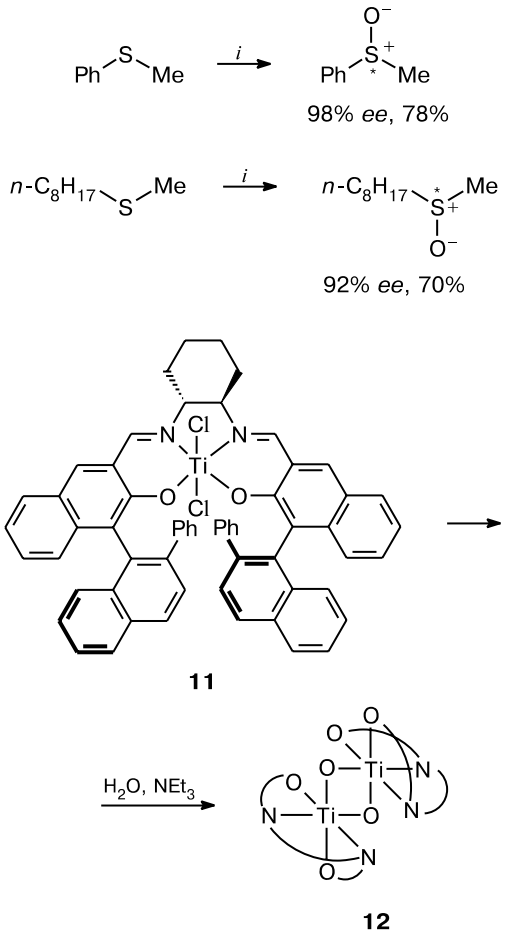
Scheme 14



no equilibrium exists between **10** and **13** or that the equilibrium leans exclusively to **10**.

According to the above result, a M(salen) complex containing a Lewis-acidic metal ion but hardly generating a peroxo species seems to be a promising candidate for the catalyst of the asymmetric BV oxidation. The zirconium ion is Lewis acidic, and the Zr—O bond is approximately 0.2 Å longer than the Ti—O bond. Thus, it is expected that Zr(salen) complexes will not give stable peroxo complexes (Scheme 17). The BV oxidation has been examined with various Zr(salen) complexes as catalysts.[20]

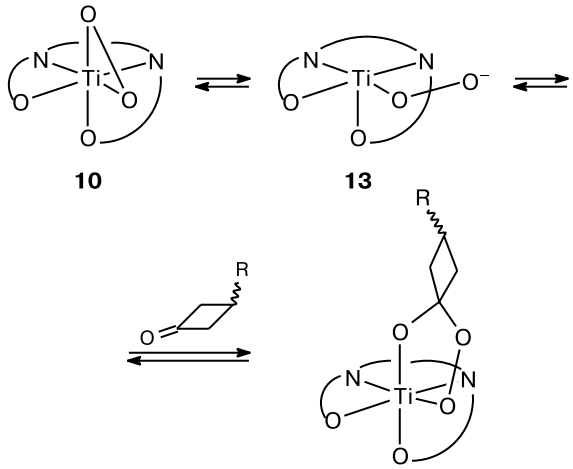
Scheme 15



i. **12**, UHP

Although most Zr(salen) complexes are poor catalysts, complex **14** shows high enantioselectivity (*ee* >80%)

Scheme 16

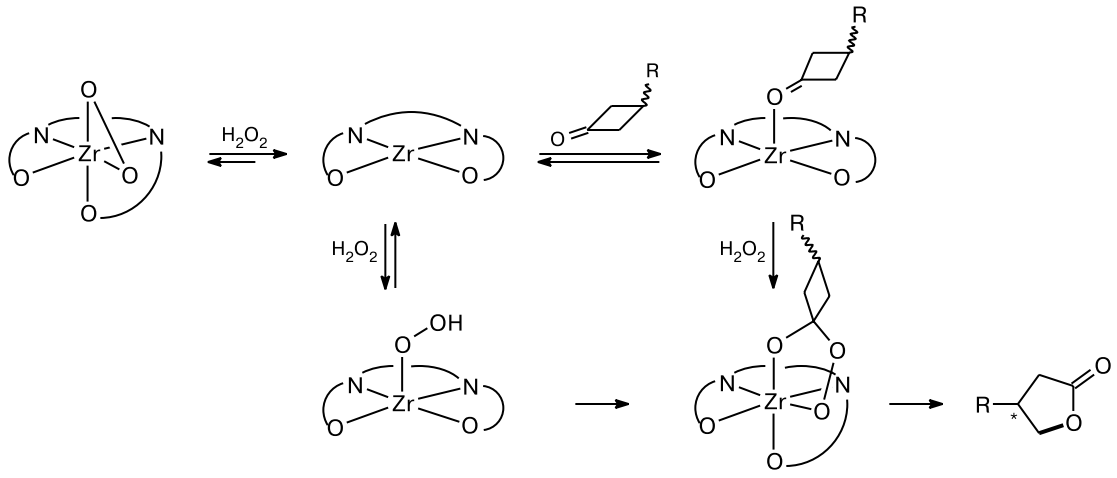


together with acceptable chemical yields in the BV oxidation of various prochiral cyclobutanones using an urea—hydrogen peroxide adduct (Scheme 18).[20]

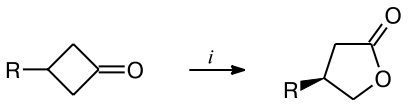
Complex **14** contains the 2-phenylnaphthyl groups of elbowed shape in positions 3 and 3′ and can form a chiral concave reaction site when exists in the *cis*-β configuration (Fig. 3). It has been reported[21] that chiral auxiliaries of concave shape generally tend to show high asymmetric induction. This may account for the excellent asymmetric catalysis of **14** and further suggests that **14** may catalyze highly enantiospecific and regioselective BV oxidation of racemic ketones.

The following examples of BV oxidation of racemic bicyclic butanones show the expected potent molecule-recognizing ability of complex **14**.[22] Before discussing the reactions, we will briefly discuss the relationship between the enantiotopos selectivity exhibited by complex **14** and the migratory aptitude. If the enantiotopos selection ob-

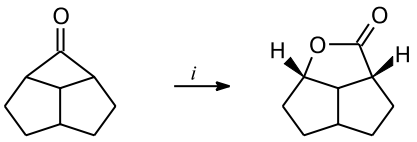
Scheme 17



Scheme 18

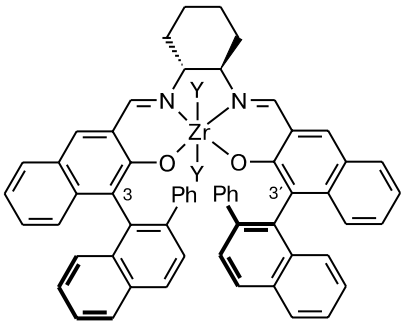


R	*ee* (%)	Yield (%)
Ph	87	68
p-ClC_6H_4	82	63
p-$MeOC_6H_4$	84	43
n-C_8H_{17}	81	63



94% *ee*, 99%

i. **14** (5 mol.%), UHP, CH_2Cl_2, ~20 °C



14: Y = PhO

served in the BV oxidation of 3-substituted cyclobutanones is equally involved in the oxidation of bicyclic butanones,

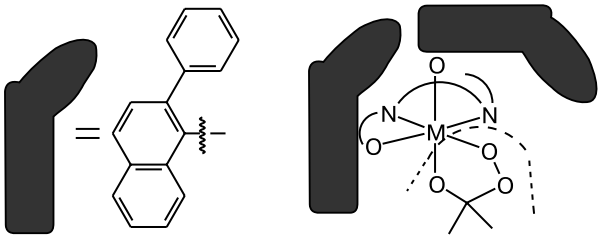
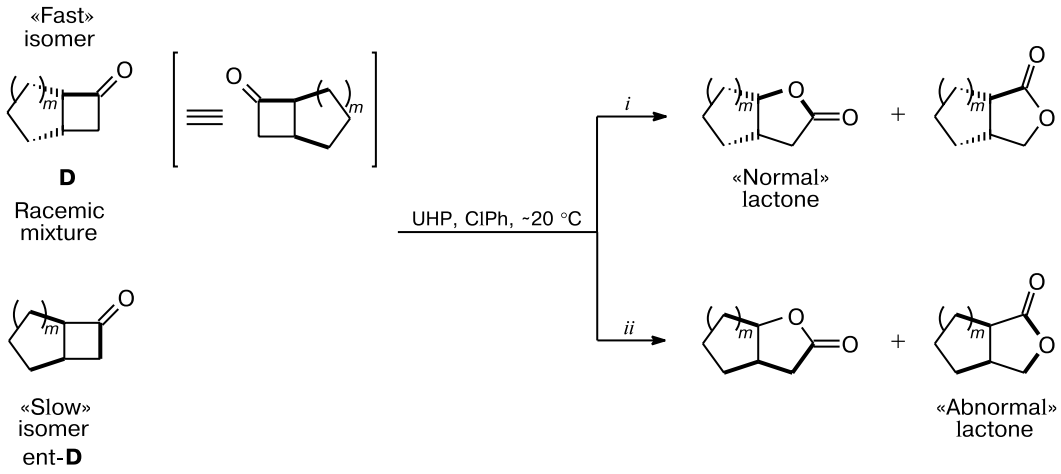


Fig. 3. Schematic model of the *cis*-β-Zr(salen) adduct with the Criegee intermediate.

the enantiotopos selection in the oxidation of one enantiomer (**D**) matches with the migratory aptitude, because both factors imply migration of the methine group. However, the enantiotopos selection mismatches with the aptitude in the oxidation of another enantiomer (ent-**D**), as these factors act in the opposite directions (Scheme 19). Thus, it is expected that the oxidation of enantiomer **D** gives a normal lactone as the major product, while the oxidation of ent-**D** gives a normal lactone only when the migratory aptitude overrides the enantiotopos selection by **14**. If the enantiotopos selection overrides the migratory aptitude, the product derived from ent-**D** should be an abnormal lactone. Despite this description, it should be added that the interaction between the salen ligand and the substrate might affect the transition state of the rearrangement of the Criegee intermediate and change the expected stereo- and regiochemical courses of the BV oxidation.

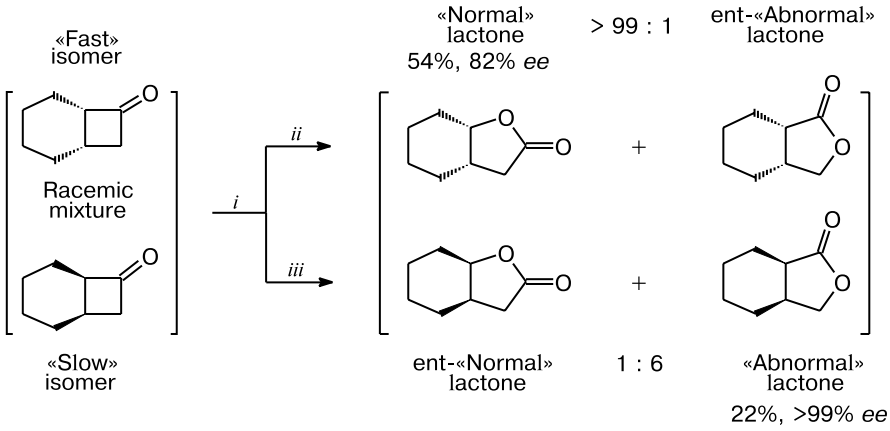
The stereochemistry of the oxidation of bicyclo[4.2.0]octan-5-one agrees with the above discussion, in particular, the fast-isomer gives exclusively the corresponding normal lactone, while the slow-isomer gives the corresponding abnormal and normal lactones in a ratio

Scheme 19



i. Matching pair; *ii*. Mismatching pair
(the bold line is the bond selected by **14**)

Scheme 20



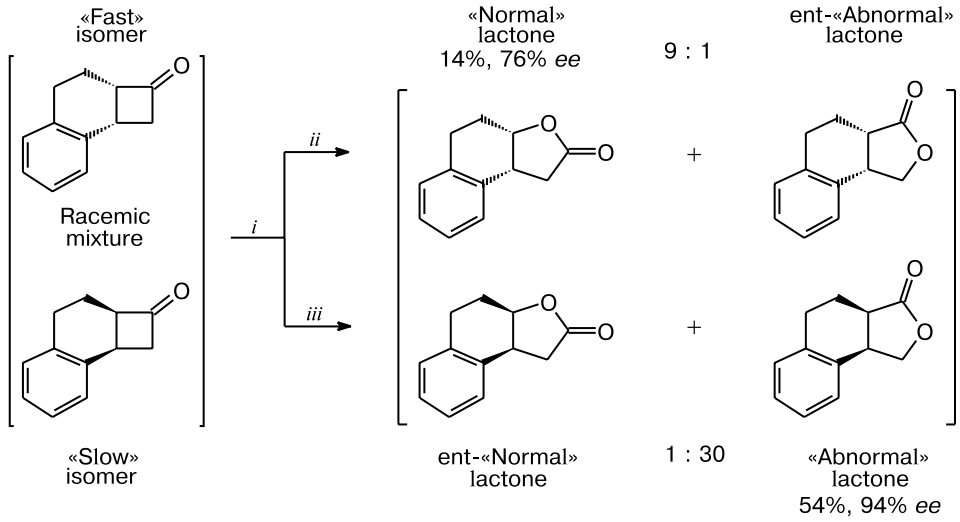
i. **14**, UHP, ClPh, ~20 °C, $k_{rel} \approx 4.2$, 76% conversion. *ii*. Matching pair; *iii*. Mismatching pair.

of 6 : 1 (Scheme 20). The enantiotopos selectivity overrides the migratory aptitude, albeit moderately.[20].

The BV oxidation of 2,3-benzobicyclo[4.2.0]octan-7-one shows considerably different stereochemistry (Scheme 21), namely, the fast-isomer gives preferentially the corresponding abnormal lactones, while the slow-isomer gives the corresponding normal and abnormal lactones in a ratio of 9 : 1. The introduction of the benzene ring favors the formation of the abnormal lactones in the reactions of both enantiomers, and the substrate—ligand interaction overrides the mismatching effect between the enantiotopos selection and the migratory aptitude.[22] Since the conversion rates of bicyclo[4.2.0]octan-5-one and 2,3-benzobicyclo[4.2.0]octan-7-one do not differ much, the substrate—ligand interaction seems to accelerate the oxidation of the enantiomer giving the abnormal lactone and to decelerate the oxidation of the enantiomer giving the normal lactone.

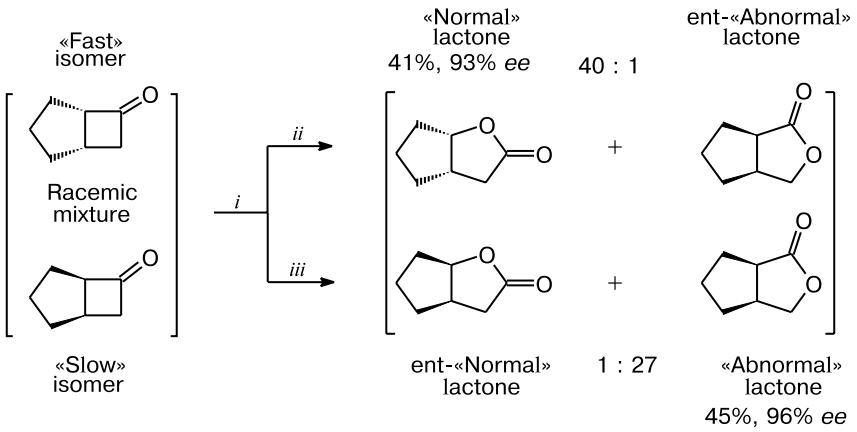
A similar result was obtained in the reaction of bicyclo[3.2.0]heptan-6-one: the fast-isomer gave the corresponding abnormal and normal lactones in a ratio of 27 : 1, while the slow isomer gave the normal and abnormal lactones in a ratio of 40 : 1 (Scheme 22). The reaction is almost complete regiodivergent parallel kinetic resolution. The substrate—ligand interaction overrides again the mismatching effect between the enantiotopos selection and the migratory aptitude. The interaction favors the formation of the abnormal lactone from the fast isomer, but it does not disfavor the formation of the normal lactone from the slow isomer.

Scheme 21



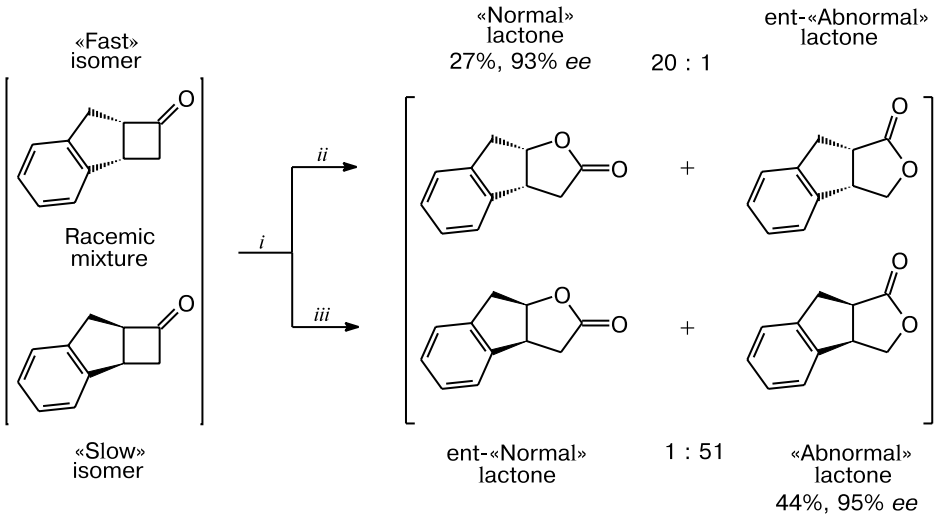
i. **14**, UHP, ClPh, ~20 °C, $k_{rel} \approx 8.0$, 68% conversion. *ii*. Matching pair; *iii*. Mismatching pair.

Scheme 22



i. **14**, UHP, ClPh, ~20 °C, $k_{rel} \approx 2.0$, 90% conversion. *ii.* Matching pair; *iii*. Mismatching pair.

Scheme 23

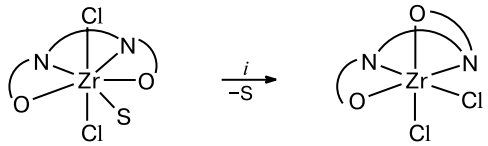


i. **14**, UHP, ClPh, ~20 °C, $k_{rel} \approx 2.9$, 74% conversion. *ii.* Matching pair; *iii*. Mismatching pair.

The oxidation of the bicyclo[3.2.0]heptan-6-one annelated to the benzene ring shows a similar stereochemistry (Scheme 23). Again, the introduction of the benzene ring favors the formation of the abnormal lactones in the reactions of both enantiomers. Thus, the regioselectivity of the oxidation of the fast isomer is further enhanced and that of the oxidation of the slow isomer is somewhat reduced.

Simple Zr(salen) complexes have been reported to have a pentagonal-bipyramidal configuration due to coordination of the solvent molecule. To eliminate the solvent molecule, refluxing in toluene is required (Scheme 24),[23] resulting in the *cis*-β configuration of the complexes.

Scheme 24



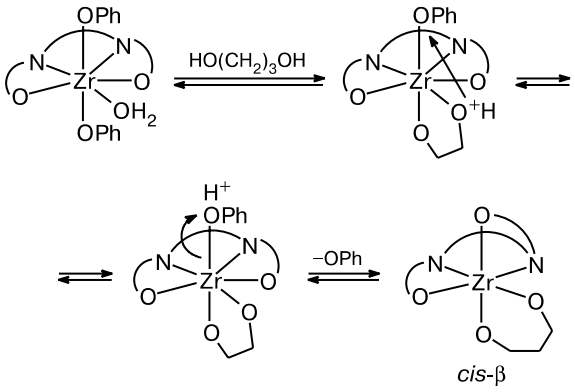
S = THF

i. Toluene (heating)

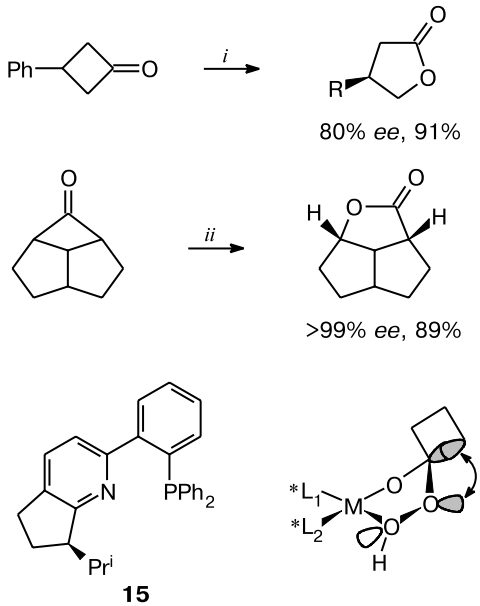
The X-ray diffraction analysis of complex **14** has also demonstrated that the complex has a pentagonal-bipyramidal configuration in which a water molecule is coordinated to the zirconium ion.[22] Complex **14** does not lose the water molecule on heating, at least, to 70 °C. However, NMR analysis has indicated that it exists as an

equilibrium mixture of *trans*- and *cis*-β-isomers in the presence of propane-1,3-diol. It has been considered that the axial phenoxy group is first replaced by the 1,3-diol and the equatorial water molecule is replaced intramolecularly by the other hydroxy group of the diol to form a six-membered chelate; the concomitant proton transfer promotes dissociation of the other phenoxy group (Scheme 25). The formation of a five membered ring is more favorable than six-membered ring formation, and the Criegee adduct forms a five-membered chelate. Thus, it is likely that **14** adopts the *cis*-β-configuration and efficiently recognizes a structural change of the substrate, as expected.

Scheme 25



Scheme 26



i. $Pd(SbF_6)_2$-**15** (5 mol.%), UHP, THF, –60 °C
ii. $Pd(SbF_6)_2$-**15** (5 mol.%), UHP, THF, –40 °C

Palladium(II)—2-(phosphinophenyl)pyridine complex **15** can serve as the catalyst for the BV oxidation[24] (Scheme 26). It has been proposed that the conformation of the chelated Criegee intermediate is regulated to allow the enantiotopos selective σ—σ* interaction with the chiral ligand **15**.

Studies into the biological and chemical asymmetric Baeyer—Villiger oxidation reactions have revealed that their stereochemistry is mainly determined by recognition of the structure of the Criegee intermediate and by regulation of the stereoelectronic requirements in its migration. Using a trial-and-error process along this line, some studies have achieved a high level of enantiotopos selectivity and regiodivergent parallel kinetic resolution in the BV oxidation of prochiral and racemic ketones, respectively. However, the chemist´s understanding of how a molecular catalyst recognizes a transition state structure and controls the conformation of the transition state is still immature. Accumulation of such knowledge will pave the way for highly efficient BV oxidation using a reasonably designed molecular catalyst.

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