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Cationic Co(III)(salen)-catalyzed enantioselective Baeyer–Villiger oxidation of 3-arylcyclobutanones using hydrogen peroxide as a terminal oxidant

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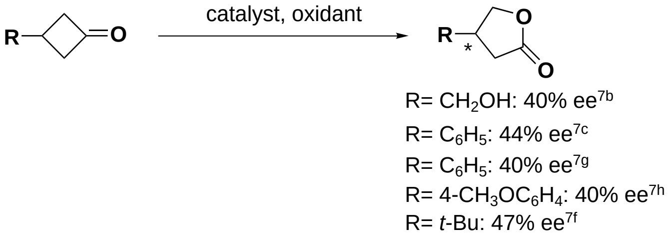
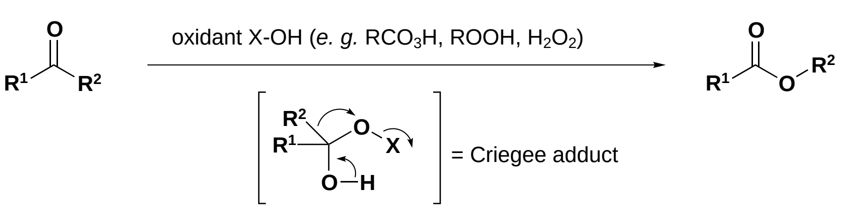
Abstract—A cationic Co(III)(salen) complex of *cis*-β-structure was found to serve as an efficient catalyst for asymmetric Baeyer–Villiger reaction of 3-substituted cyclobutanone using hydrogen peroxide as a terminal oxidant. Good enantioselectivity up to 78% ee was achieved. © 2001 Elsevier Science Ltd. All rights reserved.

Baeyer–Villiger oxidation, transformation of a carbonyl group into an ester group, is a potent synthetic tool used in a wide variety of syntheses.[1] The reaction starts with nucleophilic attack of an oxidant to the carbonyl group, and subsequent migration of the carbonyl-substituent in the intermediate Criegee adduct with retention of its configuration gives lactone (Scheme 1). The first step is accelerated by coordination of the carbonyl group to a Lewis acid. Thus, much effort has been directed to development of metal-mediated asymmetric Baeyer–Villiger (B–V) reaction.[2] In 1994, Bolm et al.[3] reported the first enantiomer-differentiating reaction of racemic 2-substituted cycloalkanone by using a Cu-bis(oxazoline) complex as the catalyst under Mukaiyama conditions (a combination of molecular oxygen and aldehyde).[4,5] Strukul et al. also reported enantiomer-differentiating B–V reaction using a chiral platinum complex as the catalyst.[6] Since then, various optically active metal complexes have been used as catalysts for asymmetric B–V reaction,[7] and good to high enantioselectivities have been achieved in the reactions of some specific substrates.[3,7a,c,8]

Prochiral 3-substituted cyclobutanones have been used as a touchstone for asymmetric B–V reaction and their B–V reactions have been studied by using the catalysts described above. However, only modest enantioselectivity has so far been achieved in these reactions (Scheme 2).



Scheme 2.



Scheme 1.

Keywords: Co(salen); asymmetric catalysis; Baeyer–Villiger oxidation; hydrogen peroxide.

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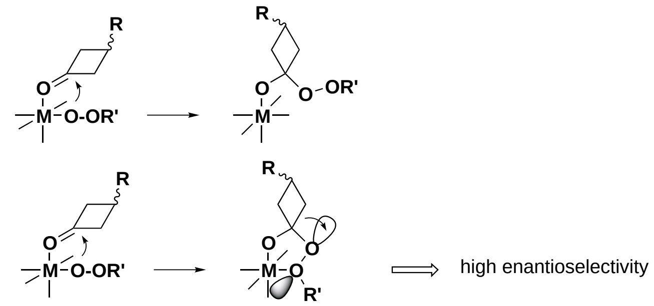
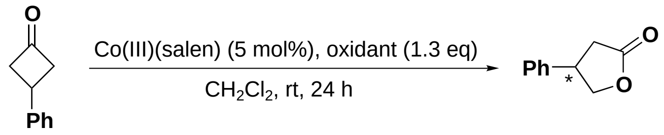


Scheme 3.

In order to achieve high enantioselectivity in these reactions, two stereochemistries must be regulated: (i) face selectivity in the formation of the Criegee adduct and (ii) enantiotopic selectivity in C–C bond migration. The face selectivity should be mainly governed by the steric factor, but the topos selectivity in the migration should be influenced by the conformation of the peroxy moiety of the adduct (Scheme 3). The C–C bond that could overlap the anti-bonding orbital of the O–O bond was considered to migrate preferentially. Thus, we expected that high enantioselectivity would be realized if the Criegee adduct forms a five-membered chelate ring with a metal center in an appropriate asymmetric atmosphere and the conformation of the O–O bond is fixed in an enantiomerically pure form.

This consideration suggested that a trigonal–bipyramidal or octahedral metal complex bearing two vacant *cis*-coordinating sites should be a suitable catalyst for asymmetric B–V reaction. We recently reported that Ti(salen) **1** of *cis*-β structure served as an efficient catalyst for asymmetric sulfoxidation (Scheme 4).[9] This titanium complex takes octahedral geometry and possesses two readily exchangeable ligands which are *cis* to each other. Thus, we examined B–V reaction with Ti(salen) **1** as the catalyst but the attempt was unsuccessful.

Table 1. Asymmetric B–V oxidation of 3-phenylcyclobutanone using Co(salen)s as the catalyst



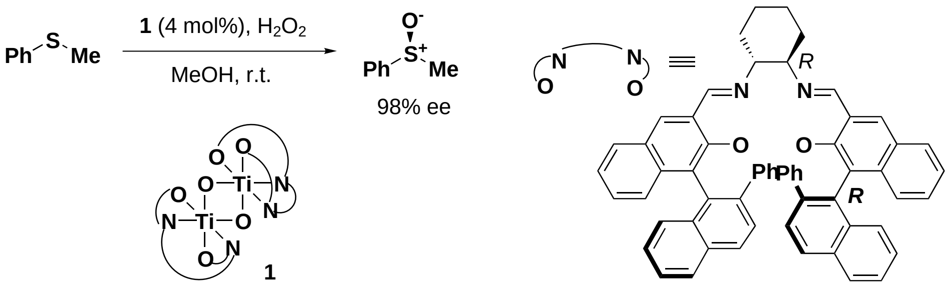
Entry	Cat.	Oxidant	Yield	% ee[a]	Config.[b]
1	**2**	H_2O_2	29	0	–
2	**2**	TBHP	72	0	–
3[c]	**2**	*m*CPBA	75	0	–
4	**3**	H_2O_2	20	0	–
5	**3**	TBHP	62	0	–
6[c]	**3**	*m*CPBA	80	0	–
7	**4**	H_2O_2	30	20	*S*
8	**4**	UHP	31	53	*S*
9	**4**	TBHP	27	0	–
10[c]	**4**	*m*CPBA	78	0	–
11	**5**	UHP	30	57	*S*
12	**6**	UHP	10	55	*S*
13	**7**	UHP	0	–	–

[a] Determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 49/1).

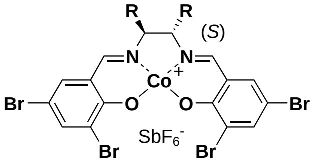
[b] Absolute configuration was determined by chiroptical comparison (Ref. 13a).

[c] Reaction was carried out at −78°C in the presence of 1 equiv. of *N*-methylmorpholine *N*-oxide.

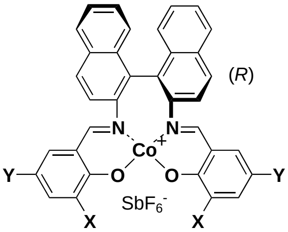
Co(III)(salen)s show high asymmetric induction[10,11] and high Lewis acidity.[11] On the other hand, Che et al. reported that iron and manganese complexes of binaphthyl Schiff base took *cis*-β structure.[12] Based on this knowledge, we next examined B–V reaction of 3-phenylcyclobutanone using cationic Co(III)(salen)s **2**–**4** as the catalyst (Table 1). Although all the catalysts promoted the desired B–V reaction, complexes **2** and **3** showed no asymmetric induction (entries 1–6). As expected, complex **4** that was considered to take a *cis*-β structure based on Che's report and to bear two vicinal coordinating sites, shows modest asymmetric induction when hydrogen peroxide, especially urea·hydrogen peroxide adduct (UHP), was used as an oxidant (entries 7 and 8). This probably suggested that the oxidants such as *t*-butyl hydroperoxide (TBHP) and *m*-CPBA attacked the carbonyl group in an intermolecular fashion giving a non-chelated Criegee adduct, while hydrogen peroxide was coordinated to the metal ion and attacked the carbonyl group to give a chelated Criegee adduct. We next examined the effect of the substituent of the salen ligand on enantioselectivity. Complexes **5** and **6** showed an equal level of enantioselectivity to complex **4** but complex **6** was less catalytically active than complexes **4** and **5** (entries 11 and 12). Introduction of an electron-donating methoxy group destroyed the catalytic activity (entry 13).



Scheme 4.



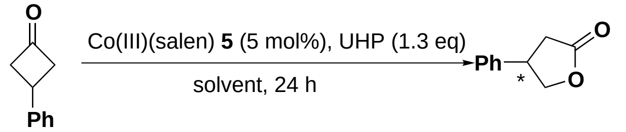
2: R= Ph
3: R= -(CH$_2$)$_4$-



4: X=Y= Br
5: X=Y= F
6: X=Y= H
7: X= MeO, Y= H

We also examined the effect of solvent and temperature on enantioselectivity (Table 2). Although specific relationship between solvent polarity and chemical yield was not observed, the reactions in polar solvents such as ethers and alcohols showed better enantioselectivities (up to 71% ee) (entries 2, 3, 4, 9, 10 and 11). The reaction at 0°C showed slightly better enantioselectivity of 75% ee with good chemical yield. It is noteworthy that 30% hydrogen peroxide can be used equally efficiently as UHP, as the terminal oxidant, when ethanol was used as the solvent (entries 6 and 7). The reaction at −20°C showed the best enantioselectivity of 77% ee. The reactions of 3-(*p*-chlorophenyl)- and 3-(*p*-methoxyphenyl)-cyclobutanones were also performed at 0°C by using aqueous hydrogen peroxide as the terminal oxidant and showed good enantioselectivity of 75 and 78% ee, respectively (Scheme 5).

Table 2. Asymmetric B–V oxidation of 3-phenylcyclobutanone using Co(salen) **5** as the catalyst

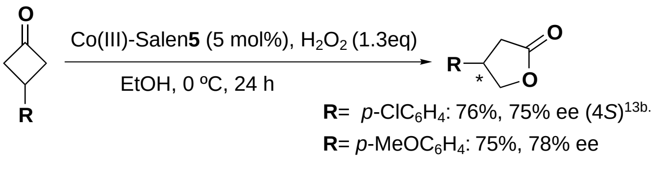


Entry	Solvent	Temp.	Yield	% ee[a]	Config.[b]
1	CH$_2$Cl$_2$	Rt	30	57	*S*
2	THF	Rt	69	70	*S*
3	CH$_3$CN	Rt	93	67	*S*
4	EtOH	Rt	87	71	*S*
5	EtOH[c]	Rt	92	69	*S*
6	EtOH	0°C	90	75	*S*
7	EtOH[c]	0°C	85	75	*S*
8	EtOH[c]	−20°C	72	77	*S*
9	MeOH	Rt	84	70	*S*
10	*i*-PrOH	Rt	92	71	*S*
11	AcOEt	Rt	87	60	*S*
12	Et$_2$O	Rt	83	69	*S*
13	Hexane	Rt	78	50	*S*
14	Benzene	Rt	22	55	*S*
15	Toluene	Rt	25	55	*S*

[a] Determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 49/1).

[b] Absolute configuration was determined by chiroptical comparison (Ref. 13a).

[c] Aqueous hydrogen peroxide (30%) was used as terminal oxidant.



R= *p*-ClC$_6$H$_4$: 76%, 75% ee (4*S*)[13b.]
R= *p*-MeOC$_6$H$_4$: 75%, 78% ee

Scheme 5.

Typical experimental procedure was exemplified by asymmetric Baeyer–Villiger reaction of 3-(*p*-methoxyphenyl)cyclobutanones with **5** as the catalyst at 0°C: 3-(*p*-methoxyphenyl)cyclobutanone (17.6 mg, 0.1 mmol) was dissolved into 0.5 ml of ethanol. To the ethanolic solution was added Co(III)(salen) complex **5** (4.3 mg, 5.0 μmol) and cooled to −20°C. To this solution was added 30% aqueous hydrogen peroxide (15 μl, 0.13 mmol) and the mixture was stirred at the temperature for 24 h. Ethanol was removed on a rotary evaporator and the residue was chromatographed on silica gel (hexane:AcOEt = 45:7) to give 3-(*p*-methoxyphenyl)butyrolactone (14.5 mg, 75%). The enantiomeric excess of the lactone was determined to be 78% ee by HPLC analysis using DAICEL CHIRALPAK AD-H (hexane:*i*-PrOH = 19:1).

In conclusion, we were able to demonstrate that a Lewis acidic metal complex bearing two vicinal open coordinating-site, can be a catalyst for asymmetric Baeyer–Villiger reaction. Further study is under progress in our laboratory.

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13. (a) Specific rotation of 4-phenylbutyrolactone (77% ee): $[\alpha]_{\mathrm{D}}^{24} = +37.0°$ (*c* 0.53, MeOH); lit.[7h] (*S*-isomer): $[\alpha]_{\mathrm{D}}^{20} = +50.4°$ (*c* 5, MeOH); (b) Specific rotation of 4-(*p*-chlorophenylbutyrolactone (75% ee): $[\alpha]_{\mathrm{D}}^{24} = +39.8°$ (*c* 0.47, $CHCl_3$); lit.[7h] (*S*-isomer): $[\alpha]_{\mathrm{D}}^{20} = +46.5°$ (*c* 0.5, $CHCl_3$).