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# Co(III)-Salen Catalyzed Carbenoid Reaction: Stereoselective [2,3]Sigmatropic Rearrangement of S-Ylides Derived from Allyl Aryl Sulfides

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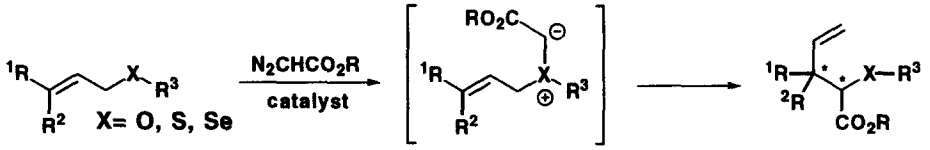
**Abstract:** Allyl aryl sulfides and diazoacetic acid esters react in the presence of optically active Co(III)-salen complex (4) with good enantioselectivity, to give the [2,3]sigmatropic rearrangement products, 2-arylthio-3-aryl-4-pentenoic acid esters, via the corresponding S-ylides. © 1997 Elsevier Science Ltd.

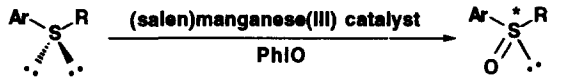
Carbon-carbon bond formation introducing asymmetric center(s) provides a very efficient method for the construction of sterically complex molecules. One such reaction is the [3,3]- or [2,3]sigmatropic rearrangement which has been widely used in the synthesis of various natural products. However, this type of reaction is a self-immolative asymmetric synthesis,[1] wherein the chirality in the substrate is transferred into the product while the original chirality is decayed, and examples of catalytic and enantioselective sigmatropic rearrangement are still rare.[2] A few years ago, Doyle *et al.* reported that the reaction of allyl ether and diazoacetate in the presence of $Rh_2(OAc)_4$ proceeded with moderate to good diastereoselectivity (79:21-97:3), giving the corresponding [2,3]sigmatropic rearrangement products by way of the intermediary oxonium ylides (Scheme 1, X= O).[3] However, no asymmetric version of this reaction has been reported. In 1995, Uemura *et al.* reported the [2,3]sigmatropic rearrangement of allylic charcogen-ylides that were prepared by the reaction of allylic sulfides or selenides with diazoacetate using Cu(I)-bis(oxazolines) or $Rh_2(5S\text{-MEPY})_4$ as a catalyst (Scheme 1, X= S or Se). These reactions proceeded with moderate enantioselectivity (up to 41% ee).[2]




**Scheme 1**

On the other hand, we recently found that the well-designed (salen)manganese(III) complex is an efficient catalyst for asymmetric oxidation of alkyl aryl sulfides (Scheme 2).[4] Furthermore, we also found that a (salen)cobalt(III) complex is an efficient catalyst for asymmetric cyclopropanation of styrene derivatives using diazoacetate as a carbenoid source (up to 96% ee). This reaction has been considered to proceed through an intermediary cobalt-carbenoid species and we expected that the reaction of allylic sulfides and diazoacetate in the presence of a (salen)cobalt(III) complex (hereafter referred to as Co-salen complex) would proceed with high enantioselectivity to give the corresponding S-ylide which undergoes [2,3]sigmatropic rearrangement.[5] Along this line, we examined the stereoselective [2,3]sigmatropic rearrangement of the S-ylide which is derived from allyl aryl sulfides and α-diazoacetates *in situ* in a catalytic and enantioselective manner using an optically active

(salen)cobalt(III) complex as a catalyst.




**Scheme 2**

We first examined the reaction using cinnamyl phenyl sulfide and *tert*-butyl diazoacetate as test materials (Table 1). Since we have found that Mn-salen catalyzed asymmetric epoxidation and asymmetric oxidation of sulfides have common features in many respects,[6] we also expected that Co-salen catalyzed asymmetric cyclopropanation and S-ylide formation would also show many similar features. Since Co-salen catalysts bearing substituents at 3- and 3'-carbons showed no catalytic activity for asymmetric cyclopropanation, we examined S-ylide formation with Co-salen catalysts (**1**-**4**) bearing no 3,3'-substituent.[7] All the reactions examined showed a similar level of diastereomer ratio (the ratio of *anti*- and *syn*-isomers), while enantiomeric excess of the major isomer was dependent on the catalysts used (entries 1-4). The catalyst bearing electron-donating methoxy groups exhibited slightly better asymmetric induction than the catalyst bearing bulky *tert*-butyl groups. Finally, catalyst **4** was found to show the best enantioselectivity of 64% ee. This strongly suggests that differentiation of the enantiotopic lone pair electrons on the sulfur atom is dictated by the chirality of the Co-salen complex but diastereoselectivity is determined by the difference in the potential energy of the two transition states (**A** and **B**). This also suggests that the S-ylide does not coordinate with the Co-salen catalyst.[8] The reaction of cinnamyl *o*-methoxyphenyl sulfides also showed a similar level of stereoselectivity (entries 5 and 6). To further improve both enantioselectivity and diastereoselectivity, we next examined the reaction using (-)-menthyl diazoacetate as a diazo compound. Both the enantioselectivity in S-ylide formation and *syn-anti* ratio of the product was improved to 74% ee and to 93:7, respectively, as expected (entry 7). This means that the sense of asymmetric induction by the (-)-menthyl moiety matches that achieved with the use of the Co-salen catalyst.

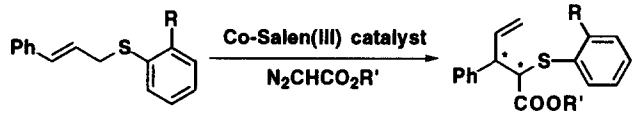
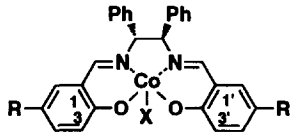


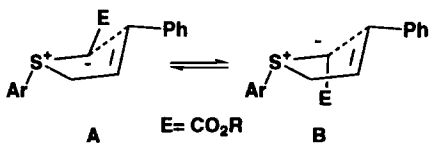

**Table 1.** Co-salen Catalyzed Asymmetric [2,3]sigmatropic rearrangement.

| Entry | Catalyst | R | R' | Yield (%) | *anti* : *syn*[a] | % ee[b] |
|---|---|---|---|---|---|---|
| 1 | **1** | H | *t*-Bu | 74 | 83:17 | 47[c] |
| 2 | **2** | " | " | 64 | 82:18 | 50[c] |
| 3 | **3** | " | " | 86 | 83:17 | 43[c] |
| 4 | **4** | " | " | 81 | 85:15 | 64[c] |
| 5 | **2** | OMe | " | 72 | 86:14 | 53[c] |
| 6 | **4** | OMe | " | 75 | 83:17 | 60[c] |
| 7 | **4** | H | (-)-menthyl | 68 | 93:7 | 74[d,e] |

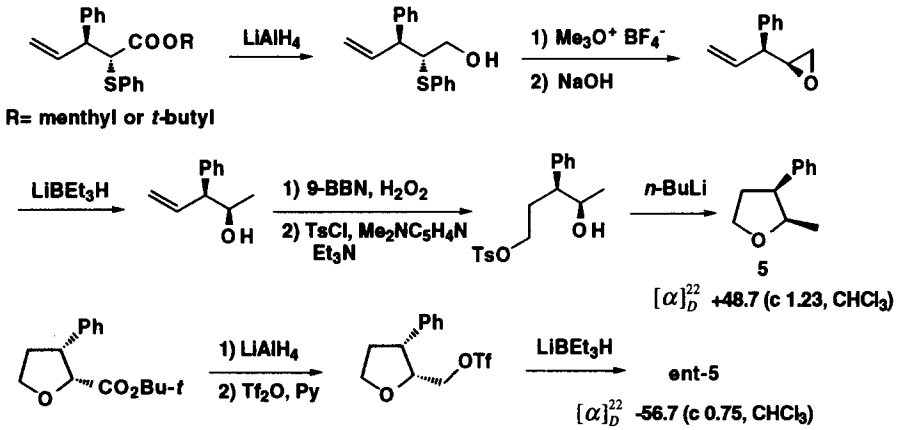
a) Determined by $^1$H NMR analysis (270 MHz).
b) The enantiomeric excess of the *anti*-isomer unless otherwise noted.
c) Determined by HPLC analysis using DAICEL CHIRALPAC AD (hexane/*i*-PrOH = 100/1).
d) The diastereomeric excess of the *anti*-isomer.
e) Determined by $^1$H NMR analysis (400 MHz).



**1**: R= *t*-Bu, X= I
**2**: R= OMe, X= I
**3**: R= *t*-Bu, X= Br
**4**: R= OMe, X= Br

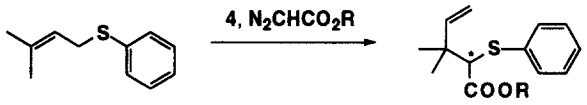


Configuration of the major isomer was determined to be 2*R*,3*S* by chemical correlation and chiroptical comparison (Scheme 3). The major *anti*-isomer was converted into (2*R*,3*S*)-2-methyl-3-phenyltetrahydrofuran **5** by using stereochemically well-established methods. On the other hand, stereochemically defined compound **ent-5** was derived from *tert*-butyl (2*R*,3*R*)-3-phenyltetrahydrofurancarboxylate.[9]

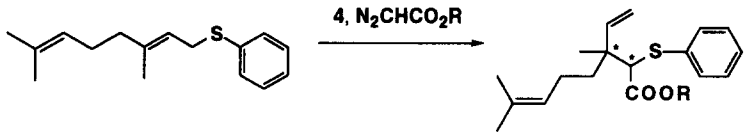



**Scheme 3**

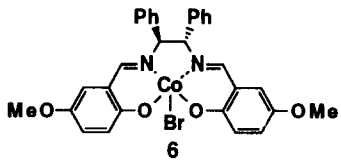
To clarify the scope of the reaction, we further examined the reactions of 3-methyl-2-butenyl phenyl sulfide and geranyl phenyl sulfide (Eqs 1 and 2). The reaction of 3-methyl-2-butenyl phenyl sulfide and (-)-menthyl diazoacetate in the presence of catalyst **4** proceeded with good stereoselectivity of 74% de.[10] As expected from the previous result that the sense of asymmetric induction by catalyst **4** matched that by (-)-menthyl moiety (*vide supra*), the same reaction in the presence of **6**, which is the enantiomer of **4**, showed low selectivity (8% de). The reaction of geranyl phenyl sulfide also proceeded with good stereoselectivity.[11]




(1)




(2)




6

Typical experimental procedure was exemplified by the reaction of cinnamyl phenyl sulfide and *tert*-butyl diazoacetate using complex **4** as a catalyst: To a dichloromethane solution (11.8 ml) of the Co(II)-salen complex[12] (53.7 mg, 0.1 mmol) was added a solution of $Br_2$ (0.12 M, 0.05 mmol) in dichloromethane (407 μl)

and the mixture was stirred for 1h at room temperature to give Co(III)-salen complex **4**. To this solution was added a mixture of cinnamyl phenyl sulfide (453 mg, 2.0 mmol) and dichloromethane (11.8 ml) and the mixture was stirred for another 10 min. *tert*-Butyl diazoacetate (281 μl, 2.0 mmol) was added to the mixture at room temperature, stirred for 24 h, and then concentrated *in vacuo*. The residue was passed through a silica gel column (hexane-AcOEt=1:0 to 30:1) to give a 85:15 mixture of isomers (554 mg, 81%). The % ee was determined as described in the footnote to Table 1 (entry 4).

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† Research Fellow of the Japan Society for the Promotion of Science.

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6 Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189-214.

7 Co-salen catalysts bearing substituents at 3- and 3'-carbons showed very poor catalytic activity for S-ylide formation reaction, as expected.

8 This means that % ees of major and minor isomers should be equal. Actually, both the isomers obtained with **4** and *tert*-butyl diazoacetate showed the same enantioselectivity of 64% ee (Table 1, entry 4).

9 Ito, K.; Yoshitake, M.; Katsuki, T. *Heterocycles* **1996**, *42*, 305-317.

10 The reaction gave a mixture of two diastereomers with $[\alpha]_D^{22} = +24.8°$ (*c* 1.97, $CHCl_3$). The diastereomers could not be separated.

11 Configuration of the major diastereomer was tentatively assigned to be *anti* by the mechanical analogy with [2,3]sigmatropic rearrangement of the S-ylide derived from cinnamyl phenyl sulfide.

12 The Co(II)-salen complex was prepared from $Co(OAc)_2$ and the corresponding Schiff base which was in turn prepared from 2-hydroxy-5-methoxybenzaldehyde and (1*R*,2*R*)-1,2-diphenylethylenediamine.

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