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Coordination Chemistry Reviews 237 (2003) 245–256

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Vanadium-catalyzed asymmetric oxidations

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Received 25 January 2002; accepted 5 September 2002

Contents

Abstract

Chirally modified vanadium complexes have been used as catalysts in enantioselective epoxidations of allylic alcohols and asymmetric sulfide to sulfoxide oxidations. For both reactions various combinations of chiral ligands and vanadium sources have been tested. The results of previous work and those of current investigations are discussed and details of the catalysis with respect to enantioselectivity and catalyst turnover is presented.

Keywords: Asymmetric catalysis; Enantioselectivity; Epoxides; Sulfoxides; Vanadium

1. Introduction

Asymmetric metal catalysis is in the focus of current chemical research, and in recent years several major breakthroughs have been achieved [1]. It was therefore not surprising that the 2001 Nobel Prize in Chemistry was awarded to three scientists for their development of catalytic asymmetric synthesis. The Royal Swedish Academy of Sciences recognized the contributions by William S. Knowles and Ryoji Noyori ‘on chirally catalyzed hydrogenation reactions’, and by K. Barry Sharpless ‘for his work on chirally catalyzed oxidation reactions’ [2]. Their fundamental findings expand the scope of asymmetric synthesis and allow a more targeted preparation of pharmaceutical products such as antibiotics, anti-inflammatory drugs and other medicines.

2. Enantioselective vanadium-catalyzed epoxidations of allylic alcohols

It was one of the 2001 Nobel Prize laureates, Sharpless and coworkers, who reported on a highly promising asymmetric vanadium catalyst as early as 1977 [3]. A combination of $VO(acac)_2$ and chiral hydroxamic acid **3** afforded optically active epoxides from the corresponding allylic alcohols such as **1** and *tert*-butyl hydroperoxide (TBHP) as oxidant with up to 50% ee (Scheme 1). With a proline-derived hydroxamic acid as chiral ligand, higher enantioselectivities (up to 80% ee) could be achieved by the same authors a few years later [4,5].

Although the enantioselectivity in this vanadium-catalyzed asymmetric epoxidation was not perfect, the process was considered a major success, because it allowed a straightforward synthesis of highly valuable synthetic intermediates (chiral epoxides) [6] from readily available starting materials (allylic alcohols). Disadvantages were the requirement of a fivefold excess of ligand

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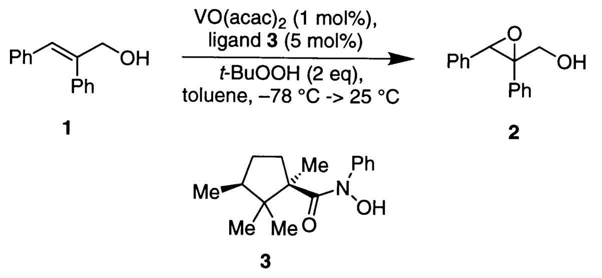
PII: S0010-8545(02)00249-7



Scheme 1. Asymmetric epoxidation according to Sharpless [3].

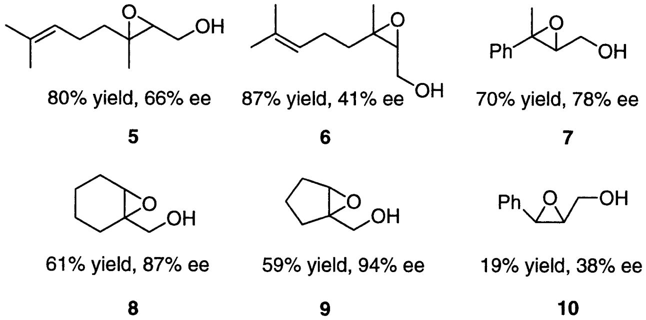
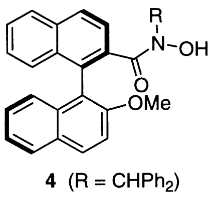


Chart 1. Epoxides and ee-values obtained with Yamamoto's chiral catalyst.

with respect to vanadium and the pronounced 'ligand-deceleration' [7], which reduced the catalytic efficiency. A few years later, the attention was drawn to another epoxidation reaction discovered by Sharpless and coworkers [8], which is still considered to be one of the most reliable methods in asymmetric oxidation catalysis. With TBHP as oxidant and in the presence of a combination of titanium tetraisopropoxide and tartrate ligands, allylic alcohols are converted to epoxides with very high enantioselectivities. The reaction is ligand-accelerated [7], can be performed catalytically and is applicable to a wide range of substrates [9]. After a period of detailed mechanistic studies and the establishment of its broad applicability, the Ti-catalyzed Sharpless epoxidation was regarded as state of the art, and many further investigations were directed towards the development of epoxidation protocols of *unfunctionalized* olefins [6d,6e,6f,6g,6h,6i,6j,6k,6l,6m,6n].

For almost two decades Sharpless' vanadium-catalyzed epoxidation of allylic alcohols remained undeveloped. In 1999, however, Yamamoto and coworkers reported on an improvement of the existing protocol, which allowed one to obtain epoxyalcohols with up to 94% ee [10]. From a series of axially-chiral ligands hydroxamic acid **4** proved to be the most efficient one (Fig. 1).

Remarkably and in contrast to the previous systems, only a small excess of ligand (7.5 mol%) with respect to vanadium [5 mol% of VO(O–*i*-Pr)$_3$] was required for high enantioselectivity. This result was interpreted as evidence for the formation of a 1:1 complex between vanadium and the hydroxamic acid. Use of triphenylmethyl hydroperoxide (TrOOH) as oxidant gave better results than application of TBHP or cumene hydroperoxide (CHP). By the use of toluene, chlorinated solvents such as dichloromethane could be avoided. Unfortunately, low temperatures (−20 °C) and extended reaction times (2–3 days) were required for high ee and yield, respectively. Chart 1 lists representative examples of optically active epoxides which became accessible from the corresponding allylic alcohols through the catalysis with this system [10].



4 (R = CHPh$_2$)

Fig. 1. Yamamoto's axially-chiral hydroxamic acid used in vanadium catalysis [10].

To increase the efficiency of this vanadium catalysis further progress was required in particular with respect to enantioselectivity, catalyst loading, type of oxidant, and reaction conditions. Based on his previous studies Yamamoto introduced a novel amino acid-based hydroxamic acid and demonstrated its applicability in the catalysis under discussion [11]. An iterative positional optimization approach [12] was used to find the most efficient ligand structure. In this protocol every component of the ligand is individually optimized for selectivity by varying its structure, while other units are kept constant. Previously, it had been demonstrated that a sequential screening of all variables could then lead to synthetically interesting catalysts [12]. In this particular case, Hoshino and Yamamoto found that hydroxamic acid **11** derived from *tert*-leucine was the most efficient ligand reaching enantioselectivities of up to 96% ee in the vanadium-catalyzed epoxidation reaction (Fig. 2).

Besides the high enantioselectivity the most remarkable aspects of this new catalytic system were the low catalyst loading (1 mol% of VO(O–*i*-Pr)$_3$ and 1.5 mol% of ligand), the possibility to use TBHP as oxidant, and the mild reaction conditions (6 h at 0 °C). Chart 2 shows representative examples (epoxides obtained from the corresponding allylic alcohols under conditions

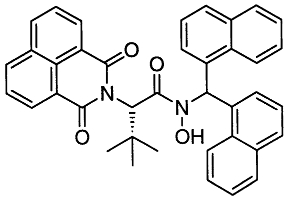


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Fig. 2. Yamamoto's amino acid-derived hydroxamic acid used in vanadium catalysis [11].

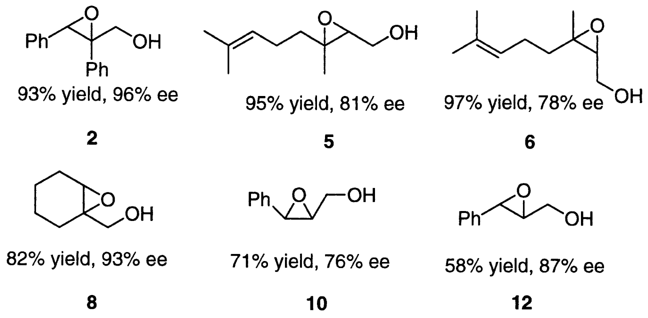


Chart 2. Epoxides and ee-values obtained with a chiral catalyst based on **11**.

which in some cases varied from the standard ones mentioned above) and reveals that this catalysis is especially suited for transformations of disubstituted allylic alcohols [11].

^{51}V-NMR studies were performed with the intention to reveal more details of the catalyst structure [11]. At room temperature in benzene-d_6 a 1:1 mixture of VO(O–i-Pr)$_3$ and **11** gave two signals. These peaks had a ratio of 95:5 at a metal-to-ligand ratio of 1:1.5 (catalysis conditions). Whereas the first signal (−537 ppm) was proposed to derive from VO(O–i-Pr)$_2$(L) (with L = the hydroxamate of **11**), the second (−633 ppm) was assigned as due to VO(O–i-Pr)$_3$. As a consequence, a species obtained from a 1:1 complexation of vanadium and ligand was proposed to be responsible for the good catalytic performance and the high enantioselectivity. This proposal is in accordance with the previous data interpretation given by Sharpless and coworkers refering to their proline-derived system [3].

At about the same time, two other approaches were reported which were directed towards an optimization of the vanadium-catalyzed epoxidation of allylic alcohols. One of them involved the synthesis and use of hydroxamic acids **15** and was described by Park and coworkers [13]. Starting from enantiopure amine **13** and through the intermediacy of hydroxylamine **14**, chiral hydroxamic acids **15** were obtained in a short reaction sequence (Scheme 2).

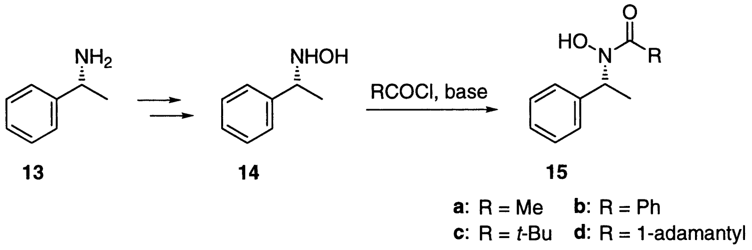
In contrast to the ligands mentioned in the previous reports, the new hydroxamic acids **15** have the sterogenic center α to the amine nitrogen. Four compounds were described and surprisingly, the steric and electronic properties of the substituent R had little effect on the enantioselectivity. Finally, the authors concluded that the hydroxamic acid bearing the least sterically demanding methyl group (**15a**) was the ligand of choice for most substrates. As oxidant, TBHP proved superior to CHP. Using 5 mol% of VO(acac)$_2$ and 15 mol% of ligand the ee-values ranged from 1 to 95%. The highest enantioselectivities (e.g. 95% ee for epoxide **2**) were obtained in reactions run at −20 °C. Unfortunately, under these conditions the reaction time was between 5 and 7 days. Interestingly, in some cases the R group and the temperature had a strong impact on the stereochemistry, and both could be used to reverse the absolute configuration of the product [13].

All hydroxamic acids introduced by Sharpless, Yamamoto, Park and Hong for the vanadium catalyzed epoxidation of allylic alcohols had either stereogenic centers or chiral axes. In 2000, the use of planar-chiral hydroxamic acids in this catalysis was described by Bolm and Kühn for the first time [14]. Previously, planar-chiral ligands had already been applied in other asymmetric catalyses, and the importance of the chiral plane on the extent of enantioselectivity had been demonstrated [15]. In this particular case, two types of planar-chiral compounds were tested. The first class belonged to the ferrocene series and involved hydroxamic acids **17**, **19** and **20** [16]. Those ferrocenes were readily available through well-established reaction sequences, which involved either the intermediacy of sulfoxide **16** [17] or oxazoline **18** [18] (Scheme 3).

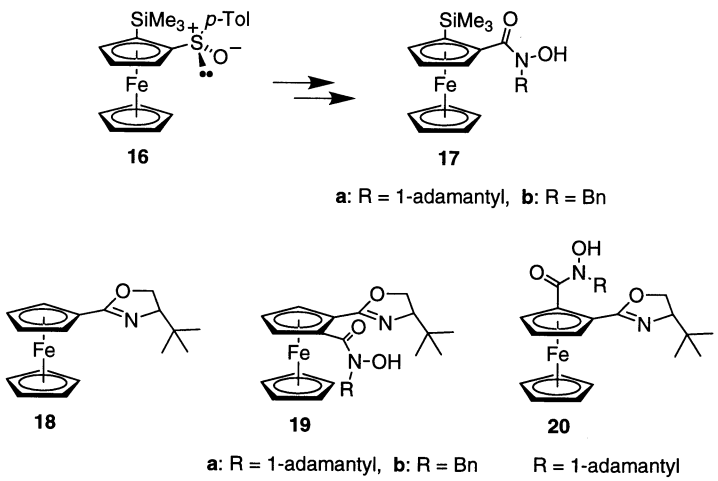
Unfortunately, with these ferrocene-type hydroxamic acids as ligands, the enantioselectivity in the vanadium-catalyzed asymmetric epoxidation of **21** remained low, and **22** was only obtained with a maximum enantiomeric excess of 33% (Scheme 4, Table 1) [16].

Interestingly, hydroxamic acids with larger substituents (adamantyl versus benzyl) gave higher enantioselectivities (Table 1, entries 1/2 and 3/4), and the planar-chirality determined the absolute configuration of the product (Table 1, entries 3/5) [16].

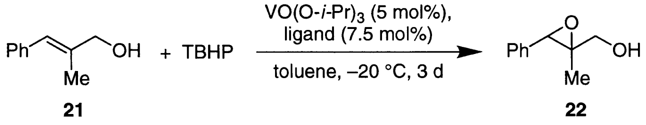
The second class of planar-chiral compounds studied by Bolm and Kühn were hydroxamic acids **24** having a [2.2]paracyclophane backbone [14]. Recently, asymmetric catalysis with chiral [2.2]paracyclophanes has



Scheme 2. Synthesis of a hydroxamic acid with a stereogenic center α to nitrogen [13].



Scheme 3. Planar-chiral hydroxamic acids based on ferrocenes [16].



Scheme 4. Asymmetric epoxidation of allylic alcohol **21**.

Table 1
Enantioselectivities from catalyses with ferrocene ligands

Entry	Ligand	Yield of **22** (%)	Ee of **22** (%)	Absolute configuration of **22**
1	**17a**	82	33	(*R*,*R*)
2	**17b**	77	12	(*R*,*R*)
3	**19a**	72	21	(*S*,*S*)
4	**19b**	76	13	(*S*,*S*)
5	**20**	89	20	(*R*,*R*)

attracted significant attention, and a number of compounds have successfully been applied as ligands in various transformations [19]. In the investigations by Bolm and Kühn, the hydroxamic acids **24** were accessed from the enantiopure [2.2]paracyclophane-4-carboxylic acid **23** [20] by reaction of its acid chloride (not shown) with the corresponding *N*-hydroxylamines (Fig. 3).

In a first screening, catalyses with **24** as ligands and CHP as oxidant gave high yields (> 86%) and enantioselectivities of up to 52% ee in the transformation of **21** to **22** (Scheme 4) [14]. Surprisingly, bulky aliphatic substituents at the nitrogen of **24** led to an increase in enantioselectivity compared to aromatic groups (Table 2). This observation was in contrast to the observations by Yamamoto and coworkers with their ligand **4** [10].

Optimizing the reaction conditions revealed that performing the catalysis at −20 °C in toluene gave the best results [14]. Furthermore, TBHP proved a better oxidant than CHP, trityl hydroperoxide (TrOOH) and 1-methylcyclohexyl hydroperoxide (MCYHP) affording **22** with higher enantiomeric excesses. Thus, under the optimized conditions and by using a combination of 5 mol% of $V(O)(O{-}i\text{-}Pr)_3$ and 7.5 mol% of **24c** as ligand, **22** was obtained with up to 71% ee. Other substrates reacted too and gave the corresponding epoxides with ee-values in the range of 38–55% (Chart 3).

Studies on the effect of the ligand-to-metal ratio showed that a lower ratio than the commonly used 1.5:1 afforded products with slightly reduced ee (67% ee with 5.5 mol% of **24c** vs. 71% ee with 7.5 mol%). Interestingly, the catalysis was inhibited when the ligand-to-metal ratio was 3. This observation was surprising because in some other systems at least a threefold ligand excess was required to obtain high enantioselectivity. It was proposed that in reactions with

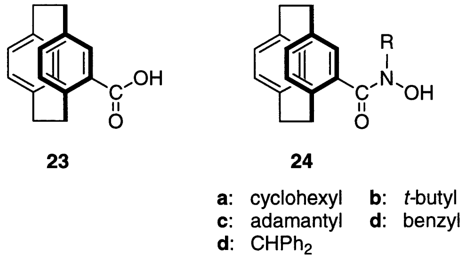


Fig. 3. [2.2]Paracyclophanes used in a vanadium-catalyzed enantioselective oxidation [14].

Table 2
Enantioselectivities from catalyses (**21** → **22**) with ligands **24** and CHP [a]

Entry	Ligand	Yield of **22** (%)	Ee of **22** (%)
1	**24a**	90	42
2	**24b**	86	46
3	**24c**	88	52
4	**24d**	87	32
5	**24e**	86	30

[a] Conditions as in Scheme 4.

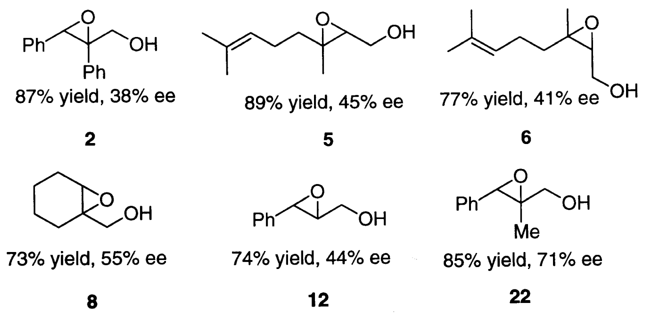


Chart 3. Epoxides and ee-values obtained with the [2.2]paracyclophane-based catalyst system.

24 either, achiral $VO(O{-}i\text{-}Pr)_3$ is more efficiently converted to an optically active vanadium species such as $VO(O{-}i\text{-}Pr)_2(L)$ (with L = the hydroxamate of **24**) or compounds $VO(O{-}i\text{-}Pr)_{3-x}(L)_x$ ($x = 1$ or 2) do not show such a significant ligand-deceleration as observed with the other ligands [14].

An interesting extension of the study on the application of [2.2]paracyclophane-based hydroxamic acids in vanadium-catalyzed oxidations focused on the use of a chiral oxidant [21]. Various achiral hydroperoxides were first tested in catalysis using **21** as substrate and **24b** as ligand (5 mol% of vanadium, 7.5 mol of **24b**). The presence of aryl groups in the oxidant had a detrimental effect on the enantioselectivity of the epoxidation (Table 3, entries 1–4). Related observations were made in oxidations giving epoxide **5**.

Next, a chiral oxygen source was tested. Enantiopure (*S*)-(1-phenyl)ethyl hydroperoxide is available by enzymatic kinetic resolution [22] and has been demonstrated to serve as an efficient chiral oxygen source in various asymmetric oxidations [23]. When this optically active hydroperoxide was applied in an epoxidation with a catalyst derived from (*S*)-**24b**, epoxide **22** with 2*S*,3*S*-configuration and an ee of 33% was obtained (Table 3, entry 5). With the enantiomeric (*R*)-**24b** as ligand (entry 6), the ee of **22** was 63% and the absolute configuration of the product was opposite (2*R*,3*R*). The combination of (*S*)-**24b** and racemic(1-phenyl)ethyl hydroperoxide (entry 7) afforded the product with 49% ee having 2*S*,3*S*-configuration as in the first case. From these results it follows, that the absolute configuration of the product is determined by the [2.2]paracyclophane ligand and not by the chiral oxygen source. The difference in the enantioselectivity (63 vs. 33% ee) indicates matched and mismatched combinations between ligand and oxidant. The intermediate ee-value for the reaction with the racemic oxidant, which is between the ones of the experiments with the single enantiomers, demonstrates that both diastereomeric combinations of the chiral ligand and the chiral hydroperoxide react at about the same rate. This general trend was confirmed in catalyses which utilized geraniol as substrate to give epoxide **5** as product [21].

A recent report by Wu and Uang involves the use of camphor based hydroxamic acids **25** and **26** in the vanadium-catalyzed epoxidation of allylic alcohols [24]. An extensive ligand screening revealed that, surprisingly, in the transformation of **1** to give **2** *N*-unsubstituted ligands (**25** with R = H) gave the highest enantioselectivities. Use of ligands with steric bulk at this position (e.g. R = benzyl, diphenylmethyl, or adamantyl) afforded products with much lower enantiomeric excesses (Fig. 4).

Finally, the ligand optimization led to hydroxamic acid **26** having aromatic substituents at the double bond (R′ = aryl). Table 4 summarizes some results from this study [24].

With a ligand **26** having a *p*-*tert*-butylphenyl substituent (R′) and with TBHP as oxidant an ee of 75% was reached in the reaction of **1** to give **2**. Remarkably, the yields were high even after relatively short reactions times (3 h at 0 °C; entries 3 and 4) being rapid compared to other systems. Thus, at the present stage these new catalysts with the camphor-based ligands

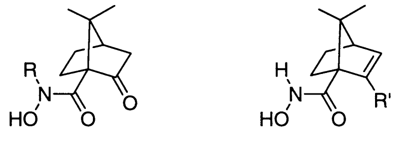


Fig. 4. Camphor-derived hydroxamic acids for asymmetric oxidations [24].

Table 3
Use of various oxidants in the reaction of **21** to give **22**

Entry	Oxidant [a]	Absolute configuration of **24b**	Ee of **22** (%)	Absolute configuration of **22**
1	**a**	*S*	72	2*S*,3*S*
2	**b**	*S*	51	2*S*,3*S*
3	**c**	*S*	46	2*S*,3*S*
4	**d**	*S*	42	2*S*,3*S*
5	(*S*)-**e**	*S*	33	2*S*,3*S*
6	(*S*)-**e**	*R*	63	2*R*,3*R*
7	*rac*-**e**	*S*	49	2*S*,3*S*

[a] **a**: TBHP; **b**: MCYHP; **c**: CHP; **d**: TrOOH; **e**: PhCH(OOH)Me.

Table 4
Results from catalyses (**1**→**2**) with ligands **26** [a]

Entry	**26** with R′	Yield of **2** (%)	Ee of **2** (%)
1	Ph	85	70
2	Tol	89	70
3	*p*-*t*-Bu–Ph	86	75
4	1-Naphthyl	88	73

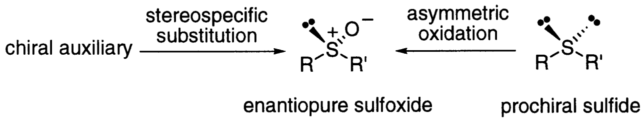
[a] VO(O–*i*-Pr)$_3$ (5 mol%), ligand (7.5 mol%), TBHP, 0 °C, 3–6 h.

appear highly promising, even though a final evaluation of their catalytic efficiency will only be possible after an investigation the scope of the substrate.

3. Asymmetric sulfide oxidations with chiral vanadium complexes

Chiral sulfoxides are important compounds in asymmetric synthesis [25,26], and more recently, their use as ligands in enantioselective catalysis has been demonstrated [27]. Of particular interest is the application of sulfoxides in biologically active systems [28]. Several methods for the synthesis of highly enantiomerically enriched sufoxides have been developed. Most of them rely on the use of chiral auxiliaries and metal catalysts involving stereospecific substitutions and enantioselective sulfide oxidations, respectively [29]. Enzymatic systems giving optically active sulfoxides have also been reported [30] (Scheme 5).

Among the metal catalysts for asymmetric sulfide oxidation titanium-based systems are the most prominent ones. After the very early work by Kagan [31] and Modena [32] in 1984, titanium catalysts received significant attention and major progress has been achieved in terms of catalyst activity and enantioselectivity [33].



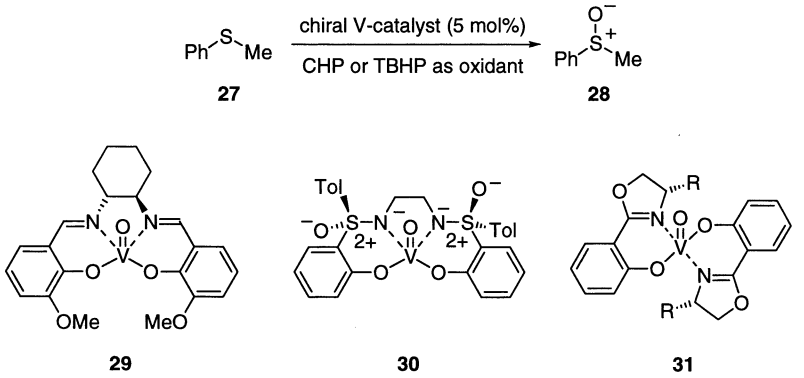
Scheme 5. General ways for the preparation of enantiopure sulfoxides.

Sulfoxidations with vanadium complexes have also been in the focus of many investigations, and the mechanisms of several catalyses have been studied in detail [34,35]. In 1986 Nakajima et al. reported on the application of catalysts bearing chiral salen-type ligands in enantioselective sulfide oxidations [36]. Using 10 mol% of tetradentate Schiff base-oxovanadium(IV) complex **29** (5 mol%) as catalyst and CHP as oxidant they achieved an enantioselectivity of 42% ee in the oxidation of methylphenyl sulfide (**27**) to the corresponding sulfoxide **28** (Scheme 6).

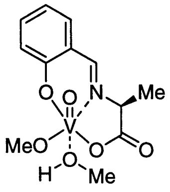
Bolm et al. attempted catalytic asymmetric sulfoxidations with vanadium(IV) complexes **30** [37] and **31** [5] having C_2-symmetric bissulfoximines and oxazolinylphenols, respectively, as ligands. Both types of catalysts showed high activity, but unfortunately, the products were racemic. Presumably, the oxidative conditions led to the formation of vanadium(V) intermediates which were unable to catalyze the sulfoxidation in an enantioselective manner.

The structurally well-characterized oxovanadium(V) complex **32** having an amino acid-derived tridentate –O–N–O-type Schiff base as ligand was reported by Fujita and coworkers to give optically active sulfoxide **28** in the asymmetric oxidation of **27** with TBHP as oxidant. However, even with 10 mol% of catalyst the highest enantioselectivity was only 14% ee [38] (Fig. 5).

In the light of these early results, the behavior of the oxidation catalyst formed in-situ from Schiff-bases **33** and vanadyl acetylacetonate introduced by Bolm and Bienewald in 1995 was remarkable [39]. For example, with this system 1 mol% of catalyst (or even 0.01 mol%) was sufficient to give optically active sulfoxides (with up to 85% ee). Furthermore, the simple reaction conditions which allow one to perform the catalysis in open vessels and the use of safe and inexpensive hydrogen peroxide as oxidant make this catalysis particularly attractive for large scale applications [40].



Scheme 6. Chiral vanadium(IV) complexes in sulfide to sulfoxide oxidations.



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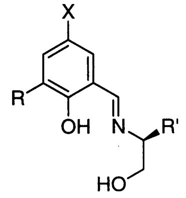


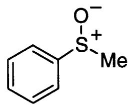
33

a: $R = R' = t\text{-Bu}, X = NO_2$
b: $R = R' = X = t\text{-Bu}$
c: $R = Ph, R' = i\text{-Pr}, X = NO_2$

Fig. 5. Oxovanadium complex and Schiff-base ligands for asymmetric sulfoxidations [38,39].

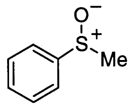
Since Schiff-bases **33** were readily available from salicylaldehydes and amino alcohols a number of compounds could easily be screened on their performance as ligands in the vanadium-catalyzed asymmetric sulfide oxidation [41]. The best results were obtained with **33** derived from *tert*-leucinol ($R' = t$-Bu). The substituent in the 3 position of the aryl group (R) had to be bulky as well, and the highest enantioselectivities were achieved with compounds having $R = tert$-butyl. The importance of electronic factors was indicated by the influence of the remote substituent X on the ee of the sulfoxidation products. Depending on the substrate, X had to be a nitro (as in **33a**) or a *tert*-butyl group (as in **33b**) for achieving the optimal enantioselectivity in the catalysis. A selection of the most significant results is shown in Chart 4.

The highest enantioselectivities were observed in the oxidation of dithioacetals [42]. These results are particularly interesting because the synthetic value of the resulting oxides has been described in numerous reports [43]. In contrast to the oxidation of simple sulfides, **33b** having a *tert*-butyl substituent in the 5 position proved superior over **33a** with a nitro group in the same position. Using a combination of 1 mol% of $VO(acac)_2$ and 1.5 mol% of **33b** as in-situ catalyst the results presented in Chart 5 were obtained.



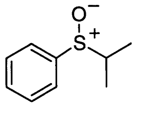
28

94% yield, 70% ee
(with **33a**)



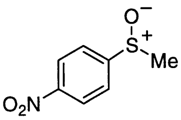
28

73% yield, 59% ee
(with **33b**)



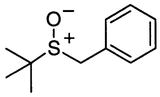
34

64% yield, 62% ee
(with **33a**)



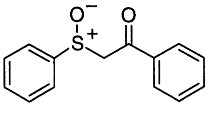
35

55% yield, 63% ee
(with **33a**)



36

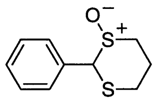
91% yield, 65% ee
(with **33a**)



37

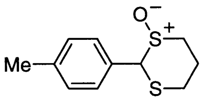
65% yield, 57% ee
(with **33b**)

Chart 4. Sulfoxides and ee-values obtained with the in-situ catalyst prepared from $VO(acac)_2$ and **33a** and **33b** as ligands [39].



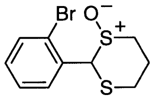
38

84% yield, 85% ee



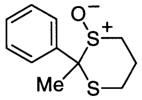
39

79% yield, 77% ee



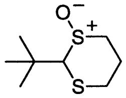
40

81% yield, 64% ee



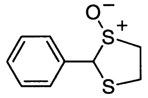
41

44% yield, 68% ee (*cis*)
37% yield, 12% ee (*trans*)



42

67% yield, 46% ee



43

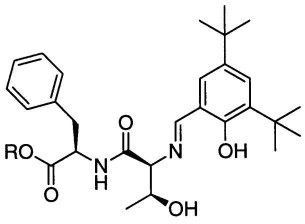
81% yield, 33% ee

Chart 5. Products and ee-values from the oxidation of dithioacetals and dithioketals with the in-situ catalyst obtained from $VO(acac)_2$ and **33b** as ligand [42].

The best ee (85%) was achieved in the oxidation of the dithioacetal of benzaldehyde (not shown) affording **38**. Only *trans*-products were observed in transformations of dithioacetals. The dithioketal from acetophenone (not shown) afforded **41** as a *cis*/*trans*-mixture with the former as the major isomer.

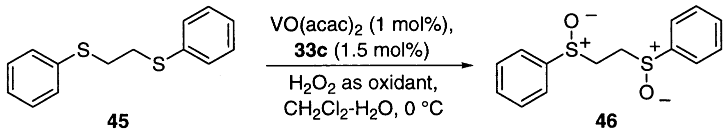
Recently, the structurally related solid phase sulfur oxidation catalysts **44** have been described [44]. However, in this case, titanium proved to be the metal of choice ($ee_{max} = 72\%$), and complexes derived from $VO(acac)_2$ gave significantly lower enantioselectivities (Fig. 6).

After the initial report by Bolm and Bienewald [39] several other groups began to investigate this vanadium catalysis, and various ligand modifications have been described. For example, Skarzewski et al. introduced Schiff-base **33c** having a phenyl substituent at C3 (R = Ph), and an *i*-Pr and a nitro groups as R′ and X, respectively [45]. With **33c** as ligand they achieved the catalytic synthesis of **38** with 88% ee, and bissulfoxide **46** was obtained from **45** with 95% ee (60% de). As before, *S*-configurated sulfoxide **28** was formed using a ligand derived from the L-amino alcohol, and (*R*)-**28** was obtained with that of D-valinol (Scheme 7).



44 R = Wang, Me

Fig. 6. Solid phase sulfur oxidation catalysts applied in Ti-catalyzed asymmetric sulfoxidations [44].

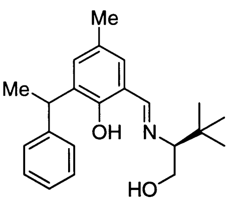


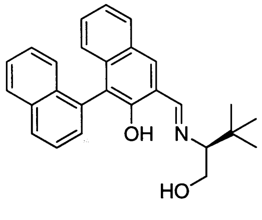
Scheme 7. Chirally modified vanadium complexes in sulfide to sulfoxide oxidations [19f,45,46].

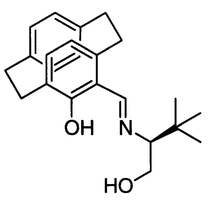
Vetter and Berkessel applied Schiff-base ligands with two elements of chirality such as **47**–**49** [19f]. The enantioselectivities in sulfoxidations of methylphenyl sulfide (**27**) to give sulfoxide **28** with vanadium catalysts derived from each diastereomer of **47**–**49** revealed significant matched-mismatched effects (for reactions at room temperature: **47**: 45 and 49% ee; **48**: 56 and 71% ee; **49**: 2 and 48% ee). The best enantioselectivity was achieved in a catalysis performed at 0 °C with **48** (matched) as ligand to give **28** with 78% ee in 92% yield. Katsuki and coworkers extended this study and obtained **28** with 88% ee using **50** as ligand (best result for methyl 2-naphthyl sulfoxide: 93% ee at 0 °C) [46] (Fig. 7).

Ellman and coworkers used the vanadium catalyst prepared from $VO(acac)_2$ and **33b** in the catalytic asymmetric synthesis of *tert*-butyl *tert*-butanethiosulfinate (**52**) [47]. With 1 mol% of the vanadium source and 1.1 mol% of **33b** as ligand, *tert*-butyl disulfide (**51**) was enantioselectively oxidized with hydrogen peroxide (30% in water) as oxidant at room temperature to give **52** with 91% ee in 98% yield. Even on a half mole scale and with a decreased catalyst loading of 0.5 mol% the loss in conversion and enantioselectivity was reported to be minor (Scheme 8).

Davis and coworkers demonstrated in numerous examples that sulfinamides and sulfinimines are extremely valuable chiral auxiliaries for asymmetric synthesis [48]. For the preparation of *tert*-butanesulfinamide (**53**) Ellman made use of **52** which was obtained by the vanadium-catalyzed enantioselective oxidation of *tert*-butyl disulfide (**51**) as described above [47]. Thus, when **52** was treated with lithium amide in ammonia, **53** was formed through a nucleophilic substitution reaction. The transformation was stereospecific, and enantiopure **53** could be obtained in 75% yield after a single recrystallization. The synthetic usefulness of *tert*-butanesulfinamide (**53**) was then illustrated by its application in the preparation of amines [49]. Thus, condensation reactions with aldehydes afforded *tert*-butanesulfinimines **54** which reacted with Grignard reagents to give primary amines (as HCl salts) after acidic hydrolysis (Scheme 9).


47


48


49

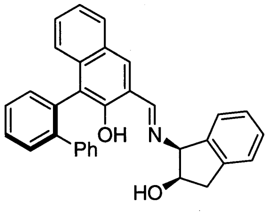
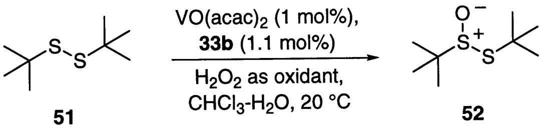

50

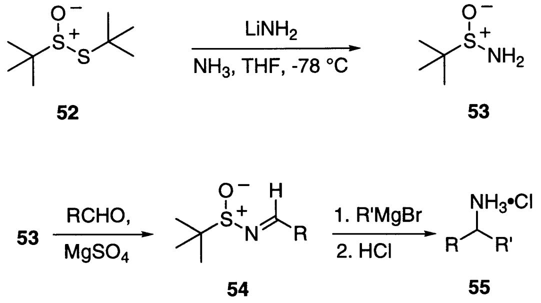
Fig. 7. Schiff-bases with two elements of chirality used in vanadium-catalyzed asymmetric sulfoxidations [19f,45,46].



Scheme 8. Vanadium-catalyzed enantioselective oxidation of *tert*-butyl disulfide [47].

Also in other asymmetric transformations *tert*-butyl *tert*-butanethiosulfinate (**52**) proved a useful intermediate which allowed the efficient preparation of compounds such as α- and β-amino acids [50], α-trifluoromethylamines [51], and several other synthetically interesting products [52].

A number of experiments have been performed with the intention to elucidate mechanistic details of the vanadium-catalyzed asymmetric sulfoxidation. For example, it was shown that the reaction is ligand-accelerated [7]; and thus, the enantioselectivity is not or only slightly affected by the presence of achiral vanadium species [39–41]. Furthermore, the enantiomeric excess of the product increases with time and



Scheme 9. Transformations of of *tert*-butanesulfinamide to give enantiopure HCl-salts of amines [49].

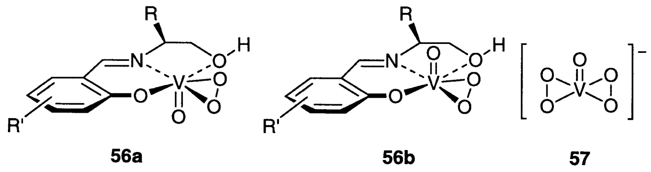


Fig. 8. Vanadium(V) species identified by ^{51}V-NMR spectroscopy.

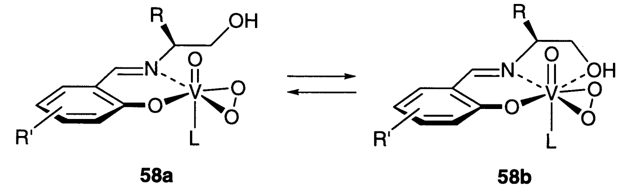


Fig. 9. Monoperoxo vanadium(V) complexes identified by ^{51}V- and ^{13}C{^{1}H}-NMR spectroscopy.

sulfide conversion [41]. This unusual behavior can either be attributed to an in-situ formation of a new catalytically active species with improved enantioselectivity, or to a (partial) blocking of less enantioselective catalysts. Furthermore, the relationship between the ee of the product and the ee of the ligand was found to be (approximately) linear [40,41]. This lack of asymmetric amplification [53] suggests that in the stereochemistry determining step of the catalysis a species bearing only a single chiral ligand is active.

NMR studies revealed the presence of various species under catalytic conditions [39–42,54,55]. On the basis of the ^{51}V-NMR data Bolm and Bienewald suggested the formation of diastereomeric vanadium(V) species **56a** and **56b** with oxoperoxo groups [42]. Besides two chiral peroxo complexes, Karpyshev et al. identified achiral diperoxo compound **57** [54] (Fig. 8).

Furthermore, the situation is complicated by the dynamic behavior of some complexes. Thus, the interpretation of the ^{51}V- and ^{13}C{^{1}H}-NMR data led Bryliakov et al. to conclude that the monoperoxo vanadium(V) complexes exists in two forms (**58a** and **58b**) [55] (Fig. 9).

Overall, the unravelling of mechanistic details and the identification of various species by NMR spectroscopy has resulted in a deeper understanding of the relevant steps of the vanadium-catalyzed asymmetric sulfoxidation. However, even at this advanced stage it is evident that further studies are required to allow both an unambiguous description of the reaction path and a clear interpretation of its stereochemical consequences.

4. Conclusions

The use of chirally modified vanadium complexes offers unprecedented opportunities in asymmetric catalysis. In both examples discussed above, the enantioselective epoxidation of allylic alcohols and the asymmetric oxidation of prochiral sulfides, significant advances have been achieved in recent years. Even though the enantioselectivities are not perfect yet, the results in terms of catalyst turnover and asymmetric induction are impressive and may serve as guideline for further investigation. Other ligands [56] and catalysts for asymmetric epoxidations and sulfoxidations will be developed, and the knowledge gained by the current studies will be useful in the discovery of novel enantioselective oxidative transformations where chiral vanadium complexes play a dominant role [57].

Acknowledgements

The support by the Deutsche Forschungsgemeinschaft (DFG) within the 'Schwerpunktprogramm Peroxidchemie' and the Fonds der Chemischen Industrie is greatly appreciated. Furthermore, I wish to express my special thanks to the PhD students who have developed the vanadium chemistry in the Bolm group during their doctoral studies, Frank Bienewald, Thi Kim Khanh Luong, and Toralf Kühn. I also thank Professor Aggarwal, University of Bristol, England, for valuable comments on the oxidation chemistry of dithioacetals and Professor Uang, National Tsing Hua University, Hsinchu, Taiwan, for sending data presented on a poster in Osaka.

References

[1] (a) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994;
(b) I. Ojima (Ed.), Catalytic Asymmetric Synthesis, 2nd ed., VCH Publisher, New York, 2000;
(c) E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer, Berlin, 1999;
(d) M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, Germany, 1998;
(e) H. Brunner, W. Zettlmeier, Handbook of Enantioselective Catalysis, vol. 1 and 2, VCH, Weinheim, 1993.

[2] http://www.nobel.se/chemistry/laureates/2001/.

[3] R.C. Michaelson, R.E. Palermo, K.B. Sharpless, J. Am. Chem. Soc. 99 (1977) 1990.

[4] K.B. Sharpless, T.R. Verhoeven, Aldrichim. Acta 12 (1979) 63.

[5] See also: C. Bolm, T.K.K. Luong, K. Harms, Chem. Ber./Recueil 130 (1997) 887.

[6] (a) C.H. Behrens, K.B. Sharpless, Aldrichim. Acta 16 (1983) 67;
(b) A.S. Rao, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 7, Pergamon Press, Oxford, 1991, p. 357;
(c) V. Schurig, F. Betschinger, Chem. Rev. 92 (1992) 873;
(d) E.N. Jacobsen, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 159;
(e) P. Besse, H. Veschambre, Tetrahedron 50 (1994) 8885;
(f) S. Pedragosa-Moreau, A. Archelas, R. Furstoss, Bull. Soc. Chim. Fr. 132 (1995) 769;
(g) T. Katsuki, Coord. Chem. Rev. 140 (1995) 189;
(h) T. Katsuki, J. Mol. Catal. 113 (1996) 87;

(i) C.T. Dalton, K.M. Ryan, V.M. Wall, C. Bousquet, D.G. Gilheany, Top. Catal. 5 (1998) 75;
(j) K. Muñiz-Fernández, C. Bolm, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, VCH-Wiley, Weinheim, 1998, p. 271;
(k) T. Katsuki, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 2, Springer, Berlin, 1999, p. 621;
(l) A. Archelas, R. Furstoss, Top. Curr. Chem. 200 (1999) 159;
(m) Y.N. Ito, T. Katsuki, Bull. Chem. Soc. Jpn. 72 (1999) 603;
(n) T. Flessner, S. Doye, J. Prakt. Chem. 341 (1999) 436.

[7] D.J. Berrisford, C. Bolm, K.B. Sharpless, Angew. Chem. Int. Ed. Engl. 34 (1995) 1059.

[8] (a) T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974;
(b) Y. Gao, R.M. Hanson, J.M. Klunder, S.Y. Ko, H. Masamune, K.B. Sharpless, J. Am. Chem. Soc. 109 (1987) 5765.

[9] (a) R.A. Johnson, K.B. Sharpless, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 103;
(b) X. Wen, I. Ojima, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, 2nd ed., VCH Publisher, New York, 2000, p. 281;
(c) T. Katsuki, V.S. Martin, Org. React. 48 (1996) 1;
(d) T. Katsuki, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, VCH-Wiley, Weinheim, 1998, p. 261.

[10] (a) N. Murase, Y. Hoshino, M. Oishi, H. Yamamoto, J. Org. Chem. 64 (1999) 338;
(b) Y. Hoshino, N. Murase, M. Oishi, H. Yamamoto, Bull. Chem. Soc. Jpn. 73 (2000) 1653.

[11] Y. Hoshino, H. Yamamtoto, J. Am. Chem. Soc. 122 (2000) 10452.

[12] K.D. Shimizu, M.L. Snapper, A.H. Hoveyda, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 3 (and references therein), Springer, Berlin, 1999, p. 1389.

[13] B. Traber, Y.-G. Jung, T.K. Park, J.-I. Hong, Bull. Korean Chem. Soc. 22 (2001) 547.

[14] C. Bolm, T. Kühn, Synlett (2000) 899.

[15] (a) C. Bolm, K. Muñiz, Chem. Soc. Rev. 28 (1999) 51;
(b) W.-P. Deng, X.-L. Hou, L.-X. Dai, Y.-H. Yu, W. Xia, Chem. Commun. (2000) 285;
(c) C. Bolm, K. Muñiz-Fernandez, A. Seger, G. Raabe, K. Günther, J. Org. Chem. 63 (1998) 7860;
(d) C. Bolm, K. Muñiz, J.P. Hildebrand, Org. Lett. 1 (1999) 491;
(e) C. Bolm, N. Hermanns, J.P. Hildebrand, K. Muñiz, Angew. Chem. Int. Ed. Engl. 39 (2000) 3465;
(f) C. Bolm, M. Kesselgruber, N. Hermanns, J.P. Hildebrand, G. Raabe, Angew. Chem. Int. Ed. Engl. 40 (2001) 1488.

[16] C. Bolm, T. Kühn, Isr. J. Chem. 41 (2001) 263.

[17] (a) D. Guillaneux, H.B. Kagan, J. Org. Chem. 60 (1995) 2502;
(b) O. Riant, G. Argouarch, D. Guillaneux, O. Samuel, H.B. Kagan, J. Org. Chem. 63 (1998) 3511.

[18] (a) T. Sammakia, H.A. Latham, D.R. Schaad, J. Org. Chem. 60 (1995) 10;
(b) Y. Nishibayashi, S. Uemura, Synlett (1995) 79;
(c) C.J. Richards, A. Mulvaney, Tetrahedron: Asymmetry 7 (1996) 1419.

[19] (a) Y.N. Belokon, M. Moscalenko, N.S. Ikonnikov, L. Yashkina, D.Y. Antonov, E.V. Vorontsov, V.I. Rozenberg, Tetrahedron: Asymmetry 19 (1997) 3245;
(b) V.I. Rozenberg, D.Y. Antonov, R.O. Zhuravsky, E.V. Vorontsov, V.N. Khrustalev, N.S. Ikonnikov, Y.N. Belokon, Tetrahedron: Asymmetry 11 (2000) 2683;
(c) P.J. Pye, K. Rossen, R.A. Reamer, N.N. Tsou, P.J. Volante, P.J. Reider, J. Am. Chem. Soc. 119 (1997) 6207;
(d) K. Rossen, P.J. Pye, A. Maliakal, P.J. Volante, J. Org. Chem. 62 (1997) 6462;
(e) P.J. Pye, K. Rossen, R.A. Reamer, P.J. Volante, P.J. Reider, Tetrahedron Lett. 39 (1998) 4441;
(f) A.H. Vetter, A. Berkessel, Tetrahedron Lett. 39 (1998) 1741;
(g) U. Wörsdörfer, F. Vögtle, M. Nieger, M. Waletzke, S. Grimme, F. Glorius, A. Pfaltz, Synthesis (1999) 597;
(h) U. Wörsdörfer, F. Vögtle, F. Glorius, A. Pfaltz, J. Prakt. Chem. 445 (1999) 341;
(i) D.S. Masterson, D.T. Glatzhofer, J. Mol. Catal. A: Chem. 161 (2000) 65;
(j) D.S. Masterson, T.L. Hobbs, D.T. Glatzhofer, J. Mol. Catal. A: Chem. 145 (1999) 75;
(k) S. Banfi, A. Manfredi, F. Montannari, G. Pozzi, S. Quici, J. Mol. Catal. A: Chem. 113 (1996) 77;
(l) M.J. Burk, W. Hems, D. Herzberg, C. Malan, A. Zanotti-Gerosa, Org. Lett. 2 (2000) 4173;
(m) A. Zanotti-Gerosa, C. Malan, D. Herzberg, Org. Lett. 3 (2001) 3687;
(n) S. Tanji, A. Ohno, I. Sato, K. Soai, Org. Lett. 3 (2001) 287;
(o) S. Dahmen, S. Bräse, Chem. Commun. (2002) 26;
(p) S. Dahmen, S. Bräse, Org. Lett. 3 (2001) 4119;
(q) R. Ruzziconi, O. Piermatti, G. Ricci, D. Vinci, Synlett (2002) 747.

[20] (a) D.J. Cram, N.L. Allinger, J. Am. Chem. Soc. 77 (1955) 6289;
(b) V. Rozenberg, N. Dubrovina, E. Sergeeva, D. Antonov, Y. Belokon, Tetrahedron: Asymmetry 9 (1998) 653 (and references therein).

[21] C. Bolm, O. Beckmann, T. Kühn, C. Palazzi, W. Adam, P. Bheema Rao, C.R. Saha-Möller, Tetrahedron: Asymmetry 12 (2001) 2441.

[22] (a) W. Adam, U. Hoch, M. Lazarus, C.R. Saha-Möller, P. Schreier, J. Am. Chem. Soc. 117 (1995) 11898;
(b) W. Adam, R.T. Fell, U. Hoch, C.R. Saha-Möller, P. Schreier, Tetrahedron: Asymmetry 6 (1995) 1047.

[23] W. Adam, P.B. Rao, H.-G. Degen, C.R. Saha-Möller, J. Am. Chem. Soc. 122 (2000) 5654.

[24] H.-L. Wu, B.-J. Uang, Poster 74 at the Third International Symposium on Chemistry and Biological Chemistry of Vanadium at Osaka, Japan, November 26–29, 2001.

[25] (a) M. Mikolajczyk, J. Drabowicz, Top. Stereochem. 13 (1982) 333;
(b) M.C. Carreño, Chem. Rev. 95 (1995) 1717;
(c) G. Solladié, in: G. Helmchen, R.W. Hoffmann, J. Mulzer, E. Schaumann (Eds.), Stereoselective Synthesis; Houben-Weyl, vol. E21, Thieme, Stuttgart, 1996, p. 1793;
(d) A.J. Walker, Tetrahedron: Asymmetry 2 (1992) 961;
(e) A.V. Mashkina, Sulfur Rep. 10 (1991) 279;
(f) G. Solladié, M.C. Carreño, in: P. Page (Ed.), Organosulfur Chemistry, vol. 1, Academic Press, New York, 1995, p. 1;
(g) M. Mikolajczyk, J. Drabowicz, P. Kielbasinski, Chiral Sulfur Reagents, CRC Press, Boca Raton, 1996.

[26] (a) C. Bolm, P. Müller, K. Harms, Acta Chem. Scand. 50 (1996) 305;
(b) C. Bolm, M. Kesselgruber, K. Muñiz, G. Raabe, Organometallics 19 (2000) 1648;
(c) C. Bolm, O. Simic, J. Am. Chem. Soc. 123 (2001) 3830 (and references therein).

[27] (a) R. Tokunoh, M. Sodeoka, K.-i. Aoe, M. Shibasaki, Tetrahedron Lett. 36 (1995) 8035;
(b) N. Khiar, I. Fernández, F. Alcudia, Tetrahedron Lett. 34 (1993) 123;
(c) J.V. Allen, J.F. Bower, J.M.J. Williams, Tetrahedron: Asymmetry 5 (1994) 1895;
(d) M.C. Carreño, J.L.G. Ruano, M.C. Maestro, L.M.M. Cabrejas, Tetrahedron: Asymmetry 4 (1993) 727;
(e) G. Celucci, D. Berta, A. Saba, Tetrahedron 53 (1997) 3843;
(f) S.L. You, Y.-G. Zhou, X.-L. Hou, L.-X. Dai, Chem. Commun. (1998) 2765;
(g) K. Hiroi, Y. Suzuki, Tetrahedron Lett. 39 (1998) 6499;

(h) K. Hiroi, Y. Suzuki, I. Abe, Y. Hasegawa, K. Suzuki, Tetrahedron: Asymmetry 9 (1998) 3797;
(i) K. Hiroi, Y. Suzuki, I. Abe, Chem. Lett. (1999) 149;
(j) Y. Suzuki, I. Abe, K. Hiroi, Heterocycles 50 (1999) 89;
(k) K. Hiroi, Y. Suzuki, I. Abe, Tetrahedron: Asymmetry 10 (1999) 1173;
(l) K. Hiroi, Y. Suzuki, I. Abe, R. Kawagishi, Tetrahedron 56 (2000) 4701.

[28] (a) P. Pitchen, C.J. France, I.M. McFarlane, C.G. Newton, D.M. Thompson, Tetrahedron Lett. 35 (1994) 485;
(b) K.M. Poss, S.T. Chao, E.M. Gordon, P.J. McCann, D.P. Santafianos, S.C. Traeger, R.K. Varma, W.N. Washburn, Tetrahedron Lett. 35 (1994) 3461;
(c) M. Matsugi, N. Fukuda, J.-i. Minamikawa, S. Otsuka, Tetrahedron Lett. 39 (1998) 5591;
(d) K. Okamoto, T. Nishino, J. Biol. Chem. 270 (1995) 7816;
(e) M. Matsugi, K. Hashimoto, M. Inai, N. Fukuda, T. Furuta, J.-i. Minamikawa, S. Otsuka, Tetrahedron: Asymmetry 6 (1995) 2991;
(f) Y. Zhang, T.W. Kensler, C.-G. Cho, G.H. Posner, P. Talalay, Proc. Natl. Acad. Sci. 91 (1994) 3147;
(g) J.K. Whitesell, M.-S. Wong, J. Org. Chem. 59 (1994) 597;
(h) C.A. Hutton, J.M. White, Tetrahedron Lett. 38 (1997) 1643;
(i) S. von Unge, V. Langer, L. Sjölin, Tetrahedron: Asymmetry 8 (1997) 1967;
(j) N. Nakajima, T. Enomoto, N. Matsuura, M. Ubukata, Bioorg. Med. Chem. Lett. 8 (1998) 3331;
(k) J.R. Henry, K.C. Rupert, J.H. Dodd, I.J. Turchi, S.A. Wadsworth, D.E. Cavender, P.H. Schafer, J.J. Siekierka, Bioorg. Med. Chem. Lett. 8 (1998) 3335;
(l) C.-C. Wang, J.J. Li, H.-C. Huang, L.F. Lee, D.B. Reitz, J. Org. Chem. 65 (2000) 2711;
(m) H. Cotton, T. Elebring, M. Larsson, L. Li, H. Sörensen, S. von Unge, Tetrahedron: Asymmetry 11 (2000) 3819;
(n) A.R. Maguire, S. Papot, A. Ford, S. Touhey, R. O'Connor, M. Clynes, Synlett (2001) 41.

[29] (a) H.B. Kagan, P. Diter, in: P.C.B. Page (Ed.), Organosulfur Chemistry, vol. 2, Academic Press, New York, 1998, p. 1;
(b) H.B. Kagan, T. Luukas, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, Germany, 1998, p. 361;
(c) H.B. Kagan, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, 2nd ed., VCH Publisher, New York, 2000, p. 327;
(d) C. Bolm, K. Muñiz, J.P. Hildebrand, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer-Verlag, Berlin, 1999, p. 697.

[30] (a) K.-H. van Pée, in: K. Drauz, H. Waldmann (Eds.), Enzyme Catalysis in Organic Chemistry, VCH, Weinheim, 1995, p. 780;
(b) H.B. ten Brink, H.L. Holland, H.E. Schoemaker, H. van Lingen, R. Wever, Tetrahedron: Asymmetry 10 (1999) 4563 (and references therein).

[31] (a) P. Pitchen, E. Duñach, M.N. Desmukh, H.B. Kagan, J. Am. Chem. Soc. 106 (1984) 8188;
(b) P. Pitchen, H.B. Kagan, Tetrahedron Lett. 25 (1984) 1049;
(c) J.-M. Brunel, P. Diter, M. Duetsch, H.B. Kagan, J. Org. Chem. 60 (1995) 8086;
(d) J.-M. Brunel, H.B. Kagan, Bull. Soc. Chim. Fr. 133 (1996) 1109;
(e) P.G. Potvin, B.G. Fieldhouse, Tetrahedron: Asymmetry 10 (1999) 1661.

[32] F. Di Furia, G. Modena, R. Seraglia, Synthesis (1984) 325.

[33] (a) R.W. Baker, G.K. Thomas, S.O. Rea, M.V. Sargent, Aust. J. Chem. 50 (1997) 1151;
(b) A. Lattanzi, F. Bonadies, A. Senatore, A. Soriente, A. Scettri, Tetrahedron: Asymmetry 8 (1997) 2473;
(c) S. Superchi, C. Rosini, Tetrahedron: Asymmetry 8 (1997) 349;
(d) M.I. Donnoli, S. Superchi, C. Rosini, J. Org. Chem. 63 (1998) 9392;
(e) Y. Yamanoi, T. Imamoto, J. Org. Chem. 62 (1997) 8560;
(f) M.T. Reetz, C. Merck, G. Naberfeld, J. Rudolph, N. Griebenow, R. Goddard, Tetrahedron Lett. 38 (1997) 5273;
(g) F. Di Furia, G. Licini, G. Modena, R. Motterle, W.A. Nugent, J. Org. Chem. 61 (1996) 5175;
(h) M. Bonchio, S. Calloni, F. Di Furia, G. Licini, G. Modena, S. Moro, W.A. Nugent, J. Am. Chem. Soc. 119 (1997) 6935;
(i) N. Komatsu, Y. Nishibayashi, T. Sugita, S. Uemura, Tetrahedron Lett. 33 (1992) 5391;
(j) N. Komatsu, M. Hashizume, T. Sugita, S. Uemura, J. Org. Chem. 58 (1993) 4529;
(k) N. Komatsu, M. Hashizume, T. Sugita, S. Uemura, J. Org. Chem. 58 (1993) 7624;
(l) C. Bolm, O.A.G. Dabard, Synlett (1999) 360.

[34] (a) T. Hirao, Chem. Rev. 97 (1997) 2707;
(b) A. Butler, M.J. Clague, G.E. Meister, Chem. Rev. 94 (1994) 625;
(c) D. Rehder, Coord. Chem. Rev. 182 (1999) 297;
(d) V. Conte, F. Di Furia, G. Licini, Appl. Catal. A: Gen. 157 (1997) 335.

[35] (a) R. Curci, F. Di Furia, R. Testi, G. Modena, J. Chem. Soc. Perkin II (1974) 752;
(b) C.K. Sams, K.A. Jørgensen, Acta Chem. Scand. 49 (1995) 939.

[36] (a) K. Nakajima, K. Kojima, T. Aoyama, J. Fujita, Chem. Lett. (1986) 1483;
(b) K. Nakajima, K. Kojima, M. Kojima, J. Fujita, Bull. Chem. Soc. Jpn. 63 (1990) 2620;
(c) C. Sasaki, K. Nakajima, M. Kojima, J. Fujita, Bull. Chem. Soc. Jpn. 64 (1991) 1318.

[37] C. Bolm, F. Bienewald, K. Harms, Synlett (1996) 775.

[38] (a) S. Colonna, A. Manfredi, M. Spadoni, L. Casella, M. Gullotti, J. Chem. Soc. Perkin Trans. 1 (1987) 71;
(b) K. Nakjima, M. Kojima, K. Toriumi, K. Saito, J. Fujita, Bull. Chem. Soc. Jpn. 62 (1989) 760.

[39] C. Bolm, F. Bienewald, Angew. Chem. Int. Ed. Engl. 34 (1995) 2640.

[40] C. Bolm, G. Schlingloff, F. Bienewald, J. Mol. Catal. A 117 (1997) 347.

[41] F. Bienewald, Dissertation at the Philipps-Universität Marburg, 1996.

[42] C. Bolm, F. Bienewald, Synlett (1998) 1327.

[43] (a) P.C.B. Page, R.D. Wilkesm, E.S. Namwindwa, M.J. Witty, Tetrahedron 52 (1996) 2125;
(b) V.K. Aggarwal, B.N. Esquivel-Zamora, G.R. Evans, E. Jones, J. Org. Chem. 63 (1998) 7306 (and references therein).

[44] S.D. Green, C. Monti, R.F.W. Jackson, M.S. Anson, S.J.F. Macdonald, Chem. Commun. (2001) 2594.

[45] (a) J. Skarzewski, E. Ostrycharz, R. Siedlecka, Tetrahedron: Asymmetry 10 (1999) 3457;
(b) J. Skarzewski, E. Ostrycharz, R. Siedlecka, M. Zielinska-Blajet, B. Pisarski, J. Chem. Res. (S) (2001) 263; J. Chem. Res. (M) (2001) 743.

[46] C. Ohta, H. Shimizu, A. Kondo, T. Katsuki, Synlett (2002) 161.

[47] (a) G. Liu, D.A. Cogan, J.A. Ellman, J. Am. Chem. Soc. 119 (1997) 9913;
(b) D.A. Cogan, G. Liu, B.J. Backes, J.A. Ellman, J. Am. Chem. Soc. 120 (1998) 8011.

[48] P. Zhou, B.-C. Chen, F.A. Davis, in: C.M. Rayner (Ed.), Advances in Sulfur Chemistry, vol. 2 (and references therein), JAI Press, Stamford, CT, 2000, p. 249.

[49] (a) G. Borg, D.A. Cogan, J.A. Ellman, Tetrahedron Lett. 40 (1999) 6709;
(b) D.A. Cogan, G. Liu, J.A. Ellman, Tetrahedron 55 (1999) 8883.

[50] (a) F.A. Davis, S. Lee, H. Zhang, D.L. Fanelli, J. Org. Chem. 65 (2000) 8704;
(b) G. Borg, M. Chino, J.A. Ellman, Tetrahedron Lett. 42 (2001)

1433;
(c) T.P. Tang, J.A. Ellman, J. Org. Chem. 64 (1999) 12;
(d) Y. Lee, R.B. Silverman, Org. Lett. 2 (2000) 303.

[51] G.K.S. Prakash, M. Mandal, G.A. Olah, Angew. Chem. Int. Ed. Engl. 40 (2001) 589.

[52] (a) J. Adrio, J.C. Carretero, J. Am. Chem. Soc. 121 (1999) 7411;
(b) D.R. Dragoli, M.T. Burdett, J.A. Ellman, J. Am. Chem. Soc. 123 (2001) 10127 (and references therein).

[53] (a) H.B. Kagan, T.O. Luukas, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 1, Springer, Berlin, 1999, p. 101;
(b) D. Fenwick, H.B. Kagan, Top. Stereochem. 22 (1999) 257;
(c) C. Girard, H.B. Kagan, Angew. Chem. Int. Ed. Engl. 37 (1998) 2923;
(d) C. Bolm, in: G.R. Stephenson (Ed.), Advanced Asymmetric Catalysis, Blackie, New York, 1996, p. 9;
(e) M. Avalos, R. Babiano, P. Cintas, J.L. Jimenez, J.C. Palacios, Tetrahedron: Asymmetry 8 (1997) 2997;
(f) K. Soai, T. Shibata, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, Wiley, New York, 2000, p. 699.

[54] N.N. Karpyshev, O.D. Yakovleva, E.P. Talsi, K.P. Bryliakov, O.V. Tolstikova, A.G. Tolstikov, J. Mol. Catal. A: Chem. 157 (2000) 91.

[55] K.P. Bryliakov, N.N. Karpyshev, S.A. Fominsky, A.G. Tolstikov, E.P. Talsi, J. Mol. Catal. A: Chem. 171 (2001) 73.

[56] (a) G. Licini, Contribution C 17 at the COST D24 Workshop, Stereocat' 2001 at Villeneuve d'Ascq, France, November 15–18, 2001;
(b) D. Rehder, D. Wang, M. Casny, G. Santoni, C. Grüning, M. Ebel, E. Kiss, Contribution I-15 at the Third International Symposium on Chemistry and Biological Chemistry of Vanadium at Osaka, Japan, November 26–29, 2001.

[57] (a) C.-Y. Chu, D.R. Hwang, S.-K. Wang, B.J. Uang, Chem. Commun. (2001) 980;
(b) S.-W. Hon, C.-H. Li, J.-H. Kuo, N.B. Barhate, Y.-H. Liu, Y. Wang, C.-T. Chen, Org. Lett. 3 (2001) 869;
(c) P.-N. Chen, W.-Y. Shih, C.-Y. Chu, B.-J. Uang, Poster P-65 at the Third International Symposium on Chemistry and Biological Chemistry of Vanadium at Osaka, Japan, November 26–29, 2001.