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Asymmetric oxidation of sulfides catalyzed by titanium and vanadium complexes in the synthesis of biologically active sulfoxides

K P Volcho, N F Salakhutdinov

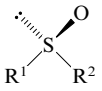
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Abstract. The published data on the asymmetric synthesis of chiral biologically active sulfoxides by oxidation of appropriate sulfides catalyzed by titanium and vanadium complexes are generalized. The bibliography includes 87 references.

I. Introduction

Sulfur-containing compounds are abundant in nature in the form of thiols, sulfides,[1] disulfides and chiral sulfoxides,[2] which are characterized by high configurational stability.



R^1, R^2 = Alk, Ar.

Optically active sulfoxides are widely used in asymmetric synthesis,[3–5] many natural[6–9] and synthetic[10–14] chiral sulfoxides exhibit high biological activities. For this reason, according to the data up to 2006, it is sulfoxidation including asymmetric that is the most common oxidation reaction in the synthesis of candidate drug molecules.[15]

The major approaches to the preparation of chiral sulfoxides of high enantiopurity include the resolution of racemates of chiral sulfoxides, asymmetric synthesis and the introduction of the sulfoxide group into an optically active compound with subsequent separation of diastereomers, and asymmetric sulfoxidation. The latter can be performed by catalytic methods using enzymes[16,17] or cell cultures,[18,19] non-metal oxidizing systems (oxidation with compounds containing a hypervalent iodine atom,[20,21] chiral phosphoryl chlorides[22] and oxaziridines[23,24] of which many are quite available[25]), as well as catalysis by metal complexes, *viz*., Mn,[26–31] Zr,[32,33] Al,[34,35] Mo,[36,37] Fe,[38,39] Mg,[40] Re,[41] W,[42] Cu,[31] Ru (Ref. 38) and, preferably, Ti and V, which are currently used in industry.[43]

The results of the application of titanium- and vanadium-containing metal complexes for asymmetric sulfoxidation are generalized in the reviews,[44–51] but it was only in two papers[52,53] that the catalytic synthesis of biologically active chiral sulfoxides using metal complex catalysts was discussed.

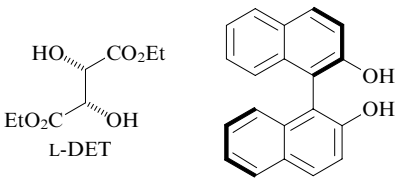
In the present review, the recent results of the application of titanium and vanadium complexes for the preparation of chiral biologically active sulfoxides by asymmetric oxidation of the corresponding sulfides are presented (diastereoselective oxidation of chiral sulfides was not considered).

II. Asymmetric synthesis of chiral sulfoxides catalyzed by titanium complexes

The first systems for asymmetric metal complex-assisted oxidation of sulfides to sulfoxides were independently suggested by Kagan[54] and Modena[55] groups in 1984. Both oxidizing systems are based on the Sharpless epoxidising reagent developed for asymmetric oxidation of allylic alcohols and consisting of equimolar amounts of titanium isopropoxide [$Ti(OPr^i)_4$] and optically active diethyl tartrate (DET) and *tert*-butyl hydroperoxide (TBHP) as an oxidant.[56] Direct application of the Sharpless system results only in achiral sulfoxides, however, the addition of 1 equiv. of water (the Kagan system)[54] or the use of a fourfold excess of DET with respect to $Ti(OPr^i)_4$ (the Modena system)[55] allowed the preparation of sulfoxides of high enantiopurity from alkyl aryl sulfides. Later it was found[57] that in some cases the replacement of TBHP by cumene hydroperoxide (CHP) increases the enantiopurity of the sulfoxides formed. In addition to D- and L-tartrates, other chiral ligands are also successfully used in homogeneous asymmetric oxidation of sulfides, for example, 1,1′-binaphthyl-2,2′-diol (BINOL) derivatives (the Uemura method).[58]

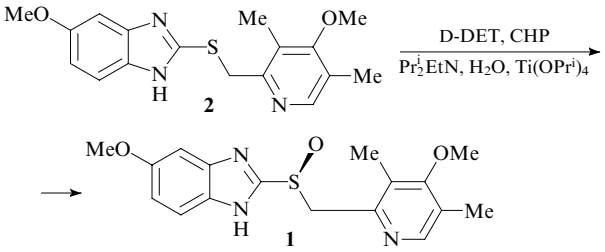
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Application of different titanium-containing oxidising systems allowed the efficient synthesis of a series of chiral sulfoxides that are of significant practical interest for pharmacology.

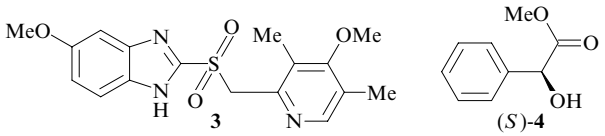
First, it is esomeprazole (**1**),† that is on sale under a trademark Nexium and is a leader in the world sale (pecuniarily) among drugs.[53] The application of the Kagan method for the oxidation of sulfide **2**, the precursor of compound **1**, afforded the virtually racemic sulfoxide.[11] This can be explained by the fact that, as a rule, the original Kagan and Modena systems cannot be applied to chiral oxidation of sulfides with bulky substituents of comparable sizes.



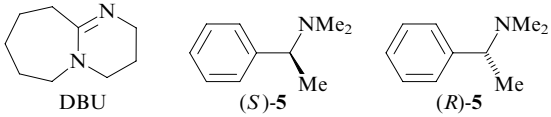
At the same time, modification of the original Kagan method afforded esomeprazole (**1**) with high enantioselectivity and in a reasonable yield.[11, 59] The following changes were introduced: first, the catalytic complex of titanium isopropoxide with D-DET and water was prepared in the presence of sulfide **2**; second, the complex obtained was equilibrated at elevated temperature before the addition of an oxidant; third, the reaction was performed in the presence of a base, preferably *N*,*N*-diisopropylethylamine (DIEA). Each of the modifications increased the enantioselectivity of the process, however, the best result was achieved upon simultaneous use of all three changes. Cumene hydroperoxide was used as an oxidant, the molar ratio titanium isopropoxide : D-DET : water was 3 : 6 : 1. The extracted raw product with the enantiomeric excess (*ee*) of up to 94% was transformed to esomeprazole sodium and crystallized, which resulted in an increase in the optical purity of the sulfoxide to virtually 100%, the yield being 55%.[11] The suggested procedure appeared efficient for relatively large-scale syntheses (up to seleral kilogrammes) of substance **1**.[11]

This is also suitable for asymmetric oxidation of other sulfides with similar structures containing an imidazole or benzimidazole substituent; *N*-methylation of the heterocycle results in a sharp decrease in the optical purity of the product.[60] It is noteworthy that Seenivasaperumal *et al.*[60] (with citation of Ref. 11) reported a yield of 78% for esomeprazole (**1**), which exceeds markedly that reported in both Ref. 11 and in a patent.[59] This discrepancy might be associated with the fact that it is the yield of the raw product without purification that is presented in Ref. 60, which does not allow the estimation of the chemoselectivity of the reaction.

A serious drawback of the procedure suggested in Ref. 11 is the formation of sulfone **3** in a substantial amount (~4%), which is difficult to separate.[61] This problem was solved by a modification of this procedure with replacement of diethyl D-tartrate by a monodentate ligand, *viz.*, methyl (*S*)-(+)-mandelate [(*S*)-**4**].[61] Compound (*S*)-**4** was used in a significant excess with respect to both titanium isopropoxide (740 mol %) and the sulfide **2** (250 mol %); the yield of esomeprazole (**1**) was also lower (up to 40%) than that reported in the original procedure,[11] but the content of sulfone **3** in the final product was less than 1%.



An important factor influencing the enantiopurity of esomeprazole[11] is the presence of a base, preferably, DIEA. So far, its role is unclear, but the use of other amines (triethylamine, 4-methylmorpholine, 1,1,3,3-tetramethylguanidine, DBU) resulted in a sharp decrease in the optical purity of the product,[11] and the use of *N*,*N*-diethylaniline as a base gave a complex mixture of products.[62] Thus, the amine structure affects considerably both the course of enantioselectice oxidation and the purity of the product formed.



The replacement of DIEA by optically active *N*,*N*-dimethyl-(*S*)-1-phenylethylamine [(*S*)-**5**] resulted in a slight increase in the yield of esomeprazole sodium (**1**) (Table 1), and the content of sulfone **3** did not exceed 0.3%.[62] Application of the enantiomer, (*R*)-**5**, instead of the compound (*S*)-**5** allowed an increase in the yield of esomeprazole sodium to 64% with the same high optical purity and insignificant content of sulfone **3**.

Table 1. Synthesis of esomeprazole (**1**) using the system of $Ti(OPr^i)_4$ with different ligands.

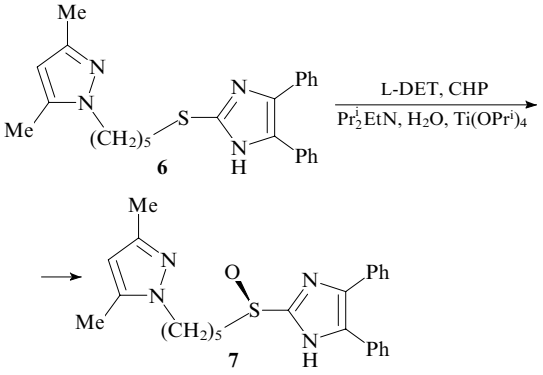
Ligands	The yield of esomeprazole sodium **1** (%)	Content of sulfone **3** (%)	Ref.
D-DET	55	up to 4	11, 61
4	40	< 1	61
D-DET + (*S*)-**5**	57	< 0.3	62
D-DET + (*R*)-**5**	64	< 0.3	62

A marked difference in the optical purity of the raw product and the yields of esomeprazole **1** sodium leads to the conclusion that the absolute configuration of *N*,*N*-dimethyl-1-phenylethylamine (**5**) affects substantially on the enantioselectivity of the reaction, *i.e.*, amine **5** plays also the role of the second chiral ligand. High yield of esomeprazole (**1**) in the synthesis by this method seems to be associated with high chemoselectivity of the processes, which is con-

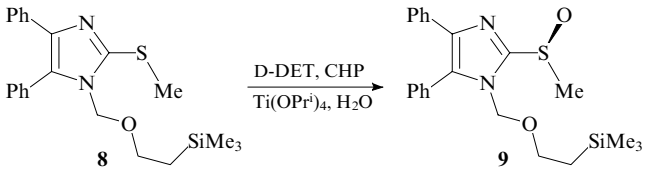
† Esomeprazole is the (*S*)-enantiomer, the racemate is referred to as omeprazole.

firmed by the formation of only an insignificant amount of sulfone **3**.

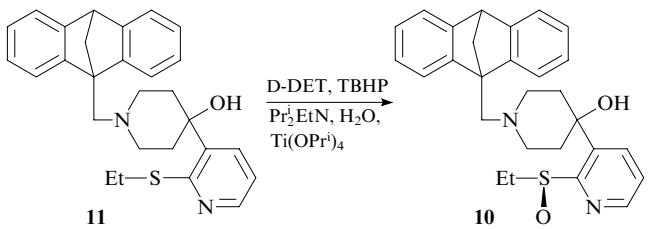
The suggested method[11] was applied for oxidation of compound **6**, a precursor of an acyl-coenzyme A: cholesterol acyltransferase inhibitor, which allowed the preparation of the target sulfoxide with *ee* of 92%,[11] whereas the nonmodified Kagan system afforded exclusively the racemic sulfoxide.[10, 63]



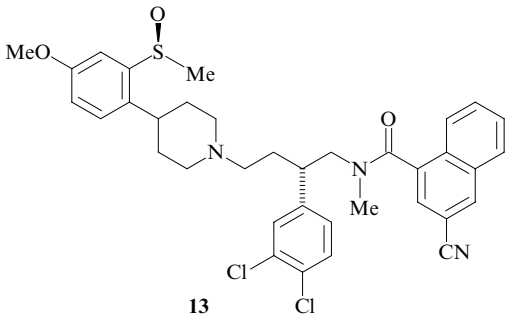
Another approach to the preparation of the optically active compound **7** consists in the oxidation by the Kagan method of sulfide **8** used as an intermediate in the synthesis of sulfoxide **7**; the chiral sulfoxide **9** was prepared with *ee* of 91% in a yield of 68%.[64]



The sulfoxide **10** tested as a drug against schizophrenia was prepared with *ee* of 93% by asymmetric oxidation of sulfide **11** using the Kagan system in the presence of DIEA, the content of the sulfone impurity being $<1\%$.[12] If *N*,*N*-diisopropylethylamine was omitted from the catalytic system, the *ee* of the product **10** decreased to 85%; moreover, up to 5% of sulfone was formed. A study of the influence of the amount of $Ti(OPr^i)_4$ and D-DET on the *ee* of sulfoxide **10** revealed that the optimum ratio was 1.45 equiv. of D-DET, 0.95 equiv. of $Ti(OPr^i)_4$ and 1 equiv. of water per equiv. of the parent sulfide. Both increase and decrease in the portion of D-DET with respect to $Ti(OPr^i)_4$ decreased the *ee* value. Recrystallisation of the raw product obtained afforded an increase in the enantiopurity of the sulfoxide **10** up to 99.5%.[12]

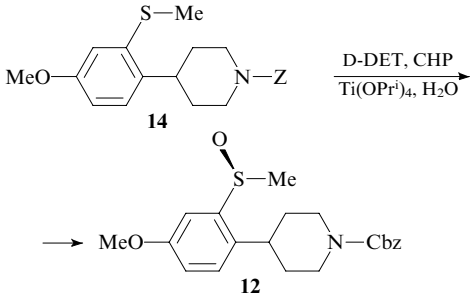


A slightly modified Kagan method was successfully used for the asymmetric synthesis of sulfoxide **12**, an important intermediate in the preparation of a neurokinin antagonist **13**.[65]



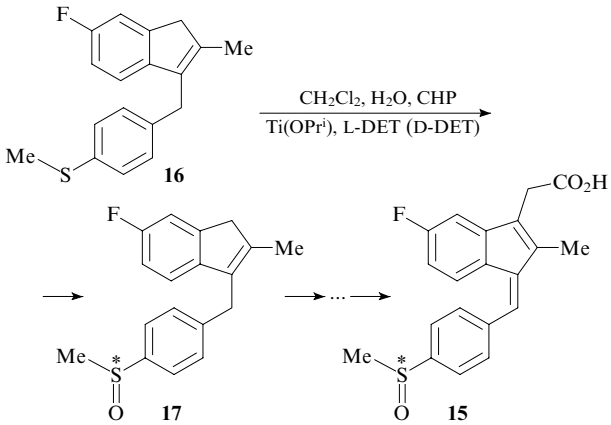
Investigations aimed at optimising the process demonstrated that it is very sensitive to temperature: for example, oxidation at -5 °C resulted in the product with *ee* 85%, a decrease in the temperature to -15 °C increased the *ee* to 94%. Important factors influencing the results of oxidation appeared to be the amount and addition rate of cumene hydroperoxide.[65] An increase in the excess of CHP from 1.05 to 1.2 equiv. resulted in a decrease in the duration of the reaction from 5–16 to 2 h, however, the content of the sulfone markedly increased.

The exothermic effect of the addition of CHP was a substantial problem in the oxidation of compound **14** leading to a decrease in the optical purity of the product upon fast addition rate of CHP.



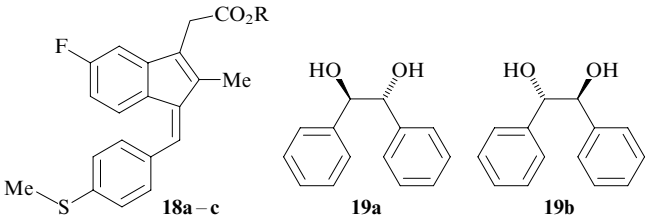
Z is benzyloxycarbonyl.

In the synthesis of the chiral nonsteroid antipyretic drug Sulindac (**15**), asymmetric oxidation of sulfide **16** to sulfoxide **17** has become one of the key steps.[66] The Kagan method using L- or D-DET allowed the preparation of both enantiomers of compound **17** in the yields of 54%–56% and *ee* ~90%.



Oxidation of compound **18a** with a carboxyl group resulted only in the racemic sulfoxide, whereas oxidation of its methyl ester **18b** afforded the corresponding sulfone in a

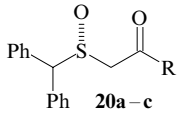
nealy quantitative yield.[66] At the same time, diols **19a**,**b** were used as ligands for oxidation of sulfides **18b**,**c** to give both enantiomers of methyl and *tert*-butyl esters of compound **15** with *ee* up to 96% and in a yield of about 50%.[67]



18a–c **19a** **19b**

R = H (**a**), Me (**b**), Bu^t (**c**).

Modafinil (**20a**) with *ee* up to 99% was prepared by asymmetric oxidation of the corresponding sulfide by the procedure similar to that described in Ref. 11: the catalytic complex of titanium isopropoxide, L-DET and water was prepared at 55 °C in the presence of the sulfide and the reaction was carried out in the presence of DIEA.[68]

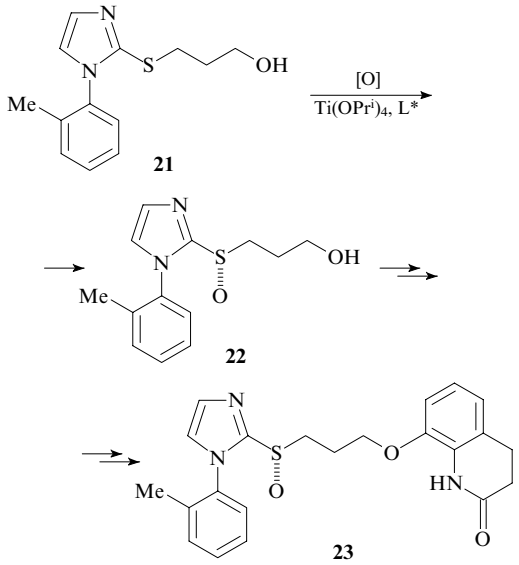


20a–c

R = NH_2 (**a**), OH (**b**), OMe (**c**).

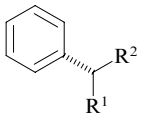
At the same time, this method appeared inefficient for the preparation of modafinic acid (**20b**) and its methyl ester (**20c**).[69] It is noted[69] that the model procedures developed, as a rule, for aryl methyl sulfides cannot be applied for the oxidation of polyfunctional sulfides without considerable modification.

The Kagan, Modena and Uemura conditions are also of little efficiency for the oxidation of sulfide **21**: sulfoxide **22**, the key intermediate in the synthesis of a platelet adhesion inhibitor OPC-29030 (**23**), was prepared with *ee* $\leqslant$ 54%.[70,71]



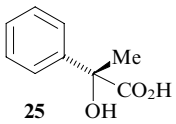
L* is a chiral ligand.

Studies of catalytic systems of Ti(OPr^i)$_4$ with 24 different ligands revealed that the best results can be achieved in the presence of mandelic acid (**24a**), compound **22** was prepared in a yield of 89% and *ee* 76%.[71]



(*R*)-**4**, **24a–d**

Compound **24**	R^1	R^2
a	OH	CO_2H
b	OMe	CO_2H
c	OH	Me
d	NH_2	CO_2H

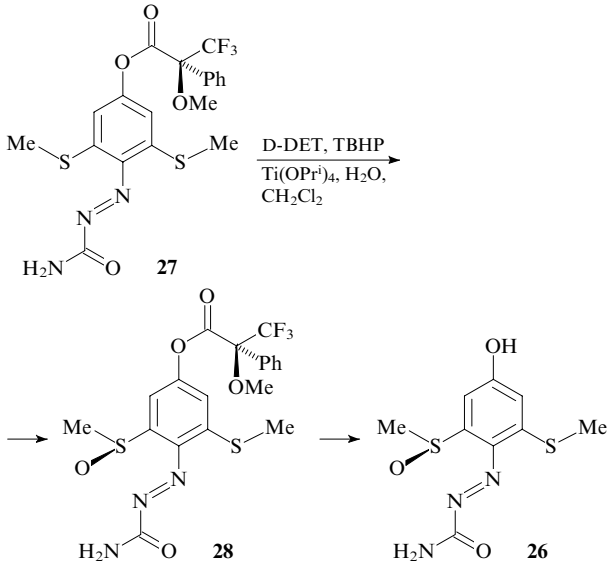


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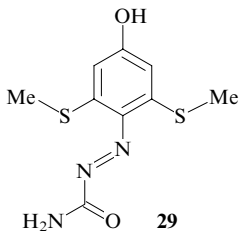
The reaction appeared to be very sensitive to the ligand structure: for example, the use of compounds (*R*)-**4** and **25** resulted in a decrease in the *ee* to 39%–48%, whereas in the presence of catalytic complexes with compounds **24b–d**, the virtually racemic product **22** was obtained.

The structure of the hydroxyalkyl substituent in sulfide **21** appeared to be no less important. Both an increase and a decrease in the length of the aliphatic chain by one methylene unit resulted in a sharp decrease in the optical purity of the product [compare with the catalytic system Ti(OPr^i)$_4$ with ligand **24a**]. If the hydroxy group was removed from compound **21**, the corresponding sulfoxide was almost racemic (*ee* 6%).[71]

The key step in the synthesis of rubroflavin **26** is asymmetric monosulfoxidation of disulfide **27** under the Kagan conditions to form[72] compound **28** in a yield of 35% and *ee* 67%.

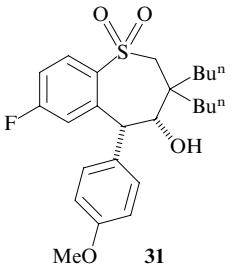


Direct oxidation of compound **29** with a phenolic group appeared ineffective, probably, due to its poor solubility in CH_2Cl_2.



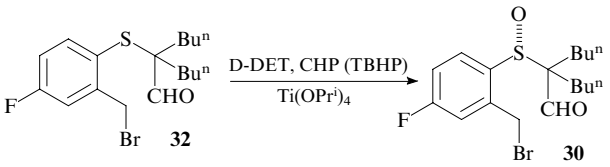
29

The chiral sulfoxide **30** was used in the enantioselective synthesis of benzothiepine **31** exhibiting ASBT inhibitory activity.[73]



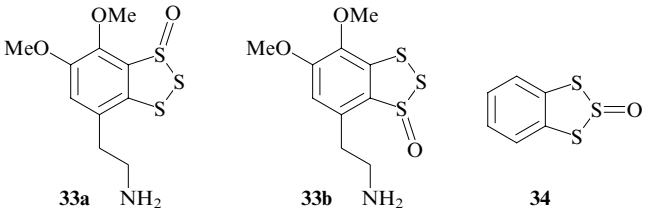
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Asymmetric oxidation of the prochiral sulfide **32** was performed using the Kagan system among others, but the *ee* of the product **30** did not exceed 20%.



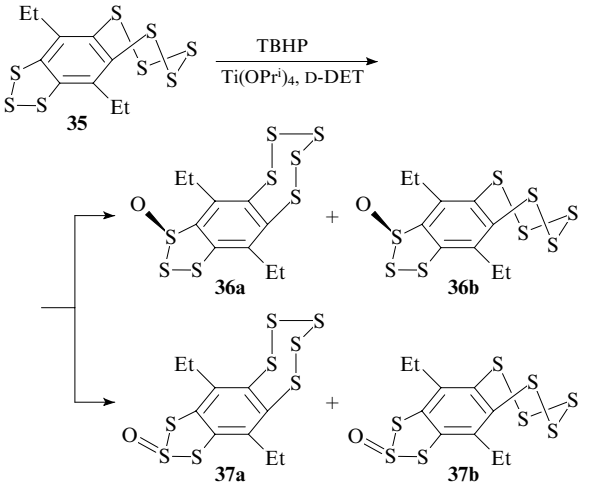
32 **30**

It is known[1] that natural benzotrithiole oxides exhibit diverse biological activities. For example, varacins B and C (**33a**,**b**) isolated from the Far East ascidian *Polycitor* manifest antimicotic and antibacterial activities,[74] and varacin C manifests also strong antitumour activity.[75] High activity against some types of tumour cell lines was also demonstrated by simpler benzotrithiole 2-oxide (**34**).[76]



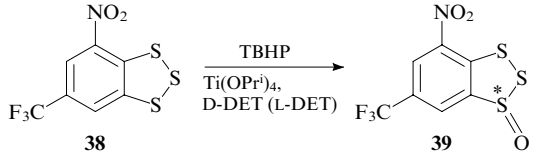
33a **33b** **34**

To date, there are only two examples of successful synthesis of chiral benzotrithiole oxides. Asymmetric oxidation of compound **35** containing simultaneously two different polysulfide rings using the Modena system afforded a mixture of monosulfoxides **36** and **37**.[77] Compounds **37a**,**b** are achiral, whereas compounds **36a**,**b** are optically active. Pairs of compounds **36a**,**b** and **37a**,**b** are conformers, but since the rate of their interconversion is low, they could successfully be isolated and studied by X-ray diffraction. Diastereoisomerism in these compounds is associated with the presence of two chirality elements, *viz*., the asymmetric sulfur atom of the sulfoxide group and the chirality plane. The reaction products were separated by column chromatography, the *ee* of compounds **36a**,**b** were 71% and 79%, respectively.



35 **36a** **36b** **37a** **37b**

Asymmetric oxidation of benzotrithiole (**38**) by the Kagan and Modena systems in the presence of L- or D-DET afforded[78,79] both enantiomers of benzotrithiole oxide **39**, the largest *ee* (up to 61%) of the product being achieved by the Modena method, while the Kagan method gave significantly lower enantiomeric excess.

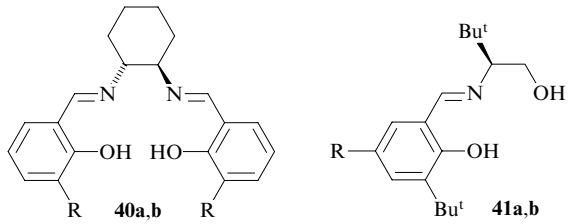


38 **39**

III. Asymmetric synthesis of chiral sulfoxides catalyzed by vanadium complexes

Oxidizing systems based on titanium isopropoxide have drawbacks substantial for their practical application. First of all, this is stringent control over the humidity of the reaction medium (because titanium isopropoxide is moisture-sensitive), which not only complicates instrumentation of the process, but can lead to irreproducible results. In addition, reliable enantioselectivity of the process can be achieved, as a rule, with large amounts of the catalyst, which leads to irreversible consumption of the reactants and difficulties with the work-up of the reaction mixtures.

The systems based on vanadium complexes have become an alternative to these systems. Vanadium complexes with chiral Schiff bases **40a**,**b** were used for the first time for asymmetric oxidation of alkyl aryl sulfides by CHP in 1986.[80] Despite high yields of sulfoxides, the enantioselectivities of the reactions did not exceed 40%. In 1995, Bolm and Bienewald[81] found that the use of vanadium complexes with ligands **41a**,**b** obtained from the corresponding salicylaldehydes and optically active β-aminoalcohols allowed preparation of sulfoxides from alkyl aryl sulfides in good yields (up to 94%) and fairly good enantioselectivities (usually, *ee* 50% – 70%).[81] Aqueous hydrogen peroxide was used as an oxidant and chiral complexes were used in catalytic amounts (0.01 mol.% – 1 mol.%).

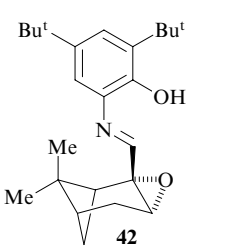


40a,**b** **41a**,**b**

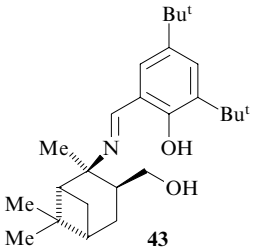
R = H (**a**), OMe (**b**). R = NO_2 (**a**), Bu^t (**b**).

The classical Bolm technique[81] based on the oxidation of prochiral sulfides with aqueous hydrogen peroxide in CH_2Cl_2 in the presence of catalytic amounts of the complex of VO(acac)$_2$ with the chiral Schiff base **41b** is unsuitable for the preparation of optically active esomeprazole (**1**) due to low conversion of the parent sulfide **2** and numerous side reactions. However, the replacement of H_2O_2 by CHP and of CH_2Cl_2 by toluene afforded compound **1** in a yield up to 62% and *ee* 14%.[79,82]

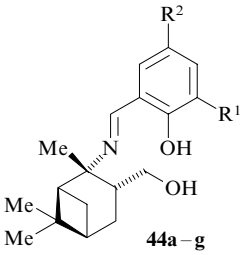
The replacement of compound **41b** by ligands **42**–**46** prepared from accessible terpenes [(−)-myrtenal, (−)- and (+)-pinenes, (+)-3-carene],[82–84] significantly influenced both the yield of compound **1** and enantioselectivity of transformations.



42

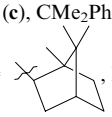


43

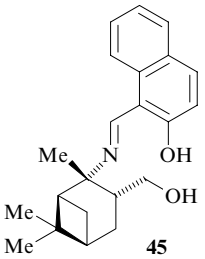


44a–**g**

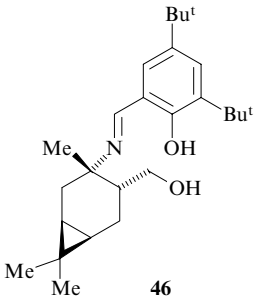
$R^1 = R^2 = Bu^t$ (**a**), H (**b**), NO_2 (**c**), CMe_2Ph (**d**);

R^1 = , R^2 = Me (**e**);

R^1 = H: $R^2 = NO_2$ (**f**), OMe (**g**).



45

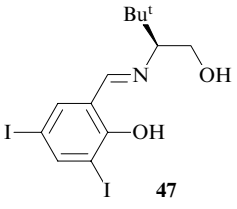


46

Thus the substitution of compound **42** for ligand **41b** allowed an increase in the yield of esomeprazole to 83% with *ee* 10%, the use of the less sterically hindered ligand **44b** increased the *ee* of sulfoxide **1** to 19%. Oxidation of sulfide **2** with cumene hydroperoxide in the presence of DIEA using the vanadyl complex with ligand **44b** resulted in an increase in the *ee* of sulfoxide **1** to 31% with simultaneous increase in the chemoselectivity of the reaction.[82]

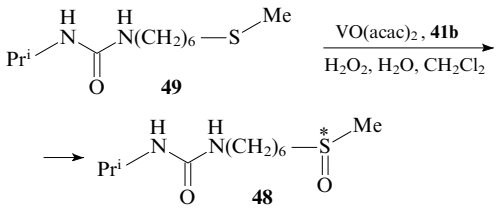
The oxidation with the latter system with monitoring of the *ee* of product **1**, revealed that it increased substantially with time, which might be explained by kinetic resolution of the sulfoxide formed. Actually, if racemic omeprazole was kept under the reaction conditions, the (*S*)-isomer (esomeprazole) with *ee* 50% was preferably obtained, whereas in the absence of DIEA, both enantiomers were consumed to form a complex mixture containing virtually no sulfoxide **1**. Remarkable that this effect of kinetic resolution was observed only when the catalitic system with ligand **44b** was used.[82]

The use of the Bolm system with ligand **47** for the synthesis of modafinil (**20a**) afforded the product in a yield of 45% and *ee* only 12%; the related compounds **20b**,**c** appeared racemic.[69]



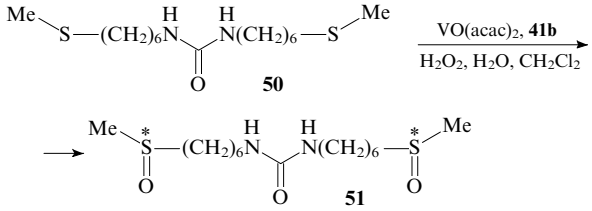
47

One of the key steps of the synthesis of the alkaloid (−)-diptocarpamine (**48**) is asymmetric sulfoxidation of the urea derivative **49**. Attempts to perform oxidation using the catalytic system $Ti(OPr^i)_4$ with diisopropyl tartrate appeared unsuccessful: in all cases, along with the starting compound, the racemic sulfoxide **48** was isolated in a yield not exceeding 35%.[85] The lack of optical induction and low yield of sulfoxide can be explained by both poor applicability of the titanium-based systems for chiral sulfoxidation of dialkyl sulfides and possible competitive complexation of $Ti(OPr^i)_4$ with the urea fragment of compound **49**.



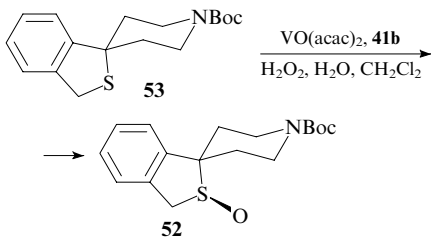
49 → **48**

Application of catalytic amounts of the complex $VO(acac)_2$ with ligand **41b** allowed the preparation[85] of the target alkaloid **48** in a yield of 91% and *ee* 45%. Similarly, oxidation of the symmetric urea derivative **50** yielded the alkaloid (−)-diptocarpidine (**51**) with *ee* 28%. Biological tests of alkaloids **48** and **51** revealed their pronounced antihypoxic activity.[86]



50 → **51**

Compound **52**, an important intermediate in the synthesis of tachykinin receptor antagonist, was prepared by asymmetric sulfoxidation of sulfide **53** using, among others, the catalytic systems including complexes of $Ti(OPr^i)_4$ with L-DET or BINOL and $VO(acac)_2$ with ligand **41b**.[87] The largest enantiomeric excess (54%) was achieved with the complex of titanium isopropoxide with DET and with the vanadium system; however, in the latter case, the yield of the sulfoxidation product was fourfold larger (80% *versus* 20% with the system $Ti(OPr^i)_4$–L-DET).



53 → **52**

Boc is *tert*-butoxycarbonyl.

* * *

Optically active sulfoxides are widely used as promising drugs. To date, numerous investigations resulted in the development of metal-complex catalytic systems for efficient sulfoxidation to chiral sulfoxides, including biologically active ones. The systems based on titanium (the Kagan

and Modena methods) and vanadium (the Bolm system) have been studied in most detail and are universal.

Although the use of the original Kagan, Modena and Bolm systems for the oxidation of polyfunctional sulfides often leads to the products with unsatisfactory enantiopurity, modification of these procedures (by alterating the reaction conditions, using different reactants and chiral and (or) achiral additives) allows, as a rule, the selection of appropriate conditions for enantiomeric sulfoxidation.

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