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Transition metal-catalyzed oxidations of bishomoallylic alcohols

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Dedicated to Professor Dr. K. Barry Sharpless.

Abstract

In recent years, new transition metal-catalyzed reactions for chemo- and stereoselective oxidations of bishomoallylic alcohols have been developed. The role of transition metals in this catalysis is connected with (i) activation of a primary oxidant (e.g. molecular oxygen, hydrogen peroxide, or *tert*-butyl hydroperoxide—reactivity), (ii) direction of the alkenol oxidation into a specific reaction channel (chemoselectivity), and (iii) control of the facial selectivity of π-bond oxygenation (stereoselectivity). The most important products which originate from these reactions are functionalized tetrahydrofurans which serve as valuable building blocks for the synthesis of e.g. polyether antibiotics or acetogenin-derived natural products. The selective formation of tetrahydropyrans in this type of chemistry is to date restricted to a structurally narrow range of substrates and the use of strongly Lewis-acidic oxidation catalysts. Likewise, only a few methods have been described so far which allow transition metal-catalyzed conversion of a bishomoallylic alcohol into an epoxyalcohol. In many other instances, the Lewis-acidity of the transition metal catalyst, which is required for peroxide or molecular oxygen activation, seems to suffice for converting an epoxyalcohol into secondary products such as functionalized tetrahydrofurans. Chemoselective oxidation of alkenols into γ,δ-unsaturated carbonyl compounds is until today still dominated by oxochromium(VI)-mediated methods. Only a few transition metal-catalyzed alternatives have been developed for this purpose so far. In view of the diversity of this chemistry, it is the aim of this review to organize the principles of transition metal-catalyzed oxidations of bishomoallylic alcohols and to present its state of the art in modern organic synthesis. An emphasis has been laid on the diastereoselective formation of functionalized cyclic ethers.

Keywords: Cobalt; Oxygen; Peroxides; Stereoselective synthesis; Transition metal catalysis; Tetrahydrofurans; Vanadium

1. Introduction [1]

The last two decades have witnessed a significant progress in the stereoselective synthesis of cyclic ethers. This development was initiated by a growing demand for synthetic polyether antibiotics [2]. In view of the significance of these compounds in particular and tetrahydrofuran-derived natural products in general [3–5], the invention of methods for stereoselectively constructing the tetrahydrofuran nucleus from δ,ε-unsaturated alcohols, e.g. **1** (Fig. 1), has received considerable attention [6,7]. It was soon recognized, that new reagents were required for this purpose, since low diastereoselectivities for tetrahydrofuran formation were frequently encountered in classical peracid-mediated bishomoallylic alcohol oxidations [8]. For toxicological reasons, it also became necessary to find substitutes for well-established reagents for oxidative ring closure reactions such as thallium(III) [9], lead(IV) [10], and mercury(II) salts [11]. Solutions for the majority of these problems were available from remarkable developments in the field of transition metal-catalyzed oxidations [12,13]. The discovery that a combination of $VO(acac)_2$ and *tert*-butyl hydroperoxide (TBHP) provides a selective oxidant for a conversion of allylic alcohols into corresponding epoxides [14–17] initiated studies on the stereoselective formation of substituted tetrahydrofurans **4** from bishomoallylic alcohols **1** [18]. In an early survey of this reaction, a surprisingly narrow structural diversity of alkenols **1** was investigated, since most known tetrahydrofuran-

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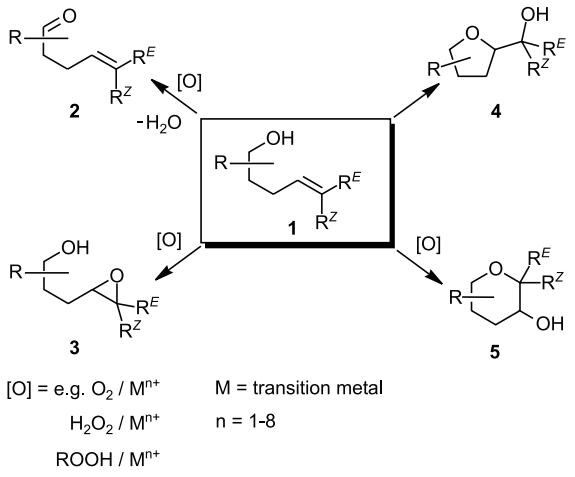


Fig. 1. Target products **2**–**5** in transition metal-catalyzed oxidations of bishomoallylic alcohols **1**.

subunits of polyether antibiotics consisted of 2,5-substituted entities [2]. Today, the knowledge about vanadium-catalyzed transformations of bishomoallylic alcohols in particular and transition metal-catalyzed oxidations of these substrates in general has increased significantly. Mild and selective methods have been developed which rely on other catalysts than the original reagent $VO(acac)_2$. Nowadays, cobalt(II) diketonates [19], vanadium(V) Schiff base complexes [20,21], *cis*-dioxomolybdenum(VI) diketonates [22,23], tungsten(VI) compounds [24], and rhenium(VII) oxo-complexes are applied for this purpose [25,26]. In most instances, molecular oxygen or hydrogen peroxide and its derivatives serve as primary oxidants which have to be activated by transition metal complexes in order to provide powerful but selective reagents. Based on the diversity of the chemistry of d-block elements, selective conversions of an alkenol **1** into the corresponding carbonyl compound **2**, epoxyalcohol **3**, tetrahydrofuran **4** [26,27], or in some instances into a tetrahydropyran **5** have become feasible [22,24,28].

In view of the diversity of this chemistry, it is the aim of this review to summarize and to organize the principles of chemoselective transition metal-catalyzed oxidations of bishomoallylic alcohols (Fig. 1) and to present its state of the art in modern organic synthesis. Emphasis has been laid on the formation of tetrahydrofurans **4**. Peracid mediated syntheses of heterocycles **4** and **5** from alkenols **1** have been omitted as well as oxidations by e.g. mercury(II) and thallium(III) salts. These aspects fall beyond the scope of a review on transition metal-catalyzed oxidations and have been covered in detailed articles elsewhere [6,11,12,29,30]. In the original concept of this work it seemed timely to include a chapter on selective metalloenzyme-catalyzed oxidations of alkenols **1** [31–33]. A survey of the literature, however, indicated that these reactions need additional research and development in order to be worked out into a useful method for organic synthesis.

2. General aspects

The concept of selective bishomoallylic alcohol oxidation requires the availability of an adequately strong oxidant for transformation of **1** either by a dehydrogenation mechanism or by an oxygenation reaction into one of the target compounds **2**–**5**. Based on thermochemical considerations, conversions of primary or secondary alcohols into corresponding carbonyl compounds (**1**→**2**) or CC π-bonds into 1,2-diol-derivatives (**1**→**3**, **1**→**4**, **1**→**5**) are feasible if molecular oxygen, hydrogen peroxide and its derivatives, or hypervalent oxo-compounds serve as oxidants [34–37].

Since the majority of transition metal-catalyzed oxidations of bishomoallylic alcohols require molecular oxygen, hydrogen peroxide, or TBHP as primary oxidant, selected properties and principles of activation of these reagents are outlined at the beginning of this review. With respect to ecological and economic considerations, molecular oxygen (50% active oxygen) and hydrogen peroxide (47% active oxygen) are considered as best oxidants (Table 1) [34–36]. In practice, *tert*-butyl hydroperoxide (TBHP) frequently is preferred for the following reasons [37,38]. The commercially available 5.5 M solution in nonane corresponds to a satisfactory active oxygen content of 11%. Further, *tert*-butanol is obtained as major co-product which is easily removed via distillation from reaction mixtures (b.p. = 83 °C). TBHP is readily soluble in organic solvents and thermally surprisingly stable under neutral conditions. A major advantage of TBHP compared with H_2O_2 also is the fact that it is less sensitive to metal contamination and does not react with most organic compounds in the absence of metal-catalysts. Hydrogen peroxide is in most instances applied as 30% aqueous solution which requires that all reagents and products are compatible with the presence of water in the reaction mixture. If this is not the case, neat urea perhydrate (urea hydrogen peroxide, UHP) may serve as alternative [34,35].

In spite of their high oxidation potentials, O_2, H_2O_2 and TBHP, if used alone, are relatively weak oxidants and require further activation [35,37]. Molecular oxygen ($^3O_2$) is a triplet diradical in its electronic ground state which precludes its direct reaction with saturated σ-bonded singlet-state molecules [36]. On the other hand, addition of triplet-dioxygen to olefinic π-bonds proceeds relatively slowly, if compared with abstractions of allylic hydrogen atoms [39]. However, coordination of $^3O_2$, for instance, as end on-bound dioxo-ligand to a transition metal complex may lift the degeneracy of its two highest half-filled orbitals which allows spin pairing in the dioxo-ligand (Fig. 2) [40,41]. The net effect is an

Table 1
Common primary oxidants in transition metal-catalyzed oxidations [34–36]

Entry	Compound [a]	Name (abbreviation)	Active oxygen (%)	Primary oxydant for metal... route [b]
1	O_2	Dioxygen	50 [c]	-peroxo, -oxo, -dioxo
2	H_2O_2	Hydrogen peroxide	47 (16) [d]	-peroxo, -oxo
3	$(H_3C)_3COOH$	*Tert*-butyl hydroperoxide (TBHP)	18 (11) [e]	-peroxy, -oxo
4	$(H_2N)_2CO \cdot H_2O_2$	Urea hydrogen peroxide (UHP)	17	-peroxo, -oxo
5	C_6H_5IO	Iodosobenzene	7	-oxo
6	$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$	Oxone®	3	-peroxo, -oxo

[a] For hydrates or mixed salts, commercially available compounds were selected which are commonly considered as suitable for storage without significant decomposition.
[b] Heterolytic activation.
[c] Based on the assumption that only one oxygen atom is used in a peroxidase-like mechanism.
[d] Figure in brackets denotes active oxygen content of a 30% (w/w) aqueous hydrogen peroxide solution.
[e] Figure in brackets is valid for a 5.5 M solution of TBHP in nonane.

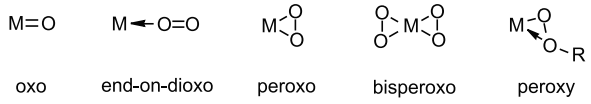
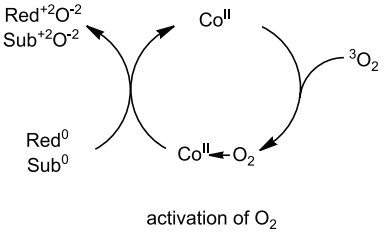


Fig. 2. Nomenclature for key functionalities which are obtainable from reactions of transition metal ions with peroxides or with molecular oxygen [38,40].

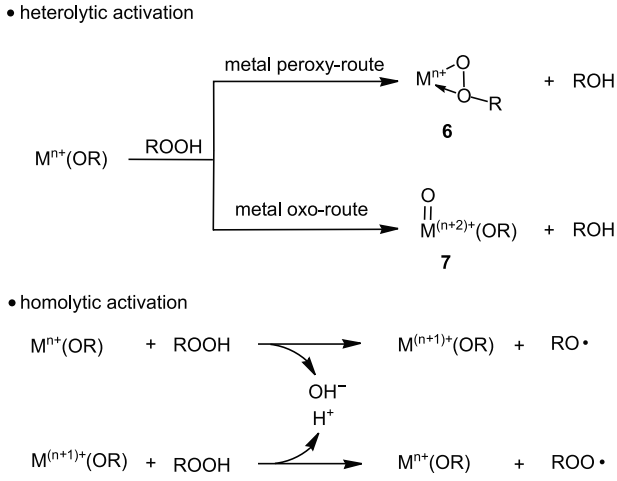
activation of molecular oxygen for selective oxidation of substrates, e.g. Sub (Scheme 1). The major issue thereby is the fact that the second oxygen atom of O_2 has to be consumed by a reducing agent Red, similarly to the formation of water in peroxidase-catalyzed reactions [19,42].

Hydrogen peroxide reacts only slowly with most organic substrates such as olefins, aromatic hydrocarbons, or alcohols. In order to serve as synthetically useful oxidant it has to be activated, for instance, by acids, bases, or UV-light or it must be converted into a peracid, a dioxirane, or a suitable persalt [35]. In the last years, activation of H_2O_2 and its derivative TBHP by transition metal ions has become more and more important. Both oxidants react basically similar with transition metals either via a heterolytic or a homolytic mechanism (Scheme 2) [38]. For example, heterolytic activation of TBHP starts with conversion of transition metal complex M^{n+} into *tert*-butyl peroxy-complex **6**. The oxidation state of the central ion is retained in this case. The reactive coordination compound **6** may deliver the terminal oxygen of the peroxy-entity to, for instance, bishomoallylic alcohol **1** [18,38]. This type of reaction is frequently observed for early transition metals with a d^0 electron configuration such as Ti^{+4}-, Zr^{+4}-,V^{+5}-, Mo^{+6}-, or W^{+6}-complexes [12]. The availability of low lying empty d-orbitals is a prerequisite for the transition metal peroxy-entity to serve as strong oxidant since the oxygen atom transfer proceeds via a nucleophilic attack of the substrate onto the σ* orbital of the OO bond (see Section 3) [43].

The reaction of hydrogen peroxide with a transition metal ion may afford a peroxo-complex (for coordination compound notation see Fig. 2). Although a peroxo-complex is structurally similar to a peroxy-complex **6**, it may behave chemically different. Since the dianionic peroxo-ligand is stronger coordinated than a peroxy-group, a conversion of a transition metal into a bisperoxo-complex often is required in order to obtain a sufficiently strong oxidant [47]. In addition, peroxo-complexes tend to decompose additional H_2O_2 in a



Scheme 1. Schematic presentation of cobalt(II)-catalzed oxygenations using molecular oxygen as primary oxidant [19,40]. Superscripts for Sub, Red, and cobalt refer to oxidation numbers.



Scheme 2. Mechanisms for heterolytic (top) and homolytic peroxide activation (bottom) [38]. R = e.g. $C(CH_3)_3$, M = transition metal, n = 1–8.

catalase-like reaction, which is not observed for peroxy-complexes [35,43–47].

The second mechanism for heterolytic activation of both oxidants, TBHP and H_2O_2, is associated with the formation of oxo-complex **7** by transfer of a peroxidic oxygen atom to M^{n+} (Scheme 2) [12,38]. This reaction causes a two electron oxidation of the central ion. It is a more common way for peroxide activation by late transition metal ions such as Os^{+8} which provides strong oxidants for organic substrates with π-bonds or filled nonbonding orbitals [38].

The third pathway for peroxide activation involves single electron transfer from a transition metal ion M^{n+} onto TBHP or H_2O_2. This reaction is followed by homolytic cleavage of an OO bond in a Fenton-type reaction (Scheme 2) [38,48]. It is obvious, that this type of peroxide activation initiates oxidations via hydrogen atom abstractions by free radical intermediates. A comparison of redox potentials of transition metal ions or compounds which are frequently applied as catalysts or reagents for oxidation of organic substrates indicates that the homolytic mechanism for peroxide activation may become important in e.g. cobalt(III)-, chromium(VI)-, vanadium(V)-, iron(III)-, or rhenium(VII)-catalyzed reactions (entries 1–5, Table 2) while titanium(IV) or tungsten(VI) compounds preferentially act as Lewis acids for heterolytic peroxide activation (entries 6,7, Table 2) [49].

Table 2
Redox potentials for selected transition metal ions or oxo-compounds [49]

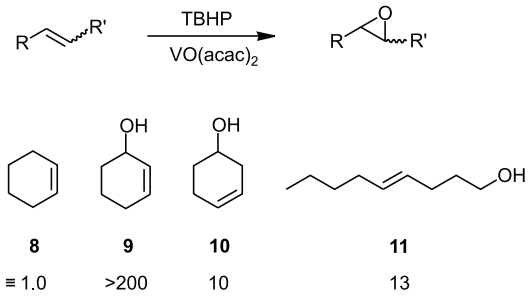
$$M^{n+} + e^- \xrightarrow{H_2O} M^{(n-1)+}$$

entry	$M^{n+} + e^-$	$M^{(n-1)+}$	E_0(V) (vs. NHE)
1	$Co^{3+} + e^-$	Co^{2+}	1.84
2	$1/2\ Cr_2O_7^{2-} + 7\ H^+ + 3\ e^-$	$Cr^{3+} + 7/2\ H_2O$	1.33
3	$VO_2^+ + 2\ H^+ + e^-$	$VO^{2+} + H_2O$	1.00
4	$Fe^{3+} + e^-$	Fe^{2+}	0.77
5	$ReO_4^- + 2\ H^+ + e^-$	$ReO_3 + H_2O$	0.77
6	$Ti(OH)^{3+} + H^+ + e^-$	$Ti^{3+} + H_2O$	0.06
7	$WO_3 + H^+ + e^-$	$1/2\ W_2O_5 + 1/2\ H_2O$	−0.03

3. Formation of tetrahydrofurans

3.1. Application of transition metal peroxy- and peroxo-mechanisms

The reagent combination of $VO(acac)_2$ and TBHP serves as efficient oxidant for epoxidation of alkenes [50,51]. Data from competition kinetic experiments in benzene ($T = 80$ °C) show, that 2-cyclohexenol (**9**) is



Scheme 3. Relative rate constants for olefin epoxidation in C_6H_6 ($T = 80$ °C) [52].

epoxidized more than 200 times faster than cyclohexene (**8**) [52]. Likewise, epoxidation of homoallylic alcohol **10** ($k^{rel} = 10$) and bishomoallylic alcohol **11** ($k^{rel} = 13$) proceed faster than the conversion of olefin **8** into cyclohexene oxide (Scheme 3).

It is known that TBHP oxidizes $VO(acac)_2$ in $C_2H_4Cl_2$ at 20 °C with a bimolecular rate constant of 12.9 $M^{-1}s^{-1}$ to afford a vanadium(V) compound [53]. It is generally accepted that this vanadium(V) compound activates TBHP via the peroxy-mechanism in order to provide an electrophilic oxidant [12,26,54]. Based on relative rate constants for olefin epoxidations (Scheme 3) and the fact that vanadium(V) complexes may adopt coordination numbers up to seven, binding of an alkenol to the intermediate vanadium(V) peroxy-complex should not only be feasible but also an important step for reactivity and selectivity control in the epoxidation reaction [50,55]. Although many vanadium(V) peroxy-complexes have been generated and investigated spectroscopically in solution, vanadium(V) *tert*-butyl peroxy-complex **12** is to date the only example which has been successfully characterized by X-ray diffraction analysis (Fig. 3) [56]. Its geometry served as starting point for a computational study on the mechanism of

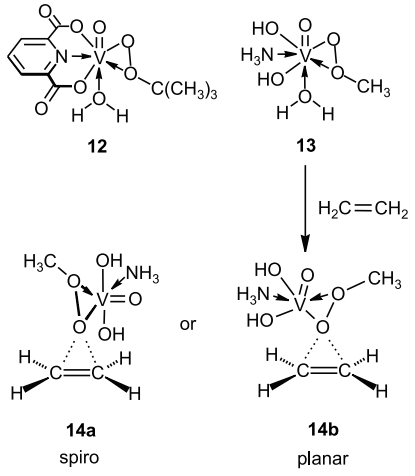
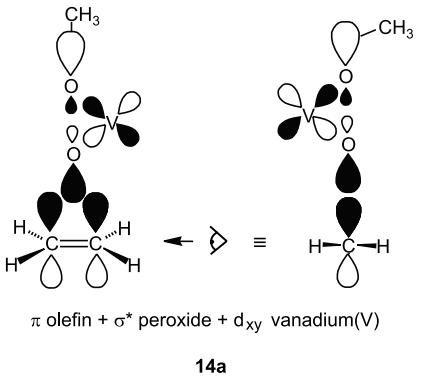


Fig. 3. Geometries of vanadium(V) peroxy-complexes **12** and **13** and proposed transition structures **14a** and **14b** for oxygen atom transfer onto ethene by peroxy-compound **13** [43,56,57].



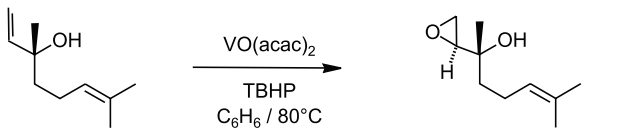
14a

Fig. 4. Favorable frontier molecular orbital interaction for oxygen atom transfer in transition structure **14a** (see Fig. 3) [43].

oxiran formation from vanadium(V) methyl peroxy-complex **13** and ethylene [43]. The graphics in Fig. 4 schematically illustrate the favorable frontier molecular orbital (FMO) interaction for CO bond formation which arises from interaction between the HOMO of the olefin and an unoccupied orbital in peroxy-complex **13**. The latter orbital is energetically located directly above the LUMO of vanadium(V) complex **13**, and principally constitutes a combination of the σ* of the OO bond and the d_{xy} orbital at vanadium(V). The FMO interaction between donor and acceptor orbitals defines a trajectory for oxygen atom transfer which requires a backside attack of the π-bond onto the peroxy-entity in transition structure **14a**. Due to a secondary orbital interaction between the lone pair at the transferable oxygen and the π*-orbital of the olefin (not shown in Fig. 4), spiro-configured intermediate **14a** should be energetically favored over planar arrangement **14b** [42,57].

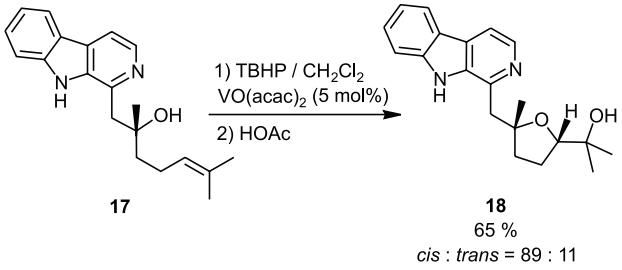
From a historic point of view, $VO(acac)_2$ was the first and in the following years most frequently used vanadium-source for catalyzing selective oxidations of bishomoallylic alcohols by TBHP [2]. Based on competition kinetic data which are given above (Scheme 3) it is obvious that a $VO(acac)_2$–TBHP-mediated oxidation of linalool **15** selectively affords allylic epoxyalcohol **16** although polar effects should have favored formation of the 6,7-epoxide (not shown in Scheme 4) [52,58].

In view of the propensity of $VO(acac)_2$ to convert alkenols upon addition of TBHP into corresponding epoxides, the standard procedure for preparation of



15 **16**
84 %
(2*S*, 3*R*) : (2*R*, 3*R*) = 75 : 25

Scheme 4. Vanadium-catalyzed epoxidation of linalool **15** [52,58].



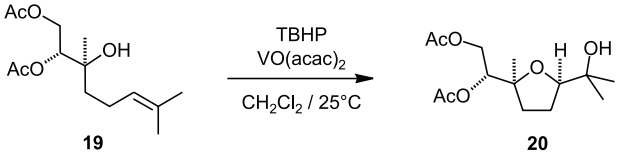
17 **18**
65 %
cis : *trans* = 89 : 11

Scheme 5. Stereoselective construction of the tetrahydrofuran subunit in the synthesis of β-carboline-derived alkaloid chrysotricine [59].

tetrahydrofurans in this type of reaction recommends treatment of the primary oxidation product with acetic acid. Acidic work-up ensures efficient formation of, for instance, tetrahydrofuran derivative **18** from tertiary alkenol **17** (Scheme 5) via a Payne-type rearrangement of an intermediate epoxyalcohol (not shown in Scheme 5). Conversion of alkenol **17** proceeds 2,5-*cis*-selectively and affords a valuable starting material for the synthesis of β-carboline-derived alkaloid chrosytricine from rubiacea *Hedyotis chrysotricha* [59].

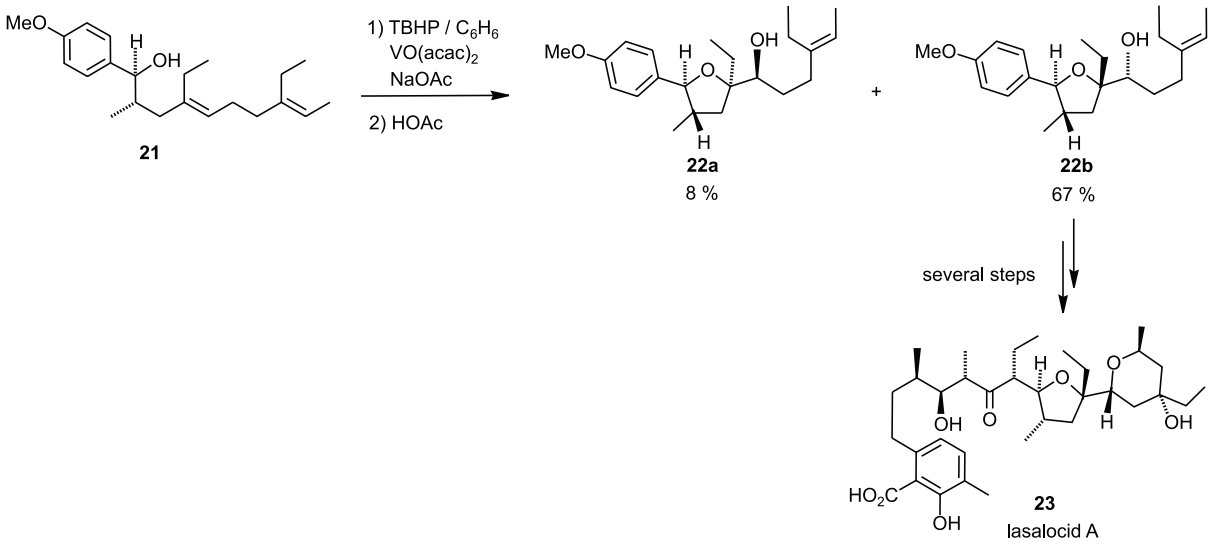
Other examples are known, such as the oxidation of linalool-derivative **19**, were alkenols are directly converted into corresponding tetrahydrofurans, e.g. heterocycle **20**, by a combination of $VO(acac)_2$ and TBHP (Scheme 6) [60]. Since $VO(acac)_2$ is not only a Lewis acid but also reacts slightly acidic, especially in the presence of traces of protic nucleophiles such as water or alcohols, it may be possible that initially formed epoxyalcohols are directly rearranged in this reaction into the desired tetrahydrofuran **20** without the necessity of adding acetic acid for driving the epoxide ring opening to completion. Formation of the 2,5-*cis*-configured isomer of **20** as major product is in line with diastereoselectivities of similar transformations using secondary 1,5,5-trisubstituted bishomoallylic alcohols as substrates. Chiral tetrahydrofuran **20** served as D-ring building block for squalene-derived polyether venustatriol [61].

In those instances where the presence of acid conflicts with efficient tetrahydrofuran formation, a two-step sequence was proposed which requires the presence of NaOAc as buffering reagent in the oxidation step [18]. Thus, reaction of 1,2,4,5-tetrasubstituted bishomoallylic alcohol **21** with TBHP and $VO(acac)_2$ in the presence of



19 **20**
90 %
cis : *trans* = 89 : 11

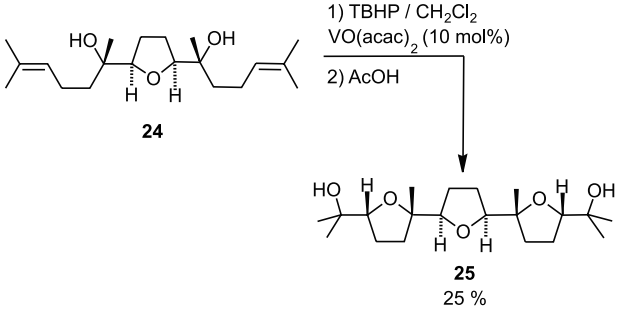
Scheme 6. Stereoselective formation of tetrahydrofuran-derived building block **20** in the total synthesis of venustatriol [60].



Scheme 7. Stereoselective synthesis of the tetrahydrofuran subunit of lasalocid A (**23**) [2,18].

NaOAc and work-up of the reaction mixture by treatment with acetic acid afforded diastereomeric tetrahydrofurans **22a** and **22b** in a ratio of 11:89. In view of relative configuration, formation of the 4-*cis*-5-*trans*-isomer **22b** is favored over 4-*trans*-5-*cis*-derivative **22a**. The intermediacy of epoxyalcohols (not shown in Scheme 7) was confirmed by adding Ac_2O and pyridine instead of HOAc in the second step of the reaction. Major product **22b** was transformed in a multi-step sequence into antibiotic lasalocid A (**23**) [2,18].

Since several physiologically active ionophors such as teurilene, glabrescol, 14-deacetyl eurylene, or longilene peroxide consist of more than one tetrahydrofuran unit, attempts were made to apply the combination of $VO(acac)_2$ and TBHP for preparation of bis- and tristetrahydrofuran-entities [2]. Thus, oxidation of substituted heterocycle **24** using TBHP and 10% of $VO(acac)_2$ allowed 2,5-*cis*-selective conversion of both bishomoallylic alcohol units in substrate **24** in a single synthetic step into tristetrahydrofuran **25** (Scheme 8) [62]. Although the yield of target product **25** remained low, the utility of the method certainly lies in its high and predictable, 2,5-*cis*-stereoselectivity for this type of substrates. This observation is noteworthy since bistetrahydrofuran-derived alkenols are known to be delicate

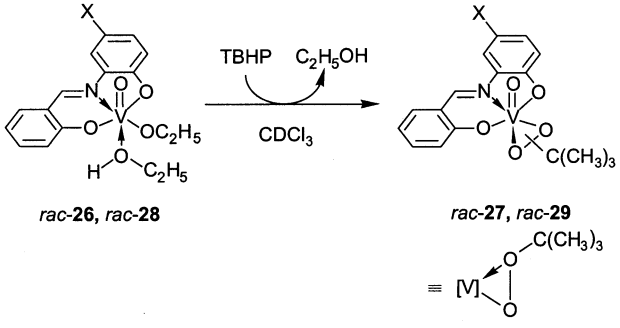


Scheme 8. Stereoselective synthesis of tristetrahydrofuran **25** [62].

substrates to selectively oxidize. A sequential construction of a tristetrahydrofuran from a suitable trienol has been shown to be associated with a change in diastereoselectivity for the formation of the third tetrahydrofuran subunit. This fact was interpreted in terms of coordination of a reaction intermediate, the corresponding bistetrahydrofuran-substituted bishomoallylic alcohol, to the transition metal catalyst which caused a change in facial selectivity for π-bond oxygenation [63].

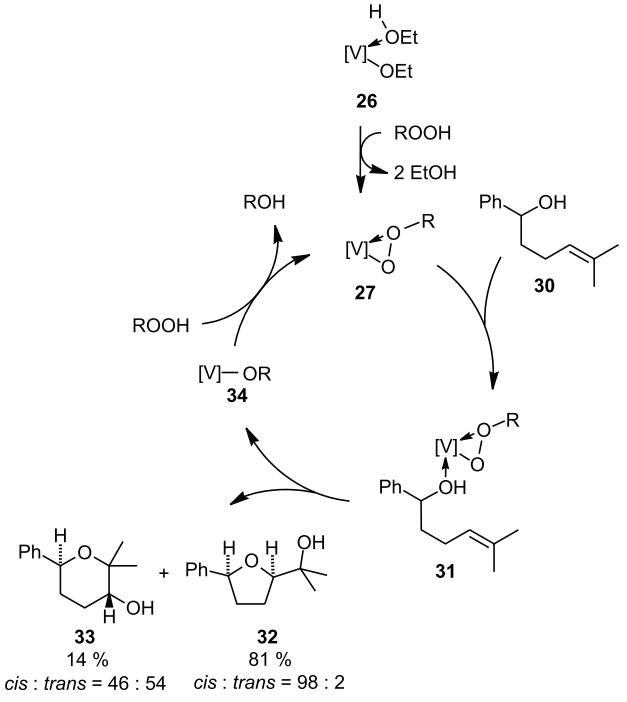
Recently, a more efficient and selective catalyst for the diastereoselective tetrahydrofuran formation from substituted bishomoallylic alcohols has been developed on the basis of vanadium(V) Schiff base complexes with tridentate ligands [20,21]. These vanadium(V) complexes, e.g. **26** and **28**, react preferentially in chlorinated solvents with TBHP to afford vanadium(V) peroxy-

Table 3
^{51}V-NMR chemical shifts for vanadium complexes **26**–**29** [20,65]

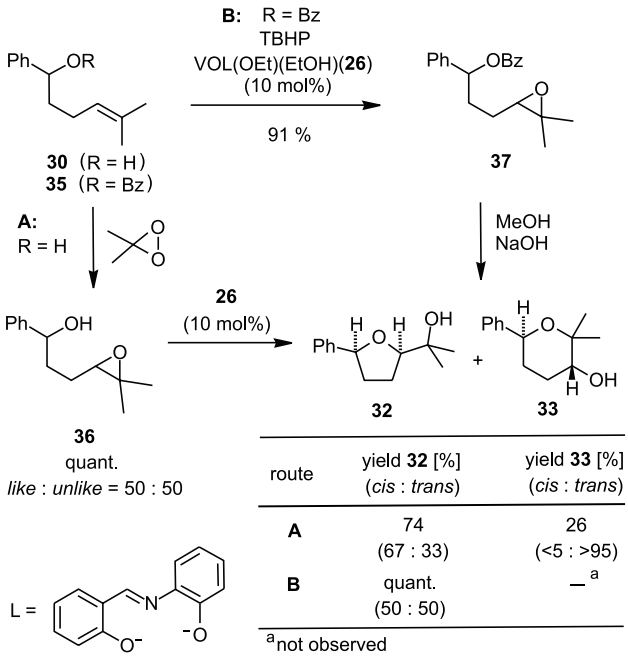


entry	X	compound	δ ^{51}V [ppm] ($CDCl_3$)
1	H	*rac*-**26**	− 530
2	H	*rac*-**27**	− 569
3	CO_2H	*rac*-**28**	− 538
4	CO_2H	*rac*-**29**	− 578

complexes, e.g. **27** and **29** (Table 3), which have been identified by IR or by ^{51}V-NMR spectroscopy or by ESI-MS spectrometry (**29**) [64,65]. In the original work on the synthesis of peroxy-complex **27** it was observed that epoxidation of unfunctionalized olefins such as cyclohexene (**8**) using TBHP as oxidant and 10 mol% of Schiff base complex **26** as catalyst is feasible while epoxidation of allylic alcohol surprisingly fails [66]. In view of these facts it is interesting to note that 1,5,5-trisubstituted bishomoallylic alcohol **30** is readily oxidized by TBHP in the presence of 10 mol% of vanadium(V) imine complex **26** to provide 2,5-disubstituted tetrahydrofuran **32** as major and tetrahydropyran **33** as minor product (Scheme 9) [20,64]. The observed 2,5-*cis*-diastereoselectivity (*cis*:*trans* = 98:2) for tetrahydrofuran formation from alkenol **30** is improved in comparison to the same transformation in the presence of TBHP and VO(acac)$_2$ (for **30**: *cis*:*trans* = 94:6). Further, thorough product analysis indicated, that the number of typical side products such as 5-methyl-4-hexeno-1-phenone (not shown in Scheme 9) and compounds originating from multiple oxidations which generally accounted for an average of 10% of reaction products from substrate **30** by TBHP in the presence of VO(acac)$_2$, could be limited to less than 2% [20]. Based on results from mechanistic studies, this reaction proceeds via a vanadium(V) peroxy-mechanism [64,65]. Thus, alkenol **30** binds to peroxy-complex **27** and affords after intramolecular, *syn*-selective oxygenation cyclic ethers **32** and **33** in an overall yield of 95%.



Scheme 9. Proposed catalytic cycle for the synthesis of cyclic ethers **32** and **33** in vanadium(V) Schiff base complex-catalyzed oxidation of bishomoallylic alcohol **30** [20,64]. R = C(CH$_3$)$_3$.

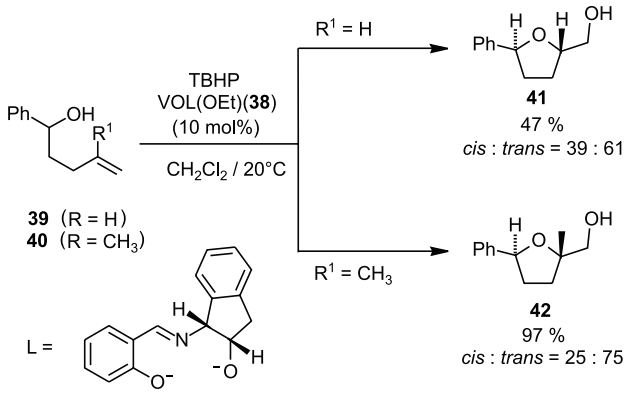


Scheme 10. Selectivities in the synthesis of cyclic ethers **32** and **33** from epoxyalcohol **36** (route A) or benzoate **37** (route B) [20,64].

Proposed vanadium(V) alkoxo-complex **34** is considered to react with TBHP for regeneration of peroxy-complex **27**. Surprisingly, ^{1}H-NMR spectroscopic monitoring of the reaction provided no experimental evidence for formation of epoxyalcohol **36** as intermediate in this type of alkenol oxidation (see Scheme 10) [20,64].

The role of the transition metal for controlling the facial selectivity in alkenol oxygenation and hence the diastereoselectivity of tetrahydrofuran formation has been demonstrated by conducting a vanadium-free epoxidation of bishomoallylic alcohol **30** using a solution of dimethyl dioxirane (DMD) as oxidant (Scheme 10) [20,64]. Treatment of an equimolar *like*/*unlike*-mixture of epoxyalcohol **36** with Lewis acid **26** affords a 74/26-distribution of tetrahydrofuran **32** (*cis*:*trans* = 67:33) and tetrahydropyran **33** (*cis*:*trans* < 5: > 95). An alternative investigation started from benzoate **37** which was epoxidized by TBHP in the presence of catalytic amounts of vanadium(V) complex **26** to afford a 50/50-mixture of *like*/*unlike*- configured epoxide **37**. Saponification of the ester **37** afforded equimolar amounts of both diastereomers of 2,5-disubstituted tetrahydrofuran **32**. Thus, formation of cyclic ether **32** from substrate **30** is by far more selective, if the reagent combination of vanadium(V) complex **26** and TBHP are used for heterocycle synthesis [20,64].

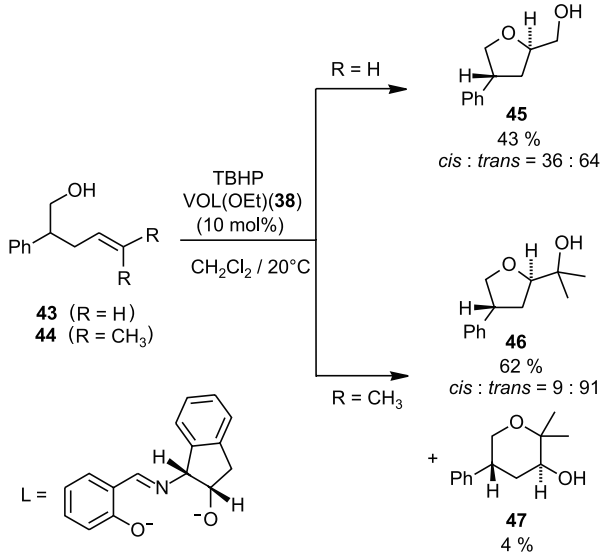
In further experiments directed towards an improvement of diastereoselective tetrahydrofuran formation from bishomoallylic alcohols, 1-amino-2-indanol-derived vanadium(V) complex **38** attracted attention since it was the most selective catalyst in a larger survey of oxidation reactions. Therefore, complex **38** was applied



Scheme 11. Formation of cyclic ethers **41** and **42** in vanadium(V) Schiff base complex-catalyzed oxidations [20,64].

in a structure-selectivity study in order to investigate diastereoselection by steric substituent effects in oxidative ring closure reactions (Schemes 11–14) [20,64]. Thus, 1-substituted bishomoallylic alkenol **39** and its 1,4-disubstituted derivative **40** were oxidized in the presence of catalytic amounts of vanadium complex **38** to afford 2,5-substituted tetrahydrofurans **41** and **42** (Scheme 11). Both transformations afforded the corresponding *trans*-substituted isomers as major products [20].

Oxidation of 2-substituted bishomoallylic alcohol **43** and its 2,5,5-trisubstituted derivative **44** with TBHP and catalytic amounts of vanadium(V) complex **38** afforded 2,4-disubstituted tetrahydrofurans **45** and **46** (Scheme 12). In addition, 4% of 3,5-*trans*-substituted tetrahydropyran **47** were obtained from oxidation of alkenol **44** [20]. Alkenols **43** and **44** are preferentially converted into *trans*-configured oxolanes. For judging the synthetic utility of this transformation it is important to

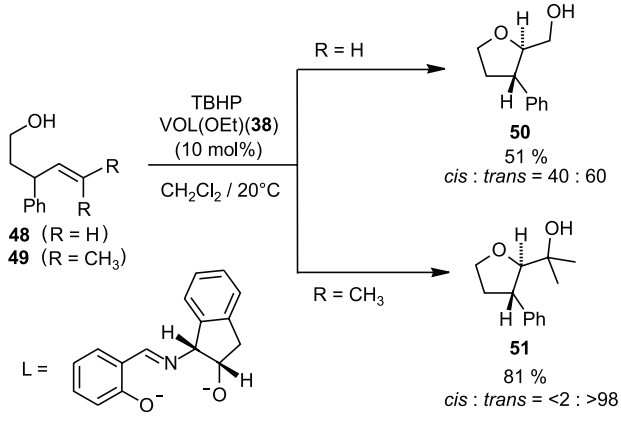


Scheme 12. Stereoselective synthesis of 2,4-*trans*-disubstituted tetrahydrofurans **45** and **46** [20,64].

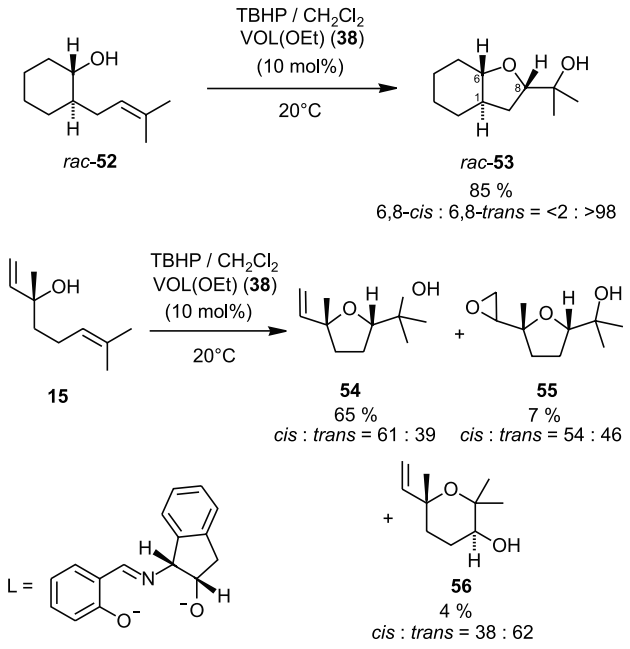
note that the selectivity for product formation which is outlined in Scheme 12 is complementary to those for both substrates in, for instance, classical halogen cyclizations [6,7,65]. The latter type of reaction provides a 2,4-*cis*-configured tetrahydrofuran as major product for conversion of substrate **43** and substituted tetrahydropyrans for halogen cyclization of **44** [65].

2,3-Disubstituted tetrahydrofurans **50** and **51** have been prepared by oxidizing 3-substituted bishomoallylic alcohol **48** and its 3,5,5-trisubstituted derivative **49** by TBHP in the presence of 10 mol% vanadium catalyst **38** (Scheme 13) [20]. In both instances, *trans*-configured isomers of heterocycles **50** and **51** were obtained as major products.

Vanadium(V) Schiff base complex **38** has been applied in the synthesis of substituted oxabicyclo[4.3.0]nonane *rac*-**53** from allyl-substituted cyclohexanol *rac*-**52** and TBHP (Scheme 14). The high diastereoselectivity for the formation of heterocyclic compound *rac*-**53** may be rationalized in view of the fact that a 2,5-*cis*- and 2,4-*trans*-substitution pattern denotes a matched-case for the formation of substituted tetrahydrofurans from this type of substrate (see Schemes 9 and 12) [64]. Additional experiments on the regioselectivity of oxidation of linalool **15** were carried out using TBHP as oxidant and indanolamine-derived vanadium(V) complex **38** as catalyst. In contrast to previous reactions, not 1,2-epoxide **16** (see Scheme 4) but linalooloxide **54** was obtained in 65% yield, besides epoxide **55** (7%) and linalool-derived tetrahydropyran **56** (4%, Scheme 14) [64]. The formation of terpene-derived tetrahydrofuran **54** proceeds 2,5-*cis*-selectively (*cis*:*trans* = 61:39). The synthetic significance of this observation is easily recognized if it is compared with selectivity data from commonly used reactions for converting tertiary bishomoallylic alcohol **15** into cyclic ethers. Thus, peracid-mediated linalool oxidations provide equimolar mixtures of *cis*/*trans*-isomers of **54** along



Scheme 13. Preparation of 2,3-*trans*-configured tetrahydrofurans **50** and **51** in vanadium(V) Schiff base complex-catalyzed oxidations [20,64].



Scheme 14. Formation of bicyclic compound *rac*-**53** and linalool-derived oxolanes **54** and **55** in vanadium(V) Schiff base complex-catalyzed oxidations [64].

with substantial amounts of both isomers of tetrahydropyran **56** [67]. A time-dependent analysis of product formation from alkenol **15** in the vanadium(V) Schiff base-catalyzed reaction illustrates that vinyl-substituted heterocycle **54** serves as starting material for the synthesis of epoxytetrahydrofuran **55** and not 1,2-epoxylinalool **16**. The unusual selectivity for linalool-oxide formation in a vanadium-catalyzed oxidation of substrate **15** may be explained by the reluctance of vanadium(V) peroxy-complex **27** to epoxidize allylic alcohols which restricts the preferential site of oxygenation to the π-system of the bishomoallyl subunit [64,66].

A model has been proposed in order to rationalize formation of major products in vanadium(V) Schiff base complex-catalyzed tetrahydrofuran syntheses from bishomoallylic alcohols. This mnemonic device may serve to predict selectivities in new vanadium(V)-catalyzed oxidations for an application in synthesis [21,64]. For a proper description of this model it is important to emphasize that the central ion in oxovanadium(V)

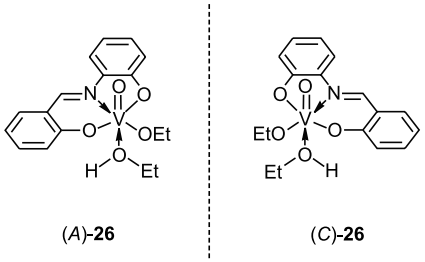


Fig. 5. Geometry of vanadium(V) Schiff base-complex (*A*)-**26** (left) and its (*C*)-enantiomer (right) [68].

compounds with tridentate Schiff base ligands is a stereogenic center [21,68] (Fig. 5).

In oxidations which are outlined in this review, either 50/50-mixtures of enantiomeric (e.g. **26**, achiral ligand, Fig. 5) or ca. equimolar mixtures of diastereomeric vanadium(V) Schiff base complexes (e.g. **38**, optically active auxiliary, Schemes 11–14) were applied as catalysts for oxidation of racemic mixtures of substrates **1**. Therefore it is reasonable to restrict the stereochemical discussion to the reaction of one enantiomer of vanadium(V) peroxy-complex, e.g. **27**, with one enantiomer of chiral bishomoallylic alcohol **1** (Fig. 6, Scheme 15). The initial step of the catalytic cycle of bishomoallylic alcohol oxidation, requires formation of a vanadium(V) peroxy-complex, e.g. **27** (TBHP activation, Scheme 9). If the equatorial binding mode in peroxy-complex **12** is taken as archetype for TBHP coordination in vanadium(V) complexes in general, either a proximal or a distal arrangement of the *tert*-

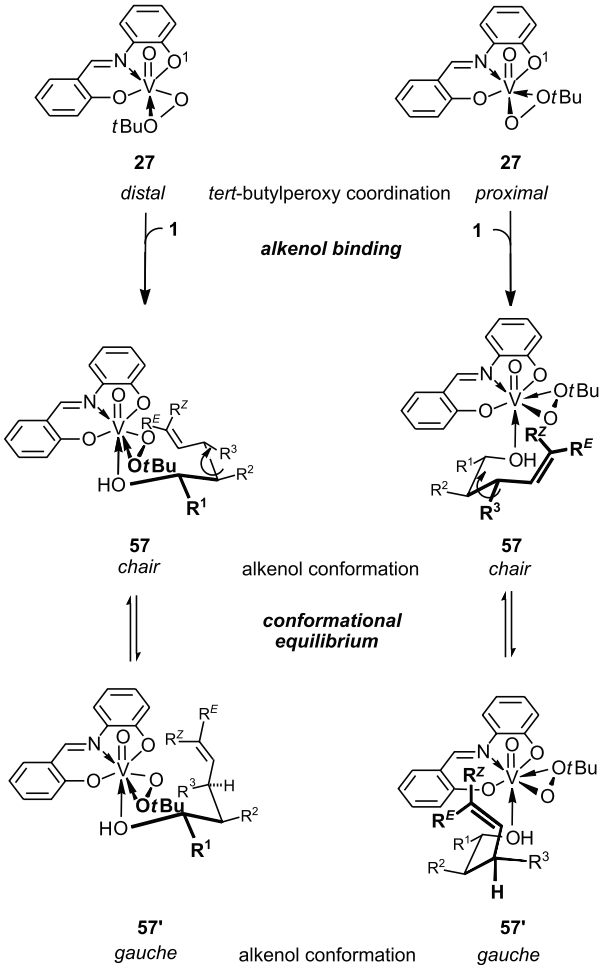
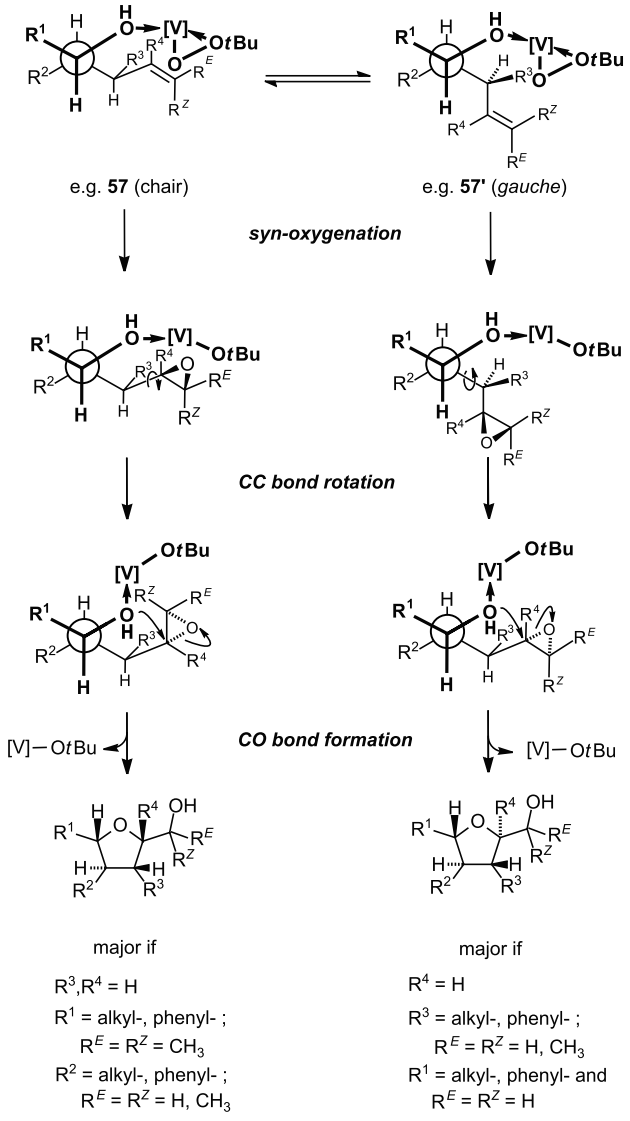


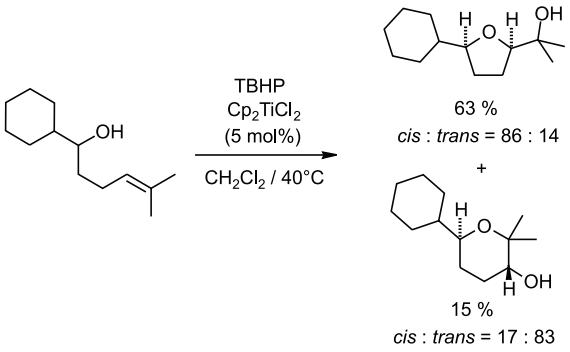
Fig. 6. Proposed modes of binding of the *tert*-butyl peroxy-ligand in vanadium(V) complex **27** (top), and structures of preferred conformers for oxygenation of alkoxo-ligands in 'loaded' compounds **57** (center and bottom). The superscript at one of the Schiff base oxygens denotes the donor atom of highest CIP-priority.



Scheme 15. Proposed stereochemical model for the formation of major products in vanadium(V) Schiff base complex-catalyzed tetrahydrofuran syntheses [64].

butyl substituent with respect to the atom of highest priority in the tridentate auxiliary (i.e. O1, Fig. 6) should be observed. Based on results from competition kinetic experiments, binding of substrate **1** to e.g. vanadium peroxy-complex **27** follows. Two aspects may contribute to rationalize substrate binding more closely. First, it is known from X-ray crystallographic data of aminophenol-derived vanadium(V) Schiff base complex **26** that ethanol may coordinate in *trans*-position to the VO double bond [69]. A long oxygen vanadium(V) connectivity which is observed for binding of a neutral ethanol molecule in coordination compound **26** has been interpreted in terms of a significant *trans*-effect of the oxo-ligand [55,64,69]. Second, substitution of an alkoxo ligand has been observed in ESI-MS investigations by reacting bishomoallylic alcohol **30** with vanadium(V) Schiff base complex **28**. Both observations point to the fact that alkenol binding to vanadium(V) complexes in non-coordinating solvents is feasible (see Table 3, Scheme 9) [65]. Since the conformational flexible alkenol ligand may adopt, for instance, a *chair*-like conformer (Fig. 6, Scheme 15, left) or a *gauche* arrangement (Fig. 6, Scheme 15, right) in 'loaded' vanadium(V) complex **57**, short distances between the peroxy-entity and the π-bond in addition to favorable a stereoelectronic alignment (see Fig. 4) allow efficient intramolecular oxygen atom transfer to take place. Thus, at least two competing pathways for oxygenation should exit which differ in facial selectivity of product formation. In this model, vanadium(V)-coordinated epoxyalcohols are formed as primary products. However, these intermediates, if they exist at all, should be very short-lived, because they have until today not been detected spectroscopically in vanadium(V) Schiff base complex-catalyzed oxidations of bishomoallylic alcohols [20,64]. Rearrangement of primary oxygenation products into tetrahydrofurans requires a stereo-controlled backside attack of the hydroxyl oxygen atom onto the C4O bond of the epoxide entity. Comparison of main products obtained from oxidation reactions (see Schemes 9–14) to those predicted as major isomers from the dual reaction channel model lead to a number of instructive results. (i) Since diastereoselectivity but not diastereospecifity is observed in all experiments, apparently both stereochemical modes of π-bond oxygenation operate for all substrates. In view of the fact that generally low diastereoselectivities are obtained for oxidation of bishomoallylic alcohols which lack in additional methyl groups at position 5 (e.g. **39**, Scheme 11, **43** in Scheme 12, **48** in Scheme 13) energetic differences between competing channels should be small, unless sterically more demanding substrates (e.g. **30**, Scheme 9, **40** in Scheme 11, **44** in Scheme 12, **49** in Scheme 13) or conformationally more rigid bishomoallylic alcohols are bound to vanadium peroxy-complexes (e.g. *rac*-**52** in Scheme 14). (ii) Even substrates with trisubstituted double bonds may show opposite facial selectivities in the oxygenation step. For instance, oxygenation of 1,5,5-bishomoallylic alcohol **30** seems to occur mainly via a chair-like transition state to afford *cis*-2,5-disubstituted tetrahydrofuran **32** as major product (Scheme 9). On the other hand, a *gauche* conformer should be preferred for oxygenation of 3,5,5-trisubstituted isomer **49** which then provides *trans*-2,3-disubstituted tetrahydrofuran **51** as diastereomerically pure product (Scheme 13). (iii) 1-Phenyl-substituted bishomoallylic alcohol **39**, 1-alkyl derivatives thereof (not shown in Scheme 11), and 1-phenyl-4-methyl-4-penten-1-ol (**40**) (all *trans*-selective) are oxygenated with opposite selectivity if compared with 1,5,5-trisubstituted substrates, e.g. **30** (*cis*-selective) [64].

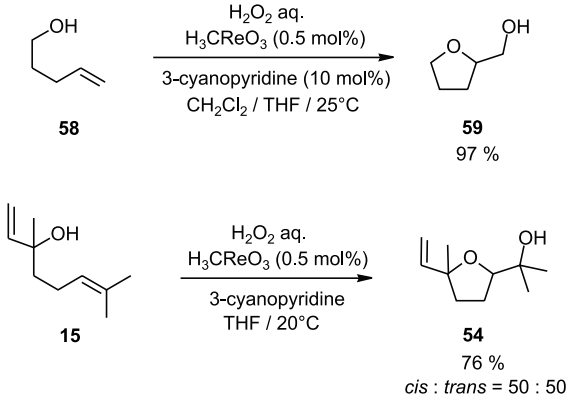
In addition to the multitude of vanadium-catalyzed reactions, a new method for the synthesis of substituted



Scheme 16. Formation of cyclic ethers in a titanium-catalyzed oxidation of a bishomoallylic alcohol [70].

tetrahydrofurans from bishomoallylic alcohols has been described recently. The methods requires Cp_2TiCl_2 as catalyst and TBHP as primary oxidant (Scheme 16) [70]. In comparison with data reported from the first study on vanadium(V) Schiff base complex-catalyzed tetrahydrofuran formation, which had appeared a year earlier, the titanium-based reaction seems to provide qualitatively similar results, but offers with respect to efficiency and diastereoselectivity for oxolane synthesis slightly inferior values.

While the majority of known tetrahydrofuran syntheses from bishomoallylic alcohols profits from reactivities and selectivities of transition metal peroxy-complexes, relatively few peroxo-complex-mediated alkenol oxidations have been reported so far for this purpose. Some more recent examples start from catalytic amounts of methyl trioxorhenium(VII) (MTO), and aqueous H_2O_2 in either heterogeneous (H_2O–CH_2Cl_2) or homogeneous mixtures (THF–H_2O) (Scheme 17) [71–74]. Addition of 3-cyanopyridine to the reaction mixture has been shown to increase the yield of tetrahydrofuran formation by tempering the Lewis acidity of the metal center and protecting primary oxidation products from further oxidation [75]. Mechanistic studies have shown that MTO is converted under these conditions into a bisperoxo-complex, presumably as its 3-cyanopyridine adduct [71–73]. In view



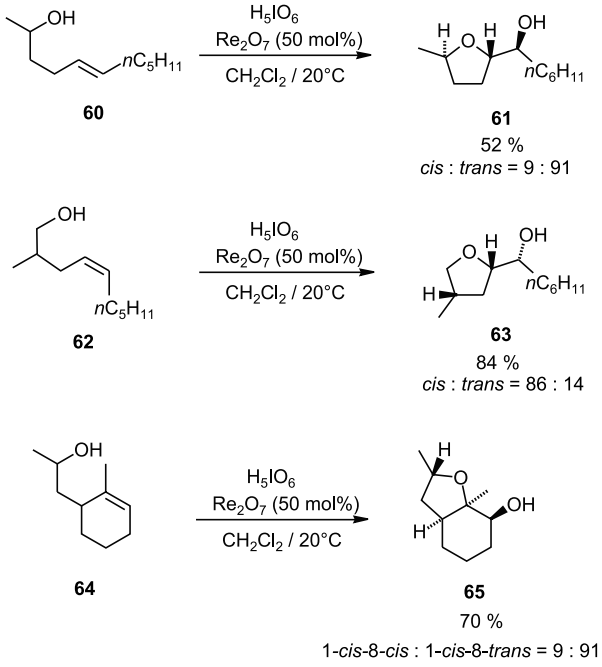
Scheme 17. Synthesis of cyclic ethers **54** and **59** using aqueous hydrogen peroxide as primary oxidant [74,75].

of the propensity of this electrophilic rhenium(VII)-based oxidant to epoxidize olefins, it its straightforward to assume the same mechanistic pathway for conversion of bishomoallylic alcohols **15** and **58** via intermediate oxiranes (not shown in Scheme 17) into substituted tetrahydrofurans **54** and **59** [75].

3.2. Transition metal oxo-compounds as selective oxidants

The reactivity of high-valent metal oxo-complexes, e.g. $CrO_3 \cdot py_2$, Re_2O_7, $AcOReO_3$, or OsO_4, towards olefins is well-documented in the literature [25,26,76,77]. In principle, the substrate is either dihydroxylated (e.g. reaction with OsO_4) or oxygenated (conversion with e.g. Re_2O_7) under these conditions. In both instances, the central ion is reduced since two electrons from the filled π-orbital of the olefin are transferred into a vacant transition metal d-orbital of suitable symmetry. CO bond formation then has to involve interaction of oxygen lone pairs of the metal oxo-fragment with the π*-orbital of the olefin [78]. The discovery, that Re_2O_7 is able to convert bishomoallylic alcohols efficiently and highly stereoselectively into substituted tetrahydrofurans if 2,6-lutidine and prior to work-up NaOOH are added, opened new perspectives for tetrahydrofuran synthesis [25]. Thus, a catalytic version of this reaction was developed which requires 10 mol% of Re_2O_7 and TBHP as oxidant [79]. Although the reactivity was largely retained with the new reagent combination, selectivity generally was lost since tetrahydrofuran **61** was obtained as an equimolar mixture of *cis*/*trans*-diastereomers starting from the (Z)-isomer of alkence **60**. In order to conduct stereoselective tetrahydrofuran syntheses from e.g. alkenols **60**, **62**, **64**, 50 mol% Re_2O_7 were necessary and H_5IO_6 served as co-oxidant to afford selectively 2,5-*trans*-disubstituted tetrahydrofurans **61** (*cis*:*trans* = 9:91) and **65** (1-*cis*-8-*cis*:1-*cis*-8-*trans* = 9:91) as major compounds or heterocycle **63** as a 86/14-mixture of *cis*/*trans*-diastereomers (Scheme 18) [79].

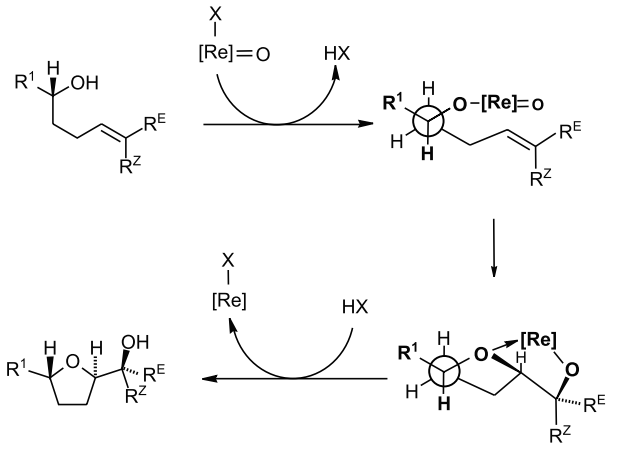
The proposed mechanism for stereoselective oxidations of bishomoallylic alcohols by rhenium(VII) oxo-complexes requires binding of e.g. an acyl rhenate(VII) to an alkenol followed by *syn*-oxygenation (Scheme 19) [26]. It is noteworthy, that the diastereoselectivities obtained in rhenium(VII) oxo-complex-mediated bishomoallylic alcohol oxidations, which are outlined in Scheme 18, are complementary to those obtained vanadium(V) peroxy-complex-mediated reactions of these substrates as long as the latter oxidation proceeds via a *chair*-like transition structure (Scheme 15, left) [64].



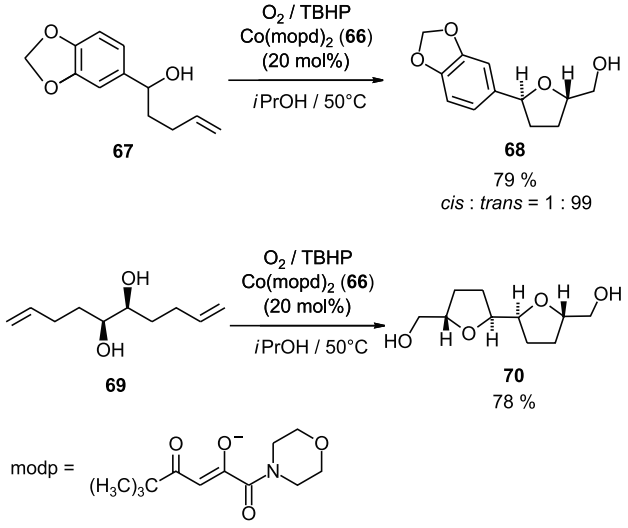
Scheme 18. Stereoselective synthesis of tetrahydrofurans in rhenium(VII)-catalyzed bishomoallylic alcohol oxidations [79].

3.3. Miscellaneous reactions

In recent years, cobalt(II) diketonate complex-catalyzed oxidations of 1-substituted bishomoallylic alcohols have provided a new and highly stereoselective synthetic access to 2,5-*trans*-configured disubstituted tetrahydrofurans [19,80,81]. Reactivity and selectivity in this type of oxidation are determined by a delicate balance between donor ability of the diketonate-chelate ligand and the electrophilicity of the transition metal ion. Thus, cobalt(II) complex **66** was found to catalyze oxidation of 1-aryl-4-penten-1-ol **67** into 2,5-*trans*-disubstituted tetrahydrofuran **68** (Scheme 20) [80,81]. This



Scheme 19. Proposed mechanism and major stereochemical pathway for rhenium(VII) oxo-compound-mediated *syn*-oxygenation [26]. X = e.g. OAc, ReO_4, R^E = *E*-arranged alkyl substituent, R^Z = *Z*-arranged alkyl substituent.

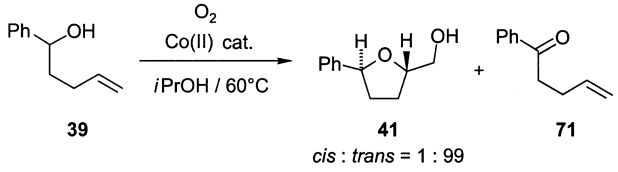


Scheme 20. Formation of 2,5-*trans*-disubstituted tetrahydrofurans **68** and **70** in cobalt(II)-catalyzed oxidations [80,81].

reaction has been successfully applied in the stereoselective synthesis of 2,5-*trans*-configured tetrahydrofuran-subunit of natural product gigantetrocin A (not shown in Scheme 20), an annonaceous acetogenin with a broad spectrum of biological activities such as cytotoxic, antimicrobial, antimalarial, antifeedent, or immunosuppressive effects [82]. A further application of this method is outlined in Scheme 20 which allowed a remarkably efficient and stereoselective synthetic access to *trans*-*trans*-configured bistetrahydrofuran building block **70** in 78% yield starting from twofold unsaturated diol **69**. Target compound **70** was converted in a five step synthesis into a building block for the synthesis of acetogenin asimilobin (not shown in Scheme 20) [82]. It is noteworthy that cobalt(II)-catalyzed oxidations of suitable bishomoallylic alcohols have been applied to prepare all-*trans*-configured tris- and tetrakistetrahydrofurans without a loss of stereoselectivity and efficiency. The mechanism of this reaction has until today not been addressed by detailed physical organic investigations and can therefore not be discussed here. Since molecular oxygen and TBHP serve as oxidant, radical intermediates are likely to take part in one or another way in the ring closure step (see also Scheme 2 and Table 2). Based on product studies and comparison to data from independent mechanistic investigations, intermediacy of free substituted 4-penten-1-oxyl radicals can be excluded [83].

An interesting version of cobalt(II)-catalyzed synthesis of tetrahydrofurans from bishomoallylic alcohols utilizes only molecular oxygen as oxidant (Table 4) [21,81,84]. The highest yields of 2,5-*trans*-configured tetrahydrofuran **41** from 1-phenyl-4-pentenol **39** were obtained in hot isopropanol. However, the reaction may also be performed in *tert*-butanol or in propionic aldehyde diethyl acetal as solvents [84]. In the absence

Table 4
Reactivity and selectivity in aerobic cobalt(II)-catalyzed oxidations of 1-phenyl-1-pentenol **39** [21,81,84]

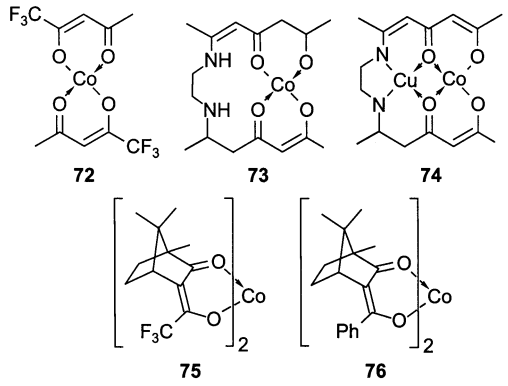


39 **41** **71**

cis : *trans* = 1 : 99

entry	Co(II) cat.	recovered **39** [%]	yield **41** [%]	yield **71** [%]
1	**72**	20	35	12
2	**73**	100	– [a]	– [a]
3	**74**	– [a]	32	15
4	**75**	50	27	– [a]
5	**76**	40	24	5

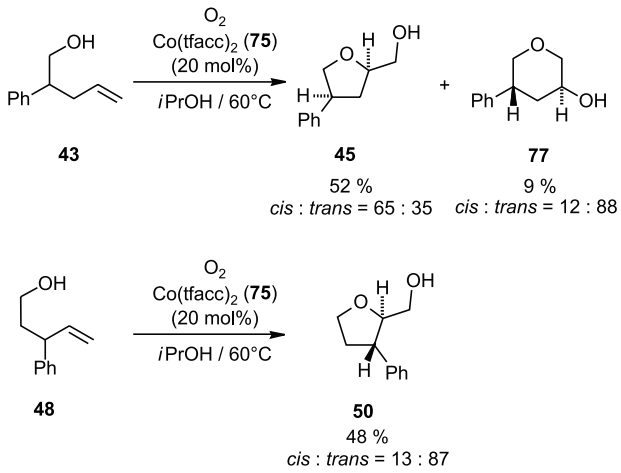
[a] not observed



72 **73** **74**

75 **76**

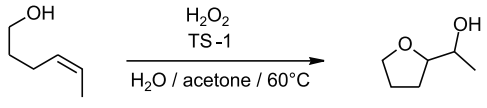
of cobalt(II) catalyst, 10% of pentenophenone **71** are formed, presumably in an autoxidation reaction. The use of cobalt(II) diketonate complexes **72**, **74**–**76** as catalysts in this reaction affords tetrahydrofuran **41** in satisfactory yields but in all cases with an excellent diastereoselectivity of *cis*:*trans* = 1:99 (Table 4, entries 1, 3–5). Two observations in this context are noteworthy. (i) Whereas heteronuclear cobalt(II) copper(II) complex **74** catalyzes tetrahydrofuran formation, monocobalt complex **73** is catalytically inactive (Table 4, entry 2–3) [84]. According to additional experimental results, the role of the copper(II) ion in this catalysis may be attributed to an increase in electrophilicity at the cobalt(II) reaction center. This fact has been shown to be a prerequisite for efficient tetrahydrofuran formation from aerobic oxidations of bishomoallylic alcohols in an additional survey on the reactivity and selectivity in cobalt(II) diketonate catalysis [84]. (ii) Camphor-derived coordination compound **75** was the only catalyst in this study to afford tetrahydrofuran **41** in satisfactory yield while simultaneously inhibiting formation of ketone **71** (Table 4, entry 4). Therefore, cobalt(II) complex **75** was



Scheme 21. Stereoselective synthesis of tetrahydrofurans **45** and **50** and tetrahydropyran **77** in aerobic cobalt(II)-catalyzed oxidations of bishomoallylic alcohols [21,84].

applied in the stereoselective synthesis of further tetrahydrofurans, e.g. **45** (*cis*:*trans* = 65:35) and **50** (*cis*:*trans* = 13:87) from 2-, and 3-substituted bishomoallylic alcohols **43** and **48** (Scheme 21) [21,84]. Although in both instances lower diastereoselectivities are observed than for the synthesis of 2,5-disubstituted isomer **41** (Table 4, *cis*:*trans* = 1:99), the data which are outlined in Table 4 and Scheme 21 provide an interesting starting point for future catalyst development, once the mechanism of this tetrahydrofuran synthesis has been fully rationalized.

Lately, synthetically useful heterogeneously catalyzed tetrahydrofuran syntheses have been reported. Thus, alkenol **78** is oxidized in hot acetone by a 30% aqueous solution of hydrogen peroxide in the presence of titanium silicate molecular sieve TS-1 to provide monosubstituted tetrahydrofuran **79** in excellent yield (Scheme 22) [85]. In view of the acidity of the catalyst, the high selectivity for the synthesis of tetrahydrofuran **79** in this reaction is remarkable. It was explained by the



78 **79**
92 %

Scheme 22. Application of heterogeneous catalysis in the synthesis of tetrahydrofuran **79** [85].

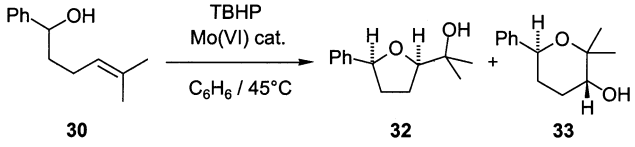
restricted geometry inside the TS-1 channel (pore sizes: 5.3 × 5.6 and 5.1 × 5.5 Å) which was considered to better support folding of the alkenol chain for tetrahydrofuran formation than for the synthesis of a tetrahydropyrans (see also Section 4).

4. Formation of tetrahydropyrans

In view of an inherent tetrahydrofuran selectivity, it is not surprising that only a few examples of selective tetrahydropyran formation have been reported so far in transition metal-catalyzed oxygenations of bishomoallylic alcohols. In general, these reactions require strongly Lewis-acidic catalysts and alkyl substituents at the terminal position of the olefinic π-bond. Thus, oxidation of 1-phenyl-5-methyl-4-hexenol **30** by TBHP using *cis*-dioxomolybdenum(VI) coordination compounds as catalysts affords 3,6-*trans*-configured tetrahydropyran **33** as major and the five-membered ring heterocycle **32** as minor product (Table 5) [22]. The selectivity for tetrahydropyran formation increases in the series of catalysts MoO_2Cl_2 (**32**:**33** = 43:57, entry 1, Table 5), MoO_2(salamp)(EtOH) (**32**:**33** = 41:59, entry 2, Table 5), $MoO_2(acac)_2$ (**32**:**33** = 9:91, entry 3, Table 5). In comparison with the data from vanadium(V) Schiff base complex-catalyzed oxidations of alkenol **30**, it is noteworthy, that formation of the minor product **32** proceeds qualitatively similarly 2,5-*cis*- and that of the major heterocycle **33** 3,6-*trans*-selectively (Table 5, Scheme 9).

Another interesting transformation which affords a substituted tetrahydropyran as major product, although only slightly in preference, was discovered by oxidizing linalool **15** with TBHP in hot CH_3CN using a heterogeneous titanium alumosilicate Beta MCM-41 catalyst (Scheme 23) [86]. Formation of six-membered ring **56** was explained by epoxidation of substrate **15** at the terminal double bond inside the Beta zeolithe's large pores. The initial oxygenation step is followed by acid-assisted isomerization of an epoxyalcohol intermediate into tetrahydropyran **56** as major and linalool oxide **54**

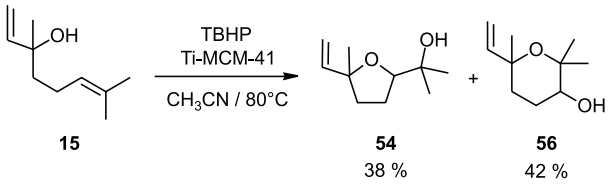
Table 5
Selective formation of tetrahydropyran **33** from phenylmethylhexenol **30** in Mo^{+6}-catalyzed oxidations [22]



30 **32** **33**

entry	Mo(VI) cat.	mol [%]	yield **32** [%] (*cis* : *trans*)	yield **33** [%] (*cis* : *trans*)
1	MoO_2Cl_2	20	37 (87 : 13)	50 (20 : 80)
2	MoO_2(salamp)(EtOH)[a]	100	29 (77 : 23)	42 (22 : 78)
3	$MoO_2(acac)_2$	20	6 (64 : 36)	59 (16 : 84)

[a] salamp = *N*-(2-hydroxyphenyl)salicylidenimine dianion, corresponds to auxiliary L in Scheme 10.



15 **54** 38 % **56** 42 %

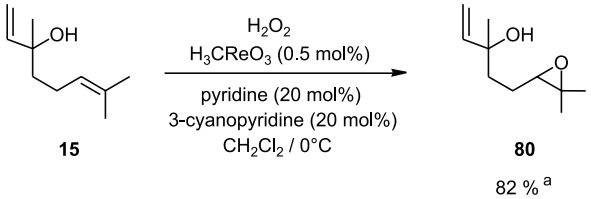
Scheme 23. Formation of linalool-derived tetrahydropyran **56** and heterocycle **54** in a heterogeneously catalyzed oxidation of linalool **15** [86].

as minor product (**56**:**54** = 53:47) [86].

5. Synthesis of bishomoallylic epoxyalcohols

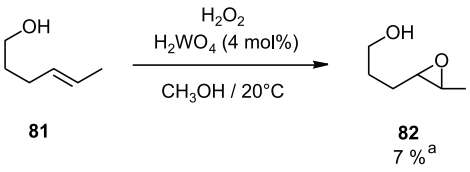
Selective conversion of a bishomoallylic alcohol into a corresponding epoxyalcohol still is a challenge, since the Lewis-acidity of most transition metal oxidation catalysts suffices to directly initiate conversion of primary product into a larger heterocycle such as a substituted tetrahydrofuran or a tetrahydropyran. Therefore, dioxiranes have become reagents of choice for this purpose [64,87], if a transition metal-free method for the synthesis of bishomoallylic epoxyalcohols is required (see Scheme 10). However, it has been outlined at the beginning of Section 3.1, that epoxyalcohols may be obtained by oxidizing bishomoallylic alcohols in the presence of TBHP and $VO(acac)_2$ (see Scheme 3) [18,51]. An alternative method uses MTO as catalyst and H_2O_2 as primary oxidant. The reaction is performed in CH_2Cl_2 at 0 °C and requires the presence of 50/50-mixture of pyridine and 3-cyanopyridine in order to convert e.g. linalool **15** into its 6,7-epoxide **80** in 82% yield (Scheme 24) [75]. The use of pyridine and 3-cyanopyridine was essential since the latter base alone was not strong enough to prevent substantial isomerization of epoxyalcohol **80** into linalooloxide **54** [75].

In view of selective oxidations under mild and neutral conditions (pH 6–7), the use of tungstic acid as catalyst for oxidation of e.g. unsaturated alcohol **81** into epoxyalcohol **82** by H_2O_2 is of interest. Unfortunately the yield of epoxyalcohol **82** did not exceed 7% (48% conversion of starting alkenol **81**). However, since the tungstate ion is less prone to metal-induced hydrogen peroxide decomposition, its application still may be



15 **80** 82 %[a]

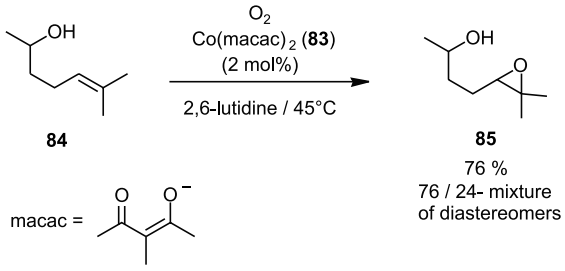
Scheme 24. Rhenium(VII)-catalyzed synthesis of linalool-derived epoxide **80** [75]. (Side product: 6% of linalooloxide **54** (*cis*:*trans* = 50:50)).



Scheme 25. Tungsten(VI)-catalyzed synthesis of epoxyalcohol **82** [88]. (A 48% conversion of **81**; 17% of cyclic ethers as side products).

superior to that of the molybdate or the vanadate ion for this purpose in regard of an economic use of the primary oxidant (Scheme 25) [88].

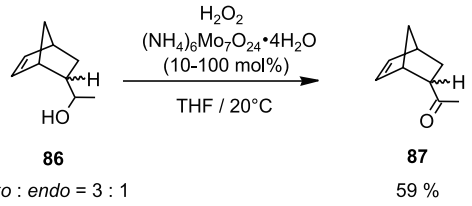
It is noteworthy at the end of this section, that a promising mild and selective method for the synthesis of epoxyalcohols has been discovered in the course of an exploration of reactivities and selectivities in aerobic cobalt(II)-catalyzed oxidations. Recent investigations have shown, that the cobalt(II) bis(3-methylacetylacetonate) complex (**83**) is the most efficient catalyst for oxidizing sulcatol **84** with molecular oxygen into epoxyalcohol **85** in 76% yield (Scheme 26). The fact, that a 76/24-mixture of diastereomers of target compound **85** was obtained strongly points to alkenol coordination to the cobalt(II) ion in the oxygenation step (see also Schemes 9 and 10) [89].



Scheme 26. Synthesis of sulcatol-derived epoxyalcohol **85** [89].

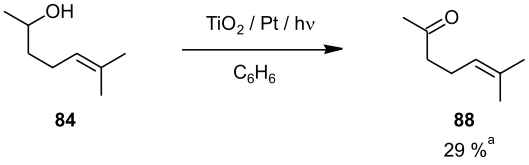
6. Preparation of γ,δ-unsaturated carbonyl compounds from bishomoallylic alcohols

The selective formation of γ,δ-unsaturated carbonyl compounds from bishomoallylic alcohols is feasible, if oxygenation of the π-bond either via a peroxy- or an oxo-mechanism does not extensively compete with an electron transfer-induced transformation of the alcohol functionality into a carbonyl group. This type of dehydrogenation mechanism requires alkenol binding to a transition metal ion which has strong oxidation potential (Table 2). Alkenol binding then is followed by transfer of a total of two electrons from the CH–OH entity onto the central ion. In view of non-catalytic processes, this chemistry is today still dominated by oxochromium(VI) reagents [90,91]. However, it has to



Scheme 27. Chemoselecitve oxidation of bishomoallylic alcohol **86** in the synthesis of unsaturated ketone **87** [92].

be pointed out that these compounds have been reported to oxygenate π-bonds of bishomoallylic alcohols to provide substituted tetrahydrofurans [26]. One of the transition metal-catalyzed methods for the syntheses of γ,δ-unsaturated carbonyl compounds from bishomoallylic alcohols requires ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ for peroxide activation and



Scheme 28. Synthesis of 6-methyl-5-hepten-2-one (**88**) [93].

H_2O_2 as primary oxidant. This reaction has been applied to convert norbornene-derived substrate **86** into ketone **87** with a yield of 59% (Scheme 27) [92].

An interesting alternative method for chemoselective oxidation has been elaborated for sulcatol **84**. Photooxidation of alkenol **84** using a heterogeneous platinized titanium dioxide catalyst affords 6-methyl-5-hepten-2-one (**88**) in excellent yield (Scheme 28) [93].

7. Summary and perspectives

Applications of transition metal-catalyzed oxidations allows a chemo-regio-, and stereoselective conversions of substituted bishomoallylic alcohol into a cyclic ether (e.g. tetra-hydrofuran), an epoxyalcohol, or an unsaturated carbonyl compound. In most instances, molecular oxygen, hydrogen peroxide, or *tert*-butyl hydroperoxide (TBHP) serve as primary oxidants. These reagents have to be activated by coordination compounds in order to serve as powerful but selective oxidants. For instance, hydrogen peroxide and *tert*-butyl hydroperoxide may be activated either by a heterolytic or a homolytic mechanism. The former reaction, which is more important in this context, involves formation of intermediate peroxo- (H_2O_2 as oxidant), peroxy- (e.g. TBHP as oxidant), or oxo-complexes. Early d^0-transition metal ions (e.g. Ti^{4+}, V^{+5}, Mo^{+6}) prefer the peroxo- or the peroxy-route, whereas oxidations using late transition metal

catalysts (e.g. Re^{+7}) may follow the oxo-mechanism. The most important products from bishomoallylic alcohol oxidations are substituted tetrahydrofurans. Since diastereoselection generally is attainable by selecting either a transition metal peroxy- or an oxo-complex-mediated reaction, several useful new syntheses of tetrahydrofuran-derived buildings blocks have emerged in the last few years. A seemingly more difficult synthetic problem is associated with a reversal of the inherent selectivity for tetrahydrofuran formation towards the synthesis of tetrahydropyrans from substituted bishomoallylic alcohols. Until today, these reactions are restricted to the use of strongly Lewis-acidic catalysts and to a structurally very narrow range of substrates. Likewise, only a few transition metal-catalyzed methods for converting bishomoallylic alcohols into corresponding epoxyalcohols or γ,δ-unsaturated carbonyl compounds have been developed so far.

The past years have seen tremendous improvements in transition metal-catalyzed oxidations of alkenols in terms of reactivity and selectivity. The major challenge for future work will certainly remain to solve the problem of auxiliary-controlled instead of a mechanism-controlled diastereoselection in tetrahydrofuran synthesis. This aspect requires a more detailed knowledge about interactions between transition metal peroxy-complexes and bishomoallylic alcohols in the transition state of the oxygenation step. Detailed physical organic investigation and hopefully X-ray crystallographic data on new transition metal peroxy-complexes may provide more structural insights for this purpose. These investigations may also lay a profound basis for accompanying computational studies which may lead to a more rational catalyst design one day. Further it remains to be seen, in which way developments of enzyme-catalyzed oxidations or new reaction media, for instance liquid ionic compounds [94], may contribute to improve stereo- and regiocontrol in the synthesis of heterocyclic compounds from bishomoallylic alcohols and their higher homologues.

Acknowledgements

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[1] The following abbreviations have been used in this review: acac, acetylacetone monoanion; DMD, dimethyl dioxirane; macac, 3-methylacetylacetone monoanion; mopd, 1-morpholinocarbamoyl-4,4-dimethyl-1,3-pentandione monoanion; MTO, methyltrioxorhenium; salamp, *N*-(2-hydroxyphenyl)salicylidenimine dianion; TBHP, *tert*-butyl hydroperoxide; tfacc, (+)-3-trifluoracetylcamphor monoanion.
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