(Schiff-base)vanadium(V) Complex-Catalyzed Oxidations of Substituted Bis(homoallylic) Alcohols − Stereoselective Synthesis of Functionalized Tetrahydrofurans

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Dedicated to Prof. Dr. K. Barry Sharpless

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Vanadium(V) complexes **4** have been prepared from tridentate Schiff-base ligands **3** and $VO(OEt)_3$. All vanadium(V) compounds were characterized (IR, UV/Vis, and ^{51}V NMR spectroscopy, and in selected examples by X-ray diffraction analysis) and were applied as oxidation catalysts for the stereoselective synthesis of functionalized tetrahydrofurans **2** starting from substituted bis(homoallylic) alcohols **1** (mono- or trisubstituted C–C double bonds). Oxidation of secondary or tertiary 1-alkyl-, 1-vinyl-, or 1-phenyl-substituted 5,5-dimethyl-4-penten-1-ols under optimized conditions [TBHP as primary oxidant and 1,2-(amino)indanol-derived vanadium(V) reagent **4g** as catalyst] provided 2,5-*cis*-configured tetrahydrofurans in synthetically useful yields and diastereoselectivities (22–96% *de*). On the other hand, *trans*-disubstituted oxolanes (62%–96 *de*) were obtained from oxidations of 2- or 3-alkyl- and 2- or 3-phenyl-substituted 5,5-dimethyl-4-penten-1-ols bis(homoallylic) alcohols. Treatment of 4-penten-1-ols (i.e. substrates with monosubstituted olefinic π-bonds) with TBHP and catalytic amounts of vanadium(V) complex **4g** furnished *trans*-disubstituted tetrahydrofurans as major products (20–96% *de*), no matter whether an alkyl or a phenyl substituent was located in position 1, 2, or 3 of the alkenol chain. The mechanism of this reaction has been investigated in detail. Based on results from ^{51}V NMR spectroscopy and competition kinetics, it proceeds by a transition metal–peroxy pathway. In an initial step, TBHP coordinates to, for example, *N*-(2-oxidophenyl)salicylideniminato-derived vanadium complex **4a**. Subsequent alkenol binding gives rise to a "loaded" vanadium(V) peroxy complex (e.g. **60**) which facilitates diastereoselective oxygen transfer, presumably onto a coordinated substrate. This step leads to the formation of functionalized tetrahydrofurans as major products. TBHP binding to the remaining vanadium(V) complex then allows a regeneration of the active oxidant, for example peroxy complex **57**. The origin of the observed diastereoselectivity in this oxidation has been studied in an independent stereochemical analysis. Thus, diastereomerically enriched epoxy alcohol (1*R*,4*R*)-**10** was prepared. Its treatment with 1,2-(amino)indanol-derived vanadium complex **4g** affords a 91:9 mixture of *cis*-2-(1-hydroxy-1-methylethyl)-5-(phenyl)tetrahydrofuran (*cis*-**6**) and *cis*-2,2-dimethyl-6-(phenyl)tetrahydropyran-3-ol (*cis*-**7**). Similarly, a 39:61 mixture of heterocycles *trans*-**6** and *trans*-**7** was obtained from epoxy alcohol (1*S*,4*R*)-**10**, if treated with Lewis acid **4g**.

Introduction

Functionalized substituted tetrahydrofurans (i.e. oxolanes) occur widely in nature as constituents of terrestrial and marine organisms.[1−4] A number of these compounds exhibit remarkable antibiotic or cytotoxic effects, which have opened perspectives for selected clinical applications.[2] This circumstance has brought about a growing demand for cyclic ethers in general and tetrahydrofuran-derived natural products in particular.[3−5] Since their supply cannot be covered from natural sources alone, the invention of methods for stereoselectively constructing the tetrahydrofuran nucleus from δ,ε-unsaturated alcohols, e.g. **1** (Figure 1), has received considerable attention.[6,7] In the last few years, the most significant progress in this field of research has originated from transition metal catalyzed oxidations[8] − transformations which utilize active oxygen compounds, such as hydrogen peroxide,[9,10] peroxo compounds,[10,11] or molecular oxygen[12] as primary oxidants. In spite of their high oxidation potentials, these reagents, if used alone, are sur-

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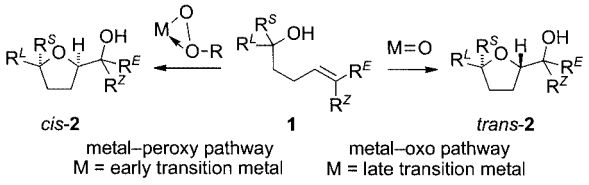


Figure 1. Mechanisms for diastereoselective syntheses of functionalized tetrahydrofurans **2** from bis(homoallylic) alcohols **1**; R^S = small substituent, R^L = large substituent, R^Z = alkyl substituent in (*Z*) arrangement, R^E = alkyl substituent in (*E*) arrangement, R = $C(CH_3)_3$, $C(CH_3)_2C_6H_5$

prisingly inert towards organic substrates. Activation by transition metal reagents, however, is attainable, and often provides powerful but selective oxidants.[8] Two major strategies have evolved for this purpose. The first route follows a transition metal−peroxo (H_2O_2 as primary oxidant) or −peroxy pathway (alkyl hydroperoxides as active oxygen source, Figure 1, left).[13,14] The second mechanism proceeds via high-valent transition metal−oxo compounds (Figure 1, right).[14] Both mechanisms open perspectives for diastereoselective tetrahydrofuran syntheses, since their facial selectivities for π-bond oxygenation may, depending on the substrate, be complementary.[8,15]

From a historical point of view, the reagent combination of [VO(acac)$_2$] [acac = acetylacetonato(−1)] and TBHP was the first and in the following years most frequently applied oxidant for converting bis(homoallylic) alcohols, by a transition metal catalyzed oxidation, into functionalized tetrahydrofurans.[2,16] This procedure has been successfully applied for the synthesis of tetrahydrofuran subunits of polyether-derived natural products such as lasalocid A,[17] ionomycin,[18] teurilene,[19] ferensimycin B,[20] glabrescol,[21] venustatriol,[22] or thyrsiferol.[23] Surprisingly, until now this method has not been further explored, either (i) by conducting a concise structure-selectivity survey or (ii) by application of auxiliaries other than exclusively diketonate ligands, in order to improve the reactivity and stereoselectivity of the active oxidant. Such achievements could have contributed to the development of reagents that were able to inhibit transformations which frequently interfere with selective tetrahydrofuran formation, for instance epoxidations of allylic π-bonds[24] or electron transfer and succeeding radical reactions.[25] Guided by these deficits of the [VO(acac)$_2$]/TBHP sytem on one side and the synthetic potential of transition metal−peroxy compounds in organic synthesis on the other, a promising new approach for constructing functionalized cyclic ethers has been developed recently.[26] Major improvements originated from the use of vanadium(v) catalysts with tridentate auxiliaries. Such reagents increase the diastereoselectivity and the efficiency for tetrahydrofuran formation from substituted bis(homoallylic) alcohols, and inhibited the above-mentioned side reactions to a significant degree. Based on these perspectives, we have extended our preliminary investigation[26] to address three major areas. (i) Alternative (Schiff-base)vanadium(v) complexes **4** were prepared and their catalytic properties for diastereoselective syntheses of functionalized tetrahydrofurans were assessed. (ii) The mechanism of the tetrahydrofuran synthesis from δ,ε-unsaturated alcohols was investigated in detail. (iii) A structure-selectivity study was performed in order to derive guidelines for predicting diastereoselectivities for any future application of this method.

Results

1. Preparation and Characterization of Vanadium(v) Complexes with Tridentate Schiff-Base Ligands

Dark-red to black vanadium(v) complexes[27] **4a**−**k** were prepared in quantitative yields by treating equimolar amounts of tris(ethoxy)- or tris(isopropoxy)vanadate[28] and dibasic tridentate Schiff-bases[29] **3a**−**k** in anhydrous EtOH (Figure 2, Table 1).[30] Vanadium(v) compounds **4** were readily soluble in DMF and CH_3CN, soluble in $CHCl_3$ and EtOH, and sparingly soluble in C_6H_6 or in hydrocarbons. Complexes **4a**−**k** were characterized by ^{51}V NMR, IR, and UV/Vis spectroscopy (Table 1). ^{51}V NMR spectra of vanadium(v) complexes **4a**, **4c**−**k** were, unless otherwise noted, recorded in EtOH and were referenced to $VOCl_3$ (δ ≡ 0 ppm) as external standard. For reasons which are unclear at the moment, no ^{51}V NMR signal was observed for *o*-anthranilic acid derived vanadium complex **4b**.[27b] In all other instances ^{51}V NMR signals were identified between δ = −518 ppm (3-aminoisoborneol-based complex **4h**, see also Figure 3) and δ = −557 ppm [(*S*)-methioninol derivative **4k**]. On standing at room temperature, dark-

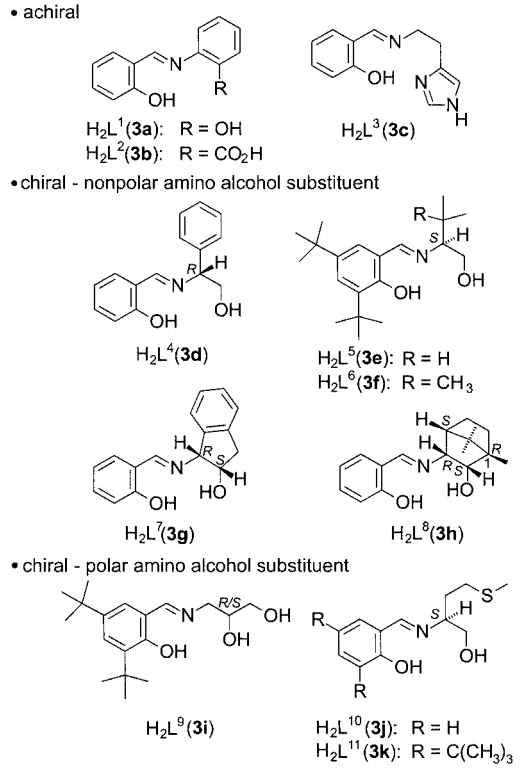
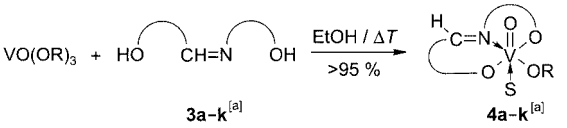


Figure 2. Structural formulae of Schiff-base auxiliaries **3a**−**k** for the synthesis of derived vanadium(v) complexes **4a**−**k** (see Table 1)

Table 1. Preparation of Schiff-base complexes **4** from tris(alkoxy)-vanadate(v) and auxiliaries **3**[a]



3a–k[a] **4a–k**[a]

S = vacant or solvent
R = *i*Pr or Et

entry	4	δ^{51}V [ppm][b]	ν(V=O) [cm^{-1}][c]	λ_{max} [nm][d] (lgε [lmol^{-1}s^{-1}])
1	**a**	−529	990	361 (3.80) 659 (2.40)
2	**b**	—[e]	996	352 (3.69)
3	**c**	−523	976	373 (2.99) 659 (2.43)
4	**d**	−538[f]	997	362 (3.15) 652 (2.20) 443 (1.88)
5	**e**	−543 / −551[g]	994	321 (3.78) 652 (2.50) 440 (2.53)
6	**f**	−533 / −549[h]	979	362 (3.19) 658 (1.94) 423 (2.33)
7	**g**	−541[i]	997	345 (3.74) 652 (2.39) 435 (2.44)
8	**h**	−518[j]	986	310 (3.61) 652 (2.74) 444 (2.38)
9	**i**	−548	966	324 (3.88) 659 (2.36) 448 (2.46)
10	**j**	−535 / −542[k]	979	320 (3.79) 659 (2.48) 447 (2.30)
11	**k**	−545 / −557[l]	983	350 (3.69) 652 (2.06) 437 (1.91)

[a] The graphic is valid for formation of vanadium compounds **4a**, **4b**, and **4d**−**k** from amino alcohol derived ligands **3a**, **3b**, and **3d**−**k** but not for the synthesis of histamine-derived complex **4c** from auxiliary **3c**. [b] Recorded in EtOH as solvent and referenced against $VOCl_3$ (≡ 0 ppm). [c] KBr disk. [d] In EtOH. [e] Not detected. [f] δ = −526 and −534 ppm (peak ratio: 1.5:1) in CD_3OD. [g] Peak ratio: 1.9:1. [h] Peak ratio: 1:2.6. [i] δ = −534 and −538 ppm (peak ratio: 1:1.2) in CD_3OD. [j] δ = −550 and −553 ppm (peak ratio: 1:3) in $CDCl_3$. [k] Peak ratio: 1.5:1. [l] Peak ratio: 1.7:1.

brown block-shaped crystals precipitated from a solution of Schiff-base complex **4a** in $CHCl_3$ which consisted, according to data from an X-ray analysis, of an oxygen-bridged dimer $[(VOL^1)_2O$, see Supporting Information; for Supporting Information see also the footnote on the first page of this article]. If dissolved in EtOH or in CD_3OD, this material gave rise to a single ^{51}V NMR signal at δ = −529 ppm which was identical to the chemical shift observed for parent vanadium complex **4a**.[26,27a] ^{51}V NMR spectra of complexes with chiral auxiliaries, such as (*S*)-valinol-, (*S*)-*tert*-leucinol-, and (*S*)-methioninol-derived coordination compounds consisted in most instances of two slightly separated lines [Δδ = 8 ppm (**4e**), 16 (**4f**), 7 (**4j**), 12 (**4k**)]. In other cases, a change from EtOH to CD_3OD [Δδ = 8 ppm (**4d**), 4 (**4g**)] or to $CDCl_3$ as solvent [Δδ = 3 ppm (**4h**)] led to a modification of the spectra from single lines to two signals with approximate peak ratios of 1:1.2 to 1:2.6 (Table 1).

IR analysis was performed on samples of vanadium(v) complexes **4a**−**k** that were embedded in KBr disks. The spectral information given in Table 1 was restricted to diagnostic absorptions of V=O stretching modes[30] because the ligands were adequately characterized prior to complex formation. These absorptions fall, with the exception of complex **4i** (966 cm^{-1}), into a narrow spectral range of 979−997 cm^{-1} (Table 1).

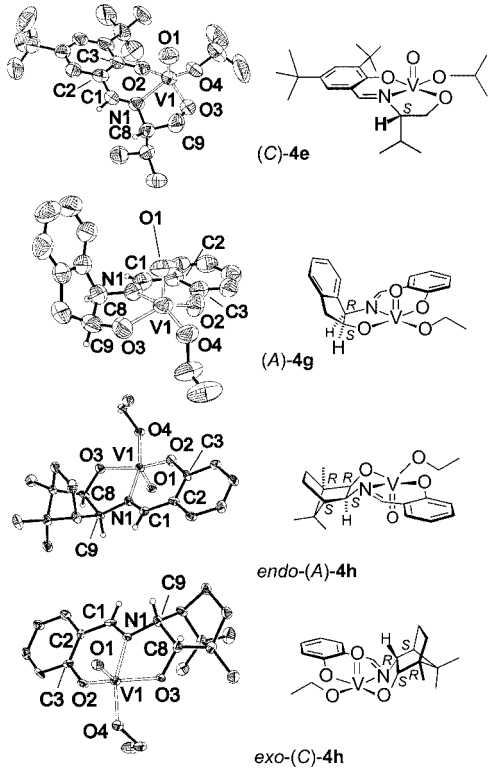


Figure 3. Solid-state structures of (Schiff-base)vanadium(v) complexes **4e**, **4g**, and **4h** (anisotropic displacement parameters drawn at the 50% probability level) showing labeling of selected non-H atoms; selected hydrogen atoms are depicted as circles of an arbitrary radius

(Schiff-base)vanadium(v) complexes **4a**−**k** exhibited relatively featureless UV/Vis spectra, if dissolved in EtOH (Table 1). An intense band was located for all compounds at λ = 310−373 nm. With the exception of three complexes [**4a** (*o*-aminophenol-derived ligand), **4b** (*o*-anthranilic acid based auxiliary), and **4c** (histamine-derived chelate)], a second less-intense absorption was noted at λ ≈ 440 nm. A third but weak band was present in UV/Vis spectra of Schiff-base complexes **4c**−**k** at λ ≈ 655 nm.

Analytical data for characterization of (Schiff-base)vanadium(v) complexes **4a**−**k** (Table 1) were supplemented by results from single-crystal X-ray diffraction analyses of compounds **4e**, **4g**, and **4h** (Figure 3, Table 2, and Supporting Information). Suitable crystals were grown from saturated solutions of vanadium complexes in 2-propanol (**4e**) or ethanol (**4g**, **4h**). Whereas the data collection for (*S*)-valinol-derived complex **4e** and (1*R*,2*S*)-(amino)indanol-based vanadium(v) compound **4g** at room temperature afforded satisfactory information for unambiguously solving and refining these structures (Figure 3, top and center), the data obtained for aminoisoborneol-derived complex **4h** under these conditions were not of sufficient quality to solve the structure. Therefore, the latter experiment was repeated at −130 °C (Supporting Information). Structure solution

Table 2. Selected bond lengths [Å] and angles [°] for (Schiff-base)vanadium(v) complexes **4g**, **4e**, *endo*-**4h**, and *exo*-**4h** (see also Supporting Information)

Entry	Parameter	(*C*)-**4e**	(*C*)-**4g**	*exo*-(*C*)-**4h**	*endo*-(*A*)-**4h**
1	V1−O1	1.562(7)	1.586(2)	1.582(4)	1.578(4)
2	V1−O2	1.864(6)	1.855(2)	1.860(5)	1.860(5)
3	V1−O3	1.846(6)	1.815(3)	1.820(4)	1.818(5)
4	V1−O4	1.773(6)	1.777(2)	1.787(4)	1.773(4)
5	V1−N1	2.165(6)	2.106(3)	2.106(5)	2.100(5)
6	N1−V1−O2	80.2(2)	82.7(1)	83.0(2)	83.1(2)
7	N1−V1−O3	76.6(2)	77.0(1)	76.6(2)	77.5(2)
8	O2−V1−O4	95.9(3)	94.0(1)	94.1(2)	94.4(2)
9	O3−V1−O4	94.2(3)	91.8(1)	90.0(2)	89.7(2)
10	N1−C8−C9−O3	−44.4(9)	22.7(4)	6.1(7)	−7.4(7)
11	C3−C2−C1−N1	10(1)	9.8(6)	−7.3(10)	7.7(10)
12	Config. at V1[a]	C	A	C	A
13	Point group	$P2_12_12_1$	$P2_12_12_1$	*P*1	*P*1
14	Offset of V1 [Å][b]	0.51	0.52	0.54	0.52
15	Configuration (amino alcohol part)	(1*S*)	(1*S*,2*R*)	(1*R*,2*S*,3*R*,4*S*)	(1*R*,2*R*,3*S*,4*S*)

[a] The stereochemical descriptor *C* refers to a clockwise and *A* to an anticlockwise configuration at the vanadium center.[31] [b] With respect to the best N1−O2−O4−O3 plane.

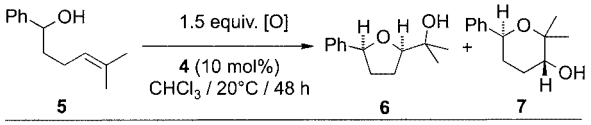
and refinement in the triclinic space group *P*1 indicated that the sample consisted of stereoisomeric complexes *exo*-**4h** and *endo*-**4h** in a 1:1 ratio (Figure 3, bottom). Despite the fact that enantiopure *exo*-configured aminoisoborneol **3h** had been applied for the synthesis of Schiff-base complex **4h**, diastereomers in regard of the configuration at C2, C3, and V1 were observed in the solid state. Samples of compounds **4e** and **4g** crystallized diastereomerically pure and exhibited in one case *C* configuration (**4e**) and in the other *A* configuration at the vanadium center (**4g**). In general, short bonds were found for V1−O1 [1.562(7) Å (**4e**), 1.586(2) Å (**4g**), 1.582(4) (*exo*-**4h**), and 1.578(4) Å (*endo*-**4h**)]. The remaining vanadium oxygen distances decreased in the series from V1−O2 (ca. 1.86 Å) to V1−O3 (ca. 1.82 Å) to V1−O4 (ca. 1.78 Å). In all complexes, relatively long V1−N1 contacts were observed (2.10−2.17 Å). Bond angles decreased from O2−V1−O4 [phenolato to ethanolato or 2-propanolato oxygen atom; 94.0(1)−95.9(3) °] to O3−V1−O4 [amino alcoholato to ethanolato or 2-propanolato oxygen atom; 89.7(2)−94.2(3) °] to N1−V1−O2 [imine nitrogen atom to phenolato oxygen atom; 80.2(2)−83.1(2) °] to N1−V1−O3 [imine nitrogen atom to amino alcoholato oxygen atom; 76.6(2)−77.5(2) °]. The torsion angle C3−C2−C1−N1 deviates from the expected 0° by ca. ±10°.

2. Vanadium(v)-Catalyzed Oxidations of Bis(homoallylic) Alcohols

In order to identify suitable conditions for an efficient conversion of substituted bis(homoallylic) alcohols into functionalized tetrahydrofurans, five variables were considered for modification: (i) amount of catalyst, (ii) solvent, (iii) reaction temperature, (iv) primary oxidant, and (v) the auxiliary (i.e. Schiff-base ligand **3**). Four of these parameters were optimized by oxidizing 5-methyl-1-phenyl-4-hexen-1-ol (**5**)[32] in the presence of *o*-aminophenol-derived vanadium(v) complex **4a**.[26] The latter complex lacks additional stereochemical information in its auxiliary and therefore allows us to uncover the basic reactivity of the system. To begin with, substrate **5** was stirred with 1.5 equiv. of TBHP in $CHCl_3$ at 20 °C. In the absence of catalyst **4a**, no conversion of alkenol **5** was observed (Table 3, Entry 1). Addition of 0.1−5 mol % of catalyst **4a** afforded at 20 °C within 48 h 79−77% of 2-(1-hydroxy-1-methylethyl)-5-phenyltetrahydrofuran (**6**)[33] besides 13−16% of the corresponding tetrahydropyran **7**[33] (GC yields; Supporting Information). An increase to 10 mol % of catalyst **4a** improved the efficiency for the synthesis of tetrahydrofuran **6** marginally (81%, *cis*/*trans* = 98:2). On the other hand, formation of tetrahydropyran **7** was slightly reduced (11%, *cis*/*trans* = 46:54), but more importantly, the synthesis of further oxidation products (see below) was almost completely prevented. These facts caused us to use 10 mol % of catalyst **4** for all subsequent transformations. The efficiency of the synthesis of disubstituted tetrahydrofuran **6** decreases upon changing the solvent from $CHCl_3$ (81%), to CH_2Cl_2 (79%), CH_3CN (33%), $(H_3CO)_2CO$ (30%), and $C_6H_5CF_3$ (24%; Supporting Information). Lowering of the reaction temperature was paralleled by a reduced turnover of alkenol **5**, which provided in this case at −20 °C within 48 h only 21% of tetrahydrofuran **6**. At that temperature, however, the selectivity for the formation of tetrahydrofuran **6** versus tetrahydropyran **7** improved from 85:15 (20 °C) to 95:5 (−20 °C; for details see Supporting Information). A change in primary oxidant from TBHP to cumene hydroperoxide (CHP), iodosobenzene (PhIO), or urea hydrogenperoxide (UHP) caused a drop in yield of target compound **6**. A variation of catalysts from **4a** to **4b**−**k** under otherwise optimized conditions (i.e. TBHP, $CHCl_3$, 20 °C, 48 h) led in all instances to tetrahydrofuran *cis*-**6** as the major product (29−84%, GC analysis). The observed diastereoselectivity

for the synthesis of oxolane **6** remained close to *cis*/*trans* = 98:2 (Table 3, Entries 5−15). Tetrahydropyran **7** was formed in all runs as a minor product (1−15%, GC analysis).

Table 3. Survey of the efficiency of primary oxidants and vanadium(v) catalysts **4** for the stereoselective synthesis of tetrahydrofuran **6** from methyl-phenylhexenol **5**

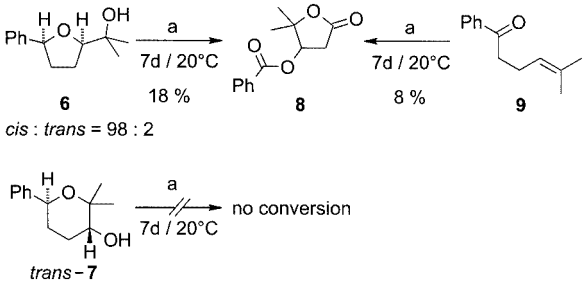


5 **6** **7**

entry	4	[O]	**6** [%] (*cis* : *trans*)[a]	**7** [%] (*cis* : *trans*)[a]
1	none	TBHP	—[b]	—[b]
2	**a**	PhIO	6 (98 : 2)	1 (41 : 59)
3	**a**	UHP	—[b]	—[b]
4	**a**	CHP	78 (98 : 2)	18 (39 : 61)
5	**a**	TBHP	81 (98 : 2)	14 (49 : 51)
6	**b**	TBHP	63 (97 : 3)	11 (29 : 71)
7	**c**	TBHP	58 (98 : 2)	6 (40 : 60)
8	**d**	TBHP	81 (97 : 3)	15 (44 : 56)
9	**e**	TBHP	29 (98 : 2)	3 (40 : 60)
10	**f**	TBHP	36 (97 : 3)	7 (30 : 70)
11	**g**	TBHP	83 (97 : 3)[c]	13 (46 : 54)[c]
12	**h**[d]	TBHP	80 (98 : 2)	14 (49 : 51)
13	**i**	TBHP	59 (98 : 2)	7 (33 : 67)
14	**j**	TBHP	82 (98 : 2)	12 (39 : 61)
15	**k**	TBHP	70 (98 : 2)	10 (33 : 67)

[a] Yields and *cis*/*trans* ratios of compounds **6** and **7** were determined, unless otherwise noted, by GC with *n*-$C_{14}H_{30}$ as internal standard. The experimental uncertainty for similarly determined yields was estimated to be ±5% and for diastereoselectivities ±1 in absolute values. [b] Not detected (GC). [c] Isolated yields: 74% of **6** (*cis*/*trans* = 97:3) and 12% of **7** (*cis*/*trans* = 46:54). [d] Used as mixture of *exo*-**4h** and *endo*-**4h** (see Figure 3).

In order to improve the mass balance in oxidations of substrate **5** which had been catalyzed by the most efficient vanadium compounds, i.e. **4a** (81% of **6**), **4d** (81% of **6**), and especially **4g** (83% of **6**), the reaction mixtures in question were further analyzed by GC. These investigations pointed to the formation of 5-methyl-1-phenylhex-4-en-1-one (**9**)[33] (**4a**: 4%; **4d** and **4g**: 1%) and in one example lactone **8** (only **4d**: 3%) in minor amounts. Based on this additional information, the stability of oxidation products under standard reaction conditions was studied. Thus, ketone **9**, tetrahydrofuran derivative **6** (*cis*/*trans* = 98:2), tetrahydropyran derivative *trans*-**7** (*cis*/*trans* = < 2:> 98) were treated with TBHP and vanadium complex **4a** in $CHCl_3$ at 20 °C for 7 d. Tetrahydropyran derivative *trans*-**7** was stable under these conditions, whereas 5-methyl-1-phenylhex-4-en-1-one (**9**) and tetrahydrofuran derivative **6** were both converted into further oxidation products (^{1}H NMR spectroscopy). Butyrolactone **8** is the only compound isolated from these mixtures in sufficient quantity to allow an unambiguous characterization so far (Scheme 1). It should be added that disubstituted tetrahydrofuran **6** itself is prone to autoxidation and on standing for several weeks in the laboratory atmosphere afforded approximately 34% of butyrolactone **8** along with additional, as yet unidentified, products.



Scheme 1. Control experiments for investigating the stability of oxidation products; reagents and conditions: (a) 1.5 equiv. TBHP, 10 mol % VOL[1](OEt)(EtOH) (**4a**)

To obtain additional information on product formation starting from 5-methyl-1-phenyl-4-hexenol (**5**) and TBHP in the presence of 10 mol % of catalyst **4g**, the reaction was monitored in two time-dependent studies. Data from GC analyses showed that the ratio of tetrahydrofuran **6** versus tetrahydropyran **7** (**6**/**7** = 86:14) and the *cis*/*trans* ratios of both cyclic ethers (for **6**: *cis*/*trans* = 97:3; for **7**: *cis*/*trans* = 46:54) remained constant throughout the conversion of **5**. This observation was noteworthy, since oxidation of a racemic mixture of alkenol **5** in the presence of vanadium(v) complex **4g** (prepared from enantiomerically pure auxiliary **3g**) might have given rise to a kinetic resolution[34] (see also Section 3). In the second time-dependent study, ^{1}H NMR spectra were recorded at reaction times of 5, 10, 30, 60, 120, and 480 min. A stacking plot of a selected spectral region is depicted in Figure 4 and illustrates that alkenol **5** was transformed into heterocycles **6** and **7** without a buildup of an additional intermediate, such as the expected epoxy alcohol **10**. The latter compound was prepared indepen-

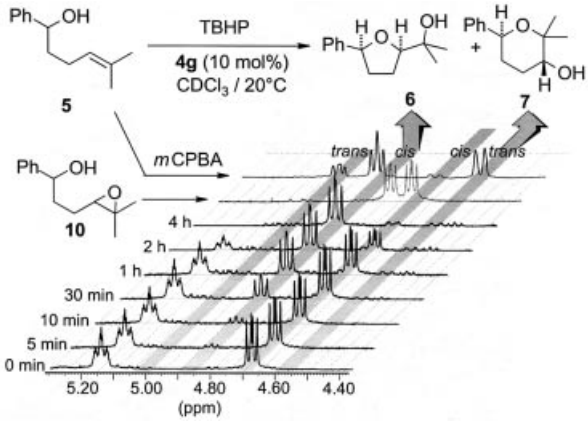
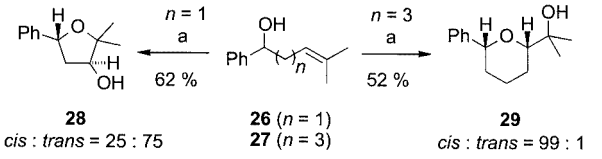


Figure 4. Stacking plot from a time-dependent ^{1}H NMR investigation of the oxidation of methyl-phenylhexenol **5** with TBHP in the presence of (Schiff-base)vanadium(v) complex **4g**; the selected spectral region depicts resonances of the olefinic and the benzylic proton in substrate **5** (t = 0 min) and benzylic protons of cyclic ethers **6** and **7** (see t = 4 h); for illustration purposes, ^{1}H NMR spectra of a 1:1 mixture of *like*- and *unlike*-configured diastereomers of epoxy alcohol **10** and a crude reaction mixture, which had been obtained from an *m*CPBA-mediated oxidation of bis-(homoallylic) alcohol **5**, have been added to this plot

dently in 99% yield by treatment of methyl-phenylhexenol **5** with dimethyldioxirane.[35] For illustration purposes, its ^{1}H NMR resonances have been added to the stacking plot in Figure 4.

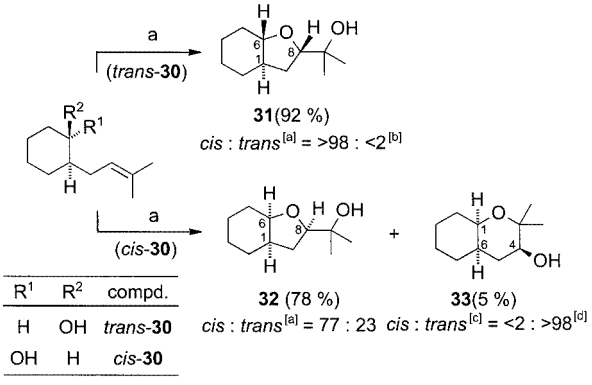
Oxidations of 1-, 2-, and 3-substituted bis(homoallylic) alcohols **5** and **11**−**15** on a preparative scale were conducted in the presence of 1-amino-2-indanol-derived catalyst **4g** (Table 3, footnote[c], Table 4). Conversion of 1-*tert*-butyl-substituted alkenol **11** under these conditions provided 71% of 5-*tert*-butyl-2-(1-hydroxy-1-methylethyl)tetrahydrofuran (**16**) (*cis*/*trans* = 91:9) and 4% of diastereomerically pure tetrahydropyran *trans*-**21** (^{1}H NMR spectroscopy). Treatment of 2-phenyl- and 2-isopropyl-substituted substrates **12** and **13**[36] with TBHP and vanadium reagent **4g** furnished 2,4-disubstituted tetrahydrofuran **17** (55%, *cis*/*trans* = 9:91) and **18** (90%, *cis*/*trans* = 19:81) as major products. In addition, *trans*-2,2-dimethyl-5-phenyltetrahydropyran-3-ol (*trans*-**22**) was obtained in 4% yield from the oxidation of alkenol **12**, whereas formation of 5-isopropyl-substituted tetrahydropyran **23** from substrate **13** was not observed in our experiments. Oxidation of 3-phenyl- and 3-isopropyl-substituted bis(homoallylic) alcohols **14** and **15** with TBHP in the presence of catalyst **4g** afforded diastereomerically pure (^{1}H NMR spectroscopy) 2,3-*trans*-configured tetrahydrofurans *trans*-**19** (76%) and *trans*-**20** (54%). 16% of *trans*-configured tetrahydropyran *trans*-**25** was obtained from isopropyl-substituted alkenol **15**, but no tetrahydropyran **24** from the oxidation of 5-methyl-3-phenylhex-4-enol (**14**).

Treatment of 4-methyl-1-phenylpentenol **26** (lower homologue of **5**) with TBHP and Schiff-base complex **4g** afforded 62% of 3-hydroxy-5-phenyl-substituted tetrahydrofuran **28** (*cis*/*trans* = 25:75, Scheme 2). 6-Methyl-1-phenyl-5-hepten-1-ol (**27**) was oxidized under these conditions into 52% of 2-(1-hydroxy-1-methylethyl)-5-phenyltetrahydropyran (**29**) (*cis*/*trans* = 99:1) and 9% of 6-methyl-5-heptenophenone[37] (not shown in Scheme 2).



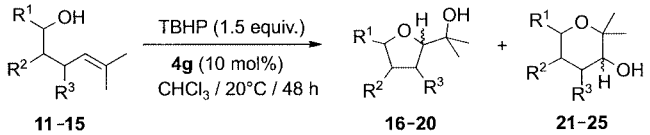
Scheme 2. Stereoselective synthesis of functionalized cyclic ethers **28** and **29**; reagents and conditions: (a) 1.5 equiv. TBHP, 10 mol % VOL^7(OEt) (**4g**), $CHCl_3$, 20 °C, 48 h

Oxidation of 2-allyl-substituted cyclohexanol *trans*-**30**[38] with TBHP and vanadium(v) catalyst **4g** yielded 92% of diastereomerically pure bicyclic tetrahydrofuran 6,8-*cis*-**31** (Scheme 3). If cyclohexanol derivative *cis*-**30**[38] was subjected to these conditions, a mixture of 78% of bicyclic tetrahydrofuran **32** (6,8-*cis*/6,8-*trans* = 77:23) and 5% of



Scheme 3. Formation of bicyclic compounds from both diastereomers of 2-allyl-substituted cyclohexanol **30**; reagents and conditions: (a) 1.5 equiv. TBHP, 10 mol % VOL^7(OEt) (**4g**), $CHCl_3$, 20 °C, 48 h; [a] stereodescriptors *cis* and *trans* refer to relative configurations at C6 and C8; [b] corresponding *trans* isomer was not detected (^{1}H NMR spectroscopy); [c] stereodescriptors *cis* and *trans* refer to relative configurations at C1 and C4; [d] corresponding *cis* isomer was not detected (^{1}H NMR spectroscopy)

Table 4. Vanadium(v)-catalyzed oxidation of 5,5-dimethyl-substituted bis(homoallylic) alcohols **11**−**15**

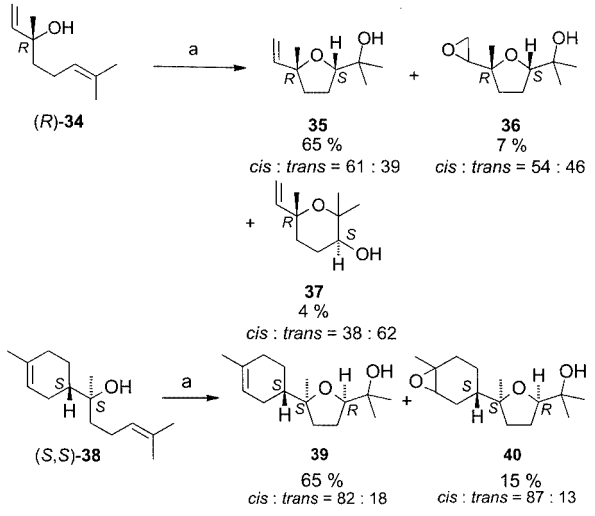


entry	**11**–**15**	R^1	R^2	R^3	**16**–**20** [%] (*cis* : *trans*)		**21**–**25** [%] (*cis* : *trans*)	
1	**11**	$C(CH_3)_3$	H	H	**16**	71 (91 : 9)	**21**	4 (<2 : >98)[a]
2	**12**	H	C_6H_5	H	**17**	55 (9 : 91)	**22**	4 (<2 : >98)[a]
3	**13**	H	$CH(CH_3)_2$	H	**18**	90 (19 : 81)	**23**	—[b]
4	**14**	H	H	C_6H_5	**19**	76 (<2 : >98)	**24**	—[b]
5	**15**	H	H	$CH(CH_3)_2$	**20**	54 (<2 : >98)	**25**	16 (<2 : >98)

[a] The corresponding *cis* isomer was not detected (^{1}H NMR spectroscopy). [b] Not detected (^{1}H NMR spectroscopy).

diastereomerically pure tetrahydropyran derivative 1,4-*trans*-**33** were obtained.

Conversion of (*R*)-linalool [(*R*)-**34**] with TBHP in $CHCl_3$ at 20 °C furnished 65% of furanoid linalool oxide **35**[39] (*cis*/*trans* = 61:39), 7% of epoxylinalool oxide **36**[39] (*cis*/*trans* = 54:46), and 4% of pyranoid linalool oxide **37**[39] (*cis*/*trans* = 38:62), if (Schiff-base)vanadium(v) complex **4g** was applied as catalyst. Treatment of (*S*,*S*)-bisabolol [(*S*,*S*)-**38**] under these conditions led to the formation of 2,2,5-substituted tetrahydrofuran **39**[40] in 65% yield (*cis*/*trans* = 82:18) and its epoxy derivative **40**[40] in 15% yield (*cis*/*trans* = 87:13) (Scheme 4).

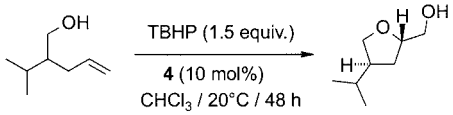


Scheme 4. Vanadium(v)-catalyzed oxidation (*R*)-linalool [(*R*)-**34**] and (*S*,*S*)-bisabolol [(*S*,*S*)-**38**]; reagents and conditions: (a) 1.5 equiv. TBHP, 10 mol % $VOL^7(OEt)$ (**4g**), $CHCl_3$, 20 °C, 48 h

Suitable conditions for diastereoselectively preparing 2-(hydroxymethyl)-4-isopropyltetrahydrofuran (**42**) from 2-isopropyl-4-penten-1-ol (**41**)[41] were found by varying catalysts **4a**−**k** (Table 5). All other parameters such as solvent, reaction temperature, required amount of catalyst and primary oxidant TBHP were assumed to follow the same trends as those which had been required for an efficient conversion of methyl-phenylhexenol **5** into tetrahydrofuran *cis*-**6**. These parameters were therefore not further modified. In the absence of a vanadium reagent **4** no reaction between isopropylpentenol **41** and TBHP was noted over 48 h (Table , Entry 1). Upon addition of 10 mol % of a vanadium(v) catalyst to the reaction mixture, oxidation of substrate **41** into 2-(hydroxymethyl)-4-isopropyltetrahydrofuran (**42**) took place (Table 5, Entries 2−12). The yields of product **42** (GC) varied between 9 and 94%. The observed diastereoselectivities ranged from 41:59 (Table 5, Entry 4) to 29:71 (Table 5, Entry 8). Based on the results, which are collected in Table 5, we restricted ourselves to the use of 1-amino-2-indanol-derived catalyst **4g** for continuing the project (Table 6, Scheme 5).

Oxidation of 1-phenyl- and 1-*tert*-butyl-4-penten-1-ol (**43**[42] and **44**[43]) with TBHP in the presence of 10 mol % of catalyst **4g** afforded 2-(hydroxymethyl)-5-phenyltetrahydrofuran (**48**) (47%, *cis*/*trans* = 39:61) and its 5-*tert*-butyl

Table 5. Screening for reactivity and selectivity: vanadium(v) catalysts **4** in the diastereoselective synthesis of tetrahydrofuran **42** from 2-isopropyl-4-penten-1-ol (**41**)

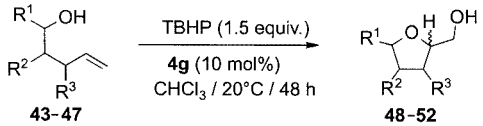


41 **42**

entry	4	conv. **41** [%][a]	**42** [%] (*cis* : *trans*)[b]
1	none	–	–
2	**a**	98	94 (30 : 70)
3	**b**	98	91 (36 : 64)
4	**c**	55	46 (41 : 59)
5	**d**	97	83 (31 : 69)
6	**e**	50	42 (39 : 61)
7	**f**	51	29 (28 : 72)
8	**g**	98	90 (29 : 71)[c]
9	**h**	91	83 (33 : 67)
10	**i**	16	9 (25 : 75)
11	**j**	98	84 (32 : 68)
12	**k**	52	47 (31 : 69)

[a] GC analysis. [b] See footnote[a] of Table 3. [c] Isolated yield: 74% of **42** (*cis*/*trans* = 29:71).

Table 6. Vanadium(v)-catalyzed oxidations of substituted 4-penten-1-ols **43**−**47**



43–**47** **48**–**52**

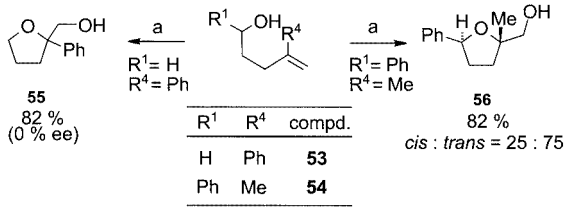
entry	**43**–**47**	R^1	R^2	R^3	**48**–**52**	[%] (*cis* : *trans*)
1	**43**	C_6H_5	H	H	**48**	47 (39 : 61)
2	**44**	$C(CH_3)_3$	H	H	**49**	59 (39 : 61)
3	**45**	H	C_6H_5	H	**50**	43 (36 : 64)
4	**46**	H	H	C_6H_5	**51**	43 (40 : 60)
5	**47**	H	H	$C(CH_3)_3$	**52**	61 (<2 : >98)[a]

[a] The corresponding *cis* isomer was not detected (^{1}H NMR spectroscopy).

derivative **49** (59%, *cis*/*trans* = 39:61) (Table 6, Entries 1 and 2). If 2-phenyl-substituted pentenol **45**[44] was treated under these conditions, 43% of 2-(hydroxymethyl)-4-phenyltetrahydrofuran (**50**) was obtained (*cis*/*trans* = 36:64, Table 6, Entry 3). Treatment of 3-phenyl- and 3-*tert*-butyl-substituted bis(homoallylic) alcohols **46**[43] and **47**[45] with TBHP and vanadium reagent **4g** provided 43% of 2-(hydroxymethyl)-3-phenyltetrahydrofuran (**51**) (*cis*/*trans* = 40:60) and diastereomerically pure (^{1}H NMR spectroscopy) 3-*tert*-butyl-2-(hydroxymethyl)tetrahydrofuran (**52**) (61%, Table 6, Entries 4 and 5).

Finally, 4-substituted 4-penten-1-ols **53**[46] and **54** were treated with TBHP and catalyst **4g** (Scheme 5). Oxidation of prostereogenic substrate **53** under such conditions furnished 82% of racemic 2-(hydroxymethyl)-2-phenyltetrahydrofuran (**55**). 4-Methyl-1-phenyl-4-penten-1-ol (**54**) was

converted into 82% of 2,2,5-trisubstituted tetrahydrofuran derivative **56** (*cis*/*trans* = 25:75) under standard conditions.

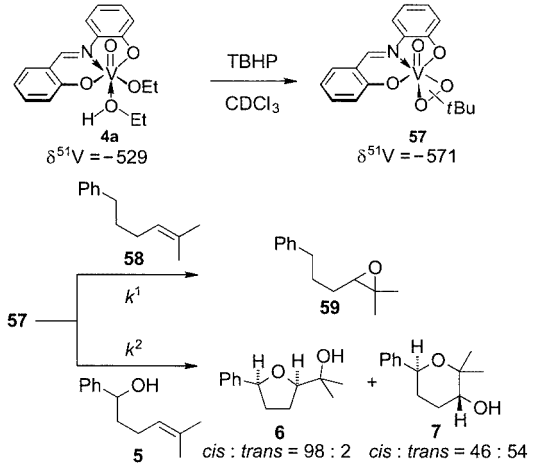


Scheme 5. Conversion of 4-substituted bis(homoallylic) alcohols **53** and **54** into cyclic ethers **55** and **56**; reagents and conditions: (a) 1.5 equiv. TBHP, 10 mol % VOL[7](OEt) (**4g**), $CHCl_3$, 20 °C, 48 h

3. Competition Kinetics and Stereochemical Studies

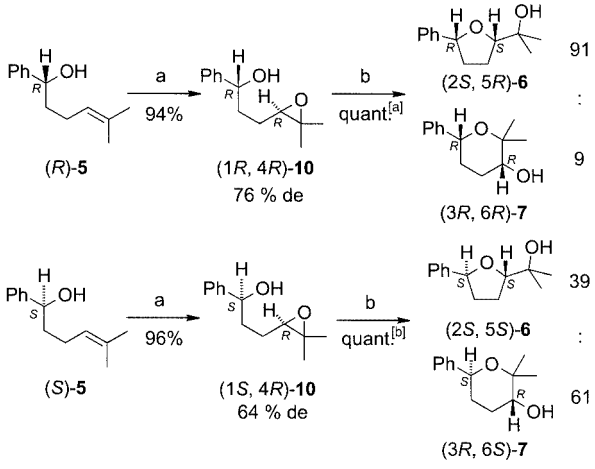
The oxidation of 5-methyl-1-phenylhex-4-enol (**5**) with TBHP in the presence of *o*-aminophenol-derived catalyst **4a** afforded 2-(1-hydroxy-1-methylethyl)-5-phenyltetrahydrofuran (**6**) and 2,2-dimethyl-6-phenyltetrahydropyran-3-ol (**7**) as major products (Table 3). Treatment of 2-methyl-6-phenyl-2-hexene (**58**)[47] under these conditions furnished 87% of epoxide **59**. Subsequently, a vanadium(v)-catalyzed oxidation of a mixture of substrates **5** and **58** was investigated. This reaction led to the formation of three products: tetrahydrofuran **6** as a mixture of *cis*/*trans* isomers, a diastereomeric mixture of tetrahydropyran *cis*-**7** and *trans*-**7**, and epoxide **59** (Scheme 6). Based on this information, a set of competition experiments was devised. Thus, defined molar ratios of substrates **5** and **58** were treated with peroxy complex **57** under pseudo-first-order conditions at 20 °C. Reaction products **6**, **7**, and **59** were quantified by GC analysis. Similarly obtained ratios of ([**6**] + [**7**])/[**59**] were plotted against the corresponding ratio of [**5**]/[**58**] to provide a linear correlation (Supporting Information). Based on a kinetic model which requires direct irreversible oxygen transfer from peroxy complex **57** to both substrates **5** and **58** under pseudo-first-order conditions, the slope of this linear correlation corresponds to the relative rate constant $k^{rel} = k^2/k^1 = 120 \pm 20$ (20 °C).[48] The large experimental error was estimated on the basis that our experiments were restricted, for analytical reasons, to an at least fivefold molar excess of fastest reacting substrate, i.e. alkenol **5**, instead of the desirable tenfold molar excess.

For a stereochemical analysis of product formation from bis(homoallylic) alcohols, a racemic mixture of methyl-phenylhexenol **5** was separated into both enantiomers (*R*)-**5** and (*S*)-**5** (HPLC, Chiracel OD column, both > 99% *ee*). Both samples were epoxidized under Shi conditions[49] in order to provide (1*R*,4*R*)-**10** in 94% yield (76% *de*, ^{1}H NMR spectroscopy) from alkenol (*R*)-**5**[50] and (1*S*,4*R*)-**10** in 96% yield (64% *de*, ^{1}H NMR spectroscopy) from (*S*)-**5**. Assignment of the (*R*) configuration at the stereocenter which was constructed in the Shi epoxidation was based on (i) the general face-selection rule for this well-established method[49] and (ii) a correlation of epoxy alcohol configurations with the geometry of rearranged products **6** and **7** (see below). Treatment of epoxy alcohol (1*R*,4*R*)-**10** with 10 mol % of vanadium(v) complex **4g** or with *p*-toluenesulfonic acid



Scheme 6. Formation of peroxy complex **57** (top) and its use in competition kinetic investigations (bottom)

(TsOH) led quantitatively to the formation of 2,5-*cis*-configured tetrahydrofuran (2*S*,5*R*)-**6** and 3,6-*cis*-configured tetrahydropyran (3*R*,6*R*)-**7** in a ratio of 91:9. Furthermore, vanadium(v)- or acid-catalyzed rearrangement of epoxy alcohol (1*S*,4*R*)-**10** furnished 2,5-*trans*-disubstituted tetrahydrofuran derivative (2*S*,5*S*)-**6** and 3,6-*trans*-substituted tetrahydropyran derivative (3*R*,6*S*)-**7** in a ratio of 39:61. Since the major component in one sample [e.g. (1*R*,4*R*)-**10**] constituted the enantiomer of the minor in the second sample [e.g. (1*S*,4*S*)-**10**], such by-products from each epoxide isomerization were readily identified.



Scheme 7. Diastereoselective conversion of alkenols (*R*)-**5** and (*S*)-**5** into corresponding cyclic ethers **6** and **7**; reagents and conditions: (a) Shi epoxidation;[49] (b) TsOH (1 equiv.) or **4g** (0.1 equiv.); [a] yields: 80% of (2*S*,5*R*)-**6**, 8% of (3*R*,6*R*)-**7**, and 12% of a 39:61 mixture of *trans*-**6** and *trans*-**7**; [b] yields: 32% of (2*S*,5*S*)-**6**, 50% of (3*R*,6*S*)-**7**, and 18% of a 91:9 mixture of *cis*-**6** and *cis*-**7**

Discussion

1. Characterization of (Schiff-base)vanadium(v) Complexes 4 and Their Conversion into Peroxy Derivatives

In a previous study, (Schiff-base)vanadium(v) complexes had been prepared by an in situ mixing of $[VO(acac)_2]$ and

imine ligands **3a**, **3d**, and **3g**. Similarly prepared vanadium reagents served as catalysts for converting selected bis(homoallylic) alcohols **1** into functionalized tetrahydrofurans **2**. TBHP had served in all instances as primary oxidant.[26] In the present report, complexes **4** were synthesized in a separate step. All vanadium reagents **4** were characterized by means of spectroscopy and elemental analysis. These results were supplemented by data from selected X-ray diffraction analyses. Similarly characterized coordination compounds **4** were applied as oxidation catalysts.

(i) IR Analysis and UV/Vis Spectra

The coordination compounds **4a**−**k** exhibited single V=O stretching bands in the region of 966−997 cm^{-1}. These absorptions were indicative of monomeric vanadium(v) compounds.[30] Up to three characteristic electronic transitions were observed in the UV/Vis spectra of the d^0 vanadium(v) compounds **4** (in EtOH). Strong absorptions in the region between 310−373 nm were assigned to intraligand π→π* transitions. Two less intense lower energy transitions were observed at ca. 440 nm and at ca. 655 nm (except for **4a**−**c**). Both transitions were, in extension to previous assignments in structurally related vanadium(v) compounds, attributed to ligand-to-metal charge transfer of the type phenolato oxygen atom → *d* and alcoholato oxygen atom → *d* [where *d* represents a vacant d orbital at the vanadium(v) center].[51]

(ii) ^{51}V NMR Shifts

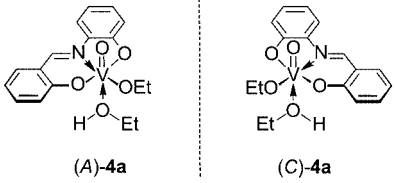
The coordination compounds **4a**, **4c**−**k** displayed ^{51}V NMR signals in the range of δ = −518 to −557 ppm which were characteristic for pentavalent vanadium(v) complexes with a coordination sphere that was dominated by O functionalities.[52] Two ^{51}V signals were observed for vanadium compounds **4d** (CD_3OD), **4e** and **4f** (both in EtOH), **4g** (CD_3OD), **4h** ($CDCl_3$), and **4j**,**k** (both in EtOH). These findings implied that at least two structurally different complexes existed in those cases. The exact origin of this observation remained unclear in the present study. In principle, it may have originated from configurational desintegrity of imine ligands, which had occurred during complex formation, or the presence of diastereomers, caused by different configurations at the vanadium center (see below), or by ligand-exchange reactions and therefore a dynamic behavior of complexes **4**. The latter reasoning was based on the well-known propensity of alkoxide ligands to be replaced by nucleophiles with higher affinity for vanadium(v), such as water or TBHP.[53] We are not able to present evidence for the former two arguments in general. However, the results from X-ray crystallographic studies of the vanadium complexes **4e**, **4g**, and **4h** provided valuable information in view of such considerations.

(iii) X-ray Crystallography

In the complexes **4e**, **4g**, and **4h**, the pentacoordinate vanadium(v) atoms are located in distorted tetragonal pyramids. The central ions are displaced from the best planes which are formed by the corresponding Schiff-base functions and the additional alcoholato oxygen atom (**4e**: 0.51 Å; **4g**: 0.52 Å; *exo*-**4h**: 0.54 Å; *endo*-**4h**: 0.52 Å; Table 2). Connectivities of V1 to O decreased in the series V1−O2 (ca. 1.86 Å, phenolato oxygen atom, part of a six-membered chelate ring) > V1−O3 (ca. 1.82 Å, alcoholato oxygen atom, part of a five-membered chelate ring) > V1−O4 (ca. 1.78 Å, ethanolato or 2-propanolato oxygen atom) > V1−O1 (1.56−1.58 Å). In analogy to investigations of structurally related complexes, the latter connectivity was interpreted as a vanadium−oxygen double bond.[30] Observed long V1−N1 distances of 2.10−2.17 Å were attributed to the well-known low affinity of neutral imino nitrogen atoms for vanadium(v) centers.[54] Bite angles in tridentate chelates decrease from N1−V1−O2 (ca. 82°) to N1−V1−O3 (ca. 77°), which is reasonable since the former describes a corner of an almost planar distorted hexagon while the latter originates from a saturated five-membered heterocyclic ring.

In regard to their general constitution, the vanadium(v) complexes **4e**, **4g**, and **4h** may be subdivided into two hemispheres. The first hosts ligands that are considered to be spectators in the oxidation catalysis (ligands that coordinate via O1−O3 and N1 to V1). This part of the compound is dominated by steric effects from the amino alcohol entity (O3, N1). The second hemisphere is more open. It consists of the vacant coordination site in *trans* position to O1 and the monovalent alcoholato ligand (connected via O4 to V1). Alkoxide ligands, however, may be displaced in solutions, e.g. by TBHP.[55] Further, neutral donor ligands, such as EtOH and 1,4-dioxane, have been found to bind in *trans*-position to V−O double bonds.[27b,56] Therefore, the second hemisphere of complexes **4** is considered to play a major role in catalysis, since it should allow peroxide and bis(homoallylic) alcohol binding (see below).

The central ion in oxovanadium(v) compounds with tridentate imine ligands of the type used in this study constitutes a stereogenic center (see Figure 5). (*S*)-Valinol-derived vanadium complex **4e** exhibits *C* configuration and (1*R*,2*S*)-aminoindanol-based compound **4g** *A* configuration at the vanadium center.[31] The absolute configuration of stereocenters in the auxiliaries of both coordination compounds is identical to that of the free ligands H_2L^5 (**3e**) and H_2L^7 (**3g**). Structure solution and refinement of complex **4h** showed that the sample, which was prepared from enantiomerically pure *exo*-configured ligand H_2L^8 (**3h**; Figure 2), consisted of two compounds: *exo*-**4h** with *C* configuration at the vanadium center and *A*-configured *endo*-**4h**. This un-



(*A*)-**4a** (*C*)-**4a**

Figure 5. Geometry of (Schiff-base)vanadium(v) complex (*A*)-**4a** (left) and its enantiomer (*C*)-**4a** (right)[31]

expected inversion of two stereocenters in a Schiff-base auxiliary, due to its reaction with $VO(OEt)_3$, is under investigation.

(iv) Reaction with TBHP

Vanadium complexes **4** reacted with TBHP.[26,27a] For example, conversion of $VOL^1(OEt)(EtOH)$ (**4a**) with a 1.5 molar excess of TBHP in $CDCl_3$ at 61 °C provided a brown solution which was characterized by a ^{51}V NMR signal shifted to high field at $\delta = -571$. In view of additional analytical data from previous studies[26,27a] and more recent results from an ESI-MS investigation of a derivative of **4a**,[57] the resonance at $\delta = -571$ ppm was assigned to peroxyvanadium(v) complex **57**. This interpretation was supported by the fact that a similarly prepared solution of **57** in CH_2Cl_2 converted 5-methyl-1-phenylhex-4-en-1-ol (**5**) in a stoichiometric reaction, at 20 °C within 48 h, into 65% of 2,5-disubstituted tetrahydrofuran **6** (*cis*/*trans* = 95:5) and 5% of 2,2-dimethyl-6-phenyltetrahydropyran-3-ol (**7**, *cis*/*trans* = 45:55).[26] In analogy to this cumulative evidence for the existence of peroxy complex **57**, ^{51}V NMR spectral changes upon addition of 1.5 equiv. of TBHP in hot $CDCl_3$ (61 °C) to phenylglycine-derived vanadium complex **4d** (^{51}V NMR: $\delta = -575$ and -580 ppm; 1.5:1 signal ratio) and to aminoindanol-derived complex **4h** (^{51}V NMR: $\delta = -574$ and -578 ppm; 1:1.2 signal ratio) were interpreted as formation of corresponding peroxy complexes.

2. Vanadium(v)-Catalyzed Oxidation of 5-Methyl-1-phenylhex-4-en-1-ol (5) and Structurally Related Derivatives

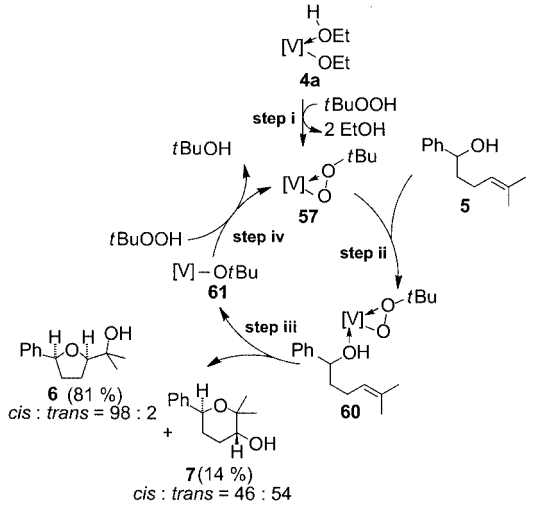
The mechanism of the tetrahydrofuran formation from bis(homoallylic) alcohol **5** and TBHP in the presence of (Schiff-base)vanadium(v) complex **4a** was investigated in detail. According to the results given above, the reaction followed a transition metal−peroxy pathway and proceeded in four major steps:[8] (i) formation of peroxyvanadium(v) complex **57**, and hence activation of TBHP, (ii) alkenol binding to intermediate **57**, (iii) stereoselective intramolecular oxygen transfer, and (iv) subsequent regeneration of peroxy complex **57** from proposed *tert*-butoxy complex **61** (Scheme 8).

(i) Formation of Peroxy Complex 57 from Vanadium Reagent 4a

TBHP is a comparatively strong oxidant[58] which, however, did not react with bis(homoallylic) alcohol **5** alone. The hydroperoxide had to be activated for this purpose e.g. by *N*-(2-oxidophenyl)salicylideniminato-derived vanadium complex **4a**. This step was associated with the formation of peroxyvanadium(v) complex **57** (see above).

(ii) Alkenol Coordination to Peroxy Complex 57

Evidence for alkenol binding to intermediate **57** was taken from results of competition kinetic experiments (Scheme 6). Thus, bis(homoallylic) alcohol **5** was oxidized 120 times faster than structurally related olefin **58** ($T = 20$ °C; Scheme 6).[59] Although it was proposed in an earlier



Scheme 8. Proposed catalytic cycle for the synthesis of cyclic ethers **6** and **7** in a (Schiff-base)vanadium(v) complex catalyzed oxidation of methyl-phenylhexenol **5**

investigation that olefin coordination to the vanadium(v) center in peroxy complex **57** was a prerequisite for selective epoxidation of nonfunctionalized alkenes,[27a] it was more likely that the origin of the observed difference in rate constants k^1 and k^2 in the present work originated from an acceleration of a rate-determining step in the alkenol oxidation. The molecular basis for this kinetic effect was considered to be associated with substrate binding via the hydroxy group to the oxophilic vanadium(v) ion,[60] which set the stage for an intramolecular π-bond oxygenation (step iii).

(iii) Stereoselective Oxygen Transfer in "Loaded" Vanadium(v) Complex 60

Coordination of TBHP and bis(homoallylic) alcohol **5** to vanadium(v) compound **4a** provided "loaded" complex **60**. Intramolecular oxygen transfer from the coordinated peroxide to the alkenol ligand in **60** proceeded stereoselectively and furnished 81% of 2,5-disubstituted tetrahydrofuran **6** (*cis*/*trans* = 98:2) and 14% of corresponding tetrahydropyran **7** (*cis*/*trans* = 46:54). The preferred trajectory for oxygen atom delivery to one of the prostereogenic faces of the (Schiff-base)vanadium(v) complex bound alkenol was reconstructed using the results from the stereochemical analysis of product formation from diastereomerically enriched epoxy alcohols **10** (Scheme 7). These studies had indicated that (1*R*,4*R*)-configured substrate **10** rearranged upon treatment with (Schiff-base)vanadium(v) complex **4g** or TsOH into a 91:9 mixture of *cis*-2,5-disubstituted tetrahydrofuran (2*S*,5*R*)-**6** and 3,6-*cis*-configured tetrahydropyran (3*R*,6*R*)-**7**. The *unlike* isomer (1*S*,4*R*)-**10** provided under the same conditions a mixture of *trans*-configured heterocycles (2*S*,5*S*)-**6** and (3*R*,6*S*)-**7**, which was surprisingly in favor of the tetrahydropyran derivative **7** [(2*S*,5*S*)-**6**/(3*R*,6*S*)-**7** = 39:61]. These results showed that the relative configuration of epoxy alcohol **10** dictated the preference for tetrahydrofuran synthesis [from (1*R*,4*R*)-**10**] or tetra-

hydropyran formation [from (1*S*,4*R*)-**10**]. In order to translate these findings into selectivity data for the vanadium(v)-catalyzed oxidation of bis(homoallylic) alcohol **5**, the structure of intermediate **60** was modeled using assumptions that related to the configuration at the vanadium center and the mode of peroxide and alkenol binding. Since compounds **4a**[61] and **5** were both applied as racemates, the following stereochemical discussion is restricted to the reaction of an arbitrarily selected enantiomer of methyl-phenylhexenol **5** [i.e. (*R*)-**5**] with a peroxyvanadium(v) complex **57** not further defined stereochemically. The mode of TBHP-binding in peroxy complex **57** was constructed by taking meridional ligation of η^2-coordinated *tert*-butylperoxy ligand in a structurally well-defined (2,6-pyridinedicarboxylato)vanadium(v) complex[62] as archetype for alkylperoxy coordination in (Schiff-base)vanadium(v) complexes in general. In regard to bis(homoallylic) alcohol coordination to peroxy complex **57**, it seems reasonable to assume that this interaction takes place in *trans* position to the V−O double bond, since neutral oxygen donor ligands such as EtOH or 1,4-dioxane have been reported to bind to that site (X-ray crystallographic studies).[27b,56,61] The geometry of a thus modeled "loaded" complex **60** did not significantly restrict the conformational space of methyl-phenylhexenol **5** unless the reacting entities, i.e. the olefinic π-bond and the transferable oxygen atom, approached. In this case, the chair-like arrangement of the ligand in *chair*-**60** was considered to be one of the more significantly populated conformers (Figures 6 and 7). Intramolecular oxygen transfer in *chair*-**60** provided vanadium(v) complex *like*-**62**. If oxygenation occurred from the opposite diastereotopic face of the π-bond, e.g. via *gauche*-**60**, complex *unlike*-**62** was formed. However, intermediates *like*-**62** and *unlike*-**62**, if they existed at all, should be very short-lived, because they have so far not been detected by ^{1}H NMR spectroscopic monitoring of (Schiff-base)vanadium(v) complex-catalyzed oxidations of substrate **5** (Figure 4). Rearrangement of primary oxygenation products *like*-**62** and *unlike*-**62** into tetrahydrofurans required a stereocontrolled backside attack of the hydroxy oxygen atom onto the C4−O bond of the epoxide entity. This step was probably paralleled by elimination of *tert*-butoxy complex **61**. Rearrangement of *like*-configured epoxy alcohol derivative *like*-**62** provided in this model *cis*-substituted heterocycles (2*S*,5*R*)-**6** and (3*R*,6*R*)-**7**. Similarly, *trans*-substituted cyclic ethers (2*S*,5*S*)-**6** and (3*R*,6*S*)-**7** were obtained from *unlike*-**62**. In view of the inherent selectivity for formation of 2,5-*cis*-configured tetrahydrofuran *cis*-**6** in (peroxy)(Schiff-base)vanadium(v) complex mediated oxidation of bis(homoallylic) alcohol **5**, product formation from this reaction should mainly proceed via *like*-**62**. However, since the experiment provided *trans*-configured products *trans*-**6** and *trans*-**7** in each case as side products, both stereochemical pathways for π-bond oxygenation should exist.

This stereochemical interpretation of the vanadium(v)-catalyzed oxidation of substrate **5** was supported by results from experiments with conformationally restricted bis(homoallylic) alcohols **30** (Scheme 3). Thus, *trans*-configured

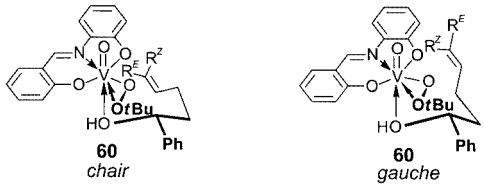


Figure 6. Proposed binding modes of the *tert*-butylperoxy ligand and 5-methyl-1-phenylhex-4-en-1-ol (**5**) in vanadium(v) complex **60**; $R^E = R^Z$ = methyl

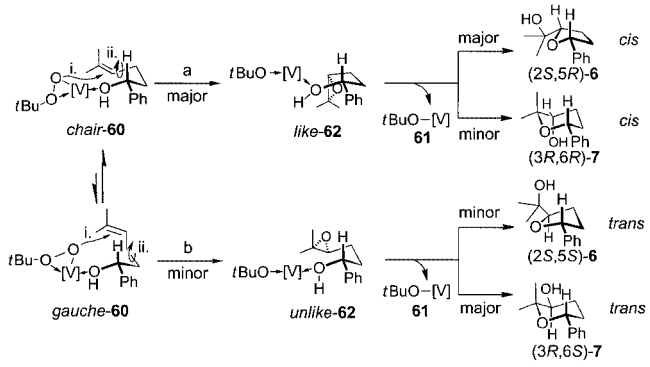


Figure 7. Stereochemical model for correlating the facial selectivity of π-bond oxygenation from "loaded" peroxy complex **60** with the geometry of similarly prepared cyclic ethers **6** and **7**

cyclohexanol derivative *trans*-**30** was oxidized under these conditions to afford diastereomerically pure bicyclic 6,8-*cis*-substituted tetrahydrofuran **31**. This notable diastereoselectivity was attributed to a more profound preference for adopting a *chair*-like conformer in the transition state of the oxygenation reaction. In this sense, it was reasonable that formation of bicyclic tetrahydrofuran **32** proceeded with significantly lower diastereoselectivity and was associated with the additional formation of 5% of *trans*-configured tetrahydropyran **33**.

(iv) Regeneration of Peroxy Complex 57 − Closing the Catalytic Cycle

The proposed *tert*-butoxyvanadium(v) complex **61** was considered to react with TBHP in order to regenerate peroxy complex **57** for selective oxygen atom transfer in another catalytic cycle. Highest selectivities for the formation of target compound **6** were achieved at 20 °C using TBHP as primary oxidant, preferentially in a solvent with low donicity (D_N) and a high dielectric constant (ε) such as $CHCl_3$.[63] Since 0.1 mol % of vanadium complex **4a** sufficed to convert bis(homoallylic) alcohol **5** in a total yield of 82% into heterocycles **6** and **7**, an estimated turnover of peroxy complex **57** in 820 catalytic cycles was achieved. For practical reasons, 10 mol % of reagent **4a** were applied in order to reduce formation of side products (see above). The efficiency of peroxide utilization with respect to formation of heterocycles **6** and **7** under these conditions was 63%. The catalytic activity of the vanadium complexes faded at the end of the oxidation reaction. The exact origin of this deactivation step was not known, but it is under investi-

gation in order to develop catalysts with improved characteristics for future projects.

Auxiliary Control in Product Formation

The observed yields of tetrahydrofuran derivative **6** were dependent on the structure of the catalyst **4**. Thus, application of vanadium(v) complexes **4a**, **4d**, **4g**, **4h**, and **4j** allowed formation of tetrahydrofuran derivative **6** in more than 80% yield (Table 3). This group of catalysts shared two common structural motifs: (a) no *tert*-butyl substituents in the *o*-hydroxybenzaldehyde entity and (b) a nonpolar amino alcohol substructure in the chelate ligand. The remaining catalysts either were prepared from 4,6-di-*tert*-butylsalicylaldehyde (**4e**, **4f**, **4i**, and **4k**) or from polar amines (i.e. **4c**, **4i**) and furnished lower yields of tetrahydrofuran **6** in the same reaction period. In spite of the observed distinct differences in reactivities, the catalysts had no significant effect on the observed diastereoselectivity for formation of target compound **6**.[64,65]

3. Structure-Selectivity Relationship in (Schiff-base)vanadium(v) Complex Catalyzed Oxidations of Bis(homoallylic) Alcohols

TBHP served as efficient primary oxidant for converting 5,5-dimethyl-substituted bis(homoallylic) alcohols (Figure 8, left) and substituted 4-penten-1-ols (Figure 8, right) into functionalized tetrahydrofurans. The reaction was catalytic in vanadium(v). The use of 1-amino-2-indanol-derived complex **4g** for this purpose is recommended since it was an efficient reagent for both peroxide activation and diastereoselective oxygen transfer to δ,ε-unsaturated alcohols (Tables 3 and 5). This reagent was superior to alternative methods which required, for example, $[VO(acac)_2]$,[2,26] molybdenum(vi) complexes,[66] and more recently $[Cp_2TiCl_2]$,[67] as catalysts. No direct comparison of the peroxyvanadium(v) complex based tetrahydrofuran formation with highly diastereoselective oxidations using stoichiometric amounts of acylrhenates(vii)[14] or oxidations which require the reagent combination of cobalt(ii) diketonate complexes, molecular oxygen *and* TBHP[68] can be made at this point because the sets of substrates in these studies did not match. Finally, it is worth mentioning that *m*CPBA is a reliable but poorly selective oxidant for converting bis(homoallylic) alcohols into functionalized tetrahydrofurans (Supporting Information).[69]

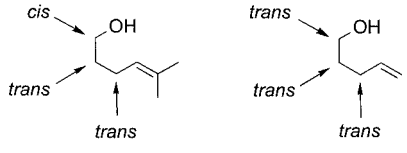


Figure 8. Guidelines for the stereoselective synthesis of functionalized tetrahydrofurans from substituted bis(homoallylic) alcohols

(i) Oxidation of 5,5-Dimethyl-Substituted Bis(homoallylic) Alcohols

1-Substituted secondary or tertiary bis(homoallylic) alkenols upon treatment with TBHP and catalyst **4g** afforded 2,5-*cis*-configured tetrahydrofuran derivatives as major compounds. Therefore, these substrates were considered to follow the same stereochemical pathway for oxygenation of the bis(homoallylic) π-bond as outlined for 5-methyl-1-phenylhex-4-en-1-ol (**5**) in Figure 7. The observed diastereoselectivities decreased from methyl-1-phenylhexenol **5** (96% *de*), to 1-*tert*-butyl derivative **11** (82% *de*), 1-methyl-1-cyclohexenyl-substituted alkenol (*S*,*S*)-**38** (64% *de*) to (*R*)-linalool (**34**, 22% *de*). It is noteworthy, that (*R*)-linalool [(*R*)-**34**] was oxidized at the bis(homoallylic) rather than at the allylic π-bond. This finding, however, may be rationalized by considering the reluctance of Schiff-base complex **4a** to catalyze the epoxidation of allylic alcohol itself which restricts the oxygen atom acceptor to the bis(homoallylic) π-bond. The fact that (*S*,*S*)-bisabolol [(*S*,*S*)-**38**] is preferentially oxidized at the bis(homoallylic) double bond that is embedded in the flexible hydrocarbon chain rather than at a more rigid cyclohexene substructure opens further useful perspectives for applications of this new method in stereoselective synthesis (Scheme 4).[70]

Finally, it is instructive to compare results from vanadium(v)-catalyzed oxidations of 4-methyl-1-phenyl-3-buten-1-ol (**26**, lower homologue of **5**) and 6-methyl-1-phenyl-5-hepten-1-ol (**27**, higher homologue of **5**) with respect to the observed diastereoselectivity. The fact that *trans*-configured tetrahydrofuran *trans*-**28** was obtained as the major product from substrate **26** was interpreted with a change in facial selectivity for π-bond oxygenation, if compared to substrate **5**. Again it is worth mentioning that epoxy alcohol intermediates were not observed in this reaction (TLC). Formation of 2,6-*cis*-disubstituted tetrahydropyran *cis*-**29** from alkenol **27** pointed to the fact that the same face-selection rule in peroxyvanadium(v) complex mediated oxygenation applied for this substrate as for its lower homologue **5**.

5,5-Dimethyl-substituted bis(homoallylic) alcohols with substituents at positions 2 and 3 were selectively oxidized in the presence of TBHP and catalyst **4g** to provide *trans*-configured tetrahydrofurans (Table 4). In extension to the stereochemical model which is outlined in Figure 6, formation of *trans*-2,4-substituted tetrahydrofurans should therefore preferably proceed via a *chair*-like arranged alkenol ligand in a "loaded" complex, similar to *chair*-**60** (see Figures 6 and 7). On the other hand a reversal of this facial selectivity in the oxygen-transfer step had to be assumed in order to explain the synthesis of diastereomerically pure 2,3-*trans*-disubstituted tetrahydrofuran derivatives, e.g. **19** and **20** (Figure 7).

(ii) Oxidation of Substituted 4-Penten-1-ols

(Schiff-base)vanadium(v)-catalyzed oxidations of 4-penten-1-ols with alkyl or phenyl groups at position 1, 2, and 3 (e.g. **41**, **43**−**47**, refer to Tables 5 and 6) proceeded in all cases more slowly and less diastereoselectively than

those outlined for their 5,5-dimethyl-substituted derivatives. *trans*-Disubstituted tetrahydrofurans were obtained as major products in all experiments. Formation of corresponding tetrahydropyrans was not observed. The same trends were noted for the reaction of TBHP and 4-methyl-1-phenyl-4-penten-1-ol (**54**) which furnished *trans*-2,5-substituted tetrahydrofuran as the major product (Scheme 5). The fact that oxidation of 1-phenyl- and 1-*tert*-butyl-substituted 4-penten-1-ols **43** and **44** were favored the *trans* isomer instead of the expected *cis* isomer (see above) pointed to a change in facial selectivity for π-bond oxygenation, which is caused by the substitution pattern at the double bond. This issue is under investigation.

Conclusion

Vanadium(v) complexes **4** with tridentate Schiff-base auxiliaries served as efficient oxidation catalysts for a chemo- and diastereoselective conversion of bis(homoallylic) alcohols into the corresponding tetrahydrofurans. The reaction follows a transition metal−peroxy mechanism. Thus, coordination of TBHP to a vanadium(v) complex was followed by alkenol binding to provide a "loaded" peroxy complex, e.g. **60**. Subsequent intramolecular stereoselective oxygen transfer affords disubstituted functionalized tetrahydrofurans. Important elementary reactions such as the formation of *tert*-butylperoxy complexes (^{51}V NMR spectroscopy), alkenol binding (competition kinetics), and stereoselective π-bond oxygenation (stereochemical analysis using diastereomerically enriched epoxy alcohols **10**) were investigated in separate experiments. Guidelines for stereoselective synthesis, which may be derived at the present state of our investigation, predict formation of *trans*-configured tetrahydrofurans from 5,5-dimethyl-substituted bis(homoallylic) alcohols with alkyl and aryl groups at position 2 or 3 as well as from 1-, 2-, and 3-alkyl- or phenyl-substituted 4-penten-1-ols. On the other hand, the vanadium(v)-catalyzed oxidation of secondary or tertiary 5,5-dimethyl-substituted δ,ε-unsaturated alkenols proceeded 2,5-*cis*-selectively. Formation of furanoid *cis*-linalool oxide (*cis*-**35**) as the major product from (*R*)-linalool [(*R*)-**34**], instead of the expected corresponding 1,2-epoxy alcohol was noteworthy and has opened new perspectives for stereoselective synthesis, e.g. for the formation of tetrahydrofuran-derived β-carboline alkaloids.[71]

Experimental Section

General Remarks: ^{1}H, ^{13}C and ^{51}V NMR spectra were recorded with Bruker AC 250 and WM 400 instruments at 20 °C in $CDCl_3$ solution (^{51}V NMR: EtOH) unless otherwise noted. Residual protons of deuterated solvents [δ_H = 7.26 ($CDCl_3$)] and the corresponding carbon resonances in ^{13}C NMR spectra [δ_C = 77.0 ($CDCl_3$)] were taken as internal standards. ^{51}V NMR: $VOCl_3$ was taken as external standard [δ_V = 0.00 ($VOCl_3$)]. IR: KBr pellets, Perkin−Elmer 1600 FT-IR spectrometer. UV/Vis: 1-cm quartz cuvettes, Perkin−Elmer 330 spectrophotometer. MS: Varian MATCH 7 spectrometer (EI, 70 eV). C,H,N,S analyses: Microanalytisches Laboratorium, Universität Würzburg, Carlo Erba 1106 or LECO CHNS-932. Solvents were purified according to standard procedures. (*R*)-Linalool [(*R*)-(**34**)], *tert*-butyl hydroperoxide (5.5 M in nonane), and $VO(Et)_3$ were obtained from Fluka or Aldrich and were used as received. Petroleum ether was distilled prior to use (b.p. 40−55 °C).

1. Preparation of Schiff Bases 3. General Procedure: Schiff bases **3** were prepared by condensation of salicylaldehydes (2 mmol, 1 equiv.) and amino alcohols (2 mmol, 1 equiv.) in refluxing ethanol (15 mL, 3−4 h). Subsequent evaporation of the solvent furnished, after extensive drying at 20 °C/10^{-2} mbar, analytically pure Schiff bases **3** in quantitative yields [exception: **3h** was purified by column chromatography (SiO_2) and obtained in 61% yield].

2,4-Di-*tert*-butyl-6-({[(1*S*)-1-(hydroxymethyl)-2-methylpropyl]-imino}methyl)phenol (3e): Yield: 0.64 g (quant.), yellow solid, m.p. 104−105 °C. $[\alpha]_D^{25}$ = −32.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz): δ = 0.96 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 7.0 Hz, 3 H), 1.31 (s, 9 H), 1.45 (s, 9 H), 1.90−2.03 (m, 1 H), 3.07 (m_c, 1 H), 3.67−3.87 (m, 2 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 7.44 (d, *J* = 2.4 Hz, 1 H), 8.40 (s, 1 H) ppm. ^{13}C NMR (63 MHz): δ = 18.8, 19.8, 29.4, 31.5, 30.1, 34.1, 35.0, 64.7, 77.9, 117.7, 126.1, 127.1, 136.7, 140.2, 158.1, 167.1 ppm. IR (KBr): $\tilde{\nu}$ = 3298 cm^{-1}, 3223, 2953, 2871, 1624, 1468, 1435, 1275, 1250, 1025, 851. MS (70 eV, EI): *m*/*z* (%) = 319 (62) [M^+], 304 (100) [$C_{19}H_{30}NO_2^+$], 276 (50) [$C_{17}H_{26}NO_2^+$], 219 (19) [$C_{13}H_{17}NO_2^+$], 162 (11) [$C_9H_8NO_2^+$], 57 (53) [$C_4H_9^+$], 41 (28) [$C_3H_5^+$]. HRMS ($C_{20}H_{33}NO_2$, 319.49): calcd. 319.2511, found 319.2510.

2,4-Di-*tert*-butyl-6-({[(1*S*)-1-(hydroxymethyl)-2,2-dimethylpropyl]-imino}methyl)phenol (3f): Yield: 0.67 g (quant.), viscous yellow oil. $[\alpha]_D^{25}$ = −36.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz): δ = 0.98 (s, 9 H), 1.31 (s, 9 H), 1.45 (s, 9 H), 2.94 (dd, *J* = 9.4, 2.9 Hz, 1 H), 3.74 (dd, *J* = 11.3, 2.9 Hz, 1 H), 3.93 (dd, *J* = 11.3, 9.5 Hz, 1 H), 7.14 (d, *J* = 2.4 Hz, 1 H), 7.41 (d, *J* = 2.4 Hz, 1 H), 8.38 (s, 1 H) ppm. ^{13}C NMR (63 MHz): δ = 27.1, 29.4, 31.5, 33.2, 34.2, 35.1, 62.5, 81.4, 117.7, 126.2, 127.2, 136.8, 140.2, 158.2, 167.2 ppm. IR (KBr): $\tilde{\nu}$ = 3387 cm^{-1}, 2960, 2907, 2869, 1631, 1474, 1440, 1172, 1062. MS (70 eV, EI): *m*/*z* (%) = 333 (90) [M^+], 318 (100) [$M^+ - CH_3$], 290 (44) [$C_{19}H_{31}NO^+$], 276 (48) [$M^+ - CH(CH_3)_3$], 219 (31) [$C_{15}H_{22}O^+$], 162 (6) [$C_{11}H_{13}^+$], 57 (35) [$C_4H_9^+$]. HRMS ($C_{21}H_{35}NO_2$, 333.5): calcd. 333.2668, found 333.2667.

(1*R*,2*S*,3*R*,4*S*)-3-[(2-Hydroxybenzylidene)amino]isoborneol (3h): Yield: 0.33 g (61%), R_f = 0.80 (Et_2O), yellow solid, m.p. 119 °C (EtOH). $[\alpha]_D^{25}$ = 32.7 (*c* = 1.0, MeOH). ^{1}H NMR (250 MHz): δ = 0.86 (s, 3 H), 1.01 (s, 3 H), 1.26 (s, 3 H), 0.91−1.22 (m, 5 H), 3.61 (d, *J* = 7.3 Hz, 1 H), 3.85 (d, *J* = 7.3 Hz, 1 H), 6.91 (m_c, 2 H), 7.27 (m_c, 2 H), 8.36 (s, 1 H) ppm. ^{13}C NMR (63 MHz): δ = 11.3, 21.5, 21.6, 26.5, 33.5, 47.2, 49.3, 53.3, 68.2, 81.6, 117.5, 118.3, 119.8, 131.7, 133.7, 137.0, 165.8 ppm. IR (KBr): $\tilde{\nu}$ = 3448 cm^{-1}, 2953, 2935, 2868, 1627, 1527, 1484, 1461, 1389, 1280, 1223, 1052, 847. MS (70 eV, EI): *m*/*z* (%) = 273 (100) [M^+], 230.1 (40) [$C_{14}H_{16}NO_2^+$], 161 (65) [$C_{10}H_{11}NO^+$], 122 (90) [$C_7H_8NO^+$], 41 (35) [$C_3H_5^+$]. $C_{17}H_{23}NO_2$ (273.4) calcd. C 74.69, H 8.48, N 5.12 found C 75.13, H 7.97, N 4.85.

3-{[(3,5-Di-*tert*-butyl-2-hydroxyphenyl)methylene]amino}propane-1,2-diol (3i): Yield: 0.61 g (quant.), viscous yellow oil. ^{1}H NMR (250 MHz): δ = 1.30 (s, 9 H), 1.44 (s, 9 H), 3.56−3.81 (m, 4 H), 3.99−4.05 (m, 1 H, 2-H), 7.10 (d, *J* = 2.4 Hz, 1 H), 7.40 (d, *J* = 2.4 Hz, 1 H), 8.41 (s, 1 H) ppm. ^{13}C NMR (63 MHz): δ = 29.4, 31.4, 34.1, 35.0, 61.9, 64.6, 71.6, 117.6, 126.1, 127.3, 136.7, 140.3, 158.0, 168.3 ppm. IR (KBr): $\tilde{\nu}$ = 3385 cm^{-1}, 2959, 1636, 1458,

1440, 1362, 1273, 1252, 1043. MS (70 eV, EI): *m/z* (%) = 307 (51) [M^+], 292 (100) [$C_{17}H_{26}NO_3^+$], 250 (24) [$C_{14}H_{20}NO_3^+$], 219 (33) [$C_{13}H_{17}NO^+$], 74 (51) [$C_3H_6O_2^+$], 57 (56) [$C_4H_9^+$]. HRMS ($C_{18}H_{29}NO_3$, 307.4): calcd. 307.2147, found 307.2148.

2,4-Di-*tert*-butyl-6-({[(1*S*)-1-(hydroxymethyl)-3-(methylthio)propyl]-imino}methyl)phenol (3k): Yield: 0.70 g (quant.), viscous yellow oil. ^{1}H NMR (250 MHz): δ = 1.32 (s, 9 H), 1.45 (s, 9 H), 1.81−1.96 (m, 2 H), 2.09 (s, 3 H), 2.08−3.63 (m, 2 H), 3.48 (m_c, 1 H), 3.65−3.79 (m, 2 H), 7.14 (d, *J* = 2.4 Hz, 1 H), 7.41 (d, *J* = 2.4 Hz, 1 H), 8.44 (s, 1 H) ppm. ^{13}C NMR (63 MHz): δ = 15.3, 29.4, 31.4, 30.7, 31.0, 34.1, 35.0, 66.1, 70.3, 117.6, 126.2, 127.3, 136.7, 140.3, 157.9, 167.6 ppm. IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 2957, 2903, 2862, 1624, 1476, 1249, 1173, 1045, 880, 826. MS (70 eV, EI): *m/z* (%) = 351 (100) [M^+], 336 (94) [$C_{19}H_{30}NO_2^+$], 277 (34) [$C_{17}H_{27}NO_2^+$], 203 (26) [$C_{13}H_{17}NO_2^+$], 118 (34) [$C_5H_{11}OS^+$], 57 (61) [$C_4H_9^+$], 41 (30) [$C_3H_5^+$]. HRMS ($C_{20}H_{33}NO_2S$, 351.6): calcd. 351.2232, found 351.2233.

2. (Schiff-base)vanadium(v) Complexes 4. General Procedure: A solution of Schiff-base ligand **3** (1 mmol) in dry ethanol (10 mL) was added under nitrogen to a solution of $VO(OEt)_3$ (1 mmol) in dry ethanol (5 mL). The reaction mixture was stirred at 20 °C for 1 h. Afterwards, the solvent was removed under reduced pressure to provide vanadium(v) complexes **4** in quantitative yields.

VOL^1(OEt)(EtOH) (4a): Yield: 0.37 g (quant.), dark brown-green microcrystalline solid. IR (KBr): $\tilde{\nu}$ = 990 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 242 (4.16), 341 (3.78), 361 (3.80), 659 (2.40) nm. ^{51}V NMR (105 MHz): δ = −529 (EtOH), −529; (CD_3OD); −529 ($CDCl_3$) ppm.

VOL^2(OEt) (4b): Yield: 0.35 g (quant.), dark-brown solid. IR (KBr): $\tilde{\nu}$ = 996 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 255 (4.16), 348 (3.69), 352 (3.69) nm. ^{51}V NMR (105 MHz): no signal detected (EtOH). $C_{17}H_{18}NO_5V$ (367.3): calcd. C 55.60, H 4.94, N 3.81; found C 53.64, H 4.62, N 3.13.

VOL^3(OEt) (4c): Yield: 0.33 g (quant.), black solid. IR (KBr): $\tilde{\nu}$ = 976 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 247 (sh), 316 (3.28), 373 (2.99), 659 (2.43) nm. ^{51}V NMR (105 MHz): δ = −523 (EtOH) ppm.

VOL^4(OEt) (4d): Yield: 0.35 g (quant.), brown crystals. IR (KBr): $\tilde{\nu}$ = 997 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 256 (4.36), 362 (3.15), 443 (1.88), 652 (2.20) nm. ^{51}V NMR (105 MHz): δ = −538 (EtOH); −526/−534 (1.5:1 in CD_3OD) ppm. VOL^4(OH)·(H_2O): $C_{15}H_{16}NO_5V$ (341.2): calcd. C 52.80, H 4.73, N 4.10; found C 53.66, H 4.80, N 2.62.

VOL^5(OEt) (4e): Yield: 0.43 g (quant.), black microcrystalline solid. IR (KBr): $\tilde{\nu}$ = 994 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 248 (4.36), 321 (3.78), 440 (2.53), 652 (2.50) nm. ^{51}V NMR (105 MHz): δ = −543/−551 (1.9:1 in EtOH); −560/−562 ppm ($CDCl_3$). $C_{22}H_{36}NO_4V$ (429.5): calcd. C 61.53, H 8.45, N 3.26; found C 61.12, H 7.85, N 3.50.

VOL^6(OEt) (4f): Yield: 0.44 g (quant.), black microcrystalline solid. IR (KBr): $\tilde{\nu}$ = 979 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 259 (4.33), 318 (3.80), 362 (3.19), 423 (2.33), 658 (1.94) nm. ^{51}V NMR (105 MHz): δ = −533/−549 (1:2.6 in EtOH); −562/−571 ($CDCl_3$) ppm. $C_{23}H_{38}NO_4V$ (443.5): calcd. C 62.29, H 8.64, N 3.16; found C 61.37, H 7.98, N 3.19.

VOL^7(OEt) (4g): Yield: 0.36 g (quant.), red crystalline solid. IR (KBr): $\tilde{\nu}$ = 997 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 272 (4.22), 345 (3.74), 435 (2.44), 652 (2.39) nm. ^{51}V NMR (105 MHz): δ = −541 (EtOH); −534/−538 (1:1.2 in CD_3OD); −542/−545 (1:1.2 in $CDCl_3$) ppm. VOL^7(OH)·(H_2O): $C_{16}H_{16}NO_5V$ (353.3): calcd. C 54.40, H 4.57, N 3.97; found C 54.35, H 3.98, N 3.93.

VOL^8(OEt) (4h): Yield: 0.38 g (quant.), red crystalline solid. IR (KBr): $\tilde{\nu}$ = 986 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 234 (4.27), 310 (3.61), 444 (2.38), 652 (2.74) nm. ^{51}V NMR (105 MHz): δ = −518 (EtOH); 550/−553 (1:3 in $CDCl_3$) ppm. VOL^8(OH)·(H_2O): $C_{17}H_{24}NO_5V$ (373.3): calcd. C 54.69, H 6.48, N 3.75; found C 54.89, H 6.28, N 3.73.

VOL^9(OEt) (4i): Yield: 0.42 g (quant.), dark brown-black solid. IR (KBr): $\tilde{\nu}$ = 966 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 231 (4.44), 324 (3.88), 448 (2.46), 659 (2.36), 659 (2.35) nm. ^{51}V NMR: δ = −548 (EtOH); −520 ($CDCl_3$) ppm. $C_{20}H_{32}NO_5V$ (417.4): calcd. C 57.55, H 7.73, N 3.36; found C 55.98, H 7.09, N 3.48.

VOL^{10}(OEt) (4j): Yield: 0.35 g (quant.), brown solid. IR (KBr): $\tilde{\nu}$ = 979 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 256 (4.32), 320 (3.79), 447 (2.30), 659 (2.48) nm. ^{51}V NMR (105 MHz): δ = −535/−542 (1.5:1 in EtOH) ppm. VOL^{10}(OH)·2(H_2O): $C_{12}H_{20}NO_6SV$ (357.3): calcd. C 40.34, H 5.64, N 3.92, S 8.97; found C 39.51, H 4.55, N 3.90, S 8.94.

VOL^{11}(OEt) (4k): Yield: 0.46 g (quant.), black microcrystalline solid. IR (KBr): $\tilde{\nu}$ = 983 cm^{-1} (V=O). UV/Vis (EtOH): λ_{max} (lg ε) = 251 (4.25), 350 (3.69), 437 (1.91), 652 (2.06) nm. ^{51}V NMR: δ = −545/−557 (1.7:1 in EtOH); −562/−573 ppm (in $CDCl_3$). $C_{22}H_{36}NO_4SV$ (461.5): calcd. C 57.25, H 7.86, N 3.03, S 6.95; found C 56.13, H 7.22, N 3.24, S 7.00.

3. Synthesis of Alkenols. General Procedure: Bis(homoallylic) alcohols were prepared from the corresponding carbonyl compounds.[73] Thus, a solution of a ketone or an aldehyde (1 equiv.) in anhydrous Et_2O (1 mL/mmol) was added dropwise at 0 °C to a suspension of $LiAlH_4$ (0.5 equiv.) in anhydrous Et_2O (5 mL/mmol). The reaction mixture was refluxed for 2 h and was subsequently cooled to 0 °C, hydrolyzed (5 mL of H_2O/mmol) and neutralized by treatment with aq. satd. NH_4Cl solution (2 mL/mmol). The organic phase was separated and the aqueous phase was extracted with Et_2O (2 × 2 mL/mmol). The combined organic layers were washed with brine (3 mL/mmol) and H_2O (2 × 3 mL/mmol) and dried (Na_2SO_4). The solvent was removed under reduced pressure (950 mbar/40 °C) to provide a residue, which was purified by distillation and in selected instances (see below) by column chromatography (SiO_2).

2,2,7-Trimethyl-6-octen-3-ol (11): 2,2,7-Trimethyl-6-octen-3-one[73a] (10.0 g, 59.4 mmol) was reduced with $LiAlH_4$ (0.5 equiv.) as described above to provide 9.47 g (94%) of alkenol **11** as a colorless liquid; b.p. 92 °C/11 mbar. ^{1}H NMR (250 MHz): δ = 0.88 [s, 9 H, $C(CH_3)_3$], 1.29 (m_c, 1 H, CH_2), 1.56 (m_c, 1 H, CH_2), 1.63 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 2.13 (m_c, 2 H, CH_2), 3.20 (dd, *J* = 10.4, 1.9 Hz, 1 H, CH), 5.15 (tquint, J_t = 7.2, J_{quint} = 1.5 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 17.7, 25.6, 25.7, 25.8, 31.5, 34.9, 79.8, 124.4, 123.1 ppm. MS (70 eV, EI): *m/z* (%) = 170 (4) [M^+], 113 (17) [$M^+ - C(CH_3)_3$], 95 (67) [$M^+ - C(CH_3)_3 - H_2O$], 82 (67) [$C_6H_{10}^+$], 69 (100) [$C_5H_9^+$]. $C_{11}H_{22}O$ (170.3): calcd. C 77.58, H 13.02; found C 78.13, H 12.86.

5-Methyl-3-phenyl-4-hexen-1-ol (14): $Hg(OAc)_2$ (0.505 g, 1.58 mmol) was added to a solution of 2-methyl-4-phenyl-3-buten-2-ol[73c] (4.00 g, 31.7 mmol) in ethyl vinyl ether (20 mL). The reaction mixture was stirred at an oil-bath temperature of 50 °C for 24 h. K_2CO_3 (0.5 g) was added and the volatiles were removed under reduced pressure (600 mbar/40 °C) to afford a residue which

was purified by column chromatography [SiO_2; petroleum ether/acetone, 9:1 (v/v)] to provide 5-methyl-3-phenyl-4-hexen-1-al (2.56 g, 43%) as a colorless liquid: R_f = 0.70 [petroleum ether/acetone, 9:1 (v/v)]. ^1H NMR (250 MHz): δ = 1.72 (s, 6 H, CH_3), 2.76 (m_c, 2 H, CH_2), 4.13 (dt, J_d = 6.7, J_t = 9.3 Hz,1 H, CH), 5.29 (dquint, J_d = 9.3, J_{quint} = 1.5 Hz, 1 H, CH), 7.15−7.36 (m, 5 H, Ar H) 9.70 (t, J_t = 2.2 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 18.7, 26.5, 39.4, 42.0, 126.7, 127.2, 128.4, 133.6, 139.8, 200.2 ppm. MS (70 eV, EI): *m/z* (%) = 188 (21) [M^+], 173 (45) [$M^+ - CH_3$], 145 (100) [$C_{11}H_{13}^+$], 117 (62) [$C_9H_9^+$]. $C_{13}H_{16}O$ (188.3): calcd. C 82.94, H 8.57; found C 83.16, H 8.51. According to the General Procedure, 5-methyl-3-phenyl-4-hexen-1-al (2.48 g, 13.2 mmol) was treated with $LiAlH_4$ (0.5 equiv.). The crude product was purified by distillation to furnish 2.00 g (80%) of alcohol **14** as a colorless liquid; b.p. 140 °C/10^{-2} mbar. ^1H NMR (250 MHz): = 1.69 (d, J_d = 1.4 Hz, 3 H, CH_3), 1.71 (d, J_d = 1.4 Hz, 3 H, CH_3), 1.81−2.03 (m, 2 H, CH_2), 3.62 (t, J_t = 6.4 Hz, 2 H, CH_2), 3.67 (dt, J_d = 6.4, J_t = 9.3 Hz, 1 H, CH), 5.30 (dquint, J_d = 9.3, J_{quint} = 1.4 Hz, 1 H, CH), 7.16−7.33 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 18.6, 26.4, 35.8, 43.6, 65.8, 126.4, 127.8, 128.6, 134.1, 143.5 ppm. MS (70 eV, EI): *m/z* (%) = 190 (10) [M^+], 145 (100) [$C_{11}H_{13}^+$], 117 (32) [$C_9H_9^+$]. $C_{13}H_{18}O$ (190.3): calcd. C 82.06, H 9.53; found C 81.73, H 9.21.

5-Methyl-3-(1-methylethyl)-4-hexen-1-ol (15): Ethyl 5-methyl-3-(1-methylethyl)-4-hexenoate[73b] (1.73 g, 8.70 mmol) was treated with $LiAlH_4$ (1.0 equiv.) as outlined above. The crude product was purified by column chromatography [SiO_2; petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)] to furnish 1.17 g (86%) of alkenol **15** as colorless liquid: R_f = 0.60 [petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)]. ^1H NMR (250 MHz): δ = 0.82 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.87 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.34−1.46 (m, 1 H, CH_2), 1.53 (m_c, 1 H, CH), 1.62 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.66−1.78 (m, 1 H, CH_2), 2.17 (m_c, 1 H, CH), 3.56 (m_c, 2 H, CH_2), 4.93 (dquint, J_d = 10.2, J_{quint} = 1.4 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 19.3, 19.8, 20.5, 26.2, 33.3, 36.4, 42.0, 62.7, 114.4, 127.7 ppm. MS (70 eV, EI): *m/z* (%) = 156 (16) [M^+], 113 (42) [$C_7H_{13}O^+$], 95 (83) [$C_7H_{12}^+$], 69 (100) [$C_5H_8^+$], 55 (53) [$C_4H_7^+$]. $C_{10}H_{20}O$ (156.3): calcd. C 76.86, H 12.90; found C 76.94, H 12.63.

4-Methyl-1-phenyl-3-penten-1-ol (26): 4-Methyl-1-phenyl-3-penten-1-one[73d] (2.0 g, 11.5 mmol) was treated with $LiAlH_4$ (0.5 equiv.) as outlined above. The crude product was purified by column chromatography [SiO_2; petroleum ether/Et_2O/CH_2Cl_2, 1:1:1 (v/v/v)] to furnish compound **26** (1.6 g, 78%) as a colorless liquid: R_f = 0.68 [petroleum ether/acetone, 3:1 (v/v)]. ^1H NMR (250 MHz): δ = 1.61 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.78 (br. s, 1 H, OH), 2.32−2.58 (m, 2 H, CH_2), 4.69 (dd, *J* = 7.7, 5.5 Hz, 1 H, CH), 5.18 (t, *J* = 8.1 Hz, 1 H, CH), 7.25−7.43 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 18.0, 25.9, 38.3, 74.0, 119.7, 125.8, 127.4, 128.3, 135.2, 144.2 ppm. MS (70 eV, EI): *m/z* (%) = 176 (3) [M^+], 158 (10) [$C_{12}H_{15}^+$], 143 (26) [$C_{11}H_{13}^+$], 107 (78) [$C_7H_7O^+$], 77 (48) [$C_6H_5^+$], 70 (100) [$C_5H_9^+$]. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.56, H 9.04.

6-Methyl-1-phenyl-5-hepten-1-ol (27): 6-Methyl-1-phenyl-5-hepten-1-one,[37] (3.2 g, 16.0 mmol) was treated with $LiAlH_4$ (0.5 equiv.) as described above. The crude product was purified by column chromatography [SiO_2; petroleum ether/acetone, 3:1 (v/v)] to provide alkenol **27** (2.9 g, 89%) as a colorless liquid: R_f = 0.79 [petroleum ether/acetone, 3:1 (v/v)]. ^1H NMR (250 MHz): δ = 1.42 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 1.67−2.00 (m, 6 H, CH_2), 2.20 (br. s, 1 H, OH), 4.48 (dd, *J* = 6.1, 5.2 Hz, 1 H, CH), 4.92 (t, *J* = 7.0 Hz, 1 H, CH), 7.17−7.20 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 16.9, 26.8, 27.3, 29.4, 40.3, 72.0, 125.9, 127.5, 129.0, 135.2, 130.4, 133.3, 146.5. MS (70 eV, EI): *m/z* (%) = 204 (1) [M^+], 171 (14) [$C_{13}H_{16}^+$], 133 (19) [$C_{10}H_{12}^+$], 120 (100) [$C_8H_9O^+$], 107 (39) [$C_7H_7O^+$], 82 (100) [$C_6H_{11}^+$], 41 (40) [$C_3H_6^+$]. $C_{14}H_{20}O$ (204.3): calcd. C 82.30, H 9.87; found C 82.23, H 9.81.

2,2-Dimethyl-6-hepten-3-ol (44): 2,2-Dimethyl-6-hepten-3-one[43] (4.0 g, 27.7 mmol) was treated with $LiAlH_4$ (0.5 equiv.) as outlined in the General Procedure. The crude material was purified by column chromatography [SiO_2; petroleum ether/Et_2O/CH_2Cl_2, 1:1:1 (v/v/v)] to afford product **44** (2.9 g, 74%) as a colorless liquid: R_f = 0.65 [petroleum ether/acetone, 3:1 (v/v)]. ^1H NMR (250 MHz): δ = 0.88 [s, 9 H, $C(CH_3)_3$], 1.37 (m_c, 1 H, CH_2), 1.62 (m_c, 1 H, CH_2), 2.10 (m_c, 2 H, CH_2), 2.30 (m_c, 2 H, CH_2), 2.39−2.52 (m, 1 H, CH), 3.21 (dd, *J* = 8.5, 1.8 Hz, 1 H, CH), 5.00 (m_c, 2 H, CH_2), 5.84 (ddt, J_d = 17.4, 10.4, J_t = 7.0 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 11.0, 25.6, 31.2, 34.9, 79.4, 114.7, 138.8 ppm. MS (70 eV, EI): *m/z* (%) = 142.2 (0.3) [M^+], 85 (38) [$C_5H_9O^+$], 71 (13) [$C_4H_7O^+$], 67 (62) [$C_5H_8^+$], 57 (100) [$C_4H_9^+$], 41 (88) [$C_3H_5^+$]. $C_9H_{18}O$ (142.2): calcd. C 76.00, H 12.76; found C 76.10, H 12.77.

4-Methyl-1-phenyl-4-penten-1-ol (54): 4-Methyl-1-phenyl-4-penten-1-one (4.0 g, 23.0 mmol) was obtained from ethyl benzoylacetate and 3-chloro-2-methyl-1-propene in extension to a published procedure[33] to afford 4-methyl-1-phenylpent-4-en-1-one. This ketone was reduced with $LiAlH_4$ (0.5 equiv.) to provide a crude product. This material was purified by column chromatography [SiO_2; petroleum ether/Et_2O/CH_2Cl_2, 1:1:1 (v/v/v)] to afford alkenol **54** (3.3 g, 81%) as a colorless liquid: R_f = 0.45 [petroleum ether/Et_2O/CH_2Cl_2, 1:1:1 (v/v/v)]. ^1H NMR (250 MHz): δ = 1.66 (s, 3 H, CH_3), 1.71−1.89 (m, 2 H, CH_2), 1.90−2.08 (m, 2 H, CH_2), 2.05 (br. s, 1 H, OH), 4.57 (dd, *J* = 5.7, 7.3 Hz, 1 H, CH), 4.64 (m_c, 1 H, CH_2), 4.67 (m_c, 1 H, CH_2), 7.18−7.32 (5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 22.5, 33.9, 36.8, 74.2, 110.1, 125.9, 127.5, 128.4, 144.6, 145.4 ppm. MS (70 eV, EI): *m/z* (%) = 176 (5) [M^+], 161 (21) [$C_{11}H_{13}O^+$], 145 (26) [$C_{11}H_{13}^+$], 104 (100) [$C_8H_8^+$], 77 (95) [$C_6H_5^+$]. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.56, H 9.04.

4. Vanadium(v)-Catalyzed Oxidations of Bis(homoallylic) Alcohols. General Procedure: Vanadium(v) complex **4** (0.1 equiv.) was added at 25 °C to a solution of alkenol (1.00 mmol) in $CHCl_3$ (5 mL/mmol). Addition of *tert*-butyl hydroperoxide (5.5 M in nonane, 1.5 equiv.) led to a change in color of the reaction mixture from brown to dark red. The solution was stirred for an additional 48 h at 25 °C. After removal of the solvent under reduced pressure (250 mbar/40 °C), the crude product was filtered through a short pad of Al_2O_3. The product was washed from the column with Et_2O. The combined organic phases were concentrated under reduced pressure to provide an oil which was purified by kugelrohr distillation and subsequent column chromatography (SiO_2). For product analysis by GC on an analytical level (≤ 0.1 mmol of alkenol), *n*-$C_{14}H_{30}$ (0.01 mmol) was added as an internal standard after separating the oxidation products from vanadium compounds by extraction [$CHCl_3$/satd. aqueous $Na_2S_2O_3$ solution (2 mL/2 mL)].

Oxidation of 5-Methyl-1-phenyl-4-hexen-1-ol (5)

2-(1-Hydroxy-1-methylethyl)-5-phenyltetrahydrofuran (6):[33] Yield: 140 mg (74%), colorless liquid, b.p. 140 °C/10^{-2} mbar (ref.[33] no data given), *cis*/*trans* = 98:2. ***cis*-6:** R_f = 0.40 [petroleum ether/acetone, 4:1 (v/v)]. ^1H NMR (250 MHz): δ = 1.15 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.66−1.80 (m, 1 H, CH_2), 1.85−1.95 (m, 2 H, CH_2), 2.05 (br. s, 1 H, OH), 2.17−2.29 (m, 1 H, CH_2), 3.80 (t, *J* = 7.3 Hz, 1 H, CH), 4.80 (dd, *J* = 8.2, 6.7 Hz,, 1 H, CH), 7.19−7.35 (m, 5 H, Ar H) ppm. ***trans*-6:** R_f = 0.42 [petroleum ether/acetone, 4:1 (v/v)]. ^1H NMR (250 MHz): δ = 1.23 (s, 3 H, CH_3), 1.74−1.96

(m, 3 H, CH_2), 2.05 (br. s, 1 H, OH), 2.24−2.36 (m, 1 H, CH_2), 3.97 (dd, J = 7.5, 6.7 Hz, 1 H, CH), 4.92 (dd, J = 8.2, 5.9 Hz, 1 H, CH), 7.19−7.35 (m, 5 H, Ar H) ppm.

2,2-Dimethyl-6-phenyltetrahydropyran-3-ol (7):[33] Yield: 24 mg (12%), colorless crystals, m.p. 141 °C (subl.), ref.[33] 142−143 °C, *cis*/*trans* = 46:54. ***cis*-7:** R_f = 0.17 [petroleum ether/acetone, 4:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.33 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.58 (br. s, 1 H, OH), 1.60−1.97 (m, 4 H, CH_2), 3.48 (t, J = 2.9 Hz, 1 H, CH), 4.70 (dd, J = 11.7, 2.9 Hz, 1 CH), 7.16−7.28 (m, 5 H, Ar H) ppm. ***trans*-7:** R_f = 0.15 [petroleum ether/acetone, 4:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.30 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.56 (br. s, 1 H, OH), 1.61−1.78 (m, 2 H, CH_2), 1.90−1.97 (m, 2 H, CH_2), 3.56 (dd, J = 11.4, 4.4 Hz, 1 H, CH), 4.57 (dd, J = 11.4, 2.0 Hz, 1 H, CH), 7.19−7.32 (m, 5 H, Ar H) ppm.

3-Benzoyloxy-2,2-dimethyl-5-γ-butyrolactone (8): A solution of 2-(1-hydroxy-1-methylethyl)-5-phenyltetrahydrofuran (**6**, 84 mg, 0.40 mmol) in $CHCl_3$ (2 mL) was treated with TBHP (110 μL, 5.5 M in nonane, 0.60 mmol) and VOL^1(OEt)(EtOH) (**4a**) (14.8 mg, 0.04 mmol). The reaction mixture was stirred at 25 °C for 7 d and subsequently filtered through a short column of aluminum oxide. The product was eluted (Et_2O). The combined organic phases were concentrated under reduced pressure and the remaining residue purified by column chromatography [SiO_2; petroleum ether/acetone, 4:1 (v/v)]. Yield: 17.2 mg (18%), colorless crystals, m.p. 89 °C, b.p. 140 °C/10^{-2} mbar (kugelrohr). R_f = 0.35 [petroleum ether/acetone, 4:1 (v/v)]. ^{1}H NMR (400 MHz): δ = 1.51 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 2.71 (dd, J = 18.4, 2.2 Hz, 1 H, CH_2), 3.18 (dd, J = 18.4, 6.8 Hz,, 1 H, CH_2), 5.46 (dd, J = 6.8, 2.2 Hz,, 1 H, CH), 7.46−7.64 (m, 3 H, Ar H), 8.03−8.05 (m, 2 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 21.8, 26.4, 36.1, 75.1, 86.5, 128.6, 128.8, 129.7, 133.7, 165.6, 173.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 161 (30) [$C_{10}H_9O_2^+$], 147 (40) [$C_9H_7O_2^+$], 129 (30) [$C_6H_9O_3^+$], 91 (97) [$C_7H_7^+$], 43 (100) [$C_2H_3O^+$]. $C_{13}H_{14}O_4$ (234.3): calcd. C 66.66, H 6.02; found C 67.13, H 5.88.

Oxidation of 2,2,7-Trimethyl-6-octen-3-ol (11)

5-*tert*-Butyl-2-(1-hydroxy-1-methylethyl)tetrahydrofuran (16): Yield: 133 mg (71%), colorless liquid, b.p. 140 °C/10 mbar (kugelrohr), *cis*/*trans* = 91:9. MS (70 eV, EI): *m*/*z* (%) = 186 (1) [M^+], 129 (5) [$M^+ - C_4H_9$], 85 (32) [$C_5H_9O^+$] 59 (100) [$C_3H_7O^+$], 57 (62) [$C_4H_9^+$], 39 (31) [$C_3H_3^+$]. $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.37, H 11.89. ***cis*-16:** R_f = 0.78 [petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.90 [s, 9 H, $C(CH_3)_3$], 1.13 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.52−1.83 (m, 4 H, CH_2), 3.54 (dd, J = 8.2, 6.4 Hz, 1 H, CH), 3.65 (dd, J = 7.5, 6.9 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 24.6, 26.3, 26.4, 27.7, 29.2, 34.6, 71.9, 85.5, 87.6 ppm. ***trans*-16:** R_f = 0.75 [petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.87 [s, 9 H, $C(CH_3)_3$], 1.10 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.60−1.90 (m, 4 H, CH_2), 3.63 (dd, J = 10.7, 6.0 Hz, 1 H, CH), 3.67 (dd, J = 9.1, 5.6 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 24.3, 26.1, 26.4, 27.6, 28.8, 33.9, 72.0, 86.4, 88.5 ppm.

***trans*-6-*tert*-Butyl-2,2-dimethyltetrahydropyran-3-ol (*trans*-21):** Yield: 7 mg (4%), colorless crystals, m.p. 43 °C, b.p. 140 °C/10 mbar (kugelrohr). R_f = 0.65 [petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.77 [s, 9 H, $C(CH_3)_3$], 1.05 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.45−1.92 (m, 4 H, CH_2), 3.04 (dd, J = 11.2, 2.4 Hz, 1 H, CH), 3.35 (dd, J = 11.0, 4.8 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 24.1, 25.6, 25.9, 27.3, 28.4, 33.5, 74.3, 74.6, 76.6 ppm. MS (70 eV, EI): *m*/*z* (%) = 186 (1) [M^+], 169 (16) [$M^+ - OH$], 129 (30) [$M^+ - C_4H_9$], 111 (27) [$M^+ - C_4H_9 - H_2O$], 85 (38) [C_5H_9O], 59 (100) [$C_3H_7O^+$], 57 (89) [$C_4H_9^+$]. $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.80, H 11.82.

Oxidation of 5-Methyl-2-phenyl-4-hexen-1-ol (12)

2-(1-Hydroxy-1-methylethyl)-4-phenyltetrahydrofuran (17): Yield: 114 mg (55%), colorless liquid, b.p. 130 °C/10^{-2} mbar (kugelrohr), *cis*/*trans* = 9:91. MS (70 eV, EI): *m*/*z* (%) = 206 (2) [M^+], 148 (100) [$M^+ - C_3H_6O$], 147 (37) [$C_{10}H_{11}O^+$], 129 (32) [$C_{10}H_9^+$], 118 (70) [$C_9H_{10}^+$], 117 (40) [$C_9H_9^+$], 104 (60) [$C_8H_8^+$], 91 (76) [$C_7H_7^+$], 59 (89) [$C_3H_7O^+$], 41 (12) [$C_3H_5^+$]. $C_{13}H_{18}O_2$ (206.3) calcd. C 75.69 H 8.80; found C 75.29 H 8.62. ***cis*-17:** R_f = 0.29 [petroleum ether/acetone, 3:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.20 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.80−2.00 (m, 1 H, CH_2), 2.27−2.39 (m, 1 H, CH_2), 3.48−3.66 (m, 1 H, CH), 3.77 (dd, J = 9.6, 7.8 Hz, 1 H, CH_2), 3.93 (dd, J = 9.5, 5.5 Hz, 1 H, CH), 4.26 (dd, J = 8.9, 7.9 Hz, 1 H, CH_2), 7.23−7.36 (m, 5 H, Ar H) ppm. ***trans*-17:** R_f = 0.31 [petroleum ether/acetone, 3:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.17 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.91−2.02 (m, 1 H, CH_2), 1.97 (br. s, 1 H, OH), 2.27−2.39 (m, 1 H, CH_2), 3.37−3.49 (ddd, J = 13.7, 9.0, 6.9 Hz, 1 H, CH), 3.84 (dd, J = 8.5, 7.0 Hz, 1 H, CH), 3.97 (t, J = 7.5 Hz, 1 H, CH), 4.25 (dd, J = 8.6, 7.0 Hz, 1 H, CH_2), 7.23−7.36 (m, 5 H, Ar H) ppm.

***trans*-2,2-Dimethyl-5-phenyltetrahydropyran-3-ol (*trans*-22):** Yield: 8.0 mg (4%), colorless liquid, b.p. 130 °C/10^{-2} mbar (kugelrohr). R_f = 0.25 [petroleum ether/acetone, 3:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.31 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.84 (s, 1 H, OH), 1.98−2.08 (m, 1 H, CH_2), 2.16−2.27 (m, 1 H, CH_2), 3.20 (m_c, 1 H, CH), 3.61 (dd, J = 3.7, 3.4 Hz, 1 H, CH_2), 3.73 (dd, J = 11.9, 10.4 Hz, 1 H, CH), 3.81 (ddd, J = 11.6, 5.5, 1.5 Hz, 1 H, CH_2), 7.20−7.36 (m, 5 H, Ar H) ppm. MS (70 eV, EI): *m*/*z* (%) = 206 (2) [M^+], 188 (6) [$C_{13}H_{16}O^+$], 148 (14) [$C_{10}H_{12}O^+$], 104 (100) [$C_8H_8^+$], 91 (19) [$C_7H_7^+$], 77 (11) [$C_6H_5^+$], 59 (34) [$C_3H_7O^+$], 41 (10) [$C_3H_5^+$]. $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.80; found C 75.33, H 8.99.

Oxidation of 2-Isopropyl-5-methylhex-4-en-1-ol (13)

2-(1-Hydroxy-1-methylethyl)-4-isopropyltetrahydrofuran (18): Yield: 149 mg (90%), colorless liquid, b.p. 120 °C/10 mbar (kugelrohr), *cis*/*trans* = 19:81. MS (70 eV, EI): *m*/*z* (%) = 172 (1) [M^+], 113 (54) [$C_7H_{13}O^+$], 95 (50) [$C_7H_{11}^+$] 59 (100) [$C_3H_7O^+$]. $C_{10}H_{20}O_2$ (172.3): calcd. C 69.72, H 11.70; found C 69.62, H 11.58. ***cis*-18:** R_f = 0.75 [petroleum ether/Et_2O/CH_2Cl_2, 2:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.87 (d, J = 6.7 Hz, 3 H, CH_3), 0.92 (d, J = 6.7 Hz, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.44 (sept, J = 6.7 Hz, 1 H, CH), 1.36−1.60 (m, 1 H, CH_2), 1.76−2.05 (m, 1 CH_2), 3.45 (dd, J = 9.1, 8.1 Hz, 1 H, CH), 3.75 (dd, J = 8.0, 5.3 Hz, 1 H, CH), 3.99 (t, J = 8.1 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 21.3, 21.6, 24.1, 27.3, 29.7, 31.8, 47.9, 71.3, 73.0, 86.6 ppm. ***trans*-18:** R_f = 0.75 [petroleum ether/Et_2O/CH_2Cl_2, 2:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.87 (d, J = 6.6 Hz, 3 H, CH_3), 0.91 (d, J = 6.6 Hz, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.48 (sept, J = 6.6 Hz, 1 H, CH), 1.37−1.59 (m, 1 H, CH_2), 1.78−1.98 (m, 1 H, CH_2), 3.38 (t, J = 8.6 Hz, 1 H, CH_2), 3.73 (dd, J = 8.6, 5.8 Hz, 1 H, CH), 4.04 (dd, J = 8.6, 5.9 Hz, 1 H, CH_2) ppm. ^{13}C NMR (63 MHz): δ = 21.3, 21.5, 24.4, 26.8, 31.2, 31.7, 47.2, 71.7, 73.0, 85.7 ppm.

Oxidation of 5-Methyl-3-phenyl-4-hexen-1-ol (14)

***trans*-2-(1-Hydroxy-1-methylethyl)-3-phenyltetrahydrofuran (*trans*-19):** Yield: 156 mg (76%), colorless liquid, b.p. 140 °C/10 mbar (kugelrohr). R_f = 0.45 [petroleum ether/CH_2Cl_2/acetone, 2:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.26 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3),

2.18 (br. s, 1 H, OH), 1.96−2.20 (m, 2 H, CH_2), 2.69 (dt, J_d = 9.5, J_t = 7.5 Hz, 1 H, CH), 2.97 (d, J = 9.5 Hz, 1 H, CH), 3.62 (dt, J_d = 11.3, J_t = 6.4 Hz, 1 H, CH_2), 3.76 (ddd, J = 11.1, 6.4, 5.8 Hz, 1 H, 5 CH_2), 7.18−7.36 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 19.0, 24.8, 38.1, 42.4, 59.7, 60.8, 68.0, 126.8, 127.4, 128.8, 141.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 206 (1) [M^+], 148 (25) [$M^+ - C_3H_8O$], 119 (40) [$C_9H_{11}^+$], 117 (100) [$M^+ - C_7H_5$], 103 (44) [$C_8H_7^+$], 91 (73) [$C_7H_7^+$], 77 (39) [$C_6H_5^+$], 59 (20) [$C_3H_7O^+$], 51 (29) [$C_4H_3^+$], 39 (31) [$C_3H_3^+$]. $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.80; found C 75.32, H 8.68.

Oxidation of 3-Isopropyl-5-methyl-4-hexen-1-ol (15)

***trans*-2-(1-Hydroxy-1-methylethyl)-3-isopropyltetrahydrofuran *trans*-(20):** Yield: 93.6 mg (54%), colorless liquid, b.p. 120 °C/10 mbar (kugelrohr). R_f = 0.70 [petroleum ether/Et_2O/CH_2Cl_2, 2:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.90 (d, J = 6.7 Hz, 3 H, CH_3), 0.93 (d, J = 6.7 Hz, 3 H, CH_3), 1.20−1.32 (m, 1 H, CH), 1.30 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.55−1.69 (m, 1 H, CH_2), 1.67 (dq, J_d = 7.3, J_q = 6.7 Hz, 1 H, CH), 1.78−1.92 (m, 1 H, CH_2), 2.62 (d, J = 9.9 Hz, 1 H, CH_2), 3.67 (dt, J_d = 11.0, J_t = 6.1 Hz, 1 H, CH_2), 3.75−3.82 (m, 1 H, CH_2) ppm. ^{13}C NMR (63 MHz): δ = 20.0, 20.4, 20.5, 25.2, 30.9, 33.9, 41.8, 60.0, 61.9, 68.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 172 (2) [M^+], 129 (18) [$M^+ - C_3H_7$], 113 (24) [$C_7H_{13}O^+$], 83 (42) [$C_5H_7O^+$], 71 (97) [$C_4H_7O^+$], 59 (100) [$C_3H_7O^+$]. $C_{10}H_{20}O_2$ (172.3): calcd. C 69.72, H 11.70; found C 69.33, H 11.45.

***trans*-4-Isopropyl-2,2-dimethyltetrahydropyran-3-ol (*trans*-25):** Yield: 27.3 mg (16%), colorless liquid, b.p. 120 °C/10 mbar (kugelrohr). R_f = 0.65 [petroleum ether/Et_2O/CH_2Cl_2, 2:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.20 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.67−1.74 (m, 1 H, CH_2), 1.82−1.95 (m, 1 H, CH), 1.97−2.06 (m, 1 H, CH), 2.07−2.15 (m, 1 H, CH_2), 3.65 (d, J = 11.2 Hz, 1 H, CH), 3.76−3.84 (m, 1 H, CH_2), 3.88−3.96 (m, 1 H, CH_2) ppm.

Oxidation of 4-Methyl-1-phenyl-3-penten-1-ol (26)

***cis*- and *trans*-3-Hydroxy-2,2-dimethyl-5-phenyltetrahydrofuran (28):** Yield: 120 mg (62%), colorless liquid, b.p. 137 °C/10 mbar (kugelrohr), *cis*/*trans* = 2:98. MS (70 eV, EI): *m*/*z* (%) = 192 (1) [M^+], 134 (73) [$C_9H_{10}O^+$], 116 (14) [$C_6H_{11}O_2^+$], 105 (27) [$C_8H_8^+$], 91 (30) [$C_7H_6^+$], 77 (22) [$C_6H_5^+$], 59 (100) [$C_3H_6O^+$]. $C_{12}H_{16}O_2$ (192.3): calcd. C 74.97, H 8.39; found C 75.03, H 8.44. ***cis*-28:** R_f = 0.57 [petroleum ether/acetone, 2:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.25 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.94 (m_c, 1 H, CH_2), 2.17 (br. s, 1 H, OH), 2.77 (m_c, 1 H, CH_2), 4.10 (dd, J = 7.1, 2.6 Hz, 1 H, CH), 5.00 (t, J = 7.4 Hz, 1 H, CH), 7.26−7.38 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 22.51, 25.8, 41.5, 76.5, 78.5, 83.5, 125.8, 127.5, 128.7, 143.1 ppm. ***trans*-28:** R_f = 0.57 [petroleum ether/acetone, 2:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.35 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 2.18 (br. s, 1 H, OH), 2.21 (dd, J = 5.2, 1.8 Hz, 1 H, CH_2), 2.27 (dd, J = 3.0, 3.7 Hz, 1 H, CH_2), 4.13 (dd, J = 2.7, 2.8 Hz, 1 H, CH), 5.20 (dd, J = 6.4, 2.8 Hz, 1 H, CH), 7.27−7.36 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 25.9, 28.5, 43.4, 76.6, 78.6, 84.0, 125.7, 127.5, 128.7, 143.4 ppm.

Oxidation of 6-Methyl-1-phenyl-5-hepten-1-ol (27)

***cis*-2-(1-Hydroxy-1-methylethyl)-6-phenyltetrahydropyran (*cis*-29):** Yield: 105 mg (52%), colorless liquid, b.p. 149 °C/10^{-2} mbar (kugelrohr). R_f = 0.66 [petroleum ether/acetone, 3:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.21 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.44−1.54 (m, 1 H, CH_2), 1.765−1.72 (m, 2 H, CH_2), 1.81−1.83 (m, 1 H, CH_2), 1.98 (m_c, 2 H, CH_2), 2.32 (br. s, 1 H, OH), 3.35 (dd, J = 9.5, 1.8 Hz, 1 H, CH), 4.42 (dd, J = 8.9, 2.1 Hz, 1 H, CH), 7.25−7.30 (m, 1 H, Ar H), 7.33−36 (m, 4 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 23.9, 24.0, 25.4, 25.9, 33.9, 72.1, 79.9, 84.7, 125.7, 127.2, 128.2, 143.43 ppm. MS (70 eV, EI): *m*/*z* (%) = 220 (1) [M^+], 162 (100) [$C_{11}H_{13}O^+$], 156 (43) [$C_9H_{15}O_2^+$], 129 (100) [$C_7H_{12}O_2^+$], 105 (66) [$C_8H_8^+$], 91 (84) [$C_7H_6^+$], 77 (41) [$C_6H_5^+$]. $C_{14}H_{20}O_2$ (220.3): calcd. C 76.33, H 9.15; found C 76.27, H 9.18.

Oxidation of *trans*-2-(3-Methyl-2-butenyl)cyclohexanol (*trans*-30)

1,6-*trans*-6,8-*cis*-8-(1-Hydroxy-1-methylethyl)-7-oxabicyclo-[4.3.0]nonane (31): Yield: 154 mg (92%), colorless liquid, b.p. 145 °C/10 mbar (kugelrohr). R_f = 0.37 [petroleum ether/Et_2O, 1:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.13 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.18−1.28 (m, 1 H, CH), 1.01−1.36 (m, 4 H, CH_2), 1.49 (dt, J_d = 9.6, J_t = 11.3 Hz, 1 H, CH_2), 1.65−1.72 (m, 1 H, CH_2), 1.77−1.82 (m, 1 H, CH_2), 1.89 (ddd, J = 11.3, 8.2, 3.6 Hz, 1 H, CH), 1.87−1.93 (m, 1 H, CH_2), 2.02 (br. s, 1 H, OH), 2.07−2.14 (m, 1 H, CH_2), 3.05 (dt, J_d = 3.4, J_t = 10.2 Hz, 1 H, CH), 3.77 (dd, J = 9.6, 3.6 Hz, 1 H, CH) ppm. ^{13}C NMR (63 MHz): δ = 24.3, 24.5, 25.8, 26.7, 29.3, 31.2, 32.0, 45.3, 71.9, 83.7, 84.3 ppm. MS (70 eV, EI): *m*/*z* (%) = 184 (3) [M^+], 102 (23) [$C_{10}H_5O_2^+$], 82 (22) [$C_6H_{10}^+$], 67 (58) [$C_5H_7^+$], 59 (100) [$C_3H_7O^+$], 41 (30) [$C_3H_6^+$]. $C_{11}H_{20}O_2$ (184.3): calcd. C 71.70, H 10.80; found C 75.32, H 8.68 (Supporting Information).

Oxidation of *cis*-2-(3-Methyl-2-butenyl)cyclohexanol (*cis*-30)

1,6-*cis*-8-(1-Hydroxy-1-methylethyl)-7-oxabicyclo[4.3.0]nonane (32): Yield: 143 mg (78%), colorless liquid, b.p. 145 °C/10 mbar (kugelrohr), *cis*/*trans* = 77:23. MS (70 eV, EI): *m*/*z* (%) = 184 (1) [M^+], 125 (44) [$C_8H_{13}O^+$], 102 (39) [$C_{10}H_5O_2^+$], 81 (93) [$C_6H_9^+$], 59 (100) [$C_3H_7O^+$]. $C_{11}H_{20}O_2$ (184.3): calcd. C 71.70, H 10.80; found C 75.32, H 8.68 (Supporting Information). **1,6-*cis*-6,8-*cis*-32:** R_f = 0.38 [petroleum ether/Et_2O, 1:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.14 (s, 3 H, CH_3), 1.24 (s, 3 H CH_3), 1.21−1.92 (m, 8 H, CH, CH_2), 1.56−1.84 (m, 2 H, CH_2), 2.12−2.23 (m, 1 H, CH_2), 3.69 (dd, J = 9.0, 7.3 Hz, 1 H, CH_2), 3.85 (dt, J_d = 5.8, J_t = 5.6 Hz, 1 H, CH_2) ppm. ^{13}C NMR (63 MHz): δ = 21.9, 23.0, 24.4, 27.8, 27.9, 29.3, 31.7, 37.4, 70.5, 77.4, 85.6 ppm. **1,6-*cis*-6,8-*trans*-32:** R_f = 0.38 [petroleum ether/Et_2O, 1:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.10 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.12−1.64 (m, CH, CH_2), 1.81−1.94 (m, 2 H, CH_2), 1.98−2.11 (m, 1 H, CH), 3.93 (dd, J = 9.1, 7.0 Hz, 1 H, CH_2), 3.95 (dd, J = 6.9, 4.3 Hz, 1 H, CH_2) ppm. ^{13}C NMR (63 MHz): δ = 20.5, 23.7, 24.0, 27.0, 27.5, 28.3, 33.5, 38.5, 72.5, 78.0, 84.0 ppm.

1,6-*cis*-1,4-*trans*-3,3-Dimethyl-2-oxabicyclo[4.4.0]decan-4-ol (33): Yield: 8.9 mg (5%), colorless liquid, b.p. 145 °C/10 mbar (kugelrohr). R_f = 0.38 [petroleum ether/Et_2O, 1:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.16 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.16−1.95 (m, 11 H, CH, CH_2), 3.40 (dd, J = 3.1, 2.9 Hz, 1 H, CH), 3.75−3.78 (m, 1 H, CH) ppm (Supporting Information).

Oxidation of (*R*)-Linalool [(*R*)-34]

2-(1-Hydroxy-1-methylethyl)-5-methyl-5-vinyltetrahydrofuran (35):[39] Yield: 111 mg (65%), colorless liquid, b.p. 80 °C/10 mbar (kugelrohr). ***cis*-35:** $[\alpha]_D^{25}$ = +29.1 (*c* = 1.1, $CHCl_3$), ref.[39] $[\alpha]_D^{25}$ = +11.7 (*c* = 0.1, MeOH). R_f = 0.48 [petroleum ether/Et_2O/acetone, 5:2:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.11 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.75−1.89 (m, 4 H, CH_2), 2.05 (br. s, 1 H, OH), 3.84 (dd, J = 7.6, 6.6 Hz, 1 H, CH), 4.97 (dd, J = 10.6, 1.8 Hz, 1 H, CH_2), 5.17 (dd, J = 17.4, 1.8 Hz, 1 H, CH_2), 5.96 (dd, J = 17.4, 10.6 Hz, 1 H, CH) ppm. ***trans*-35:** $[\alpha]_D^{25}$ = −13.1 (*c* = 1.0, $CHCl_3$), ref.[39] $[\alpha]_D^{25}$ = −10.1 (*c* = 0.1, MeOH). R_f = 0.45 [petroleum ether/Et_2O/acetone, 5:2:1 (v/v/v)]. ^{1}H NMR

(250 MHz): δ = 1.10 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.29 (s, 3 H CH_3), 1.66−1.74 (m, 1 H, CH_2), 1.75−1.93 (m, 3 H, CH_2), 2.05 (br. s, 1 H, OH), 3.78 (t, *J* = 7.1 Hz, 1 H, CH), 4.98 (dd, *J* = 10.6, 1.8 Hz, 1 H, CH_2), 5.18 (dd, *J* = 17.4, 1.8 Hz, 1 H, CH_2), 5.85 (dd, *J* = 17.4, 10.6 Hz, 1 H, CH) ppm.

2-(1-Hydroxy-1-methylethyl)-5-methyl-5-(oxiran-2-yl)tetrahydrofuran (36):[39] Yield: 13.0 mg (7%), colorless liquid, b.p. 80 °C/10 mbar (kugelrohr, ref.[39] no data available), *cis*/*trans* = 54:46.

2,2,6-Trimethyl-6-vinyltetrahydropyran-3-ol (37):[39] Yield: 7.4 mg (4%), colorless liquid, b.p. 80 °C/10 mbar (kugelrohr, ref.[39] no data given), *cis*/*trans* = 38:62.

Oxidation of (*S*,*S*)-Bisabolol [(*S*,*S*)-38]

2-(1-Hydroxy-1-methylethyl)-5-methyl-5-(1-methylcyclohex-1-en-4-yl)tetrahydrofuran (39):[40] Yield: 155 mg (0.65 mmol, 65%), colorless liquid, b.p. 125 °C/10^{-2} mbar (kugelrohr, ref.[40] no data available), *cis*/*trans* = 82:18. ***cis*-(2*R*,5*S*,1′*S*)-39:** $[\alpha]_D^{25}$ = −32.8 (*c* = 1.0, $CHCl_3$), ref.[40] $[\alpha]_D^{25}$ = −64.1 (*c* = 0.5, MeOH). R_f = 0.65 [petroleum ether/Et_2O/acetone, 5:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.10 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.51−2.01 (m, 11 H, CH, CH_2), 2.05 (br. s, 1 H, OH), 3.76 (dd, *J* = 7.3, 7.0 Hz, 1 H, CH), 5.34−5.37 (m, 1 H, CH) ppm. ***trans*-(2*S*,5*S*,1′*S*)-39:** R_f = 0.62 [petroleum ether/Et_2O/acetone, 5:1/1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.06 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.51−2.01 (m, 11 H, CH, CH_2), 2.05 (br. s, 1 H, OH), 3.75 (dd, *J* = 10.8, 6.6 Hz, 1 H, CH), 5.34−5.37 (m, 1 H, CH) ppm.

2-(1-Hydroxy-1-methylethyl)-5-methyl-5-(6-methyl-7-oxabicyclo-[4.1.0]hept-3-yl)tetrahydrofuran (40):[40] Yield: 37.8 mg (15%), colorless liquid, b.p. 125 °C/10^{-2} mbar (kugelrohr, ref.[40] no data available), *cis*/*trans* = 87:13. ***cis*-40**: R_f = 0.55 [petroleum ether/Et_2O/acetone, 5:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.11 (s, 3 H, CH_3), 1.19 (s, 6 H, CH_3), 1.29 (s, 3 H, CH_3), 1.51−2.01 (m, 11 H, CH, CH_2), 2.05 (br. s, 1 H, OH), 2.97 (dd, *J* = 6.1, 5.4 Hz, 1 H, CH), 3.65 (dd, *J* = 9.0, 6.1 Hz, 1 H, CH) ppm. ***trans*-40:** R_f = 0.55 [petroleum ether/Et_2O/acetone, 5:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 1.05 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.51−2.01 (m, 11 H, CH, CH_2), 2.05 (br. s, 1 H, OH), 2.96−2.99 (m, 1 H, CH), 3.64 (dd, *J* = 11.5, 4.6 Hz, 1 H, CH) ppm.

Oxidation of 3-(Hydroxymethyl)-2-methyl-5-hexene (41)

2-(Hydroxymethyl)-4-isopropyltetrahydrofuran (42):[41] Yield: 77.1 mg (74%), colorless liquid, b.p. 95 °C/10 mbar (kugelrohr), *cis*/*trans* = 29:71. ***cis*-42:** R_f = 0.48 [petroleum ether/acetone, 4:1 (v/v)]. ^{1}H NMR (600 MHz): δ = 0.87 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.93 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.34 (m_c, 1 H, CH_2), 1.47 (sept, *J* = 6.6 Hz, 1 H, CH), 1.98 (m_c, 1 H, CH), 2.00 (m_c, 1 H, CH_2), 3.45 (t, *J* = 7.9 Hz, 1 H, CH_2), 3.51 (dd, *J* = 11.6, 5.9 Hz, 1 H, CH_2), 3.69 (dd, *J* = 11.6, 3.1 Hz, 1 H, CH_2), 3.96 (t, *J* = 7.9 Hz, 1 H, CH_2), 4.05 (m_c, 1 H, CH) ppm. ***trans*-42:** R_f = 0.47 [petroleum ether/acetone, 4:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 0.87 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.93 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.47 (sept, *J* = 6.6 Hz, 1 H, CH), 1.64 (dt, J_d = 12.5, J_t = 8.5 Hz, 1 H, CH_2), 1.82 (ddd, *J* = 12.7, 8.5, 4.8 Hz, 1 H, CH_2), 1.93 (m_c, 1 H, CH), 3.40 (t, *J* = 8.8 Hz, 1 H, CH_2), 3.47 (dd, *J* = 11.5, 6.2 Hz, 1 H, CH_2), 3.62 (dd, *J* = 11.5, 3.5 Hz, 1 H, CH_2), 4.02 (dd, *J* = 8.2, 7.5 Hz, 1 H, CH_2), 4.08 (m_c, 1 H, CH) ppm.

Oxidation of 1-Phenyl-4-penten-1-ol (43)

2-(Hydroxymethyl)-5-phenyltetrahydrofuran (48):[74a] Yield: 84 mg (47%), colorless liquid, b.p. 135 °C/10^{-2} mbar (ref.[74a] no data given), *cis*:*trans* = 39:61. MS (70 eV, EI): *m*/*z* (%) = 178 (10) [M^+], 160 (19) [$C_{11}H_{12}O^+$], 147 (100) [$C_{10}H_{11}O^+$], 129 (49) [$C_{10}H_9^+$], 91 (75) [$C_7H_7^+$], 77 (18) [$C_6H_5^+$], 41 (17) [$C_3H_5^+$]. $C_{11}H_{14}O_2$ (178.2) calcd. C 74.13, H 7.92; found C 73.54, H 7.90. ***cis*-48:** R_f = 0.19 [petroleum ether/acetone, 2:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.74−1.87 (m, 2 H, CH_2), 1.91−2.09 (m, 1 H, CH_2), 2.04 (s, 1 H, OH), 2.20−2.37 (m, 1 H, CH_2), 3.67 (ddd, *J* = 17.1, 11.5, 6.1 Hz, 2 H, CH_2), 4.13 (m, 1 H, CH), 4.84 (dd, *J* = 7.8, 6.6 Hz, 1 H, CH), 7.17−7.29 (m, 5 H, Ar H) ppm. ***trans*-48:** R_f = 0.21 [petroleum ether/acetone, 2:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.74−1.87 (m, 2 H, CH_2), 1.91−2.09 (m, 1 H, CH_2), 2.04 (s, 1 H, OH), 2.20−2.37 (m, 1 H, CH_2), 3.67 (ddd, *J* = 15.0, 11.6, 3.4 Hz, 2 H, CH_2), 4.29 (m_c, 1 H, CH), 4.92 (dd, *J* = 7.8, 6.3 Hz, 1 H, CH), 7.17−7.29 (m, 5 H, Ar H) ppm.

Oxidation of 2,2-Dimethyl-6-hepten-3-ol (44)

5-*tert*-Butyl-2-(hydroxymethyl)tetrahydrofuran (49):[74a,74b] Yield: 94 mg (59%), colorless liquid, b.p. 100 °C/10^{-2} mbar (kugelrohr), *cis*/*trans* = 39:61. ***cis*-49:** R_f = 0.66 [petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.89 [s, 9 H, $C(CH_3)_3$], 1.62−1.89 (m, 4 H, CH_2), 3.46 (dd, *J* = 11.2, 6.1 Hz, 1 H, CH_2), 3.65 (dd, *J* = 11.2, 8.4 Hz, 1 H, CH_2), 3.61 (m_c, 1 H, CH), 4.00 (m_c, 1 H, CH) ppm. ***trans*-49:** R_f = 0.64 [petroleum ether/Et_2O/CH_2Cl_2, 4:1:1 (v/v/v)]. ^{1}H NMR (250 MHz): δ = 0.88 [s, 9 H, $C(CH_3)_3$], 1.55−1.96 (m, 4 H, CH_2), 3.48 (dd, *J* = 11.4, 6.3 Hz, 1 H, CH_2), 3.65 (dd, *J* = 11.4, 9.6 Hz, 1 H, CH_2), 3.66 (m_c, 1 H, CH), 4.01 (m_c, 1 H, CH) ppm.

Oxidation of 2-Phenyl-4-penten-1-ol (45)

2-(Hydroxymethyl)-4-phenyltetrahydrofuran (50): Yield: 77.1 mg (43%), colorless liquid, b.p. 145 °C/10^{-2} mbar (kugelrohr), *cis*/*trans* = 36:64. MS (70 eV, EI): *m*/*z* (%) = 178 (3) [M^+], 147 (82) [$C_{10}H_{11}O^+$], 129 (41) [$C_{10}H_9^+$], 119 (50) [$C_9H_{11}^+$], 91 (100) [$C_7H_7^+$], 77 (14) [$C_6H_5^+$], 41 (34) [$C_3H_5^+$]. $C_{11}H_{14}O_2$ (178.2) calcd. C 74.13, H 7.92; found C 72.61, H 8.00 (Supporting Information). ***cis*-50:** R_f = 0.60 [petroleum ether/acetone, 2:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 1.86 (dt, J_d = 12.3, J_t = 10.5 Hz, 1 H, CH_2), 2.28 (ddd, *J* = 12.3, 7.4, 6.3 Hz, 1 H, CH_2), 2.34 (br. s, 1 H, OH), 3.47 (m_c, 1 H, CH_2), 3.61 (dd, *J* = 11.6, 5.8 Hz, 1 H, CH_2), 3.75 (m_c, 1 H, CH_2), 3.76 (dd, *J* = 11.0, 8.6 Hz, 1 H, CH), 4.22 (dd, *J* = 8.6, 7.0 Hz, 1 H, CH_2), 4.33 (m_c, 1 H, CH), 7.16−7.32 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 35.7, 45.0, 64.7, 74.3, 80.5, 126.6, 127.2, 128.6, 141.2 ppm. ***trans*-50:** R_f = 0.60 [petroleum ether/acetone, 2:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 2.08 (dt, J_d = 12.9, J_t = 7.9 Hz, 1 H, CH_2), 2.18 (ddd, *J* = 12.9, 8.8, 5.8 Hz, 1 H, CH_2), 2.34 (br. s, 1 H, OH), 3.42 (quint, *J* = 7.9 Hz, 1 H, CH), 3.55 (dd, *J* = 11.6, 5.8 Hz, 1 H, CH_2), 3.71 (dd, *J* = 11.6, 8.5 Hz, 1 H, CH_2), 3.73 (t, *J* = 8.6 Hz, 1 H, CH_2), 4.24 (dd, *J* = 8.6, 7.0 Hz, 1 H, CH_2), 4.30 (m_c, 1 H, CH), 7.16−7.32 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 35.6, 45.4, 65.1, 74.8, 79.9, 126.7, 127.2, 128.6, 141.9 ppm.

Oxidation of 3-Phenyl-4-penten-1-ol (46)

2-(Hydroxymethyl)-3-phenyltetrahydrofuran (51): Yield: 77.1 mg (43%), colorless liquid, b.p. 125 °C/10^{-2} mbar (kugelrohr), *cis*/*trans* = 40:60. MS (70 eV, EI): *m*/*z* (%) = 178 (4) [M^+], 160 (13) [$C_{11}H_{12}O^+$], 147 (100) [$C_{10}H_{11}O^+$], 118 (16) [$C_9H_{10}^+$], 117 (56) [$C_9H_9^+$], 91 (81) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$], 41 (10) [$C_3H_5^+$]. $C_{11}H_{14}O_2$ (178.2) calcd. C 74.13, H 7.92; found C 73.12, H 8.28. ***cis*-51:** R_f = 0.39 [petroleum ether/acetone, 3:1 (v/v)]. ^{1}H NMR (250 MHz): δ = 2.17−2.40 (m, 2 H, CH_2), 3.19 (dd, *J* = 6.4, 5.2 Hz, 2 H, CH_2), 3.54 (t, *J* = 7.6 Hz, 1 H, CH), 3.94 (td, J_t = 8.5, J_d = 7.6 Hz, 1 H, CH_2), 4.16 (m_c, 1 H, CH), 4.21 (m_c, 1 H,

CH_2), 7.23−7.36 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 32.1, 46.4, 63.2, 67.6, 82.0, 126.8, 127.6, 128.7, 140.8 ppm. ***trans*-51:** R_f = 0.41 [petroleum ether/acetone, 2:1 (v/v)]. ^1H NMR (250 MHz): δ = 2.12−2.39 (m, 2 H, CH_2), 3.19 (q, J = 8.6 Hz, 1 H, CH), 3.52 (t, J = 7.6 Hz, 1 H, CH_2), 3.75 (dd, J = 11.8, 2.9 Hz, 1 H, CH), 3.93 (m_c, 1 H, CH), 4.00 (td, J_t = 8.2, J_d = 7.0 Hz, 1 H, CH_2), 4.11 (td, J_t = 8.2, J_d = 4.6 Hz, 1 H, CH_2), 7.23−7.36 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 35.3, 46.0, 62.7, 68.2, 86.3, 126.7, 127.5, 128.4, 141.1 ppm.

Oxidation of 3-*tert*-Butyl-4-penten-1-ol (47)

***trans*-3-*tert*-Butyl-2-(hydroxymethyl)tetrahydrofuran (*trans*-52):** Yield: 97.1 mg (61%), colorless liquid, b.p. 110 °C/10^{-2} mbar (kugelrohr). R_f = 0.60 [petroleum ether/acetone, 4:1 (v/v)]. ^1H NMR (250 MHz): δ = 0.96 [s, 9 H, $C(CH_3)_3$], 0.87−0.96 (m, 1 H, CH), 1.56−1.70 (m_c, 1 H, CH_2), 1.85−1.97 (m_c, 1 H, CH_2), 2.62 (dd, J = 4.7, 2.9 Hz, 1 H, CH_2), 2.82 (ddd, J = 9.3, 3.8, 2.9 Hz, 1 H, CH), 2.91 (dd, J = 4.7, 3.8 Hz, 1 H, CH_2), 3.68 (m, 1 H, CH_2), 3.78 (m, 1 H, CH_2) ppm. ^{13}C NMR (63 MHz): δ = 27.9, 32.1, 33.3, 49.3, 54.6, 62.0, 80.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 158 (1) [M^+], 141 (8) [$C_9H_{17}O^+$], 127 (14) [$C_8H_{15}O^+$] 69 (18) [$C_4H_6O^+$], 57 (100) [$C_4H_9^+$], 41 (34) [$C_3H_6^+$]. $C_9H_{18}O_2$ (158.2): calcd. C 68.31, H 11.47; found C 68.77, H 11.18.

Oxidation of 4-Phenyl-4-penten-1-ol (53)

2-(Hydroxymethyl)-2-phenyltetrahydrofuran (55): Yield: 146 mg (82%), colorless liquid, b.p. 155 °C/10^{-2} mbar (kugelrohr), (*S*)/(*R*) = 50:50. R_f = 0.40 [petroleum ether/acetone, 2:1 (v/v)]. ^1H NMR (250 MHz): δ = 1.78−1.91 (m_c, 1 H, CH_2), 1.92−2.04 (m_c, 1 H, CH_2), 2.12 (ddd, J = 15.7, 12.1, 7.1 Hz, 1 H, CH_2), 2.37 (dt, J_d = 12.1, J_t = 8.2 Hz, 1 H, CH_2), 2.75 (br. s, 1 H, OH), 3.66 (dd, J = 12.8, 11.8 Hz, 2 H, CH_2), 3.99 (ddt, J_d = 15.7, 8.2, J_t = 7.1 Hz, 2 H, CH_2), 7.22−7.41 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 26.1, 33.9, 68.4, 68.9, 87.4, 125.3, 127.0, 128.2, 144.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 178 (0.1) [M^+], 147 (100) [$C_{10}H_{11}O^+$], 105 (95) [$C_7H_5O^+$], 77 (36) [$C_6H_5^+$] 51 (10) [$C_4H_3^+$]. $C_{11}H_{14}O_2$ (178.2): calcd. C 74.13, H 7.92; found C 74.46, H 8.74 (Supporting Information).

Oxidation of 1-Phenyl-4-methyl-4-penten-1-ol (54)

2-(Hydroxymethyl)-2-methyl-5-phenyltetrahydrofuran (56): Yield: 114 mg (0.82 mmol, 82%), colorless liquid, b.p. 145 °C/10^{-2} mbar (kugelrohr), *cis*/*trans* = 25:75. MS (70 eV, EI): *m*/*z* (%) = 161 (32) [$C_{11}H_{13}O^+$], 117 (5) [$C_9H_{10}^+$], 77 (7) [$C_6H_5^+$] 43 (100) [$C_2H_3O^+$]. $C_{12}H_{16}O_2$ (192.3): calcd. C 74.97, H 8.39; found C 74.68, H 8.49. *cis*-**56**: R_f = 0.50 [petroleum ether/Et_2O/CH_2Cl_2 = 1:1:1 (v/v/v)]. ^1H NMR (250 MHz): δ = 1.32 (s, 3 H, CH_3), 1.75−2.00 (m, 2 H, CH, CH_2), 2.07−2.16 (m, 1 H, CH_2), 2.18 (br. s, 1 H, OH), 2.27−2.39 (m, 1 H, CH), 3.55 (dd, J = 18.4, 11.2 Hz, 2 H, CH_2), 5.00 (dd, J = 9.0, 6.0 Hz, 1 H, CH), 7.25−7.33 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 24.0, 35.0, 35.7, 69.7, 80.9, 84.1, 126.4, 128.0, 128.9, 142.7 ppm. ***trans*-56:** R_f = 0.45 [petroleum ether/Et_2O/CH_2Cl_2 = 1:1:1 (v/v/v)]. ^1H NMR (250 MHz): δ = 1.34 (s, 3 H, CH_3), 1.74−1.85 (m, 1 H, CH_2), 1.87−2.00 (m, 1 H, CH_2), 2.04−2.17 (m, 1 H, CH_2), 2.25−2.36 (m, 1 H, CH), 2.48 (br. s, 1 H, OH), 3.54 (s, 2 H, CH_2), 4.93 (dd, J = 9.3, 5.5 Hz, 1 H, CH_2), 7.19−7.35 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 24.7, 34.4, 36.0, 69.1, 82.5, 84.3, 126.4, 128.0, 128.9, 142.7 ppm.

5. Epoxidation of 5-Methyl-1-phenyl-4-hexen-1-ol (5)

***rac*-4,5-Epoxy-5-methyl-1-phenyl-1-hexanol (10):** Dimethyldioxirane (11.56 mL of a 0.05 M solution in acetone, 0.578 mmol) was added dropwise at 0 °C over a period of 15 min to a solution of 5-methyl-1-phenyl-4-hexen-1-ol (**5**) (100 mg, 0.526 mmol) in acetone (10 mL). The reaction mixture was allowed to warm to 25 °C within 30 min. After complete consumption of alkenol **5** and dimethyldioxirane (KI/starch test), the solvent was removed under reduced pressure (650 mbar/40 °C) to provide epoxy alcohol **10** (108 mg, 99%) as an analytically pure colorless liquid (50:50 mixture of diastereomers): b.p. 140 °C/10 mbar (kugelrohr). MS (70 eV, EI): *m*/*z* (%) = 206 (1) [M^+], 148 (14) [$C_{10}H_{12}O^+$], 104 (100) [$C_8H_8^+$], 77 (47) [$C_6H_5^+$], 59 (36) [$C_3H_7O^+$]. $C_{13}H_{18}O_2$ (206.3): calcd. C 75.69, H 8.80; found C 75.79, H 8.89. ***like*-10:** R_f = 0.40 [petroleum ether/acetone, 4:1 (v/v)]. ^1H NMR (400 MHz): δ = 1.26 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.51−1.69 (m, 2 H, CH_2), 1.71−1.89 (m, 1 H, CH_2), 1.88−1.96 (m, 1 H, CH_2), 2.70 (dd, J = 7.6, 4.8 Hz, 1 H, CH), 4.80 (dd, J = 7.4, 5.7 Hz,, 1 H, CH), 7.23−7.36 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 18.6, 25.2, 35.9, 58.8, 64.2, 74.1, 125.9, 127.6, 128.6, 144.5 ppm. ***unlike*-10:** R_f = 0.40 [petroleum ether/acetone, 4:1 (v/v)]. ^1H NMR (400 MHz): δ = 1.24 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.58−1.64 (m, 2 H, CH_2), 1.82−1.92 (m, 1 H, CH_2), 1.95−2.04 (m, 1 H, CH_2), 2.75 (t, J = 6.3 Hz, 1 H, CH), 4.73 (dd, J = 5.7, 7.7 Hz, 1 H, CH), 7.19−7.35 (m, 5 H, Ar H) ppm. ^{13}C NMR (63 MHz): δ = 18.7, 24.8, 25.4, 35.9, 58.6, 64.3, 73.7, 125.7, 127.5, 128.4, 144.5 ppm.

(1*R*,4*R*)-4,5-Epoxy-5-methyl-1-phenyl-1-hexanol [(1*R*,4*R*)-10] and (1*S*,4*R*)-4,5-Epoxy-5-methyl-1-phenyl-1-hexanol [(1*S*,4*R*)-10]: A racemic mixture of 5-methyl-1-phenyl-4-hexen-1-ol (**5**) was separated into (*S*)-**5** and (*R*)-**5** (both > 99% *ee*) by HPLC [Chiralcel OD (21 × 250 mm); *i*PrOH/*n*C_6H_{14}, 1:99 (v/v)]. **(*R*)-5:** $[\alpha]_D^{25}$ = +13.4 (*c* = 1.24, $CHCl_3$). **(*S*)-5:** $[\alpha]_D^{25}$ = −11.2 (*c* = 1.24, $CHCl_3$) {ref.[50a]: $[\alpha]_D^{25}$ = −10.7 (*c* = 1.60, $CHCl_3$)}. A solution of (*R*)- or (*S*)-5-methyl-1-phenyl-4-hexen-1-ol (**5**, 19.0 mg, 0.526 mmol) in dimethoxymethane/CH_3CN/aq. $Na_2B_4O_7$ buffer (0.05 M)/4 × 10^{-4} M aq. Na_2EDTA buffer, 2:1:1:1 (v/v/v/v, total volume of 2.5 mL), 1,2-4,5-di-*O*-isopropylidene-β-D-*erythro*-2,3-hexodiulo-2,6-pyranose[49] (7.74 mg, 0.03 mmol), and *n*Bu_4HSO_4 (1.5 mg, 0.004 mmol) was treated at −10 °C over a period of 2 h with a solution of Oxone® (85 mg, 0.138 mmol) and K_2CO_3 (80 mg, 5.8 mmol) in aq. Na_2EDTA buffer (4 × 10^{-4} M, 0.65 mL) and H_2O (0.65 mL) using a syringe pump. After addition was complete, the reaction mixture was diluted with petroleum ether (10 mL) and H_2O (10 mL). Epoxy alcohols **10** were extracted from this mixture with petroleum ether (2 × 10 mL). The combined organic phases were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford products **10** as colorless liquids. **(1*R*,4*R*)-10:** Yield: 19.4 mg (0.094 mmol, 94%), *like*/*unlike* = 88:12 (according to ^1H NMR spectroscopy). **(1*S*,4*R*)-10:** Yield: 19.8 mg (0.096 mmol, 96%), colorless liquid, *like*/*unlike* = 82:18 (according to ^1H NMR spectroscopy). Both samples were immediately used in the succeeding two experiments.

Formation of Tetrahydrofuran Derivative (2*S*,5*R*)-6 and Tetrahydropyran Derivative (3*R*,6*R*)-7: A solution of (1*R*,4*R*)-**10** (19.4 mg, 0.094 mmol) in $CDCl_3$ (0.7 mL) was treated with *p*-toluenesulfonic acid (34.4 mg, 0.20 mmol) or with $VOL^7(OEt)$ (**4g**, 3.7 mg, 0.01 mmol) and stirred at 25 °C for 2 h. After removal of the solvent under reduced pressure (250 mbar/40 °C), the products were filtered through a short pad of Al_2O_3 using Et_2O as eluent. The combined organic phases were concentrated under reduced pressure to provide an oil, which was purified by column chromatography [SiO_2; petroleum ether/acetone, 4:1 (v/v)]. Yield: 19.0 mg (98%), colorless liquid, (2*S*,5*R*)-**6**/(3*R*,6*R*)-**7** = 91:9 (^1H NMR spectroscopy). **(2*S*,5*R*)-6:** $[\alpha]_D^{25}$ = −21.0 (*c* = 0.50, $CHCl_3$). R_f = 0.40 [petroleum ether/acetone, 4:1 (v/v)]. **(3*R*,6*R*)-7:** $[\alpha]_D^{25}$ = −2.6 (*c* = 0.50, $CHCl_3$). R_f = 0.17 [petroleum ether/acetone, 4:1 (v/v)].

Formation of Tetrahydrofuran Derivative (2*S*,5*S*)-6 and Tetrahydropyran Derivative (3*R*,6*S*)-7: A solution of (1*S*,4*R*)-**10** (19.8 mg, 0.096 mmol) in $CDCl_3$ (0.7 mL) was treated with *p*-toluenesulfonic acid (34.4 mg, 0.20 mmol) or with $VOL^7(OEt)$ (**4g**, 3.7 mg, 0.01 mmol) and was stirred at 25 °C for 2 h. After removal of the solvent under reduced pressure (250 mbar/40 °C) the products were filtered through a short pad of aluminum oxide using Et_2O as eluent. The combined organic phases were concentrated under reduced pressure to provide an oil, which was purified by column chromatography [SiO_2; petroleum ether/acetone, 4:1 (v/v)]. Yield: 18.9 mg (97%), colorless liquid, (2*S*,5*S*)-**6**/(3*R*,6*S*)-**7** = 39:61 (^{1}H NMR spectroscopy). **(2*S*,5*S*)-6:** $[\alpha]_D^{25}$ = +49.7 (*c* = 0.50, $CHCl_3$). R_f = 0.42 [petroleum ether/acetone, 4:1 (v/v)]. **(3*R*,6*S*)-7:** $[\alpha]_D^{25}$ = +27.0 (*c* = 0.50, $CHCl_3$). R_f = 0.15 [petroleum ether/acetone, 4:1 (v/v)].

6. X-ray Crystallographic Study: Suitable crystals of vanadium(v) complexes **4e**, **4g**, and **4h** were grown by slowly concentrating saturated solutions in EtOH at room temperature. CCDC-197917 (**4h**), -197918 [$(VOL^1)_2O$, see Supporting Information], -197919 (**4g**), and -197920 (**4e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. For details on crystallographic investigations see Supporting Information.

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[1] The following abbreviations have been used: acac = acetylacetone monoanion, CHP = cumene hydroperoxide, DMD = dimethyl dioxirane, TBHP = *tert*-butyl hydroperoxide, UHP = urea hydrogen peroxide. Unless otherwise noted by a proper stereodescriptor, all graphics refer to racemic.

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