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Diastereoselective Epoxidation and Bishydroxylation of Cyclic *tert*-Butyl Allyl Peroxides

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Abstract: The epoxidation and the OsO_4-catalyzed bishydroxylation of cyclic *tert*-butyl allyl peroxides **1 - 6** have been investigated. The epoxidation of **1, 2, 3, 5** carried out with four different oxidants proceeded mainly with high *anti*-selectivity referred to the ^{t}BuOO group leading to the epoxides **12-15a,b**. The nucleophilic ring-opening of the epoxides **12-15a,b** was accomplished with H_2O or MeOH catalyzed by BF_3*Et_2O and proceeded with very high regio- and diastereoselectivity yielding new functionalized *tert*-butyl peroxides **18-23a,b**. Analogous high *anti*-selectivity was observed in the OsO_4-catalyzed bishydroxylation of **1 - 6** with ^{t}BuOOH to the corresponding diols **18c, 20c, 25, 26a,b, 22c**, and **27a,b**.

The direct transformation of C-H bonds into C-O functionalities is one of the outstanding problems of the oxidation chemistry.[1] One example for this transformation, the acyloxylation of allylic C-H bonds using per-esters or diacyl peroxides in the presence of copper catalysts, is the so called Kharasch-Sosnovsky reaction.[2] Besides this, similar transformations of olefins into allylic peroxides were achieved by the copper catalyzed oxidation with hydroperoxides, described first by Kharasch, Fono, Treibs and Pellmann in the 1950's.[3]

Since the early work of Kharasch some considerations about the mechanism of the copper catalyzed peroxygenation reaction have been made by Sosnovsky and Lawesson,[4] Kochi,[5] and recently by Minisci.[6] By contrast, until now the synthetic application of the *tert*-butyl allyl peroxides, e.g. the further functionalization of the olefinic double bond, has not yet been investigated. This is probably due to the conditions of the Kharasch reaction using the olefinic substrate in large excesses or even as solvent in the preparation of the allylic peroxides. Therefore this reaction is not very useful for synthetic applications especially when more expensive olefins are to be converted into the corresponding allylic peroxides.

Recently we could show that the *tert*-butyl allyl peroxides **1 - 6** (figure 1) are available in moderate yields (corresponding to the olefins) by a modification of the „Kharasch oxidation" using copper N-oxide complexes, for example $[Cu(bipyO_2)_3]Cl_2$, and excess *tert*-butyl hydroperoxide in acetonitrile at 25-40 °C.[7]

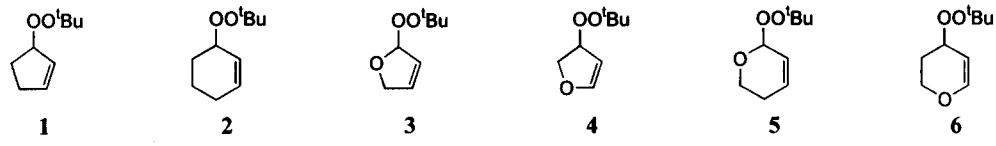
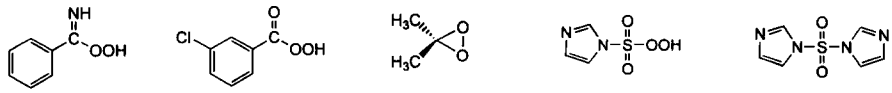


Figure 1

The present publication deals with the further oxyfunctionalization of the *tert*-butyl allyl peroxides **1** - **6**. We focused on the epoxidation of the double bond and following nucleophilic ring opening of the corresponding epoxides as well as on the OsO_4-catalyzed bishydroxylation to the corresponding *cis*-diols. It was anticipated that these transformations could lead to new functionalized peroxides. In particular, when **3** - **6** are introduced the oxidation products would represent interesting peroxy sugar derivatives. On the other hand it was interesting to evaluate the influence of the *tert*-butyl peroxy group on the diastereoselectivities in these reactions. The ^{t}BuOO group was expected to cause an *anti*-directing effect in both the epoxidation reactions with organic peracids and in the bishydroxylation process. Similar directing effect has been previously shown in the epoxidations of allylic ethers and esters [8] in contrast to the *syn*-selective epoxidation of allylic alcohols.[9]

Epoxidation of the Allylic Peroxides

The epoxidations of **1**, **2**, **3**, and **5** respectively were carried out with four different epoxidation agents (figure 2): **A**) benzimidic peracid (**7**) *in situ* generated ($PhCN/H_2O_2/K_2CO_3$),[10] **B**) m-chloroperbenzoic acid (mCPBA, **8**)/$NaHCO_3$,[11] **C**) dimethyldioxirane (DMD, **9**) *in situ* generated ($KHSO_5$/acetone/$NaHCO_3$)[12] and **D**) 1-imidazolylsulfonic peracid (**10**) *in situ* generated (Im_2SO_2 (**11**)/H_2O_2/NaOH).[13]

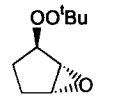
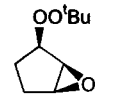
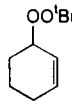
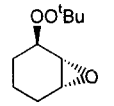
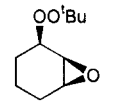
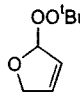
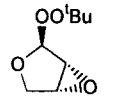
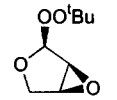
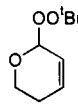
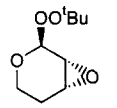
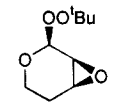


7 8 9 10 11

Figure 2

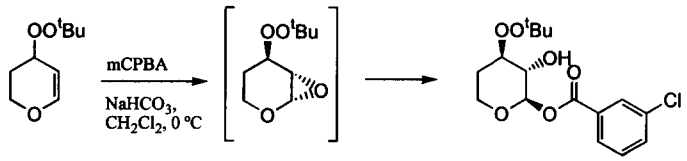
The corresponding new (acid sensitive) peroxy epoxides **12-15** were isolated in good yields (table 1) and the corresponding diastereoisomers **a** and **b** separated by flash chromatography. The structures of **12-15a,b** were determined by NMR spectroscopy (^{1}H NMR, ^{13}C NMR, H,H-COSY, H,H-NOESY and C,H-COSY measurements) and their purity was certified by elemental analysis.

Table 1: Epoxidation of Allylic Peroxides **1**, **2**, **3**, **5** with the Oxidants A, B, C, D

Entry	Educt	Oxidant [a]	Conv.[b] [%]	Yield [c] [%] (Σ Epoxides)	Diastereomers [d] major	Diastereomers [d] minor	de [e] [%]
							
1	**1**	A	99	97	**12a** (47)	**12b** (38)	9
2	**1**	B	94	89	**12a** [f]	**12b** [f]	59
3	**1**	C	98	91	**12a** [f]	**12b** [f]	69
4	**1**	D	n.d.	[g]	**12a** (79) [h]	**12b** [i]	95
							
5	**2**	A	99	94	**13a** (49)	**13b** (37)	13
6	**2**	B	95	90	**13a** [f]	**13b** [f]	56
7	**2**	C	92	95	**13a** [f]	**13b** [f]	71
8	**2**	D	60	[g]	**13a** (87)	**13b** [i]	91
							
9	**3**	A	95	94	**14a** (81)	**14b** (7)	75
10	**3**	B	15	90	**14a** [f]	**14b** [f]	95
11	**3**	C	76	93	**14a** (90)	**14b** [i]	96
12	**3**	D	80	[g]	**14a** (77)	**14b** [k]	> 99
							
13	**5**	A	97	88	**15a** (42)	**15b** (43)	0
14	**5**	B	55	92	**15a** [f]	**15b** [f]	9
15	**5**	C	75	95	**15a** [f]	**15b** [f]	0
16	**5**	D	51	[g]	**15a** (59)	**15b** [i]	71

a) **A**: 3 eq. $PhCN/H_2O_2/K_2CO_3$ in MeOH at 25 °C (12 h); **B**: 2 eq. mCPBA/$NaHCO_3$ in CH_2Cl_2 at 25 °C (10 h); **C**: 3 eq. $KHSO_5/NaHCO_3$ in acetone at 25 °C (12 h); **D**: 4 eq. Im_2SO_2/H_2O_2/NaOH in MeOH at 10 °C (3 h). b) Conversion of **1**,**2**,**3** and **5** determined by GLC. c) Isolated mixture of diastereomeric epoxides with respect to conversion. d) In parentheses yield of isolated pure diastereomer with respect to conversion. e) Analysis of the crude product (GLC, ^1H NMR). f) Diastereomers were not separated. g) Only main diastereomer was isolated. h) Yield referred to starting material. i) Minor diastereomer was not isolated. k) Diastereomer was not detected in the crude reaction mixture.

Attempts to isolate the epoxides from the reactions of the enol ethers **4** and **6** were not successful. Instead, the oxidation of **6** with mCPBA yielded the 4-*tert*-butylperoxy-3-hydroxy-2-(3-chlorobenzoyl)oxytetrahydropyran (**17**, 70% yield of pure diastereomer, scheme 1) which is undoubtedly the ring-opening product of the intermediate *anti*-epoxide **16**. The formation of **17** is in agreement with the results obtained in the oxidation of other aldehyde enol ethers by mCPBA.[14]



6 **16** **17**

Scheme 1

The main effects observed in these reactions (table 1) are as follows: The *anti*-products were obtained as the major diastereoisomers (with exception of entries 13 and 15) in agreement with the proposed *anti*-directing effect of the ^{t}BuOO group. Compared to MeO, BnO or OAc groups, the ^{t}BuOO substituent exhibits a stronger *anti*-directing effect. This is demonstrated in the epoxidation with mCPBA (entry 6). While the epoxidation of **4** led to a *syn/anti* ratio of 1:3.5, lower *syn/anti*-ratios for the epoxidations of the corresponding acetate (1:1.5), methyl ether (1:1.23), and benzyl ether (1:1.27) have been reported previously.[8]

Remarkable differences in the diastereoselectivities were observed for the different oxidants used. Generally, the highest de values were obtained with the imidazolyl sulfonic peracid (**10**) which is in accordance with the high diastereoselectivity found in the epoxidation of other olefins with a number of arene sulfonic peracids.[13] This fact may be due to the increased steric hindrance caused by the tetrahedral configuration of the sulfur atom compared with the planar mCPBA. The lowest *anti*-selectivity was found for peroxy benzimidic acid in agreement with the reported low selectivity for this oxidant.[15] Surprisingly, in the majority the diastereoselectivities found with DMD *in situ* generated are somewhat higher than those obtained with mCPBA. This finding has been also described in the diastereoselective epoxidation of various cyclic allylic compounds with isolated DMD,[16] for example, 3-hydroperoxy-1-cyclohexene is converted into the *anti*-epoxide (de 82%).[17] The increased *anti*-attack of the DMD (compared to mCPBA) is attributed to steric reasons as well as dipole dipole interactions.

Furthermore, the diastereoselectivity of the epoxidation strongly depends on the structure of the substrates. It was established that, for each oxidant, the diastereoselectivities increase in the order **5** < **6** < **2** ≈ **1** < **3**, which correlates well with the C=C-C-O dihedral angles Φ (measured with Dreiding models) when the peroxy group is arranged in the conformationally preferred pseudoequatorial position.

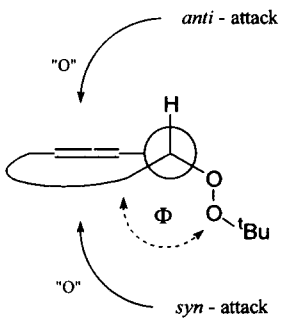


Figure 3

Therefore, the different diastereoselectivities may be rationalized in terms of greater steric hindrance of the *syn*-side attack during the oxygen transfer step, which is influenced by the dihedral angle Φ (figure 3). Analogous dependence on the dihedral angle Φ was observed in the epoxidation of other allylic substituted cycloolefins with peracids[8] and with DMD as well.[16] For example, higher *anti*-selectivity was observed for pseudoaxial allylic ethers compared with the pseudoequatorial isomers.[8] Despite the steric effects, polar effects as dipole dipole interactions may also play a role (see ref. 16).

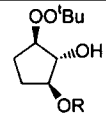
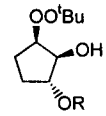
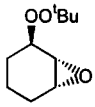
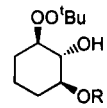
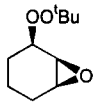
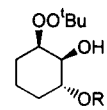
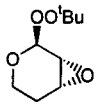
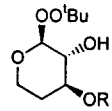
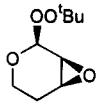
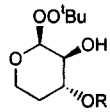
Ring Opening of the Peroxy Epoxides

Attempts to open the epoxide rings of **12a,b**, **13a,b** and **15a,b** with H_2O or MeOH as nucleophiles under alkaline conditions were not successful (no reaction at room temperature, decomposition at elevated temperatures). Similarily, the acid-catalyzed reactions led also to decomposition products.

The desired reactions have been achieved with BF_3*Et_2O as Lewis acid catalyst under mild conditions (25 °C) to yield the corresponding diols **18a,b**, **20a,b** and **22a,b** or the methoxy compounds **19a,b**, **21a,b** and **23a,b** in good yields (table 2). The ring-opening products **18-23a,b** were isolated as pure diastereoisomers, their corresponding isomers were only detected in traces in the crude reaction mixture (GLC or ^{1}H NMR). The structures of **18-23a,b** were confirmed by ^{1}H NMR spectroscopy (including COSY and NOESY experiments).

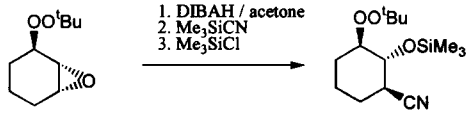
The observed high diastereoselectivity is in agreement with the *anti*-selective ring opening of other types of epoxides by Lewis acid catalysts reported to proceed in a S_N2-like process.[18] Additionally, a high regio-selectivity is observed, in which the ^{t}BuOO group directs the attack of the nucleophile almost quantitatively to the remote epoxide carbon atom of the peroxy epoxides. This result corresponds with the reported regio-directing effect of other bulky substituents in Lewis acid catalyzed epoxide ring-opening reactions.[18]

Table 2: Nucleophilic Ring-Opening of the Epoxides **12a,b**, **13a,b**, and **15a,b** with H_2O or MeOH (Catalyst BF_3*Et_2O).[a]

Entry	Epoxide		Nucleophile	Product [b]	R		Yield [c] [%]
1		**12a**	H_2O		H	**18a**	85
2			MeOH		CH_3	**19a**	65
3		**12b**	H_2O		H	**18b**	80
4			MeOH		CH_3	**19b**	65
5		**13a**	H_2O		H	**20a**	91
6			MeOH		CH_3	**21a**	82
7		**13b**	H_2O		H	**20b**	80
8			MeOH		CH_3	**21b**	84
9		**15a**	H_2O		H	**22a**	68
10			MeOH		CH_3	**23a**	63
11		**15b**	H_2O		H	**22b**	69
12			MeOH		CH_3	**23b**	76

a) Reaction conditions: 1) H_2O: 25 °C, 4h, solvent THF/H_2O; 2) MeOH: 25 °C, 6h, solvent MeOH. b) Main diastereomer shown, other isomers (regio- or diastereoisomers) were only detected in traces (GLC, ^1H NMR spectroscopy). c) Isolated pure diastereomer with respect to starting material.

In a preliminary experiment it was shown that the Lewis acid catalyzed ring-opening reaction of the peroxy epoxides can also be carried out with other than oxygen nucleophiles (scheme 2). Treatment of **13a** with Me_3SiCN in the presence of $^iBu_2(O^iPr)Al$ [19] gave the cyano derivative **24** as pure diastereoisomer (isolated product: 43%).



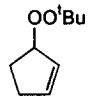
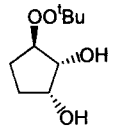
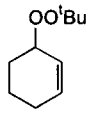
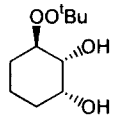
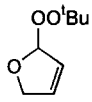
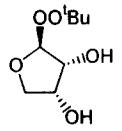
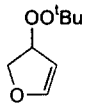
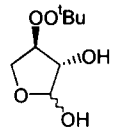
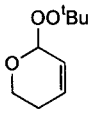
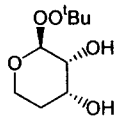
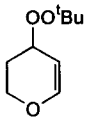
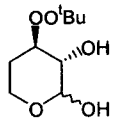
13a **24**

Scheme 2

Osmium-Catalyzed Bishydroxylation of Allylic Peroxides

The cyclic allylic peroxides **1** - **6** have been also oxidized with *tert*-butyl hydroperoxide in acetone (25 °C) in the presence of a catalytic amount OsO_4 (0.2 mol%) and $BnMe_3N^+OAc^-$ as base by a modification of the Sharpless procedure.[20] The corresponding bishydroxy compounds were isolated in moderate to good yields (table 3).

Table 3: OsO_4 - Catalyzed Bishydroxylation of Allylic Peroxides **1** - **6** with ^tBuOOH

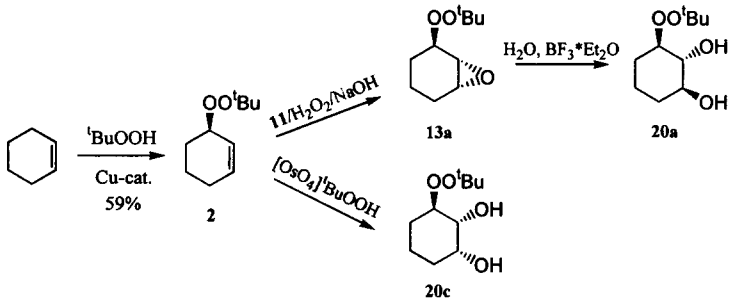
Entry	Starting Material		Products [a]		Yield [b] [%]
1		**1**		**18c**	73
2		**2**		**20c**	70
3		**3**		**25**	58
4		**4**		**26a,b** [c]	25 [d]
5		**5**		**22c**	61
6		**6**		**27a,b** [e]	38 [d]

a) Main diastereomer shown. Other diastereoisomers were only detected in traces (GLC, ^1H NMR). Structures were determined by ^1H NMR spectroscopy and purity was checked by elemental analysis. b) Isolated pure diastereoisomer with respect to starting material. c) Mixture of (2*R**,3*S**,4*R**)-epimer (**26a**) and (2*S**,3*S**,4*R**)-epimer (**26b**); ratio **26a** : **26b** = 2 : 1 determined by ^1H NMR spectroscopy. d) Low yield after chromatographic purification. e) Mixture of (2*R**,3*S**,4*R**)-epimer (**27a**) and (2*S**,3*S**,4*R**)-epimer (**27b**); ratio **27a** : **27b** = 2 : 1 determined by ^1H NMR spectroscopy.

As shown in table 3 the peroxy diols **18c**, **20c**, **22c**, and **25** were obtained as single diastereoisomers (the corresponding isomers were only detected in traces). The bishydroxylation of the furan and pyran derivatives **4** and **6** yielded mixtures of the diastereoisomers **26a,b** and **27a,b** which result from the known epimerization reaction of 2-hydroxy furans and -pyrans at the C-2 atom. Despite this, in all cases the OsO_4-catalyzed bishydroxylation occurred selectively *anti* to the ^tBuOO group in agreement with the main *anti*-directing effect of other allylic groups (OH, OMe).[21]

Summary

By applying different oxidants, the *tert*-butyl allyl peroxides **1** - **6**, which are easily available from the corresponding cyclic olefins by copper-catalyzed peroxygenation, have been transformed into new 1,2,3-trisfunctionalized cycloalkane derivatives with acceptable yields and high diastereoselectivity. For example, by starting from cyclohexene the diastereomeric dihydroxy *tert*-butyl peroxides **20a** and **20c** were isolated in overall yields of 47 % (**20a**, de > 86%) and 41% (**20c**, de > 95%), of the pure diastereoisomers.



Scheme 3

Investigations to achieve the enantioselective *tert*-butyl peroxylation of cyclic olefins by using chiral copper catalysts should be of interest, thus rendering the preparation of 1,2,3-trisfunctionalized cycloalkanes as **12-15** and **18-27** with enantiomeric excesses.

EXPERIMENTAL PART

Unless otherwise noted ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 (300 MHz) spectrometer using $CDCl_3$ as solvent and hexamethyldisiloxane (HMDSO) as internal reference.[22] ^1H NMR COSY and NOESY experiments were carried out on a Varian Unity 500 (500 MHz) NMR spectrometer. GLC-MS analyses

were performed on a Varian Saturn II spectrometer. Elemental analyses were performed on a Leco CHNS-932 analyzer. IR spectra were measured using a Philips PU 9624 FT-IR spectrometer.
The modified preparation of the known[3,23] allyl *tert*-butyl peroxides **1 - 6** and the separation of the regioisomers is described otherwise.[7] H_2O_2 was a commercial product and used as 33% (Merck) or 70% aqueous solution (Peroxid-Chemie). *Tert*-butyl hydroperoxide (commercial product, 80%, Fluka) was distilled prior use. m-Chloroperbenzoic acid (**8**; 70%) was commercially available from Fluka. The contents of peroxide were determined by iodometric titration before use. Silica gel 60 (40 μm, for flash chromatography, Baker) was used for column chromatography. Solvents were purified according to standard methods and distilled prior use.

General Procedure for the Epoxidation Reactions
Method A: To a well stirred solution of 1 mmol of the appropriate *tert*-butyl allyl peroxide (**1 - 6**) in 5 ml MeOH 1.5 mmol benzonitrile, 2.5 mmol H_2O_2 (33%) and 25 mg K_2CO_3 were added. After 2h stirring at room temperature the addition of the same amounts of benzonitrile, H_2O_2 and K_2CO_3 was repeated and stirring was continued for further 10h (TLC analysis). The excess H_2O_2 was destroyed by the addition of Pd charcoal, the solvent was evaporated in vacuo to about a half and the remaining solution was extracted several times with pentane (5 x 5 ml). The combined organic phases were washed with saturated $NaHCO_3$ and brine and finally dried with $MgSO_4$. The solvent was evaporated *in vacuo* and the crude product chromatographed on silica gel. The conversions and de-values were determined directly from the crude reaction mixture by GLC and by ^1H NMR spectroscopy.
Method B: A solution of 1 mmol of the corresponding *tert*-butyl allyl peroxide in 10 ml CH_2Cl_2 was stirred at room temperature and 170 mg $NaHCO_3$ were added. To this suspension 2 mmol mCPBA were added and stirring was continued for 10 h (monitored by TLC). The reaction mixture was treated with 10 ml water and extracted with pentane (5 x 15 ml). The combined organic phases were washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4$. The solvent was evaporated and the residue analyzed by GLC and ^1H NMR spectroscopy and purified by column chromatography.
Method C: To a well stirred mixture of 3 ml acetone (purified as usual in dioxirane generation[12]), 1 ml water, 370 mg $NaHCO_3$ and 1 mmol of the *tert*-butyl allyl peroxide a solution of 3 mmol Oxone® in 3.5 ml water was added dropwise over 2 h at room temperature. The stirring was continued for 10 h (TLC analysis). Then the mixture was treated with 20 ml water and extracted with pentane (5 x 15 ml). The combined organic phases were washed with saturated $NaHCO_3$, water, and brine and dried over $MgSO_4$. After evaporation of the solvent the crude product was analyzed by GLC and ^1H NMR spectroscopy (determination of conversions and the de values) and purified by column chromatography.
Method D: A solution of 1 mmol of the corresponding *tert*-butyl allyl peroxide and 4 mmol 1,1'-bissulfonylimidazole (**11**) in 15 ml MeOH was cooled down to 10 °C with stirring and 10 mmol H_2O_2 (70%) were added. While stirring ca. 0.4 ml 10N NaOH were added dropwise to the mixture so that the base was immediately consumed and the mixture was only weakly alkaline. The end of the reaction (ca. 3h) was indicated by the complete consumption of **11** (TLC) and by the increased pH of the mixture (pH ~ 9). After addition of 10 ml ice-cold water the mixture was extracted with ether (5 x 10 ml). The combined organic phases were washed with saturated $NaHCO_3$, water, and brine and dried over $MgSO_4$. After evaporation of the solvent *in vacuo* the crude product was purified and analyzed as described above.

(1*R,2*R**,3*R**)-1-*tert*-Butylperoxy-2,3-epoxycyclopentane (12a)**[24] and **(1*R**,2*S**,3*S**)-1-*tert*-Butylperoxy-2,3-epoxycyclopentane (12b):**[24] a) According to *method A* 475 mg (3 mmol) **1** were oxidized yielding 501 mg (97%) of a mixture of the diastereomeric epoxides **12a** and **12b** (**12a** : **12b** = 1.2 : 1, GLC). After column chromatography (n-hexane/EtOAc 15:1) 245 mg (47%) pure **12a** and 196 mg (38%) pure **12b** were obtained as colourless oils. **12a**: Elemental analysis: $C_9H_{16}O_3$ (172.22), calc.: C, 62.80; H, 9.30; found: C, 62.40; H, 9.41%. ^1H NMR: δ [ppm] 1.22 (s, 9H, ^{t}Bu), 1.50-1.84 (m, 3H), 1.94 (ddd, 1H, J_1 = 13.2 Hz, J_2 = 7.9 Hz, J_3 = 1.2 Hz), 3.51 (s, br, 1H, epoxy-H), 3.67 (d, 1H, epoxy-H, J = 2 Hz), 4.54 (d, 1H, CH-OO, J = 5.7 Hz). ^{13}C NMR: δ [ppm] 25.20 (CH_2), 25.75 (CH_2), 26.37 (CH_3), 56.78 (CH-O), 57.07 (CH-O), 80.31 (C-OO), 83.05 (CH-OO). **12b**: Elemental analysis: $C_9H_{16}O_3$ (172.22), calc.: C, 62.80; H, 9.30; found: C, 62.50; H, 9.35%. ^1H NMR: δ [ppm] 1.26 (s, 9H, ^{t}Bu), 1.53-1.80 (m, 3H), 2.08 (dd, 1H, J_1 = 13.7 Hz, J_2 = 8.5 Hz), 3.44 (d, 1H, epoxy-H, J = 2

Hz), 3.61 (d, 1H, epoxy H, J = 2.5 Hz), 4.49 (dd, 1H, CH-OO, J_1 = 8.4 Hz, J_2 = 7.8 Hz). ^{13}C NMR: δ [ppm] 21.80 (CH_2), 25.45 (CH_2), 26.37 (CH_3), 55.65 (CH-O), 55.82 (CH-O), 80.35 (C-OO), 83.86 (CH-OO).
b) According to *method B* 156 mg (1 mmol) **1** were oxidized yielding 154 mg (89%) of a mixture of the diastereomeric epoxides **12a,b** after column chromatography (n-hexane/EtOAc 10:1). The isomer ratio was determined directly from the crude mixture (**12a** : **12b** = 3.9 : 1).
c) Following *method C* 78 mg (0.5 mmol) **1** were epoxidized. After the usual work up and chromatographic purification 78 mg (91%) of the isomeric mixture of **12a,b** were obtained (isomer ratio **12a** : **12b** = 5.5 : 1).
d) According to *method D* 78 mg (0.5 mmol) **1** were oxidized. The analysis of the crude reaction mixture (GLC) showed an isomer ratio of **12a** : **12b** ≈ 40 : 1. After column chromatography (n-hexane/EtOAc 15:1) 68 mg (79%) pure **12a** were obtained. All analytical data were consistent with **12a** prepared following *method A*.

(1*R,2*R**,3*R**)-1-*tert*-Butylperoxy-2,3-epoxycyclohexane (13a)** and **(1*R**,2*S**,3*S**)-1-*tert*-Butylperoxy-2,3-epoxycyclohexane (13b):** a) 3-*tert*-Butylperoxycyclohexene (**2**) (510 mg, 3 mmol) was oxidized according to *method A* using 9 mmol PhCN and 15 mol H_2O_2. After the usual work up 524 mg (91%) of a mixture of the diastereomeric epoxides **13a,b** were obtained (isomer ratio **13a** : **13b** = 1.3 : 1, GLC). After column chromatography (n-hexane/EtOAc 15:1) 273 mg (49%) pure **13a** and 205 mg (37%) pure **13b** were isolated as colourless oils. **13a**: Elemental analysis: $C_{10}H_{18}O_3$ (186.25) calc.: C, 64.50; H, 9.68; found: C, 64.10; H, 9.81%. ^{1}H NMR (500 MHz): δ [ppm] 1.10 (dddd, 1H, H-6_{ax}, J_1 = 12.7 Hz, J_2 = 12.0 Hz, J_3 = 9.3 Hz, J_4 = 3.2 Hz), 1.20 (m, 1H, H-5_{ax}), 1.22 (s, 9H, ^{t}Bu), 1.36 (m, 1H, H-5_{eq}), 1.67 (dddd, 1H, H-4_{ax}, J_1 = 15.5 Hz, J_2 = 10.2 Hz, J_3 = 5.7 Hz, J_4 = 2.4 Hz), 1.73 (dddd, 1H, H-6_{eq}, J_1 = 12.7 Hz, J_2 = 6.5 Hz, J_3 = 6.0 Hz, J_4 = 2.4 Hz), 1.96 (d"t", 1H, H-4_{eq}, J_1 = 15.5 Hz, J_2 = 4.5 Hz), 3.19 (m, 1H, epoxy H-3_{syn}), 3.36 (d, 1H, epoxy H-2_{syn}, J = 3.7 Hz), 4.18 (dd, 1H, H-1_{ax}, J_1 = 9.3 Hz, J_2 = 5.9 Hz). ^{13}C NMR: δ [ppm] 14.78 (CH_2), 24.35 (CH_2), 24.69 (CH_2), 26.36 (CH_3), 52.82 (O-CH), 53.14 (O-CH), 77.37 (OO-CH), 80.27 (OO-C). **13b**: Elemental analysis: $C_{10}H_{18}O_3$ (186.25) calc.:C, 64.50; H, 9.68; found: C, 64.20; H, 9.78%. ^{1}H NMR (500 MHz): δ [ppm] 1.20 (m, 1H, H-5_{ax}), 1.22 (s, 9H, ^{t}Bu), 1.37 (m, 1H, H-6_{ax}), 1.55 (m, 2H, H-4_{ax}/H-6_{eq}), 1.75 (m, 2H, H-4_{eq}/H-5_{eq}), 3.25 (m, 1H, epoxy H-3_{anti}), 3.43 (dd, 1H, epoxy H-2_{anti}, J_1 = 4 Hz, J_2 = 1.6 Hz), 4.25 (ddd, 1H, H-1_{ax}, J_1 = 9.5 Hz, J_2 = 4.6 Hz, J_3 = 1.7 Hz). ^{13}C NMR: δ [ppm] 19.75 (CH_2), 23.01 (2 CH_2), 26.43 (CH_3), 52.36 (CH-O), 53.78 (CH-O), 79.47 (CH-OO), 80.09 (C-OO).
b) Following *method B* 170 mg (1 mmol) **2** were oxidized. After the usual work up and purification by column chromatography 168 mg (90%) of a mixture of the diastereomeric epoxides **13a,b** were obtained. GLC analysis of the crude product showed an isomer ratio of **13a** : **13b** = 3.5 : 1.
c) The epoxidation of 85 mg (0.5 mmol) **2** according to *method C* gave 81 mg (88%) **8a,b** as diastereomeric mixture. The isomer ratio was determined by GLC to be **13a** : **13b** = 5.8 : 1.
d) According to *method D* 170 mg (1 mmol) **2** were oxidized (conversion 60%, GLC). After the usual work up and column chromatography (n-hexane/EtOAc 15:1) 96 mg (52%) pure **13a** were obtained. All data were in agreement with those obtained from **13a** prepared according to *method A*. The isomer ratio **13a** : **13b** in the crude product was found to be **13a** : **13b** = 21 : 1 (GLC).

(2*S,3*R**,4*R**)-2-*tert*-Butylperoxy-3,4-epoxytetrahydrofuran (14a)** and **(2*S**,3*S**,4*S**)-2-*tert*-Butylperoxy-3,4-epoxytetrahydrofuran (14b):** a) According to *method A* 475 mg (3 mmol) **3** were epoxidized to yield 489 mg (93%) **14a,b** as diastereomeric mixture after the usual work up. Analysis of the crude reaction product indicated an isomer ratio **14a** : **14b** = 7.1 : 1 (GLC). After flash chromatography 402 mg (77%) pure **14a** and 34 mg (6%) pure **14b** were isolated. **14a**: Elemental analysis: $C_8H_{14}O_4$ (174.19), calc.: C, 55.20; H, 8.05; found: C, 55.30; H, 7.82%. ^{1}H NMR : δ [ppm] 1.24 (s, 9H, ^{t}Bu), 3.71 (d, 1H, epoxy H, J = 2.6 Hz), 3.80 (d, 1H, epoxy H, J = 2.6 Hz), 3.92 (d, 1H, CH_2O, J = 10.4 Hz), 4.00 (d, 1H, CH_2-O, J = 10.4 Hz), 5.46 (s, 1H, CH-OO). ^{13}C NMR: δ [ppm] 26.29 (CH_3), 54.02 (CH-O), 54.40 (CH-O), 67.19 (CH_2-O), 81.01 (C-OO), 103.30 (CH-OO). **14b**: Elemental analysis: $C_8H_{14}O_4$ (174.19), calc.: C, 55.20; H, 8.05; found: C, 55.25; H, 7.98%. ^{1}H NMR : δ [ppm] 1.27 (s, 9H, ^{t}Bu), 3.74 (dd, 1H, epoxy H, J_1 = 2.4 Hz, J_2 = 0.75 Hz), 3.77 (d, 1H, epoxy H, J = 2.4 Hz), 3.83 (dd, 1H, CH_2O, J_1 = 10.8 Hz, J_2 = 0.75 Hz), 4.25 (d, 1H, CH_2O, J = 10.8 Hz), 5.51 (s, 1H, CH-OO). ^{13}C NMR: δ [ppm] 26.31 (CH_3), 54.54 (CH-O), 54.99 (CH-O), 67.61 (CH_2O), 81.62 (C-OO), 104.19 (CH-OO).

b) Following *method B* 158 mg (1 mmol) **3** were oxidized to give after usual work up (conversion 15%, GLC) 24 mg (14%) **14a,b** as diastereomeric mixture. The isomer ratio was determined by GLC to be **14a** : **14b** ≈ 90 : 1.
c) According to *method C* 79 mg (0.5 mmol) **3** were epoxidized (conversion 76%, GLC). After the usual work up 61 mg (70%) **14a,b** were isolated as diastereomeric mixture. GLC analysis of the crude product indicated an isomer ratio **14a** : **14b** = 52 : 1.
d) The epoxidation of 158 mg (1 mmol) **3** according to *method D* (conversion 80%, GLC) gave 107 mg (61%) pure **14a** after the usual work up and column chromatography (n-hexane/EtOAc 15:1). All data were in full agreement with the data obtained according to *method A*. The isomer **14b** was not detected in the crude reaction mixture (ratio **14a** : **14b** > 200 : 1).

(2*S,3*R**,4*R**)-2-*tert*-Butylperoxy-3,4-epoxytetrahydropyran (15a)** and **(2*S**,3*S**,4*S**)-2-*tert*-Butylperoxy-3,4-epoxytetrahydropyran (15b)**: a) According to *method A* 345 mg (2 mmol) **5** were epoxidized. After the usual work up 323 mg (86%) **15a,b** were isolated as diastereomeric mixture. Analysis of the crude product (GLC) showed a 1:1 mixture of **15a** and **15b**. After column chromatography (n-hexane/EtOAc 10:1) 154 mg (41%) pure **15a** and 158 mg (42%) pure **15b** were obtained as colourless oils. **15a**: Elemental analysis: $C_9H_{16}O_4$ (188.22); calc.: C, 57.34; H, 8.57; found: C, 57.38; H, 8.63%. ^{1}H NMR (500 MHz): δ [ppm] 1.29 (s, 9H, ^{t}Bu), 1.88 (dddd, 1H, H-5_{eq}, J_1 = 15.4 Hz, J_2 = 5.0 Hz, J_3 = 4.0 Hz, J_4 = 3.5 Hz), 2.09 (ddd, 1H, H-5_{ax}, J_1 = 15.4 Hz, J_2 = 9.8 Hz, J_3 = 6.3 Hz), 3.04 (d, 1H, epoxy H-3_{syn}, J = 4.0 Hz), 3.35 („t", 1H, epoxy H-4_{syn}, J ≈ 3.9 Hz), 3.49 (ddd, 1H, H-6_{eq}, J_1 = 11.7 Hz, J_2 = 6.3 Hz, J_3 = 3.5 Hz), 3.81 (ddd, 1H, H-6_{ax}, J_1 = 11.7 Hz, J_2 = 9.9 Hz, J_3 = 5.0 Hz), 5.37 (s, 1H, H-2, CH-OO). ^{13}C NMR: δ [ppm] 23.21 (CH_2), 26.32 (CH_3), 47.82 (CH-O), 49.96 (CH-O), 55.26 (CH_2-O), 81.29 (C-OO), 98.10 (CH-OO). **15b**: Elemental analysis: $C_9H_{16}O_4$ (188.22), calc.: C, 57.43; H, 8.57; found: C, 57.29; H, 8.68%. ^{1}H NMR (500 MHz): δ [ppm] 1.29 (s, 9H, ^{t}Bu), 1.94 (m, 2H, CH_2), 3.32 (m, 2H, epoxy H, H-3_{anti}/H-3_{syn}), 3.53 (ddd, 1H, H-6_{eq}, J_1 = 11.0 Hz, J_2 = 4.6 Hz, J_3 = 2.2 Hz), 3.87 („t"d, 1H, H-6_{ax}, J_1 ≈ 11 Hz, J_2 = 4.0 Hz), 5.42 (d, 1H, H-2, J = 3 Hz). ^{13}C NMR: δ [ppm] 24.41 (CH_2), 26.35 (CH_3), 48.85 (CH-O), 49.35 (CH-O), 55.73 (CH_2-O), 81.10 (C-OO), 96.67 (CH-OO).
b) The epoxidation of 86 mg (0.5 mmol) **5** according to *method B* (conversion 55%) gave 48 mg (51%) of a diastereomeric mixture of **15a,b**. The isomer ratio was determined by GLC and found to be **15a** : **15b** = 1.2 : 1.
c) According to method C 86 mg (0.5 mmol) **5** were oxidized (conversion 75%) and yielded 65 mg (69%) **15a,b** (mixture of isomers) after usual work up. Isomer ratio **15a** : **15b** = 1 : 1 (GLC analysis of the crude product).
d) Following the procedure of *method D* 172 mg (1 mmol) **5** were epoxidized (conversion 51%) and yielded 56 mg (30%) pure **15a** after work up and chromatography (n-hexane/EtOAc 10:1). The isomer ratio determined from the crude product was **15a** : **15b** = 6 : 1.

(2*R,3*S**,4*R**)-4-*tert*-Butylperoxy-3-hydroxy-2-(3-chlorobenzoyl)oxytetrahydropyran (17):** According to *method B* 50 mg (0.29 mmol) **6** were oxidized with mCPBA (3 eq.)/$NaHCO_3$(6 eq.) at 0 °C in 10 ml n-hexane. After 6h the reaction mixture was worked up as usual (*method B*). After column chromatography (n-hexane/EtOAc 5:1) 70 mg (70%) pure **17** were obtained as light-yellowish oil. Elemental analysis: $C_{16}H_{21}ClO_6$ (344.77); calc.: C, 55.73; H, 6.14; Cl, 10.28; found C, 55.57; H, 6.20; Cl, 10.11%. IR (KBr, neat): ν [cm^{-1}] 3460 (OH), 3080 (CH), 2980 (CH), 1736 (C=O), 1255 (C-O), 1074 (C-O). ^{1}H NMR : δ [ppm] 1.26 (s, 9H, ^{t}Bu), 1.73 (d"t"d, 1H, H-5_{ax}, J_1 = 12 Hz, J_2 = 10.5 Hz, J_3 = 4.5 Hz), 2.05 (d"t"d, 1H, H-5_{eq}, J_1 = 12.8 Hz, J_2 = 4.5 Hz, J_3 = 2.8 Hz), 3.06 (d, 1H, OH, J = 2.2 Hz, disappeared with D_2O), 3.64 (ddd, 1H, H-6_{ax}, J_1 = 12 Hz, J_2 = 10.5 Hz, J_3 = 2.8 Hz), 3.85 (ddd, 1H, H-3_{ax}, J_1 = 7.9 Hz, J_2 = 7.1 Hz, J_3 = 2.2 Hz, OH-coupling, signal changes to dd with D_2O), 4.06 (dt, 1H, H-6_{eq}, J_1 = 12 Hz, J_2 = 4.4 Hz), 4.14 (ddd, 1H, H-4_{ax}, J_1 = 10.1 Hz, J_2 = 7.9 Hz, J_3 = 5 Hz), 5.75 (d, 1H, H-2_{ax}, J = 7 Hz), 7.36 (t, 1H, Ar, J = 8 Hz), 7.52 (d, 1H, Ar, J = 8 Hz), 7.97 (d, 1H, Ar, J = 8 Hz), 8.07 (s, 1H, Ar).

General Procedure for the Nucleophilic Ring Opening of Epoxides 12-15 a,b
A) Reaction with H_2O: To a well stirred solution of 0.5 mmol of the appropriate epoxide in a mixture of 3 ml absolute THF and 2 ml H_2O, 20 µl freshly distilled BF_3*Et_2O were added at room temperature and the stirring

continued for 4 h (TLC monitoring). When the reaction was complete, 10 ml of saturated aqueous $NaHCO_3$ were added under vigorous stirring. The mixture was extracted with ether (5 x 10 ml), the combined organic phases were washed with saturated aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. Then the solvent was evaporated *in vacuo* and the crude product purified by column chromatography.
B) Reaction with MeOH: The appropriate epoxide (0.5 mmol) was dissolved in 5 ml absolute MeOH. Under vigorous stirring 20 µl freshly distilled BF_3*Et_2O were added and the resulting mixture stirred for further 6 h (TLC monitoring). After completion of the reaction 10 ml sat. aqu. $NaHCO_3$ were added and the obtained mixture concentrated *in vacuo* to about 4 ml, followed by extraction with n-pentane (5 x 10 ml). The combined pentane phases were washed with saturated aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product purified by chromatography.

(1*R,2*R**,3*S**)-1-*tert*-Butylperoxy-2,3-dihydroxycyclopentane (18a):** Following *procedure A* 125 mg (0.72 mmol) **12a** were allowed to react with THF/H_2O. After the described work up and column chromatography (n-hexane/EtOAc 2:1) 116 mg (85%) pure **18a** were obtained as colourless oil. Elemental analysis: $C_9H_{18}O_4$ (190.24); calc.: C, 56.84; H, 9.47; found: C, 56.95; H, 9.90 %. ^{1}H NMR : δ [ppm] 1.24 (s, 9H, ^{t}Bu), 1.71 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.77 (s, br, 2H, 2OH, disapp. with D_2O), 3.98 ("t", 1H, CH-O, J = 6.4 Hz), 4.03 (m, 1H, CH-O, J_1 = 6.1 Hz, J_2 = 5.3 Hz), 4.28 (dt, 1H, H-1, J_1 = 6.5 Hz, J_2 = 5.0 Hz).

(1*R,2*S**,3*R**)-1-*tert*-Butylperoxy-2,3-dihydroxycyclopentane (18b):** The reaction of 111 mg (0.65 mmol) **12b** with THF/H_2O as described above yielded 98 mg (80%) pure **18b** after column chromatography (n-hexane/EtOAc 2:1) as colourless oil. Elemental analysis: $C_9H_{18}O_4$ (190.24); calc.: C, 56.84; H, 9.47; found: C, 56.73; H, 9.50 %. ^{1}H NMR : δ [ppm] 1.23 (s, 9H, ^{t}Bu), 1.45 (m, 1H, CH_2), 1.59 (m, 1H, CH_2), 2.06 (m, 2H, CH_2), 2.85 (s, br, 2H, 2OH), 3.88 ("t"d, 1H, H-2$_{anti}$, J_1 = 4.53 Hz, J_2 = 3.6 OH-coupling, signal changes to triplett with D_2O), 4.13 ("q", 1H, H-3$_{syn}$, J = 5.5 Hz), 4.52 (d"t", 1H, H-1, J_1 = 7.6 Hz, J_2 = 5.0 Hz).

(1*R,2*R**,3*S**)-1-*tert*-Butylperoxy-2-hydroxy-3-methoxycyclopentane (19a):** Following the general *procedure B* 142 mg (0.82 mmol) **12a** were converted with MeOH/BF_3*Et_2O to yield 107 mg (65%) pure **19a** as colourless oil after column chromatography (n-hexane/EtOAc 5:1). Elemental analysis: $C_{10}H_{20}O_4$ (204.26); calc.: C, 58.80; H, 9.87; found: C, 58.67; H, 9.90%. ^{1}H NMR : δ [ppm] 1.23 (s, 9H, ^{t}Bu), 1.67 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 2.45 (s, br, 1H, OH), 3.37 (s, 3H, OCH_3), 3.57 ("q", 1H, H-3$_{anti}$, J ≈ 6.5 Hz), 4.08 ("t", 1H, H-2$_{syn}$, J ≈ 5.8 Hz), 4.25 (dt, 1H, H-1, J_1 = 7.3 Hz, J_2 = 5.9 Hz).

(1*R,2*S**,3*R**)-1-*tert*-Butylperoxy-2-hydroxy-3-methoxycyclopentane (19b):** Following the above procedure 30 mg (0.17 mmol) **12b** were allowed to react with MeOH/BF_3*Et_2O yielding 22 mg (65%) pure **19b** as colourless oil after column chromatography (n-hexane/EtOAc 5:1). Elemental analysis: $C_{10}H_{20}O_4$ (204.26); calc.: C, 58.80; H, 9.87; found: C, 58.69; H, 9.77%. ^{1}H NMR : δ [ppm] 1.23 (s, 9H, ^{t}Bu), 1.55 (m, 2H, CH_2), 1.97 (m, 1H, CH_2), 2.09 (m, 1H, CH_2), 2.65 (d, 1H, OH, disapp. with D_2O, J = 3.3 Hz), 3.35 (s, 3H, OCH_3), 3.68 (ddd, 1H, H-3$_{syn}$, J_1 = 6.5 Hz, J_2 = 4.0 Hz, J_3 = 3.3 Hz), 4.06 (dt, 1H, H-2$_{anti}$, J_1 = 4.0 Hz, J_2 = 3.3 Hz, signal changes to dd with D_2O), 4.46 ("t"d, 1H, H-1, J_1 ≈ 7.0 Hz, J_2 = 4.6 Hz).

(1*R,2*R**,3*S**)-1-*tert*-Butylperoxy-2,3-dihydroxycyclohexane (20a):** According to the general *procedure A* 100 mg (0.54 mmol) **13a** were hydrolyzed with $THF/H_2O/BF_3$*Et_2O yielding after column chromatography (n-hexane/EtOAc 2:1) 100 mg (91%) pure **20a** as colourless oil which solidifies below 20 °C. Elemental analysis: $C_{10}H_{20}O_4$ (204.26); calc.: C, 58.80; H, 9.87; found: C, 58.53; H, 10.01%. ^{1}H NMR : δ [ppm] 1.25 (s, 9H, ^{t}Bu), 1.27 (m, 3H), 1.71 (m, 1H, CH_2), 1.94 (m, 2H, CH_2), 2.83 (s, br, 1H, OH), 3.40 (t, 1H, H-2$_{ax}$, J = 9 Hz), 3.46 (td, 1H, H-3$_{ax}$, J_1 = 9 Hz, J_2 = 5 Hz), 3.57 (s, br, 1H, OH), 3.76 (ddd, 1H, H-1$_{ax}$, J_1 = 10.3 Hz, J_2 = 8.3 Hz, J_3 = 5 Hz).

(1*R,2*S**,3*R**)-1-*tert*-Butylperoxy-2,3-dihydroxycyclohexane (20b):** As described above 120 mg (0.65 mmol) **13b** were converted and yielded 105 mg (80%) pure **20b** as colourless oil (white crystals mp < 25 °C) after column chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_{10}H_{20}O_4$ (204.26); calc.: C, 58.80; H,

9.87; found: C, 58.75; H, 9.76%. ^{1}H NMR : δ [ppm] 1.23 (s, 9H, ^{t}Bu), 1.52 (m, 4H, 2 CH_2), 1.96 (m, 2H, CH_2), 2.44 (s, br, 1H, OH), 2.93 (d, 1H, OH, J = 7.8 Hz), 3.44 (m, with D_2O dd, 1H, H-2_{ax}, J_1 = 9 Hz, J_2 = 2.6 Hz), 3.77 (td, 1H, H-3_{ax}, J_1 = 9.5 Hz, J_2 = 4.4 Hz), 4.39 (dt, 1H, H-1_{eq}, J_1 = 4.3 Hz, J_2 = 2.8 Hz).

(1*R,2*R**,3*S**)-1-*tert*-Butylperoxy-2-hydroxy-3-methoxycyclohexane (21a):** According to the *procedure B* 150 mg (0.8 mmol) **13a** were treated with MeOH/BF_3*Et_2O to yield 137 mg (82%) pure **21a** as colourless oil after column chromatography (n-hexane/EtOAc 5:1). Elemental analysis: $C_{11}H_{22}O_4$ (218.29); calc.: C, 60.52; H, 10.16; found: C, 59.89; H, 9.99%. ^{1}H NMR (CD_3NO_2) : δ [ppm] 1.12 (m, 2H, CH_2), 1.24 (s, 9H, ^{t}Bu), 1.70 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 3.06 (td, 1H, H-3_{ax}, J_1 = 10 Hz, J_2 = 4.2 Hz), 3.19 (s, 1H, OH), 3.43 (s, 3H, OCH_3), 3.50 ("t", 1H, H-2_{ax}, J = 9 Hz), 3.79 (ddd, 1H, H-1_{ax}, J_1 = 10.8 Hz, J_2 = 9.1 Hz, J_3 = 4.5 Hz).

(1*R,2*S**,3*R**)-1-*tert*-Butylperoxy-2-hydroxy-3-methoxycyclohexane (21b):** According to the procedure above 80 mg (0.43 mmol) **13b** were allowed to react with MeOH/BF_3*Et_2O. After column chromatography (n-hexane/EtOAc 5:1) 79 mg (84%) pure **21b** were isolated. Elemental analysis: $C_{11}H_{22}O_4$ (218.29); calc.: C, 60.52; H, 10.16; found: C, 60.31; H, 9.97%. ^{1}H NMR : δ [ppm] 1.23 (s, 9H, ^{t}Bu), 1.45 (m, 3H), 1.75 (m, 3H), 2.51 (d, 1H, OH, J = 3.6 Hz), 3.37 (s, 3H, OCH_3), 3.44 (td, 1H, H-3_{ax}, J_1 = 6.4 Hz, J_2 = 3.5 Hz), 3.90 (ddd, 1H, H-2_{ax}, J_1 = 6.4 Hz, J_2 = 3.6 Hz, J_3 = 2.6 Hz, signal changes to dd with D_2O), 4.23 (d"t", 1H, H-1, J_1 = 8 Hz, J_2 ≈3 Hz).

(2*S,3*R**,4*S**)-2-tert-Butylperoxy-3,4-dihydroxytetrahydropyran (22a):** From the reaction of 65 mg (0.35 mmol) **15a** with THF/H_2O/BF_3*Et_2O according to *procedure A* 50 mg (68%) pure **22a** were obtained as colourless oil after column chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_9H_{18}O_5$ (206.24); calc.: C, 52.41; H, 8.80; found: C, 52.20; H, 8.95%. ^{1}H NMR : δ [ppm] 1.28 (s, 9H, ^{t}Bu), 1.70 (qd, 1H, H-5_{ax}, J_1 = 12 Hz, J_2 = 5 Hz), 1.93 (ddt, 1H, H-5_{eq}, J_1 = 12 Hz, J_2 = 5 Hz, J_3 = 2 Hz), 2.70 (s, br, 2H, 2 OH), 3.35 ("t", 1H, H-3_{ax}, J = 8.3 Hz), 3.49 (td, 1H, H-6_{ax}, J_1 = 12 Hz, J_2 = 2 Hz), 3.70 (ddd, 1H, H-4_{ax}, J_1 = 12 Hz, J_2 = 8.3 Hz, J_3 = 5 Hz), 4.00 (ddd, 1H, H-6_{eq}, J_1 = 12 Hz, J_2 = 4.9 Hz, J_3 = 2 Hz), 4.71 (d, 1H, H-2_{ax}, J = 8 Hz).

(2*S,3*S**,4*R**)-2-*tert*-Butylperoxy-3,4-dihydroxytetrahydropyran (22b):** Following the procedure above 54 mg (0.29 mmol) **15b** were transformed into **22b** (pure diastereomer) yielding 42 mg (69%) as colourless oil after column chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_9H_{18}O_5$ (206.24); calc.: C, 52.41; H, 8.80; found: C, 52.38; H, 8.56%. ^{1}H NMR : δ [ppm] 1.27 (s, 9H, ^{t}Bu), 1.65 (qd, 1H, H-5_{ax}, J_1 = 13 Hz, J_2 = 5.2 Hz), 1.94 (dtd, 1H, H-5_{eq}, J_1 = 13 Hz, J_2 = 4.8 Hz, J_3 = 2 Hz), 2.50 (s, br, 2H, 2 OH), 3.50 (dd, 1H, H-3_{ax}, J_1 = 10 Hz, J_2 = 4.4 Hz), 3.70 (m, 2H, 2 H-6, CH_2O, H-5), 3.90 (m, 1H, H-4_{ax}), 5.35 (d, 1H, H-2_{eq}, J = 4.4 Hz).

(2*S,3*S**,4*R**)-2-*tert*-Butylperoxy-3-hydroxy-4-methoxytetrahydropyran (23a):** According to *procedure B* 41 mg (0.22 mmol) **15a** were converted using MeOH/BF_3*Et_2O. After column chromatography (n-hexane/EtOAc 3:1) 30 mg (63%) pure **23a** were isolated as colourless oil. Elemental analysis: $C_{10}H_{20}O_5$ (220.26); calc.: C, 54.35; H, 9.15; found: C, 54.38; H, 9.35%. ^{1}H NMR : δ [ppm] 1.27 (s, 9H, ^{t}Bu), 1.52 (dtd, 1H, H-5_{ax}, J_1 = 13 Hz, J_2 = 12 Hz, J_3 = 5 Hz), 2.48 (s, br, 1H, OH), 3.36 (m, 3H), 3.42 (s, 3H, OCH_3), 4.00 (ddd, 1H, H-6_{eq}, J_1 = 12 Hz, J_2 = 4.5 Hz, J_3 = 2 Hz), 4.72 (d, 1H, H-2_{ax}, J = 8 Hz).

(2*S,3*R**,4*S**)-2-*tert*-Butylperoxy-3-hydroxy-4-methoxytetrahydropyran (23b):** As described above 36 mg (0.19 mmol) **15b** were transformed and yielded 32 mg (76%) pure **23b** (colourless oil) after chromatography (n-hexane/EtOAc 3:1): Elemental analysis: $C_{10}H_{20}O_5$ (220.26); calc.: C, 54.35; H, 9.15; found: C, 54.35; H, 9.28%. ^{1}H NMR : δ [ppm] 1.28 (s, 9H, ^{t}Bu), 1.52 (dtd, H-5_{ax}, J_1 = 13 Hz, J_2 = 11 Hz, J_3 = 5 Hz), 2.06 (ddt, 1H, H-5_{eq}, J_1 = 13 Hz, J_2 = 4.4 Hz, J_3 = 2 Hz), 2.20 (s, br, 1H, OH), 3.36 (m, 1H, H-4_{ax}), 3.40 (s, 3H, OCH_3), 3.65 (m, 1H, H-3_{ax}), 3.72 (ddd, 1H, H-6_{eq}, J_1 = 12 Hz, J_2 = 5 Hz, J_3 = 2.7 Hz), 3.90 ("t"d, 1H, H-6_{ax}, J_1 = 12 Hz, J_2 = 2 Hz), 5.36 (d, 1H, H-2_{eq}, J = 4 Hz).

(1*R,2*R**,3*R**)-3-*tert*-Butylperoxy-2-trimethylsilyloxycyclohexane-1-carbonitrile (24):** Modifying a procedure of Imi,[19] 1.5 mmol dry acetone were added at 0 °C (N_2 atmosphere) to a well stirred solution of 1.5

mmol diisobutylaluminiumhydride in 5 ml dry n-hexane (prepared from commercial 1M DIBAH in n-hexane, Aldrich). After additional stirring at room temperature for 20 min, 1.5 mmol (200 µl) cyanotrimethylsilane (Aldrich) were added and stirring was continued for 2 h. Then the epoxide **13a** (1 mmol, 186 mg) was added and stirring continued for further 15 h. After that time the mixture was treated with 2 mmol (~ 253 µl) chlorotrimethylsilane. The solvent was removed *in vacuo* and the crude product was purified by chromatography (n-hexane/EtOAc 15:1) yielding 124 mg (43%) pure **24** as colourless oil. Elemental analysis: $C_{14}H_{27}NO_3Si$ (285.46); calc.: C, 58.90; H, 9.53; N, 4.91; found: C, 58.76; H, 9.59; N, 4.53%. IR (KBr, neat): ν [cm^{-1}] 2950 (CH), 2242 (CN). ^{1}H NMR : δ [ppm] 0.20 (s, 9H, $SiMe_3$), 1.22 (s, 9H, ^{t}Bu), 1.25 (m, 1H, H-5_{ax}), 1.33 (m, 1H, H-4_{ax}), 1.55 ("q"d, 1H, H-6_{ax}, J_1 ≈13 Hz, J_2 = 3.6 Hz), 1.76 (dm, 1H, H-5_{eq}, J_1 = 13.4 Hz, J_2 ≈ 4 Hz), 2.03 (dm, 1H, H-6_{eq}, J_1 ≈ 12 Hz), 2.22 (d, 1H, H-4_{eq}, J ≈ 12 Hz), 2.48 (ddd, 1H, H-1_{ax}, J_1 = 12 Hz, J_2 = 9 Hz, J_3 = 4 Hz), 3.64 ("t"d, 1H, H-3_{ax}, J_1 ≈ 9 Hz, J_2 = 4.5 Hz), 3.68 ("t", 1H, H-2_{ax}, J ≈ 9 Hz).

Catalytic Bishydroxylation of Allyl *tert*-Butyl Peroxides

General procedure: The bishydroxylation reactions were carried out modifying the method of Sharpless.[20] To a well stirred mixture of 0.5 mmol benzyltrimethylammonium acetate in 4 ml acetone 1 mmol of the appropriate allyl *tert*-butylperoxide **1 - 6** and 1.5 mmol *tert*-butyl hydroperoxide were added. The mixture was cooled to 0 °C and 0.1 ml of the OsO_4-catalyst solution (prepared from 0.02 g OsO_4, 4 ml ^{t}BuOH and 0.02 ml ^{t}BuOOH) were added and stirring continued for 1 h at 0 °C. The ice-bath was removed and stirring was continued for 10 h at room temperature. After addition of 10 ml ether, the mixture was cooled down to 0 °C and treated with 10 ml 10% aqueous Na_2SO_3. After stirring for 1 h at room temperature the mixture was saturated with NaCl, the organic layer was separated and the aqueous phase extracted with ether (5 x 15 ml). The combined organic phases were washed with brine and dried with $MgSO_4$. After removing the solvent *in vacuo*, the residue was purified by column chromatography.

(1*R,2*R**,3*R**)-1-*tert*-Butylperoxy-2,3-dihydroxycyclopentane (18c):** According to the procedure above 156 mg (1 mmol) **1** were oxidized to yield 138 mg (73%) pure **18c** as colourless oil after column chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_9H_{18}O_4$ (190.24); calc.: C, 56.83; H, 9.54; found: C, 56.53; H, 9.60%. ^{1}H NMR (500 MHz) : δ [ppm] 1.24 (s, 9H, ^{t}Bu), 1.48 (ddt, 1H, H-5_{syn}, J_1 = 14.1 Hz, J_2 = 9.9 Hz, J_3 = 5.5 Hz), 1.72 (dddd, 1H, H-4_{anti}, J_1 = 13.9 Hz, J_2 = 9.4 Hz, J_3 = 5.4 Hz, J_4 = 3.4 Hz), 1.94 (dddd, 1H, H-4_{syn}, J_1 = 13.9 Hz, J_2 = 9.9 Hz, J_3 = 6.6 Hz, J_4 = 5.4 Hz), 2.16 (d"t"d, 1H, H-5_{anti}, J_1 = 14.2 Hz, J_2 = 8.8 Hz, J_3 = 6.6 Hz), 2.58 (s, br, 1H, OH-3), 2.81 (s, br, 1H, OH-2), 4.08 ("t"d, 1H, H-2_{syn}, J_1 = 4.8 Hz, J_2 = 2.4 Hz {OH-coupling, disappeared with D_2O}), 4.16 ("t"dd, 1H, H-3_{syn}, J_1 = 4.6 Hz, J_2 = 3.5 Hz, J_3 = 2 Hz {OH-coupling, disappeared with D_2O}), 4.46 (dt, 1H, H-1, J_1 = 8.4 Hz, J_2 = 5.3 Hz). ^{13}C NMR: δ [ppm] 24.99 (CH_2), 26.21 (CH_3), 28.94 (CH_2), 72.55 (CH-O), 78.04 (CH-O), 80.50 (C-OO), 88.49 (CH-OO).

(1*R,2*R**,3*R**)-1-*tert*-Butylperoxy-2,3-dihydroxycyclohexane (20c):** In a similar manner 170 mg (1mmol) **2** were oxidized to yield 143 mg (70%) pure **20c** as colourless oil (white needles < 20 °C) after work up and column chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_{10}H_{20}O_4$ (204.26); calc.: C, 58.80; H, 9.87; found: C, 58.54; H, 10.02%. ^{1}H NMR (500 MHz) : δ [ppm] 1.15 (m, 1H, CH_2), 1.22 (s, 9H, ^{t}Bu), 1.36 ("t"m, 1H, CH_2, J_1 ≈13 Hz), 1.50 (d"quint", 1H, H-5_{eq}, J_1 ≈13 Hz, J_2 ≈3.5 Hz), 1.70 („qt", 1H, H-5_{ax}, J_1 = 13.2 Hz, J_2 = 3.5 Hz) 1.84 (dm, 1H, H_{eq}, J_1 ≈13 Hz), 1.90 (dm, 1H, H_{eq}, J_1 ≈ 13 Hz), 3.30 (s, br, 2H, 2 OH), 3.62 (dd, 1H, H-2_{ax}, J_1 = 8.7 Hz, J_2 = 3.1 Hz), 4.02 (dt, 1H, H-3_{eq}, J_1 = 3.5 Hz, J_2 = 3 Hz), 4.12 (ddd, 1H, H-1_{ax}, J_1 = 11 Hz, J_2 = 8.9 Hz, J_3 = 4.5 Hz). ^{13}C NMR: δ [ppm] 18.27 (CH_2), 26.38 (CH_3), 27.40 (CH_2), 29.41 (CH_2), 69.51 (CH-O), 75.83 (CH-O), 80.90 (C-OO), 82.53 (CH-OO).

(2*S,3*R**,4*R**)-2-*tert*-Butylperoxy-3,4-dihydroxytetrahydrofuran (25):** As mentioned above 128 mg (0.8 mmol) **3** were oxidized. After chromatography (n-hexane/EtOAc 2:1) 89 mg (58%) pure **25** were isolated as colourless oil. Elemental analysis: $C_8H_{16}O_5$ (192.21); calc.: C, 49.99; H, 8.39; found: C, 49.65; H, 8.52%. ^{1}H NMR: δ [ppm] 1.24 (s, 9H, ^{t}Bu), 2.80 (s, br, 1H, OH), 3.10 (s, br, 1H, OH), 3.93 (dd, 1H, CH_2O, J_1 = 10.2 Hz, J_2 = 2.3 Hz), 4.15 (m, 2H), 4.31 (m, 1H, H-4), 5.38 (d, 1H, H-2, J = 2.5 Hz).

(2*R,3*S**,4*R**) and (2*S**,3*S**,4*R**)-4-*tert*-Butylperoxy-2,3-dihydroxytetrahydrofuran (26a,b):** Following the general procedure 130 mg (0.82 mmol) **4** were oxidized and gave 40 mg (25%, colourless oil) **26a,b** as mixture of epimers (**26a**:**26b** = 2:1, determined by ^{1}H NMR spectroscopy) after chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_8H_{16}O_5$ (192.21); calc.: C, 49.99; H, 8.39; found: C, 49.45; H, 8.32%. ^{1}H NMR (mixture of **26a,b**): **26a:** δ [ppm] 1.23 (s, 9H, ^{t}Bu), 2.83 (s, br, 1H, OH), 3.79 (s, br, 1H, OH), 3.81 (dd, 1H, H-5$_{syn}$, J_1 = 10.4 Hz, J_2 = 2.5 Hz), 4.18 (dd, 1H, H-5$_{anti}$, J_1 = 10.4 Hz, J_2 = 5.4 Hz), 4.27 (m, 1H, H-3$_{syn}$), 4.52 (dt, 1H, H-4, J_1 = 5.3 Hz, J_2 = 2.5 Hz), 5.40 (dd, 1H, H-2$_{syn}$, J_1 = 4.2 Hz, J_2 = 3.8 Hz {OH-coupling, signal changes to dublett with D_2O}). **26b**: δ [ppm] 1.23 (s, 9H, ^{t}Bu), 3.27 (d, br, 1H, OH, J = 9 Hz), 3.74 (s, br, 1H, OH), 4.05 (dd, 1H, H-5$_{syn}$, J_1 = 10.6 Hz, J_2 = 2.4 Hz), 4.19 (dd, 1H, H-5$_{anti}$, J_1 = 10.6 Hz, J_2 = 5.5 Hz), 4.40 (m, 1H, H-3$_{syn}$), 4.49 (ddd, 1H, H-4, J_1 = 5.5 Hz, J_2 = 2.4 Hz, J_3 = 1.5 Hz), 5.18 (d, 1H, H-2$_{anti}$, J = 9 Hz {OH-coupling, signal changes to singlet with D_2O}).

(2*S,3*R**,4*R**)-2-*tert*-Butylperoxy-3,4-dihydroxytetrahydropyran (22c):** According to the procedure above 88 mg (0.51 mmol) **5** were oxidized yielding 65 mg (61%) pure **22c** as colourless oil after chromatography (n-hexane/EtOAc 2:1). Elemental analysis: $C_9H_{18}O_5$ (206.23); calc.: C, 52.41; H, 8.80; found: C, 52.30; H, 8.95%. ^{1}H NMR: δ [ppm] 1.26 (s, 9H, ^{t}Bu), 1.79 (m, 2H, 2 H-5), 2.99 (s, br, 2H, 2 OH), 3.64 (dd, 1H, H-3$_{syn}$, J_1 = 5.4 Hz, J_2 = 3.3 Hz), 3.83 (m, 2H, 2 H-6), 4.00 (dt, 1H, H-4$_{syn}$, J_1 = 6.6 Hz, J_2 = 3.8 Hz), 5.15 (d, 1H, H-2, J = 5.4 Hz).

(2*R,3*S**,4*R**) and (2*S**,3*S**,4*R**)-4-*tert*-Butylperoxy-2,3-dihydroxytetrahydropyran (27a,b):** According to the general procedure 172 mg (1 mmol) **6** were oxidized. After column chromatography (n-hexane/EtOAc 2:1) 78 mg (38%, colourless oil) **27a,b** were isolated as mixture of epimers (**27a**:**27b** = 2:1, determined by ^{1}H NMR spectroscopy). Elemental analysis: $C_9H_{18}O_5$ (206.23); calc.: C, 52.41; H, 8.80; found: C, 52.41; H, 8.85%. ^{1}H NMR (mixture of **27a,b**): **27a**: δ [ppm] 1.24 (s, 9H, ^{t}Bu), 1.64 (m, 1H, H-5$_{ax}$), 1.97 (m, 1H, H-5$_{eq}$), 2.90 (s, br, 2H, 2 OH), 3.46 (m, 1H, H-6$_{eq}$), 3.70 (dd, 1H, H-3$_{ax}$, J_1 = 8.4 Hz, J_2 = 3.1 Hz), 3.95 ("t"d, 1H, H-6$_{ax}$, $J_1 \approx$ 11 Hz, J_2 = 3 Hz), 4.24 (ddd, 1H, H-4$_{ax}$, J_1 = 9.6 Hz, J_2 = 8.4 Hz, J_3 = 4.8 Hz), 5.19 (d, 1H, H-2$_{eq}$, J = 3.1 Hz). **27b**: δ [ppm] 1.23 (s, 9H, ^{t}Bu), 1.70 (m, 1H, H-5$_{ax}$), 2.00 (m, 1H, H-5$_{eq}$), 2.90 (s, br, 2H, 2 OH), 3.46 (m, 1H, H-3$_{ax}$), 3.65 (m, 1H, H-6$_{ax}$), 3.95 (m, 1H, H-6$_{eq}$), 4.02 (ddd, 1H, H-4$_{ax}$, J_1 = 11 Hz, J_2 = 9 Hz, J_3 = 4.5 Hz), 4.53 (d, 1H, H-2$_{ax}$, J = 7 Hz).

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