Steric and Electronic Effects in the Diastereoselective Catalytic Epoxidation of Cyclic Allylic Alcohols with Methyltrioxorhenium (MTO)

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The steric effects of allylic substituents in the epoxidations with methyltrioxorhenium/urea/hydrogen peroxide adduct (MTO/UHP) have been assessed for a series of 3-alkyl-substituted cyclohexenes. The *trans* selectivity increases with the size of the substituent and the diastereoselectivities follow an excellent linear correlation with the steric substituent constants of Taft (E_s) or Charton (ν). Good *cis* selectivity is observed in the epoxidation of the cyclic allylic alcohols 2-cyclopentenol and 2-cyclohexenol due to a hydroxy-directing effect through hydrogen bonding; however, for 2-cycloheptenol and 2-cyclooctenol hydrogen bonding is ineffective and steric interactions cause a higher *trans* selectivity. The conformationally fixed *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenols serve as suitable substrates for gauging the dihedral angle of the transition states for the oxygen transfer in these epoxidations. Thus, the MTO/UHP oxidant favours a *quasi-equatorial* arrangement of the hydroxy group for effective hydrogen bonding (hydroxy-group directivity), in analogy to *m*-chloroperbenzoic acid (*m*-CPBA) and dimethyldioxirane (DMD), and a dihedral angle of ca. 130° is suggested.

Introduction

The control of chemo-, regio-, and diastereoselectivity in oxidations is a key feature in organic synthesis[1], and can be accomplished with a wide variety of stoichiometric or catalytic oxidants. These oxidants include the stoichiometric peracids and dioxiranes, and catalytic systems with transition-metal catalysts.[1][2]

Over the last few years, methyltrioxorhenium (MTO) has been shown to be an efficient and versatile oxidation catalyst with interesting selectivity behaviour. High chemoselectivity is observed in MTO-catalysed sulfoxidations and Si−H insertions;[3] regioselectivity is displayed in the oxidation of geraniol,[4] which is oxidised preferentially to the 6,7-epoxide rather than to the 3,4-epoxide, and in the oxidation of 2-methylnaphthalene to Vitamin K_3.[5] The regio- and diastereoselectivities observed in the epoxidation of allylic alcohols are of particular interest, as they give insight into the transition-state geometry.[4]

The transition states of epoxidations are affected by both the steric and the electronic influences of substituents, and these determine the sense and the extent of the diastereoselectivity. In the epoxidation of chiral cyclic allylic alcohols it has been shown that steric and electronic factors and, thus, the diastereoselectivity, depend on both the oxidising agent and the ring size,[2d,6] for which the dihedral angle α (C=C−C−O) plays a pivotal role. The dihedral angle may be gauged from the diastereoselectivities observed in the oxidation of the conformationally fixed allylic alcohols *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenol. Based on the diastereoselectivity of the oxidation of these substrates with various oxidants, the preferred dihedral angles of each oxidant may be estimated. The VO(acac)$_2$-catalysed epoxidation was shown to favour a quasi-axial hydroxy conformation[6b] and, hence, a dihedral angle α of 40−50°, while for epoxidations with *m*-chloroperbenzoic acid (*m*-CPBA) and dimethyldioxirane (DMD) a quasi-equatorial arrangement of the hydroxy group is preferred[6b,6c] with a dihedral angle $130° < \alpha < 140°$ for cyclic allylic alcohols.[1a,6c]

In order to differentiate between the steric and electronic factors which act in the hydroxy-directing effect of allylic substituents in MTO-catalysed epoxidations, a set of 2-cycloalkenols of varying ring size and cyclohexene derivatives, which bear alkyl or hydroxy functionalities in the allylic position, were studied. The observed selectivities were compared to those of the reported stoichiometric oxidants *m*-CPBA and DMD in order to deduce a likely dihedral angle and therewith a plausible transition-state geometry. Structural fine-tuning was probed through the angular dependence of the diastereoselectivity for the conformationally fixed *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenols.

Results and Discussion

The series of 3-alkyl-substituted cyclohexenes **1a−d** (Table 1) provide a quantitative measure of purely steric effects for the MTO-catalysed epoxidations, since electronic interactions with the allylic substituent are not possible.

No differences in the *cis*/*trans* ratios between the two MTO-based systems MTO/UHP (UHP = urea/hydrogen peroxide adduct) and MTO/H_2O_2 (30%)/pyridine were observed within the experimental error. As is evident, the *trans* diastereoselectivity increases with increasing size of the allylic alkyl substituent. When the *trans*/*cis* ratios were plotted against the Taft steric substituent constants E_s[11] (Figure 1) or the Charton steric parameter ν[11] (data not shown), which are both linear functions of the van der Waals radii

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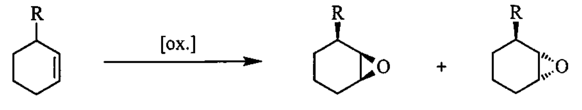
Table 1. Epoxidation of the 3-alkyl-substituted cyclohexenes **1a−d**



1a-d *cis*-**(6a-d)** *trans*-**(6a-d**

Entry	R		[a]	MTO/UHP	MTO/H_2O_2[b]	*m*-CPBA[c]	DMD[d]
1	Me	(**1a**)	convn.	31	82	81	≥ 99
			m.b.	82	63	81	≥ 99
			d.r.	49:51	50:50	48:52	52:48
2	Et	(**1b**)	convn.	62	−	92	≥ 99
			m.b.	≥ 95	−	92	≥ 99
			d.r.	46:54	−	53:47	45:55
3	*i*Pr	(**1c**)	convn.	53	−	−	59
			m.b.	≥ 95	−	−	59
			d.r.	27:73	−	−	22:78
4	*t*Bu	(**1d**)	convn.	88	≥ 95	75	94
			m.b.	91	91	75	≥ 99
			d.r.	9:91	7:93	10:90	5:95

[a] Conversions, mass balances, and diastereomeric ratios (*cis*/*trans*) were determined by ^{1}H-NMR spectroscopy and are given in%; error ca. ± 5% of stated values. − [b] In the presence of 12 mol-% pyridine. − [c] For Entry 1 see ref.[7]; for Entry 2 see ref.[8]; for Entry 4 see ref.[9] − [d] For Entries 1, 2, 4 see ref.[10]

of the substituents,[12] excellent linear correlations were obtained, with correlation coefficients r^2 = 0.992 (E_s) and 0.996 (ν). The selectivities for the epoxidation of the cyclohexenes **1a−d** by DMD obey a similar correlation with the Taft E_s values (r^2 = 0.980), albeit with a larger absolute value for the slope (|*m*| = 0.828) than is observed with MTO/UHP (|*m*| = 0.636). As expected, DMD is slightly more sensitive to steric effects than MTO/UHP, and this may be explained by the fact that the C−O bond length (138.8 pm[13]) in the dioxirane is shorter by ca. 30% than the Re−O ones (190.4 and 191.8 pm[14]) in the peroxorhenium functionality. In the case of *m*-CPBA, the slope of the correlation line (|*m*| = 0.636) is the same as that of the rhenium catalyst and demonstrates that the steric influences on both oxidation systems are comparable.

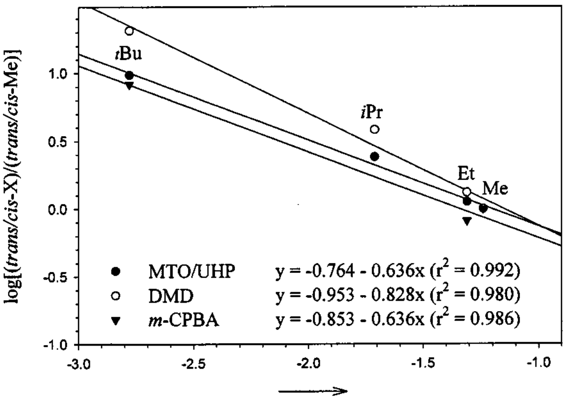
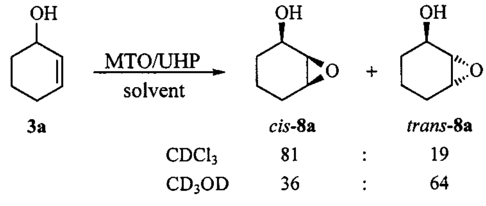


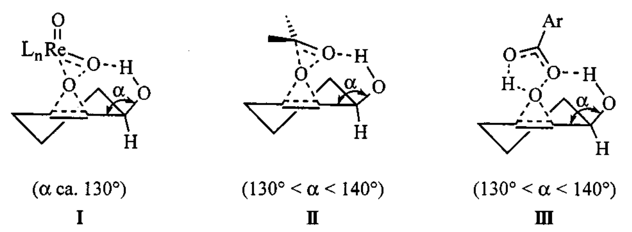
Figure 1. Diastereoselectivity (*trans*/*cis*) in the epoxidation of 3-alkyl-substituted cyclohexenes **1a−d** versus Taft's steric substituent constant E_s

While only steric effects operate in the MTO-catalysed epoxidation of the 3-alkyl-substituted cyclohexenes **1a−d** and are responsible for the *trans* selectivity obtained for **1c**, **d**, these influences cannot explain the high *cis* selectivity observed for the corresponding allylic alcohol derivative **3a** (Scheme 1), as the size of the hydroxy functionality should be comparable to that of a methyl substituent. A hydroxy-directing effect is at work, which through hydrogen bonding steers the oxidant to the *cis* π face of the double bond with respect to the allylic hydroxy group. That the interaction between the hydroxy substituent of allylic alcohols and the oxidant involves hydrogen bonding was recently shown for a set of acyclic allylic alcohols with 1,3-allylic strain.[4] The inversion in the diastereoselectivity (Scheme 1) in $CDCl_3$ versus [D$_4$]methanol supports the proposed hydrogen-bonding mechanism. The CD_3OD intervenes through external hydrogen bonding in the association between the substrate and oxidant. Thus, CD_3OD, which is present in a large excess, intervenes with the hydrogen bonding between the substrate and the oxidant, and, therefore, the transition state **I** (Figure 2) no longer applies. Instead of electronic effects, steric ones dominate to account for the appreciable *trans* selectivity.



Scheme 1. Solvent dependence in the MTO-catalyzed diastereoselective (*cis*/*trans*) epoxidation of 2-cyclohexenol (**3a**)

The cyclic allylic alcohols **2−5** in Table 2 have been chosen to assess the competition between electronic (*cis* selectivity through hydrogen bonding) and steric (*trans* selectivity) effects by comparison with the standard oxidants DMD and *m*-CPBA. For the latter, the mechanism of oxygen-transfer through assisted hydrogen bonding (Figure 2)



(α ca. 130°) **I**

(130° < α < 140°) **II**

(130° < α < 140°) **III**

Figure 2. Transition states for the epoxidation of 2-cyclohexenol (**3a**) by MTO/UHP and MTO/H_2O_2 (30%)/pyridine (**I**), DMD (**II**), and *m*-CPBA (**III**)

is well established.[2m] The dihedral angle α (C=C−C−O) will dictate whether hydrogen bonding is involved, which is a function of the favoured conformation. For this set of conformationally flexible cycloalkenols the α angle varies systematically from 120° to 199°,[6b,6c] as displayed in the favoured ground-state conformations in Table 2. The data for MTO (Entries 1, 2, 5, 8, and 12) show a regular trend: With increasing dihedral angle α the diastereoselectivity changes from 80:20 (Entries 1 and 2) for **2** (α ca. 120°) to ≤ 5:95 (Entry 12) for **5** (α ca. 199°). Thus, the pronounced *cis* selectivity for cyclopentenol **2** displays control through hydrogen bonding between the allylic hydroxy functionality and the peroxorhenium complex similar to the transition-state structure **I** in Figure 2, while the exclusive *trans* selectivity for cyclooctenol **5** speaks for purely steric interactions. That in the latter case steric rather than electronic interactions dominate is demonstrated by the lack of solvent effects. In $CDCl_3$ as well as in CD_3OD the same high (*cis*/*trans* = 5:95) *trans* selectivity is observed, a finding that cannot be reconciled in terms of hydrogen bonding. Analogous trends apply to DMD (Entries 3, 6, 10, and 13) and *m*-CPBA (Entries 4, 7, 11, and 14), commensurate with the hydrogen-bonded transition-state geometries **II** and **III** (Figure 2).

The shortcoming of these conformationally flexible cycloalkenols **2−5** is that the optimal dihedral angle α for stereoselective oxygen transfer is difficult to be reliably defined and recourse must be taken in rigid derivatives, namely the *tert*-butyl-substituted ones **3b**, **c** (Table 3). Thus, for *trans*-5-*tert*-butyl-2-cyclohexenol (**3b**) the dihedral angle is 110°, for the *cis* isomer **3c** it is 140°,[6c] with the hydroxy group in the pseudo-axial position for **3b** and pseudo-equatorial for **3c**. As for the flexible 2-cycloalkenols **2**, **3a**, **4**, and **5**, the oxidation of the rigid **3b**, **c** by MTO/UHP also proceeded cleanly in good yields to the *syn*- and *anti*-epoxides **8b**, **c** without any enone formation (Table 3, Entries 1, 3, 7, 9). With MTO/H_2O_2 (30%)/pyridine (Entries 2 and 8) as oxidant the yields are better than with MTO/UHP (Entries 1 and 7); however, minor amounts of the enone **12b** were obtained. In the nonprotic $CDCl_3$ solvent, the *syn*-epoxides **8b**, **c** were obtained preferentially with no significant difference in the diastereoselectivities between the two MTO-based oxidants. The diastereoselectivity is slightly higher for the *cis* substrate **3c** (*syn*/*anti* 84:16 and 80:20; Entries 7 and 8) than for *trans* one **3b** (*syn*/*anti* 72:28; Entries 1 and 2). As for the solvent effects with **3c**, the *syn*/*anti* ratio is diminished from 84:16 ($CDCl_3$; Entry 7) to 50:50 (CD_3OD; Entry 9), while for **3b** it is even reversed from *syn*/*anti* 72:28 ($CDCl_3$; Entry 1) to 15:85 (CD_3OD; Entry 3). These data once more emphasize the importance of hydrogen bonding in the stereocontrol of oxygen transfer for these substrates. Thus, if the hydroxy-directing effect is suppressed in protic solvents, steric influences become more important in determining the *syn*/*anti* ratio and even result in *anti* selectivity in the case of **3b** with MTO/UHP (Entry 3). Similar behaviour is observed in the epoxidation of the diastereomeric substrates **3b**, **c** by DMD (Entries 4, 5, 10, 11) and by *m*-CPBA (Entries 6 and 12) and, therefore, the similar hydrogen-bonded transition-state structures **I−III** apply (Figure 2). However, as the difference in the diastereoselectivities for **3b**, **c** with the MTO oxidants (Entries 1, 2, 7, and 8) is smaller than with DMD (Entries 4 and 10) or *m*-CPBA (Entries 6 and 12), a slightly smaller dihedral (α ca. 130°) is suggested for MTO/UHP and MTO/H_2O_2 (30%)/pyridine than for DMD or *m*-CPBA (130° < α < 140°).[1a,6c,17]

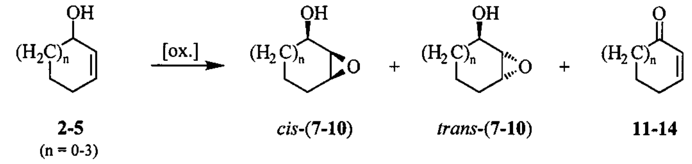
The present study demonstrates that the conformationally fixed *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenols (**3b**, **c**) serve as useful stereochemical probes to explore the transition-state geometry of metal-catalysed oxidations, in the present case the epoxidation with the MTO/UHP and MTO/H_2O_2 oxidants. Such stereochemical studies provide valuable mechanistic data on the steric and electronic effects in oxygen-transfer processes.

Experimental Section

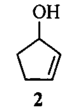
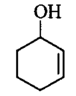
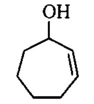
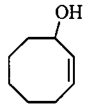
General: ^1H- and ^{13}C-NMR spectra were measured with a Bruker AC 200 (^1H-NMR: 200 MHz, ^{13}C-NMR: 50 MHz) and AC 250 (^1H-NMR: 250 MHz, ^{13}C-NMR: 63 MHz) with $CDCl_3$ or CD_3OD as internal standards. For TLC runs, precoated silica-gel foils 60 F_{254} (5 × 10 cm) from Merck were used. Spots were visualized by irradiation under a UV lamp or by treatment with the phosphomolybdic acid test spray. For peroxide tests, potassium iodide/starch paper from Merck was used. The mass balances were determined gravimetrically or by ^1H-NMR spectroscopy, and the conversions and diastereomeric ratios only by the latter, with naphthalene as internal standard. − Solvents and commercially available chemicals were purified by standard procedures. Hydrogen peroxide was employed as the urea adduct (UHP) or as a 30% aqueous solution. Dimethyldioxirane (DMD)[18] and methyltrioxorhenium (MTO)[19] were prepared according to literature procedures, as were also the 3-alkyl-substituted cyclohexenes **1b**,[20] **1c**,[21] and **1d**[22] and the conformationally fixed *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenols (**3b**, **c**).[23] The cyclic alcohols 2-cyclopentenol (**2**),[24] 2-cyclohexenol (**3a**),[25] and 2-cyclooctenol (**5**)[26] were synthesized by photooxygenation of the corresponding cycloalkenes and subsequent reduction with triphenylphosphane according to literature procedures.[2i]

3-Methylcyclohexene (1a): A Grignard reagent was prepared from 1.80 g (74.0 mmol) of magnesium turnings in 10 mL of diethyl ether and 7.8 mL (124 mmol) of methyl iodide. A solution of 10.0 g (62.1 mmol) of bromocyclohex-2-ene in 15 mL of diethyl ether was added dropwise to the reaction mixture and stirred for 2 h. After aqueous work-up, the reaction mixture was extracted with diethyl ether (3 × 100 mL), the combined organic phases were washed with sat. NH_4Cl (50 mL), H_2O (50 mL), and sat. NaCl (50

Table 2. Diastereoselectivities (*cis*/*trans*) in the epoxidation of the cycloalkenols **2−5**



2-5 (n = 0-3) *cis*-(**7-10**) *trans*-(**7-10**) **11-14**

entry	substrate[b]	oxidant	solvent	mass balance[a] [%]	convn[a] [%]	selectivity[a]			ref
						chemo enone	chemo epoxide	diastereo (*cis*:*trans*)	
1	 **2** (envelope, 120°)	MTO/UHP	$CDCl_3$	≥95	52	≤5	95	80 : 20	[c]
2		MTO/H_2O_2[d]	$CDCl_3$	79	93	≤5	95	83 : 17	[c]
3		DMD	acetone	≥95	≥95	22	78	52 : 48	[c]
4		*m*-CPBA	CH_2Cl_2	≥99	80	≤1	99	84 : 16	6b
5	 **3a** (half chair, 139°)[f]	MTO/UHP	$CDCl_3$	≥95	76	≤5	95	81 : 19[e]	[c]
6		DMD	acetone	≥95	≥95	30	70	47 : 53	16
7		*m*-CPBA	CH_2Cl_2	≥99	83	≤1	99	95 : 5	6b
8	 **4** (chair, 180°)	MTO/UHP	$CDCl_3$	71	92	≤5	95	45 : 55	[c]
9		MTO/H_2O_2[d]	$CDCl_3$	72	≥95	≤5	95	37 : 63	[c]
10		DMD	acetone	≥95	72	38	62	33 : 67	[c]
11		*m*-CPBA	CH_2Cl_2	≥99	95	≤1	99	61 : 39	6b
12	 **5** (199°)	MTO/UHP	$CDCl_3$	≥95	89	≤5	95	≤5 : 95[g]	[c]
13		DMD	acetone	≥95	≥95	≤5	95	≤5 : 95	16
14		*m*-CPBA	CH_2Cl_2	≥99	81	≤1	99	≤1 : 99	6b

[a] Determined by ^{1}H-NMR spectroscopy; error ca. ±5% of stated values. − [b] In parentheses are given the favoured ground-state conformations (cf. ref.[15]) and dihedral C=C−C−O angles α (determined by AM1 calculations). − [c] This work. − [d] In the presence of 12 mol-% pyridine. − [e] In [D$_4$]methanol the *cis*/*trans* ratio is 36:64. − [f] See ref.[6c] − [g] In [D$_4$]methanol the *cis*/*trans* ratio is 5:95.

mL), dried with $MgSO_4$, and the solvent was removed under reduced pressure (0°C/200 mbar). The crude product was purified by fractional distillation (bp 97−98°C; ref.[27] bp 101°C) to yield 2.68 g (31%) of a colorless oil. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (d, J = 7.1 Hz, 3 H, CH_3), 1.40−2.26 (m, 7 H, 3-H, 4-H, 5-H, 6-H), 5.47−5.65 (m, 2 H, 1-H, 2-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 21.7, 25.1 (2 t, 1 q, C-4, C-5, CH_3), 30.1 (d, C-3), 31.3 (t, C-6), 126.3 (d, C-1), 133.5 (d, C-2).

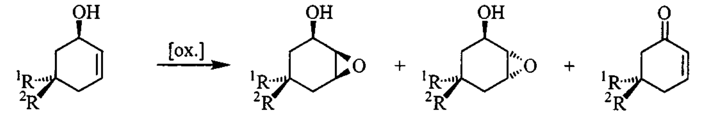
2-Cycloheptenol (4):[28] A solution of 2.6 mL (22.5 mmol) of cycloheptene and ca. 5 mg of tetraphenylporphine in 35 mL of dichloromethane was irradiated with two external Philips G 198/2 SON 250-W sodium lamps at −15°C for 3 h while a slow stream of dry oxygen gas was passed continuously through the reaction mixture. The hydroperoxide was then reduced with triphenylphosphane (1.0 equiv.) at 0°C, the reaction mixture warmed up to ambient temperature (ca. 20°C), and stirred until the peroxide test (KI/HOAc) was negative. After removal of the solvent under reduced pressure (0°C/50 mbar), the crude material was purified by flash chromatography over silica gel [petroleum ether (boiling range 30−50°C)/diethyl ether, 4:1; R_f = 0.45] to yield 1.89 g (45%) of a colourless oil. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.23−2.63 (m, 8 H, 4-H, 5-H, 6-H, 7-H), 4.37 (dm, J = 6.6 Hz, 1 H, 1-H), 5.63−5.80 (m, 2 H, 2-H, 3-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.6, 26.8, 28.6 (3 t, C-5, C-6, C-7), 36.6 (t, C-4), 72.1 (d, C-1), 130.0 (d, C-2), 137.8 (d, C-3).

General Epoxidation Procedure with MTO/UHP: To a solution of the MTO catalyst (1 mol-%) in deuteriochloroform or [D$_4$]methanol (0.6 mL) was added the urea/hydrogen peroxide adduct (1.0 equiv.). The resulting mixture was stirred for 10 min before addition of the alkene (0.33 mmol; 1.0 equiv.). After stirring at ambient temperature for 6−24 h, the crude reaction mixture was submitted to ^{1}H- and ^{13}C-NMR analysis, with naphthalene as internal standard for the former (error ± 5%). The quantitative product data are given in Tables 1−3.

General Epoxidation Procedure with MTO/H_2O_2 (30%)/Pyridine: To the allylic alcohol (0.33 mmol) were added solutions of MTO (0.5 mol-%; 32.1 mM solution in deuteriochloroform) and pyridine (12 mol-%; 352 mM solution in deuteriochloroform). Subsequently, 1.5 equiv. of 30% H_2O_2 was added at 0°C and the reaction mixture stirred at ambient temperature (ca. 20°C) for 24 h. The crude reaction mixture was analyzed by ^{1}H- and ^{13}C-NMR spectroscopy, with naphthalene as internal standard for the former (error ± 5%). The quantitative product data are given in Tables 1−3.

Epoxidation of 3-Isopropylcyclohexene (1c) by DMD: To 800 mg (6.44 mmol) of the alkene **1c** in acetone (10 mL) was added dropwise 1.1 equiv. of dimethyldioxirane (0.080 M solution in acetone) at ambient temperature (ca. 20°C). The solution was stirred at ca. 20°C for 2 h and the solvent removed (40°C/18 mbar). The crude product mixture was dried with $MgSO_4$, the remaining solvent re-

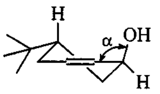
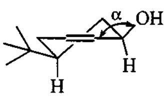
Table 3. Diastereoselectivities (*syn*/*anti*) in the epoxidation of the conformationally fixed cyclohexenols **3b**, **c**



3b,c *syn*-**8b,c** *anti*-**8b,c** **12b**

3b: $R^1 = t$Bu; $R^2 = H$

3c: $R^1 = H$; $R^2 = t$Bu

entry	substrate[b]	oxidant	solvent	mass balance[a] [%]	convn[a] [%]	selectivity[a] chemo		diastereo	ref
						enone	epoxide	(*syn*:*anti*)	
1		MTO/UHP	$CDCl_3$	≥95	75	≤5	95	72 : 28	[c]
2		MTO/H_2O_2[d]	$CDCl_3$	≥95	≥95	17	83	72 : 28	[c]
3		MTO/UHP	CD_3OD	≥95	25	≤5	95	15 : 85	[c]
4		DMD	CCl_4/acetone (9:1)	≥95	≥95	33	67	58 : 42	6c
5	**3b** (α ca. 110°)	DMD	MeOH/acetone (9:1)	≥95	92	15	85	29 : 71	6c
6		*m*-CPBA	CH_2Cl_2	≥99	92	3	97	90 : 10	6b
7		MTO/UHP	$CDCl_3$	≥95	77	≤5	95	84 : 16	[c]
8		MTO/H_2O_2[d]	$CDCl_3$	82	≥95	9	91	80 : 20	[c]
9		MTO/UHP	CD_3OD	≥95	83	≤5	95	50 : 50	[c]
10		DMD	CCl_4/acetone (9:1)	≥95	≥95	43	57	82 : 18	6c
11	**3c** (α ca. 140°)	DMD	MeOH/acetone (9:1)	≥95	60	20	80	38 : 62	6c
12		*m*-CPBA	CH_2Cl_2	≥99	93	≤1	99	98 : 2	6b

[a] Determined by ^1H-NMR spectroscopy; error ca. ± 5% of stated values. – [b] In parentheses the preferred dihedral C=C−C−O angles α (cf. ref.[6c]). – [c] This work. – [d] In the presence of 12 mol-% pyridine.

moved under reduced pressure, and purified by fractional Kugelrohr distillation (60−80°C/40 mbar) to afford 533 mg (59%) of a mixtures of the epoxides *cis*- and *trans*-**6c** as a colourless oil. The diastereomeric ratio (22:78) was determined by ^1H-NMR spectroscopy (error limit ± 5%) and gas chromatography.

(1*S,2*R**,3*R**)-3-Isopropyl-1,2-epoxycyclohexane (*cis*-6c):** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94 [d, J = 6.7 Hz, 3 H, $CH(CH_3)_2$], 1.02 [d, J = 6.7 Hz, 3 H, $CH(CH_3)_2$], 1.11−2.11 [m, 8 H, 3-H, 4-H, 5-H, 6-H, $CH(CH_3)_2$], 3.07−3.14 (m, 2 H, 1-H, 2-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.8, 20.4 [2 q, $CH(CH_3)_2$], 20.5, 20.6, 23.7 (3 t, C-4, C-5, C-6), 31.0 [d, $CH(CH_3)_2$], 42.0 (d, C-3), 52.0, 54.6 (2 d, C-1, C-2).

(1*R,2*S**,3*R**)-3-Isopropyl-1,2-epoxycyclohexane (*trans*-6c):** ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 [d, J = 6.7 Hz, 3 H, $CH(CH_3)_2$], 0.96 [d, J = 6.7 Hz, 3 H, $CH(CH_3)_2$], 1.11−2.11 [m, 8 H, 3-H, 4-H, 5-H, 6-H, $CH(CH_3)_2$], 2.90 (dm, J = 4.0 Hz, 1 H, 1-H), 3.07−3.14 (m, 1 H, 2-H; overlaps with signals of *cis* isomer). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.5, 19.3[2 q, $CH(CH_3)_2$], 22.2, 23.6, 25.1 (3 t, C-4, C-5, C-6), 31.0 [d, $CH(CH_3)_2$], 40.5 (d, C-3), 52.9, 55.3 (2 d, C-1, C-2). – $C_9H_{16}O$ (140.3): calcd. C 77.08, H 11.51; found C 76.73, H 11.08.

The allylic alcohols **2** and **4** (1.00−2.00 mmol) were epoxidized with DMD analogous to olefin **1c**. The mass balance was determined gravimetrically and the conversions and diastereomeric ratios by ^1H NMR. The quantitative product data are given in Table 2.

The epoxides **6a**,[10] **6b**,[10] **6d**,[9][10] **7**,[29] **8a**,[10] **8b**,[6c] **8c**,[6c] **9**,[30] **10**,[31] and the enones **11**,[32] **12a**,[33] **12b**,[6c] **13**,[34] and **14**[35] were identified by comparison of their characteristic ^1H- and ^{13}C-NMR signals with literature data.

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