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Solvent Effects in the Dimethyldioxirane Oxidation of Allylic Alcohols: Evidence for Hydrogen Bonding in the Dipolar Transition State of Oxygen Transfer

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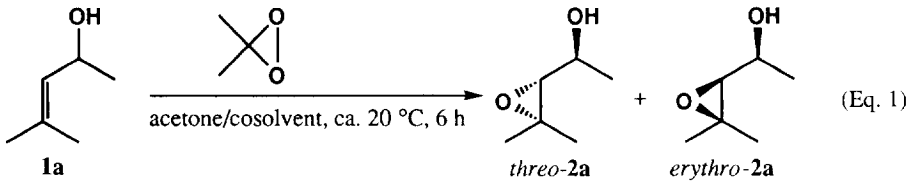
Abstract: A notably higher diastereoselectivity is observed in the dimethyldioxirane epoxidation of chiral allylic alcohols when less polar solvent mixtures are employed; this is interpreted in terms of a dipolar transition state with OH association through hydrogen bonding to the dioxirane, for which a preferential dihedral angle of >130° is estimated.

The advantages of dioxiranes, especially the isolated dimethyldioxirane (DMD), in synthetic chemistry has been well-documented in olefin epoxidations, heteroatom oxidations and CH insertions during the last years[2]. The preparation of isolated DMD (as acetone solution) is simple[3] and the reaction procedure is convenient to afford the desired products highly selectively and cleanly.

Despite the numerous application of dioxiranes in synthesis, questions remain in regard to the mechanism of the oxygen transfer in these various oxidations. For CH insertions, recently additional evidence for a radical pathway has been documented[4], whereas former results strongly supported an oxenoid-type insertion into the C-H σ bond[5]. With respect to heteroatom oxidations, we have shown that N oxidation proceeds by an S_N2-type mechanism rather than electron transfer[6]. That dioxiranes are indeed electrophilic oxidants, was established in the selective oxidation of thianthrene-5-oxide at the sulfide site[7]. In regard to epoxidations, evidence for a *spiro* transition state in the attack of DMD on the C-C double bond has been reported[8], but also in this case the electronic structure of the transition state was not detailed.

In this context, the possible generation of a dipolar transition state (heterolysis of the peroxide bond through nucleophilic attack) was the object of vivid discussion. Were this the case, a stabilizing influence by hydroxy groups could provide a hint for charge separation in the transition state through hydrogen bonding. In view of our success in employing stereochemical probes to assess directing effects of hydroxy groups in photooxygenations[9], we applied these to DMD epoxidations. The diastereoselectivities in the epoxidation of



1a *threo*-**2a** *erythro*-**2a** (Eq. 1)

chiral allylic alcohols were so much lower than for *m*CPBA, that a transition state with hydrogen bonding analogous to that for *m*CPBA was argued against for DMD, at least in acetone as solvent[10]. Nonetheless, the solvent effects observed on the rates of the epoxidation of ethyl *trans*-cinnamate strongly suggested partial

charge separation in the transition state for oxygen transfer[11]. Were the proposed dipolar transition state stabilized by the proximate hydroxy group in the chiral allylic alcohol, attack would be preferred from the diastereotopic face of the π bond on which the OH group is located. Thus, the lack of diastereoselectivity in the above-mentioned examples may arise through interference of the hydrogen bonding in the transition state by the polar solvent acetone. Indeed, recently it was reported[12] that the diastereoselectivity in the oxidation of cyclohex-2-enol can be notably affected by solvent tuning, i.e. the use the unpolar CCl_4 as cosolvent led to an enhanced *cis* selectivity. These results are very much in line with those we have already presented[1] in part and presently we report the details.

The oxidation of 4-methylpent-3-en-2-ol (Eq. 1) with dimethyldioxirane (1.1 equiv.) in acetone as solvent has been previously described[10]; the two diastereomeric epoxides are obtained in moderate selectivity. The same reaction was also carried out in different solvent mixtures through the addition of a cosolvent with different hydrogen bond capacities[13] than acetone (Table 1). This set of experiments reveals the same trend that was

Table 1: Solvent Effects in the Diastereoselectivity in Dimethyldioxirane Epoxidation of Allylic Alcohol **1a**

cosolvent	solvent ratio[a]	*threo*-**2a** : *erythro*-**2a** diastereoselectivity [%][b,c]
methanol	1:1	60 : 40
ethyl acetate	1:1	71 : 29
none	/	76 : 24
CCl_4	1:1	76 : 24
hexane	1:1	77 : 23
CCl_4	1:9	82 : 18
hexane	1:9	82 : 18

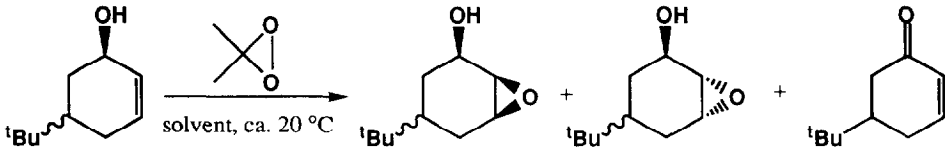
[a] Acetone and cosolvent mixtures. [b]Determined by ^{1}H NMR analysis directly on the crude product mixture (error ± 5% of the stated values). [c] Mass balances and conversions were in all cases >90%.

obtained in the oxidation of cyclohex-2-enol[12], i.e. the higher the hydrogen bonding capacity of the medium, the lower is the *threo* selectivity of the epoxidation. Nevertheless, the DMD diastereoselectivities are still remarkably lower (≤ 82:18) than those observed for *m*CPBA (95 : 5)[16].

To gain further insight into the geometry of the proposed H bonding in the transition state, we performed oxidations of the known[14] conformationally fixed cyclic allylic alcohols *trans*-**1b** and *cis*-**1b** (Table 2) in three solvent mixtures of different HBD capacity. For *trans*-**1b**, in which the OH functionality is located in the *pseudoaxial* position, *anti* attack is favored when the reaction was run in acetone/MeOH or pure acetone, whereas the selectivity is inverted to a modest *syn* selectivity in the acetone/CCl_4 (1:9) solvent mixture. A notable solvent effect is also observed for *cis*-**1b**; in this case the *anti* selectivity (38 : 62) observed for the mixture acetone/MeOH was inverted to a moderate *syn* selectivity of 60 : 40 in acetone and further enhanced to 82 : 18 when CCl_4 was employed as cosolvent.

Conclusive stereochemical evidence was obtained for the oxidation of isophorol (**1c**), in which the OH functionality is also located preferentially in the pseudoequatorial position,[15] under the above described conditions (Eq. 2).The *syn* diastereoselectivity of the epoxidation in this example is the highest of the three cyclic substrates employed in all three solvents. In fact, in the nonpolar solvent mixture (acetone/CCl_4), the diastereoselectivity is as high as the one observed for *m*CPBA[15]. In all herein examined oxidations of the cyclic

Table 2: DMD Oxidations of Conformationally Fixed Cyclohex-2-en-1-ols (**1b**)



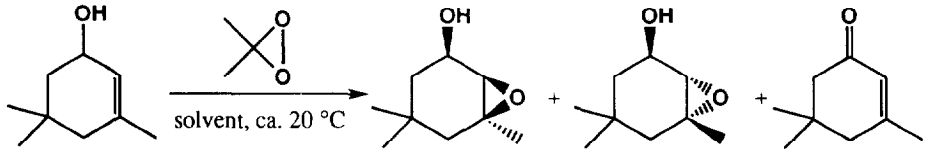
1b **2b** **3b**

substrate	solvent	time[a] [h]	diastereoselectivity[b,c] *syn* : *anti*	chemoselectivity[c] **2b** : **3b**
trans-**1b**	acetone/MeOH (1:9)	2 (92%)	29 : 71	85 : 15
trans-**1b**	acetone	10	30 : 70	58 : 42
trans-**1b**	acetone/CCl_4 (1:9)	8	58 : 42	67 : 33
cis-**1b**	acetone/MeOH (1:9)	2 (60%)	38 : 62	80 : 20
cis-**1b**	acetone	4	60 : 40	43 : 57
cis-**1b**	acetone/CCl_4 (1:9)	12	82 : 18	57 : 43

[a] Mass balances >95%, conversions >95%, unless noted in parenthesis [b] With respect to the OH group. [c] The data was determined by ^{1}H NMR analysis directly on the crude product mixture (error ± 5% of the stated values).

allylic alcohols the amount of enone formation (which will be discussed in detail separately) is highest in acetone and decreases in both solvent mixtures employed.

Table 3: Solvent Effect in the DMD Oxidation of Isophorol (**1c**)



(Eq. 2)

1c *cis*-**2c** *trans*-**2c** **3c**

solvent	time [h]	diastereoselectivity[a] *cis*-**2c** / *trans*-**2c**	product distribution[a,b] **2c** : **3c**
acetone/MeOH (1:9)	1.5	62 : 38	92 : 8[c]
acetone	0.5	83 : 17	77 : 23
acetone/CCl_4 (1:9)	12	96 : 4	92 : 8

[a] Determined by ^{1}H NMR analysis directly on the crude product mixture (error ± 5% of the stated values). [b] Mass balances and conversions were >95%. [c] Conversion 66%.

As already pointed out, the present[1] and previous[12] results of solvent effects clearly suggest an association of the dioxirane to the adjacent hydroxy functionality of the chiral allylic alcohols in the transition state through hydrogen bonding. Nevertheless, several facts indicate a somewhat different quality of hydrogen bonding with DMD compared to *m*CPBA. For instance, the solvent effect for *m*CPBA epoxidations is relatively small, i.e. even excellent hydrogen bonding solvents like alcohols do not perturb the existent strong association. This is different in the epoxidations performed by dimethyldioxirane. Furthermore, the results in Table 1 show that the solvent effect on the diastereoselectivity in the epoxidation of acyclic allylic alcohol (**1a**) is not as prominent as for the cyclic ones (Tables 2 and 3). Apparently, only conformationally fixed hydroxy groups as in cyclic

substrates can exert a significant effect, whereas the essentially freely rotating hydroxyethyl group of the acyclic substrate, although encumbered by 1,3-allylic strain, is less effective so that π-facial differentiation by attractive interactions such as hydrogen bonding is reduced and lower diastereoselectivity is the consequence.

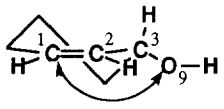
The results in Table 1 and Eq. 1 also provide valuable mechanistic information on the preferred orientation of hydrogen bonding for DMD. Since the oxidation of 4-*tert*-butylcyclohexene with DMD yields the corresponding epoxides quantitatively with no stereochemical preference (d.r. 50 : 50), the observed stereoselectivities for the allylic alcohols **1b** are solely a function of the electronic and steric influences exerted by the adjacent hydroxy group. For *trans*-**1b** mainly steric reasons are controlling the diastereoselectivity when the reaction is performed in either acetone/MeOH or pure acetone and, thus, the epoxidation occurs preferentially *anti* to the OH functionality. On the other hand, a slight *syn* selectivity is obtained in the less polar solvent mixture acetone/CCl_4. This solvent change promotes the association between DMD and the substrate and thereby inverts the sense in the diastereoselectivity, but the hydroxy functionality is not sufficiently well aligned to achieve high selectivity. In contrast, the allylic alcohols *cis*-**1b** and **1c** show a more pronounced solvent effect. For *cis*-**1b** again an *anti* selectivity is observed when the reaction is performed in the polar solvent mixture acetone/MeOH, in which mainly steric factors are conducting the π-facial attack. Due to the further outward pointing position of the OH functionality in *cis*-**1b** compared to *trans*-**1b**, the selectivity is lower for the former. Moreover, the solvent change from the acetone/MeOH mixture to pure acetone leads already to an inversion of the diastereoselectivity for *cis*-**1b** and when the unpolar acetone/CCl_4 medium is employed, a significantly higher *syn* selectivity is observed. The hydroxy functionality in these substrates is favorably oriented to allow a *contrasteric* preference through association even in acetone as solvent, an effect that is further substantiated in the unpolar acetone/CCl_4 solvent mixture.

Apparently, the C_1-C_2-C_3-O_9 dihedral angle of the hydroxy functionality with respect to the double bond in the cyclohexenols is decisive for stereocontrol; thus, AM1 calculations were performed on the ground state conformations to estimate these angles (Table 4). The data suggest that a dihedral angle of >130° is presumably

Table 4: Dihedral Angles in Cyclohex-2-en-1-ols

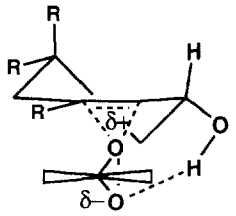
cyclohexenol	angle[a] [°]
parent (**1d**)	139.1
trans-**1b**	109.5
cis-**1b**	139.5
1c	137.1

[a] Determined by AM1 calculations



dihedral angle
C_1-C_2-C_3-O_9

Figure 1: Preferred Transition State Geometry



favorable for the association between the allylic hydroxy group and the dioxirane in the transition state for the oxygen transfer (Figure 1); for comparison, in the case of *m*CPBA epoxidations, this angle is ca. 120°[16]. Since the calculated dihedral angles of *cis*-**1b** and **1c** are approximately the same, if such geometrical effects were to operate exclusively, similar diastereoselectivities should be expected; nevertheless, although the trends and the sense are the same, significant differences in the extent of stereocontrol are noted. The higher substituted double bond in isophorol (**1c**) is more nucleophilic and charge transfer to the electrophilic dioxirane is further progressed along the transition state coordinate of this S_N2 process with resultant stronger polarization or more pronounced heterolysis of the peroxide bond. Consequently, the more negatively charged oxygen atom of the dioxirane moiety will form a stronger hydrogen bond with the hydroxy functionality, which is manifested by the higher diastereoselectivity.

In conclusion, the conformationally fixed chiral allylic alcohols **1** employed in the present study have served as useful stereochemical tool to explore the transition state structure of the dimethyldioxirane epoxidation. These useful probes allow to sense the efficiency of intramolecular hydrogen bonding between the allylic hydroxy group and the dioxirane moiety in the dipolar transition state, while fine-tuning of the diastereoselectivity can be achieved by changing appropriately the polarity and hydrogen-bonding ability of the medium. We contend that such stereochemical studies nicely complement kinetic ones to provide mechanistic insight into the complexities and intricacies of oxygen transfer processes not only for dioxirane, but generally.

Experimental Section

General Aspects

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer by using $CDCl_3$ as internal standard. Potassium iodide- starch paper (Merck) was used for peroxide tests. Dimethyldioxirane was prepared according to our described procedure[3], all starting materials (**1a**, *cis*-**1b**[14], *trans*-**1b**[14], **1c**[15]) were made according to literature-known procedures. The relative stereochemistry of the products was determined by comparison of the spectral data with those given in the literature or by indepent preparation according to literature procedures. Commercial compounds were used as received, solvents were purified and dried by reported standard methods.

General procedure for the oxidations of allylic alcohols by dimethyldioxirane: The allylic alcohols were dissolved in the required amount of the appropriate cosolvent and 1.0-1.1 equiv. of dimethyldioxirane (0.05-0.10 M solution in acetone) were rapidly added at room temperature (ca. 20 °C). The solution was stirred at room temperature, until the peroxide test was negative. The solvent was removed *in vacuo* (20 °C, 20 mbar) to yield a mixture of the corresponding epoxides and enones in high purity.

α,3,3-Trimethyl-2-oxiranemethanol (2a): According to the general procedure, the reaction of 72.0 mg (0.72 mmol) alcohol **1a** with a 0.93 M solution of dimethyldioxirane (8.00 mL, 74.0 mmol) in MeOH (8.0 mL) yielded 83.5 mg (99%) of the diastereomeric epoxides **2a**. *threo* -**2a** [(*S**, *R**)-**2a**]: ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 1.22 (d, *J* = 6.5 Hz, 3H), 1.28 (s, 3H), 1.31 (s, 3H), 2.54 (bs, 1H), 2.70 (d, *J* = 8.0 Hz, 1H), 3.62 (dq, J_1= 8.0 Hz, J_2= 6.5 Hz, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 19.0 (q), 19.2 (q), 24.9 (q), 59.4 (s), 67.0 (d), 68.5 (d). *erythro*-**2a** [(*S**, *S**)-**2a**]: ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 1.33 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.36 (s, 3H), 2.54 (bs, 1H), 2.62 (d, *J* = 7.9 Hz, 1H), 3.52 (dq, J_1= 7.9 Hz, J_2= 6.3 Hz, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 18.6 (q), 20.9 (q), 24.8 (q), 59.3 (s), 66.2 (d), 67.1 (d). For detailed reaction conditions and diastereoselectivities in the epoxidation of **1a**, cf. Table 1.

Epoxidation of Alcohol *trans*-1b: According to the general procedure, the reaction of 40.0 mg (0.27 mmol) alcohol *trans*-**1b** with a 0.062 M solution of dimethyldioxirane (4.40 mL, 0.27 mmol) in MeOH (39.6 mL) yielded 44.3 mg (100%) of a mixture of the diastereomeric epoxides **2b** and enone **3b**. (*1R**, *2R**, *4R**, *6S**)-4-(1,1-Dimethylethyl)-7-oxabicyclo[4.1.0]heptan-2-ol (**2b**): ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.80 (s, 9H), 1.23-2.14 (m, 6H), 3.06-3.10 (m, 1H), 3.24 (dd, J_1 = 5.4 Hz, J_2 = 3.6 Hz, 1H), 4.37 (d, *J* = 2.3 Hz, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 26.0 (t), 27.2 (q), 27.3 (t), 31.4 (s), 32.7 (d), 53.8 (d), 56.4 (d), 64.0 (d). (*1S**, *2R**, *4R**, *6R**)-4-(1,1-Dimethylethyl)-7-oxabicyclo[4.1.0]heptan-2-ol (**2b**): ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.80 (s, 9H), 1.19-2.11 (m, 6H), 3.25 (t, *J* = 4.4 Hz, 1H), 3.43 (bs, 1H), 4.18 m, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 24.5 (t), 27.1 (q), 27.9 (t), 31.7 (s), 35.1 (d), 53.1 (d), 53.6 (d), 65.9 (d). 5-(1,1-Dimethylethyl)-cyclohex-2-en-1-one (**3b**): ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.90 (s, 9H), 1.82-2.61 (m, 5H), 6.01 (d, *J* = 9.8 Hz, 1H), 7.02 (ddd, J_1 = 9.8 Hz, J_2 = 6.1 Hz, J_3 = 2.1 Hz, 1H).^{13}C-NMR (50 MHz, $CDCl_3$): δ= 26.9 (q), 27.4 (d), 32.2 (s), 40.0 (t), 45.2 (d), 129.2 (d), 150.9 (d), 201.1 (s). For detailed reaction conditions, product ratios and diastereoselectivities in the epoxidation of *trans*-**1b**, cf. Table 2.

Epoxidation of Alcohol *cis*-1b: According to the general procedure, the reaction of 54.0 mg (0.35 mmol) alcohol *trans*-**1b** with a 0.056 M solution of dimethyldioxirane (6.25 mL, 0.35 mmol) in MeOH (56.3 mL) yielded 57.3 mg (97%) of a mixture of the diastereomeric epoxides **2b** and enone **3b**. (*1R**, *2R**, *4S**, *6S**)-4-

(1,1-Dimethylethyl)-7-oxabicyclo[4.1.0]heptan-2-ol (**2b**): ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.81 (s, 9H), 0.92-1.80 (m, 5H), 2.9 (bs, 1H), 3.25-3.35 (m, 2H), 3.90-3.99 (m, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 24.1 (t), 26.9 (q), 28.9 (t), 32.1 (d), 43.4 (s), 55.1 (d), 55.9 (d), 70.0 (d). (*1S*, 2R*, 4S*, 6R**)-4-(1,1-Dimethylethyl)-7-oxabicyclo[4.1.0]heptan-2-ol (**2b**): ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.82 (s, 9H), 0.93-1.84 (m, 6H), 3.09 (dd, J_1= 3.7Hz, J_2 = 1.3 Hz, 1H), 3.19-3.36 (m, 1H), 3.89-4.01 (m, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 26.2 (t), 27.0 (q), 28.3 (t), 33.0 (s), 36.0 (d), 54.8 (d), 57.2 (d), 67.6 (d). For detailed reaction conditions, product ratios and diastereoselectivities in the epoxidation of *cis*-**1b**, cf. Table 2.

4,4,6-Trimethyl-7-oxabicyclo[4.1.0]heptan-2-ol (**2c**): According to the general procedure, the reaction of 49.0 mg (0.35 mmol) alcohol **1a** with a 0.057 M solution of dimethyldioxirane (6.50 mL, 0.37 mmol) in CCl_4 (58.5 mL) yielded 53.2 mg (99%) of a mixture of the diastereomeric epoxides **2c** and isophorone (**3c**). (*1R*, 2R*, 6S**)-**2c**: ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.83 (s, 3H), 0.86 (s, 3H), 1.31 (s, 3H), 1.44-1.67 (m, 5H), 3.20 (d, J = 2.1 Hz, 1H), 4.12 (ddd, J_1= 10.9 Hz, J_2= 6.0 Hz, J_3= 2.1 Hz, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 24.6 (q), 26.3 (q), 31.1 (q), 31.2 (s) , 39.6 (t), 42.1 (t), 61.6 (s), 62.3 (d), 66.6 (d). (*1S*, 2R*, 6R**)-**2c**: ^{1}H-NMR (200 MHz, $CDCl_3$): δ= 0.94 (s, 3H), 0.99 (s, 3H), 1.31 (s, 3H), 1.4-1.7 (m, 4H), 2.02 (bs, 1H), 2.94 (s, 1H), 4.1-4.2 (m, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ= 24.1 (q), 28.5 (q), 28.9 (s), 31.6 (q), 42.4 (t), 42.5 (t), 59.4 (s), 61.0 (d), 65.8 (d). For detailed reaction conditions, product ratios and diastereoselectivities in the epoxidation of **1c**, cf. Table 3.

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