Solvent Effects in the Regio- and Diastereoselective Epoxidations of Acyclic Allylic Alcohols by Dimethyldioxirane: Hydrogen Bonding as Evidence for a Dipolar Transition State

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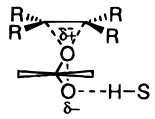
A mechanistically significant solvent effect is observed in the regioselectivity of the geraniol epoxidation by dimethyldioxirane. In hydrogen-bonding solvents (MeOH), the 6,7-epoxide is preferred over the 2,3-epoxide (74:26), which reveals that the more nucleophilic 6,7 double bond (the 2,3 double bond is inductively deactivated by the allylic hydroxy group) is preferentially attacked by the electrophilic dimethyldioxirane. In MeOH, both regioisomeric dipolar transition states are equally well stabilized by interaction through intermolecular hydrogen bonding with solvent molecules. In the nonpolar CCl_4, intramolecular hydrogen bonding with the allylic hydroxy functionality favors attack at the 2,3 double bond and proportionally more 2,3-epoxide is formed. Similarly, also the π-facial selectivity in the dimethyldioxirane epoxidation of methyl-substituted chiral acyclic allylic alcohols is controlled by intermolecular *versus* intramolecular hydrogen bonding. Thus, higher *threo* selectivities are obtained in the nonpolar CCl_4 by stabilization of the diastereomeric transition state with minimal allylic strain through intramolecular hydrogen bonding with the allylic hydroxy group. The geometry of the dipolar transition state for the dimethyldioxirane epoxidations is similar to that of *m*-CPBA, but with apparently a slightly larger (ca. 130°) dihedral angle α to relieve 1,2-allylic strain.

Introduction

For some time it has been recognized that the hydroxy group directs the π-facial selectivity in the epoxidation of allylic alcohols for a variety of oxidizing agents,[1] provided the substrate possesses allylic strain.[2] Such stereochemical studies have revealed valuable mechanistic information on the transition state geometry of oxygen transfer processes. Particularly informative have been, for example, *m*-CPBA and vanadium-catalyzed epoxidations, in which the oxidant associates in different ways with the hydroxy functionality, i.e., through hydrogen bonding with *m*-CPBA *versus* metal-alkoxide bond formation for vanadium.[3] As a consequence of the domination of 1,3-allylic strain ($A^{1,3}$) for *m*-CPBA *versus* 1,2-allylic strain ($A^{1,2}$) for vanadium in the highly ordered associate, the π-facial selectivity in the epoxide formation of a chiral allylic alcohol possessing either strain is opposite for the two oxidants, namely, *threo* for *m*-CPBA *versus erythro* for vanadium. This change has been ascribed to differing dihedral angles α in the associate of the allylic substrate and oxygen transfer agent in the transition state, in particular ca. 120° for *m*-CPBA and ca. 50° for the vanadium/tBuOOH system.

In this context, only little is known to date on such hydroxy-directed stereochemical probing in dimethyldioxirane (DMD) chemistry; unquestionably, such information should be desirable for stereoselective synthesis with this now popular oxidant.[4] It has been proposed that the attack on the double bond by this electrophilic oxidizing agent proceeds through a *spiro* rather than a *planar butterfly* transition state.[5] The electronic nature of the transition state still remains unclear, i.e., whether the epoxidation is synchronous or whether some dipolar character applies. Also the possibility of a *bona fide* diradical process, which was proposed already in early investigations on dioxiranes,[6] was again invoked.[7]

Recently it was found that these epoxidations can be assisted through polar solvents, as demonstrated by kinetic experiments.[8] Partial charge separation was proposed in the dimethyldioxirane epoxidation, and hence, the dipolar transition state shown was suggested.



Analogous to the *m*-CPBA or vanadium-catalyzed epoxidations, a hydroxy-directing effect was expected for DMD in the oxidation of chiral allylic alcohols which possess allylic strain, but in acetone/CH_2Cl_2 (ca. 1:1) as solvent

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the diastereoselectivities were generally low.[9] Nevertheless, appreciable effects could be observed for cyclic allylic alcohols; the diastereoselectivities were significantly enhanced in nonpolar solvents incapable of hydrogen bonding.[10,11]

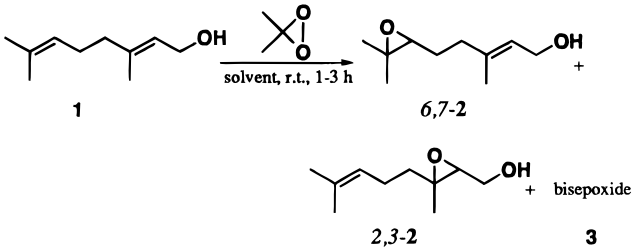
Analogous studies on directing effects in the $^1O_2$ ene reaction showed that cyclic substrates behave differently from acyclic ones[12] in their propensity to conduct the π-facial attack on the double bond. In view of this happenstance, a detailed study on the hydroxy-directing effect in the DMD epoxidations appeared to us to be in order to assess the regio- and diastereoselectivity for acyclic allylic alcohols as a function of solvent polarity. Geraniol was chosen to probe the regioselectivity, since it contains an allylic alcohol functionality as well as an unfunctionalized double bond, both of the same degree of substitution, i.e., trialkyl substituted. For this purpose, the hydrogen-bonding ability of the solvent[13] was varied to assess, through changes in the regioselectivity, the relative rate of DMD epoxidation of the allylic hydroxy-substituted *versus* the unfunctionalized double bonds in geraniol (**1**). In addition, the chiral, acyclic allylic alcohols **4a**−**g** were selected to determine the diastereoselectivity as a function of solvent polarity. The degree and type of methyl substitution of the simplest chiral allylic alcohol **4a** was successively varied to investigate the importance of 1,3- *versus* 1,2-allylic strain in the epoxidation with DMD as reflected by the diastereomeric ratio (dr). It was anticipated that the preferred π-facial attack (*threo versus erythro*) as a function of allylic strain and hydrogen-bonding ability of the medium should provide information on the transition state geometry of the hydroxy-directed epoxidation. Solvents which showed the largest effect in similar investigations on cyclic substrates were employed as cosolvent with acetone, namely, CCl_4 and MeOH (both 9:1 relative to acetone).[10,11] Unfortunately, acetone is unavoidable in view of the preparation of DMD.[14]

Results

As already reported,[9] the oxidation of geraniol (**1**) with 1 equiv of DMD in pure acetone yields a mixture of the monoepoxides *6,7*-**2** and *2,3*-**2** and the bisepoxide **3** (dr 50:50) in a ratio of 73:17:10, whereas at a large excess (5 equiv) of DMD the bisepoxide is formed exclusively. The formation of bisepoxide must be avoided since it masks the determination of the regioselectivity. Therefore, the oxidations of geraniol were run to only ca. 30% conversion by employing a deficiency (0.3 equiv) of DMD. Indeed, as the results in Table 1 show, the bisepoxide was not detected.

A significant solvent effect is observed on the product distribution of the two regioisomeric epoxides **2** in this series. In acetone/MeOH (1:9), the solvent mixture of highest hydrogen-bonding capacity, the epoxidation of the

Table 1. Solvent Effects on the Regioselectivity in the Epoxidation of Geraniol (1)



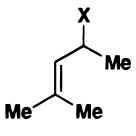
entry	equiv[a]	solvent	convsn[b,c] [%]	product distribution[c] *6,7*-**2**	*2,3*-**2**	**3**[d]
1	1	acetone	93	73	17	10
2	0.3	acetone/MeOH (1:9)	27	88	12	
3	0.3	acetone	28	74	26	
4	0.3	acetone/CCl_4 (1:9)	27	51	49	
5	5	acetone	>95			95

[a] Equivalents of DMD relative to geraniol. [b] Mass balances >90%. [c] Determined by ^{1}H NMR analysis directly on the crude product mixture (error ± 5% of the stated values). [d] Diastereomeric ratio 50:50.

6,7 double bond is preferred (88:12) over the 2,3 one, whereas in pure acetone the ratio decreases to 74:26. In acetone/CCl_4 (1:9), the least polar medium, the attack is completely unselective, since the two regioisomers were obtained in a 51:49 ratio.

Solvent effects on the diastereoselectivity were tested for the set of allylic alcohols **4** and are compiled in Table 2. Clearly, the diastereoselectivity in the epoxide formation depends on the substitution pattern of the allylic alcohol **4**. In pure acetone (medium B), for substrates without allylic strain there is essentially no diastereoselectivity observed (entries 1 and 5), whereas substrates with a methyl group at the R_1 or R_3 position (entries 3 and 8) show a distinct *threo* selectivity in the epoxidation by DMD. This selectivity is higher in the case of 1,3-allylic (**4d**) than 1,2-allylic strain (**4b**). Further introduction of methyl groups as in derivatives **4e** (entry 11), **4f** (entry 14), and **4g** (entry 16) leads in all cases to an enhanced diastereoselectivity, even though in some cases no increased allylic strain is evident. For instance, comparison of the pair **4d** and **4e** (entries 8 and 11) and the pair **4f** and **4g** (entries 14 and 16), in which only R_2 is changed from hydrogen to methyl (constant allylic strain), reveals a significantly greater diastereoselectivity for the higher substituted allylic alcohol in both cases.

Also several derivatives of allylic alcohol **4e**, which was chosen as a representative example, were oxidized with DMD under conditions B in Table 2. In contrast to the parent alcohol **4e**, a low *erythro* selectivity was displayed in the epoxidations of methyl ether **5e** (38:62), trimethylsilyl ether **6e** (46:54), and the acetate **7e** (42:58), for which high conversions (>95%) and mass balances (>90%) were obtained.



5e: X = OMe
6e: X = $OSiMe_3$
7e: X = OAc

In all cases in which either 1,2- or 1,3-allylic strain is present, also a notable solvent effect can be perceived.

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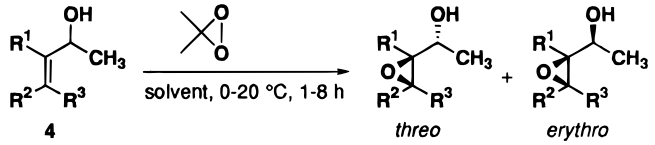
Table 2. Solvent Effects on the Diastereoselectivities in the DMD Epoxidations of Allylic Alcohols



entry	substr	R^1	R^2	R^3	medium[a]	mb[b] [%]	convsn[c,d] [%]	dr[d] *threo*:*erythro*
1	**4a**	H	H	H	B	97	89	50:50
2	**4b**	CH_3	H	H	A	90	>95	57:43
3	**4b**	CH_3	H	H	B	73	>95	60:40
4	**4b**	CH_3	H	H	C	81	>95	70:30
5	**4c**	H	CH_3	H	B	99	78[e]	53:47
6	**4c**	H	CH_3	H	C	78	>95[e]	56:44
7	**4d**	H	H	CH_3	A	100	86	64:36
8	**4d**	H	H	CH_3	B	84	>95	67:33
9	**4d**	H	H	CH_3	C	98	>95	85:15
10	**4e**	H	CH_3	CH_3	A	100	>95	59:41
11	**4e**	H	CH_3	CH_3	B	96	87	76:24
12	**4e**	H	CH_3	CH_3	C	100	>95	82:18
13	**4f**	CH_3	H	CH_3	A	99	>95	82:18
14	**4f**	CH_3	H	CH_3	B	96	>95	87:13
15	**4f**	CH_3	H	CH_3	C	100	>95	91:9
16	**4g**	CH_3	CH_3	CH_3	B	100	>95	> 95:5

[a] (A) MeOH/acetone (9:1), (B) acetone, (C) CCl_4/acetone (9:1). [b] Mass balance. [c] Yields >95% in all cases. [d] Determined by ^1H NMR analysis of characteristic signals (error ± 5% of the stated values). [e] Epoxide/enone ca. 90:10.

Thus, for substrates **4b** (entries 2−4), **4d** (entries 7−9), **4e** (entries 10−12), and **4f** (entries 13−15) the diastereoselectivity is enhanced with decreasing solvent polarity, i.e., in the order acetone/MeOH (1:9) > acetone > acetone/CCl_4 (1:9). For derivative **4g**, already in pure acetone the highest possible diastereoselectivity of >95:5 was obtained. In contrast, the same diastereoselectivities within experimental error (entries 5 and 6) were observed for the substrate **4c** without any allylic strain, when the solvent was changed from acetone to the less polar mixture acetone/CCl_4 (1:9). Furthermore, as expected, in all these epoxidations no *cis*−*trans* isomerization occurred.

Discussion

The present results on the regioselectivity in the DMD epoxidation of geraniol (**1**) in Table 1 and on the diastereoselectivities of the chiral allylic alcohols **4** (Table 2) as a function of solvent polarity provide convincing experimental evidence for a hydroxy-directing effect. Thus, the hydroxy group of the substrate associates with the incoming dioxirane oxidant in the transition state to reconcile the observed solvent polarity trends. We propose that also here the hydrogen-bonding ability of the solvent is the principal molecular feature in controlling the selectivity.

Let us first take up the regioselectivity results for geraniol (Table 1). The convenience of this substrate is the fact that the regioselectivity in the epoxidation of the 6,7 *versus* the 2,3 double bond provides a relative rate measure in terms of the ratio of the two possible monoepoxides *6,7*-**2** and *2,3*-**2**, an intramolecular competition experiment that obviates recourse to cumbersome absolute rate studies. Since the two double bonds are trisubstituted, the inductive electron withdrawal by the hydroxy group will lower the nucleophilicity of the 2,3 double bond, and if this electronic property is the decisive reactivity factor, preferential epoxidation of the 6,7 double bond would be expected. Indeed, in the most polar medium, i.e., 9:1 methanol and acetone, the regioselectivity 88:12 (Table 1) bears out this expectation. Intermolecular hydrogen bonding with methanol stabilizes the dipolar transition state sufficiently so that the allylic hydroxy functionality does not come into the act. In contrast, in the least polar medium, i.e., 9:1 CCl_4 and acetone, external hydrogen bonding is of no consequence and the dipolar transition state should seek assistance through intramolecular hydrogen bonding by the allylic hydroxy functionality. Therefore, since internal hydrogen bonding is more effective for dioxirane attack on the 2,3 double bond (six-membered ring is conformationally preferred), its epoxidation should prevail. The observed 51:49 regioselectivity (Table 1) bears out the right trend, but the effect is not sufficient to invert the ratio in favor of the epoxide *2,3*-**2**. However, it should be kept in mind that there is still 10% acetone in this medium and its polar nature moderates the effect apparently through association with the allylic hydroxy group and additionally through possible polar stabilization of the transition state for the *6,7*-epoxide. As a matter of fact, the 74:26 regioselectivity (Table 1) in pure acetone as solvent confirms this counteracting trend. It is for this reason that the observed regioselectivities for geraniol (**1**) are not dramatic but mechanistically significant in that they reflect a superposition of two electronic effects, namely, the nucleophilic reactivity, which favors the 6,7 over the 2,3 double bond, counteracted by assistance through intramolecular (allylic hydroxy group) *versus* intermolecular (solvent) hydrogen bonding.

The diastereoselectivity results for DMD epoxidations of the chiral allylic alcohols **4** (Table 2) corroborate the conclusions reached from the regioselectivities of geraniol (**1**). Appreciable π-facial selectivities can only be expected if intramolecular hydrogen bonding by the allylic hydroxy functionality operates and allylic strain helps in differentiating energywise appropriate conformations in the transition state.

Thus, it is not surprising that the two substrates **4a** and **4c** (entries 1 and 5, Table 2), which do not possess any allylic strain, do not display any diastereoselectivity in the dioxirane epoxidation and also no solvent effects. In the case of substrate **4b** with 1,2-allylic strain only,

the diastereoselectivity is quite low, but increases regularly from methanol to CCl_4 as cosolvents and for acetone it is intermediate. Again, in the polar methanol, intramolecular association of the incoming dioxirane with the allylic hydroxy functionality is offset by external hydrogen bonding with the solvent and the inherent 1,2-allylic strain essentially does not come to fruition in steering the π-facial attack; consequently, a poor diastereoselectivity is observed. In the nonpolar CCl_4 as cosolvent (entry 4), the trend to higher *threo* diastereoselectivity is evident, but the effect is small.

The action of 1,3-allylic strain in the substrates **4d** (entries 7−9) and **4e** (entries 10−12) is more pronounced in controlling the expected π-facial selectivity. Thus, in the nonpolar CCl_4 as cosolvent, the medium of highest stereocontrol through intramolecular hydrogen bonding with the allylic hydroxy group, essentially the same but relatively high (dr ca. 85:15) diastereoselectivities for both derivatives **4d** and **4e** (entries 9 and 12) are manifested. When both *threo*-directing 1,2- and 1,3-allylic strain operate in concert, as in the substrate **4f** (entries 13−15), it is not surprising that in the nonpolar cosolvent CCl_4 the π-facial diastereoselectivity is enhanced to as much as 91:9 and a pronounced solvent effect operates. Nevertheless, the highest diastereoselectivity is displayed by the tetrasubstituted derivative **4g** even in pure acetone. This was unexpected since an additional methyl group at the R_2 position exerts no further allylic strain when compared to **4f**. This higher diastereoselectivity may result from stronger hydrogen bonding to the adjacent allylic hydroxy functionality presumably on account of larger charge separation in the transition state for the peroxide bond cleavage. Moreover, despite their higher nucleophilicity, tetrasubstituted alkenes can be less reactive than trisubstituted ones in DMD epoxidations due to counteracting steric effects.[5] Consequently, for such substrates a higher demand is placed on the adjacent allylic hydroxy group to overcome this steric barrier through hydrogen bonding and, hence, a higher π-facial selectvity is observed. This effect was also noted in the diastereoselective epoxidation of cyclic allylic alcohols.[10b]

Clearly, the diastereoselective epoxidations of the chiral allylic alcohols **4** in Table 2 establish evidence for an interaction of the OH functionality with the dipolar transition state in the dioxirane S_N2 attack, which is stabilized through intramolecular hydrogen bonding with the allylic hydroxy group, unless a polar solvent interferes. Further support for this proposed association is also gained from the DMD epoxidation of methyl ether **5e**, trimethylsilyl ether **6e**, and acetate **7e** of allylic alcohol **4e**. While the free hydroxy group in **4e** directs the DMD attack to an extent of 76:24 (*threo* to *erythro*) even in acetone as solvent, all three derivatives **5e**−**7e**, which due to the lack of the proton cannot involve H-bonding, yield the corresponding epoxides in a low (maximum 38:62) *erythro* selectivity. Therefore, merely steric factors are ineffective in governing the π-facial selectivity in such DMD epoxidations.

The question that remains concerns the preferred transition state geometry with respect to the dihedral angle α for optimal internal hydrogen bonding. Comparison with the proposed transition state structures for *m*-CPBA and vanadium-catalyzed epoxidations (Figure 1) provides a clue. The preferred *threo* diastereoselectivities obtained for DMD resemble closely those for *m*-CPBA rather than those for vanadium, except that the

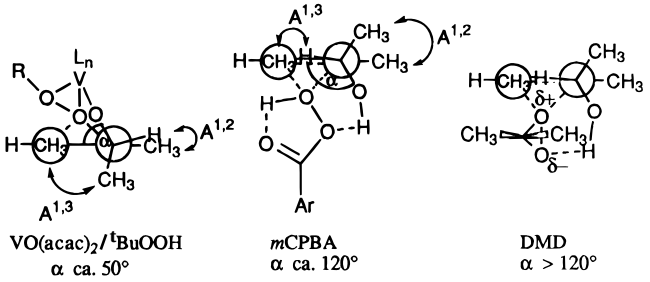


Figure 1. Preferred transition states in the epoxidations of chiral allylic alcohol **4f** with different oxidants.

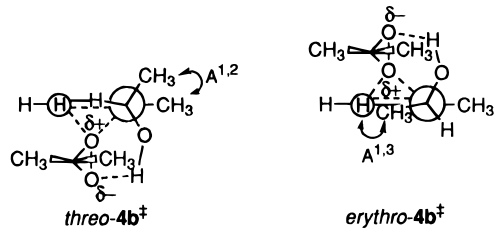


Figure 2. Diastereomeric transition states in the epoxidation of **4b**.

stereocontrol is generally lower for the DMD epoxidation. This trend may be explained by the fact that the symmetrical dioxirane peroxide bond is much less polarized in the transition state than the already inherently polarized peroxide bond in the peracid and the adjacent hydroxy group hydrogen bonds considerably less effectively for DMD. This is supported by the appreciable solvent effect for DMD but not for *m*-CPBA on the diastereoselectivity.

The surprising result that the epoxidation of allylic alcohol **4b** (1,2-allylic strain) proceeds *threo* selectively with DMD in all three solvents employed (entries 2−4, Table 2), whereas the peracid yields the *erythro* product but in low selectivity (45:55),[15] offers an additional reason for the similar yet differentiated diastereoselectivities between these two oxidants. The two transition states for the diastereomeric epoxides are shown in Figure 2 for DMD. If a dihedral angle α of ca. 120° applies, there is no dominant steric interaction that should direct the π-facial attack. In the *threo* transition state, the two methyl groups are not close enough together to exert appreciable 1,2-allylic strain, while for the *erythro* attack the 1,3-strain is not significant since the steric interaction between H and CH_3 is not effective. A dihedral angle α smaller than 120° will tend to bring the two methyl groups responsible for the 1,2-allylic strain in the *threo* transition state closer together, this geometry will be disfavored, and a low *erythro* selectivity is expected. In contrast, if the dihedral angle α is larger than 120°, the 1,2-allylic strain ($A^{1,2}$) in the *threo* case will be decreased but the small 1,3-strain ($A^{1,3}$) in the *erythro* transition state will be increased, which seems to be responsible for the fine tuning in the observed diastereoselectivities. Therefore, while the exact dihedral angle is open to debate, the trends in the moderate but mechanistically relevant π-facial selectivities suggest that for DMD a larger angle applies than for *m*-CPBA. With the assumption that for *m*-CPBA a dihedral angle of 120° operates,[3] we had estimated for the cyclic allylic alcohols

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an angle α of ca. 130°,[10b] which is a reasonable guess also for the acyclic ones examined herein.

Conclusion

Altough on kinetic grounds skepticism has been expressed[16] as to whether the observed directing effects in the dioxirane epoxidations of allylic alcohols derive from assistance by the hydroxy functionality through intramolecular hydrogen bonding with the peroxide bond, our present regioselectivities (relative rates) and stereoselectivities (π-facial reactivities) provide convincing experimental evidence in favor. A dipolar transition state applies for this oxygen transfer process, which is stabilized by hydrogen-bonding solvents or by hydrogen bridging with an adjacent allylic hydroxy functionality. These results substantiate previous reports that such coordinative effects operate in the diastereoselective DMD epoxidations of cyclic allylic alcohols[10,11] and cyclic allylic ammonium salts.[17] Since no *cis*−*trans* isomerizations were observed in these epoxidations, radical-type processes[7] are unlikely.

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Supporting Information Available: Experimental procedures with the characterization of all products (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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