Diastereoselective Photooxygenation of Chiral Naphthyl Alcohols: The Hydroxy Group Directing Effect in Singlet Oxygen [4 + 2] Cycloaddition to Arenes

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Received February 13, 1995[⊗]

Abstract: A series of chiral naphthyl alcohol derivatives **1** was prepared and submitted to sensitized photooxygenation. The corresponding endoperoxides **2** were formed in high yields through [4 + 2] cycloaddition of singlet oxygen. The π-facial selectivity of singlet oxygen attack was determined and the stereochemistry of the product assigned for representative cases (**1a,h**) by X-ray analysis of the triols **3** derived from the endoperoxides by reduction. In the photooxygenation of the alcohols **1a−g** in nonpolar solvents, the (αR^*,$1R^*$,$4S^*$)-configurated endoperoxides **2a−g** were formed preferentially (diastereomeric ratio (dr) $\geq$ 85:15). Increase in solvent polarity or protection of the hydroxy group as the acetate in **1i** or as the silyl ether in **1j** led to substantial loss of diastereoselectivity. Placement of a methyl group at C2, as in alcohol **1h**, gave high but opposite π-facile selectivity (dr = 94:6), i.e., (αR^*,$1S^*$,$4R^*$)-**2h** was formed as major product. The observed substitution effects on the π-facial selectivity are rationalized in terms of steric and electronic control. Thus, hydrogen bonding operates between the unprotected hydroxy group and the incoming singlet oxygen dienophile. *Peri* strain leads to an effective energy discrimination of the respective diastereomeric transition states and, consequently, high π-facial selectivities. An alkyl substituent at C2, however, induces additional *ortho* strain of 1,3-allylic origin, which overrides the effect of *peri* strain to afford highly selectively the opposite stereoisomer.

Introduction

The [4 + 2] cycloaddition between singlet oxygen and conjugated dienes was discovered as early as 1867, when Fritzsche reported the reversible formation of a product (later assigned as the corresponding endoperoxide) in the self-sensitized photooxygenation of naphthacene.[1] At that time, neither the structure of the cycloadduct nor the nature of the oxidizing species as singlet oxygen was recognized. It took almost 80 years until the pioneering work of Dufraisse[2] and that of Schenck on the synthesis of ascaridole[3] again focused interest on the chemistry of the excited state dienophile singlet oxygen. Ever since, the synthetic utility of endoperoxides has been established by numerous applications.[4] Surprisingly little, however, is known about the sterochemical features in singlet oxygen [4 + 2] cycloadditions, in sharp contrast to the classical Diels−Alder reaction.[5] For the latter, many studies have revealed the directing ability of adjacent stereogenic centers on the π-facial selectivity.[6]

Since we recently established the steering propensity of allylic hydroxy[7] and amino[8] functionalities in the singlet oxygen ene reaction, it was of interest to extend this concept for the singlet oxygen [4 + 2] cycloadditions. Indeed, in a previous Communication,[9] we reported that a strategically placed hydroxy group exerts remarkable stereocontrol in the [4 + 2] cycloaddition of chiral naphthyl alcohols. Furthermore, the stereocontrolling ability of other functional groups (X = Cl, Br, SiR_3) at the stereogenic center in chiral naphthalene derivatives was established,[10] and this method was exploited in the highly diastereoselective photooxygenation of chiral phenol derivatives.[11]

The choice of chiral naphthalene derivatives as model compounds to probe π-facial stereocontrol has proven most convenient since these substrates combine several beneficial features. Thus, the starting alcohols are readily available, and the substitution pattern at the naphthalene core can be easily varied, which allows the steric and electronic effects to be systematically studied. Fortunately, the [4 + 2] cycloaddition of singlet oxygen to naphthalene derivatives gives high yields ($\geq$95%) of the corresponding endoperoxides,[12] which is essential for determining reliably substituent effects on the π-facial

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[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1995.

(1) Fritzsche, M. *C. R. Acad. Sci.* **1867**, *64*, 1035.
(2) Moureu, C.; Dufraisse, C.; Dean, P. M. C. R. *Hebd. Sci.* **1926**, *182*, 1440.
(3) Schenck, G. O.; Ziegler, K. *Naturwissenschaften* **1944**, *32*, 157.
(4) Clennan, E. L.; Foote, C. S. In *Organic Peroxides*; Ando, W., Ed.; Wiley & Sons: Chichester, 1992; Section 245.
(5) (a) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Chapter 7. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. (c) Ciganek, E. *Org. React. (N. Y.)* **1984**, *32*, 1.
(6) (a) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 663. (b) Brown, F. K.; Houk, K. N.; Burnell, D. J.; Valenta, Z. *J. Org. Chem.* **1987**, *52*, 3050. (c) Tripathy, R.; Franck, R. W.; Onan, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 3257. (d) Fisher, M. J.; Hehre, W. J.; Kahn, S. D.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 4625. (e) Ishida, M.; Beniya, Y.; Inagaki, S.; Kato, S. *J. Am. Chem. Soc.* **1990**, *112*, 8980. (f) Macaulay, J. B.; Fallis, A. G. *J. Am. Chem. Soc.* **1990**, *112*, 1136. (g) Coxon, J. M.; McDonald, D. Q. *Tetrahedron Lett.* **1992**, *33*, 651. (h) Ishida, M.; Aoyama, T.; Beniya, Y.; Yamabe, S.; Kato, S.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3430.
(7) Adam, W.; Nestler, B. *J. Am. Chem. Soc.* **1992**, *114*, 6549.
(8) Adam, W.; Brünker, H.-G. *J. Am. Chem. Soc.* **1993**, *115*, 3008.
(9) Adam, W.; Prein, M. *J. Am. Chem. Soc.* **1993**, *115*, 3766.
(10) Prein, M.; Adam, W.; Maurer, M.; Peters, E. M.; Peters, K.; von Schnering, H. G. *Chem. Eur. J.* **1995**, *1*, 89.
(11) Adam, W.; Prein, M. *Tetrahedron Lett.* **1994**, *35*, 4331.

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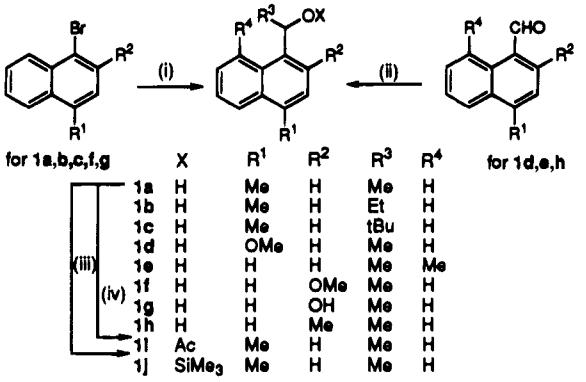
Scheme 1. Preparation of the Naphthyl Alcohols **1**[a]



[a] Conditions: (i) (1) Mg, THF, reflux; (2) R^3CHO, THF, 0 °C to reflux, 2−5 h; (3) NH_4Cl (aqueous); (ii) (1) MgMeI, Et_2O, 0 °C to room temperature, 5−16 h; (2) NH_4Cl (aqueous); (iii) Ac_2O, pyridine, room temperature, 24 h; (iv) Me_3SiCl, imidazole, CH_2Cl_2, room temperature, 48 h.

selectivity. Most importantly, the *peri* hydrogen atom provides a stereochemical anchor, which discriminates between the different rotamers, a prerequisite for high diastereoselectivity.

We now report full experimental details on the stereochemistry of the photooxygenation of chiral naphthyl alcohols. The previous study[9] has been extended, and the effects of substitution on the naphthalene core and substitution type at the chirality site on the degree and sense of the π-facial selectivity in the hydroxy-directed singlet oxygen [4 + 2] cycloaddition have been systematically studied. Thus, alcohols **1a−c** (cf. Scheme 1) should reveal the steric effect of the aliphatic substituent at the stereogenic center on the π-facial selectivity, while the photooxygenation of the derivatives **1d−h**, which differ by the substitution pattern of the naphthalene core, should reveal the influence of special geometrical features. Especially the effectes of increased *peri* strain, as in alcohol **1e**, and of *ortho* strain, as in derivative **1h**, on the degree and sense of the diastereoselectivity should provide closer insight into the reaction mechanism. Finally, in the photooxygenation of the naphtalene derivatives **1i,j**, the influence of electron-donating and -accepting groups at the stereogenic center is tested. The present results provide an updated mechanistic picture of the hydroxy group directing effect in the singlet oxygen [4 + 2] cycloaddition.

Results

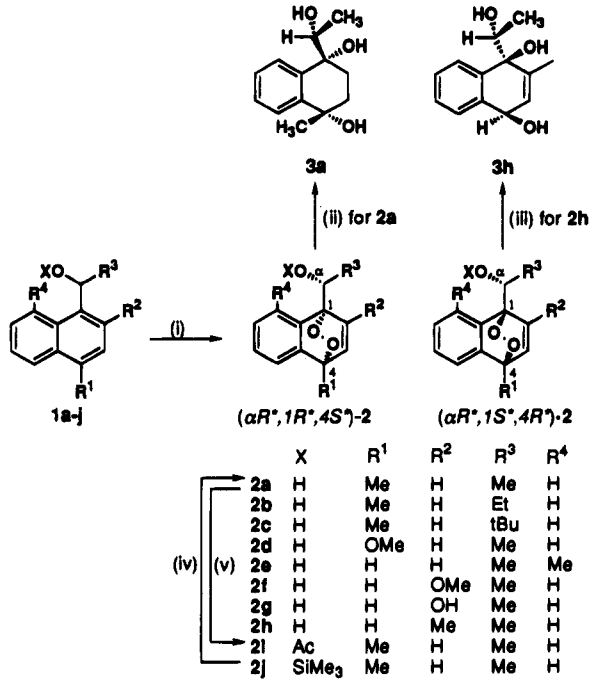
The desired starting alcohols were obtained either by Grignard reaction of the respective bromo-substituted naphthalenes with an aliphatic aldehyde (derivatives **1a−c,f,h**) or by addition of methylmagnesium iodide to the corresponding naphthyl aldehydes (alcohols **1d,e,g**) (Scheme 1). Acetate **1i** and silyl ether **1j** were obtained from alcohol **1a** by standard methods.

On sensitized photooxygenation in $CDCl_3$ at −30 °C, the chiral naphthyl alcohols **1** gave the corresponding endoperoxides **2** (Scheme 2). Due to the appreciable thermal lability of the endoperoxides **2**,[12] the conversions, yields, and product compositions were determined directly by low-temperature ^1H NMR analysis of the crude product mixtures. The results are summarized in Table 1.

In the photooxygenation of the 1,4-substituted naphthyl alcohol **1a** at −30 °C, good (82:18 to 86:14) π-facial selectivity was observed for the nonpolar solvents chloroform (entry 1), dichloromethane (entry 3), and toluene (entry 4), while the

(12) (a) Wasserman, H. H.; Larsen, D. L. *J. Chem. Soc., Chem. Commun.* **1972**, 253. (b) van den Heuvel, C. J. M.; Steinberg, H.; de Boer, Th. J. *Recl.: J. R. Neth. Chem. Soc.* **1980**, *99*, 109.

Scheme 2. Photooxygenation and Stereochemical Correlation of the Naphthyl Alcohols **1**[a]



[a] Conditions: (i) $^1O_2$; (ii) H_2, Pd/C, EtOAc, 0 °C, 2 h; (iii) $LiAlH_4$, Et_2O, 0 °C, 3 h; (iv) $(nBu)_4NF$, −30 °C, 48 h; (v) Ac_2O, pyridine, −25 °C, 48 h.

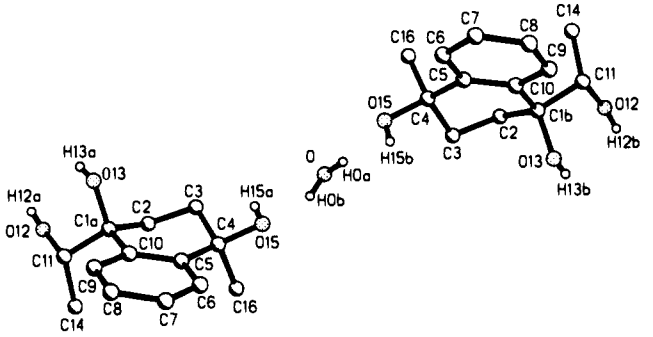


Figure 1. X-ray structure of triol **3a**.

diastereoselectivity dropped significantly when the more polar solvents acetonitrile (entry 5), acetone (entry 6), and methanol (entry 7) were used. Furthermore, photooxygenation at −70 °C in chloroform led to an increase in diastereoselectivity to 90:10 (entry 2).

The (αR^*,1R^*,4S^*) stereochemistry for the major isomer could be unequivocally assigned on the basis of an X-ray structure determination for triol **3a** (Figure 1). The latter was obtained by hydrogenation of the endoperoxide (αR^*,1R^*,4S^*)-**2a** (Scheme 2).

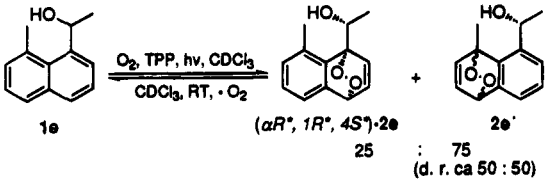
Within the error limit, the same selectivities as for alcohol **1a** were encountered in the photooxygenation of the chiral alcohols **1b,c** (entries 8, 9), which differ in the aliphatic substituent R at the stereogenic center. For the *tert*-butyl derivative **1a**, the diastereomeric ratio (dr) of the endoperoxides **2c** changed with reaction time; i.e., while at short photooxygenation times and low conversion an 87:13 ratio in favor of (αR^*,1R^*,4S^*)-**2c** was found (entry 9), the (αR^*,1S^*,4R^*) isomer was preferred (5:95) on prolonged photooxygenation (entry 10). The kinetically controlled endoperoxide (αR^*,1R^*,4S^*)-**2c** did not persist under the photooxygenating conditions and reverted back to the starting material. Thus, the thermodynamically more stable (αR^*,1S^*,4R^*) isomer ac-

Table 1. Photooxygenation Conditions[a] and Product Data for Chiral Naphthyl Alcohols **1**

entry	substrate	solvent	time (h)	temp (°C)	conv (%)	yield[b] (%)	diastereoselectivity[c] (dr, %)
1	**1a**	$CDCl_3$	4	−30	>95	>95	85:15
2	**1a**	$CDCl_3$	5	−70	>95	>95	90:10
3	**1a**	CH_2Cl_2	5	−35	>95	>95	86:14
4	**1a**	$C_6D_5CD_3$	10	−30	>95	>95	82:18
5	**1a**	CD_3CN	10	−30	>95	>95	61:39
6	**1a**	CD_3COCD_3	5	−30	87	>95	58:42
7	**1a**	CD_3OD	28	−35	95	95	55:45
8	**1b**	$CDCl_3$	6	−30	>95	>95	88:12
9	**1c**	$CDCl_3$	2.5	−30	30	>95	87:13
10	**1c**	$CDCl_3$	48	−30	60	~70	~5:95
11	**1d**	$CDCl_3$	0.5	−30	96	96	79:21
12	**1e**	$CDCl_3$	4	−30	>95	25[d]	≥95:5
13	**1f**	$CDCl_3$	2.5	−30	>95	>95	91:9
14	**1g**	$CDCl_3$	2.5	−30	>95	69[e]	≥95:5
15	**1h**	$CDCl_3$	6	−30	>95	>95	6:94
16	**1h**	CH_2Cl_2	6	−30	>95	>95	6:94
17	**1h**	CD_3OD	5	−25	45	>95	25:75
18	**1i**	$CDCl_3$	6	−30	21	>95	56:44
19	**1j**	$CDCl_3$	5	−30	68	>95	58:42

[a] Tetraphenylporphine (TPP) was used as sensitizer, except for entries 5, 7, and 15, for which Rose Bengal was employed. ^1H NMR spectra were taken on the crude product mixtures at −20 °C. [b] Yield of 1,4-endoperoxides **2**. [c] Ratio of (αR*,1R*,4S*)- and (αR*,1S*,4R*)-**2** diastereomers determined by NMR analysis of appropriate, characteristic proton signals; error ~5% of the stated values. [d] 75% of the 5,8-endoperoxide **2e'** (dr ~50:50) was obtained. [e] 31% of 1,2-naphthoquinone was detected.

Scheme 3. Product Distribution in the Photooxygenation of Naphthyl Alcohol **1e**



cumulated in the course of the reaction. Careful monitoring of the reaction progress revealed that this behavior was unique for the β-branched alcohol **1c** and did not occur in the photooxygenation of the other derivatives of **1**.

A slight decrease in diastereoselectivity (79:21) was observed in the photooxygenation of the 4-methoxy-substituted chiral naphthyl alcohol **1d** (entry 11). Unfortunately, the resulting endoperoxide **2d** readily fragmented under extrusion of acetaldehyde at −20 °C, which severely hampered the determination of the exact π-facial selectivity for the initial singlet oxygen attack.

The [4 + 2] cycloaddition of the 1,8-disubstituted naphthyl alcohol **1e** (entry 12) is complicated by the fact that both monosubstituted aromatic rings compete for singlet oxygen to give the two regioisomeric endoperoxides **2e** and **2e'** in a 25:75 ratio (Scheme 3). While the major regioisomer **2e'**, which does not bear the chiral group at the reactive ring, no diastereoselectivity was observed (~50:50), the minor regioisomer **2e** was formed with complete π-facial selectivity (≥95:5).

The chiral naphthyl alcohols **1f,g** (entries 13, 14), which contain an oxygen substituent at C2, showed high π-facial selectivity (90:10 and ≥95:5) in the singlet oxygen [4 + 2] cycloaddition. However, naphthol **1g** yielded besides the endoperoxide **2g** appreciable amounts (31%) of the fragmentation product 1,2-naphthoquinone (Scheme 4). The latter was also obtained from the 2-methoxysubstituted endoperoxide **2f** on attempted silica gel-catalyzed enol ether hydrolysis.

Also for the 1,2-disubstituted naphthyl alcohol **1h**, high (94:6) π-facial selectivity was observed for the singlet oxygen [4 + 2] cycloaddition in the nonpolar solvents chloroform (entry 15) and dichloromethane (entry 16), while the diastereomeric

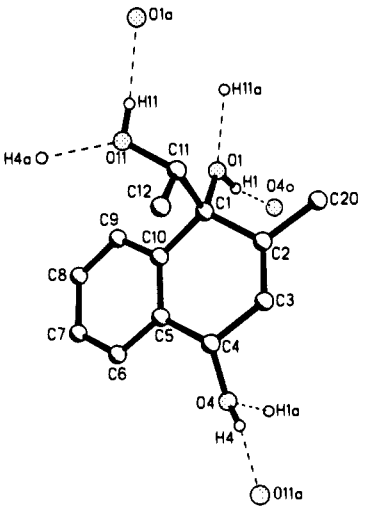
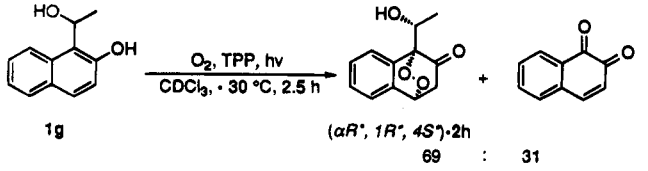


Figure 2. X-ray structure of triol **3h**.

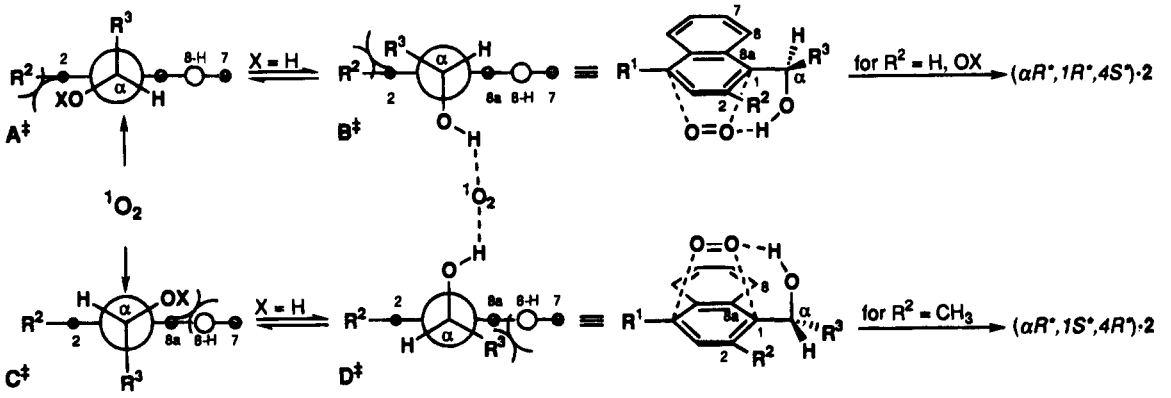
Scheme 4. Product Distribution in the Photooxygenation of Naphthyl Alcohol **1g**



ratio dropped to 75:25 when protic methanol was used as solvent (entry 17). Since the methyl substituent at C2 adds additional steric strain to the starting alcohol **1h** (see Discussion), the relative stereochemistry of the resulting endoperoxides **2h** could not be directly correlated to that of the cycloadducts of alcohol **1a** like for endoperoxides **2b−g**. An X-ray analysis (Figure 2) of the triol **3h**, which was obtained by $LiAlH_4$ reduction of the major diastereomer **2h** (Scheme 2), was essential to assign the configuration of the endoperoxide **2h**. Indeed, the opposite sense of π-facial selectivity applies in the photooxygenation of alcohol **1h** compared to **1a−g**, i.e., (αR*,1S*,4R*)-**2h** was formed as the major product.

Finally, in the photooxygenations of the acetate **1i** (entry 18, 56:44) and the silyl ether **1j** (entry 19, 58:42), a dramatic drop

Scheme 5. Stereochemical Course for the [4 + 2] Cycloaddition of Chiral Naphthyl Alcohols **1** and Singlet Oxygen



in diastereoselectivity was observed compared to the parent alcohol **1a**. In these cases, the stereochemistry was assigned by chemical correlation of the endoperoxides **2i,j** to the parent system ($\alpha R^*,1R^*,4S^*$)-**2a**. Thus, the latter was acylated to give ($\alpha R^*,1R^*,4S^*$)-**2i** as major diastereomer, while fluoride ion-catalyzed desilylation of the crude photooxygenate of **2j** confirmed the preference for ($\alpha R^*,1R^*,4S^*$)-**2j**.

Discussion

The results on the stereochemical course of the photooxygenation of chiral alcohols **1a–h** clearly demonstrate that an unprotected hydroxy group efficiently steers the singlet oxygen [4 + 2] cycloaddition in nonpolar solvents. Masking of the hydroxy group either by electron acceptors, as in acetate **1j**, or by electron donors, as in the silyl ether **1j**, causes loss of stereocontrol. Therefore, a free hydroxy group is essential for π-facial stereocontrol. Steric effects are of secondary importance, since the derivatives **1a–c** show almost identical diastereoselectivities. Equally mechanistically informative is the fact that both the increased *peri* strain in alcohol **1e** and the incorporation of an oxy substituent at C2 (alcohols **1f,g**) increase diastereoselectivity. Moreover, the introduction of *ortho* strain, as in alcohol **1h**, also results in high π-facial selectivity (94:6), but in the opposite stereochemical sense to that observed for alcohol **1a**.

A mechanistic rationalization of the foregoing results is possible in terms of synergistic action of steric and electronic control (Scheme 5). Minimization of *peri* strain should lead to transition state $\mathbf{A}^{\ddagger}$ as the preferred conformation, which bears the hydrogen atom proximate to the *peri* hydrogen atom 8-H. Sterically controlled attack on this energy-favored rotamer would give the observed ($\alpha R^*,1R^*,4S^*$) diastereomer for the free alcohols (X = H). Increase of the size of X, as in acetate **1i** (X = Ac) or silyl ether **1j** (X = $SiMe_3$), significantly reduces the steric control, and a drop in π-facial selectivity is encountered.

This rationale based on simple steric bias, however, does not satisfactorily explain the small influence of a bulky R^3 substituent at the stereogenic center and the loss of stereocontrol which occurs in more polar solvents during the photooxygenation of alcohols **1a,h**. We propose that hydrogen bonding between the free hydroxy group and the incoming singlet oxygen dienophile, as illustrated by transition states $\mathbf{B}^{\ddagger}$ and $\mathbf{D}^{\ddagger}$ (Scheme 5), is operating.[13] Transition state $\mathbf{B}^{\ddagger}$ is preferred over $\mathbf{D}^{\ddagger}$ in energy because *peri* strain between R^3 and 8-H is significant in the latter. Thus, the ($\alpha R^*,1R^*,4S^*$)-diastereomeric endoperoxides benefit from this attractive electronic interaction and are formed highly selectively.

The mechanism in Scheme 5 nicely accounts for the loss of stereocontrol as the solvent polarity is increased (Table 1, entries 5–7 and 16). Thus, the directing effect through hydrogen bonding is reduced and diastereoselectivity is lost. Furthermore, lower temperatures (entry 2) or increased *peri* strain, as in the 1,8-disubstituted derivative **1e**, will enhance the energy discrimination between the hydrogen-bonded transition states $\mathbf{B}^{\ddagger}$ and $\mathbf{D}^{\ddagger}$ and, consequently, will lead to higher diastereoselectivities. Although for substrate **1e** the 5,8-endoperoxide regioisomer is preferred (Scheme 3), this happenstance does not contradict the proposed attractive interaction between singlet oxygen and the hydroxy group. The regiochemistry of singlet oxygen attack is determined by the overall electron density of the competing aromatic rings. Since it is well-known that allylic alcohols react significantly slower with singlet oxygen than their parent olefins,[14] the preferential attack at the methyl-substituted aromatic ring should be and is observed. Assistance by the hydroxy group efficiently discriminates only the diastereotopic faces of substrate **1e** for attack at the less reactive hydroxyethyl-substituted ring, and no stereocontrol should be expected in the formation of the 5,8-endoperoxide (50:50).

Although concerted synchronous transition states are shown in Scheme 5, the above-mentioned stereochemical arguments for the proposed mechanism of singlet oxygen [4 + 2] cycloadditions (Scheme 5) also apply to other reaction pathways. Namely, a reversible exciplex[15] with a partial negative charge on singlet oxygen, a perepoxide zwitterionic intermediate, or a concerted asynchronous transition state[16] all would also experience stabilization through hydrogen bonding. For the oxygen-substituted naphthalene derivatives **1d,f,g**, unsymmetrical attack is highly likely and can explain some special features of π-facial selectivity in the present systems. Thus, the reduced (79:21) diastereoselectivity in the photooxygenation of alcohol **1d** is attributed to unsymmetrical attack at the electron-rich C3–C4 bond, which is located farther away from the stereogenic center. The higher degree of π-facial selectivity for alcohols **1f,g**, on the other hand, is explained in terms of an unsymmetrical attack of singlet oxygen on the C1–C2 bond, which is in close proximity to the directing unit.

In contrast, in the [4 + 2] cycloaddition of alcohol **1h**, the sense of the stereocontrol is reversed due to the *ortho* strain

(13) Hydrogen bonding between the hydroxy group and singlet oxygen, which is presumably partially negatively charged in the encounter complex, is in best agreement with the experimental results. For example, electrostatic attraction between the lone pairs of the nucleophilic oxygen substituent with the incoming electrophilic singlet oxygen dienophile, as previously discussed (cf. refs 6–8), would be expected to lead to a high π-facial selectivity for the silyl ether **1j**.

(14) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979.

(15) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053.

(16) Clennan, E. L. *Tetrahedron* **1991**, *47*, 1343.

caused by the methyl group at C2,[17] which overrides the effect of *peri* strain for this substrate. Consequently, transition state $\mathbf{D}^{\ddagger}$ is favored over $\mathbf{B}^{\ddagger}$ on account of reduced *ortho* strain in the former, and (αR*,1*S**,4*R**)-**2h** is formed as the major diastereomer (Scheme 5). This electornic interaction goes hand-in-hand with steric stereocontrol. Thus, transition state $\mathbf{C}^{\ddagger}$ is favored over $\mathbf{A}^{\ddagger}$, and sterically controlled attack of singlet oxygen gives the (αR*,1*S**,4*R**) diastereomer.

Summary

In the present study, we have demonstrated that the directing effect of a strategically placed hydroxy group on singlet oxygen in the [4 + 2] cycloaddition of chiral naphthyl alcohols can lead to very high diastereoselectivities. The proposed mechanistic rationalization, which is based on a synergistic effect of steric and electronic control (hydrogen bonding with the incoming dienophile), is substantiated by the observed solvent and substituent effects. *Peri* strain is responsible for the discrimination in energy of the respective conformers in the transition state. *Ortho* strain, however, as in derivative **1h**, is even more effective in dictating sense and extent of stereocontrol. The present hydroxy group directing effect, discovered in the photooxygenation of naphthyl substrates, combined with the steering propensities of other functional groups, should be helpful in achieving high diastereoselectivities in the singlet oxygen [4 + 2] cycloaddition to chiral, open-chain dienes.

(17) Broeker, J. L.; Hoffmann, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006.

Acknowledgment. Generous financial support by the Deutsche Forschungsgemeinschaft (SFB 347, "Selektive Reaktionen Metall-aktivierter Moleküle") is gratefully appreciated. M.P. thanks the Fonds der Chemischen Industrie for a doctoral fellowship (1993−95). Part of this work was presented at the 25th Reaction Mechanisms Conference, Notre Dame, IN, June 10−15, 1994.

Supporting Information Available: Detailed experimental procedures and spectral data of compounds **1**−**3**; graphical representations, crystallographic data, and tables of atomic coordinates and interatomic distances from the X-ray studies of triols **3a**,**h** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9504808