Diastereoselective Singlet Oxygen Ene Reaction (Schenck Reaction) and Diastereoselective Epoxidations of Heteroatom-Substituted Acyclic Chiral Olefins: A Mechanistic Comparison

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Abstract: The directing propensity of allylic and homoallylic heteroatom substituents on the diastereoselective singlet oxygen ene reaction (Schenck reaction) of acyclic, chiral olefins has been investigated. These extensive stereochemical results offer evidence for our proposed mechanism of the diastereoselective singlet oxygen ene reaction. Thus, provided a substrate possesses sufficient 1,3-allylic strain to populate preferentially the appropriate conformation, the photooxygenation is directed *threo*-selectively by intramolecular hydrogen bonding in the *threo*-**A** exciplex of allylic alcohols, while electron-accepting or bulky substituents result in the *erythro*-configurated products. A detailed comparison of the diastereoselectivities for the singlet oxygen ene reaction with those of the epoxidation by *m*-chlorobenzoic acid (mCPBA) and dioxirane of several judiciously chosen substrates showed that both oxygen transfer processes are influenced similarly by allylic and homoallylic substituents. Thus, it is shown that the acyclic, allylic alcohol **1a** is epoxidized highly *threo*-selectively by methyl(trifluoromethyl)dioxirane due to hydrogen bonding in the transition state and that bulky and/or electron-accepting substituents direct all three oxidants *erythro*-selectively. These pronounced steering effects on the diastereoselectivity of oxygen transfer processes (photooxygenation and epoxidation) should be valuable for the rational design of stereocontrolled oxyfunctionalizations by $^1O_2$, *m*CPBA, and dioxiranes.

Introduction

The ene reaction of singlet oxygen ($^1O_2$) with alkenes, the so-called Schenck reaction,[2] constitutes a convenient route to allylic hydroperoxides.[3] Much work has been carried out in recent years on such photooxygenations, particularly on its diastereo- and regioselectivity.[4−12] The prominent controlling factor for the regioselectivity in the Schenck reaction[2] is the by now classical *cis* effect,[4] but more recently, *gem*-directing[5] and "nonbonding large group" interactions have been recognized.[6] Furthermore, very high regioselectivity is exercised by silyl[7] and stannyl substituents.[8]

In regard to the diastereoselectivity for the $^1O_2$ ene reaction, π-facial differentiation has been abundantly documented[9] for cyclic and bicyclic substrates, whereas for acyclic olefins, such diastereomeric control has been described only recently.[10−12] Among the earliest examples count acyclic unsaturated silyl cyanhydrines[10] and olefins with phenyl substituents[11] at an allylic chirality center, for which again the *cis* effect in conjunction with 1,3-allylic strain is held responsible as the steering factor. Most recently we showed that hydroxy[12] and amino[13] functionalities at an allylic chirality center direct the singlet oxygen ene reaction *threo*-selectively, whereas acylated chiral allylic amines are photooxygenated *erythro*-selectively.[13] Unfortunately, not much is known to date on the directing effects of other heteroatom substituents.

For *m*CPBA epoxidations of acyclic chiral olefins, it is abundantly documented[14] that the diastereoselectivity of the epoxidation can be determined by the directing effect of an allylic hydroxy group and steric interactions of the oxidant with substituents at the stereogenic center. Thus, allylic alcohols, which possess 1,3-allylic strain, are epoxidized in a highly *threo*-

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selective manner, whereas olefins with a large substituent at the allylic chirality center undergo epoxidation *erythro*-selectively.[15]

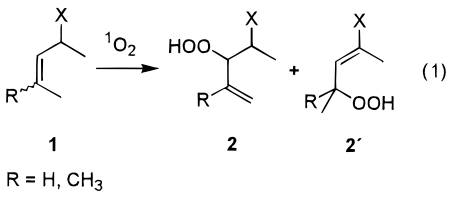
In comparison, little is known presently on diastereoselective epoxidations of chiral acyclic olefins with dioxiranes.[16] Only few examples show that the diastereoselectivity of this reaction may also be influenced by large substituents at the allylic chirality center or by an allylic ammonium or hydroxy group. Thus, in a very recent publication, it was shown by Asensio[16e] that the diastereoselectivity of the epoxidation of cyclic allylic ammonium salts by dimethyl- and methyl(trifluoromethyl)-dioxirane is directed by intramolecular hydrogen bonding, while Murray[16f] showed the same for the epoxidation of cyclohex-2-en-1-ol by dimethyldioxirane. Results similar to Murray's for the cyclic system were obtained by us for the epoxidation of the acyclic, chiral alcohol **1a** by dimethyldioxirane.[16g]

The main issue of this work was to investigate the directing effect of several heteroatom substituents on the diastereoselectivity of the singlet oxygen ene reaction of acyclic, chiral olefins. On one hand, we were interested in knowing whether homoallylic hydroxy functionalities can direct the singlet oxygen ene reaction *threo*-selectively, like allylic alcohols,[12] amines,[13] and ammonium chlorides[13] do; on the other hand, we wanted to probe whether electron-accepting or partially negatively charged substituents at the stereogenic allylic position would generally direct the photooxygenation *erythro*-selectively, as observed for acylated allylic amines.[13] This would provide relevant evidence for the mechanism we have suggested for the singlet oxygen ene reaction[13b] and would open new synthetic applications of the diastereoselectively controlled Schenck reaction.

Futhermore, it was of mechanistic interest to explore the geometric details in the oxygen transfer process of the singlet oxygen ene reaction by comparing its diastereoselectivities with those of the epoxidation by *m*CPBA, since much valuable information has been accumulated on the transition state for the later oxidation through such stereochemical probes.[12,14,16e−g] Additionally, the dioxirane epoxidations of the same set of chiral substrates were to be examined to assess its propensity for stereocontrolled oxyfunctionalizations. It was relevant to determine whether the same substituent effects, which determine the diastereoselectivity in the singlet oxygen ene reaction, may serve for the design of diastereoselective epoxidations by *m*CPBA and dioxiranes. Herein we present our results of this intensive study which provides valuable mechanistic insight into the diastereoselective oxidations by $^1O_2$, *m*CPBA, and dioxiranes.

Results

Photooxygenations. Photooxygenation of the allylic substrates **1a**−**m** afforded the regioisomeric allylic hydroperoxides **2** and **2′** by means of the singlet oxygen ene reaction (eq 1). As



starting materials for the $^1O_2$ oxidations of the hydroperoxide **1b**, the alkene **1d**, and the halides **1l,m**, isomeric mixtures of (*E*)-(2-methyl-3-penten-2-yl) hydroperoxide [(*E*)-**1′b**], of (*E*)-2,2,3,5-tetramethyl-3-hexene [(*E*)-**1′d**], of (*E*)-4-chloro-4-methyl-2-pentene [(*E*)-**1′l**], and of (*E*)-4-bromo-4-methyl-2-pentene [(*E*)-**1′m**] were used. The (*E*)-**1′b**, (*E*)-**1′l**, and (*E*)-**1′m** isomers survived the photooxygenation conditions and the substrates **1b** and **1l,m** were photooxygenated selectively. (*E*)-**1′d** gave with singlet oxygen the corresponding hydroperoxide, which was also isolated and fully characterized, as described earlier.[13b]

The observed product ratios in Table 1 were determined by ^1H NMR spectroscopy directly on the crude product mixtures. Control experiments such as the irradiation of substrates **1a**−**m** in the absence of sensitizer and prolonged photooxygenation of the corresponding hydroperoxides established that all starting materials and products persisted under the oxidation conditions. Photooxygenations in CCl_4 and $CDCl_3$ were performed at −25 °C and that of acetone at 0 °C. A control experiment with substrate **1a** showed that there is no significant temperature effect.

The photooxygenation of the derivatives **1a,d**−**f** in carbon tetrachloride (entries 1, 23, 27, and 32) was described previously[12,13] and was additionally performed in acetone. The allylic alcohol **1a** (entries 1−3) afforded in acetone, like in methanol,[12] predominantly the *threo*-configurated hydroperoxide (*R**,*R**)-**2a** in high regio- but only moderate *threo*-diastereoselectivity. In contrast, from the allylic hydroperoxide **1b** (entries 11 and 12), the bis-hydroperoxides **2b** were obtained in a moderately *erythro*-selective but also highly regioselective reaction. Due to their instability under the conditions of silica gel chromatography, the bis-hydroperoxides **2b** were reduced to the corresponding diols **3b**, which were isolated and fully characterized. The photooxygenation of the homoallylic alcohol (*Z*)-**1c** (entries 17 and 18) gave only the hydroperoxides **2c**, but in little if any diastereoselectivity.

The chiral olefin **1d** (entries 23 and 24) and the acylated allylic amines **1e** (entries 27 and 28) and **1f** (entries 32 and 33) gave in carbon tetrachloride (entries 23, 27, and 32) predominantly the *erythro*-configurated products (*R**,*S**)-**2d**−**f**, in diastereoselectivities identical within the error (ca. 5% of the stated value) to those observed in acetone (entries 24, 28, and 33). The regioisomeric product was only detected in the case of derivative **1f**; its diastereomeric ratio (*Z*)-**2′f**:(*E*)-**2′f** was 95:5 in both solvents (entries 32 and 33).

The sulfone **1g** afforded in carbon tetrachloride (entry 36) as well as in acetone (entry 37) only one product, the *erythro*-configurated (*R**,*S**)-**2g**. The photooxygenation of the sulfoxides **1h,i** (entries 40 and 41) was complicated in view of the fact that a 1:1 mixture of the diastereomers **1h,i** had to be used because all attempts to separate them by chromatography

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Table 1. Regio- and Diastereoselectivity in the Photooxygenation and *m*CPBA and DMD Epoxidations of Chiral, Allylic Olefins[a]

entry	substrate	X	R	oxidant	solvent	time (h)	conv (%)	yield[b] (%)	**2:2′**	*erythro*:*threo*	*Z*:*E*
1[c]	**1a**	OH	Me	$^1O_2$	CCl_4	2	>95	89[d]	96:4	7:93	*e*
2[c]	**1a**	OH	Me	$^1O_2$	methanol	2	>95	>95	>97:3	27:73	*f*
3	**1a**	OH	Me	$^1O_2$	acetone-d_6	2	>95	>95	96:4	31:69	*e*
4	**1a**	OH	Me	*m*CPBA	CCl_4	12	>95	>95		5:95	
5	**1a**	OH	Me	*m*CPBA	methanol-d_4	10	>95	>95		6:94	
6	**1a**	OH	Me	*m*CPBA	acetone-d_6	8	>95	>95		7:93	
7[g,h]	**1a**	OH	Me	DMD	acetone	8	>95	>95		24:76	
8[h]	**1a**	OH	Me	DMD	CCl_4[i]	8	>95	>95		18:82	
9	**1a**	OH	Me	TFD	acetone-d_6[j]	0.5	>95	>95		40:60	
10	**1a**	OH	Me	TFD	CCl_4	0.5	60	>95		8:92	
11	**1b**	OOH	Me	$^1O_2$	CCl_4	7	77	>95	>95:5	66:34	*f*
12	**1b**	OOH	Me	$^1O_2$	acetone-d_6	5	>95	>95	>95:5	70:30	*f*
13[k]	**1b**	OOH	Me	*m*CPBA	acetone-d_6	5	>95	>95		75:25	
14[k]	**1b**	OOH	Me	*m*CPBA	CCl_4	2	80	>95		72:28	
15[k]	**1b**	OOH	Me	DMD	acetone	5	>95	>95		69:31	
16[k]	**1b**	OOH	Me	TFD	CCl_4	0.5	80	>95		80:20	
17	(*Z*)-**1c**	CH_2OH	H	$^1O_2$	CCl_4	2	51	79[d]	>95:5	45:55	*f*
18	(*Z*)-**1c**	CH_2OH	H	$^1O_2$	acetone-d_6	2[l]	>95	>95	>95:5	45:55	*f*
19	(*Z*)-**1c**	CH_2OH	H	*m*CPBA	acetone-d_6	2	>95	>95		36:64	
20	(*Z*)-**1c**	CH_2OH	H	*m*CPBA	CCl_4	2	>95	>95		26:74	
21	(*Z*)-**1c**	CH_2OH	H	DMD	acetone	2	>95	>95		38:62	
22	(*Z*)-**1c**	CH_2OH	H	TFD	CCl_4	0.5	80	>95		24:76	
23[m]	**1d**	tBu	Me	$^1O_2$	CCl_4	5	>95	88[d]	>95:5	71:29	*f*
24	**1d**	tBu	Me	$^1O_2$	acetone-d_6	2	>95	>95	>95:5	73:27	*f*
25	**1d**	tBu	Me	*m*CPBA	acetone-d_6	0.75	>95	>95		>95:5	
26	**1d**	tBu	Me	DMD	acetone	8	>95	82[d]		>95:5	
27[m]	**1e**	NHBoc	Me	$^1O_2$	CCl_4	8	>95	76[d]	*f*,*n*	76:24	*f*
28	**1e**	NHBoc	Me	$^1O_2$	acetone-d_6	3	>95	90[d]	*f*,*n*	78:22	*f*
29	**1e**	NHBoc	Me	*m*CPBA	acetone-d_6	7	>95	>95		56:44	
30	**1e**	NHBoc	Me	*m*CPBA	$CDCl_3$	7	>95	>95		35:65	
31	**1e**	NHBoc	Me	DMD	acetone	7	>95	90[d]		62:38	
32[m]	**1f**	$NBoc_2$	Me	$^1O_2$	CCl_4	3	>95	91[d]	86:14	95:5	95:5
33	**1f**	$NBoc_2$	Me	$^1O_2$	acetone-d_6	5	>95	>95	85:15	95:5	95:5
34	**1f**	$NBoc_2$	Me	*m*CPBA	acetone-d_6	5	75	>95		77:23	
35	**1f**	$NBoc_2$	Me	DMD	acetone	3	>95	88[d]		75:25	
36	**1g**	SO_2Ph	Me	$^1O_2$	CCl_4	20	87	87[d]	>95:5	>95:5	*f*
37	**1g**	SO_2Ph	Me	$^1O_2$	acetone-d_6	70	75	>95	>95:5	>95:5	*f*
38	**1g**	SO_2Ph	Me	*m*CPBA	acetone-d_6	8	>95	>95		>95:5	
39	**1g**	SO_2Ph	Me	DMD	acetone	8	>95	87[d]		>95:5	
40[o]	**1h**	SOPh	Me	$^1O_2$	$CDCl_3$	6.5	>95	94[d]	*p*	>95:5	*p*
41[o]	**1i**	SOPh	Me	$^1O_2$	$CDCl_3$	6.5	>95	94[d]	*p*	85:15	*p*
42	(*Z*)-**1j**	COOEt	H	$^1O_2$	CCl_4	15	>95	77[d]	91:9	78:22	78:22
43	(*Z*)-**1j**	COOEt	H	$^1O_2$	acetone-d_6	2[l]	66	>95	90:10	65:35	70:30
44	(*Z*)-**1j**	COOEt	H	*m*CPBA	acetone-d_6	2	>95	>95		49:51	
45	(*Z*)-**1j**	COOEt	H	DMD	acetone	2	>95	>95		51:49	
46	(*E*)-**1j**	COOEt	H	$^1O_2$	CCl_4	60	55	>95	33:67	49:51	44:56
47	(*Z*)-**1k**	COOH	H	$^1O_2$	CCl_4	13	>90	>95	93:7	79:21	77:23
48	(*Z*)-**1k**	COOH	H	$^1O_2$	acetone-d_6	2[l]	80	>95	>95:5	70:30	68:32
49[q]	(*Z*)-**1k**	COOH	H	$^1O_2$	CCl_4	8	50	>95	95:5	85:15	74:26
50	(*Z*)-**1k**	COOH	H	*m*CPBA	acetone-d_6	2	>95	>95		60:40	
51	(*Z*)-**1k**	COOH	H	*m*CPBA	CCl_4	2	>95	>95		46:54	
52	(*Z*)-**1k**	COOH	H	DMD	acetone	8	>95	>95		46:54	
53	**1l**	Cl	Me	$^1O_2$	$CDCl_3$	3.5	70	81[d]	>95:5	85:15	*f*
54	**1l**	Cl	Me	$^1O_2$	acetone-d_6	2	50	>90	>95:5	>90:10	*f*
55	**1l**	Cl	Me	*m*CPBA	acetone-d_6	1	50	>90		90:10	
56	**1l**	Cl	Me	DMD	acetone	7	>95	>95		90:10	
57	**1m**	Br	Me	$^1O_2$	$CDCl_3$	1	65	78	*f*,*r*	89:11	*f*

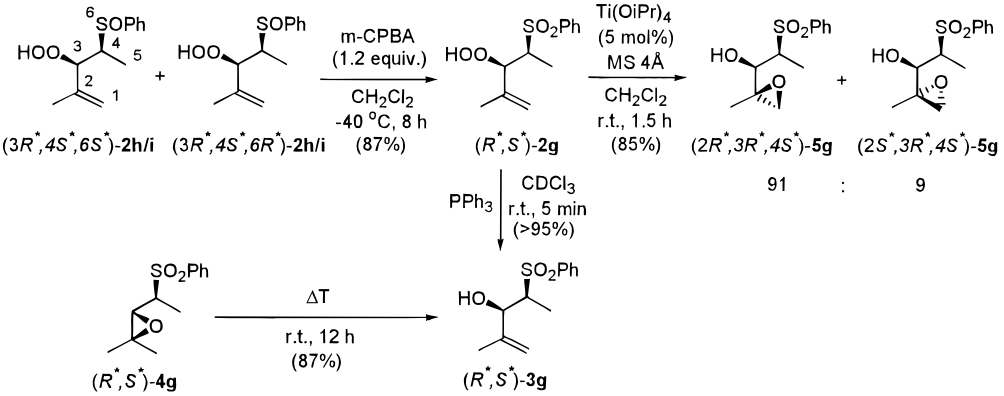
[a] The photooxygenations were performed with two external 250 W sodium lamps and tetraphenylporphine as the sensitizer at −25 °C; control experiments showed that there is no significant temperature effect on the diastereoselectivity. [b] The yields, diastereomeric ratios, and regioselectivities were determined directly on the crude product mixture by ^{1}H NMR spectroscopy (error ±5% of the stated value); mass balances >95%, except where stated by means of footnotes in this table. [c] Reference 12. [d] Yield of isolated material. [e] The regioisomer was observed in form of its ring tautomer. [f] No regioisomeric products were detected. [g] Reference 16d. [h] Reference 16g. [i] A 90:10 mixture with acetone was used. [j] A 88:12 mixture with $CDCl_3$ was used. [k] After reduction of **4b** with triphenylphosphine to **4a**. [l] Two 400 W sodium lamps. [m] Reference 13b. [n] Mass balance 90%. [o] Photooxygenation was carried out on a 1:1 mixture of the diastereomeric sulfoxides **1h**,**i**; the relative configuration of the sulfoxides was not assigned; one of the diastereomers gave the corresponding hydroperoxides **2h/i** in a diastereometric ratio of >95:5, the other in 85:15. [p] The reaction mixture contained 8% of (*Z*)-**2′h/i**, which can derive from **1h** as well as from **1i**. [q] In the presence of 2 equiv pyridine. [r] Mass balance 78%.

failed.[17] Photooxygenation of **1h,i** (1:1) gave a mixture of the two *erythro*-configurated, diastereomeric hydroperoxy sulfoxides *erythro*-**2h/i**, one of the two possible *threo*-configurated hydroperoxy sulfoxides *threo*-**2h/i**, and the *Z*-configurated regioisomeric product (*Z*)-**2′h/i**. This complex mixture of diastereomers could not be separated by silica gel chromatography. Therefore, from the diastereomeric ratio *erythro*(1)-**2h/i**:*erythro*(2)-**2h/i**:*threo*-**2h/i**:(*Z*)-**2′h/i** = 45:40:7:8, it was estimated that the two diastereomeric sulfoxides **1h** and **1i** gave the corresponding product pairs *erythro*-**2h**/*threo*-**2h** and *erythro*-**2i**/*threo*-**2i** in diastereoselectivities of >95:5 and 85:15.

Photooxygenation of the ester (*Z*)-**1j** (entries 42 and 43) afforded in a highly regioselective but moderately diastereo-

(17) Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 2100−2104.

Scheme 1

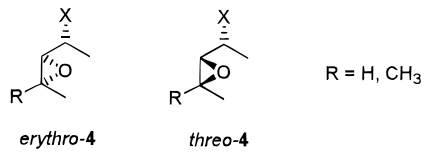


selective reaction predominantly the *erythro*- and *Z*-configurated products. The photooxygenation of the (*E*)-**1j** diastereomer (entry 46), which unlike all other substrates possesses no 1,3-allylic strain, showed no diastereoselectivity. Furthermore, the regioselectivity was not only poor but even inverted in comparison to its (*Z*)-**1j** isomer (entries 42 and 43).

The Schenck ene reaction of the carboxylic acid (*Z*)-**1k** (entries 47 and 48) gave the corresponding hydroperoxides **2k** and **2′k** in a regio- and diastereoselectivity quite similar to that observed in the photooxygenation of the ester (*Z*)-**1j** (entries 42 and 43). In the presence of 2 equiv of pyridine, the selectivities were slightly increased (entry 49).

From the allylic chloride **1l** (entries 53 and 54) and the bromide **1m** (entry 57) also only the respective hydroperoxides **2l,m** were obtained highly *erythro*-selectively. Due to their instability under the conditions of silica gel chromatography, the hydroperoxides were reduced to the corresponding alcohols **3l,m**, which were isolated and fully characterized.

Epoxidations. Epoxidation of the substrates **1a**−**g**, (*Z*)-**1j**, (*Z*)-**1k**, and **1l** with *m*CPBA, dimethyldioxirane (DMD) or bis-(trifluoromethyl)dioxirane (TFD) led in very clean reactions to the corresponding diastereomeric epoxides **4**. The allylic



alcohol **1a** gave with *m*CPBA (entries 4−6) in very high diastereoselectivities (identical within the experimental error) to the *threo*-configurated epoxide **4a** in acetone, methanol, and carbon tetrachloride. The diastereoselectivity in the epoxidations of **1a** with DMD (entry 7) and TFD (entry 9) was significantly lower in acetone. However, in both epoxidations, a significant solvent effect was observed on the diastereoselectivity (entries 7−10), which was notably higher in CCl_4 (entries 8 and 10) than in acetone (entries 7 and 9).

Epoxidation of the allylic hydroperoxide **1b** with *m*CPBA, DMD, and TFD afforded after reduction the epoxides **4a** in a moderate *erythro*-selectivity (entries 13−16). In acetone as well as in carbon tetrachloride, the epoxidations of the homoallylic alcohol (*Z*)-**1c** (entries 19−22) gave the known[18] epoxides **4c** in moderate *threo*-selectivity, which again was somewhat higher in the nonpolar CCl_4 (entries 20 and 22) *versus* acetone (entries 19 and 21).

For the epoxidation of the chiral alkene **1d** (entries 25 and 26) with *m*CPBA and DMD in acetone, only one diastereomer was obtained. In contrast, the *m*CPBA and DMD oxidations of the carbamate **1e** (entries 29 and 31) gave in acetone the epoxides **4e** in only a slight excess of the *erythro*-configurated stereoisomer, but in $CDCl_3$ (entry 30), *m*CPBA expressed a slight preference for the *threo*-product. The diastereoselectivities for the epoxidation of the imidodicarbonate **1f** (entries 34 and 35) were somewhat higher. The epoxidations of the sulfone **1g** led only to the *erythro*-configurated (*R**,*S**)-**4g** (entries 38 and 39).

The reaction of the ester (*Z*)-**1j** was not diastereoselective at all both with *m*CPBA and DMD (entries 44 and 45). The *m*CPBA epoxidation of the acid (*Z*)-**1k** in acetone showed a moderate *erythro*-selectivity (entry 50), while the DMD epoxidation in acetone and that of *m*CPBA in carbon tetrachloride were unselective (entries 51 and 52). The oxidation of the allylic chloride **1l** with DMD and *m*CPBA afforded also in high diastereoselectivities the *erythro*-configurated epoxide (*R**,*S**)-**4l** (entries 55 and 56).

Stereochemical Assignments. The relative configurations of the hydroperoxides **2a,d**−**f** were already assigned previously.[13b] The hydroperoxide **1b** afforded after photooxygenation and reduction directly the known[12] diastereomeric 4-methyl-4-pentene-2,3-diol (**3b**). The configurations of the hydroperoxides **2c** were determined by chemical correlation with the literature-known[19] diastereomeric 2-methyl-4-pentene-1,3-diol (**3c**).

The *erythro* configuration of the hydroperoxide **2g** was deduced from the small coupling constant of the α protons at the sulfur- and oxygen-bearing carbon atoms.[20] Additionally, the hydroperoxide was transformed by titanium-catalyzed oxygen transfer to the epoxides (2*R**,3*R**,4*S**)-**5g** and (2*S**,-3*R**,4*S**)-**5g** in a diastereomeric ratio of 91:9 (Scheme 1). For the major isomer, an X-ray structure determination established rigorously the (2*R**,3*R**,4*S**)-**5g** geometry (Figure 1).

The configuration of the hydroperoxides **2h/i** was determined again from the coupling constants of the α protons at the sulfur- and oxygen-bearing carbon atoms.[20] Furthermore, the *erythro*-configurated main isomers **2h/i** were chemically correlated with the hydroperoxide (*R**,*S**)-**2g** (Scheme 1). The configuration of the regioisomeric product **2′h/i** was established by NOE experiments (Figure 2), in which a significant enhancement of the signal for the olefinic proton was observed on irradiation of the methyl group attached to the double bond.

The configurations of the hydroperoxides **2j,k** were determined by chemical correlation to the literature-known[19] diastereomeric diols **3c**. The relative configuration of the regioisomeric products **2′j** and **2′k** was assessed by NOE experiments (Figure 2); for the corresponding *E* isomers, no such effects were observed.

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(19) Heathcock, C. H.; Finkelstein, B. L.; Jarvi, E. T.; Radel, P. A.; Hadley, C. R. *J. Org. Chem.* **1988**, *53*, 1922−1942.

(20) (a) Carretero, J. C.; Garcia Ruano, J. L.; Martinez, M. C.; Rodriguez, J. H.; Alcudia, F. *Tetrahedron* **1985**, *41*, 2419−2433. (b) Brunet, E.; Garcia Ruano, J. L.; Martinez, M. C.; Rodriguez, J. H.; Alcudia, F. *Tetrahedron* **1984**, *40*, 2023−2034.

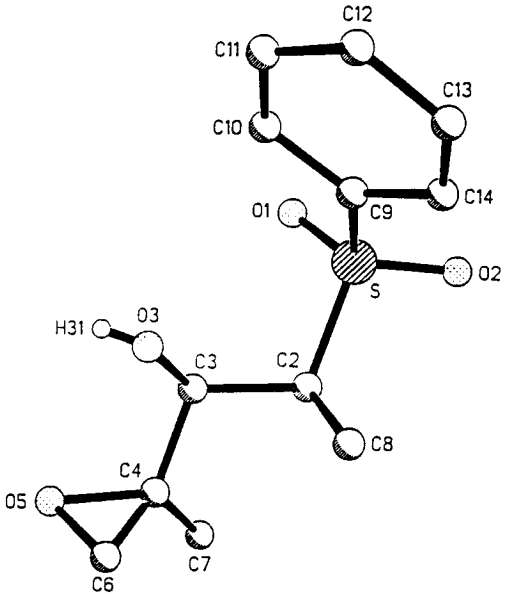


Figure 1. X-ray structure of sulfone (2*R**,3*R**,4*S**)-**5g**.

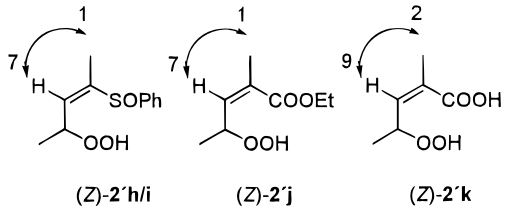


Figure 2. NOE experiments of the diastereomeric hydroperoxides **2′**.

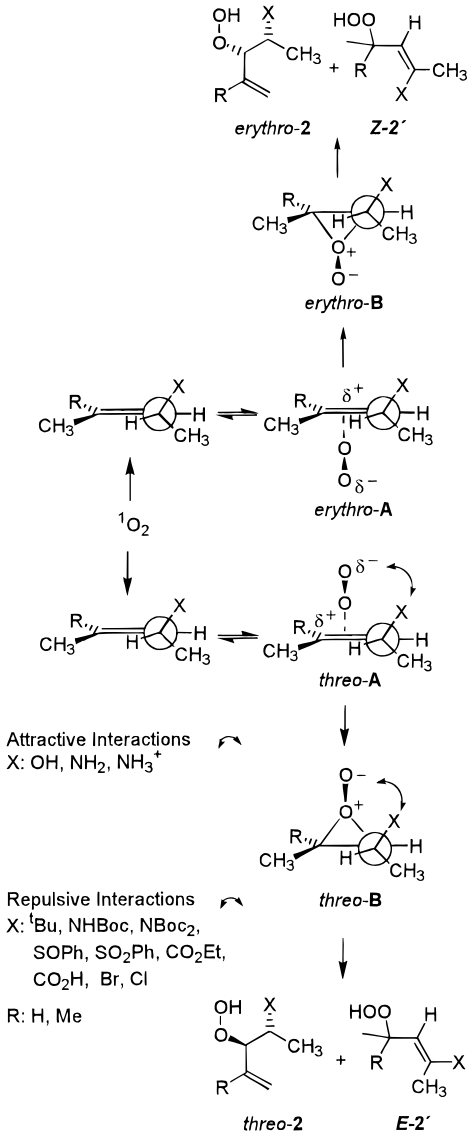
The chloro- and the bromohydrins **3l** and **3m** were chemically correlated to the known[21] *cis*- and *trans*-configurated epoxides (*cis*,*trans*)-2-methyl-3-(1-methylethenyl)oxirane (*cis*,*trans*-**6**).

The carbamate **1e** gave with *m*CPBA in deuteriochloroform (entry 30) a 65:35 diastereomeric mixture of epoxides **4e** with an inverse stereochemistry to that found in the epoxidations with *m*-CPBA and DMD in acetone (entries 29 and 31). Since it is known that in methylene chloride carbamates are epoxidized by *m*CPBA in a moderately *threo*-selective manner,[22] consequently, the main diastereomer in the epoxidation of carbamate **1e** with mCPBA and DMD in acetone should be *erythro*-configurated.

The epoxide **4g** was rearranged to the alcohol (*R**,*S**)-**3g**, which was also obtained by reduction of the hydroperoxy sulfone (*R**,*S**)-**2g** (Scheme 1). In view of the established sterically controlled attack of *m*CPBA in the epoxidations of allylic silanes,[15a−c] sulfones,[15b] and phosphine oxides,[15e] the main diastereomers in the epoxidations of the olefins **1d,f** are assumed to have the *erythro* configuration.

Since the diastereomeric epoxides **4j,k** were obtained in low diastereoselectivities (entries 44−46 and 50−51), their relative configurations were not assigned. An attempt to assign the stereochemistry of the chloro epoxide **4l** by chemically correlating it to the epoxy alcohol **4a** of known configuration[34] failed unfortunately. For example, the conversion of **4l** to **4a** with potassium hydroxide or $(Bu)_4NOH$ in methylene chloride at room temperature or the conversion of **4a** to **4l** with $SOCl_2$ in diethyl ether at 0 °C gave complex mixtures of unidentified compounds. Therefore, the configurational assignments of the diastereomeric epoxides are based on their characteristic ^1H NMR spectra. Thus, since for all *erythro*-configurated epoxides investigated here the epoxy protons α to the stereogenic center are shifted upfield compared to their *threo*-configurated diastereomers, the *major* isomer of the epoxide **4l** of the epoxidation of chloride **1l** is assumed to have the *erythro* configuration.

Scheme 2



Discussion

In recent publications[12,13] we showed that the Schenck reaction is a convenient tool for the diastereoselective synthesis of allylic hydroperoxides with β-hydroxy and β-amino substituents from chiral allylic alcohols and amines and selected derivatives. Previously we suggested a mechanism,[13b] in which the high diastereoselectivity is explained in terms of the reversible formation of perepoxide-like structured diastereomeric exciplexes **A** or *bona fide* perepoxide **B** intermediates during the oxyfunctionalization step (Scheme 2).

The *threo*-selective photooxygenation of allylic alcohols, amines, and ammonium salts, whose conformational preference is fixed by 1,3-allylic strain,[23] was rationalized in terms of stabilization of the *threo*-configurated *threo*-**A** exciplex by hydrogen bonding between the substituent X and the incipient negatively charged dioxygen molecule. Thus, the *threo*-**B** perepoxide and the *threo*-configurated hydroperoxide **2** are formed preferentially. The *erythro*-selectivity found in the

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photooxygenation of the acylated allylic amines, which also possess 1,3-allylic strain,[23] was rationalized in terms of steric and electrostatic repulsion of the X substituent and the incipient negatively charged dioxygen molecule in the *threo*-**A** exciplex. Thus, the *threo*-configurated exciplex is destabilized and the *erythro*- and *Z*-configurated hydroperoxides are formed preferentially.

The high regioselectivity of these photooxygenations was accounted for in terms of the hindered rotation about the allylic chirality center. Because of 1,3-allylic strain, the allylic hydrogen atom at the tertiary carbon atom can hardly achieve a conformation perpendicular to the olefinic plane and is not abstracted.

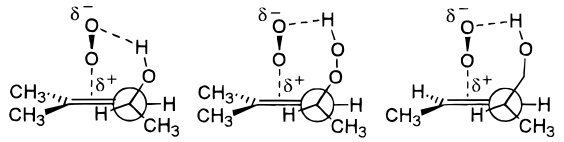
From the mechanism suggested in Scheme 2 we conclude that quite generally acyclic, chiral olefins undergo regio- and diastereoselective Schenck reactions provided two requisites are met: (1) the chiral substrate possesses a preferred conformation dictated by 1,3-allylic strain[23] and (2) the allylic chirality center bears a functionality which interacts with the incipient negatively charged dioxygen molecule in the *threo*-**A** exciplex through attractive (hydrogen bonding) or repulsive (electrostatic/steric) means. We shall first analyze our present singlet oxygen diastereoselectivities from this mechanistic perspective and subsequently compare them with those of the peracid and dioxirane epoxidations. We contend that the oxygen transfer from the peracids to olefins is a particularly suitable model for comparison because its transition state geometry is akin to the perepoxide-like structures **A** and **B** in the singlet oxygen ene reaction and fortunately its *butterfly* mechanism is well established.[24]

The results in Table 1 reveal that electron-accepting X substituents like SO_2Ph (entries 36 and 37), COOEt (entries 42 and 43), COOH (entries 47−49), Cl (entries 53 and 54), and Br (entry 57) at the allylic chirality center all promote highly regioselective singlet oxygen ene reactions in moderate to good *erythro* stereocontrol. As proposed for the acylated allylic amines, this can be explained by electrostatic and steric repulsions between the substituent X and the negatively charged oxygen atom in the *threo*-**A** exciplex (cf. Scheme 2). Thus, the energy-favored *erythro*-**A** exciplex and *erythro*-**B** perepoxide are formed, which lead to the *erythro*-**2** and (*Z*)-**2′** hydroperoxides.

Steric reasons alone cannot be responsible for the aforementioned *erythro* diastereoselectivities. This is clearly demonstrated for the photooxygenation of the allylic halides **1l,m** (entries 53 and 57), the ester (*Z*)-**1j** (entry 42), and the acid (*Z*)-**1k** (entry 47) in halogenated solvents (CCl_4 and $CDCl_3$). Their diastereoselectivities are all higher than for the *tert*-butyl derivative **1d** (entry 23). The steric demand of the *tert*-butyl group is certainly higher than that of the chloro substituent.

The importance of the 1,3-allylic strain for the regio- and diastereoselectivity of the singlet oxygen ene reaction of acyclic chiral olefins is once more shown by the photooxygenation of the ester (*E*)-**1j** (entry 46). Since the chirality center in this stereoisomer rotates essentially freely, the Schenck reaction is not diastereoselective at all. Furthermore, the regioselectivity is inverted in comparison to the (*Z*)-**1j** isomer (entry 42). The reason is that in the (*E*)-**1j** isomer the hydrogen atom at the chirality center readily aligns perpendicularly to the olefinic plane and its abstraction leads preferentially to the α,β-unsaturated ester hydroperoxides (*Z*,*E*)-**2′j**.

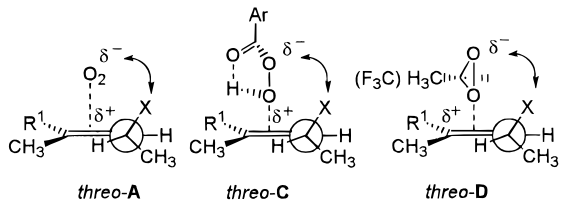
In contrast to the high *threo*-selectivity in the photooxygenation of the chiral allylic alcohol **1a** (entry 1), the Schenck reactions of the chiral allylic hydroperoxide **1b** (entry 11) and the homoallylic alcohol (*Z*)-**1c** (entry 17) exhibited little if any stereocontrol. Clearly, the hydroxy functionality in these substrates does not stabilize the *threo*-**A** exciplex. This can be rationalized in terms of the *threo*-configurated exciplexes *threo*-**A/1a**−**c**. Whereas favorable hydrogen bonding (six-membered



threo-**A/1a** *threo*-**A/1b** *threo*-**A/1c**

ring) stabilizes the *threo*-**A/1a** complex, the seven-membered rings in the *threo*-**A/1b,c** exciplexes do less so. Therefore, no significant steering control is exercised by the OH group for the hydroperoxide **1b** and the homoallylic alcohol (*Z*)-**1c** and the Schenck ene reaction proceeds in low diastereoselectivity.

In view of the epoxide-like geometry proposed[13b] for the exciplex **A** and certainly for the perepoxide **B** (Scheme 2), it should be mechanistically instructive to compare the singlet oxygen diastereoselectivities with those of *bona fide* epoxidations by peracids.[14,15,24] It is widely accepted that in the peracid epoxidation of alkenes the *butterfly* transition state applies, which results from nucleophilic attack of the double bond on the peroxide bond of the oxidant.[24] In the case of allylic alcohols, a strong hydrogen bond is formed[14] and, provided 1,3-allylic strain operates, the *threo*-**C** transition state is favored in



threo-**A** *threo*-**C** *threo*-**D**

R^1 = H, CH_3

energy compared to that with the *erythro*-geometry in view of methyl−methyl repulsion in the latter. Consequently, the *threo*-configurated epoxy alcohols are formed preferentially. Quite analogously, the preferred transition state geometry of the photooxygenation possesses the structure represented by the *threo*-**A** exciplex. In this context, it should be noted that contrary to the six-membered ring proposed here for the hydrogen bonding in the singlet oxygen ene reaction[13b] and other publications,[14g] Sharpless favors a five-membered ring for the hydrogen bonding in the diastereoselective epoxidation of allylic alcohols.[14c]

As already pointed out in the Introduction, only little is known on the diastereoselective epoxidation of allylic alcohols by dioxiranes. Recently Murray[25] proposed on the basis of solvent effects on the rate of DMD epoxidations that a spiro-type transition state with partial charge separation operates. Moreover, theoretical work by Bach[26] on the reaction coordinate for the parent dioxirane epoxidation of ethylene suggests that a spiro-perpendicular transition state is the lowest energy pathway. Consequently, analogous to the structures *threo*-**A/1a** for singlet oxygen and *threo*-**C**/**1a** for *m*CPBA, the *threo*-**D**/**1a** transition state for dioxirane should be favored in energy because of stabilization of the incipient partially negatively charged external

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dioxirane oxygen atom through hydrogen bonding. This was previously suggested[16c] and expected in view of minimized 1,3-allylic strain.[23] Very recent results by Asensio[16e] and Murray[16f] for the epoxidations of cyclic allylic alcohols and ammonium salts support this suggestion.

Our results for the epoxidation of the acyclic allylic alcohol **1a** by DMD in acetone display only a moderate *threo* diastereoselectivity[16d,g] (entry 7), definitely lower than for *m*CPBA (entry 6) but somewhat higher than for singlet oxygen (entry 3). Since an appreciable solvent effect is observed on the *threo* diastereoselectivities of the photooxygenation of the allylic alcohol **1a** in CCl_4 *versus* acetone (entries 1 and 3), it was necessary to investigate the solvent effect on the epoxidation of allylic alcohol **1a** by dioxirane. Therefore, the epoxidation with DMD was performed in the precence of a large excess of carbon tetrachloride[16g] (90:10 CCl_4/acetone; entry 8). Under these conditions, the *threo*-configurated epoxide **4a** was obtained in a little higher diastereoselectivity than in acetone alone (entry 7). Furthermore, when the trifluoromethyl-substituted dioxirane (TFD) was used as oxidant, since it can be prepared as ketone-free solutions,[27] indeed, in acetone-d_4 (entry 9) only a low *threo*-selectivity was obtained, while in carbon tetrachloride (entry 10) it was again high. Thus, we conclude that, in the epoxidation of acyclic, allylic alcohols by dioxiranes, hydrogen bonding operates in the transition state *threo*-**D**, quite analogous to the transition states *threo*-**C** for *m*CPBA and *threo*-**A** for singlet oxygen. However, despite the similarity in the transition states for these three oxidants, marked differences apply in the quality of hydrogen bonding. For example, for the *m*CPBA epoxidations of the allylic alcohol **1a** in methanol-d_4, acetone-d_6, and carbon tetrachloride (entries 4−6), within the error limits the same diastereoselectivities were obtained. This means that the hydrogen bonding in the *threo*-**C** transition state for *m*CPBA is so strong that even methanol cannot perturb it. In contrast, for the singlet oxygen and TFD, hydrogen bonding in the *threo*-**A** exciplex and the *threo*-**D** transition state is much weaker and the diastereoselectivity is significantly lower in methanol-d_4 (entry 2) and acetone-d_6 (entries 3 and 9) than in carbon tetrachloride (entries 1 and 10).

Additional mechanistic insight is provided by the diastereoselectivities in the singlet oxygen, *m*CPBA, DMD, and TFD oxidations of the allylic hydroperoxide **1b** (entries 11−16) and the homoallylic alcohol (*Z*)-**1c** (entries 17−22). The moderate *threo*- or even *erythro*-diastereoselectivities observed for all three oxidants imply little if any steering effect by the homoallylic hydroxy or homoallylic-like hydroperoxy functionality through hydrogen bonding. As pointed out already for the Schenck reaction of these substrates (entries 11, 12, 17, and 18), the *threo*-**A/1b,c** transition states possess an unfavorable geometry for hydrogen bonding, which results in poor stereocontrol. Similarly, poor hydrogen bonding also operates in the transition states for the *m*CPBA (*threo*-**C**) and DMD/TFD (*threo*-**D**) epoxidations of the allylic hydroperoxide **1b** (entries 13−16). Thus, not the *threo*- but the *erythro*-configurated epoxide **4b** is formed preferentially. Had hydrogen bonding been appreciable, 1,3-allylic strain would have dictated a high *threo*-selectivity. For the homoallylic alcohol (*Z*)-**1c** the situation seems to be somewhat different. Whereas the singlet oxygen ene reaction of this substrate is not diastereoselective at all (entries 17 and 18), the *m*CPBA and dioxirane epoxidations give the epoxide **4c** in a moderate *threo*-selectivity (entries 19−22); the latter are even higher in the nonpolar CCl_4 (entries 20 and 22) than in acetone (entries 19 and 21). Since due to steric effects *erythro*-**4c** would have been expected as the main product, a modest stabilization of *threo*-**C** and *threo*-**D** by hydrogen bonding might be responsible for this moderate diastereoselectivity.

Erythro-controlling effects on the epoxidation of acyclic chiral olefins are displayed by large X groups at the allylic chirality center. For example, it is known[15] that substrates with large X substituents are attacked by *m*CPBA preferentially from the side opposite to X and, therefore, the *erythro*-configurated epoxides are favored. A similar trend has been observed for the DMD[16a,b] epoxidation of acyclic olefins.

The observed *erythro* selectivities in the oxidations of the substrates **1d,g** (entries 23−26 and 36−39) for the three oxidants $^1O_2$, *m*CPBA, and DMD nicely corroborate these expectations. Furthermore, the very high diastereoselectivities of the *m*CPBA and DMD epoxidations of the *tert*-butyl-substituted alkene **1d** (entries 25 and 26) show that these epoxidations are more subject to steric influence of the X substituent than the singlet oxygen ene reaction. The latter exhibits only a moderate *erythro*-selectivity in the oxidation of *tert*-butyl derivative **1d** (entries 23 and 24).

Unlike the singlet oxygen ene reaction, the *m*CPBA and DMD epoxidations of the substrates **1e,f** (entries 29−31 and 34 and 35) and (*Z*)-**1j,k** (entries 44 and 45 and 50−52) exhibit only moderate if any *erythro*-diastereoselectivity. For the singlet oxygen ene reaction, the moderate to high diastereoselectivities were explained by the electrostatic repulsion of the partially negatively charged singlet oxygen and the X substituent. This repulsion seems not to be decisive for the *m*CPBA and DMD epoxidations. However, as was clearly shown by the highly diastereoselective epoxidations of the allylic chloride **1l** (entries 55 and 56), the *m*CPBA and DMD reactions depend not only on steric but also on electronic influence.[43] These electronic effects might be of electrostatic nature, as described for the singlet oxygen ene reaction.

In conclusion, the above extensive stereochemical results demonstrate that heteroatom-substituted acyclic, chiral olefins with 1,3-allylic strain can nicely be employed for the diastereoselective synthesis of oxyfunctionalized molecules through the singlet oxygen ene reaction and the *m*CPBA and DMD/TFD epoxidations. Thus, *threo*-selectivity can be achieved by X substituents, which act through hydrogen bonding. Indeed, it has been convincingly demonstrated by the TFD epoxidation of **1a** that hydrogen bonding is the decisive factor in the diastereoselective epoxidation of acyclic allylic alcohols by dioxirane. In contrast, substrates which possess sterically demanding and/or partially negatively charged X substituents are oxidized *erythro*-selectively by all three oxidants.

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Supporting Information Available: Experimental details for the preparation, purification, and characterization of all mentioned compounds and the crystallographic data for (2*R**,3*R**,4*S**)-**5g** (24 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.

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