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π-Facial Selectivity of the Singlet Oxygen [4+2] Cycloaddition to Chiral Naphthalene Derivatives: The Directing Effect of Carbon-Containing Substituents

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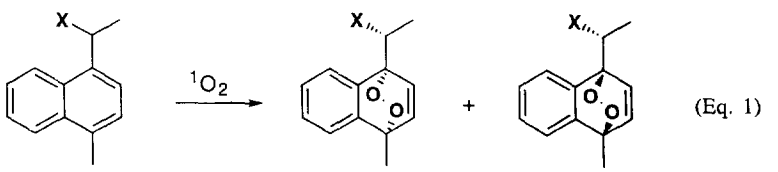
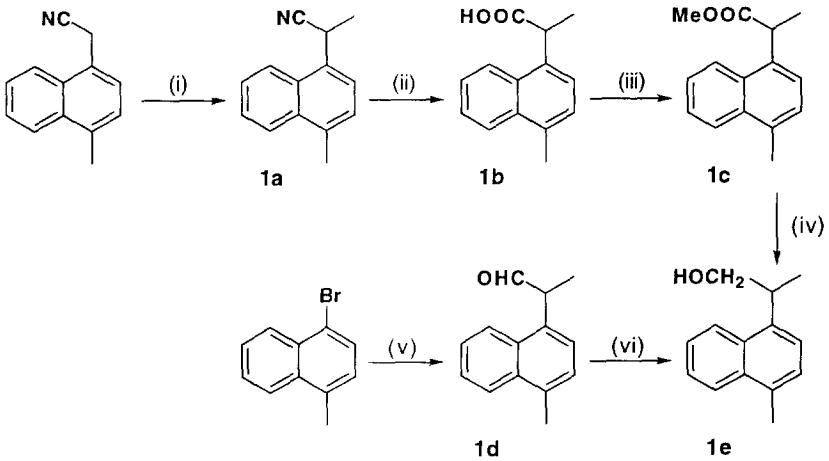
Abstract: *A set of five chiral naphthalene derivatives* **1** *gave on photooxygenation the corresponding endoperoxides in excellent yields; the diastereoselectivity of singlet oxygen attack was determined and the directing effect of various carbon-containing substituents (CN, COOH, COOMe, CHO, CH_2OH) was rationalized in terms of attraction or repulsion in the transition state through electronic and steric effects.*

The [4+2] cycloaddition of dienic substrates with singlet oxygen has become a useful preparative method due to the synthetic versatility of the resulting endoperoxide products.[1] For effective stereoselective synthesis, however, knowledge on the π-facial directing effect of functional groups in chiral dienes on the singlet oxygen attack is essential, but scarce to date. In view of this happenstance, we recently started a systematic study on the substrate-controlled, diastereoselective singlet oxygen [4+2] cycloaddition.[2] Thus, for 5-substituted 1,3-cyclopentadienes [3] it was demonstrated that the π-facial selectivity is controlled by steric bias.[2e] More demanding to achieve efficient stereocontrol are substrates for which the directing substituent is not directly attached to the ring system. Conformational preferences in the ground and/or transition state raise additional mechanistic complexities and have prompted numerous studies on the classical Diels-Alder reaction.[4] For the singlet oxygen dienophile we have recently shown [2a-c] that strategically placed heteroatom substituents (X = OH, Cl, Br, SiR_3) cause remarkable diastereoselectivities (d.r. ≤ 95 : 5) in the endoperoxidation of chiral naphthalene derivatives **1** (Eq. 1).



1 *like*-**2** *unlike*-**2** (Eq. 1)

It was of general interest to assess whether a similar directing effect is also exerted by carbon-containing substituents at the chirality center. Due to their ready accessibility and clean reaction with singlet oxygen,[2a-c,5] chiral naphthalene derivatives were again chosen as model substrates. The carbonyl derivatives **1a-d** (X = COOH, COOR, CHO, CN) and the alcohol **1e** (X = CH_2OH) were prepared from the available precursors (Scheme 1). In the photooxygenation of the latter substrate, it was of interest to determine



Scheme 1: (i) step 1: $NaNH_2$, Et_2O, reflux, 0.5 h; step 2: MeI, rt, 18 h, 76%. (ii) NaOH(aq), EtOH, reflux, 20 h, 77%. (iii) MeOH, HCl (g), reflux, 5 h, 80%. (iv) $LiAlH_4$, Et_2O, reflux, 14 h, 87%. (v) step 1: Mg, THF; step 2: ethyl pyruvate, rt, 3 h; step 3: $LiAlH_4$, Et_2O, rt, 12 h; step 4: H_2SO_4, Et_2O, reflux, 5 h, 59%. (vi) $NaBH_4$, MeOH, rt, 3 h, 94%.

whether the well-documented, *like*-directing propensity of the free hydroxy groups (hydrogen bonding to singlet oxygen [2a-d,6]) may be extended from the benzylic (Eq. 1, X = OH) to the homobenzylic position.

On photooxygenation at subambient temperatures in nonpolar solvents, the chiral naphthalenes **1a-e** afforded the corresponding endoperoxides **2a-e** (Eq. 1) in nearly quantitative yields. Reaction conditions and diastereoselectivities, the latter determined by NMR spectroscopy on the crude reaction mixtures, are summarized in Table 1. While the nitrile **1a** and the aldehyde **1d** showed poor π-facial control (entries

Table 1: Diastereoselectivities in the Photooxygenation of the Chiral Naphthalene Derivatives **1**

entry	substrate	substituent	time (h)	conversion [a] (%)	endoperoxide **2** (%)	diastereoselectivity *like*-**2** : *unlike*-**2**
1	**1a**	CN	6	40	≥ 95	51 : 49 [b]
2	**1b**	COOH	5	90	≥ 95	21 : 79
3	**1b**	COOH [c]	4	90	> 95	10 : 90
4	**1c**	COOMe	6	≥ 95	≥ 95	22 : 78
5	**1d**	CHO	16	48	ca. 90	60 : 40 [b]
6	**1e**	CH_2OH	5	≥ 95	≥ 95	90 : 10

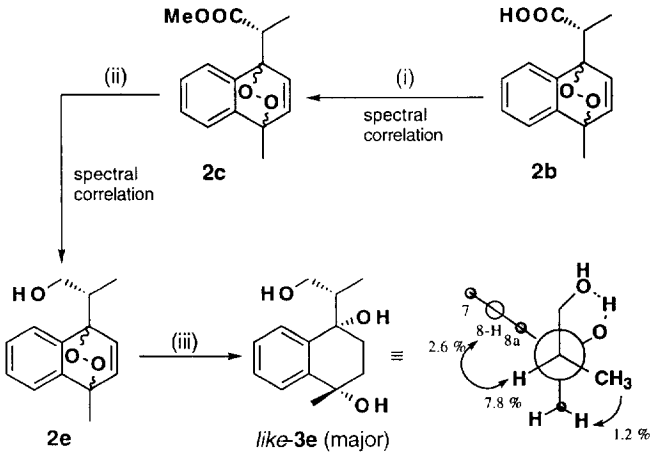
a) Photooxygenations were carried out at - 30 °C in $CDCl_3$ with tetraphenylporphine (TPP) as sensitizer; NMR spectra were taken on the crude product mixture at - 20 °C.

b) The relative stereochemistry was not assigned.

c) The photooxygenation was carried out in presence of 2.0 equiv. pyridine.

1 and 5), good to high diastereoselectivities were observed for the derivatives **1b,c,e** (entries 2-4 and 6). Remarkably, for the free acid **1b** the preference for *unlike* attack was enhanced when the photooxygenation was carried out in the presence of two equivalents of pyridine (entry 3).

The diastereoselectivities for derivatives **1a,d** are too low to speculate on their sense as well as origin. For the other endoperoxides **2b,c,e**, the relative stereochemistry of singlet oxygen attack was established by a combination of NMR spectroscopy and chemical transformations (Scheme 2). NOE



Scheme 2: (i) CH_2N_2, $CDCl_3$, - 25 °C, 15 h, ca. 90%; (ii) $LiAlH_4$, Et_2O, 0 °C, 2 h; (iii) H_2, Pd/C, EtOAc, 0 °C, 2 h, 75%.

experiments on triol **3e** clearly demonstrated the *like* configuration for the major diastereomer, a result that is in good agreement with the *like*-directing propensity of the free hydroxy group in the previously examined chiral naphthyl alcohols.[2a-c] Once the geometry of the derivative **2e** was assigned, the endoperoxides **2b,c** were spectrally correlated. Thus, the ester **2c** was converted to alcohol **2e** by careful $LiAlH_4$ reduction (preservation of the peroxide functionality) and the *unlike* configuration for the major isomer of the former was confirmed by spectral comparison. Diazomethane esterification of the acid **2b** and spectral correlation with cycloadduct **2c** showed that also the free acid **1b** reacted preferentially to the *unlike* endoperoxide.

A mechanistic rationale of the present stereochemical results is featured in Fig. 1. Thus, for the

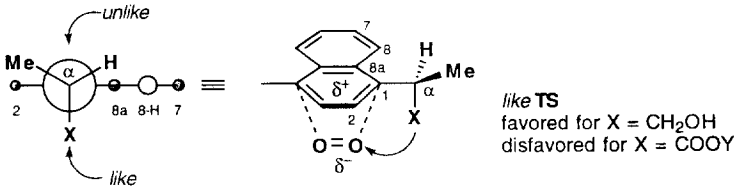


Figure 1: Transition States for the *like* Attack of Singlet Oxygen on the Chiral Naphthalene Substrates **1**.

conformation with minimal *peri* strain, the free hydroxy group of alcohol **1e** directs the dienophile contrasterically to the *like* face of the aromatic system through hydrogen bonding to the incoming singlet oxygen molecule,[6] which bears a partial negative charge in the transition state or intermediary exciplex.[7] In contrast, for the acid **1b** and the ester **1c** electrostatic repulsion [8] between singlet oxygen and the benzylic

substituent disfavors the *like* approach and, therefore, prefers the *unlike* diastereoselectivity. For the latter substrates, additionally also steric hindrance may operate in controlling *unlike* π-facial selectivity.

In conclusion, not only heteroatom but also carbon-containing substituents at the stereogenic center can steer efficiently the singlet oxygen attack on chiral naphthalene derivatives. For synthetic utility, it should be worthwhile to probe whether the observed directing effects can be exploited in the endoperoxidation of open-chain dienes or for the closely related Diels-Alder reaction with ordinary carbon dienophiles.

EXPERIMENTAL

General Aspects

Melting points were determined on a Büchi SMP-20 apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 1420 ratio recording infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer by using $CDCl_3$ as internal standard. Combustion analyses were carried out by the Microanalysis Division of the Institute of Inorganic Chemistry, University of Würzburg. Column chromatography was run on silica gel (63 - 200 μm) from Woelm as stationary phase, with an absorbant / substrate ratio of ca. 100 : 1. For thin layer chromatography (TLC), Polygram SIL G/UV_{254} (40x80 mm) plates from Macherey and Nagel were used. UV detection (254 nm) was employed for the naphthalene derivatives, peroxides were made visible by means of 10% aqueous KI spray and subsequent exposure to a heatgun.

All commercial compounds were used as received, solvents were purified and dried by reported standard methods. $CDCl_3$ for photooxygenations was filtered through basic alumina prior to use. 1-Bromo-4-methylnaphthalene [9] was prepared according to previously described procedures.

α,4-Dimethyl-1-naphthalenacetonitrile (1a)

Nitrile **1a** was prepared from 2.14 g (11.8 mmol) 4-methyl-1-naphthalenacetonitrile [10] exactly as previously described for α-methyl-1-naphthalenacetonitrile. [11] After column chromatography [silica gel/petroleum ether (30-50)/Et_2O (4 : 1) as eluent], 1.75 g (76%) yellowish powder was obtained, mp 56-57 °C (petroleum ether). IR (CCl_4): ν = 3060 cm^{-1}, 2960, 2920, 2210 (CN), 1585, 1505, 1440, 1380, 830. ^1H-NMR (200 MHz, $CDCl_3$): δ = 1.78 (d, *J* = 7.2 Hz, 3 H), 2.72 (s, 3 H), 4.63 (q, *J* = 7.2 Hz, 1 H), 7.34 (d, *J* = 7.9 Hz, 1 H), 7.57-7.63 (m, 3 H), 7.93-7.97 (m, 1 H), 8.06-8.11 (m, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 19.5 (q), 20.5 (q), 28.1 (d), 121.9 (s), 122.5 (d), 124.3 (d), 125.3 (d), 125.9 (d), 126.2 (d), 126.4 (d), 129.7 (s), 130.7 (s), 133.0 (s), 135.2 (s). Anal Calcd for $C_{14}H_{13}N$ (195.3): C, 86.11; H, 6.71; N 7.17. Found: C, 86.05; H, 6.84; N 6.81.

α,4-Dimethyl-1-naphthalenacetic acid (1b)

To a solution of 1.45 g (7.42 mmol) nitrile **1a** in ethanol (50 mL) and water (15 mL), NaOH (2.30 g, 57.5 mmol) was added and the mixture was brought to reflux for 20 h. The solvent was evaporated at 40 °C/20 Torr, 4 N HCl (40 mL) and methyl *tert.*-butyl ether (MTB, 150 mL) were added and the aqueous layer was extracted with methyl *tert.*-butyl ether (3 x 100 mL). The combined organic layers were washed with water (3 x 20 mL) and dried over anydrous $MgSO_4$. Evaporation of the solvent at 30 °C/20 Torr and recrystallization from Et_2O gave 1.23 g (77%) acid as tan colored powder, mp 125-126 °C (Et_2O). IR ($CHCl_3$): ν = 3280-2910 cm^{-1} (OH), 3370, 2970, 1660 (C=O), 1560, 1440, 1390, 830. ^1H-NMR (200 MHz, $CDCl_3$): δ = 1.69 (d, *J* = 7.2 Hz, 3 H), 2.70 (s, 3 H), 4.30 (q, *J* = 7.2 Hz, 1 H), 6.03 (br s, 1 H), 7.31 (d, *J* = 7.9 Hz, 1 H), 7.40 (d, *J* = 7.9 Hz, 1 H), 7.52-7.58 (m, 2 H), 8.03-8.08 (m, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 17.7 (q), 19.5 (q), 43.2 (d), 123.7 (d), 123.7 (d), 124.6 (d), 125.1 (d), 125.8 (d), 126.3 (d), 131.5 (s), 133.1 (s), 134.4 (s), 134.9 (s), 178.2 (s, C-12). Anal Calcd for $C_{14}H_{14}O_2$ (214.3): C, 78.48; H, 6.59. Found: C, 78.46; H, 6.45.

Methyl α,4-dimethyl-1-naphthalenacetate (1c)
A solution of 600 mg (2.80 mmol) carboxylic acid **1b** in MeOH (50 mL) was saturated with dry HCl gas and brought to reflux for 5 h. The yellow solution was concentrated to 10 mL at 20 °C/20 Torr. Water (15 mL) and ether (40 mL) were added and the aqueous layer was extracted with ether (2 x 30 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 x 15 mL) and brine (2 x 15 mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated at 20 °C/20 Torr. Column chromatography of the residue on silica gel [petroleum ether (30-50)/ Et_2O (10 : 1)] as eluent gave 512 mg (80%) ester **1c** as yellowish oil. IR ($CHCl_3$): ν = 3040 cm^{-1}, 2940, 1720 (C=O), 1570, 1490, 1410, 820, 740. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.65 (d, *J* = 7.1 Hz, 3 H), 2.69 (s, 3 H), 3.66 (s, 3 H), 4.49 (q, *J* = 7.1 Hz, 1 H), 7.29-7.38 (m, 2 H), 7.53-7.60 (m, 2 H), 8.03-8.12 (m, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 18.2 (q), 19.5 (q), 41.2 (d), 52.1 (q), 123.5 (d), 124.1 (d), 125.0 (d), 125.5 (d), 125.9 (d), 126.4 (d), 131.2 (s), 133.0 (s), 133.8 (s), 134.9 (s), 175.7 (s). Anal Calcd for $C_{15}H_{16}O_2$ (228.3): C, 78.92; H, 7.06. Found: C, 78.74; H, 7.15.

Ethyl α-hydroxy-α,4-dimethyl-1-naphthalenacetate
To the Grignard reagent, prepared from 9.00 g (40.7 mmol) 1-bromo-4-methylnapthalene and 990 mg (40.7 mmol) magnesium turnings in 130 mL THF, ethyl pyruvate (4.73 g, 40.7 mmol) was added at 0 °C and the mixture was stirred at room temperature (ca. 20 °C) for 3 h. Standard workup and recrystallization of the oily residue from pentane gave 7.92 g (75%) hydroxy ester as yellowish powder, mp 78-79 °C (pentane). IR ($CHCl_3$): ν = 3500 cm^{-1} (OH), 3060, 2960, 1700 (C=O), 1590, 1440, 1120. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.1 Hz, 3 H), 2.00 (s, 3 H), 2.70 (s, 3 H), 3.67 (br s, 1 H), 4.08-4.27 (m, 2 H), 7.30 (d, *J* =7.4 Hz, 1 H), 7.45-7.57 (m, 3 H), 8.01-8.05 (m, 1 H), 8.20-8.25 (m, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 19.7 (q), 27.2 (q), 62.2 (t), 75.9 (s), 123.9 (d), 124.8 (d), 125.3 (d), 125.4 (d), 125.5 (d), 125.8 (d), 131.0 (s), 133.4 (s), 135.0 (s), 135.5 (s), 178.0 (s). Anal Calcd for $C_{16}H_{18}O_3$ (258.3): C, 74.40; H, 7.02. Found: C, 74.58; H, 6.90.

2-(4-Methyl-1-naphthyl)-1,2-propanediol
To a suspension of 658 mg (17.3 mmol) $LiAlH_4$ in ether (50 mL), a solution of 3.00 g (11.6 mmol) ethyl α-hydroxy-α,4-dimethyl-1-naphthalenacetate in ether (100 mL) was added dropwise. The mixture was stirred at room temperature (ca. 20 °C) for 12 h and carefully hydrolyzed with aqueous NH_4Cl. Standard workup gave 2.63 g (99%) diol as colorless cubes, mp 95-96 °C (Et_2O/pentane).IR ($CHCl_3$): ν = 3520 cm^{-1} (OH), 3320, 2980, 1580, 1360, 1100, 1020. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.79 (s, 3 H), 2.10 (br s, 1 H), 2.68 (s, 3 H), 2.70 (br s, 1 H), 3.82 (d, *J* = 11.2 Hz, 1 H), 4.28 (d, *J* = 11.2 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 7.49-7.56 (m, 3 H), 8.02-8.07 (m, 1 H), 8.67-8.72 (m, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 19.7 (q), 26.3 (q), 70.0 (t), 76.1 (s), 123.7 (d), 125.1 (d), 125.1 (d), 125.2 (d), 125.8 (d), 126.9 (d), 131.0 (s), 133.9 (s), 134.8 (s), 137.7 (s). Anal Calcd for $C_{14}H_{16}O_2$ (216.3): C, 77.75; H, 7.46. Found: C, 77.71; H, 7.67.

α,4-Dimethyl-1-naphthalenacetaldehyde (1d)
A solution of 1.00 g (4.67 mmol) 2-(4-Methyl-1-naphthyl)-1,2-propanediol and 0.5 mL H_2SO_4 in ether (40 mL) was heated to reflux for 4 h. Water (10 mL) was added and the aqueous layer was extracted with ether (3 x 15 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 x 10 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent at 20 °C/20 Torr and chromatography of the residue on silica gel [petroleum ether (30-50)/Et_2O (4 : 1) as eluent] gave 722 mg (79%) aldehyde **1d** as colorless oil. IR ($CHCl_3$): ν = 3040 cm^{-1}, 2920, 1720, 1590, 1450, 1310. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 7.0 Hz, 3 H), 2.71 (s, 3 H), 4.36 (qd, *J* = 7.0 Hz, 1.4 Hz, 1 H), 7.19 (d, *J* = 7.3 Hz, 1 H), 7.35 (d, *J* = 7.3 Hz, 1 H), 7.48-7.65 (m, 2 H), 8.01-8.11 (m, 2 H), 9.75 (d, *J* = 1.4 Hz, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 14.6 (q), 19.5 (q), 48.7 (d), 123.5 (d), 125.2 (d), 125.3 (d), 125.8 (d), 126.3 (d), 126.4 (d), 127.3 (s), 132.2 (s), 132.4 (s), 134.4 (s), 201.4 (d). Anal Calcd for $C_{14}H_{14}O$ (216.3): C, 84.81;

H, 7.12. Found: C, 84.65; H, 6.68.

α,4-Dimethyl-1-naphthalenethanol (1e)
To a solution of 300 mg (1.51 mmol) aldehyde **1d** in methanol (10 mL), $NaBH_4$ (70.0 mg, 1.85 mmol) was added. The solution was stirred at room temperature (ca. 20 °C) for 3 h and the solvent was evaporated at 20 °C/20 Torr. Column chromatography of the residue on silica gel [petroleum ether (30-50)/EtOAc (5 : 1) as eluent] gave 285 mg (94%) alcohol **1e** as colorless syrup. IR (CCl_4): ν = 3540 cm^{-1} (OH), 3040, 2940, 1580, 1440, 1380, 1010, 980, 825. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.44 (d, *J* = 5.7 Hz, 3 H), 1.70 (br s, 1 H), 2.71 (s, 3 H), 3.77-3.99 (m, 3 H), 7.34 (br s, 2 H), 7.53-7.62 (m, 2 H), 8.04-8.11 (m, 1 H), 8.18-8.23 (m, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 17.9 (q), 19.5 (q), 36.1 (d), 68.0 (t), 122.6 (d), 123.5 (d), 125.0 (d), 125.4 (d), 125.6 (d), 126.3 (d), 131.9 (s), 132.9 (s), 133.0 (s), 137.5 (s). Anal Calcd for $C_{14}H_{16}O$ (200.3): C, 88.96; H, 8.05. Found: C, 84.37; H, 7.89.

General Procedure for Photooxygenations
A solution of the naphthalene derivative **1** (200 μmol) and a catalytic amount of tetraphenylporphine (TPP) in $CDCl_3$ (1 mL) was irradiated at -30 °C by means of two OSRAM Vialox NAV-E (250 W) sodium lamps, while a gentle stream of dried oxygen gas was allowed to pass through the solution. NMR spectra were taken directly on the crude product mixtures, for details cf. Table 1. Control experiments assured that the cycloadducts were stable under the reaction conditions, i.e. the d.r. values did not change on prolonged photooxygenation. The labile endoperoxides reverted to the corresponding naphthalenes by loss of dioxygen and were, therefore, characterized spectroscopically.

1-(1-Cyanoethyl)-1,4-dihydro-4-methyl-1,4-epidioxynaphthalene (2a)
Mixture of diastereomers (51 : 49) ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.4 Hz, 3 H), 1.68 (d, *J* = 7.4 Hz, 3 H), 1.90 (s, 2 x 3 H), 3.67 (q, *J* = 7.4 Hz, 1 H), 3.68 (q, *J* = 7.4 Hz, 1 H), 6.81 (s, 2 H), 6.83, d, *J* = 8.2 Hz, 1 H), 6.95 (d, *J* = 8.2 Hz, 1 H), 7.23-7.62 (m, 2 x 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$, only resolved resonances are listed): δ = 12.9 (2 x q), 15.8 (q), 15.9 (q), 26.8 (d), 27.1 (d), 79.1 (s), 79.3 (s), 82.4 (s), 83.1 (s), 120.2 (d), 120.5 (d), 120.7 (d), 120.8 (d), 121.7 (s), 121.8 (s), 126.8 (d), 126.9 (d), 127.0 (d), 127.3 (d), 133.0 (d), 134.1 (s), 135.1 (s), 140.9 (d), 141.0 (d).

1-(1-Carboxyethyl)-1,4-dihydro-4-methyl-1,4-epidioxynaphthalene (2b)
Like-**2b** (minor isomer, only resolved resonances are listed): ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.4 Hz, 3 H), 1.88 (s, 3 H), 3.38 (q, *J* = 7.4 Hz, 1 H), 6.47 (br s, 1 H), 6.73 (d, *J* = 8.2 Hz, 1 H), 6.91 (d, *J* = 8.2 Hz, 1 H), 7.24-7.43 (m, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.2 (q), 15.8 (q), 41.8 (d), 78.6 (s), 83.1 (s), 120.4 (d), 121.0 (d), 126.1 (d), 126.3 (d), 137.1 (d), 139.0 (d), 175.1 (s).*Unlike*-**2b** (major isomer): ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.61 (d, *J* = 7.3 Hz, 3 H), 1.88 (s, 3 H), 3.41 (q, *J* = 7.3 Hz, 1 H), 6.25 (br s, 1 H), 6.74 (d, *J* = 8.2 Hz, 1 H), 6.98 (d, *J* = 8.2 Hz, 1 H), 7.24-7.43 (m, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 15.8 (q), 41.3 (d), 78.7 (s), 81.6 (s) 120.2 (d), 120.9 (d), 126.7 (d), 126.8 (d), 135.8 (d), 139.1 (d), 141.0 (s), 141.1 (s), 175.2 (s).

1,4-Dihydro-1-[1-(methoxycarbonyl)ethyl]-4-methyl-1,4-epidioxynaphthalene (2c)
Like-**2c** (minor isomer, only resolved resonances are listed): ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.61 (d, *J* = 7 1 Hz, 3 H), 1.88 (s, 3 H), 3.75 (s, 3 H), 6.73 (d, *J* = 8.2 Hz, 1 H), 7.09 (d, *J* = 8.2 Hz, 1 H), 7.17-7.33 (m, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.0 (q), 16.0 (q), 39.0 (d), 52.4 (q), 80.5 (s), 84.9 (s), 120.3 (d), 120.5 (d), 126.7 (d), 127.0 (d), 136.3 (d), 138.2 (d), 173.1 (s). *Unlike*-**2n** (major isomer): ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 7.2 Hz, 3 H), 1.89 (s, 3 H), 3.51 (q, *J* = 7.2 Hz, 1 H), 3.79 (s, 3 H), 6.75, (d, *J* = 8.3 Hz, 1H), 7.16-7.34 (m, 5 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.2 (q), 16.1 (q), 39.5 (d), 52.6 (q), 78.8 (s), 84.6 (s), 120.3 (d), 120.3 (d), 126.9 (2xd), 135.4 (d), 138.3 (d), 139.3 (s), 140.3 (s), 173.7 (s).

1,4-Dihydro-1-[1-(methoxycarbonyl)ethyl]-4-methyl-1,4-epidioxynaphthalene (2c) from endoperoxide 2b: According to the general procedure, a sample of 45.0 mg (210 µmol) of the carboxylic acid **1b** was photooxygenated in $CDCl_3$. At - 25 °C diazomethane (420 µmol, ether solution) was added and the mixture stored at -25 °C overnight. The diastereomers of endoperoxide **2c** (yield ca. 90%) were identified by their characteristic NMR resonances.

1,4-Dihydro-1-(1-formylethyl)-4-methyl-1,4-epidioxynaphthalene (2d)
Major isomer: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 7.2 Hz, 3 H), 1.93 (s, 3 H), 3.51 (qd, *J* =7.2 Hz, 2.0 Hz, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 6.89 (d, *J* = 8.3 Hz, 1 H), 7.11-7.39 (m, 4 H), 9.99 (d, *J* = 2.0 Hz, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 9.0 (q), 15.9 (q), 46.9 (d), 78.3 (s), 81.9 (s), 120.2 (d), 120.5 (d), 126.2 (d), 126.9 (d), 135.6 (d), 138.5 (s), 139.9 (d), 140.5 (s), 210.5 (d). *Minor isomer*: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 7.2 Hz, 3 H), 1.90 (s, 3 H), 3.46 (brq, *J* = 7.2 Hz, 1 H), 6.77-6.83 (m, 2 H), 7.11-7.36 (m, 4 H), 10.00 (d, *J* = 1.9 Hz, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 9.0 (q), 16.0 (q), 46.1 (d), 78.3 (s), 80.6 (s), 120.1 (d), 120.6 (d), 126.1 (d), 126.7 (d), 135.0 (d), 138.3 (s), 139.3 (d), 140.8 (s), 201.5 (d).

1,4-Dihydro-1-[(2-hydroxy-1-methyl)ethyl)]-4-methyl-1,4-epidioxynaphthalene (2e)
Like-**2e** (major isomer): ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.9 Hz, 3 H), 1.89 (s, 3 H), 2.33 (br s, 1 H), 2.85-2.94 (m, 1 H), 3.75 (dd, *J* = 11.5 Hz, 4.4 Hz, 1H), 3.97 (dd, *J* = 11.5 Hz, 5.9 Hz, 1 H), 6.76 (d, *J* = 8.2 Hz, 1 H), 6.92 (d, *J* = 8.2 Hz, 1 H), 7.23-7.38 (m, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.4 (q), 15.9 (q), 35.6 (d), 63.9 (t), 78.2 (s), 84.1 (s), 120.1 (d), 120.8 (d), 126.5 (d), 126.6 (d), 131.6 (d), 139.4 (d), 139.6 (s), 140.5 (s). *Unlike*-**2e** (minor isomer, only resolved resonances are listed): ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.44 (d, *J* = 6.8 Hz, 3 H), 1.88 (s, 3 H), 3.83 (dd, *J* = 11.0 Hz, 6.1 Hz, 1 H), 4.08 (dd, *J* = 11.0 Hz, 7.1 Hz, 1 H), 7.53-7.59 (m, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 12.1 (q), 15.9 (q), 34.8 (d), 64.3 (t), 78.1 (s), 84.8 (s), 120.2 (d), 121.2 (d), 126.1 (d), 126.3 (d), 131.0 (d), 137.3 (d).

1,4-Dihydro-1-[(2-hydroxy-1-methyl)ethyl)]-4-methyl-1,4-epidioxynaphthalene (2e) from endoperoxide 2c: According to the general procedure, a sample of 50.0 mg (250 µmol) of the ester **1c** was photooxygenated for 6 h in CH_2Cl_2 (*like*-**2c**:*unlike*-**2c** = 22 : 78). The solvent was evaporated at -10 °C/0.01 Torr and precooled (0 °C) ether (4 mL) and 19.0 mg (500 µmol) $LiAlH_4$ were added. The mixture was stirred at 0 °C for 2 h and aqueous NH_4Cl (0.3 mL) was added. The solvent was evaporated at -10 °C/0.01 Torr and the residue extracted with $CDCl_3$ (0.7 mL). The diastereomers of endoperoxide **2e** were identified by their characteristic NMR resonances.

(*1R*,4R)-1,2,3,4-Tetrahydro-1-[(*R**)-2-hydroxy-1-methylethyl]-naphthalene-1,4-diol** (*like*-**3e**): According to the general procedure, a sample of 260 mg (1.30 mmol) alcohol **1e** was photooxygenated in CH_2Cl_2 (*like*-**2e** : *unlike*-**2e** = 89 : 11). The solvent was evaporated at -10 °C/0.01 Torr and precooled (0 °C) ethyl acetate (10 mL) and Pd/C (15 mg) were added. The mixture was hydrogenated at 1 atm H_2 pressure until negative peroxide test (KI/HOAc) (1.5 h). The catalyst was removed by filtration and the solvent was evaporated at 20 °C/20 Torr. Column chromatography of the residue on silanated silica gel [petroleum ether (30-50)/Et_2O (10 : 1) as eluent] gave 234 mg (76%) *like*-triol **3e** (d.r. ≥ 95 : 5) as yellowish syrup. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 7.1 Hz, 3 H), 1.44-1.63 (m, 2 H), 1.67 (s, 3 H), 1.80-2.12 (br s, 3H), 2.23-2.48 (m, 2 H), 2.65-2.80 (m, 1 H), 3.63 (dd, *J* = 11.5 Hz, 4.9 Hz, 1 H), 3.98 (dd, *J* = 11.5 Hz, 6.0 Hz, 1 H), 7.26-7.44 (m, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 13.3 (q), 19.0 (t), 24.0 (q), 29.0 (t), 38.2 (d, C-10), 64.2 (t), 76.1 (s), 81.7 (s), 120.8 (d), 121.2 (d), 127.7 (d), 127.9 (d), 138.3 (s), 139.5 (s). Anal Calcd for $C_{14}H_{20}O_3$ (236.3): C, 71.16; H, 8.53. Found: C, 70.80; H, 8.88.

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