Synthesis and photochemistry of (2S,4R)- and (2R,4R)-1,2,3,4-tetrahydro-4-ethyl-1,1,4-trimethyl-3Z-ethylidene-2-naphthalenols

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Synthesis and photochemistry of (2*S*,4*R*)- and (2*R*,4*R*)-1,2,3,4-tetrahydro-4-ethyl-1,1,4-trimethyl-3*Z*-ethylidene-2-naphthalenols

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Abstract. The synthesis and photochemistry of optically pure (2*S*,4*R*)- and (2*R*,4*R*)-1,2,3,4-tetrahydro-4-ethyl-1,1,4-trimethyl-3*Z*-ethylidene-2-naphthalenols **10a** and **11a** are described. Naphthalenols **10a** and **11a** were prepared in seven steps from 2-phenylbutanenitrile. Synthesis is mainly based upon acylation of isobutene by the optically active 2-methyl-2-phenylbutanoyl chloride (**5**), and a Wittig reaction, while the ethylidene naphthalenones **8a** and **9a** are separated by HPLC. Under inert conditions, irradiation of both alcohols gives rise to *E*–*Z* isomerization, followed by photodegradation reactions, leading to the formation of indane **12** by the elimination of formaldehyde. Irradiation of oxygenated solutions of **10a** reveals a rapid photoaddition of oxygen to the double bond, leading to the stereo- and regioselective formation of hydroperoxide **13** and epoxy alcohol **15a**, which hydrolyses on standing to triol **16a**. The observed stereochemistry is explained by the stereoselective coordination of the hydroxyl group at the chiral allylic site with the attacking electrophilic oxygen. In the case of **11a** a more complicated reaction mixture was obtained in which, analogously, the epoxy alcohol **15b** and triol **16b** were present. Semi-empirical MNDO, AM1 and PM3 calculations revealed that, in the preferential ground state conformation, the hydroxyl group occupies an orthogonal position with respect to the exocyclic double bond. Fluorescence measurements revealed that the reactive state in the photochemistry of these naphthalenol systems under inert conditions is the triplet state. In the photoreactions of optically pure compounds **10a** and **11a**, we were unable to identify products analogous to **2**, which are claimed to originate from the racemic precursors **1** via a planar 1,3 OH shift from a singlet (in the double bond) excited state. Clean photochemical reactions were observed only when **10a** and **11a** were irradiated in oxygenated solutions, resulting in stereo- and regiospecific photoproducts.

Introduction

Quantum-chemical calculations concerning the photochemical *E*–*Z* isomerization of olefins, based on the pioneering work of Mulliken¹, reveal that excitation of the double bond results in a 90°-twisted diradicaloid structure². In biradicals a small polarizing perturbation causes a complete polarization of the excited singlet states, a phenomenon often referred to as sudden polarization³. Although the phenomenon of sudden polarization does not seem to have any consequence for the *E*–*Z* isomerism as such, it may lead to reactions such as an attack by a polar solvent on the highly polarized alkene. Studies by Marshall⁴ and Kropp⁵ have already implicated the presence of polar intermediates in the photochemical addition of alcohols to alkenes. In these additions *E*–*Z* isomerization of the olefin is followed by protonation of the transoid intermediate. However, more recently it has been concluded that photoaddition of water and alcohols to 3-nitrostyrenes occurs via a planar polarized triplet state⁶. Twisting of the alkene moiety in *T*₁ results in deactivation, only to the ground state.

Although the photochemistry of alkenes in both inert and hydroxylic solvents is well documented, the photochemistry of bichromophoric compounds with suitably posi-

tioned hydroxyl groups has enjoyed only limited study^{7–9}. A remarkable photochemical rearrangement has been claimed to occur in the 2-propenol units of both 9-hydroxygermacrene B¹⁰(3) and 1,2,3,4-tetrahydro-4-ethyl-1,1,4-trimethyl-3*Z*-alkylidene-2-naphthalenol compounds^{10,11} **Z-1a** (Scheme 1). Upon UV irradiation of a racemic mixture¹² of (2*R*,4*R*)- and (2*S*,4*S*)-**1a**, not only has a fast *E*–*Z* isomerization been observed, yielding a photostationary state for *E*/*Z* of approximately 1:1, but also a slow stereospecific formation in low yields, of photoproduct **2a**¹¹.

The experimental data presented here, suggest that the photoreactivity is controlled by the preferred conformation of the ground state^{13–15}, a phenomenon well-known in photochemistry. It has been reported that the diastereomeric alcohols **1b** (a racemic mixture of 2*S*,4*R* and 2*R*,4*S*) do not give **2** due to a difference in conformation. This stereospecificity in the photoreactivity of **1a** is interesting. It has been postulated that differentiation of reactivity originates from a preferential twisting of the polarized singlet excited ene moiety, dictated by the steric interactions of stereocentres. It should be noted, however, that direct excitation of the olefinic chromophore in **1** into its *S*₁ state, must be considered unlikely due to the fact that simple alkenes exhibit poor absorption in the spectral

Scheme 1.

regions accessible to the photochemical equipment employed. Actually, the alkyl benzene chromophore in **1** might be expected to be primarily excited. Such an aromatic chromophore is known to be able to sensitize the triplet state of alkyl ethylenes (E_T 84 kcal/mol for benzene, 81 kcal/mol for tetrahydronaphthalene and 79 kcal/mol for ethene)¹⁶. As a consequence, this would produce the triplet rather than the singlet-excited state of the exocyclic double bond in **1**. Another unresolved difference in the comparison between germacrol **3** and **1a,b** is found in the results of the photoreactivity in methanol. An efficient reaction was found for germacrol, but for the naphthalenol derivatives methanol addition was observed. Moreover, a strong inhibition of reactivity was found in polar non-hydroxylic solvents¹⁷. The conflicting experimental results of **1a** in comparison with **1b** and **3** and increasing mechanistical interest in stereochemistry combined with photochemistry of hydroxylic bichromophoric compounds, motivated us to reinvestigate the photochemistry of the 2-naphthalenol compounds. Hence, in this paper we present the synthesis and characterization of the

optically active starting materials for **1a** and **1b** (referred to as **11a** and **10a**, respectively)¹² and a study of the photochemical behaviour of the 2-naphthalenols **10a** and **11a** in various solvents as well as in the presence of oxygen.

Results

Synthesis

The reaction route for the synthesis of the optically pure (2S,4R)- and (2R,4R)-1,2,3,4-tetrahydro-4-ethyl-1,1,4-trimethyl-3Z-ethylidene-2-naphthalenols **10a** and **11a** is outlined in Scheme 2.

In this preparative procedure the optically pure (*R*)-2-methyl-2-phenylbutanoic acid^a (**4**) is employed as a key starting material for the synthesis of the naphthalenol derivatives. The racemic acid is prepared by the methylation of 2-phenylbutanenitrile^a, followed by hydrolysis^{18,19}. Resolution of the racemic acid was achieved by fractional crystallization of the quinine salts from aqueous ethanol. The progress of the resolutions is easily followed by the determination of the melting point of the salts. The formation of optically pure **4** by resolution was verified by the determination of the optical rotation: $[\alpha]_D^{25} -29.2^\circ$ (*c* 4.9, benzene)^{20,21}. The absolute configuration, as evidenced by Cram et al. by relating the configuration of acid **4** to that of 2-phenylbutane, is *R*²². The corresponding (*R*)-2-methyl-2-phenylbutanoyl chloride^a **5** is easily obtained by reaction of thionyl chloride with butanoic acid **4**.

An essential step in the reaction route is the synthesis of the optically pure polyalkylnaphthalenone **6**. Racemic, crowded polyalkyl-3,4-dihydro-2(1*H*)-naphthalenones are usually synthesized via Friedel-Crafts alkylation using dihydro-2,2,5,5-tetraalkyl furanone²³. To obtain optically pure material, it is highly desirable to use another method in which the synthesis is based upon acylation of the branched alkene (isobutene) by the optically pure 2-methyl-2-phenylbutanoyl chloride **5**, followed by Friedel-Crafts cyclization of the resulting unsaturated ketones to the polyalkyl 3,4-dihydro-2(1*H*)-naphthalenones²⁴. In or-

^a For Chem. Abstr. names, see Experimental.

Scheme 2.

Figure 1. Plots of the induced proton chemical shift $\Delta\nu$ of ketones **8a** and **9a**, versus the amount of shift reagent added.

der to avoid extensive rearrangements, the acylation was carried out with a minimal amount of stannic chloride in carbon disulfide, resulting in a mixture of an unsaturated ketone, the corresponding tertiary chloride and the desired final product. All intermediates were isolated and cyclized with boron trifluoride etherate in dichloromethane. Oxidation with SeO_2 furnishes optically pure 1,4-dihydro-1-ethyl-1,4,4-trimethyl-2,3-naphthalenedione **7** ($[\alpha]_D^{25} 100^\circ$, c 2, methanol). A Wittig reaction on **7**, using ethylenephosphorane, gives rise to the α,β -unsaturated ketones **8a** and **9a** in a ratio of 40:60. Both ketones were isolated in pure form by HPLC. Small traces of *E* isomers were easily separated from the *Z* isomers by column chromatography.

In order to distinguish between the 1-ethyl-1,4,4-trimethyl and the 4-ethyl-1,1,4-trimethyl derivatives, two different methods were used: first, by correlating relative positions of the ^{13}C -NMR resonances of the quaternary carbons in several tetraalkylnaphthalenediones, by changing the substituents on the quaternary carbon from methyl to ethyl and the carbonyl to ethylidene; second, by carrying out ^1H -NMR Eu(fod)_3 experiments. Using the former method

to determine the structure of both ketones, we compared the ^{13}C -NMR resonances of the quaternary carbons of 1,4-dihydro-1,1,4,4-tetramethyl-2,3-naphthalenedione, 1,4-dihydro-1-ethyl-1,4,4-trimethyl-2(1*H*)-naphthalenedione and 3,4-dihydro-1,1,4,4-tetramethyl-3*Z*-ethylidene-2(1*H*)-naphthalenedione¹⁷ to the resonances of the optical pure ketones **8a** and **9a**. Upon replacement of one methyl by an ethyl group in the dione derivatives, the ^{13}C -NMR resonance of the corresponding quaternary carbon is shifted downfield by 4.0 ppm, from 51.6 to 55.6 ppm. Going from dione to ethylidene group in the tetramethyl derivative, its ^{13}C -NMR resonance undergoes an upfield shift of 8.8 ppm, from 51.6 to 42.8 ppm. Taking these data into account, the isomer showing chemical shifts of 49.2 and 45.8 ppm is proposed to be **8a** while the isomer featuring chemical shifts of 42 and 53.4 ppm represents ketone **9a**.

The ^1H -NMR Eu(fod)_3 shift experiments, as shown in Figure 1 for the α,β -unsaturated ketones **8a** and **9a**, indicate that for a given amount of reagent added, both methyl groups on C1 in ketone **8a** are shifted to a larger extent than in ketone **9a** in which only one methyl group on C1 exhibits such a large shift. A strong indication is the difference in shift of the ethyl group: in the case of ketone **8a**, this group is slightly affected upon adding the shift reagent, whereas in **9a** the ethyl group is shifted to an even larger extent than the two methyl groups at C4.

Upon LiAlH_4 reduction of ketone **8a**, the diastereomeric allylic alcohols **10a** (2*S*,4*R*) and **11a** (2*R*,4*R*) are formed in a ratio of 70:30. Both diastereomers are distinguished by determination of the configuration on C2. This was realized initially by the assignment of the quaternary carbons C1 and C4 and adjacent substituents in a two-dimensional (2D) NMR INADEQUATE experiment (see Figure 2) and a heteronuclear $^1\text{H}/^{13}\text{C}$ 2D chemical-shift correlation NMR spectrum²⁵, followed by ^1H -NMR Eu(fod)_3 experiments to correlate the shift of the protons closest to the hydroxyl group and/or to the shift of the ethyl and methyl substituents on C4 (see Figure 3).

From the results presented in these figures an unambiguous assignment of the configurations for both diastereomers was obtained. In the INADEQUATE-2D-COSY-like symmetry experiment (INADSYM) for **10a** the whole skeleton of the molecule could be traced by determination of the ^{13}C - ^{13}C connectivities, thereby starting from the clearly assignable signal of the ethyl group (C12) at 9.8

^b fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato.

Figure 2. Two dimensional INADEQUATE spectrum of **10a** showing ^{13}C - ^{13}C connectivities. The horizontal F2 axis represents ^{13}C chemical shifts or couplings. The F1 axis represents $0.55 \times ^{13}\text{C}$ chemical shifts. SW1/SW = 3.6, τ = 6 ms, 256 increments with a spectral width of 17 kHz; 32 scans per increment.

Figure 3. Plots of the induced proton chemical shift $\Delta\delta$ of naphthalenols **10a** and **11a**, versus the amount of shift reagent added.

ppm which is connected to the methylene at $0.55 \times 38 = 20.9$ ppm on the F1 axis. In Figure 2 the correlations appear as off-diagonal cross-peaks of the two adjacent carbon atoms as in COSY. Coordinates of cross-peaks are given in the ^{13}C chemical shifts or ^{13}C - ^{13}C couplings on the F2 domain (horizontal axis) and $0.55 \times$ shifts or couplings ($SW1/SW2 = 3.6$) on the F1 domain (vertical axis), respectively.

From Figure 2 it can be clearly seen that the quaternary carbon at 39.6 ppm is correlated with two methyl groups at approximately half shifts (0.55) of 0.55×26.0 and 30.0 ppm, respectively, and therefore it is denoted as C1; the other quaternary carbon at 42.8 ppm is correlated to the methylene (C11) and one methyl group at approximately half shifts of $(0.55) \times 38.0$ and 31.7 ppm, respectively (hence denoted as C4).

In a 2D-XHCORR experiment, the ^{13}C signals for **10a** and **11a** were found to be correlated with the proton resonances in the ^1H spectrum (see experimental section for more details). The next step in the determination of the configuration of **10a** and **11a**, is to examine the shift of proton resonances from the methyl and ethyl groups at C1 and C4 upon addition of Eu(fod)_3 . Figure 3 clearly shows that in case of **10a** the methyl signal (C12) is shifted to much larger extent than that of **11a**, where only one methyl (C7 or C8) exhibits a very large shift. As a consequence, the hydroxyl group in the molecule has to be attached to the same side as the ethyl group of the alcohol **10a** and to the opposite side in **11a**. Hence, we assign the 2S,4R configuration to alcohol **10a** and the 2R,4R configuration to alcohol **11a**.

Photochemistry

In order to reconsider the mechanism of the photochemical rearrangements for the racemic naphthalenol compounds **1a** and **1b**, we reinvestigated the photochemical behaviour of these compounds, using the optically pure enantiomers **10a** and **11a** as starting materials. Irradiations were conducted in inert medium as well as in media potentially capable of entering into a (photo)reaction with the substrates. Inert conditions were obtained by purging the solution continuously with a stream of dry argon, and using *n*-hexane (spectroscopic grade) as solvent. Photolysis experiments were carried out in oxygenated solutions of *n*-hexane or in protic solvents (2% H_2O in CH_3CN or MeOH) to study the possible photoaddition of oxygen, water or methanol to the double bond and the subsequent behaviour. Studies were performed by photolyzing $4 \cdot 10^{-3}$

Scheme 3.

M solutions of the substrates in 500 ml of solvent. Kinetics of formation and disappearance of materials were monitored by GC analysis.

In inert medium, UV irradiation of alcohol **10a** results primarily in a fast *E*-*Z* isomerization around the double bond. Prolonged irradiation leads to formation of (*Z*)- and (*E*)-1-ethyl-1,3,3-trimethyl-2-ethylideneindanes **12a** and **12b** in addition to (*Z*) and (*E*) ketones **8a** and **8b** in low yields (Scheme 3).

As can be clearly seen from the chromatograms (GC) in Figure 4, the 1:1 photostationary state for the *Z* and *E* isomers of both alcohols is reached in about 10 minutes. Evaluation of the data at longer photolysis times (Table II, experimental section) shows that prolonged irradiation led to the almost complete photodecomposition of both *E* and *Z* isomers, affording a complicated reaction mixture. Despite repeated column chromatography, and HPLC, only mixtures of photoproducts could be isolated in low yields, together with an unidentified polar polymer with an elemental composition of approximately $\text{-C}_4\text{H}_6\text{O-}$ as one of the main products.

The combination of ^1H -NMR and GC/MS analysis of the major fractions resulted in the characterization of *E* and *Z* ketones **8a,b** and *E*- and *Z*-indanes **12a** and **12b**. It should be noted that alcohol **11a** shows similar photochemical behaviour to **10a**. No indication of the allylic rearrangement in the 2-propenol unit, as suggested in Scheme 1, for the 2-naphthalenol enantiomer **11a** was obtained. Again, ^1H -NMR spectra and GC/MS analysis indicated a fast *E*-*Z* isomerization as the primary and major photoprocess, while prolonged irradiation ulti-

Figure 4. Stack plot of GC chromatograms of aliquots taken from the irradiation mixture of **10a** (*Z*) after photolysis for 1, 5 and 10 minutes and 2 hours, showing the *Z*/*E* isomerization.

mately led to the previously mentioned degradation products and the indanes by loss of formaldehyde.

UV Irradiation of **10a** in oxygen-saturated hexane for 15 minutes at temperatures below 0°C, results in the formation of two products **14** and **15a**, in 34 and 60% yield at 50% conversion, respectively. We assume that **14** originates from the main photoproduct **13** (see Discussion). Irradiations were stopped at maximum concentrations of the photoproducts at a *Z/E* isomer ratio of approximately 7:3. Longer photolysis times enhance the complexity of the reaction mixtures. Isolation of the photoproducts was accomplished by column chromatography using hexane/ethyl acetate (96:4) as eluent. Structures of photoproducts were determined on the basis of two-dimensional $^1\text{H}/^{13}\text{C}$ correlation spectra and available data from the literature on the photooxidation of allylic alcohols. The proton spectrum of the first eluted product **14** shows vinylic resonances at 6.44, 5.23 and 5.51 ppm in which the proton at 6.44 ppm is coupled to the protons at 5.23 and 5.51 ppm (3J 10.67 and 16.82 Hz). The vinylic resonances each represent a single hydrogen. The ^{13}C -NMR spectrum of **15a** shows three resonances at 65.63 (s) and 58.85 (d) (-C-O-oxirane) and 77.04 (d, -CH-O, alcohol) ppm. For a more detailed structural elucidation we refer to the Discussion, since 2D-NMR $^1\text{H}/^{13}\text{C}$ correlation experiments do not give absolute proof on the connectivities of oxygen^{26a}. Photoproduct **15a**, obtained in relatively high yield, is readily hydrolysed on standing in CDCl_3 in the presence of light and water to compound **16a**. In the ^{13}C -NMR spectrum three -C-O- resonances are visible at 67.82 (s), 62.54 (d) and 62.41 (d) ppm, respectively, and the methyl on C9 of the exocyclic oxygenated double bond has shifted down-field (7 ppm). 2D-NMR $^1\text{H}/^{13}\text{C}$ correlation experiments revealed the structure of triol **16a** (see Scheme 4 and Experimental Section for further details). Irradiation of **11a** in the presence of oxygen results in a more complicated reaction mixture. Repeated flash column chromatography still affords mixtures of photoproducts. However, characteristic ^1H -NMR resonances in combination with the results obtained for naphthalenol **10a**, indicate that an epoxy alcohol and a triol are present in the collected fractions [i.e. δ 3.33 (q) and δ 3.62 (s) for the epoxy alcohol **15b** and δ 4.33 (q) and 3.18 (s) for the triol **16b**]. No ene reaction was found, such as had been observed for **10a**. Instead, characteristic signals in the ^1H -NMR spectra of other fractions showed a singlet at 5.8 ppm and a quartet at 4.5 ppm.

Since photoaddition of oxygen and subsequent photochemistry turned out to be selective we studied the photochemical behaviour of both alcohols **10a** and **11a** in the protic solvents methanol and water and under inert conditions. However, irradiation of **10a** and **11a** in methanol does not result in photoaddition to the exocyclic double bond of either the *E* or *Z* isomer, but an unidentified polymer was found as the main product (after photolysis

Figure 5a. UV absorption spectra of **10a** (dotted lines) and reference alcohol **17** (solid lines) in *n*-hexane with maxima at 264 nm. Figure 5b. Normalized fluorescence spectra of both compounds. The structure of reference alcohol **17** is depicted in the insert of the fluorescence spectrum.

for 8 h). The photochemical behaviour observed in *n*-hexane does not occur in methanol.

Photoaddition of water to the exocyclic double bond was pursued by dissolving both starting materials in CH_3CN as co-solvent. In 100% CH_3CN , only *E-Z* isomerization was observed, secondary photochemical processes being very slow. Upon addition of 2% (10 ml, 0.5 mol) water to the photostationary mixture (1:1) still no photoaddition to the exocyclic double bond was observed.

Fluorescence studies

In order to increase our insight into the mechanistic details of the photochemical behaviour of the 2-naphthalenol derivatives we examined whether reactions occur via the singlet (S_1) or triplet (T_1) excited state. To decide whether S_1 or T_1 is the reactive state, we measured the UV absorption and fluorescence spectra of naphthalenol **10a** and reference alcohol **17**, in which the exocyclic double bond is absent (ketone **6** is reduced to the corresponding alcohol **17**). If a photoreaction takes place via the singlet state of the exocyclic double bond in **10a**, this state should either be populated by direct excitation or by singlet-singlet energy transfer from the singlet excited state of the aromatic moiety. Although both processes are *a priori* quite improbable, it can be seen from Figure 5a that the UV absorption spectra of **10a** and **17** are identical in shape. Thus, the exocyclic double bond exhibits poor absorption in the spectral regions accessible to our photochemical equipment. Hence, a singlet reaction would only be expected if singlet-singlet energy transfer takes place. If energy is transferred from the S_1 of alkylbenzene towards the S_1 of ethylidene the fluorescence intensity for **10a** must be lower than for the reference compound **17**. However the fluorescence spectra in Figure 5b show that (also at 77K) both compounds emit light of the same wavelength with an almost equal quantum yield. No quenching of fluorescence in **10a** as compared to **17** was observed and thus no indication for singlet-singlet energy transfer was obtained (note that in fact the fluorescence of **10a** is slightly more intense than that of **17**, see Figure 5b).

Conformational studies

The conformational properties of **10a,b** and **11a,b** were investigated on the basis of three semi-empirical MO calculations: MNDO²⁷, AM1²⁸ and PM3²⁹. In these compounds, the exocyclic double bond can adopt two possible orientations, one in which the hydroxyl group is situated in the plane of the exocyclic double bond and one in which the hydroxyl group is oriented in an orthogonal position with respect to this plane. In the starting geometries the dihedral angles are set to 0° for the planar naphthalenol conformers and 90° for the orthogonal con-

Scheme 4.

formers. Steric energy was minimized by means of MM calculations. The geometries of 2*R*,4*R* and 2*S*,4*R* were optimized further using the MNDO, AM1 and PM3 Hamiltonians of the Mopac program²⁷⁻²⁹. The relative populations of all stable conformers of 10*a*,*b* and 11*a*,*b* were calculated from the Boltzmann equation based on heats of formation at 0° only. Table I shows that all methods of calculation for all conformers lead to the conclusion that, for diastereomers 10*a*, 10*b* and 11*a*, 11*b* the preferential conformation is the orthogonal orientation. Although local minima for the planar geometries are found, the planar conformation is unfavourable in view of the very low populations calculated by MNDO, AM1 and PM3.

Discussion

The optically pure 2-naphthalenols 10*a* and 11*a* were prepared in seven steps from 2-phenylbutanenitrile (see Scheme 2). Enantiomerically pure 2-methyl-2-phenylbutanoic acid (97.5 g, e.e. > 99%) was obtained after five recrystallizations of the salt of quinine and racemic 2-methyl-2-phenylbutanoic acid in 60% aqueous ethanol. The conditions for the acylation of isobutene with butanoyl chloride 5 were optimized; excess isobutene and 0.6 equiv. SnCl₄ were used, resulting in a mixture of ketones containing 45% 2-chloro-2,5-dimethyl-5-phenyl-4-heptanone (6*a*) and 40% 2,5-dimethyl-5-phenyl-1-hepten-4-one (6*b*) and 15% of the naphthalenone 6. Further cyclization was accomplished with excess of boron trifluoride etherate to avoid rearrangement to side-products²⁴. Eventually, naphthalenone 6 was obtained in 45% overall yield. Some difficulties arose in the separation of the ethylidenenaphthalenones 8*a* and 9*a*. Repeated argentation chromatography did not result in the separation of both isomers. HPLC using rather critical conditions 99.75% hexane and 0.25% ethyl acetate saturated with 0.1% water) allowed separation of 8*a* and 9*a*. GLC showed both ketones to still contain 5% of the other isomer. The *E* isomers were separated easily from the *Z* isomers but were formed in very low yields, due to the steric interactions of the phosphorane with the bulky methyl and ethyl groups of the dione 7. Finally, the optically pure 2-naphthalenols 10*a* and 11*a* were obtained in a ratio of 3:7 upon reduction with LiAlH₄. The characterization and assignment of the isomers is outlined above.

Under inert conditions, both optically pure compounds 10*a* and 11*a*, gave a complex mixture of photoproducts, when irradiated for long periods. Only *E* and *Z* isomerization and photodegradation reactions were observed, resulting in the formation of (*E*)- and (*Z*)-1-ethyl-1,3,3-trimethyl-2-ethylideneindanes 12*a*,*b*. Since the weakest bond could well be the C1-C2 (or C3-C4), formation of the indanes probably originates from the benzylallylbiradical 12*c*, as the initial intermediate (Scheme 5) which, by

Scheme 5.

loss of CH₂O and recombination of the radical sites, can yield the indane. As an alternative, the ketones 8*a* and 8*b* (M⁺ 242) might be formed in low yield by loss of hydrogen. Under inert conditions, we did not obtain any evidence for the formation of the photoproducts found by Peijnenburg et al.¹¹.

Upon UV irradiation of compound 10*a* in the presence of oxygen, we observed a fast reaction leading to the regio- and stereospecific formation of two photoproducts. Product 14, the alcohol derivative of the allylic hydroperoxide 13, is without doubt the result of allylic oxidation of the C=C double bond in a stereo- and regioselective ene reaction, the hydroperoxide group in 13 being easily converted to its alcohol, on C3, under the experimental conditions used, by performing column chromatography on silica gel. The ene reaction of olefins has been understood for three decades and is considered to proceed with singlet oxygen as the reactive species³⁰. In the mechanism of the ene region, the stereochemical selectivities have attracted considerable attention. Three pronounced effects of regioselectivity have been observed: the *cis* or *syn* effect³¹, the *gem* effect³², and the large-group effect^{33,34}. In the by now well-known *cis* effect there is a strong preference for hydrogen abstraction on the higher substituted side of trisubstituted olefins. In the *gem* effect, electron-withdrawing groups in either vinylic or allylic relationship, or e.g. α,β -unsaturated ketones, increase the tendency for geminal hydrogen abstraction. This effect has also been recognized for non-bonding large groups, where regioselective double-bond formation occurs at the substituent with the (larger) groups at the same carbon of the olefin. Although these factors were rationalized in terms of rotational barriers^{32b}, it was pointed out later that barriers to rotation do not dictate regioselectivity, but regioselective ene-product distribution depends on the free-energy difference of the isomeric transition states³⁴. It is also generally accepted that methyl and methylene hydrogens are reactive, and that isopropyl C-H and certain conformationally inaccessible hydrogens are not; this explains why in the exciplex or perepoxide, hydrogen abstraction occurs only from C-H10 and not from C-H2. The latter hydrogen occupies the inaccessible (quasi) equatorial position; cf. Matush and Schmidt³⁵. It should be noted that in apolar solvents (hexane) the ene region is strongly favoured over dioxetane formation at the experimental temperatures. Decomposition of the dioxetanes would lead to the corresponding ketones in the reaction

Table I Heats of formation (ΔH_f) and relative populations (at 0°C) of all stable conformers of *Z* and *E* isomers of (2*S*,4*R*)-10*a*,*b* and (2*R*,4*R*)-11*a*,*b*.

Naphthalenol conformer	Heats of formation ΔH_f (Kcal/mol)			Relative population (%)		
	MNDO	AM1	PM3	MNDO	AM1	PM3
10 <i>a</i> <i>Z</i> -2 <i>S</i> ,4 <i>R</i> (orthog)	-4.8	-35.5	-41.5	100.0	99.7	100
<i>Z</i> -2 <i>S</i> ,4 <i>R</i> (planar)	-0.2	-32.3	-36.6	0.0	0.3	0.0
11 <i>a</i> <i>Z</i> -2 <i>R</i> ,4 <i>R</i> (orthog)	-4.4	-36.1	-42.2	99.7	99.2	100
<i>Z</i> -2 <i>R</i> ,4 <i>R</i> (planar)	-1.2	-33.5	-36.3	0.3	0.8	0.0
10 <i>b</i> <i>E</i> -2 <i>S</i> ,4 <i>R</i> (orthog)	-1.8	-33.3	-41.7	99.8	96.5	99.5
<i>E</i> -2 <i>S</i> ,4 <i>R</i> (planar)	+1.7	-31.5	-38.1	0.2	3.5	0.5
11 <i>b</i> <i>E</i> -2 <i>R</i> ,4 <i>R</i> (orthog)	-1.2	-33.6	-42.1	95.8	96.5	100
<i>E</i> -2 <i>R</i> ,4 <i>R</i> (planar)	+0.5	-31.8	-37.7	4.2	3.5	0.0

mixtures; however, no such ketones were found. As a result the occurrence of the ene region implicated the formation of $^1\Delta$ oxygen in the reaction mixture, generated either by triplet or singlet quenching of the naphthalenol derivative, concomitant with deactivation to the ground state or inter-system crossing, respectively³⁶.

The $^1\text{H-NMR}$ spectrum of **15a** indicates that the double bond has been photo-oxygenated, since in combination with resonances of 3.52 (q) and 3.40 (d) ppm, olefinic resonances are absent. However, on the basis of spectral data in the literature²⁶ and our own spectral data we could establish the molecular structure of **15a** as being the epoxy alcohol depicted in Scheme 4. The structure of photoproduct **15a** concurs with the results reported by Adam et al. for the photo-oxygenation of olefins in the presence of titanium(IV) catalysts²⁶. In particular, the anomalous low-field ^{13}C shift for the (doublet) hydroxy carbon at 78 ppm of (*R**,*S**)- α -(1,1-dimethylethyl)-2-methyloxiranemethanol is in excellent agreement with our own data (77 ppm). In combination with the other data and the subsequent hydrolysis to triol **16a** in which the relief of rigidity is evidenced by the upfield shifting of the methyl group at C9, product **15a** is hence identified as the epoxy alcohol shown in Scheme 4.

Formation of an epoxide is not a straightforward reaction since on singlet photo-oxygenation hydroperoxides and dioxetanes are generally formed as the main products. In certain circumstances epoxidation may occur. Epoxide formation strongly depends on the sensitizer that is used and to a lesser extent on the solvent. Solvents in which the lifetime of singlet oxygen is longer, ought to favour epoxide formation, and especially in apolar solvents, longer lifetimes engender relatively high yields of epoxide. Dependent on the nature and amount of the sensitizer, strained olefins like adamantylideneadamantane in dye-sensitized oxidation give either dioxetane or the epoxide in high yields^{37,38}. Epoxidation is suppressed completely by adding a radical scavenger³⁸ and greater amounts of sensitizer (*i.e.* formation of the dimer of Rose Bengal acts as an electron donor) results in increased amounts of epoxide. Also, in the sensitized oxidation of alkenes by dicyanoanthracenes (DCA) in which the anion of DCA produces the olefinic radical cation, oxiranes are formed^{39,40}. In both types of oxidation, quenching with oxygen may lead to epoxidation via a (second) electron transfer (small exothermic) of the olefinic radical cation to oxygen, leading to a superoxide radical anion $\text{O}_2^{\cdot-}$. Although we are aware of the fact that epoxidation might be the result of triplet oxidation of the olefin, in a thermal process, high-triplet-state olefins are quenched efficiently by oxygen. Hence, intersystem crossing from triplet to the groundstate is probably the most significant pathway.

Since we are dealing with a strained electron-rich olefin in a non-planar triplet state, involvement of charge-transfer intermediates of oxygen or even a 1,4 biradical⁴¹ are readily formed. As a matter of fact in the initial exciplex with triplet oxygen, electron-rich olefins, such as the ene moiety of **10a**, may act as an electron donor to produce an olefinic radical cation and a superoxide radical anion. The subsequent oxidation of the olefin involving the superoxide anion may then result in formation of epoxides (radical autoxidation). A subsequent reaction of the olefin **10a** involving the superoxide radical anion would then account for the high yield of epoxy alcohol **15a** together with the typical singlet-oxygen-derived product like the allylic hydroperoxide.

Concerning the stereochemistry of the photo-oxygenations only two photoproducts with a pronounced stereo- and regioselectivity were found (> 95%). The determination of the stereochemistry of these products is very cumbersome. Configurational assignment is mainly based on fac-

tors controlling the regio- and stereochemistry of the ene reaction and formation of epoxides combined with our own chemical experiments on the crowded tetraalkyl naphthalenols. As might be expected from steric shielding by the bulky ethyl and methyl groups the attack of singlet oxygen in blocked from this side and attack occurs exclusively at the side of the resident hydroxyl group. The observed high regio- and diastereoselectivities can be explained only by the stereoelectronic properties of the hydroxyl functionality, since steric control alone cannot account for the observed diastereoselectivities, also for **14**, **15a** and **15b**. Coordination of the hydroxyl group at the allylic stereocentre with the incoming electrophilic singlet oxygen generates a perepoxide-like transition state leading to only one isomer for these rigid allylic alcohols. The unique coordinating *cis* effect of the hydroxyl group dictating regioselectivity and diastereoselectivity was recently reported for flexible chiral allylic alcohol derivatives by Adam et al.^{42,43}.

For compound **15a**, the observed stereoselectivity is somewhat puzzling, since to some extent, although relatively slow, *Z-E* isomerization took place, indicating that oxygen quenches the triplet state effectively. Singlet quenching would lead to enhanced intersystem crossing and consequently faster *Z-E* isomerization. One explanation for our observations might be that the stereoselective photochemical epoxidation is controlled by the *cis* effect of the hydroxylic stereocentre on C2, leading to a preferential attack of oxygen on the less hindered hydroxylic side of the starting material. It is reasonable to assume that in both photochemical pathways one initial, common transition state, *e.g.* an exciplex with perepoxide geometry, is involved in which steric interaction and allylic strain is minimized⁴⁴. Attack only at the hydroxylic side implies that the classical *cis* effect operates for the *E*-isomer and thus reactivity is less. Although absolute proof was not obtained, we have tentatively assigned the stereochemistry of the reaction products as depicted in Scheme 4.

Upon stereoselective hydrolysis of the epoxy alcohol, by decomposition in the presence of light and water in CDCl_3 , triol **16a** is readily formed. Nucleophilic attack on the less shielded side of C9 gives only one stereoisomer in which the proton chemical shifts for C2 are almost identical to that in **14** indicating that the hydroxyl groups are oriented in the same direction.

For the diastereomer **11a** the regio- and stereochemical selectivities are apparently lower. $^1\text{H-NMR}$ spectra indicate formation of epoxy alcohol **15b** and triol **16b** as the main products, in which the configurations are opposite those in **15a** or **16a**. Surprisingly for **11a** no ene reaction was found. Instead, several products were formed presumably by competing ene reactions with inversed regioselectivity, which could be explained by the fact that in **11a** the higher activation energy, due to larger steric interactions of the ethyl group with the allylic moiety, could diminish regioselective reactivity⁴⁵ and lead to other competing reactions. As a matter of fact we anticipated that photo-oxidation of the exocyclic double bond would lead to the formation of photoproducts similar to **2a** in Scheme 1. Although no proof for such a product was obtained, the quartet appearing at 4.5 ppm in combination with the singlet at 5.8 ppm does indicate that addition of oxygen and an allylic migration of the double bond in an ene-like reaction pathway do occur.

When the mechanistic details of the photochemical behaviour of the 2-naphthalenol derivatives were reconsidered, an important aspect was whether the reaction took place via the planar or orthogonal ("twisted") state or via both species. Excited alkenes in both the singlet and triplet states are able to twist efficiently. However, simple alkenes are known to exhibit poor absorption in the

spectral regions accessible to our photochemical equipment, and alkylbenzenes sensitize triplet formation of double bonds as a result of high intersystem crossing yields and energy transfer⁴⁶. Hence, a singlet reaction would only be possible if singlet-singlet-energy transfer occurred. The fluorescence measurements show that singlet-energy transfer to the double bond is very unlikely, even at lower temperatures (77K). Apparently, the reactive state in the photochemistry of these naphthalenol systems is the triplet state. Hence, a large increase in the dipole moment as the twist angle of the double bond approaches 90° (referred to as sudden polarization) which is possible for olefin singlet states as the reactive intermediates, is not plausible, as is confirmed by the absence of addition reactions in hydroxylic solvents. In the photoaddition of water and methanol to 3-nitrostyrenes, an efficient addition occurs only from a planar polarized triplet state⁶. Therefore the absence of photoaddition of the triplet states of both naphthalenol compounds and the fast *E*-*Z* isomerization, might be an experimental indication that the intermediate is a twisted biradical exhibiting efficient *E*-*Z* isomerization as the major deactivation pathway to the ground state⁶.

Another aspect of photochemical behaviour which we investigated was the conformation of the ground-state geometries of the starting materials. Semi-empirical quantum-chemical calculations (MNDO, AM1 and PM3) for the naphthalenol starting materials show that not only in the 2*S*,4*R*¹¹ but also in the 2*R*,4*R* isomer an orthogonal orientation of the hydroxyl group is preferred over a planar one (*i.e.* the hydroxyl group in the plane of the exocyclic double bond). If conformational control plays an important role (the conformation in the excited state might be different as a result of the twisting double bond), the hydroxyl group does not occupy an ideal position to react in a planar fashion with the double bond in either of the diastereoisomers, as proposed earlier¹¹.

In the photoreaction of optically pure compounds **10** and **11** we have in fact been unable to identify products analogous to **2**, which it is claimed is formed from the racemic precursors **1** via a planar 1,3 OH shift from a singlet (in the double bond) excited state. Although it is still difficult to find out if there were errors in the earlier work, we examined the spectral properties of compounds **1a** and **5a** (Ref. 11) on the one hand and **10a** and **11a** on the other. Apart from their optical purity these pairs of compounds should be identical. Since the first difference occurs in the spectral data of **17a** (Ref. 11) and **8a**, and given the fact that we had to separate the isomeric, optically pure, naphthalenones **8a** and **9a** by HPLC, we suppose that the chemical purity of the compounds studied in the earlier work is doubtful. It should be noted that the wavelengths of the maximum absorptions of **1a** and **5a** (240 and 245 nm, in Ref. 11, respectively) are different from what one would expect for a tetrahydronaphthalene derivative (about 270 nm); for compounds **10a** and **17** the agreement is much better.

Experimental^c

General procedures

All solvents and commercial reagents were reagent grade and dried with the appropriate drying agents. Argon was dried consecutively over concentrated sulfuric acid and KOH pellets. Column chromatography was performed using Merck silica gel 60, 230–400 mesh as the stationary phase. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AM200 or a Bruker AM400 spectrometer using tetramethylsilane (TMS; 0 ppm) as internal standard. GC analyses were

carried out on a Kipp Analytica 8200 instrument with FID detection (25 m×0.25 mm ID, column type: WCOT fused silica, stationary phase CP SIL-8 CB, film thickness 0.25 μm). All HPLC separations were run on a system which consists of a LKB 2248 pump, a 16×100 mm Lichrosorb 60 (5 μm) column, and a LKB 2510 UV detector (254 nm). Mass spectral data were obtained on a Hewlett Packard 5970A system by electron ionization at 70 eV. Fluorescence spectra were recorded on a Spex Fluorolog II emission spectrometer⁴⁷. The excitation wavelength was 255 nm. All samples for fluorescence measurements were degassed by purging with argon for at least 15 min and had an absorbance (1 cm) of 0.10±0.04. Normalization was performed by dividing the fluorescence intensities for both compounds by the absorption at λ_{max}. Electronic absorption spectra were recorded on a Hewlett-Packard 8451 A diode-array spectrophotometer⁴⁷. Samples for low-temperature (77K) measurements were degassed by four freeze-pump-thaw cycles.

(-)(2*R*)-2-Methyl-2-phenylbutanoic acid (**4**)^d

Racemic acid was prepared by the methylation of 2-phenylbutanenitrile^e (95%) followed by hydrolysis of the 2-methyl-2-phenylbutanenitrile^{18,19}. To a solution of diisopropylamine (72 g, 0.71 mol) in 1 l THF at 0°C and 276 ml 2.5M BuLi in hexane was added slowly at -20°C 100 g (0.69 mol) 2-phenylbutanenitrile. After stirring for 4 h the MeI (101 g, 0.71 mol) was added rapidly with external cooling (temperature was kept below 0°C). After stirring for 2 h the reaction mixture was allowed to warm to room temperature. A minimum amount of water was added to dissolve the precipitated salt. The resulting mixture was extracted with ether. The organic phase was washed with water, dried, and evaporated to give 104 g of a residual oil which appeared to be 95% pure 2-methyl-2-phenylbutanenitrile. ¹H NMR (CDCl₃) δ: 7.28–7.45 (5H, m, Ar), 1.95 (2H, m, H3), 1.68 (3H, s, H5), 0.93 (3H, t, H4).

Subsequently, the crude nitrile mixture was held at reflux with 80 g (1.43 mol) of potassium hydroxide and 1 l of diethylene glycol for 24 h. The solution was cooled, mixed with three volumes of water, and the resulting mixture was extracted with ether. The aqueous phase was acidified with cold concentrated HCl; the acid that separated was extracted with ether. The ether layer was washed with water, dried over MgSO₄ and evaporated to give 117 g (0.66 mol, yield 92%) almost white solid material. This material was crystallized from pentane at 0°C to give 104 g of racemic 2-methyl-2-phenylbutanoic acid; m.p. 56.0–57.5° (reported 56–58.9°); yield 86%.

¹H NMR (CDCl₃) δ: 11.72 (1H, s, H1), 7.20–7.40 (5H, m, Ar), 2.10 (1H, m, H3), 1.99 (1H, m, H3), 1.55 (3H, s, H5), 0.85 (3H, t, H4). ¹³C NMR (CDCl₃) δ: 182.85 (s, C1), 142.79 (s, Ar), 128.35 (2C, d, Ar), 126.84 (d, Ar), 126.23 (2C, d, Ar), 50.33 (s, C2), 31.56 (t, C3), 21.25 (q, C5), 9.02 (q, C4).

To obtain optically pure material^{20,21}, quinine (832 g, 2.57 mol) and racemic acid (685 g, 3.84 mol) were dissolved in 2500 ml ethanol and 1075 ml water. Upon cooling (4°C, slowly), the solution deposited the quinine salt (350 g; m.p. 118–121°C) which after five recrystallizations and conversion to the acid, gave 97.5 g white pure (-) crystals; m.p. 86.2–87.0°C; [α]_D²⁵ -29.2° (c 4.9, benzene) and e.e. > 99%. Lit. [α]_D²⁵ -29.5° (c 4.8, benzene)¹⁸.

(-)(2*R*)-2-Methyl-2-phenylbutanoyl chloride (**5**)^f

A mixture of 97.5 g (0.55 mol) of **4** and 132 g (1.11 mol) of thionyl chloride was stirred for 20 h. The excess thionyl chloride was evaporated under vacuum. Two successive portions of anhydrous toluene were added and evaporated under vacuum. The residue was distilled to give 105 g (95% yield) of acid chloride as a colourless liquid b.p. 122–124°C.

¹H NMR (CDCl₃) δ: 7.20–7.40 (5H, m, Ar), 2.20 (1H, m, H3), 1.99 (1H, m, H3), 1.63 (3H, s, H5), 0.87 (3H, t, H4). ¹³C NMR (CDCl₃) δ: 178.85 (s, C1), 140.42 (s, Ar), 128.88 (2C, d, Ar), 128.21 (d, Ar), 126.79 (2C, d, Ar), 60.70 (s, C2), 31.49 (t, C3), 22.13 (q, C5), 8.74 (q, C4).

(1*R*)-3,4-Dihydro-1-ethyl-1,4,4-trimethyl-2(1*H*)-naphthalenone (**6**)

A three-necked jacketed reaction vessel equipped with a magnetic stirrer, thermometer and a gas inlet tube was charged with butanoyl chloride **5** (33 g, 0.17 mol) and freshly distilled carbon disulfide as solvent²⁴. The mixture was cooled to just below -10°C by means of

^d Chem. Abstr. name: α-ethyl-α-methylbenzeneacetic acid.

^e Chem. Abstr. name: α-ethylbenzeneacetonitrile.

^f Chem. Abstr. name: α-ethyl-α-methylbenzeneacetyl chloride.

^c For numbering of C atoms see Schemes 1 and 4.

Table II Irradiations of (Z)-ethylidenenaphthalenols in inert^a and oxygenated^b solutions.

Naphthalenol	Amount (mg)	Time (min)	Yield (%) ^c				
			(Z) ^c	(E) ^c	12	8	? ^d
10a or 11a ^a	500	15	50	50	—	—	—
		60	40	40	5 ^e	—	5
		480	< 5	< 5	15	< 5	> 70
10a ^b 11a ^b	400	15	(Z) ^c	(E) ^c	14	15	
			35	15	17	30	
		15	30	10	—	23	

^a Irradiations in inert conditions were conducted with ≈ 500 ml *n*-hexane containing ≈ 2 mmole of naphthalenol. ^b Irradiations were conducted in the presence of a continuous stream of dried oxygen in ≈ 400 ml *n*-hexane. ^c Yields, determined by gas-chromatographic analysis of aliquots removed periodically from the irradiation mixture. ^d Decomposed and polymerized materials. ^e All percentages based on isolated yields unless indicated otherwise.

a closed circuit filled with methanol and 26 g (0.10 mol) stannic chloride was added. Subsequently the excess isobutene was condensed in a cold trap and slowly passed into the stirred reaction mixture through the gas inlet tube. The progress of the reaction was followed by taking aliquots periodically for ¹H-NMR measurements. After stirring for 24 h, when all starting material had disappeared, the reaction mixture was poured into ice-water. The mixture was extracted with ethyl ether, and the organic layer washed with 10% sodium hydroxide, then with water and dried with MgSO₄ monohydrate. Removal of the solvents gave a residue which was eluted with hexane/dichloromethane 2:1 (v/v) over silica. The major fraction containing a mixture (28.1 g) of three ketones was collected. Column chromatography (silica 60, hexane-ethyl acetate 95:5 (v/v)) afforded a chloride **6a** (45%), an alkene **6b** (40%) and the naphthalenone **6** (15%), respectively (*R_f* 0.18).

(5*R*)-2-Chloro-2,5-dimethyl-5-phenyl-4-heptanone (**6a**). ¹H NMR (CDCl₃) δ : 7.20–7.46 (5H, m, Ar), 2.75 (2H, AB *J_{ab}* 12.7 Hz, H3), 1.98 (2H, m, H6), 1.66 (3H, s, H1 or H8), 1.61 (3H, s, H8 or H1), 1.45 (8H, s, H9), 0.77 (3H, t, H7). ¹³C NMR (CDCl₃) δ : 208.76 (s, C4), 142.02 (s, Ar), 128.76 (2C, d, Ar), 126.88 (d, Ar), 126.40 (2C, d, Ar), 67.95 (s, C2), 56.15 (s, C5), 51.47 (t, C3), 31.96 (t, C6), 31.86 (q, C1 or C8), 29.66 (q, C8 or C1), 20.36 (q, C9), 8.48 (q, C7).

(5*R*)-2,5-Dimethyl-5-phenyl-1-hepten-4-one (**6b**). ¹H NMR (CDCl₃) δ : 7.20–7.46 (5H, m, Ar), 4.82 (1H, m, H1 *cis* or *trans*), 4.55 (1H, m, H1 *trans* or *cis*), 2.90 (2H, AB *J_{ab}* 12.7 Hz, H3), 2.0 (2H, m, H6), 1.62 (3H, s, H8), 1.48 (3H, s, H9), 0.77 (3H, t, H7). ¹³C NMR (CDCl₃) δ : 209.48 (s, C4), 142.21 (s, Ar), 139.36 (s, C2), 128.36 (2C, d, Ar), 126.55 (d, Ar), 126.30 (2C, d, Ar), 114.13 (t, C1), 55.97 (s, C5), 46.13 (t, C3), 29.52 (t, C6), 22.22 (q, C8), 20.16 (q, C9), 8.38 (q, C7).

Compounds **6a** and **6b** were cyclized to the corresponding naphthalenone **6** with BF₃·OEt₂ in dichloromethane²⁴. Subsequently, all ketones (28.1 g, ≈ 0.127 mol) were dissolved in 250 ml dichloromethane to which 135 ml of BF₃·OEt₂ was added. After refluxing for three days the mixture was poured into a mixture of crushed ice–water, and made basic with ammonia. Usual work-up and column chromatography with hexane/ethyl acetate 95:5 (v/v), afforded 17.85 g (overall yield 45%) of pure **6**. Upon addition of (+)-Eu(hfc)₃⁸ (9.4 mg, 0.0078 mmol) to a solution of **6** (20 mg, 0.078 mmol) in *d*-benzene, the enantiomeric excess was found to be > 99%, ($[\alpha]_D^{25} - 24.2^\circ$, c 2, methanol). Upon addition of (+)-Eu(hfc)₃ to a solution of racemic material, the individual methyl signals of the enantiomers could be resolved easily. Anal. calcd.: C 83.28, H 9.32; found: C 83.34, H 9.10%. ¹H NMR (CDCl₃) δ : 7.20–7.46 (4H, m, Ar), 2.63 (2H, AB *J_{ab}* 12.9 Hz, H3), 1.98 (2H, m, H7), 1.42 (3H, s, H9), 1.34 (3H, s, H10 or H11), 1.30 (3H, s, H11 or H10), 0.67 (3H, t, Hg). ¹³C NMR (CDCl₃) δ : 213.45 (s, C2), 144.35 (s, C5 or C6), 141.50 (s, C6 or C5), 126.90 (d, Ar), 126.81 (d, Ar), 126.41 (d, Ar), 126.61 (d, Ar), 52.49 (t, C3), 52.38 (s, C1), 37.99 (s, C4), 33.96 (t, C7), 31.22 (q, C10 or C11), 30.55 (q, C11 or C10), 28.32 (q, C9), 9.87 (q, C8).

(1*R*)-1,4-Dihydro-1-ethyl-1,4,4-trimethyl-2,3-naphthalenedione (**7**)

6 (47.4 g, 0.22 mol) and selenium dioxide (25.1 g, 0.23 mol) were dissolved in 500 ml of dioxane and the mixture was heated under

reflux for 30 h²⁴. The solution was filtrated over hyflo and the solvent evaporated. Crystallisation in the cold from pentane and rapid filtration gave a yellow solid. However on storage at room temperature **7** turned out to be a yellow oil; storage at 4°C gave yellow crystals. ¹H NMR (CDCl₃) δ : 7.27–7.38 (4H, m, Ar), 1.97 (1H, m, H7), 1.83 (1H, m, H7), 1.57 (3H, s, H10 or H11), 1.52 (3H, s, H9), 1.46 (3H, s, H11 or H10), 0.74 (3H, t, H8). ¹³C NMR (CDCl₃) δ : 205.65 (s, C2 or C3), 205.44 (s, C3 or C2), 141.12 (s, C5 or C6), 139.10 (s, C6 or C5), 128.06 (d, Ar), 128.03 (d, Ar), 126.53 (d, Ar), 126.35 (d, Ar), 55.57 (s, C1), 50.99 (s, C4), 34.65 (t, C7), 28.03 (q, C9), 25.29 (q, C10 or C11), 23.21 (q, C11 or C10), 9.18 (q, C8).

(4*R*)-3,4-Dihydro-4-ethyl-1,1,4-trimethyl-3*Z*-ethylidene-2(1*H*)-naphthalenone (**8a**) and 3,4-dihydro-1-ethyl-1,4,4-trimethyl-(3*Z*)-ethylidene-2(1*H*)-naphthalenone (**9a**)

n-Butyllithium (24 ml of a 2.5 M solution in hexane, 0.06 mol) was added dropwise to a stirred suspension of 21.9 g (0.06 mol) ethyltriphenylphosphonium bromide in 100 ml of anhydrous diethyl ether, whereupon the deep red colour of the ethylenephosphorane was produced¹¹. The mixture was then stirred for 3 h at room temperature. At the end of this period 13.8 g (0.06 mol) of **7** was added dropwise, whereupon a white precipitate formed. The mixture was then cooled and filtered. The filtrate was washed with water, the organic layer separated and dried over MgSO₄. Evaporation of the solvents left a residue which was purified by column chromatography using hexane/ethyl acetate 95:4 (v/v) as eluent *R_f* 0.21 and 0.18. Separation of both isomers was carried out with HPLC on silica (5 μ m) using *n*-hexane/ethyl acetate/water, 99.75:0.25:0.001 as eluent, yielding 5.6 g of ketone **8a** and 6.4 g of ketone **9a**. The corresponding *Z* isomers were separated from the *E* isomers, yield < 5%. GLC showed the original product mixture to contain ketones **8a** (m.p. 65–67.2°C) and **9a** (m.p. 50.1–52.3°C) in a ratio of 40:60.

8a. ¹H NMR (CDCl₃) δ : 7.21–7.33 (4H, m, Ar), 5.75 (1H, q, H9), 1.81 (3H, d, H10), 1.53 (2H, m, H11), 1.51 (3H, s, H7 or H8), 1.48 (3H, s, H8 or H7), 1.41 (3H, s, H13), 0.71 (3H, t, H12). ¹³C NMR (CDCl₃) δ : 209.65 (s, C2), 143.82 (s, C5 or C6), 143.06 (s, C6 or C5), 142.81 (s, C3), 126.88 (d, Ar), 126.81 (d, Ar), 126.58 (d, Ar), 125.42 (d, Ar), 124.97 (d, C9), 49.18 (s, C4), 45.81 (s, C1), 37.83 (t, C11), 29.60 (q, C13), 25.99 (q, C7 or C8), 23.07 (q, C8 or C7), 14.96 (q, C10), 8.73 (q, C12). GC/MS: 242.2 (M⁺), 227.1, 215.1, 214.2, 213.2 (base peak), 198.2, 171.3, 170.2, 155.2, 141.2, 129.1, 115.1, 43.1.

9a. ¹H NMR (CDCl₃) δ : 7.21–7.40 (4H, m, Ar), 5.81 (1H, q, H10), 2.15 (1H, m, H7), 1.85 (1H, m, H7), 1.83 (3H, d, H11), 1.43 (3H, s, H9), 1.41 (3H, s, H12 or H13), 1.38 (3H, s, H13 or H12), 0.65 (3H, t, H8). ¹³C NMR (CDCl₃) δ : 209.65 (s, C2), 146.01 (s, C5 or C6), 144.26 (s, C6 or C5), 140.87 (s, C3), 126.78 (d, Ar), 126.74 (d, Ar), 126.70 (d, Ar), 124.45 (d, Ar), 124.27 (d, C10), 53.44 (s, C1), 42.0 (s, C4), 34.02 (t, C7), 30.53 (q, C12 or C13), 29.55 (q, C13 or C12), 27.60 (q, C9), 14.97 (q, C11), 9.65 (q, C8).

(2*S*,4*R*)- and (2*R*,4*R*)-1,2,3,4-tetrahydro-4-ethyl-1,1,4-trimethyl-3*Z*-ethylidene-2-naphthalenol (**10a/11a**)¹²

To a stirred solution of 1 g (3.4 mmol) naphthalenone **8a** in 25 ml anhydrous ether was added 0.19 g (3.4 mmol) LiAlH₄. After 30 min additional stirring 0.5 ml of water, 0.3 ml of a 5*N* NaOH solution, and 5 ml of water were added, respectively. Filtration, separation of the organic layer, and removal of the solvent afforded 0.94 g of a

⁸ hfc = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorato.

mixture of **10a** (m.p. 52.0–53.6°C) and **11a** (m.p. 69.9–71.6°C) in a ratio of 70:30. Separation was accomplished by repeated column chromatography with hexane/ethyl acetate, 96:4 (v/v) as eluent.

(2S,4R)-**10a**. ^1H NMR (CDCl_3) δ : 7.18–7.38 (4H, m, Ar), 5.72 (1H, q, H9), 4.52 (1H, s, H2), 2.05 (1H, m, H11), 1.86 (3H, d, H10), 1.81 (1H, m, H11), 1.56 (3H, s, H7 or H8), 1.38 (3H, s, H13), 1.07 (3H, s, H8 or H7), 0.48 (3H, t, H12). ^{13}C NMR (CDCl_3) δ : 143.44 (s, C5), 142.92 (s, C6), 140.78 (s, C3), 126.77 (d, Ar), 126.50 (d, Ar), 126.06 (d, Ar), 125.92 (d, Ar), 123.29 (d, C9), 73.93 (d, C2), 42.75 (s, C4), 39.60 (s, C1), 37.95 (t, C11), 31.74 (q, C13), 29.99 (q, C7 or C8), 25.97 (q, C8 or C7), 13.12 (q, C10), 9.80 (q, C12). GC/MS: 244.3 (M^+), 226.2, 215.2, 197.2 (base peak), 182.15, 171.1, 167.15, 157.15, 156.15, 155.1, 141.05, 128.1, 115.1, 91.15, 43.1, 32.0, 29.1.

(2R,4R)-**11a**. ^1H NMR (CDCl_3) δ : 7.12–7.38 (4H, m, Ar), 5.72 (1H, q, H9), 4.58 (1H, s, H2), 2.15 (1H, m, H11), 1.82 (1H, m, H11), 1.81 (3H, d, H10), 1.55 (3H, s, H13), 1.48 (3H, s, H7 or H8), 1.08 (3H, s, H8 or H7), 0.48 (3H, t, H12). ^{13}C NMR (CDCl_3) δ : 142.60 (s, C5), 141.89 (s, C6), 140.95 (s, C3), 126.50 (d, Ar), 125.88 (d, Ar), 126.06 (d, Ar), 125.92 (d, Ar), 121.00 (d, C9), 74.44 (d, C2), 43.51 (s, C4), 39.60 (s, C1), 37.54 (q, C13), 35.84 (t, C11), 29.64 (q, C7 or C8), 26.63 (q, C8 or C7), 13.14 (q, C10), 9.65 (q, C12). GC/MS: 244 (M^+), 226.2, 216.2, 215.2, 197.2 (base peak), 186.1, 182.2, 171.2, 157.15, 155.1, 128.0, 115.1, 91.1, 77.1, 55.0, 43.1, 41.1, 29.1, 28.1.

(1R,2S)-1,2,3,4-tetrahydro-1-ethyl-1,4,4-trimethyl-2-naphthalenol (17)

To a stirred solution of 1 g (4.6 mmol) naphthalenone **6** in 25 ml anhydrous ether was added 0.26 g (4.6 mmol) LiAlH_4 . After 30 min additional stirring 0.5 ml of water, 0.3 ml of a 5N NaOH solution, and 5 ml of water were added respectively. Filtration, separation of the organic layer, removal of the solvent, and separation accomplished by column chromatography with hexane/ethyl acetate 96:4 (v/v), as eluent, afforded 0.3 g pure (1R,2S)-naphthalenol **17**. ^1H NMR (CDCl_3) δ : 7.20–7.33 (4H, m, Ar), 3.92 (1H, dd, H2), 2.05 (1H, dd, H3), 1.73 (1H, dd, H3), 1.54 (2H, m, H7), 1.38 (6H, s, H10 and H11), 1.33 (3H, s, H9), 0.83 (3H, t, H8). ^{13}C NMR (CDCl_3) δ : 144.05 (s, C5 or C6), 141.59 (s, C6 or C5), 127.36 (d, Ar), 126.79 (d, Ar), 125.97 (d, Ar), 125.31 (d, Ar), 73.13 (d, C2), 42.44 (s, C1), 42.41 (t, C3), 35.16 (s, C4), 34.03 (t, C7), 32.57 (q, C10 or C11), 28.29 (q, C11 or C10), 23.43 (q, C9), 9.65 (q, C8).

Irradiation procedure

All photochemical experiments (as shown in Table II on **10a** and **11a**) were performed in 500 ml solvent of spectroscopic grade, containing 2 mmol of olefin. Irradiations were performed using a 500-W medium pressure Hg lamp (Hanau TQ78) through quartz. Cooling of the lamp was accomplished by means of a closed circuit filled with methanol. In this way the temperature in the reaction vessel was maintained below 0°C. When using inert conditions, the solvent was purged by a stream of dry argon, to remove traces of oxygen before and during irradiation. All photoreactions were monitored by means of gas chromatography. After irradiation, the solvents were removed on a rotatory evaporator. The reaction mixtures were separated by means of HPLC (hexane/ethyl acetate/water 99.75:0.25:0.001) or repeated column chromatography, using hexane/ethyl acetate (96:4) as eluent.

Characterisation of photoproducts¹²

(2S,4R)-1,2,3,4-Tetrahydro-4-ethyl-1,1,4-trimethyl-3E-ethylidene-2-naphthalenol (**10b**). ^1H -NMR (CDCl_3) δ : 7.22–7.42 (4H, m, Ar), 5.85 (1H, q, H9), 3.83 (1H, d, H2), 2.25 (1H, m, H11), 2.03 (1H, m, H11), 1.86 (3H, d, H10), 1.54 (3H, s, H7 or H8), 1.39 (3H, s, H13), 1.20 (3H, s, H8 or H7), 0.84 (3H, t, H12). ^{13}C NMR (CDCl_3) δ : 143.30 (s, C5), 141.96 (s, C6), 138.72 (s, C3), 126.82 (d, Ar), 126.10 (d, Ar), 125.97 (d, Ar), 125.88 (d, Ar), 123.36 (d, C9), 73.98 (d, C2), 43.8 (s, C4), 39.64 (s, C1), 32.84 (q, C8 or C7), 34.04 (t, C11), 29.14 (q, C13), 25.56 (q, C8 or C7), 15.49 (q, C10), 10.44 (q, C12). GC/MS: 229.3 ($\text{M}^+ - \text{CH}_3$), 226.4 ($\text{M}^+ - \text{H}_2\text{O}$), 215.5, 197.2, 174.1, 173.1, 173.1, 159.1, 145.2 (base peak), 128.2, 117.1, 91.1, 77.1, 43.2, 39.1.

(2R,4R)-1,2,3,4-Tetrahydro-4-ethyl-1,1,4-trimethyl-3E-ethylidene-2-naphthalenol (**11b**). ^1H NMR (CDCl_3) δ : 7.18–7.37 (4H, m, Ar), 5.74 (1H, q, H9), 3.88 (1H, d, H2), 2.35 (1H, m, H11), 2.15 (1H, m, H11), 1.91 (3H, d, H10), 1.62 (3H, s, H13), 1.32 (3H, s, H8 or H7), 1.24 (3H, s, H7 or H8), 0.60 (3H, t, H12). ^{13}C NMR (CDCl_3) δ : 143.12 (s, C5), 142.34 (s, C6), 140.94 (s, C3), 126.48 (d, Ar), 126.09 (d, Ar), 125.53 (d, Ar), 125.53 (d, Ar), 121.03 (d, C9), 74.46 (d, C2), 43.19 (s, C4), 39.35 (s, C1), 35.84 (t, C11 or

C13), 32.58 (q, C13 or C11), 29.64 (q, C7 or C8), 26.63 (q, C7 or C8), 15.05 (q, C10), 10.41 (q, C12). GC/MS: 244.1 (M^+), 229.2, 226.2, 216.1, 215.3, 197.2, 173.2, 159.3, 145.2 (base peak), 128.1, 117.1, 77.2, 43.1.

(4R)-3,4-Dihydro-4-ethyl-1,1,4-trimethyl-3Z / E-ethylidene-2(1h)-naphthalenones (**8a/8b**). GC/MS: 242.2 (M^+), 227.1, 215.1, 214.2, 213.2 (base peak), 198.2, 171.3, 170.2, 155.2, 141.2, 129.1, 115.1 43.1. GC/MS: 242.3 (M^+), 227.2, 215.2, 214.2, 213.2 (base peak), 198.2, 197.2, 182.5, 171.2, 170.2, 155.1, 141.2, 128.1, 115.1 43.1, 41.1.

(1R)-1-Ethyl-1,3,3-trimethyl-2E / Z-ethylideneindanes (**12a/12b**). ^1H NMR (CDCl_3) δ : 7.41–7.15 (4H, m, Ar), 5.52 and 5.42 (1H, q), 1.90 and 1.85 (3H, d), 2.05, 1.77 and 1.67 (2H, m), 1.48 and 1.43 (3H, s), 1.33 and 1.30 (3H, s), 1.29 and 1.27 (3H, s), 0.52 and 0.50 (3H, t). GC/MS: 214.3 (M^+), 199.2, 186.2, 185.2 (base peak), 170.15, 157.2, 155.15, 143.0, 128.1, 115.1, 91.1, 77.1, 41.1, 32.0, 29.1, 28.0. GC/MS: 214.20 (M^+), 199.2, 186.1, 185.1 (base peak), 170.15, 155.15, 143.1, 128.1, 91.2, 77.1, 41.1, 32.0, 29.1, 28.0.

(2S,3R,4R)-1,2,3,4-Tetrahydro-1-ethyl-1,4-trimethyl-2-ethenyl-2,3-naphthalenediol (**14**). ^1H NMR (CDCl_3) δ : 7.14–7.37 (4H, m, Ar), 6.44 (1H dd, H9, 3J 10.67 and 16.82 Hz) 5.51 (1H, dd, H10, *trans*, 2J 1.9 and 3J 16.82 Hz), 5.23 (1H, dd, H10, *cis*, 2J 1.9 Hz and 3J 10.67 Hz), 2.70 (1H, s, H₂), 2.10 (1H, m, H11), 2.02 (1H, m, H11), 1.52 (3H, s, H13), 1.34 (3H, s, H8 or H7), 1.32 (3H, s, H7 or H8), 0.82 (3H, t, C12). ^{13}C NMR (CDCl_3) δ : 139.04 (s, C5 or C6), 138.02 (s, C6 or C5), 135.11 (d, C9), 127.52 (d, Ar), 127.48 (d, Ar), 127.26 (d, Ar), 126.88 (d, Ar), 112.12 (t, C10), 69.03 (d, C2), 65.63 (s, C3), 43.23 (s, C4) 39.20 (s, C1), 32.78 (t, C11), 32.54 (q, C13), 28.03 (q, C7 or C8), 26.83 (q, C8 or C7), 9.98 (q, C12).

(2S,3R,4R,3'S)-1,2,3,4-Tetrahydro-4-ethyl-1,1,4-trimethyl-2-naphthalenol-3-spiro-2'-(3-methyloxirane) (**15a**). ^1H NMR (CDCl_3) δ : 7.18–7.35 (4H, m, Ar), 3.52 (1H, s, H2), 3.40 (1H, q, H9), 1.95 (1H, m, H11), 1.82 (1H, m, H11), 1.62 (3H, d, H10), 1.43 (3H, s, H13), 1.38 (3H, s, H8 or H7), 1.28 (3H, s, H7 or H8), 0.63 (3H, t, C12). ^{13}C NMR (CDCl_3) δ : 143.82 (s, C5 or C6), 141.22 (s, C6 or C5), 127.03 (d, Ar), 126.60 (d, Ar), 126.25 (d, Ar), 125.00 (d, Ar), 77.04 (d, C2), 65.63 (s, C3), 58.85 (d, C9), 43.23 (s, C4), 39.2 (s, C1), 31.24 (t, C11), 31.06 (q, C13), 27.89 (q, C7 or C8), 25.04 (q, C8 or C7), 15.17 (q, C10), 11.08 (q, C12).

(2S,3S,4R,1'R)-1,2,3,4-Tetrahydro-1-ethyl-2-(1'-hydroxyethyl)-1,4,4-trimethyl-2,3-naphthalenediol (**16a**). ^1H NMR (CDCl_3) δ : 7.18–7.30 (4H, m, Ar), 4.4 (1H, q, H9), 3.05 (1H, s, H2), 2.18 (2H, m, H11), 1.55 (3H, s, H13), 1.34 (3H, d, H10), 1.32 (3H, s, H8 or H7), 1.28 (3H, s, H7 or H8), 0.87 (3H, t, H12). ^{13}C NMR (CDCl_3) δ : 140.71 (s, Ar), 139.10 (s, Ar), 126.61 (d, Ar), 126.43 (d, Ar), 126.31 (d, Ar), 125.97 (d, Ar), 67.82 (s, C3), 62.54 (d, C9), 62.41 (d, C2), 41.42 (s, C1), 34.55 (s, C4), 31.13 (q, C8), 31.02 (t, C12), 29.59 (q, C13), 27.50 (q, C7), 22.51 (q, C10), 10.04 (q, C12).

(2R,3S,4R,3'R)-1,2,3,4-Tetrahydro-4-ethyl-1,1,4-trimethyl-2-naphthalenol-3-spiro-2'-(3-methyloxirane) (**15b**). ^1H NMR (CDCl_3) δ : 7.20–7.40 (4H, m, Ar), 3.62 (1H, s, H2), 3.33 (1H, q, H9), 1.82 (2H, m, H11), 1.52 (3H, d, H10), 1.43 (3H, s, H13), 1.41 (3H, s, H8 or H7), 1.35 (3H, s, H7 or H8), 0.55 (3H, t, H12). ^{13}C NMR (CDCl_3) δ : 142.41 (s, Ar), 140.57 (s, Ar), 127.31 (d, Ar), 126.44 (d, Ar), 126.28 (d, Ar), 126.02 (d, Ar), 77.1 (d, C2) 64.31 (s, C3), 61.14 (d, C9), 42.21 (s, C1), 40.01 (s, C4), 33.24 (q, C8), 30.04 (t, C12), 28.32 (q, C13), 26.41 (q, C7), 15.60 (q, C10), 10.20 (q, C12).

(2R,3R,1'S)-1,2,3,4-tetrahydro-1-ethyl-3-(1'-hydroxyethyl)-1,1,4-trimethyl-2,3-naphthalenediol (**16b**). ^1H NMR (CDCl_3) δ : 7.18–7.34 (4H, m, Ar), 4.33 (1H, q, H9), 3.18 (1H, s, H2), 1.80 (2H, m, H11), 1.56 (3H, s, H13), 1.43 (3H, d, H10), 1.41 (3H, s, H7 or H8), 1.38 (3H, s, H8 or H7), 0.58 (3H, t, H12).

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