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AN EXPERIMENTAL STUDY ON THE MECHANISM AND STEREOCHEMISTRY OF A PHOTOCHEMICAL [1,3]-OH SHIFT. A NON-WOODWARD AND HOFFMANN REACTION PATH FOR PHOTOCHEMICAL SIGMATROPIC REACTIONS

W.J.G.M. Peijnenburg* and H.M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

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Abstract - An experimental study on the photochemistry of the 4-methyl, 4-ethyl disubstituted 3-alkylidene-2-naphthalenol derivatives 1a,b and 5a,b is presented. It is shown that occurrence of a [1,3]-OH shift is dependent only on the ground-state conformation of the substrate. This conformation in its turn is fixed by the chirality at C_2 and C_4. In case of compounds 1a,b the hydroxyl group is located in the plane of the exocyclic double bond. Excitation of this favourable conformation results in a 90°-twist of the exocyclic double bond. Due to the interaction between the substituents at C_4 and C_9 preferential formation of just one twisted geometry takes place. The stereochemical outcome of the resulting [1,3]-OH shift agrees well with the one expected in case of a planar shift. Further evidence in favour of the occurrence of a non-Woodward and Hoffmann reaction path is obtained from the irradiation of 5a,b; despite a favourable ground-state conformation for a suprafacial shift to occur, this shift does not take place. Instead a 90°-twisted intermediate is formed, from which solely a radiationless transition to the ground state is observable. The stereostructure of the photoproducts formed was established by means of low temperature NOE measurements.

Introduction

During our investigations on the photochemistry of rigid 1,5-dienes it was found that irradiation of 8-hydroxygermacrene B leads to an exclusive [1,3]-OH shift[1]. Following the Woodward and Hoffmann rules of conservation of orbital symmetry[2], a photochemical [1,3] sigmatropic shift is expected to proceed in a suprafacial way. However, the orbital symmetry arguments deal only with strictly concerted conversions and no attention is paid to local geometry changes which effectuate the course of the overall process. Yet it is well-known in alkene photochemistry that twisting of the excited double bond occurs in order to diminish electronic repulsion between the antibonding p-orbitals. In unsymmetrically substituted alkenes this twist will be accompanied by a complete charge separation in the orthogonal situation[3]. Based on this phenomenon, known as "Sudden Polarization", we proposed a mechanism for photochemical sigmatropic reactions as depicted in Figure 1 for the photochemical [1,3]-OH shift in 2-propen-1-ol[4].

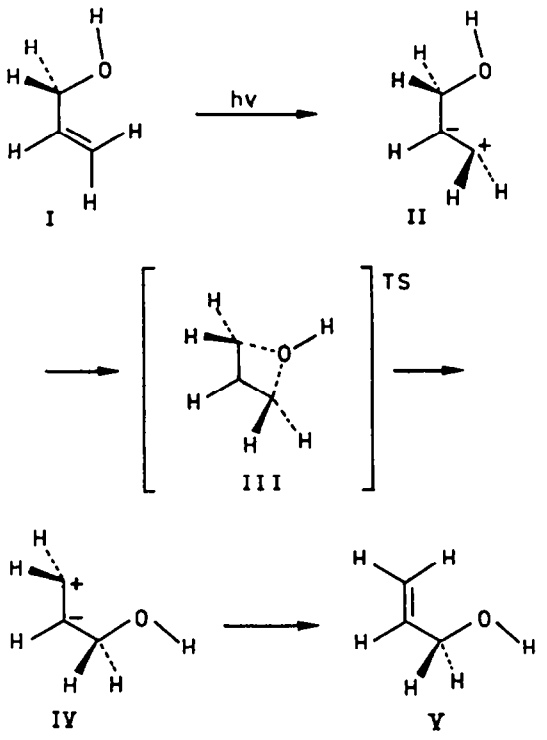


Figure 1. The proposed mechanism of the planar [1,3]-OH shift in 2-propen-1-ol.

For 2-propen-1-ol (I) this polarization leads to a positive charge on the terminal carbon atom and a negative charge on the central carbon atom (II). The hydroxyl group, which has a partially negative charge, may now shift towards the positively charged terminus in the plane of the carbon atoms via a transition state of C_{2v}-symmetry (III). After a radiationless transition from a second twisted conformation (IV) the reaction proceeds on the ground state potential surface towards the shifted product (V). MNDO-CI calculations for various photochemical shifts showed the activation energy for this planar mechanism to be considerably smaller than for the mechanism based on the Woodward and Hoffmann rules[5].

Up to now relatively little attention has been paid to the stereochemical aspects of photochemical sigmatropic rearrangements. Most of this work was directed to [1,3]-C shifts, which were studied in detail by Cookson and co-workers[6]. Irradiation of cyano-3-phenylcyclohexylidene methyl acetate showed that E-Z equilibration is faster than the [1,3]-benzylic shift and therefore no conclusions regarding the stereochemical fate of the allylic terminus could be obtained (see Figure 2).

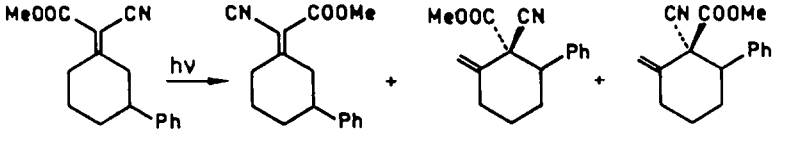


Figure 2. Photochemistry of cyano-3-phenylcyclohexylidene methyl acetate.

In the abscence of steric factors the twisting motion of the exocyclic double bond takes place in two opposite directions, thus accounting for the scrambling of the chirality at the terminal carbon atoms.

We now wish to report the results of an experimental study on the photochemistry of the 4-methyl, 4-ethyl disubstituted 3-alkylidene-2-naphthalenol derivatives 1a,b and 5a,b. Irradiation of these diastereoisomeric compounds leads, because of the large steric interaction between the allylic ethyl group and the vinylic alkyl group, to a preferential twisting of the exocyclic double bond into one direction. The stereochemical outcome of the subsequent [1,3]-OH shift delivers to our knowledge the first experimental evidence of the occurrence of a planar photochemical [1,3] sigmatropic shift in acyclic alkenes.

Results

Upon direct irradiation of (2RS,4SR)-1a in n-hexane fast E-Z isomerization around the exocyclic double bond could be observed. This led to the formation of a mixture of the E- and Z-isomers 2a and 1a respectively in a ratio of approximately 50:50. Further irradiation of this mixture resulted in the clean formation of the diastereoisomeric product mixtures 3a and 4a in a ratio of 85:15.
The influence of the C_9-alkyl group becomes clear from the observed photochemical behaviour of the product formed by substitution of the C_9(Me) by the more bulky ethyl group (compound 1b). Irradiation of the rapidly formed 50:50 mixture of 1b and 2b results in an even more stereoselective [1,3]-OH shift, yielding 3b and 4b in a ratio of 93:7 (see Figure 3).

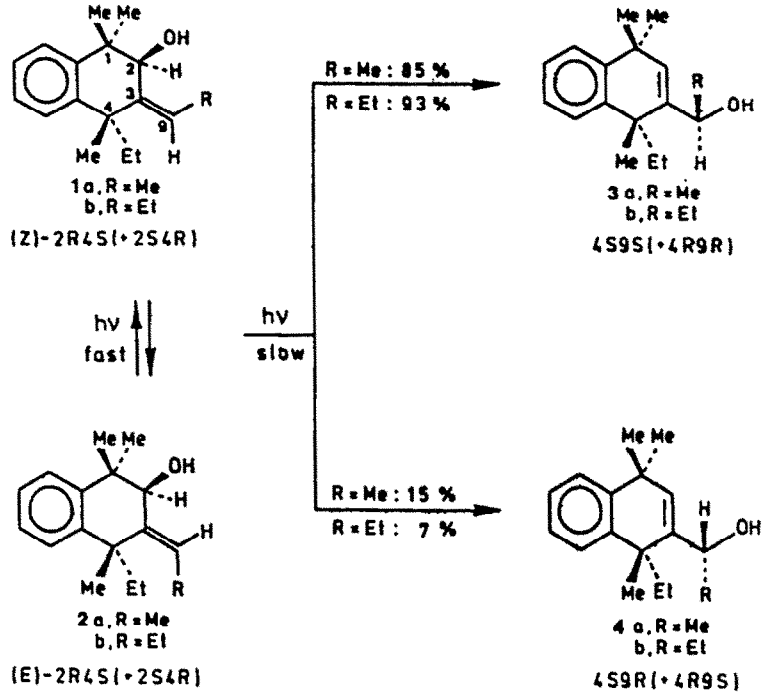


Figure 3. Photochemistry of (2RS,4SR)-1a,b upon irradiation in n-hexane.

Irradiation of either (2SR,4SR)-5a or (2SR,4SR)-5b in n-hexane also gave rise to the initial formation of a 50:50 mixture of the E- and Z-isomers 6a,b and 5a,b respectively. However upon prolonged irradiation no further photoproducts were formed. This clearly demonstrates the unique properties of the compounds studied. Dependent on the chirality at C_2 and C_4, either a highly stereospecific [1,3]-OH shift takes place or no shift at all is observed. Initial formation of a 50:50 mixture of 5a,b and 6a,b was also observed upon irradiation of 5a,b in methanol.

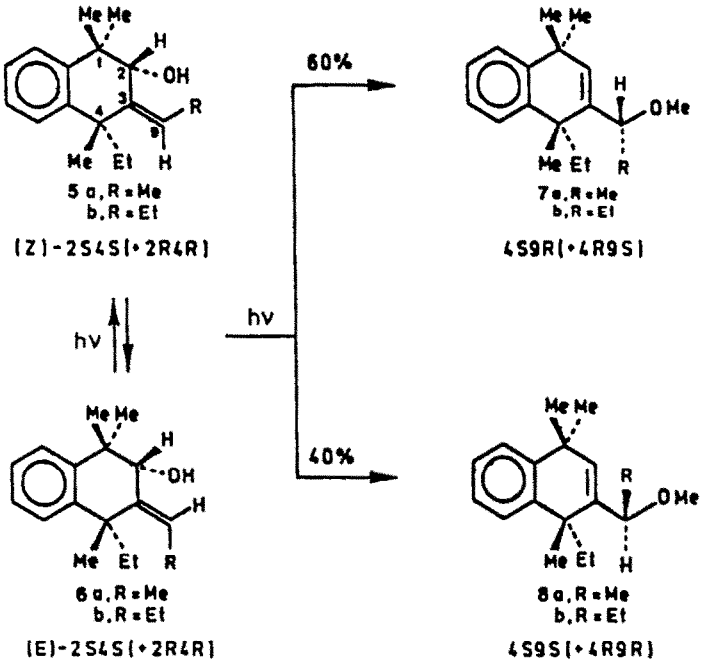


Figure 4. Photochemistry of (2SR,4SR)-5a,b upon irradiation in methanol.

Besides this general behaviour the two additional photoproducts 7a,b and 8a,b were formed in ratios of 60:40. These products arise from the addition of methanol to the excited double bond of either 5a,b or 6a,b. No [1,3]-OH shift could be established (see Figure 4).

The fact that the [1,3]-OH shift does not occur for compounds 5a,b and 6a,b in n-hexane indicates a lower reactivity than for compounds 1a,b and 2a,b, but does not exclude the possibility of its appearance in methanol. Therefore a control experiment was set up in order to make sure no photochemical substitution reaction occurs which would convert 3a,b and 4a,b into 7a,b and 8a,b. No reaction could be observed upon prolonged irradiation of both 3a,b and 4a,b in methanol.

Discussion

The observation of an unequal product distribution upon irradiation of the 50:50 mixture of 1a,b and 2a,b clearly indicates the occurrence of a non-Woodward and Hoffmann reaction path for photochemical sigmatropic [1,3]-OH shifts. For following the Woodward and Hoffmann rules of conservation of orbital symmetry, a photochemical [1,3]-OH shift is predicted to proceed in a suprafacial fashion. A suprafacial [1,3]-OH shift will always be accompanied with complete transfer of the chirality at C_2 in the starting products towards C_9 in the photoproducts 3a,b and 4a,b.

As shown in Figure 5 a relative configuration of 2R4S(2S4R) of the Z-isomers 1a,b will lead to the formation of a 4S9R(4R9S)-configuration of the products formed upon suprafacial migration of the hydroxyl group. Similarly the same relative configuration of 2R4S(2S4R) of the E-isomers 2a,b will result in a 4S9S(4R9R)-configuration of the photoproducts.

Because of the presence of the unequal substituents at C_2 and C_4 the transition states for these two suprafacial shifts would be diastereoisomeric of nature. Going from the starting geometry to the transition state, the interaction between the trans oriented vinylic substituent at C_9 and the alkyl substituents at C_4 will increase. This interaction will be largest in case of a trans oriented

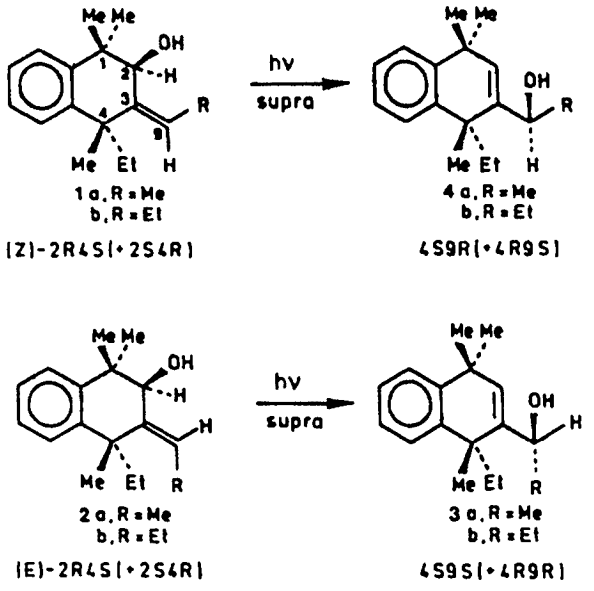


Figure 5. Products expected from a suprafacial [1,3]-OH shift in 1a,b and 2a,b.

methyl or ethyl group (compounds 2a,b). Therefore, the activation energy of a suprafacial [1,3]-OH shift will be lowest for compounds 1a,b, thus leading to excess formation of 4a,b. From this it may be concluded that, apart from conformational aspects (vide infra), the observed stereoselectivity (yielding predominantly 3a,b) makes a suprafacial mechanism rather improbable.

The observed stereospecificity agrees well with the one expected in case of a planar [1,3]-OH shift. Bearing in mind the knowledge about the photochemical behaviour of excited alkenes, direct irradiation of either 1a or 2a will lead to a 90°-twist of the exocyclic double bond in order to diminish the electronic repulsion between the antibonding p-orbitals. This twist will be accompanied by a complete charge separation in the orthogonal situation ("Sudden Polarization", vide supra). In view of the inequality of the substituents at both C_4 and C_9, twisting of the exocyclic double bond may take place in two opposite directions. Due to the in case of compounds 1a and 2a large steric interaction between the C_4(Et) and the C_9(Me), preferential formation of just one twisted geometry will take place i.e. the one in which the vinylic methyl group is turned away from the allylic ethyl group (reaction route A in Figure 6).

Thereupon, MNDO-calculations on the preferential conformation of 1a and 2a show that in the ground state a small sp_2-sp_2 torsion around the exocyclic double bond of 3° respectively 8° is present. Again this distortion is caused by the interaction between the C_4(Et) and the C_9(Me) and is directed in the same way as in the case of structure 9a. Thus it is evident that excitation of these slightly distorted conformations will lead to the preferential formation of the 90°-twisted geometry 9a. From this polarized structure either a radiationless transition to the ground state, yielding the (isomerized) reactants 1a and 2a, or a planar [1,3]-OH shift may occur. As shown in Figure 6 there is now only one way in which the migrating hydroxyl group can approach C_9. This will lead to the formation of a relative (4SR,9SR)-configuration in the thus formed product 3a.

Likewise, formation of 4a to a smaller extent can in the framework of a planar [1,3]-OH shift be explained by assuming a planar shift starting from the 90°-twisted geometry 10a (route B, Figure 6). Due to the in this case unfavourable ground-state distorsion of the exocyclic double bond in the starting products 1a and 2a and because of the interaction between the C_4(Et) and the C_9(Me), formation of this intermediate will hardly take place.

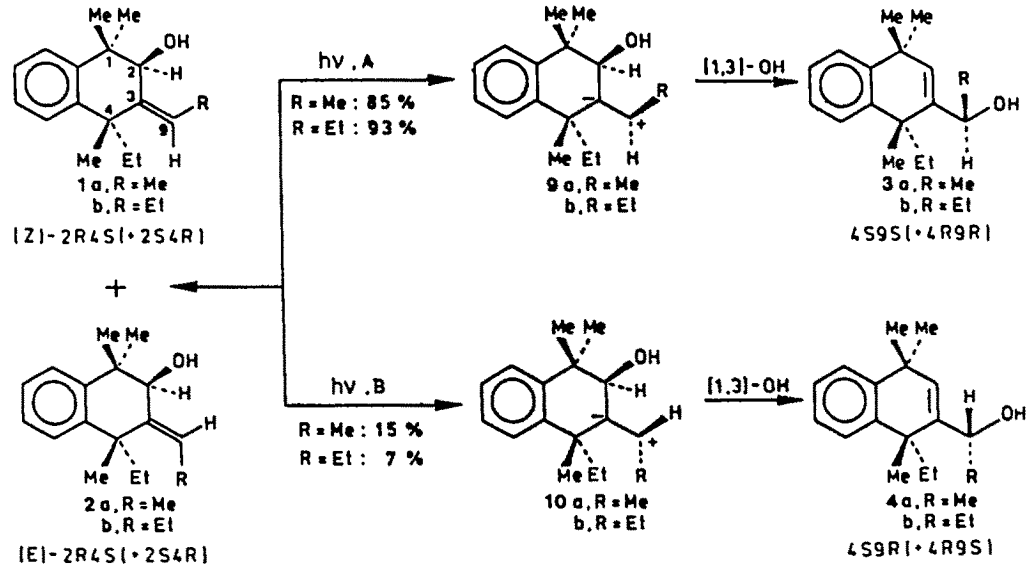


Figure 6. Products resulting from a planar [1,3]-OH shift in 1a,b and 2a,b.

The planar mechanism is strongly supported by the observed photochemistry of 1b and 2b. In case of compounds 1b and 2b an even larger interaction between the substituents at C_4 and C_9 exists. Because of this large interaction intermediate 10b will be formed to an even lesser extend, thereby explaining the observed increase in stereoselectivity of the [1,3]-OH shift upon substitution of the vinylic methyl group by the more bulky ethyl group.

Besides this, the photochemical behaviour of (2RS,4RS)-5a,b delivers additional evidence for the occurrence of a planar [1,3]-OH shift. Irradiation of these compounds in n-hexane or methanol does not result in the occurrence of a [1,3]-OH shift. In order to give an explanation for this apparent contradictory behaviour a conformational analysis of both 5a and 6a, using the semi-empirical MNDO-method[7], was performed. In these compounds the exocyclic double bond can adapt two possible orientations leading to a stable conformer, one in which the hydroxyl group is located in the plane of the exocyclic double bond and one in which the hydroxyl group is situated out of this plane. These conformers can be denoted as S respectively R[8]. First of all the steric energy of the conformers was minimized by means of MM2 calculations[9]. Coordinates found in this way were used as starting values for the MNDO-calculations. The heats of formation and relative populations of the fully relaxed geometries for both 5a and 6a are given in the Tables I and II.

The calculations clearly show a preferential ground state conformation in which the hydroxyl group is located out of the plane of the exocyclic double bond. Again this is caused by the large steric interaction between the substituents at the exocyclic double bond and the C_4(Et). In Figure 7 the preferential ground-state conformation of 5a is depicted. Dreiding molecular models clearly show the corresponding 3-propylidene derivatives 5b and 6b to possess a similar preferential conformation.

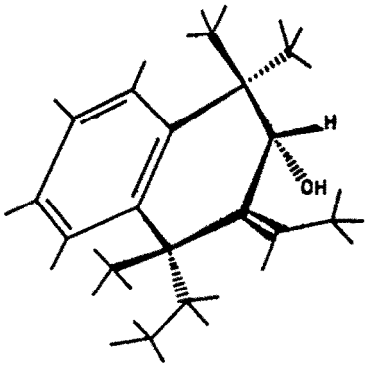


Figure 7. Preferential conformation of (Z)-2S4S-5a.

Table I. Heats of Formation (ΔH_f) and Relative Populations (at 0 °C) of All Stable Conformers of (Z)-(2S4S)-5a.

Conformer	ΔH_f (Kcal mol^{-1})	Relative Populations (%)
S	-0.121	$4.4\ 10^{-3}$
R	-5.542	99.9956

Table II. Heats of Formation (ΔH_f) and Relative Populations (at 0 °C) of All Stable Conformers of (E)-(2S4S)-6a.

Conformer	ΔH_f (Kcal mol^{-1})	Relative Populations (%)
S	1.865	0.03
R	-2.447	99.97

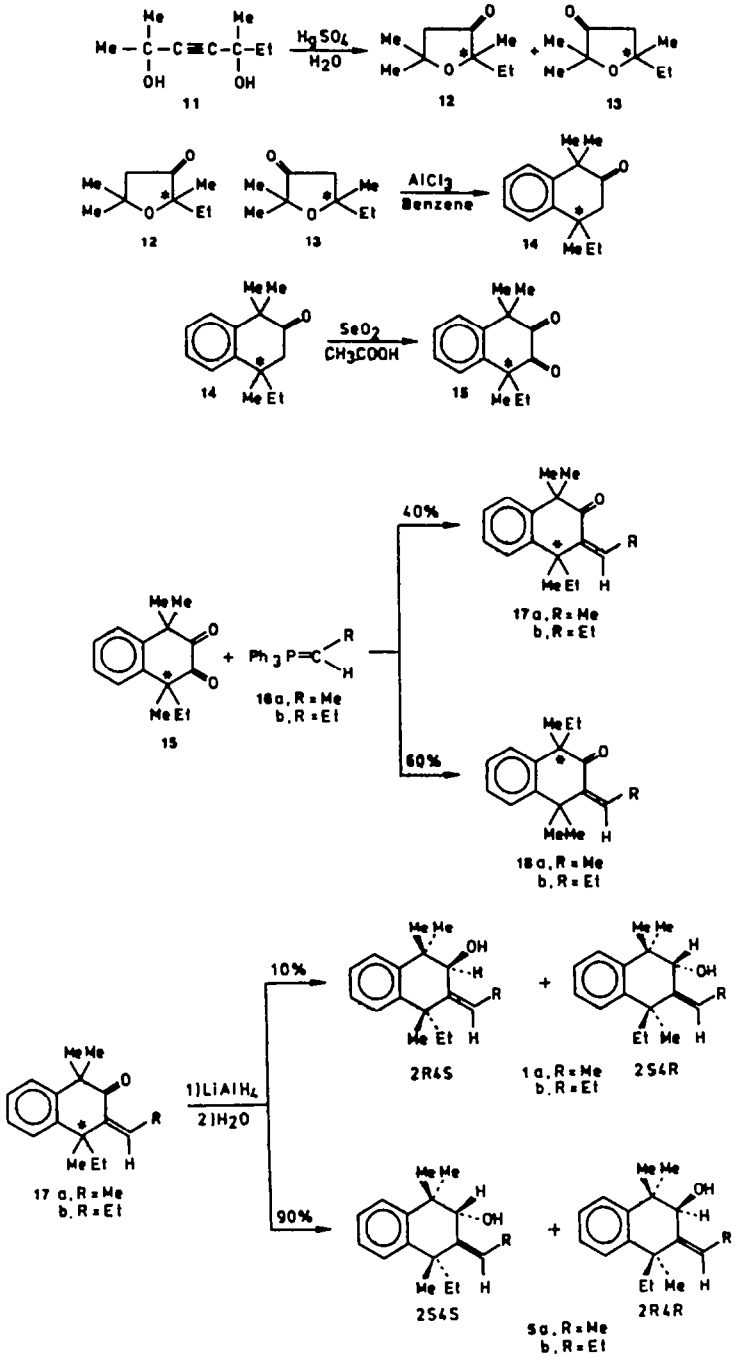
Concerning the mechanism of a photochemical [1,3]-OH shift, the conformation in which the hydroxyl group is located in the plane of the exocyclic double bond is in favour for a planar shift to occur. Regarding the very low relative populations of this (S)-conformation in both 5a and 6a (<0.03%), a planar [1,3]-OH shift is not very likely in these compounds. On the other hand, a location of the hydroxyl group out of the plane of the exocyclic bond is necessary for a suprafacial shift to take place. Thus the non-occurrence of a [1,3]-OH shift upon irradiation of a 50:50 mixture of 5a,b and 6a,b gives an extra indication in favour of a non-Woodward and Hoffmann reaction path. Despite the favourable ground-state conformation of 5a,b and 6a,b for a suprafacial shift to occur, this shift does not take place. Instead a 90°-twisted (polarized) intermediate is formed (as could be proven by irradiation of 5a,b in methanol), from which solely a radiationless transition to the ground state is observable.

Besides this, the absence of products derived from a [1,3]-OH shift in the irradiation of 5a,b and 6a,b likely indicates the occurrence of a non-radical process. For in that case cleavage of the C_2-hydroxyl bond will be followed by recombination of the hereby formed (bi)radicals. This recombination is independent of the conformation of the substrate. Hence formation of a biradicalar intermediate is expected to give rise to the occurrence of a photochemical [1,3]-OH shift in all substrates.

Experimental Section

Synthesis of Reactants of Interest

The reaction route for the synthesis of the diastereoisomeric mixtures of (2RS,4SR)- and (2RS,4RS)-3,4-dihydro-4-ethyl-1,1,4-trimethyl-(Z)-3-ethylidene-2-(1H)-naphthalenol (1a and 5a respectively), (2RS,4SR)- and (2RS,4RS)-3,4-dihydro-4-ethyl-1,1,4-trimethyl-(Z)-3-propylidene-2(1H)-naphthalenol (1b and 5b respectively) is outlined in Scheme I.



Scheme I. Reaction Route for the Synthesis of the Photochemical Reactants 1a,b and 5a,b.

Hydration of the acetylenic γ-diol 11 in the presence of $HgSO_4$ yielded a mixture of the isomeric tetrahydrofuranones 12 and 13 in an equal ratio. Upon Friedel-Crafts cyclialkylation of this mixture with benzene in the presence of $AlCl_3$, the tetrasubstituted naphthalenone derivative 14 could be isolated. Upon SeO_2-oxidation and subsequent Wittig-reaction of the resulting diketone 15, using the alkylidenephosphoranes 16a and 16b, the isomeric α,β-unsaturated ketones 17a,b and 18a,b were obtained in ratios of 40:60. In order to distinguish the 1-ethyl-1,4,4-trimethyl and 4-ethyl-1,1,4-trimethyl derivatives, ^1H NMR Eu(fod)$_3$ shift experiments were carried out. As indicated in Figure 8 for the 3-ethylidene derivatives 17a and 18a, the results show clearly that the C_1-methylene protons in case of compound 18a display a larger shift than the corresponding C_4-methylene protons of compound 17a.

Besides this, addition of Eu(fod)$_3$ to compound 17a causes a rather large shift of the two C_1(Me) groups. In case of compound 18a however only one C_1(Me) group displays this behaviour. As Eu(fod)$_3$ is known to form stable complexes with the carbonyl group, these results strongly confirm the proposed structures. Thereupon, a Z-configuration of both exocyclic double bonds could be deduced from comparison of the induced chemical shifts of the vinylic methyl and hydrogen substituents upon addition of Eu(fod)$_3$ (see Figure 8).

Similarly, ^1H NMR Eu(fod)$_3$ shift experiments on 17b and 18b enabled an unambiguous structure determination of these compounds.

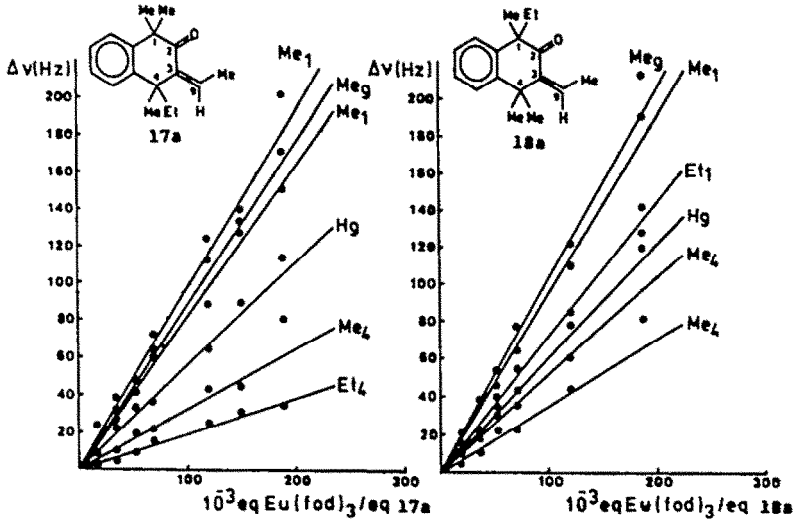


Figure 8. Plot of the induced chemical shift, Δν, versus the amount of added shift reagent for protons of 17a and 18a.

Separation of the isomeric ketones 17a,b and 18a,b could be accomplished by using argentation chromatography. Upon $LiAlH_4$-reduction of the racemic mixture of 17a (17b), the diastereoisomeric allylic alcohols 1a (1b) and 5a (5b) were formed in ratios of 10:90. Thus nearly complete asymmetric induction occurs. An explanation of this phenomenon is based on the conformation of the substrate. As the bulky ethyl group shields one side of the plane of the carbonyl group, hydride-attack is more likely to occur from the opposite side. This implies that a R(S)-configuration on C_4 results in a preferential hydride-attack yielding predominantly an R(S)-configuration on C_2.

Structural Assignment of Photoproducts

The structure elucidation of the various photoproducts was accomplished by comparison of the relative positions and multiplicities of the ^{1}H- and ^{13}C-NMR resonances. The relative configurations at C_4 and C_9 of the products derived from a [1,3]-OH shift, 3a,b and 4a,b, were deduced from the relative configurations of the corresponding methyl ethers 7a,b and 8a,b. In order to correlate these products, the allylic alcohols 3a,b and 4a,b were separately methylated to yield 8a,b and 7a,b respectively (as shown by GLC). Since this reaction does not affect the chirality at either C_4 or C_9, the correlation between 3a,b, 8a,b and 4a,b, 7a,b is evident. In order to establish the stereostructure of both 7a,b and 8a,b, low temperature difference nuclear Overhauser enhancement (NOE) measurements were performed[10,11]. Irradiation of the methoxy group produced enhancement of several other proton resonances in each case. As shown in Tables III and IV, the most significant result of these measurements is the observation of enhancement of the vinylic $C_2(H)$ in 7a,b and not in 8a,b, at temperatures below -20 °C.

Table III. Observed NOE (%) of $C_2(H)$ upon Irradiation of $C_9(OMe)$ at Several Temperatures for Compounds 7a and 8a.

Temperature (K)	Compound 7a	Compound 8a
293	1.3	0.2
273	0.9	0.6
253	3.2	0.3
233	4.8	0.9
213	7.4	1.1
203	9.3	0.8

Table IV. Observed NOE (%) of $C_2(H)$ upon Irradiation of $C_9(OMe)$ at Several Temperatures for Compounds 7b and 8b.

Temperature (K)	Compound 7b	Compound 8b
293	-0.3	0.2
273	0.6	0.4
253	1.5	0.3
233	3.6	1.0
213	5.3	0.8
203	6.8	0.9

Since a linear relationship between the observed NOE and the sixth power of the internuclear distance has been established by Bell and Saunders[12], these results indicate that at low temperatures the internuclear $C_2(H)$-$C_9(OMe)$ distance in compounds 7a,b is considerably smaller than in case of compounds 8a,b. Dreiding molecular models show that in the preferential conformation of both 7a,b and 8a,b the $C_9(H)$ is located in an anti-position to the C_2-C_3 double bond, thereby minimizing the interaction between the substituents at C_9 and C_4. In case of a relative (4SR,9SR)-configuration, $C_9(OMe)$ and $C_4(Et)$ are located on the same side of the plane of the C_2-C_3 double bond. A relative (4SR,9RS)-configuration on the other hand implies a location of the $C_9(OMe)$ and the $C_4(Et)$ on opposite sides of the plane of the C_2-C_3 double bond. Dependent on the chirality at C_4 the $C_4(Et)$ shields one side of this plane. This means that in case of a relative (4SR,9SR)-configuration the $C_9(OMe)$ is directed away from the $C_4(Et)$, which leads to an increase of the $C_2(H)$- $C_9(OMe)$ internuclear distance. Thus, based on the results of the low temperature NOE experiments, a (4SR,9SR)-configuration can be assigned to compounds 8a,b and 3a,b. As in case of a relative (4SR,9RS)-configuration the $C_4(Et)$-$C_9(OMe)$ internuclear distance is much larger, the $C_9(OMe)$ will hardly be

influenced by this substituent. This implies that in the preferential conformation the C_9(OMe) is located near the vinylic C_2(H), thus accounting for the observed enhancement of the ^1H NMR signal of this proton upon irradiation of the C_9(OMe) resonance. So compounds 7a,b and 4a,b have a (4SR,9RS)-configuration.

Materials and Methods. Preparation of compounds

^1H and ^{13}C NMR spectra were recorded at 200 respectively 50 MHz on a Bruker AC 200 NMR spectrometer, interfaced with an ASPECT 3000 computer. An internal field-frequency lock was used. Chemical shifts were referenced against tetramethylsilane (δ= 0 ppm), which was added as a small trace. NOE difference spectra were obtained using the method of Hall and Sanders[10] with the following timings: pre-irradiation (5 sec), delay (50 msec), 90° pulse (3 µsec) and acquire one transient (2.7 sec). Eight transients were collected at each site during each pass around the full frequency list until 200 transients had been accumulated at every site. Thoroughly degassed CD_2Cl_2 was used as a solvent. Gas chromatograms were recorded using a Kipp Analytica 8200 equipped with a flame-ionization detector. Columns used were Chrompack fused silica wall, open tubular columns with CP Wax 51 as liquid phase (25 m x 0.23 mm). The UV measurements were performed on a Perkin-Elmer 124 spectrofotometer. Argentation chromatography was performed using impregnated silica, prepared by evaporating to dryness of a slurry of silica (type 60, Merck) and 10% $AgNO_3$ in CH_3CN.

Irradiation Procedure

Irradiations were performed using a 500 Watt medium pressure mercury lamp (Hanau TQ718) through quartz. Cooling of the lamp and the reaction vessel was accomplished by means of a closed circuit filled with methanol. The temperature in the reaction vessel was maintained at $\pm$ 0 °C. A 6 x 10^{-3} molar solution of the various compounds in n-hexane or methanol (both p.a.) was used. Before and during irradiation, the reaction mixture was purged by a stream of dry nitrogen in order to remove all traces of oxygen. All irradiations were followed by means of GLC. Upon GLC indicating the presence of sufficient amounts of photoproducts to be identified by means of ^1H and ^{13}C NMR spectroscopy (usually at approximately 5% conversion), the irradiation was stopped and the solvent removed on a rotatory evaporator. The crude reaction mixture was separated by means of repeated argentation chromatography.

2-Ethyldihydro-2,5,5-trimethyl-3(2H)-furanone (12) and 5-ethyldihydro-2,2,5-trimethyl-3(2H)-furanone (13)[13].

To a mixture of 27 g of HgO, 30 mL of conc. H_2SO_4 and 100 mL of water was added with cooling 300 g (1.92 mol) 2,5-dimethyl-3-heptyn2,5-diol (11). The mixture was stirred for 2h at 70 °C. After cooling to room temperature and filtration, the aqueous layer was extracted with two 300-mL portions of ether. The combined organic extracts were neutralized with a saturated $NaHCO_3$-solution, washed with brine, dried over $MgSO_4$ and evaporated. Distillation (20 mm, 73-74 °C) afforded 208 g (69%) of 12 and 13 in a ratio of 50:50 (as indicated by GLC).

^1H NMR ($CDCl_3$) δ .85 (t,3H), 0.94 (t,3H), 1.23 (s,6H), 1.24 (s,3H), 1.31 (s,3H), 1.34 (s,3H), 1.40 (s,3H), 1.56 (m,4H), 2.43 (m,4H); ^{13}C NMR ($CDCl_3$) δ 214.49 (s), 214.15 (s), 83.72 (s), 80.48 (s), 78.64 (s), 75.98 (s), 49.72 (t), 46.44 (t), 35.26 (t), 32.34 (t), 30.66 (q), 30.31 (q), 27.79 (q), 26.66 (q), 26.27 (q), 24.61 (q), 8.79 (q), 8.51 (q).

3,4-Dihydro-4-ethyl-1,1,4-trimethyl-2(1H)-naphthalenone (14)[14].

To a stirred solution of 208 g (1.33 mol) of 12 and 13 in 750 mL of anhydrous benzene was added gradually anhydrous, powdered $AlCl_3$ (316 g, 2.37 mol) while maintaining the temperature between 40 and 50 °C by external cooling. The solution was then heated at reflux for 2h, cooled and poured into one liter of ice and water containing 150 mL of conc. HCl. The aqueous layer was washed with four 200-mL portions of ether. The combined organic layers were washed with a saturated $NaHCO_3$-solution, dried over $MgSO_4$ and concentrated in vacuo.
Chromatography (silica 60, n-hexane-ether 3:1 (v/v)) afforded 50.7 g (18%) of 14.
^1H NMR ($CDCl_3$) δ .60 (t,3H), 1.27 (s,3H), 1.30 (s,3H), 1.40 (s,3H), 1.79 (q,2H), 2.57 (AB-q, A 2.50, B 2.64, J_{AB}= 12.8 Hz, 2H), 7.09-7.45 (m,4H); ^{13}C NMR ($CDCl_3$) δ 213.89 (s), 145.19 (s), 142.36 (s), 127.82 (d), 127.68 (d), 127.33 (d), 125.49 (d), 53.32 (s), 53.22 (s), 38.85 (t), 34.79 (t), 32.10 (q), 31.47 (q), 29.26 (q), 10.79 (q).

1,4-Dihydro-1-ethyl-1,4,4-trimethyl-2,3-naphthalenedione (15).

To a solution of 50.7 g (0.23 mol) of 14 in 250 mL of glacial acetic acid was added 30 g (0.27 mol) SeO_2. The mixture was heated at reflux for 4h. The cooled solution was thoroughly filtered and the solvent removed in vacuo. The residu was dissolved in 200 mL of ether, washed with water and a saturated $NaHCO_3$-solution. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. This afforded 52.8 g (97%) of 15.
^1H NMR ($CDCl_3$) δ .71 (t,3H), 1.43 (s,3H), 1.48 (s,3H), 1.54 (s,3H), 1.87 (m,2H), 7.13-7.48 (m,4H); ^{13}C NMR ($CDCl_3$) δ 206.32 (s), 206.10 (s), 141.84 (s), 139.80 (s), 128.91 (d), 128.81 (d), 127.33 (d), 127.15 (d), 56.34 (s), 51.74 (s), 35.40 (t), 28.73 (q), 26.00 (q), 23.96 (q), 9.97 (q).

3,4-Dihydro-4-ethyl-1,1,4-trimethyl-(Z)-3-ethylidene-2(1H)-naphthalenone and 3,4-dihydro-1-ethyl-1,4,4-trimethyl-(Z)-3-ethylidene-2(1H)-naphthalenone (17a and 18a respectively).

n-Butyllithium (187 mL of a 1.6 M solution in n-hexane, 0.30 mol) was added dropwise to a stirred suspension of 102.2 g (0.28 mol) (ethyl)triphenylphosphonium bromide in 200 mL of anhydrous ether, whereupon the deep red color of the ethylidenephosphorane 16a was produced. The mixture was then stirred for 2h at room temperature. At the end of this period 52.8 g (0.23 mol) of 15 was added dropwise, whereupon a white precipitate formed. The mixture was then cooled and filtered by suction. The filtrate was washed with water, the organic layer separated and dried over $MgSO_4$. Removal of ether left a residue which was separated by repeated argentation chromatography using n-hexane-ether 95:5 (v/v) as eluent. Thus 3.2 g of 17a and 4.5 g of 18a could be obtained (total yield = 14%). The corresponding E-isomers were not detected as byproducts. GLC showed the original product mixture to contain 17a and 18a in a ratio of 40:60.
17a; ^1H NMR ($CDCl_3$) δ .70(t,3H), 1.38 (s,3H), 1.40 (s,3H), 1.46 (s,3H), 1.78 (d,3H), 2.05 (q,2H), 5.74 (q,1H), 7.10-7.46 (m,4H); ^{13}C NMR ($CDCl_3$) δ 209.98 (s), 145.27 (s), 144.08 (s), 143.83 (s), 129.05 (d), 127.73 (d), 127.63 (d), 125.52 (d), 125.30 (d), 50.19 (s), 43.08 (s), 38.89 (t), 30.63 (q), 28.66 (q), 24.16 (q), 16.13 (q), 9.77 (q).
18a; ^1H NMR ($CDCl_3$) δ .63 (t,3H), 1.37 (s,3H), 1.42 (s,3H), 1.49 (s,3H), 1.80 (d,3H), 2.09 (q,2H), 5.81 (q,1H), 7.10-7.49 (m,4H); ^{13}C NMR ($CDCl_3$) δ 210.25 (s), 147.09 (s), 144.87 (s), 141.92 (s), 129.30 (d), 127.79 (d), 127.40 (d), 126.00 (d), 125.75 (d), 54.49 (s), 46.84 (s), 35.09 (t), 31.61 (q), 30.60 (q), 27.03 (q), 16.02 (q), 10.72 (q).

3,4-Dihydro-4-ethyl-1,1,4-trimethyl-(Z)-3-propylidene-2(1H)-naphthalenone and 3,4-dihydro-1-ethyl-1,4,4-trimethyl-(Z)-3-propylidene-2(1H)-naphthalenone (17b and 18b respectively).

The same procedure was used as for the preparation of 17a and 18a. Starting from 50.0 g (0.22 mol) of 15, 3.0 g of 17b and 3.9 g of 18b were obtained after repeated argentation chromatography using n-hexane-ether 9:1 (v/v) as eluent.

17b; ^{1}H NMR ($CDCl_3$) δ .63 (t,3H), 1.00 (t,3H), 1.40 (s,3H), 1.43 (s,3H), 1.49 (s,3H), 2.10 (q,2H), 2.20 (m,2H), 5.63 (t,1H), 7.09-7.48 (m,4H); ^{13}C NMR ($CDCl_3$) δ 209.73 (s), 145.17 (s), 143.78 (s), 141.88 (s), 127.87 (d), 127.72 (d), 126.93 (d), 126.13 (d), 125.35 (d), 54.30 (s), 42.86 (s), 34.89 (t), 32.18 (t), 29.39 (q), 24.31 (q), 23.55 (q), 15.27 (q), 10.62 (q).

18b; ^{1}H NMR ($CDCl_3$) δ .67 (t,3H), 1.00 (t,3H), 1.42 (s,3H), 1.43 (s,3H), 1.50 (s,3H), 2.12 (q,2H), 2.19 (m,2H), 5.67 (t,1H), 7.14-7.53 (m,4H); ^{13}C NMR ($CDCl_3$) δ 210.12 (s), 145.58 (s), 144.01 (s), 143.24 (s), 128.79 (d), 127.70 (d), 127.30 (d), 125.94 (d), 124.16 (d), 53.55 (s), 49.92 (s), 38.84 (t), 31.24 (t), 30.79 (q), 27.50 (q), 23.62 (q), 15.54 (q), 9.63 (q).

(2RS,4SR)- and (2RS,4RS)-3,4-Dihydro-4-ethyl-1,1,4-trimethyl-(Z)-3-propylidene-2(1H)-naphthalenol (1b and 5b respectively).

The same procedure was used as for the reduction of 17a. Starting from 3.0 g (11.7 mmol) of 17b, 3.0 g of a mixture of 1b and 5b was obtained. GLC showed this mixture to contain 10% of 1b and 90% of 5b. Separation was accomplished using repeated argentation chromatography with n-hexane-ether 9:1 (v/v) as eluent.

1b; ^{1}H NMR ($CDCl_3$) δ .86 (t,3H), 1.05 (t,3H), 1.20 (s,3H), 1.41 (s,3H), 1.51 (s,3H), 2.03 (q,2H), 2.22 (m,2H), 4.47 (s,1H), 5.53 (t,1H), 6.97-7.33 (m,4H); ^{13}C NMR ($CDCl_3$) δ 143.64 (s), 142.82 (s), 140.74 (s), 129.63 (d), 128.61 (d), 128.39 (d), 127.85 (d), 126.79 (d), 75.65 (d), 44.26 (s), 40.22 (s), 38.69 (t), 36.81 (t), 31.06 (q), 27.62 (q), 21.71 (q), 15.81 (q), 10.57 (q).

UV (EtOH) λ_{max} 250 nm.

(2RS,4SR)- and (2RS,4RS)-3,4-Dihydro-4-ethyl-1,1,4-trimethyl-(Z)-3-ethylidene-2(1H)-naphthalenol (1a and 5a respectively).

To a stirred suspension of 0.5 g (13.2 mmol) of $LiAlH_4$ in 50 mL of anhydrous ether was added dropwise, at 0 °C, a solution of 3.2 g (13.2 mmol) of 17a in 25 mL ether. After 30 min. additional stirring the reaction mixture was allowed to warm to room temperature. After addition of respectively 1 mL of water, 1 mL of a 5N NaOH solution and 5 mL of water, filtration, separation of the organic layer and removal of the solvent afforded 3.0 g (94%) of a mixture of 1a and 5a. GLC showed a composition of 10% of 1a and 90% of 5a. Separation was accomplished by using repeated argentation chromatography with n-hexane-ether 9:1 (v/v) as eluent.

1a; ^{1}H NMR ($CDCl_3$) δ .73 (t,3H), 1.24 (s,3H), 1.32 (s,3H), 1.40 (s,3H), 1.80 (d,3H), 2.03 (q,2H), 4.53 (s,1H), 5.80 (q,1H), 7.03-7.33 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.13 (s), 143.78 (s), 142.73 (s), 128.43 (d), 127.81 (d), 127.50 (d), 127.02 (d), 126.36 (d), 75.50 (d), 43.49 (s), 40.63 (s), 36.20 (t), 32.62 (q), 29.40 (q), 20.31 (q), 15.14 (q), 10.17 (q); UV (EtOH) λ_{max} 240 nm.

5a; ^{1}H NMR ($CDCl_3$) δ .87 (t,3H), 1.28 (s,3H), 1.35 (s,3H), 1.49 (s,3H), 1.81 (d,3H), 1.97 (q,2H), 4.47 (s,1H), 5.69 (q,1H), 7.07-7.38 (m,4H); ^{13}C NMR ($CDCl_3$) δ 144.57 (s), 143.04 (s), 141.94 (s), 129.23 (d), 127.87 (d), 127.58 (d), 127.14 (d), 127.01 (d), 75.02 (d), 45.65 (s), 43.64 (s), 39.05 (t), 31.10 (q), 27.07 (q), 23.89 (q), 14.21 (q), 10.89 (q); UV (EtOH) λ_{max} 245 nm.

5b; ^{1}H NMR ($CDCl_3$) δ 1.05 (t,3H), 1.10 (t,3H), 1.15 (s,3H), 1.45 (s,3H), 1.57 (s,3H), 2.00 (q,2H), 2.23 (m,2H), 4.75 (s,1H), 5.69 (t,1H), 7.08-7.43 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.43 (s), 144.58 (s), 143.20 (s), 130.07 (d), 128.39 (d), 127.47 (d), 127.26 (d), 126.48 (d), 70.29 (d), 42.23 (s), 39.45 (s), 37.82 (t), 34.30 (t), 30.57 (q), 27.65 (q), 21.71 (q), 15.99 (q), 9.36 (q).
UV (EtOH) λ_{max} 240 nm.

(1SR,9RS)-1,4-Dihydro-1-ethyl-1,4,4-trimethyl-2(1-methoxyethyl)-naphthalene (7a).

A mixture of 0.015 g (0.63 mmol) of NaH and 15 mL of THF was heated to 40 °C, followed by addition of 0.1 g (0.7 mmol) of CH_3I. A solution of 0.1 g (0.41 mmol) of 4a in 10 mL of THF was added dropwise. Then the mixture was kept at 40 °C for 90 min. After cooling the reaction mixture, hydrolysis was performed by dropwise addition of excess of water. The aqueous layer was separated and extracted twice with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. GLC showed 7a to be the main product present. No traces of 8a could be detected. Evaporation and subsequent column chromatography (Woelm silica, n-hexane-ether 95:5 (v/v)) yielded 0.055 g (52%) of 7a.
^{1}H NMR ($CDCl_3$) δ .50 (t,3H), 1.26 (s,3H), 1.32 (d,3H), 1.35 (s,3H), 1.42 (s,3H), 1.79 (q,2H), 3.23 (s,3H), 3.91 (q,1H), 5.84 (s,1H), 7.11-7.38 (m,4H); ^{13}C NMR ($CDCl_3$) δ 148.54 (s), 143.25 (s), 138.73 (s), 133.49 (d), 127.43 (d), 127.10 (d,2x), 126.98 (d), 75.74 (d), 57.05 (q), 43.16 (s), 41.92 (s), 34.92 (t), 34.57 (q), 33.88 (q), 24.99 (q), 23.75 (q), 11.02 (q).

(1SR,9SR)-1,4-Dihydro-1-ethyl-1,4,4-trimethyl-2(1-methoxyethyl)-naphthalene (8a).

Starting from 0.14 g (0.58 mmol) of 3a, the same procedure was used as for the methylation of 4a. GLC indicated 8a to be the main product formed, no traces of 7a could be detected. Column chromatography (Woelm silica, n-hexane-ether 95:5 (v/v)) yielded 0.09 g (61%) of 8a.
^{1}H NMR ($CDCl_3$) δ .43 (t,3H), 1.28 (s,3H), 1.34 (d,3H), 1.36 (s,3H), 1.42 (s,3H), 1.76 (q,2H), 3.28 (s,3H), 3.97 (q,1H), 5.87 (s,1H), 7.15-7.40 (m,4H); ^{13}C NMR ($CDCl_3$) δ 146.78 (s), 141.56 (s), 139.51 (s), 134.12 (d), 128.11 (d), 127.31 (d), 126.98 (d), 126.78 (d), 74.92 (d), 56.33 (q), 44.03 (s), 39.86 (s), 35.13 (t), 34.11 (q), 33.70 (q), 24.40 (q), 23.47 (q), 10.81 (q).

(1SR,9RS)-1,4-Dihydro-1-ethyl-1,4,4-trimethyl-2(1-methoxypropyl)-naphthalene (7b).

The same procedure was used as for the preparation of compounds 7a and 8a. Starting from 0.1 g (0.39 mmol) of 4b, a 20 % conversion was achieved after stirring for 5 h. GLC indicated 7b to be the main product present, 8b could not be detected. Column chromatography (Woelm silica, n-hexane-ether 99:1 (v/v)) yielded 0.01g (46%) of 7b.
^{1}H NMR ($CDCl_3$) δ .59 (t,3H), .87 (t,3H), 1.25 (s,3H), 1.36 (s,3H), 1.43 (s,3H), 1.73 (q,2H), 2.01 (m,2H), 3.27 (s,3H), 4.06 (t,1H), 5.57 (s,1H), 7.13-7.42 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.37 (s), 142.11 (s), 141.47 (s), 133.57 (d), 131.94 (d), 129.88 (d), 126.94 (d), 126.73 (d), 78.32 (d), 57.16 (q), 40.85 (s), 38.17 (s), 33.54 (t), 32.72 (t), 31.23 (q), 30.02 (q), 24.07 (q), 15.19 (q), 12.33 (q).

(1SR,9SR)-1,4-Dihydro-1-ethyl-1,4,4-trimethyl-2(1-methoxypropyl)-naphthalene (8b).

Compound 8b was prepared in the same way as compounds 7a,b and 8a. Starting from 0.2 g of 3b, column chromatography (Woelm silica, n-hexane-ether 99:1 (v/v)) yielded 0.04 g (20%) of 8b. As indicated by GLC, 8a was not present in the crude reaction mixture.

^{1}H NMR ($CDCl_3$) δ .52 (t,3H), .95 (t,3H), 1.28 (s,3H), 1.39 (s,3H), 1.48 (s,3H), 1.69 (q,2H), 2.06 (m,2H), 3.24 (s,3H), 4.03 (t,1H), 5.55 (s,1H), 7.10-7.38 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.85 (s), 142.06 (s), 140.80 (s), 132.68 (d), 131.86 (d), 130.14 (d), 127.98 (d), 125.61 (d), 77.92 (d), 56.77 (q), 40.89 (s), 37.82 (s), 33.35 (t), 33.01 (t), 31.55 (q), 30.52 (q), 24.85 (q), 15.37 (q), 11.96 (q).

Spectral Data for the Remaining Photoproducts

2a; ^{1}H NMR ($CDCl_3$) δ .63 (t,3H), 1.21 (s,3H), 1.27 (s,3H), 1.43 (s,3H), 1.88 (d,3H), 2.13 (q,2H), 4.29 (s,1H), 5.73 (q,1H), 7.11-7.35 (m,4H); ^{13}C NMR ($CDCl_3$) δ 144.23 (s), 143.53 (s), 143.48 (s), 129.24 (d), 128.93 (d), 127.85 (d), 127.04 (d), 126.62 (d), 78.32 (d), 45.31 (s), 42.44 (s), 40.46 (t), 28.00 (q), 24.51 (q), 21.78 (q), 15.20 (q), 11.50 (q).

3a; ^{1}H NMR ($CDCl_3$) δ .47 (t,3H), 1.30 (s,3H), 1.31 (d,3H), 1.33 (s,3H), 1.36 (s,3H), 1.81 (q,2H), 3.89 (q,1H), 5.58 (s,1H), 7.10-7.40 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.54 (s), 142.09 (s), 140.16 (s), 132.16 (d), 128.32 (d), 127.26 (d), 126.85 (d), 126.74 (d), 72.98 (d), 43.83 (s), 40.37 (s), 35.07 (t), 33.81 (q), 33.12 (q), 25.06 (q), 24.21 (q), 11.16 (q).

4a; ^{1}H NMR ($CDCl_3$) δ .49 (t,3H), 1.24 (s,3H), 1.30 (d,3H), 1.36 (s,3H), 1.39 (s,3H), 1.82 (q,2H), 3.94 (q,1H), 5.81 (s,1H), 7.13-7.39 (m,4H); ^{13}C NMR ($CDCl_3$) δ 146.39 (s), 143.87 (s), 139.96 (s), 132.76 (d), 127.83 (d), 127.51 (d), 127.06 (d), 126.54 (d), 73.14 (d), 43.27 (s), 40.83 (s), 35.01 (t), 34.36 (q), 33.67 (q), 25.48 (q), 23.73 (q), 11.05 (q).

6a; ^{1}H NMR ($CDCl_3$) δ .70 (t,3H), 1.20 (s,3H), 1.25 (s,3H), 1.41 (s,3H), 1.79 (d,3H), 2.11 (q,2H), 4.21 (s,1H), 5.64 (q,1H), 7.05-7.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 145.64 (s), 143.92 (s), 142.83 (s), 129.77 (d), 128.79 (d), 127.27 (d), 127.06 (d), 126.83 (d), 77.06 (d), 45.09 (s), 43.09 (s), 37.64 (t), 30.56 (q), 26.63 (q), 23.47 (q), 13.95 (q), 10.43 (q).

2b; ^{1}H NMR ($CDCl_3$) δ .97 (t,3H), 1.10 (t,3H), 1.22 (s,3H), 1.38 (s,3H), 1.45 (s,3H), 2.05 (q,2H), 2.37 (m,2H), 3.95 (s,1H), 5.44 (t,1H), 7.00-7.43 (m,4H); ^{13}C NMR ($CDCl_3$) δ 144.02 (s), 141.77 (s), 141.58 (s), 129.15 (d), 128.19 (d), 127.69 (d), 126.92 (d), 125.02 (d), 77.38 (d), 45.86 (s), 43.36 (s), 40.29 (t), 37.84 (t), 29.03 (q), 26.49 (q), 22.36 (q), 15.89 (q), 10.23 (q).

3b; ^{1}H NMR ($CDCl_3$) δ .62 (t,3H), .98 (t,3H), 1.21 (s,3H), 1.31 (s,3H), 1.48 (s,3H), 1.65 (q,2H), 1.89 (m,2H), 3.86 (t,1H), 5.49 (s,1H), 7.10-7.36 (m,4H); ^{13}C NMR ($CDCl_3$) δ 146.13 (s), 143.62 (s), 140.17 (s), 130.81 (d), 129.36 (d), 129.21 (d), 128.60 (d), 126.81 (d), 75.41 (d), 42.32 (s), 39.86 (s), 37.18 (t), 34.36 (q), 34.25 (t), 31.27 (q), 25.13 (q), 15.88 (q), 12.02 (q).

4b; ^{1}H NMR ($CDCl_3$) δ .65 (t,3H), 1.01 (t,3H), 1.17 (s,3H), 1.33 (s,3H), 1.41 (s,3H), 1.71 (q,2H), 1.93 (m,2H), 3.91 (t,1H), 5.51 (s,1H), 7.08-7.32 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.51 (s), 144.51 (s), 140.86 (s), 131.35 (d), 130.10 (d), 129.63 (d), 127.98 (d), 126.47 (d), 74.92 (d), 41.81 (s), 39.23 (s), 6.73 (t), 33.92 (t), 33.71 (q), 31.61 (q), 25.01 (q), 16.12 (q), 12.23 (q).

6b; ^{1}H NMR ($CDCl_3$) δ 1.01 (t,3H), 1.19 (t,3H), 1.22 (s,3H), 1.41 (s,3H), 1.59 (s,3H), 2.12 (q,2H), 2.30 (m,2H), 4.05 (s,1H), 5.45 (t,1H), 7.10-7.40 (m,4H); ^{13}C NMR ($CDCl_3$) δ 144.45 (s), 142.95 (s), 141.59 (s), 130.10 (d), 128.22 (d), 127.77 (d), 127.50 (d), 126.93 (d), 75.31 (d), 43.52 (s), 40.44 (s), 39.03 (t), 34.81 (t), 31.34 (q), 27.02 (q), 21.84 (q), 15.10 (q), 10.79 (q).

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