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THE EFFECTS OF SUBSTITUENTS AND SOLVENT POLARITY ON PHOTOCHEMICAL [1,3] SIGMATROPIC SHIFTS. EXPERIMENTAL EVIDENCE IN FAVOUR OF THE OCCURRENCE OF SUDDEN POLARIZATION IN ACYCLIC ALKENES

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Abstract - Further experimental evidence regarding the occurrence of sudden polarization in acyclic alkenes is presented. It is shown that the yield of formation of the product derived from an intramolecular photochemical [1,3]-OR shift in 1 is dependent only on the polarity of the solvent employed. This result could be well explained in terms of a stabilization of the zwitterionic intermediate formed upon irradiation of 1 by reorientation polarization of the dipole solvent molecules. Besides this, it was found that replacement of the alkyl group at the terminal carbon atom of the C_3–C_9 exocyclic double bond in 1 by a phenyl substituent led to the occurrence of a photochemical [1,3]-H shift. This directive effect of the substituents at the exocyclic double bond could be well explained on the basis of the sudden polarization model.

Introduction

In a previous contribution from our laboratories we presented the first experimental evidence regarding the occurrence of a planar photochemical [1,3] sigmatropic shift in unsaturated hydrocarbons[1]. A central role in this planar mechanism is taken by the relaxation of an excited double bond towards a 90°-twisted intermediate. In the case of nonsymmetrical alkenes the twisting motion is accompanied by a relocalization of the electrons. This "Sudden Polarization" effect has first been described theoretically by Salem and co-workers[2] and has thereafter been found to persist by many theoretical calculations at different levels of sophistication[3]. Up till now however, only the excited state reactivities of β-t-butylstyrene derivatives and of some substituted cycloheptatrienes have been well elucidated on the basis of the sudden polarization model[4,5]. On the other hand as in the case of the intramolecular cycloaddition in which a triene is converted into a bicyclo[3.1.0]hexene, no experimental support regarding the proposed two step mechanism based upon the concept of sudden polarization was found[6]. Instead recent publications even strengthen the arguments against the validity of the sudden polarization model in this specific case; the theoretically predicted[7] effects of substituents on the charge distribution in the zwitterionic states found no experimental support[8].

We now wish to present further experimental evidence in favour of the occurrence of sudden polarization in excited unmsymmetrical alkenes. First of all the yields of formation of the products derived from a planar photochemical [1,3]-OH shift in 3,4-dihydro-1,1,4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenol (1) were determined as a function of solvent polarity. A similar study of the effects of solvent polarity on photoinduced chemical reactions was performed by Verhoeven and co-workers, who elegantly studied the effect of solvent dynamics on the rate of electron transfer in an extensive series of molecules containing electron donor and acceptor groups separated by an elongated paraffinic spacer[9].
Furthermore a directive effect of the substituents at the exocyclic double bond of a number of model compounds is reported. It is shown that dependent on the nature of these substituents either a photochemical [1,3]-H or [1,3]-OH shift takes place.

Results and Discussion

The Effect of Solvent Polarity on Photochemical [1,3]-OH Shifts

Upon direct irradiation of 1 in various solvents, fast E-Z isomerization around the exocyclic double bond could be observed. This led to the formation of a 50:50 mixture of 1 and 2. Further irradiation of this mixture resulted in the clean formation of 3, the product derived from a photochemical [1,3]-OH shift in either 1 or 2 (see Figure 1).

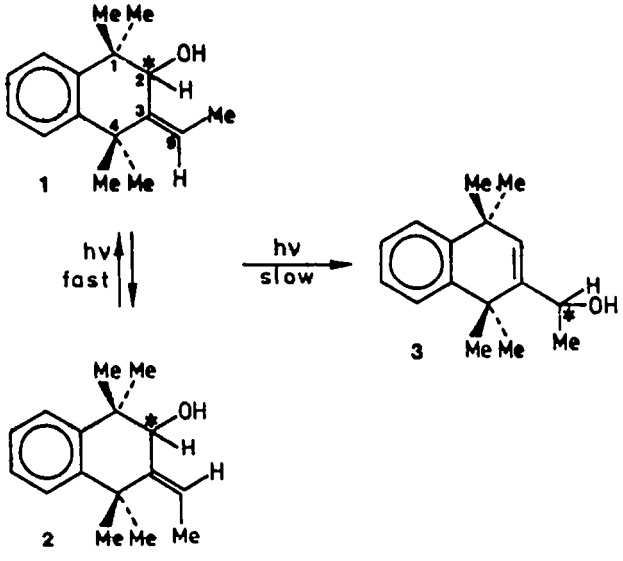


Figure 1. Photochemistry of compound 1 upon irradiation in various solvents.

It should be noted that a location of the hydroxyl group in the plane of the exocyclic double bond is a prerequisite for a photochemical planar [1,3]-OH shift to take place[1]. Clearly, in compounds 1 and 2 the presence of the four equivalent alkyl substituents at C_1 and C_4, will make the occurrence of such a conformation quite feasible.

In order to investigate the influence of solvent polarity on a photochemical [1,3]-OH shift, the irradiation was performed in a variety of solvents. A 0.01 molar solution of 1 in the differential solvents was irradiated during four hours. At regular intervals of time and at the end of this period the composition of the resulting product mixture was analyzed by means of GLC. In Table I the relative yields of formation of compound 3 after four hours of irradiation are depicted for several solvents; the yield of formation of compound 3 upon irradiation of 1 in n-hexane is given the reference value of 1. The in comparison to acetonitrile even more polar solvents methanol and ethanol could not be used since in these solvents a disturbing addition of solvent to the exocyclic double bond takes place (vide infra).

Table I. Relative yields of formation of 3 upon irradiation of a 50:50 mixture of 1 and 2 in various solvents.

Solvent	E_T[a]	Relative yield
n-hexane	30.9	1
cyclohexane	31.2	0.98
diethylether	34.6	0.65
2-Me-tetrahydrofuran	36.5	0.49
acetonitrile	46.0	0.15

[a]The solvent parameter E_T is based on the solvatochromism of pyridinium-N-phenolbetaine in various solvents[10].

From this Table it may be concluded that the yield of formation of compound 3 decreases going from a highly apolar solvent like n-hexane to the in this series most polar solvent, acetonitrile. This result is a clear support in favour of the sudden polarization model. Excitation of either 1 or 2 will be followed by a 90°-twist around the exocyclic double bond, accompanied with a complete separation of charge in the orthogonal situation. In the case of allylic alcohols this polarization leads to a negative charge on the central carbon atom C_3 and a positive charge on the terminal carbon atom C_9[11]. In case of a polar solvent this positive charge will be partly shielded by reorientation polarization of dipolar solvent molecules, thus lowering the total energy contents of the zwitterionic intermediate. This implies that in the orthogonal situation the energy difference between the S_1 and the S_0 will decrease upon transfer from an apolar to a polar solvent. However, since the nonadiabatic coupling between these states is inversely proportional to their energy difference[12], a radiationless transition from the 90°-twisted intermediate to the ground state will become more likely to occur in polar solvents, thus decreasing the yield of formation of 3 in these solvents.
Another effect of performing the irradiation of 1 and 2 in polar solvents will be an increase of the activation enthalpy for the planar [1,3]-OH shift in these compounds. Schematically the potential energy profiles for a planar [1,3]-OH shift in both a polar (---) and an apolar (——) solvent are depicted in Figure 2. Since the planar transition state bears no polar character[11], the polarity of the solvent applied will not affect its energy contents. Hence, as can be seen from Figure 2, the potential energy difference between the stabilized 90°-twisted conformation and the transition state will increase upon increasing solvent polarity, thus again decreasing the yield of formation of compound 3.

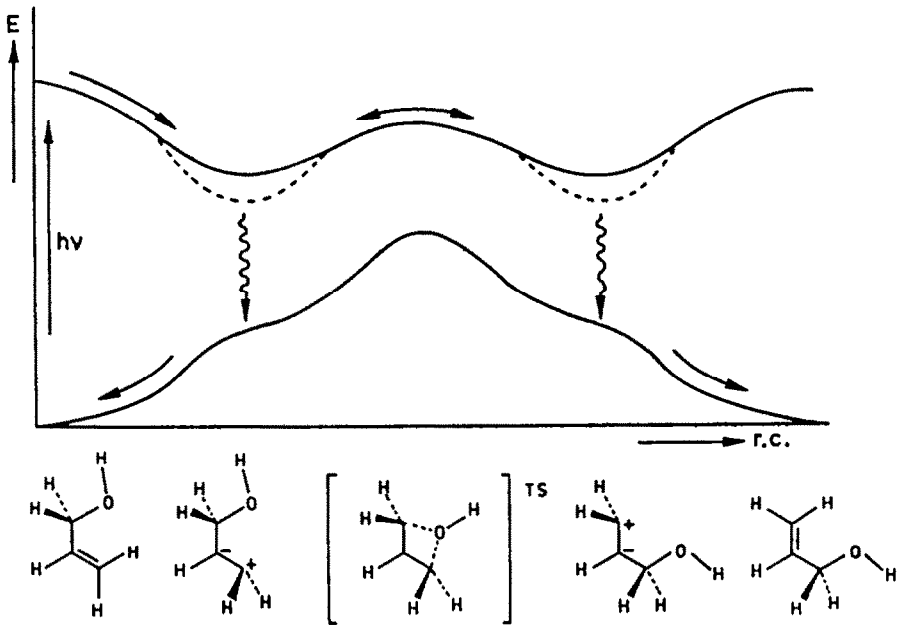


Figure 2. Potential energy curves of the ground and first singlet excited state for a photochemical planar [1,3]-OH shift in both a polar (---) and an apolar (——) solvent.

Taking into account the two effects described above, an estimate can be made of the maximum difference of the activation enthalpy, $\Delta(E_{akt})_{max}$, for the planar [1,3]-OH shift in a polar solvent like acetonitrile and an apolar solvent like n-hexane. Regarding the observed relative yields of formation of 3 depicted in Table I (1 and 0.15 respectively), the $\Delta(E_{akt})_{max}$ is calculated to amount 1.5 kcal/mol.

Summarizing it may be concluded that these results strongly support the mechanism of a planar photochemical [1,3]-OH shift whereas they contradict the mechanism of a suprafacial shift. For in that case, since no polar intermediate is involved, no solvent effect at all would be observable[1].

Substituents Effect on Photochemical [1,3] Sigmatropic Shifts

In the preceding section the photochemical behaviour of some 3-alkylidene-2-naphthalenol derivatives having an alkyl substituent at C_9 was described. Replacement of this substituent by a phenyl group causes a rather radical change in the photochemical behaviour of the thus obtained 3-phenylmethylene-2-naphthalenol derivatives. In first instance fast E-Z isomerization around the exocyclic double bond was observed upon irradiation of 4 in either n-hexane or acetonitrile, which again led to the formation of an approximately 50:50 mixture of 4 and 5. In contradistinction to compounds 1 and 2 no photochemical [1,3]-OH shift was observed upon further irradiation of this mixture. Instead the clean formation of 6 was perceptible (see Figure 3).

In compounds 4 and 5 two chromophoric phenyl groups are present whereas it is to be expected that the presence of just one phenylmethylene fragment will suffice in order to initiate the photochemical reactions of the thus obtained cyclohexanol derivatives. Indeed the same reactions as in the case of compound 4 took place upon irradiation of (E)-2-phenylmethylene-cyclohexanol 7a in either n-hexane or acetonitrile (see Figure 4).

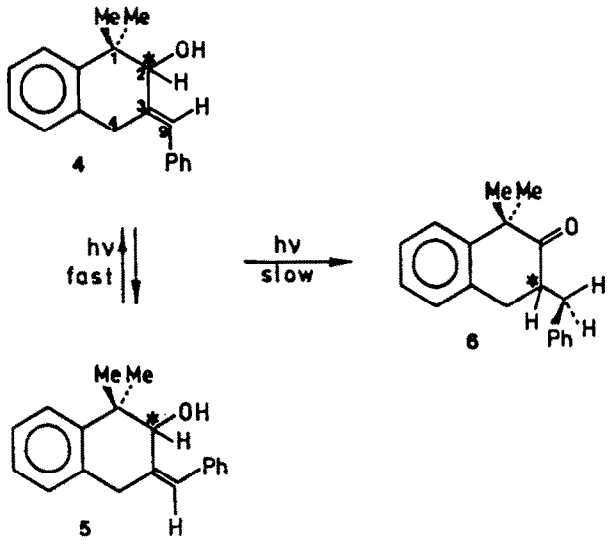


Figure 3. Photochemistry of compound 4 upon irradiation in either n-hexane or acetonitrile.

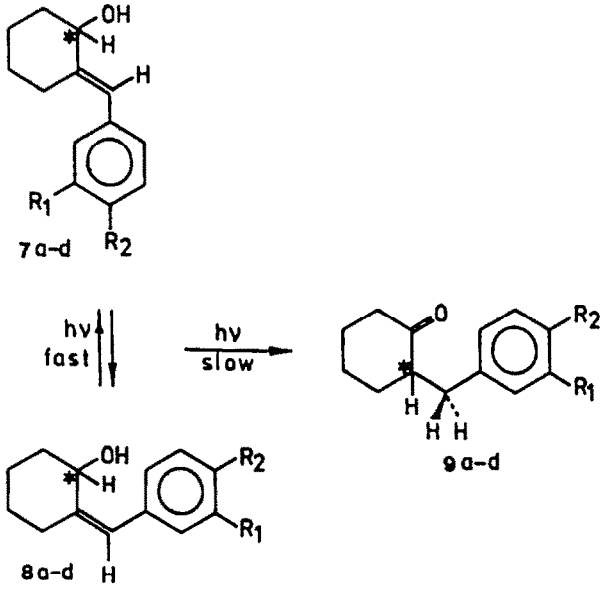
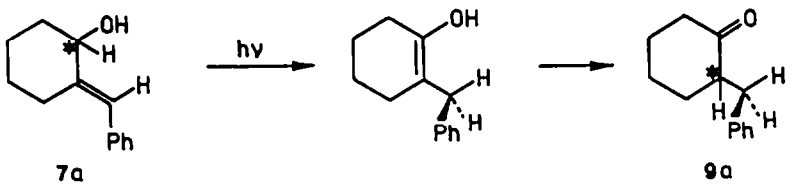


Figure 4. Photochemistry of compounds 7a (R_1=H, R_2=H), 7b (R_1=H, R_2=Cl), 7c (R_1=H, R_2=F) and 7d (R_1=OMe, R_2=H) upon irradiation in either n-hexane or acetonitrile.

Formation of the products 6 and 9a is initiated by a photochemical [1,3]-H shift in either 4,5 or 7a,8a. This shift will be followed by keto-enol tautomerism of the resulting enol, as indicated in Figure 5 for the cyclohexanol derivative 7a.



7a 9a

Figure 5. Formation of photoproducts upon irradiation of 7a.

Thus a clear directive effect of the substituents at the exocyclic double bond is perceptible. This directive effect can be well explained using the concept of sudden polarization. Excitation of either 4,5 or 7a,8a will again be followed by a 90° rotation around the exocyclic double bond, leading to the formation of a negatively charged central carbon atom and a positively charged terminal carbon atom[11]. In case of a phenyl substituent at this carbon atom, the positive charge will be partially delocalized by resonance over the electron-donating phenyl group. This delocalization decreases the polar character of the terminal carbon atom of the exocyclic double bond, thus lowering the driving force for migration of the partially negatively charged hydroxyl group. Hence, an increase of the activation energy of the [1,3]-OH shift in these compounds is expected (i.e. compared to the case of an alkyl substituent at C_9 like in compounds 1 and 2). We previously calculated the activation energy of the planar [1,3]-OH shift in 2-propenol to be 17 kcal/mol, whereas comparable calculations on the photochemical [1,3]-H shift in propene revealed an activation energy of 35.5 kcal/mol. Apparently, upon replacing the alkyl substituent at the terminal carbon atom by a phenyl substituent, the activation energy of the [1,3]-OH shift becomes higher than the energy required for the corresponding photochemical [1,3]-H shift. Moreover this latter shift will hardly be affected by the aforementioned delocalization of the positive charge at the terminal carbon atom.

Further evidence in favour of the sudden polarization model was obtained upon irradiation of 7a in methanol. Irradiation of 7a in methanol led, apart from fast E-Z isomerization, to formation of the methyl ether 10a. This product arises from the addition of methanol to the excited double bond of either 7a or 8a (see Figure 6).

The first conclusion that can be drawn from this experiment is that apparently the addition of methanol is energetically more feasible than the [1,3]-H shift since formation of 9a was not observed. Besides this the formation of the methanol addition product clearly supports the supposed polar character of the singlet excited state of 7a, 8a.

As stated before[11] it is the strong electronegative character of the hydroxyl group which invokes the observed charge separation in the excited exocyclic double bond. In case of a phenyl substituent at the terminal carbon atom, the hereby formed positive charge is stabilized by resonance over the phenyl group. It is to be expected that this latter effect will be drastically diminished by the introduction of electron-withdrawing substituents at the phenyl group. Nevertheless, as indicated in Figure 4, irradiation of the compounds having either a

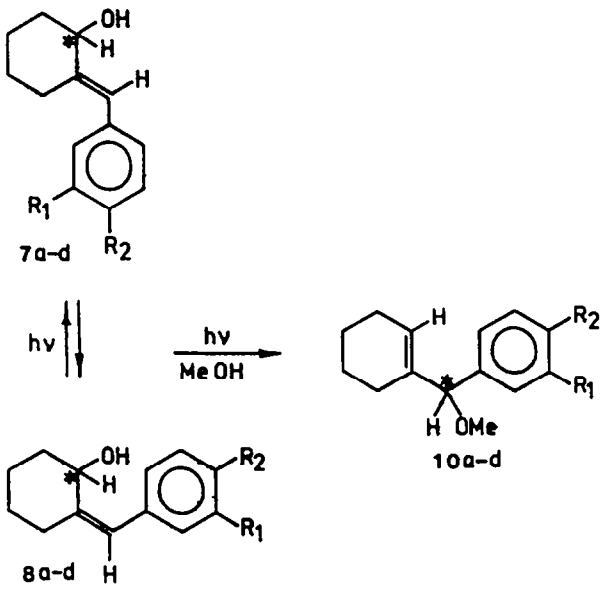


Figure 6. Photochemistry of compounds 7a (R_1=H, R_2=H), 7b (R_1=H, R_2=Cl), 7c (R_1=H, R_2=F) and 7d (R_1=OMe, R_2=H) upon irradiation in methanol.

p-Cl (7b), p-F (7c), or a m-OMe (7c) substituent as the electron-withdrawing group did not affect their photochemical behaviour compared to the unsubstituted situation (7a). Clearly the influence of the strong electronegative hydroxyl group is stronger than the opposite effect of electron-withdrawing substituents at the terminus of the allylic fragment.

Upon application of the strong electron-withdrawing p-CN group (7e), the situation changed drastically. Upon irradiation of 7e in either n-hexane or methanol only fast E-Z isomerization was observed, leading to formation of a 50:50 mixture of 7e and the corresponding Z-isomer 8e; despite prolonged irradiation no further photoproducts could be detected. From this observation it becomes clear that in this specific case the influence of the phenyl substituent exceeds the influence of the hydroxyl group. Hence a negative charge, partially delocalized by resonance over the electron-withdrawing p-cyanophenyl group at the allylic terminus is formed. This will preclude both the addition of methanol and the [1,3]-H shift. This latter effect is in accord with ground-state analogy where hydrogen shifts to a cationic centre are common, but those to an anionic centre are rare[5].

Another interesting feature is the observation that in case of a [1,3]-H shift it is always the hydrogen attached to the carbon atom bearing the hydroxy functionality that displays the shift, whereas especially in case of compound 4 a [1,3]-H shift of the C_4-protons is quite feasible since this would lead to formation of a C_3-C_4 double bond conjugated to the endocyclic phenyl group. Apparently the presence of the hydroxyl functionality is a prerequisite for the occurrence of a [1,3]-H shift in 4. To test this hypothesis the tertiary alcohol 11 was synthesized. In this compound the presence of the C_9-phenyl group will preclude a [1,3]-OH shift whereas the alternative [1,3]-Me shift is rather unlikely to occur regarding the high activation energy calculated for this reaction (62.5 kcal/mol)[11].

Upon irradiation of 11 in both n-hexane and acetonitrile only fast E-Z isomerization around the exocyclic double bond was observable; no products derived from a migration of the C_4-hydrogens could be detected (see Figure 7).

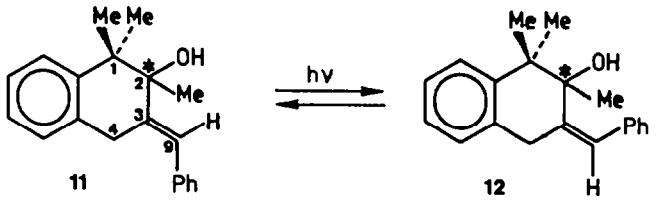


Figure 7. Photochemistry of compound 11 upon irradiation in n-hexane or acetonitrile.

The results depicted in this paragraph once again demonstrate the unique properties of the compounds studied. The presence of a subtile interplay between the various factors govering the course of the photochemical reactions of the compounds studied is clearly shown. First of all a chromophoric group is needed in order to initiate the photochemical reactions. Thereupon in the case of acyclic alkenes a 90°-twist of the excited double bond will take place, accompanied by a charge separation in the orthogonal situation. At this point both the solvent applied and the substituents at the excited double bond will have a profound and directive influence on the subsequently occuring [1,3] sigmatropic shift.

Experimental Section

Synthesis of Reactants of Interest

For the preparation of 3,4-dihydro-1,1,4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenol 1 the same reaction route was used as for the synthesis of the corresponding 4-ethyl-1,1,4-trimethyl-2(1H)-naphthalenol derivatives previously described by us[1,13,14]. A Z-configuration of the exocyclic double bond could be deduced from ^{1}H NMR Eu(fod)$_3$ shift experiments[1]. 3,4-Dihydro-1,1-dimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenol 4 was synthesized starting from 3,4-dihydro-2(1H)-naphthalenone. Methylation of this compound, using a twofold excess of methyliodide, was followed by a base catalyzed aldol condensation with benzaldehyde. This reaction is known to yield an E-configuration around the exocyclic double bond of the thus formed α,β-unsaturated ketone[15]. Addition of the grignard reagens MeMgI to this ketone yielded the tertiary alcohol 11 whereas upon LiAlH$_4$-reduction 4 was obtained in almost quantitative yield. All 2-(phenylmethylene)-cyclohexanol derivatives were prepared by either LiAlH$_4$- or NaBH$_4$-reduction of the α,β-unsaturated ketones obtained by base catalyzed aldol condensation of cyclohexanone with the corresponding benzaldehyde derivatives. As mentioned before this reaction is known to yield an E-configuration around the exocyclic double bond.

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. This enabled an unambiguous structural assignment of all products formed upon E-Z-isomerization, methanol-addition and [1,3] migration of the hydroxyl group. Comparison of the relative positions and multiplicities of the ^{1}H- and ^{13}C-NMR resonances of the products derived from a photochemical [1,3]-H shift and subsequent keto-enol tautomerism left two possibilities regarding the location of the carbonyl group i.e. based upon these data either the presence of a cyclohexyl-phenyl-ketone or a 2-benzyl-cyclohexanone derivative could be deduced. Upon comparison of the ^{1}H- and ^{13}C-NMR spectra of the photoproducts with

the spectra of authentic samples of the corresponding cyclohexyl-ketones, the photoproducts could unambiguously be identified as 2-benzyl-cyclohexanone derivatives. Similarly, the structure of the product derived from a photochemical [1,3]-H shift upon irradiation of 4 could unambiguously be assigned.

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. 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.

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 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. Products were separated by column chromatography (silica gel, type 60 Merck, or silica Woelm as stationary phase), generally using n-hexane-ether 9:1 (v/v) as eluent.

3,4-Dihydro-1,1,4,4-tetramethyl-2(1H)-naphthalenone.
This compound was prepared according to a somewhat modified procedure described by Bruson and co-workers[14]. To a stirred solution of 200 g (1.41 mol) of 2,2,5,5-tetramethyl-3(2H)-furanone in 750 mL of anhydrous benzene was added gradually anhydrous, powdered $AlCl_3$ (283 g, 2.12 mol) while maintaining the temperature between 40 and 50 °C by external cooling. The solution was then heated at reflux for 1h, cooled and poured into one liter of ice and water containing 175 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 5:1 (v/v)) afforded 115.3 g (41%) of 3,4-dihydro-1,1,4,4-tetramethyl-2(1H)-naphthalenone. ^1H NMR ($CDCl_3$) δ 1.17 (s,6H), 1.32 (s,6H), 2.48 (s,2H), 6.87-7.35 (m,4H).

1,4-Dihydro-1,1,4,4-tetramethyl-2,3-naphthalenedione.
To a solution of 115.3 g (0.57 mol) of 3,4-dihydro-1,1,4,4-tetramethyl-2(1H)-naphthalenone in 250 mL of glacial acetic acid was added 72 g (0.60 mol) SeO_2. The mixture was heated at reflux for 3h. The cooled solution was thoroughly filtered and the solvent removed in vacuo. The residu was dissolved in 250 mL of ether, washed with water, a saturated $NaHCO_3$-solution and again with water. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. This afforded 115 g (92%) of 1,4-dihydro-1,1,4,4-tetramethyl-2,3-naphthalenedione. ^1H NMR ($CDCl_3$) δ 1.14 (s,6H), 1.22 (s,6H), 7.00-7.33 (m,4H); ^{13}C NMR ($CDCl_3$) δ 204.47 (s), 140.54 (s), 128.35 (d), 126.41 (d), 51.61 (s), 27.10 (q).

3,4-Dihydro-1,1,4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenone.
n-Butyllithium (160 mL of a 1.6 M solution in n-hexane, 0.26 mol) was added dropwise to a stirred suspension of 88.6 g (0.24 mol) (ethyl)triphenylphosphonium bromide in 200 mL of anhydrous ether. The dark red coloured mixture was then stirred for 2h at room temperature. At the end of this period 38.3 g (0.18 mol) of 1,4-dihydro-1,1,4,4-tetramethyl-2,3-naphthalenedione 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 column chromatography using n-hexane-ether 85:15 (v/v) as eluent. Thus 9.8 g (24%) of 3,4-dihydro-1,1,4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenone was isolated. The corresponding E-isomer could not be detected as a byproduct. ^1H NMR ($CDCl_3$) δ 1.30 (s,6H), 1.36 (s,6H), 1.64 (d,3H), 5.55 (q,1H), 6.81-7.23 (m,4H); ^{13}C NMR ($CDCl_3$) δ 209.77 (s), 146.51 (s), 144.39 (s), 143.59 (s), 130.25 (d), 128.30 (d,2x), 125.12 (d), 124.42 (d), 50.29 (s), 42.86 (s), 30.54 (q,2x), 28.82 (q,2x), 15.83 (q).

3,4-Dihydro-1,1,4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenol (1).
To a stirred suspension of 2.5 g (66 mmol) of $LiAlH_4$ in 150 mL of anhydrous ether was added dropwise, at 0 °C, a solution of 15 g (65.2 mmol) of 3,4-dihydro- 1,1, 4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenone in 100 mL ether. After 30 min. additional stirring the reaction mixture was allowed to warm to room temperature. After addition of respectively 5 mL of water, 5 mL of a 5 N NaOH solution and 30 mL of water, filtration, separation of the organic layer and removal of the solvent afforded 14.5 g (96%) of 1. ^1H NMR ($CDCl_3$) δ .90 (s,3H), 1.29 (s,3H), 1.39 (s,3H), 1.41 (s,3H), 1.65 (d,3H), 4.34 (s,1H), 5.60 (q,1H), 6.80-7.21 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 146.03 (s), 145.12 (s), 142.19 (s), 128.08 (d), 127.43 (d), 127.08 (d), 126.60 (d), 122.01 (d), 75.32 (d), 40.48 (s), 39.74 (s), 37.48 (q), 34.01 (q), 31.07 (q), 26.70 (q), 14.00 (q). UV (EtOH) λ_{max} 260 nm.

3,4-Dihydro-1,1-dimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenone.
A solution of 2.5 g of sodium hydroxide in 60 mL of water was added with stirring to a mixture of 11 g (0.10 mol) of benzaldehyde and 12 g (0.07 mol) of 3,4-dihydro-1,1-dimethyl-2(1H)-naphthalenone (prepared by alkylation of 3,4-dihydro-2(1H)-naphthalenone[16]) in 200 mL of water at room temperature. The mixture was stirred overnight at room temperature, and extracted with two 300-mL portions of ether. After removal of the solvent the crude 3,4-dihydro-1,1-dimethyl-3-(hydroxyphenylmethyl)-2(1H)-naphthalenone was dissolved in 150 mL of 96% ethanol, acidified with 20 mL of concentrated hydrochloric acid and heated at 50° for 15 minutes. 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 11.4 g (63%) of 3,4-dihydro-1,1-dimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenone. ^1H NMR ($CDCl_3$) δ 1.48 (s,6H), 4.13 (m,2H), 6.83-7.56 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 202.62 (s), 142.43 (s), 137.37 (s), 136.23 (s), 134.54 (s), 131.51 (d), 131.10 (d), 129.56 (d,2x), 129.28 (d), 129.01 (d, 2x), 128.07 (d), 127.60 (d), 125.64 (d), 48.03 (s), 33.80 (t), 25.47 (q,2x).

3,4-Dihydro-1,1-dimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenol (4).
The same procedure was used as for the $LiAlH_4$-reduction of 3,4-dihydro-1,1,4,4-tetramethyl-(Z)-3-ethylidene-2(1H)-naphthalenone. Starting from 11.4 g (0.04 mol) of 3,4-dihydro-1,1-dimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenone, 11.1 g

(97%) of 4 was obtained. ^{1}H NMR ($CDCl_3$) δ 1.23 (s,3H), 1.40 (s,3H), 3.86 (m,2H), 4.08 (s,1H), 6.53 (s,1H), 6.98-7.39 (m,9H); ^{13}C NMR ($CDCl_3$) δ 143.81 (s), 138.46 (s), 137.50 (s), 133.65 (s), 129.96 (d), 129.48 (d), 129.14 (d), 128.66 (d,2x), 127.34 (d), 126.68 (d), 126.41 (d,2x), 125.53 (d), 82.32 (d), 41.50 (s), 32.66 (t), 30.41 (q), 25.91 (q). UV (EtOH) λ_{max} 275 nm.

(E)-2-(Phenylmethylene)-cyclohexanol (7a)[17].
A solution of 2 g of sodium hydroxide in 50 mL of water was added with stirring to a mixture of 5 g (0.05 mol) of benzaldehyde and 14 g (0.14 mol) of cyclohexanone in 200 mL of water at room temperature. The mixture was stirred overnight at room temperature. The resulting precipitate was filtered with suction and washed thoroughly with water. The crude 2-(hydroxyphenylmethyl)-cyclohexanone was dissolved in 150 mL of 96% ethanol, acidified with 20 mL of concentrated hydrochloric acid and heated at 50° for 15 minutes. Cooling in ice gave 7.5 g of crude crystalline material which was recrystallized from ethanol to yield 6.5 g (74%) of (E)-2-(phenylmethylene)-cyclohexanone. Reduction was achieved by adding dropwise, at 0 °C, a solution of 6.5 g (34.9 mmol) of this ketone in 35 mL of anhydrous ether to a stirred solution of 1.35 g (35.64 mmol) of $LiAlH_4$ in 100 mL of anhydrous ether. After 30 min. additional stirring the reaction mixture was allowed to warm to room temperature. Addition of respectively 3 mL of water, 3 mL of a 5N NaOH solution and 20 mL of water, filtration, separation of the organic layer and removal of the solvent afforded 6.5 g (99%) of 7a. ^{1}H NMR ($CDCl_3$) δ 1.25-2.92 (m,8H), 4.14 (m,1H), 6.47 (s,1H), 6.97-7.26 (m,5H); ^{13}C NMR ($CDCl_3$) δ 144.95 (s), 138.42 (s), 129.52 (d, 2x), 128.64 (d,2x), 126.69 (d), 121.36 (d), 74.04 (d), 37.17 (t), 28.00 (t), 27.66 (t), 23.95 (t). UV (EtOH) λ_{max} 260 nm.

(E)-2-[(4-Chlorophenyl)methylene]-cyclohexanol (7b).
The same procedure was used as for the synthesis of 7a except for the fact that $NaBH_4$ was used as the reducing agent: to a stirred solution of 5 g (22.7 mmol) of (E)-2-[(4-chlorophenyl)methylene]-cyclohexanone in 50 mL of 96% ethanol and 3 mL of 0.5 N sodium hydroxide, was added in small portions, whilst stirring, 0.4 g (10.7 mmol) of $NaBH_4$ at such a rate that the temperature of the solution was maintained at 18-25 °C. After completion of the addition stirring was continued for one hour. Removal of the ethanol, extraction with ether, drying over $MgSO_4$ and removal of solvent left 4.5 g (89%) of 7b. ^{1}H NMR ($CDCl_3$) δ 1.15-2.92 (m,8H), 4.20 (m,1H), 6.49 (s,1H), 6.85-7.27 (m,4H); ^{13}C NMR ($CDCl_3$) δ 145.87 (s), 136.97 (s), 132.51 (s), 130.83 (d,2x), 128.88 (d,2x), 120.18 (d), 74.08 (d), 37.34 (t), 28.04 (t), 27.83 (t), 24.13 (t). UV (EtOH) λ_{max} 270 nm.

(E)-2-[(4-Fluorophenyl)methylene]-cyclohexanol (7c).
Using the same procedure as for the preparation of 7b, 6.3 g of 7c was obtained with an overall yield of 68%. ^{1}H NMR ($CDCl_3$) δ 1.18-2.91 (m,8H), 4.17 (m,1H), 6.57 (s,1H), 6.83-7.40 (m,4H); ^{13}C NMR ($CDCl_3$) δ 162.06 (d,J_{C-F}=234 Hz), 145.22 (s), 134.64 (s), 131.25 (d,2x), 120.34 (d), 115.58 (dd,2x,J_{C-F}=21 Hz), 74.12 (d), 37.39 (t), 28.12 (t), 27.85 (t), 24.25 (t). UV (EtOH) λ_{max} 275 nm.

(E)-2-[(3-Methoxyphenyl)methylene]-cyclohexanol (7d).
Exactly the same procedure was followed as for the synthesis of 7a. Starting from 20 g (0.20 mol) of cyclohexanone and 9.9 g (0.07 mol) of 3-methoxy-benzaldehyde, 8.8 g (55%) of 7d was obtained. ^{1}H NMR ($CDCl_3$) δ 1.16-2.93 (m,8H), 3.63 (s,3H), 4.09 (m,1H), 6.42 (s,1H), 6.59-7.14 (m,4H); ^{13}C NMR ($CDCl_3$) δ 160.26 (s), 145.57 (s), 140.16 (s), 129.87 (d), 122.36 (d), 121.33 (d), 115.43 (d), 112.50 (d), 74.31 (d), 55.87 (q), 37.43 (t), 28.27 (t), 28.08 (t), 24.23 (t). UV (EtOH) λ_{max} 265 nm.

(E)-2-[(4-Cyanophenyl)methylene]-cyclohexanol (7e).
The same procedure was used as for the synthesis of 7b. Thus 5.2 g (overall yield 45%) of 7e was obtained. ^{1}H NMR ($CDCl_3$) δ 1.01-2.80 (m,8H), 4.22 (m,1H), 6.53 (s,1H), 7.26-7.63 (m,4H); ^{13}C NMR ($CDCl_3$) δ 148.35 (s), 143.59 (s), 132.26 (d, 2x), 129.19 (d,2x), 119.50 (s), 119.18 (d), 109.42 (s), 73.38 (d), 37.26 (t), 27.94 (t), 27.82 (t), 24.12 (t). UV (EtOH) λ_{max} 275 nm.

3,4-Dihydro-1,1,2-trimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenol (11).
To a stirred suspension of 103.1 g (0.62 mol) of $MeMgI$ in 450 mL of anhydrous ether was added dropwise, at 0 °C, a solution of 9.5 g (36.3 mmol) of 3,4-dihydro-1,1-dimethyl-(E)-3-(phenylmethylene)-2(1H)-naphthalenone in 50 mL ether. After 1h of additional stirring at 30 °C the reaction mixture was poured very slowly into a mixture of 8.25 g (0.16 mol) of NH_4Cl and 500 g of ice. An extra amount of ether was added, the organic layer was separated and the solvent removed. Column chromatography (silica 60, chloroform-ether 3:1 (v/v)) afforded 2.3 g (21%) of 11. ^{1}H NMR ($CDCl_3$) δ 1.14 (s,3H), 1.26 (s,3H), 1.40 (s,3H), 3.87 (AB-q, A 3.72, B 4.02, J_{AB}=18.0 Hz,2H), 6.80 (s,1H), 6.85-7.51 (m,9H); ^{13}C NMR ($CDCl_3$) δ 146.04 (s), 143.37 (s), 138.78 (s), 134.01 (s), 129.91 (d,2x), 129.17 (d), 129.04 (d, 2x), 128.46 (d), 127.12 (d), 126.73 (d), 126.39 (d), 122.28 (d), 77.50 (s), 43.97 (s), 33.55 (t), 28.19 (q), 24.93 (q), 22.84 (q). UV (EtOH) λ_{max} 270 nm.

Spectral Data for the Photoproducts

2; ^{1}H NMR ($CDCl_3$) δ 1.03 (s,3H), 1.28 (s,3H), 1.40 (s,3H), 1.49 (s,3H), 1.73 (d,3H), 3.64 (s,1H), 5.37 (q,1H), 6.78-7.23 (m,4H); ^{13}C NMR ($CDCl_3$) δ 146.92 (s), 146.05 (s), 142.30 (s), 128.89 (d), 128.83 (d), 127.59 (d), 126.84 (d), 124.95 (d), 75.45 (d), 40.54 (s), 39.80 (s), 35.39 (q), 33.26 (q), 32.32 (q), 26.56 (q), 16.59 (q).

3; ^{1}H NMR ($CDCl_3$) δ 1.35 (s,12H), 1.41 (d,3H), 3.75 (q,1H), 5.63 (s,1H), 6.91-7.27 (m,4H); ^{13}C NMR ($CDCl_3$) δ 144.72 (s), 142.96 (s), 139.67 (s), 128.49 (d), 128.04 (d), 127.36 (d), 126.89 (d), 126.15 (d), 73.51 (d), 44.06 (s), 41.58 (s), 32.36 (q), 30.22 (q), 26.38 (q).

5; ^{1}H NMR ($CDCl_3$) δ .99 (s,3H), 1.43 (s,3H), 3.80 (m,2H), 4.46 (s,1H), 6.62 (s, 1H), 6.93-7.42 (m,9H); ^{13}C NMR ($CDCl_3$) δ 143.05 (s), 137.92 (s), 137.22 (s), 134.39 (s), 129.87 (d), 129.68 (d), 129.03 (d,2x), 128.86 (d), 128.36 (d, 2x), 128.13 (d), 127.94 (d), 126.56 (d), 75.51 (d), 41.72 (s), 35.84 (t), 31.16 (q), 26.08 (q).

6; ^{1}H NMR ($CDCl_3$) δ 1.28 (s,3H), 1.31 (s,3H), 2.43-3.63 (m,5H), 6.75-7.43 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 214.69 (s), 144.32 (s), 140.41 (s), 135.01 (s), 129.79 (d), 129.08 (d,2x), 128.85 (d,2x), 127.73 (d), 127.33 (d), 126.99 (d), 126.75 (d), 48.46 (s), 48.06 (t), 36.26 (t), 34.71 (d), 28.91 (q), 27.43 (q).

8a; ^{1}H NMR ($CDCl_3$) δ 1.20-2.94 (m,8H), 4.78 (m,1H), 6.26 (s,1H), 6.93-7.24 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 143.91 (s), 138.05 (s), 129.37 (d, 2x), 128.03 (d, 2x), 125.64 (d), 121.60 (d), 66.39 (d), 35.11 (t), 33.29 (t), 28.91 (t), 21.03 (t).

9a; ^{1}H NMR ($CDCl_3$) δ 1.20-3.31 (m,11H), 6.85-7.15 (m,5H); ^{13}C NMR ($CDCl_3$) δ 211.98 (s), 140.81 (s), 129.69 (d,2x), 129.32 (d,2x), 126.72 (d), 53.20 (d), 42.96 (t), 36.37 (t), 34.30 (t), 29.08 (t), 26.03 (t).

10a; ^{1}H NMR ($CDCl_3$) δ 1.19-2.65 (m,8H), 3.18 (s,3H), 4.32 (s,1H), 5.81 (m,1H), 6.90-7.16 (m,5H); ^{13}C NMR ($CDCl_3$) δ 141.73 (s), 137.80 (s), 129.23 (d,2x), 128.45 (d,2x), 127.34 (d), 124.66 (d), 83.37 (d), 55.93 (q), 28.38 (t), 27.87 (t), 26.19 (t), 22.29 (t).

8b; ^{1}H NMR ($CDCl_3$) δ 1.22-3.00 (m,8H), 4.73 (m,1H), 6.33 (s,1H), 6.90-7.25 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 144.46 (s), 136.08 (s), 133.62 (s), 130.91 (d,2x), 129.43 (d,2x), 124.51 (d), 66.48 (d), 35.62 (t), 33.68 (t), 29.13 (t), 21.53 (t).

9b; ^{1}H NMR ($CDCl_3$) δ 1.18-3.20 (m,11H), 6.84-7.24 (m,4H); ^{13}C NMR ($CDCl_3$) δ 212.29 (s), 138.99 (s), 134.76 (s), 130.78 (d,2x), 128.48 (d,2x), 53.16 (d), 42.91 (t), 35.75 (t), 34.34 (t), 28.91 (t), 26.03 (t).

10b; ^{1}H NMR ($CDCl_3$) δ 1.11-2.96 (m,8H), 3.29 (s,3H), 4.55 (s,1H), 5.93 (m,1H), 6.79-7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 143.16 (s), 138.69 (s), 131.96 (s), 130.23 (d,2x), 128.55 (d,2x), 123.28 (d), 81.06 (d), 56.02 (q), 27.78 (t), 26.39 (t), 24.21 (t), 23.64 (t).

8c; ^{1}H NMR ($CDCl_3$) δ 1.20-2.93 (m,8H), 4.68 (m,1H), 6.40 (s,1H), 6.91-7.39 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 162.66 (d,J_{C-F}=246 Hz), 143.91 (s), 134.14 (s), 131.55 (d,2x), 125.16 (d), 115.72 (dd,2x,J_{C-F}=20 Hz), 66.78 (d), 35.33 (t), 33.43 (t), 28.97 (t), 21.23 (t).

9c; ^{1}H NMR ($CDCl_3$) δ 1.21-3.33 (m,11H), 6.89-7.42 (m,4H); ^{13}C NMR ($CDCl_3$) δ 213.58 (s), 163.15 (d,J_{C-F}=240 Hz), 139.68 (s), 131.01 (d,2x), 116.13 (dd, 2x,J_{C-F}=22 Hz), 54.56 (d), 42.44 (t), 35.82 (t), 33.62 (t), 29.35 (t), 26.37 (t).

10c; ^{1}H NMR ($CDCl_3$) δ 1.23-2.95 (m,8H), 3.31 (s,3H), 4.38 (s,1H), 6.01 (m,1H), 6.89-7.45 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 162.86 (d,J_{C-F}=243 Hz), 137.68 (s), 132.05 (s), 131.36 (d,2x), 120.17 (d), 116.56 (dd,2x,J_{C-F}=20 Hz), 86.18 (d), 55.85 (q), 31.27 (t), 27.16 (t), 23.73 (t), 22.86 (t).

8d; ^{1}H NMR ($CDCl_3$) δ 1.23-2,89 (m,8H), 3.59 (s,3H), 4.77 (m,1H), 6.20 (s,1H), 6.68-7.16 (m,4H); ^{13}C NMR ($CDCl_3$) δ 160.20 (s), 144.14 (s), 139.47 (s), 129.98 (d), 125.63 (d), 122.15 (d), 115.24 (d), 112.86 (d), 66.50 (d), 55.96 (q), 35.11 (t), 33.29 (t), 28.92 (t), 21.04 (t).

9d; ^{1}H NMR ($CDCl_3$) δ 1.22-3.29 (m,11H), 3.65 (s,3H), 6.54-7.36 (m,4H); ^{13}C NMR ($CDCl_3$) δ 214.21 (s), 160.68 (s), 143.08 (s), 130.27 (d), 122.58 (d), 116.04 (d), 112.24 (d), 58.38 (q), 53.42 (d), 43.18 (t), 36.58 (t), 34.49 (t), 29.06 (t) 26.57 (t).

10d; ^{1}H NMR ($CDCl_3$) δ 1.20-2.24 (m,8H), 3.26 (s,3H), 3.68 (s,3H), 4.40 (s,1H), 5.72 (m,1H), 6.54-7.50 (m,4H); ^{13}C NMR ($CDCl_3$) δ 160.42 (s), 143.63 (s), 138.59 (s), 129.71 (d), 125.94 (d), 119.78 (d), 113.20 (d), 112.93 (d), 88.29 (d), 56.97 (q), 55.77 (q), 26.45 (t), 24.30 (t), 23.42 (t), 23.36 (t).

8e; ^{1}H NMR ($CDCl_3$) δ 1.13-2.75 (m,8H), 4.63 (m,1H), 6.33 (s,1H), 7.22-7.69 (m,4H); ^{13}C NMR ($CDCl_3$) δ 147.06 (s), 142.95 (s), 132.86 (d,2x), 130.27 (d, 2x), 124.06 (d), 119.89 (s), 110.03 (s), 66.14 (d), 36.28 (t), 35.21 (t), 28.67 (t), 20.76 (t).

12; ^{1}H NMR ($CDCl_3$) δ 1.17 (s,3H), 1.30 (s,3H), 1.37 (s,3H), 3.76 (AB-q, A 3.63, B 3.89, J_{AB}=19.0 Hz,2H), 6.61 (s,1H), 6.91-7.47 (m,9H); ^{13}C NMR ($CDCl_3$) δ 146.65 (s), 143.19 (s), 139.46 (s), 134.57 (s), 129.92 (d,2x), 129.76 (d, 2x), 129.12 (d), 128.97 (d), 128.13 (d), 127.22 (d), 126.88 (d), 124.31 (d), 80.02 (s), 45.25 (s), 40.47 (t), 29.62 (q), 25.62 (q), 21.67 (q).

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