group at the central nitrogen atom may quench the fluorescence. This substitution effect on the fluorescence was also appeared in Sm^{3+} complexes.[6]

Conclusions

The Judd-Ofelt intensity parameters Ω_λ ($\lambda = 2$, 4, 6) for Dy^{3+} complexes with terdentate ligands have been determined to demonstrate the sensitivity of these intensity parameters to ligand environment. For Dy^{3+} ion, $U^{(2)}$ matrix elements for most of transitions in an UV-near IR spectral range are very small except only one transition $^6H_{15/2} \rightarrow ^6F_{11/2}$, peaking at 7760 cm^{-1}. It was found that the evaluation of the three intensity parameters running over the full UV-near IR spectral range accompanied large uncertainty in regression analysis. Hence, the five transitions in the near IR spectral range have been considered in this study. Among the three Ω parameters Ω_2 shows the most sensitivity to minor changes in the ligand enviorment. Although $U^{(6)}$ matrix elements for most of the transitions are large, Ω_6 was found to be insensitive to ligand effect. Contrary to Ω_2 and Ω_6 values, the large root-mean-deviations appeared in the Ω_4 parameters and even negative values of Ω_4 was obtained for Dy^{3+}(aquo) and the Dy^{3+} : MIDA solution. It shows that Ω_4 may behave as a fitting parameter. The Ω_2 (complex)/Ω_2 (aquo) ratios were used to discuss the ligand effect according to coordination geometry. The large difference in the ratio was found between $Dy(ODA)_3{}^{3-}$ and $Dy(DPA)_3{}^{3-}$. It could be attributable to differences in electron densities at the central atoms of each ligand. Consequently, pyridyl donor group interacts with the f electrons of Dy^{3+} more than ether oxygen donor group does. Contrary to expectation, the Ω_2 ratio for $Dy(MIDA)_3{}^{3-}$ was found to be equal to that for $Dy(IDA)_3{}^{3-}$.

It suggests that methyl $vs.$ hydrogen substitution at the central nitrogen donor atom of the ligands may not significantly affect their complexation with Dy^{3+} ion.

The ligand effects on complexation with Dy^{3+} ion were also investigated in terms of fluorescencing oscillator strengths for the transitions $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{15/2}$, which are hypersensitive to ligand environment. Similar results were obtained on $Dy(ODA)_3{}^{3-}$ and $Dy(DPA)_3{}^{3-}$. For $Dy(IDA)_3{}^{3-}$ and $Dy(MIDA)_3{}^{3-}$, the fluorescence of Dy^{3+} was much more intensified by coordinating with IDA than with MIDA. It could be attributed to that the substitution of methyl group at the central nitrogen atom quenchs the fluorescence possibly.

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Photochemistry of Conjugated Polyacetylenes: Photoaddition Reactions of 1-Phenyl-1,3,5-hexatriynes to Tetrahydrofuran

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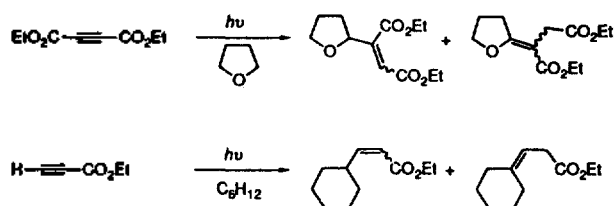
Received August 8, 1992

Photolysis of 1-phenyl-1,3,5-hexatriynes in deaerated tetrahydrofuran gave photoreduction and photoaddition products, while photolysis of 1-phenyl-1,3,5-hexatriynes in deaerated alcoholic solvents (methanol, i-propanol) yielded dark red products, probably oligomers or decomposition products of reactants, as exclusive major products. A plausible mechanism for the reaction is proposed.

Introduction

In photoaddition reactions of alkynes, proton or hydrogen abstraction by alkynes from substrates or solvents is the initial step. Radical photoaddition reaction to acetylenes oc-

curs with cyclic ethers such as tetrahydrofuran[1], and saturated hydrocarbons such as cyclohexane.[2] Although the reaction with tetrahydrofuran does not require a triplet sensitizer, efficient addition of tetrahydropyran or dioxan is only achieved when a ketone is added to promote the formation

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of radicals.

Simple acetylenes such as dec-1-yne or dec-5-yne are photoreduced on irradiation in hydrocarbon solvents.[3] Conjugated diynes, such as dodeca-5,7-diyne, undergo photoreduction at one triple bond and photopolymerization on irradiation in *n*-pentane or alcohols.[4] Photolysis of 1-(1-naphthyl)-1,3-butadiynes in methanol yields protonated polar photoaddition and photoreduction products. The *cis* photoreaction products undergo secondary photocyclization reaction to give phenanthrene derivatives on extended irradiation.[5]
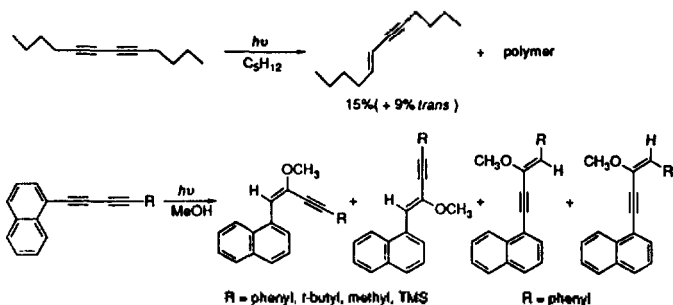
1-Phenyl-1,3,5-heptatriyne (PHT), a conjugated polyacetylene occurring in high concentration in the leaves of the tropical weeds *Bidens pilosa L., Coreopsis lanceolate, Bidens radiata,* and *Bidens ferulaefolia,* has been reported to be phototoxic to a variety of microorganisms through membrane damage.[6] [11] We have previously reported the photoreaction of PHT with undecylenic acid methyl ester (UAME) as a model reaction for PHT phototoxic action *via* the viral membrane damage.[12] When PHT was irradiated with UAME in tetrahydrofuran (THF) solution, the major reaction was addition of PHT to THF, and we investigated the reaction in detail.

Results and Discussion

Photoaddition Reaction of PHT and 1,6-Diphenyl-1,3,5-hexatriyne (DPH) to THF. Irradiation of PHT in deaerated solution of THF at 350 nm yields two photoreduction products (1, 2) and eight 1:1 photoaddition products (3-10). Red products, probably oligomers, were obtained as byproducts in the reaction.
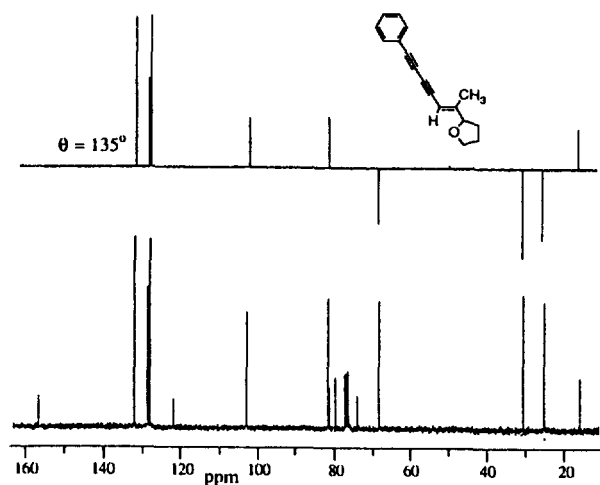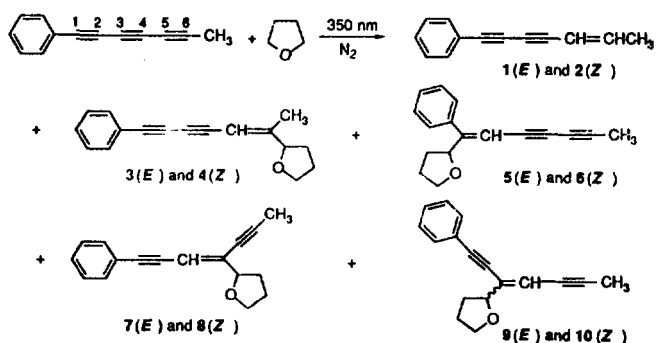

Figure 1. ^{13}C-NMR and DEPT spectra (75 MHz) or *E*-PHT-THF C(5)-C(6) photoadduct.

The structure of the products was determined by various spectral methods. The UV absorption spectra of PHT-THF photoadducts show less fine structure than those of the parent PHT suggesting the collapse of the conjugated triyne units. The shape of the absorption spectrum of the reduction product 1 is strikingly similar to that of *cis*-isomer 2. The UV spectra of the *E*-PHT-THF photoadducts are very similar to those observed in the corresponding *Z*-PHT-THF photoadducts. FT-IR spectra of the photoadducts, 3, and 4, show the acetylenic stretching bands at 2210 and 2133, 2212 and 2133 cm^{-1}, respectively.

The ^{1}H-NMR spectra of the photoadducts 3-10 show similar trends. The resonance of the olefinic proton in *E*-isomers was shifted downfield with respect to that of *Z*-isomers due to the hydrogen bonding between the olefinic proton and oxygen atom in THF ring. The upfield shift of the substituted α-proton of the parent THF ring in *E*-isomers is caused by the anisotropy effect of the vicinal triple bond.

The regiochemical configuration of the isolated photoadducts 3-10 was determined by assuming that the photoaddition reaction occurs on one of the triple bonds of PHT. The chemical shifts of the methyl carbon of the parent PHT remain unchanged in the photoadducts 5-10 indicating that the photoaddition reaction does not occur on the C(5)-C(6) triple bond of PHT. However, it appeared at 16.3 and 17.4 ppm in the photoadducts 3 and 4 indicating the addition to occur on the C(5)-C(6) triple bond. As shown in Figure 1, there is no difficulty in distinguishing the regiochemistry of the olefinic proton and THF ring. The signal at 156.5 ppm which is inactive in distortionless enhanced by polarization transfer (DEPT) experiment is assigned to the olefinic quaternary carbon attached to the THF ring in 3. The carbon at 102.8 ppm is assigned to the olefinic primary carbon. The largest upfield shift of the olefinic primary carbon in the photoadducts relative to the unsubstituted ethylene (123.5 ppm) is produced by the anisotropic effect of the conjugated triple bond. The downfield shift of the quaternary carbon is caused by α-effects of the methyl group and THF ring.

The signals of the conjugated acetylenic carbons of the photoadducts 3-6 appear between 64 and 84 ppm. These upfield shifts of the inner carbons are probably due to the

anisotropic effects of the conjugated triple bonds. In the photoadducts **7-10**, the downfield shifts are caused by the diamagnetic anisotropy effects of the benzene ring and double bond indicating that the photoaddition reactions occurred on C(3) and C(4) carbons in the photoadducts **7-10**. Results from the various spectral analyses of photoadducts **7** and **8** were similar to those of photoadducts **9** and **10** indicating that two pairs have the same regiochemical orientation as the parent PHT and must differ only in the position of the THF ring and the olefinic proton. It has not been possible to assign the regiochemistry due to difficulty in analyzing the small differences in the NMR spectra of these two pairs.

The E and Z photoaddition and reduction products are formed concurrently and are interconvertible on further irradiation of UV light.

Photolysis of 1,6-diphenyl-1,3,5-hexatriyne (DPH) in deaerated THF solution at 350 nm yields four 1:1 DPH-THF photoadducts **11-14** as major products. In the photoreaction, reduction product of DPH was not isolated and red products, probably oligomers or polymers, were obtained as major byproducts. The E and Z photoaddition products are formed concurrently and undergoes rapid interconversion on continued irradiation.


11 (*E*) and 12 (*Z*)   **13 (*E*) and 14 (*Z*)**
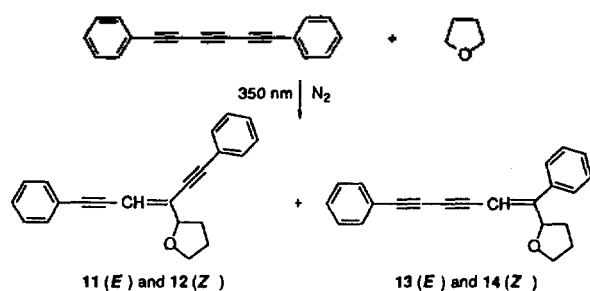
Reaction Mechanism. The lowest singlet excited state of acetylenes has the transoid zwitterionic structure with a HCC angle of about 120°.[16] In more extensively conjugated systems, the charge distribution in the excited state can be determined by evaluating the site and type of photoaddition reaction. It is theoretically possible to have three pairs of regiochemical isomers of 1:1 photoadducts which can be formed on any one of the C(1)-C(2), C(3)-C(4), and C(5)-C(6) triple bonds of the parent triynes (R=methyl). Each pair differs in the position of the THF ring or the olefinic proton. Each of these regiochemical isomers can exist in either E or Z form and give a total of 12 stereochemically distinct compounds. In the photoreaction of triynes with THF, however, only eight 1:1 photoadducts which were formed by the reaction on the C(1)-C(2) **(5, 6)**, C(3)-C(4) **(7-10)**, and C(5)-C(6) **(3, 4)** triple bonds were isolated. The photoadducts **3** and **4** are major products in the photoreaction of PHT with THF, while **5** and **6** are minor products. The photoreduction products **1** and **2** are isolated as minor products. The photoreaction products seem to originate from the triplet excited state, because oxygen quenches the photoreduction and photoaddition almost completely.

Scheme 1 shows a neutral or slightly charge-separated T_1 state. On the basis of the photoadducts, a diradical intermediate partially delocalized all over C(1)-C(6) of the PHT is proposed. In the intermediate, the developed charge is on one of the three sp^2 orbitals (C(1), C(2), C(3) or C(4)),
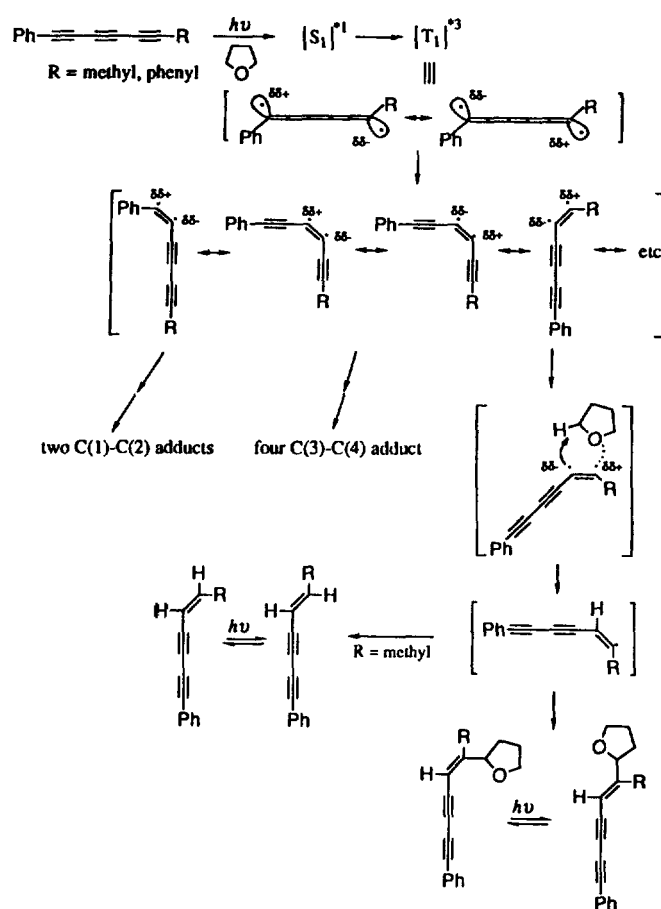
Scheme 1. A plausible mechanism for photoreaction of 1-phenyl-1,3,5-hexatriynes with tetrahydrofuran.

C(5), C(6)) because the C(1) and C(6) carbons have sp^2 hybridization. The charge in this orbital cannot be delocalized over the aromatic ring because the orbital is perpendicular to the aromatic p orbital system; therefore only the inductive effect contributes to the charge separation of the intermediate and structure (b) becomes the major contributor.
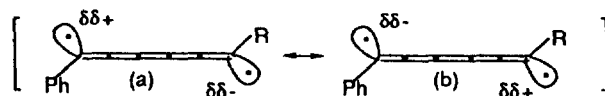
Even though no evidence for charge-transfer complex could be found by inspection of the UV spectrum of PHT in THF, the photoreduction and photoaddition reaction may be produced *via* a charge-transfer complex between PHT and THF, since this seems to be a frequently observed process in related systems.[14-16] Therefore, the vinyl radical intermediates are formed by α-hydrogen abstraction of C(5), C(4), C(3), and C(2) carbons of the parent PHT, different from the photoreactions of 1-aryl-1,3-butadiynes with methanol.

Experimental

Both ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM 300 spectrometer with chemical shifts referenced against the residual proton and carbon of the solvent CDCl$_3$. Distor-

Photochemistry of Conjugated Polyacetylenes

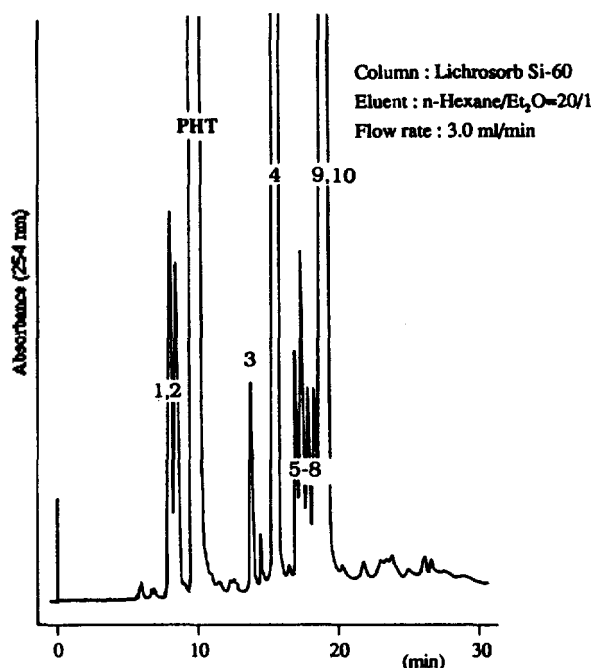*Bull. Korean Chem. Soc., Vol. 13, No. 6, 1992* **657**

Figure 2. HPLC elution profile of the photolysis mixture of 1-phenyl-1,3,5-heptatriyne (PHT) and tetrahydrofuran.

tionless enhanced by polarization transfer (DEPT) experiment was carried out on a Bruker AM 300 spectrometer. Ultraviolet spectra were recorded on a Shimadzu 3100C spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC/MS interface by the electron impact (EI) method. FT-IR spectra were recorded on a Bomem MB-100 spectrometer in NaCl cell. High performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatography equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector.

Materials

1-Phenyl-1,3,5-heptatriyne (PHT) and 1,6-diphenyl-1,3,5-hexatriyne (DPH) were prepared using the method described in ref. 17. Column chromatography was performed by using Kiesel gel 60 (70-230 mesh). Extra pure solvents were used after purification by distillation or standard methods.[18]

Irradiation of PHT in THF

A 4 mM THF solution of PHT was deoxygenated by N_2 bubbling and was irradiated with 350 nm UV light in a Rayonet Photochemical Reactor (Model RPR-208) equipped with RUL 350 nm lamps for 24 h. The resulting photoreaction mixture was concentrated *in vacuo* and subjected to column chromatography using *n*-hexane/diethyl ether (10/1, v/v) as an eluent. The HPLC profile of the photolysis mixture is illustrated in Figure 2. The reduction photoproducts **1** and **2** were isolated by a normal phase HPLC using a Lichrosorb Si-60 column and *n*-hexane eluent. The PHT-THF photoadducts **3-10** were isolated by a normal phase HPLC using *n*-hexane/diethyl ether (20/1, v/v) as an eluent. The mixture of PHT-THF photoadducts **3** and **8** were isolated by a reverse phase HPLC using a Lichrosorb RP-18 column and MeOH/H₂O (20/1, v/v) as an eluent.

Compound 1. UV (*n*-Hexane): λ_{max} 319, 299, 281, 262, 252, 240, 229 nm; MS (70 eV): m/e 166 (M⁺, 28.2), 165 (M⁺ -H, 100); ¹H-NMR (CDCl₃, 300 MHz): δ7.42 (m, 2H), 7.26 (m, 3H), 6.30 (d, quartet, 1H, $J=15.8$ Hz, =CHCH₃), 5.54 (d, quartet, 1H, $J=15.8$ Hz, =CH), 1.77 (d,d, 3H, -CH₃); ¹³C-NMR (CDCl₃, 75 MHz): δ140.3, 132.4, 129.0, 128.4, 122.0, 109.8, 80.8, 80.4, 76.6, 72.9, 18.9 ppm: 0.8% (isolated yield).

Compound 2. UV (*n*-Hexane): λ_{max} 320, 299, 280, 262, 252, 239, 230 nm; MS (70 eV): m/e 166 (M⁺, 69.2), 165 (M⁺ -H, 100), ¹H NMR (CDCl₃, 300 MHz): δ 7.43 (m, 2H), 7.27 (m, 3H), 6.12 (d, quartet, 1H, $J=10.8$ Hz, =CHCH₃), 5.53(d, quartet, 1H, $J=10.8$ Hz, =CH), 1.89 (d, d, 3H, -CH₃); ¹³C-NMR (CDCl₃, 75 MHz): δ 143.0, 132.4, 129.0, 128.4, 122.0, 109.1, 81.7, 78.8, 78.0, 74.0, 16.5 ppm: 0.8% (isolated yield).

Compound 3. UV (MeOH): λ_{max} 318, 299, 283 (sh), 247, 218 nm; IR (NaCl): 3040, 2975, 2867, 2210, 2133, 1621, 1490, 1441, 1364, 1177, 1068, 921, 842, 755, 689 cm⁻¹; MS (70 eV): m/e 236 (M⁺, 31.0), 221 (M⁺-CH₃, 13.2), 178 (M⁺-C₃H₆O, 47.9), 165 (PHT+H, 100); ¹H-NMR (CDCl₃, 300 MHz): δ7.51 (m, 2H), 7.33 (m, 3H), 5.74 (s(broad), 1H, =CH), 4.36 (t(broad), 1H, -CHC₃H₆O), 3.90 (m, 2H), 2.12 (m, 1H), 1.95 (s(broad), 3H, -CH₃), 1.91 (m, 2H), 1.68 (m, 1H); ¹³C-NMR(CDCl₃, 75 MHz): δ156.5, 132.3, 128.9, 128.3, 122.1, 102.8, 81.7, 81.4, 79.8, 77.0, 74.2, 68.7, 31.2, 25.8, 16.3 ppm: 0.5% (isolated yield).

Compound 4. UV (*n*-Hexane): λ_{max} 328, 316, 305, 298, 285, 268 (sh), 257 nm; IR (NaCl): 3060, 2958, 2868, 2212, 2133, 1610, 1490, 1442, 1376, 1320, 1179, 1059, 929, 823, 756, 689 cm⁻¹; MS (70 eV): m/e 236 (M⁺, 45.8), 221 (M⁺-CH₃, 4.9), 178 (M⁺-C₃H₆O, 35.0), 165 (PHT+H, 100); ¹H NMR (CDCl₃, 300 MHz): δ 7.41 (m, 2H), 7.23 (m, 3H), 5.39 (s (broad), 1H, =CH), 4.89 (t(broad), 1H, -CHC₃H₆O), 3.81 (m, 2H), 2.14 (m, 1H), 1.91 (m, 2H), 1.75 (d, 3H, -CH₃), 1.55 (m, 1H); ¹³C-NMR (CDCl₃, 75 MHz): δ 157.7, 132.3, 128.9, 128.3, 122.0, 104.8, 81.8, 79.1, 78.6, 77.4, 74.1, 69.0, 30.8, 26.5, 17.4 ppm: 5.3% (isolated yield).

Compound 5. UV (*n*-Hexane): λ_{max} 289, 279 (sh), 250, 236 nm; MS (70 eV): m/e 236 (M⁺, 28.2), 221 (M⁺-CH₃, 4.9); ¹H-NMR (CDCl₃, 300 MHz): δ 7.33 (m, 2H), 7.23 (m, 3H), 5.65 (d, 1H, =CH), 5.15 (quartet, 1H, -CHC₃H₆O), 3.81 (m, 2H), 2.10 (m, 1H), 1.95 (d, 3H, -CH₃), 1.84 (m, 2H), 1.63 (m, 1H); ¹³C-NMR (CDCl₃, 75 MHz): δ 157.4, 138.8, 128.1, 128.0, 127.8, 108.8, 81.9, 80.7, 79.5, 71.3, 68.8, 63.6, 31.5, 26.4, 4.8 ppm: 0.7% (isolated yield).

Compound 6. NMR spectrum of this photoproduct could not be obtained due to too low isolation yield. However, the compound **6** was compared with the photoisomerization product (*cis*-isomer) of compound **5** by HPLC analysis and confirmed to be *cis*-isomer of compound **5**.

Compound 7. UV (*n*-Hexane): λ_{max} 316, 304 (sh), 297, 287, 250 nm; MS (70 eV): m/e 236 (M⁺, 34.5), 221 (M⁺ -CH₃, 8.4), 178 (M⁺-C₃H₆O, 39.2), 165 (PHT+H, 100); ¹H NMR (CDCl₃, 300 MHz): δ 7.41 (m, 2H), 7.25 (m, 3H), 5.89 (m, 1H, =CH), 4.46 (t(broad), 1H, -CHC₃H₆O), 3.92 (m, 1H), 3.81 (m, 1H), 2.02 (d, 3H, -CH₃), 1.89 (m, 3H); ¹³C-NMR (CDCl₃, 75 MHz): δ 135.1, 132.4, 128.4, 128.3, 123.2, 114.6, 96.7, 93.5, 86.4, 82.2, 80.2, 69.0, 31.8, 25.5, 4.8 ppm: 1.6% (isolated yield).

Compound 8. UV (MeOH): λ_{max} 327, 315, 305, 286, 268, 257, 246, 223, 216 nm; MS (70 eV): m/e 236 (M⁺, 7.5), 221 (M⁺-CH₃, 2.3), 178 (M⁺-C₃H₆O, 20.5), 165 (PHT+H, 100); ¹H-NMR (CDCl₃, 300 MHz): δ 7.35 (m, 2H), 7.23 (m, 3H), 5.92 (s, 1H, =CH), 4.97 (t, 1H, -CHC₃H₆O), 3.96 (m, 1H),

3.82 (m, 1H), 2.12 (m, 1H), 1.98 (s(broad), 3H, -CH₃), 1.89 (m, 3H); ¹³C-NMR (CDCl₃, 75 MHz): δ 137.9, 131.4, 128.4, 128.3, 123.2, 115.0, 98.6, 91.8, 85.7, 77.7, 77.0, 69.2, 31.3, 26.6, 4.7 ppm: 0.6% (isolated yield).

Compound 9. UV (n-Hexane): λ_max 318, 299, 289 (sh), 248, 217 nm; MS (70 eV): m/e 236 (M⁺, 26.8), 221 (M⁺-CH₃, 5.8), 178 (M⁺-C₃H₆O, 7.1), 165 (PHT+H, 100); ¹H-NMR (CDCl₃, 300 MHz): δ 7.38 (m, 2H), 7.23 (m, 3H), 6.04 (d, 1H, =CH), 4.39 (t, d, 1H, -CHC₃H₆O), 3.92 (m, 1H), 3.78 (m, 1H), 2.06 (m, 1H), 2.03 (s, 3H, -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 137.2, 131.7, 128.2, 128.1, 123.6, 112.5, 101.6, 95.1, 87.5, 80.5, 76.6, 69.0, 31.7, 25.4, 4.8 ppm: 1.2% (isolated yield).

Compound 10. UV (n-Hexane): λ_max 316, 298, 288, 272 (sh), 242, 218 nm; MS (70 eV): m/e 236 (M⁺); ¹H-NMR (CDCl₃, 300 MHz): δ 7.36 (m, 2H), 7.27 (m, 3H), 5.86 (d, 1H, =CH), 4.75 (t, d, 1H, -CHC₃H₆O), 3.91 (m, 1H), 3.81 (m, 1H), 1.92 (m, 1H), 1.87 (d, 3H, -CH₃), 1.78 (m, 2H), 1.49 (m, 1H) ppm: 7.2% (isolated yield).

Irradiation of DPH in THF

A 4 mM THF solution of DPH was deoxygenated by N₂ bubbling and was irradiated at 350 nm in a Rayonet Photochemical Reactor for 48 h. The resulting photoreaction mixture was concentrated *in vacuo* and subjected to column chromatography using n-hexane/diethyl ether (9/1, v/v) as an eluent. The DPH-THF photoadducts 11-14 were isolated by a normal phase HPLC using a Lichrosorb Si-60 column and n-hexane/diethyl ether (7/1, v/v) as an eluent.

Compound 11. UV (n-Hexane): λ_max 347 (sh), 323, 258, 247, 217 nm; MS (70 eV): m/e 298 (M⁺, 100), 241 (M⁺-C₃H₅O, 41.3), 226 (DPH, 5.8); ¹H-NMR (CDCl₃, 300 MHz) δ 7.37 (m, 4H), 7.25 (m, 6H), 6.10 (s, 1H, =CH), 5.13 (t, 1H, -CHC₃H₆O), 4.02 (m, 1H), 3.88 (m, 1H), 2.21 (m, 1H), 2.08 (m, 1H), 1.85 (m, 2H); ¹³C-NMR (CDCl₃, 75 MHz): δ 137.5, 131.6, 131.4, 128.6, 128.5, 128.3 (4), 128.2 (2), 123.0 (5), 123.0 (0), 115.9, 99.8, 94.0, 87.8, 85.8, 77.7, 69.4, 31.5, 28.7 ppm.

Compound 12. UV (n-Hexane): λ_max 348, 323, 258, 250 (sh), 218 nm; MS (70 eV): m/e 298 (M⁺, 100), 241 (M⁺-C₃H₅O, 17.9), 227 (DPH+H, 11.7), 226 (DPH, 9.6); ¹H-NMR (CDCl₃, 300 MHz): δ 7.42 (m, 4H), 7.25 (m, 6H), 6.16 (d, 1H, =CH), 4.54 (t,d, 1H,-CHC₃H₆O), 4.01 (m, 1H), 3.85 (m, 1H), 2.17 (m, 1H), 2.07 (m, 1H), 1.91 (m, 2H); ¹³C-NMR (CDCl₃, 75 MHz): δ 136.6, 131.7, 131.6, 128.6 (2), 128.5 (8), 128.4, 128.3, 123.5, 123.0, 98.0, 96.5, 87.6, 86.5, 80.2, 69.1, 31.9, 25.5 ppm.

Compound 13. UV (n-Hexane): λ_max 321, 308, 288, 270 (sh), 258, 230 nm; MS (70 eV): m/e 298 (M⁺, 100), 241 (M⁺-C₃H₅O, 34.9), 226 (DPH, 42.0); ¹H NMR (CDCl₃, 300 MHz): δ 7.38 (m, 4H), 7.26 (m, 6H), 5.76 (s(broad), 1H, =CH), 5.20 (t(broad), 1H, -CHC₃H₆O), 3.93 (m, 1H), 3.83 (m, 1H), 2.15

(m, 1H), 1.88 (m, 3H) ppm.

Compound 14. UV (n-Hexane): λ_max 325, 310, 291 (sh), 273 (sh), 260 nm; MS (70 eV): m/e 298 (M⁺, 100); ¹H NMR (CDCl₃, 300 MHz): δ 7.38 (m, 4H), 7.26 (m, 6H), 5.98 (d, 1H, =CH), 4.80 (t,d, 1H, -CHC₃H₆O), 3.93 (m, 1H), 3.83 (m, 1H), 2.15 (m, 1H), 1.88 (m, 3H) ppm.

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