results from an increase in the separation of the donor and acceptor by ~6 Å. The largest drop in rate occurs when the first proline is added (factor of >100). The separation between the donor and acceptor increased by ~3 Å. This large decrease in rate is attributed to an increase in the outer-sphere reorganizational energy and a decrease in the electronic coupling factor,[19] with the latter predominating. For cases where the distances are fixed during the electron-transfer process, quantitative estimates for the decrease in rate could be obtained. However, because the rate of electron transfer is slow compared to proline isomerization in this study, quantification of the data as a function of distance cannot be done.

When $[(NH_3)_5Os^{II}–]$ is used in place of $[H_2O(NH_3)_4Ru^{III}–]$ as a donor, the driving force for the intramolecular electron-transfer reaction can be increased by about 0.6–0.7 V.[20] This is expected to increase the rate of electron transfer by 5 orders of magnitude ($t_{1/2} < 1$ s).[20] For such a fast reaction the question is whether the intramolecular electron-transfer reaction will take place at the long distance of the fully trans isomer or whether electron transfer will wait for the cis–trans isomerization to occur ($t_{1/2} \sim$ 1–2 min), to bring the donor and acceptor into close proximity. Furthermore, with these fast rates proline oligomers will be rigid spacers, thus allowing quantification of the decrease in rate of electron transfer with distance. The osmium(II)–cobalt(III) proline series is currently being investigated to address these issues.[20]

Acknowledgment. This work was supported by the National Institutes of Health (Grant GM 26324). S.I. is the recipient of a National Institutes of Health Career Development Award (AM 00734) (1980–1985) and a Camille and Henry Dreyfus Teacher–Scholar Award.

Registry No. $[SO_4(NH_3)_4$Ru–(iso-(Pro))–Co$(NH_3)_5](BF_4)_3\cdot HBF_4$, 88510-36-5; $[SO_4(NH_3)_4$Ru–(iso-(Pro)$_2$)–Co$(NH_3)_5](BF_4)_3\cdot HBF_4$, 88524-99-6; $[SO_4(NH_3)_4$Ru–(iso-(Pro)$_3$)–Co$(NH_3)_5](BF_4)_3\cdot HBF_4$, 88525-02-4; $[SO_4(NH_3)_4$Ru–(iso-(Pro)$_4$)–Co$(NH_3)_5](BF_4)_3\cdot HBF_4$, 88525-05-7; $[(NH_3)_5$CoPro$]^{2+}$, 68582-22-9; $[(NH_3)_5$Co(Pro)$_2]^{2+}$, 68582-28-5; $[(NH_3)_5$Co(Pro)$_3]^{2+}$, 88525-06-8; $[(NH_3)_5$Co(Pro)$_4]^{2+}$, 68582-19-4; $[(NH_3)_5$CoPro-iso$]^{2+}$, 88496-37-1; $[(NH_3)_5$Co(Pro)$_2$-iso$]^{2+}$, 88496-39-3; $[(NH_3)_5$Co(Pro)$_3$-iso$]^{2+}$, 88525-07-9; $[(NH_3)_5$Co(Pro)$_4$-iso$]^{2+}$, 88525-08-0.

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Photochemistry of 2-Phenyl-1,2-dihydronaphthalene. A Competition between a Singlet State Di-π-methane Rearrangement and a Ring-Opening Reaction

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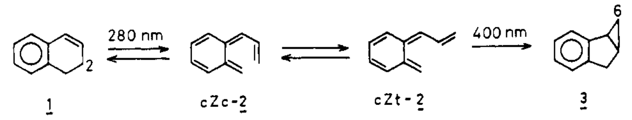
Abstract: Irradiation of 2-phenyl-1,2-dihydronaphthalene (**4**) at 300 nm in hexane leads to three primary photoproducts: *endo*- and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-**5** and *exo*-**5**) and 7,12-dihydrodibenzo[*a,d*]cyclooctatetraene (**6**). Irradiation of labeled **4** (**4**-*3,4*-d_2) showed that **5** arises via a di-π-methane rearrangement as well as via electrocyclic ring opening, single bond rotation, and photocycloaddition. The di-π-methane rearrangement proceeds partly as a triplet reaction, giving both epimers of **5**, but mainly as a stereoselective singlet reaction, giving only *endo*-**5**. The pathway via ring opening and cycloaddition yields *exo*-**5**, which arises from that conformer of **4** having the phenyl group in the pseudoequatorial position (PE-**4**). The other conformer (PA-**4**) yields mainly **6** (Scheme VI) because the ring opening can be followed by an 8π-electrocyclic ring closure. On irradiation of **4** at 254 nm the stereoselectivity of the singlet reactions is less clear, because *endo*-**5** and *exo*-**5** are interconverted. Parallel with the interconversion 2-benzylideneindan (**7**) is formed as a secondary photoproduct under these conditions.

The photochemistry of 1,2-dihydronaphthalenes has been studied for over 10 years. In 1971 Salisbury[1] proposed the reaction mechanism, given in Scheme I for the conversion of the parent compound (**1**) into benzobicyclo[3.1.0]hex-2-ene (**3**). It was based on the observation that a broad spectrum of wavelengths was needed to bring about the conversion. A long-wavelength absorption band, corresponding to the supposed pentaene intermediate (*cZc*-**2**) has actually been observed in low-temperature irradiations of some 1,2-dihydronaphthalene derivatives.[2,3]

We anticipated that 2-phenyl-1,2-dihydronaphthalene (**4**) might be a derivative of **1** of special interest in photochemical studies, because it can also be conceived as a 3-phenylpropene able to undergo a di-π-methane rearrangement. The reaction mechanism of the basic di-π-methane rearrangement is given in Scheme II in terms of intermediate diradical structures.[4] Recently, indications for the existence of such intermediates have been found[5], but concerted reactions of this kind cannot be excluded.

Scheme I



Scheme II

Scheme III

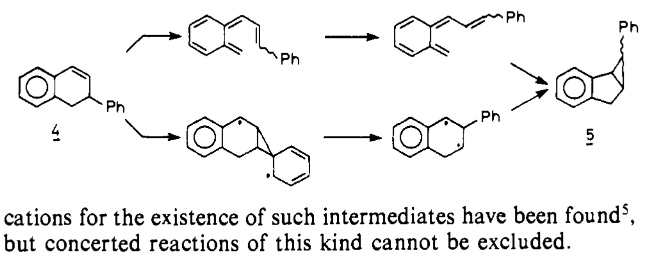


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Table I. Composition (in %) of the Mixture of Photoproducts from 4-*3,4-d*$_2$[a]

	irradiation conditions	6-*6,7-d*$_2$	*exo*-5-*1,5-d*$_2$	*exo*-5-*1,6-d*$_2$	*endo*-5-*1,6-d*$_2$	7-*d*$_2$
A	HPM,[b] quartz, hexane	4	40	<5	27	24
B	HPM, Pyrex, hexane	4	64	<5	27	
C	300 nm, Pyrex, hexane	5	33	12	50	
D	254 nm, quartz, hexane	8	14% *exo*-5-*1,5-d*$_2$ + *exo*-5-1,6-*d*$_2$ 51% *endo*-5-*1,5-d*$_2$ + *endo*-5-*1,6-d*$_2$			27
E	300 nm, Pyrex, acetone			48	52	
F	300 nm, Pyrex, hexane, 1,3-cyclohexadiene (3 × 10^{-3} M)	15	27		58	

[a] Irradiation was done under various conditions and continued until all starting material had disappeared. [b] High pressure mercury lamp (Philips HPK-125). [c] In all experiments *endo-5-1,5-d*$_2$ might have been present, but the amount was always less than 5%.

Application of this scheme to **4** leads to the same photoproduct as should be expected via the pathway of Salisbury, viz., 6-phenylbenzobicyclo[3.1.0]hex-2-ene (**5**) (Scheme III). However, formation of this product via a di-π-methane rearrangement should be accompanied by a net migration of the phenyl substituent from C(2) to C(3). This implies that the pathway of the formation of **5** can be established by introducing a marker at C(2) or C(3) of **4**.

The possible competition between two distinct photoreactions leading to the same product led us to an investigation of the photochemistry of **4** and its 3,4-dideuterio derivative (**4**-*3,4-d*$_2$).

Results

Irradiation of 2-Phenyl-1,2-dihydronaphthalene (4). Irradiation of **4** dissolved in hexane in a quartz tube with a high-pressure mercury lamp (HPM) led to complete disappearance of the starting compound within 3.5 h. Separation of the product mixture by column chromatography on silica gel gave three fractions.

The NMR spectrum of the first fraction revealed the presence of an ArCH=CH—CH$_2$Ar moiety (two broadened doublets and a doublet of triplets) and an ArCH$_2$Ar unit (singlet at 4.03 ppm). Together with the presence of eight aromatic protons and the parent peak in the mass spectrum at *m/e* 206, the data point to 7,12-dihydrodibenzo[*a,d*]cyclooctatetraene (**6**). The structure was confirmed by comparison of the NMR spectrum with those of the known 12-oxa analogue[6] and the 12-methyl derivative.[7]

Identification of the second product as 2-benzylidene indan (**7**) from its NMR spectrum was only tentative, because the spectrum had only a few characteristic features (broad signal at 3.9 and a quintet at 6.6 ppm). The structure was definitely established by an independent synthesis of **7** through irradiation of 2-benzyl-1*H*-indene.[8]

The third fraction was a mixture of *endo*-**5** and *exo*-**5**. Separation of the epimers was rather difficult, but small samples of the pure compounds were obtained by column chromatography on alumina. The compounds were identified by comparison of their NMR spectra with those reported in the literature.[9]

Irradiation of **4** in Pyrex gave *exo*-**5**, *endo*-**5**, and **6** but not **7**. Irradiation of *exo*-**5** as well as *endo*-**5** in hexane at 254 nm and following their photoconversion with NMR revealed interconversion of the epimers and rapid formation of **7** under these conditions (Scheme IV).

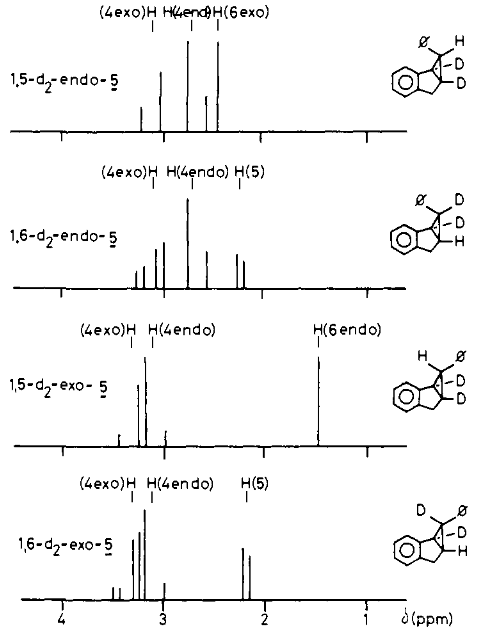
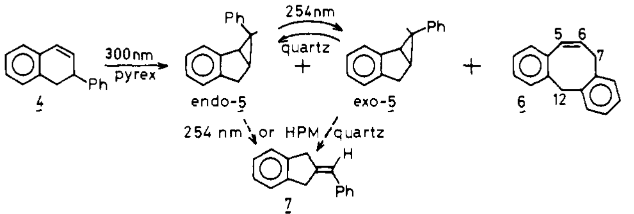


Figure 1. Simulated spectra of *endo*-**5** and *exo*-**5**, deuterated at C(1) and C(5) or C(1) and C(6).

Scheme IV



Irradiation of 3,4-dideuterio-2-phenyl-1,2-dihydronapthalene (4-*3,4-d*$_2$). In an initial experiment **4**-*3,4-d*$_2$ was irradiated in Pyrex in order to prevent interconversion of the endo/exo epimers of the deuterated photoproduct **5**. As expected deuterated **7** was not formed under these conditions. The product **6** arose as its 6,7-dideuterio derivative (**6**-*6,7-d*$_2$) as appeared from the absence of the H(6) signal in the NMR spectrum and the presence of a signal at 3.19 ppm (H(7)) corresponding to only one proton.

In the fraction containing the photoproduct **5** four different species might be present, viz., *endo*-**5**-*1,5-d*$_2$ and *exo*-**5**-*1,5-d*$_2$, formed via the upper route of Scheme III, and *endo*-**5**-*1,6-d*$_2$ and *exo*-**5**-*1,6-d*$_2$, formed via a di-π-methane rearrangement. In order to analyze the composition of the fraction, NMR spectra at 90 MHz were designed for all four species by considering the changes which will occur in the known spectra of *endo*-**5** and *exo*-**5** when deuterium is introduced in the indicated positions and then simulating the spectra (Figure 1). The simulated spectra show that the estimation of the relative concentrations of *endo*-**5**-*1,5-d*$_2$ and *exo*-**5**-*1,5-d*$_2$ in product mixtures can rather well be based on the different positions of H(6).

Estimation of the ratio *endo*-**5**-*1,6-d*$_2$/*exo*-**5**-*1,6-d*$_2$ will be less accurate, because their patterns largely overlap. In the NMR spectrum of the product mixture before separation the signal of the H(7) protons of **6** at 3.19 ppm introduces an additional inaccuracy in the evaluation of the relative concentrations of

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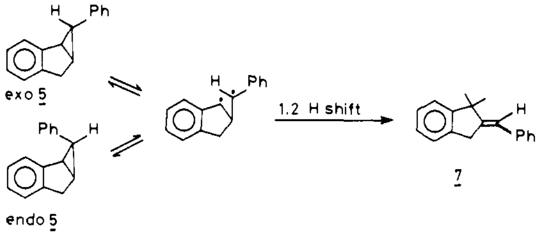
Scheme V



endo-**5**-*1,6*-d_2 and *exo*-**5**-*1,6*-d_2. Comparison of the NMR spectrum of the product fraction containing **5** from **4**-3,4-d_2 with the spectra in Figure I revealed, however, clearly that *exo*-**5**-*1,5*-d_2 and *endo*-**5**-*1,6*-d_2 had been formed as the main products. The amounts of endo-**5**-*1,5*-d_2 and *exo*-**5**-*1,6*-d_2 can not have been more than ca. 5%, based on the total amount of nonpolymeric products.

In Table I results are given of irradiations of **4**-*3,4*-d_2 under varying conditions. The percentages of the photoproducts have been estimated from the NMR spectra of the irradiation mixtures and consequently refer to the total amount of nonpolymeric products. The accuracy of the data is certainly not better than ca. 5%. In some experiments NMR spectra were traced after varying time intervals. It appeared that the product ratios were independent of the irradiation time within the accuracy of the method.

Discussion

Formation of 7. It is clear that **7**, only formed on irradiation at 254 nm, is not a primary photoproduct. It arises from *exo*- or *endo-5* under these conditions via homolytic fission of the C(1)–C(6) bond in **5**, which is also responsible for the interconversion of the epimers of **5**. Its formation must be due to a 1,2-H shift, which has been observed previously in comparable cases[10,11] (Scheme V).

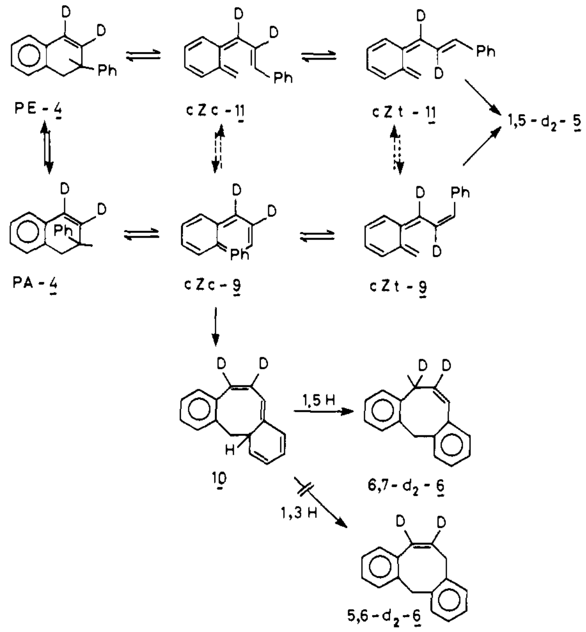
Establishment of the labeling of **7** from its NMR spectrum in experiment A showed that the olefinic proton is still present, whereas the signal at 3.9 ppm is strongly reduced. Apparently, the product is mainly **7**-*1,1*-d_2. this must originate from 1,5-deuterated **5**. Indeed, *exo*-**5**-*1,5*-d_2 is the main, primary photoproduct of **4**-*3,4*-d_2 (see B), when irradiation below 300 nm is exclused without other variations of the experimental conditions.

Formation of 6. The structure of **6** suggests that it is formed via an electrocyclic ring closure of a phenyl-substituted pentaene intermediate, corresponding to *cZc*-**2** and having the phenyl group in the "internal" position (*cZc*-**9**, Scheme VI). The deuterium incorporation in **6**-*6,7*-d_2 shows that the aromaticity, lost in the formation of the ring-closure product (**10**), is restored via a thermal, suprafacial 1,5-H shift rather than through a photochemical 1,3-H shift.

Formation of 5 via the Salisbury Mechanism. The compound **4** occurs in two conformations, and in one of our earlier papers[12] the ground-state conformational equilibrium of the pseudoaxial (PA) and pseudoequatorial (PE) conformers has been studied by using a 500-MHz ^{1}H NMR; at ambient temperature the fraction of PA-**4** (x_{PA}) appeared to be 0.31.

It has been suggested that ground-state conformational populations can control the stereoselectivity of photoreactions.[13,14] According to the Woodward–Hoffmann rules a compound like **4** may undergo two possible modes of conrotatory, electrocyclic ring opening. The more favorable process is that in which the pseudoaxial substitutent at C(2) moves into the "internal" and the pseudoequatorial substituenmt into the "external" position of the resulting pentaene (see Scheme VI).

Scheme VI



Courtot et al.[14] have connected the phenomenon with the principle of least motion;[15] the pseudoequatorial substituent is more or less in the "plane" of **4** and needs only a small displacement to end up in the external position of the conjugated pentaene. According to this principle the product **6** should originate from PA-**4**, whereas **5**-*1,5*-d_2 should mainly arise from PE-**4**, providing no photochemical equilibration of the intermediates (**9** and **11**) occurs. This condition will best be met in irradiations in the presence of a triplet quencher (F). In that experiment the largest percentage of **6** is found, and the ratio **6**-*6,7*-d_2/(**6**-*6,7*-d_2 + **5**-*1,5*-d_2) agrees surprisingly well with the fraction of PA-**4** in the ground-state conformational equilibrium (x_{PA} = 0.31).[12] However, as both products **5**-*1,5*-d_2 and **6**-*6,7*-d_2 are formed by two photochemical steps this agreement might be fortuitous, because it requires besides a coincidence of reaction rates also that the di-π-methane reaction from both PA-**4** and PE-**4** are equally efficient. Moreover, it is not sure that the cis–trans isomerizations of **9** and **11** are quenched for 100% under the experimental conditions used.

A remarkable point is that the 1,5-deuterated product **5**, which must have been formed via the Salisbury mechanism and certainly more via *cZc*-**11** than *cZc*-**9**, is nearly exclusively found as the exo isomer (*exo*-**5**-*1,5*-d_2) in all relevant experiments. This result is only understandable when the last step in the main route to **5**-*1,5*-d_2, viz., the conversion of *cZt*-**11** into *exo*-**5**-*1,5*-d_2, proceeds stereoselectively as a $_{\pi}4_a + _{\pi}2_s$ photocycloaddition. In several studies on the photochemistry of methyl-substituted dihydronaphthalenes[3,16] the stereochemical control of the formation of the benzobicyclo[3.1.0]hex-2-ene derivative could not be determined, because of 1,7-H shifts in the pentaene intermediates, but in two cases[17,18] it was found that the final photocycloaddition step proceeded with complete lack of orbital symmetry control. Fukui and Tanaka[19] argued that these results are covered by the cross-bicyclization concept.

Di-π-methane Rearrangement of 4. Table I shows that in all experiments performed with **4**-*3,4*-d_2 considerable amounts of the

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1,6-dideuterated product **5** are formed, pointing to the occurrence of a di-π-methane rearrangment. In general, this photoreaction is a singlet reaction in acyclic systems as well as in cyclic systems containing an exocyclic double bond, because in such compounds the triplet state is deactivated in a free rotor process.[20] In rigid cyclic systems it can proceed as a triplet reaction.

Indeed, the rigid substrate **4** undergoes the di-π-methane rearrangement in the presence of a triplet sensitizer (E). Under these conditions it is the only photoreaction of **4**, leading to nearly equal amounts of *endo*- and *exo*-5. However, also in the presence of a triplet quencher (F) 1,6-dideuterated **5** is formed. This singlet reaction is apparently a concerted process, because it proceeds quite stereospecifically; only ***endo*-5-*1,6-d*$_2$** is formed. In the absence of a sensitizer or quencher both the singlet and triplet reaction occur; this is especially apparent in experiment C.

The lower yields of the rearrangement product in the experiments A and B are probably due to the presence of long-wavelength irradiation which promotes the photocycloaddition of the pentaene intermediates although it is not indispensable for this reaction (see C). In experiment D the percentages of *endo*- and *exo*-**5** have not been determined separately, because of strong interconversion of the epimers in this experiment.

In conclusion, the investigation demonstrates that the photochemical formation of 6-phenylbenzobicyclo[3.1.0]hex-2-ene occurs simultaneously via two distinct pathways, viz., via an electrocyclic ring opening, single bond rotation, and a final cycloaddition step, as formulated for other 1,2-dihydronaphthalenes and through a di-π-methane rearrangement; the latter reaction proceeds as a singlet as well as a triplet reaction.

Experimental Section

^{1}H NMR spectra were recorded on a Varian T60 or a Bruker WH90 spectrometer in $CDCl_3$. For high-resolution spectra, a Bruker Wm200 or a Bruker WM500 instrument was used; δ values are given in ppm relative to Me_4Si as internal standard and J values are expressed in Hz. Mass spectra were recorded on a Varian MAT SM-2B and UV spectra on a Perkin-Elmer 555 instrument. Melting points were determined by using a Leitz melting point microscope and are uncorrected. Gas chromatography (GLC) was performed by using either a Varian aerograph, series 1200, or a Hewlett-Packard 5710A instrument fitted with a 10% w/w SE-30 column on Chromosorb WHP with dimensions 6 ft × 118 in. o.d. and a flame ionization detector. For column chromatography silica (Merck, Kieselgel 60, and for HPLC Merck, Kieselgel 60H) or alumina (Baker, Aluminum oxide, neutral) were used. HPLC separations were carried out on a Miniprep LC of Jobin-Yvon S. A. fitted with a Waters Associates Differential Refractometer R404 and a Pye Unicam LC-UV Detector.

2-Phenyl-1,2-dihydronaphthalene (4). 3-Phenyl-1-tetralone,[21] prepared from 3,4-diphenylbutanoic acid,[22] was reduced with $NaBH_4$ in ethanol[23] and then dehydrated with *p*-toluenesulfonic acid in toluene.[24] The product was purified by chromatography on silica and elution with hexane: yield, 89%; mp 35–37 °C (lit.[25] 35–37 °C).

3,4-Dideuterio-2-phenyl-1,2-dihydronaphthalene (4-*3,4-d*$_2$). A mixture of 3-phenyl-1-tetralone[21] (1.06 g, 4.77 mmol) and anhydrous K_2CO_3 (0.1 g; 7.2 mmol) was refluxed in 2 mL of D_2O, and the product was isolated by extraction with dry ether, drying over Na_2SO_4, and evaporation in vacuo, as described by Gatto et al.[26] Because of the insolubility of 3-phenyl-1-tetralone in D_2O we used, however, a much longer reflux time (16 h) and repeated the procedure twice to get 98% D incorporation: yield, 0.86 g (81%); H NMR (60 MHz) 2.9–3.5 (m, 3 H, benzylic protons), 7.0–7.5 (m, 8 H, aromatic protons), 8.0 (m, 1 H, H(8)).

The deuterated tetralone (0.5 g) was dissolved in dry ether and added dropwise to a solution of $LiAlD_4$ (0.2 g) in 10 mL of dry ether. After the solution was refluxed for 3 h, a mixture of 0.5 mL of D_2O and 10 mL of dry ether was added carefully and the solution was filtered through hyflo. The ether layer was separated, dried over Na_2SO_4, and evaporated in vacuo, yielding 0.39 g (77%) of 1,2,2-trideuterio-1-deuteroxy-3-phenyltetralin.

Tosyl OH was dissolved in a small amount of D_2O and evaporated to dryness. This procedure was repeated twice, and 0.05 g of the resulting TsOD was added to a solution of the deuterated 1-hydroxy-3-phenyltetralin (0.3 g) in dry toluene (25 mL). After completion of the dehydration the reaction mixture was washed with saturated solutions of $NaHCO_3$ and NaCl and dried over Na_2SO_4. After filtration and evaporation 0.25 g (95%) of **4-*3,4-d*$_2$** was isolated (D incorporation 98% at C(3), 100% at C(4)): ^{1}H NMR 2.7–3.3 (m, 2 H, H(1) and H(1′)), 3.74 (d of d, 1 H, H(2)), 6.9–7.3 (m, 4 H, aromatic protons), 7.26 (s, 5 H, phenyl).

Irradiations. Direct irradiations were carried out under anaerobic conditions using 10^{-3} M solutions in hexane. A high-pressure mercury arc (Philips HPK 125 W) and a quartz vessel were used when a broad spectrum of wavelengths was needed including those below 300 nm. A Pyrex vessel was used if radiation with a wavelength shorter than 300 nm had to be excluded. Irradiations at 254 nm and 300 nm were carried out in a Rayonet Photochemical Reactor or by using fluorescent tubes of Sylvania, Blacklite. Sensitized irradiations were carried out in acetone as solvent and sensitizer, using a 300-nm lamp and a Pyrex vessel. In experiment F the triplet quencher 1,3-cyclohexadiene was present in a concentration of 3×10^{-3} M. The concentration ratios of the components of the product mixtures were determined from the NMR spectra as described in the text.

The irradiation products were isolated by column chromatography on silica gel using hexane as eluent. Final purifications were carried out by using HPLC (silicagel/hexane) or TLC (silica gel/hexane). A mixture of *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (***endo*-6**) and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (**exo-6**) could be separated on alumina (column 25 × 1.4 cm) using hexane as eluent and collecting very small fractions.

Physical Data of the Products. *endo*-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-5). This compound has been isolated from irradiation mixtures of **4**: NMR (200 MHz, $CDCl_3$) 2.25 (m, 1 H, H(5), $J_{1,5}$ = 6.2 Hz, $J_{4endo,5}$ = 1.0, $J_{4exo,5}$ = 6.4, $J_{5,6exo}$ = 8.0), 2.43 (t, 1 H, H(6_{exo}), $J_{1,6exo}$ = 8.0), 2.68 (br d, 1 H, H(4_{endo}), $J_{1,4endo}$ = 1.3, $J_{4endo,4exo}$ = 17.4, $J_{4endo,5}$ = 1.0), 2.91 (m, 1 H, H(1), 3.10 (d of d, 1 H, H(4_{exo}), 6.6–7.45 (m, 9 H, aromatic H).

***exo*-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-5).** NMR (200 MHz, $CDCl_3$) 1.49 (t, 1 H, H(6_{endo}), $J_{1,6endo}$ = 3.0 Hz, $J_{5,6endo}$ = 3.4), 2.20 (m, 1 H, H(5), $J_{1,5}$ = 6.2, $J_{4endo,5}$ = 1.2, $J_{4exo,5}$ = 6.0), 2.65 (m, 1 H, H(1), $J_{1,4endo}$ = 1.3), 3.12 (br d, 1 H, H(4_{endo}), $J_{4endo,4exo}$ = 17.4), 3.33 (d of d, 1 H, H(4_{exo}), 6.9–7.4 (m, 9 H, aromatic H).

1,6-Dideuterio-*endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-5-1,6-*d*$_2$) (non aromatic protons): 90 MHz ^{1}H NMR 2.25 (br d, 1 H, H(5), $J_{4exo,5}$ = 6.4 Hz), 2.68 (br d, 1 H, H(4_{endo}), $J_{4endo,4exo}$ = 17.4), 3.10 (d, of d, 1 H, H(4_{exo}).

1,5-Dideuterio-*exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-5-*1,5-d*$_2$) (non-aromatic protons): 90 MHz ^{1}H NMR 1.49 (s, 1 H, H(6_{endo}), 3.12 (d, 1 H, H(4_{endo}), $J_{4endo,4exo}$ = 17.4), 3.33 (d, 1 H, H(4_{exo}).

7,12-Dihydrobenzo[*a*,*d*]cyclooctatetraene (6): ^{1}H NMR 3.19 (br d, 2 H, H(7), $J_{6,7}$ = 7.6 Hz), 4.03 (s, 1 H, H(12), 5.98 (d, of t, 1 H, H(6), $J_{5,6}$ = 10.6 Hz), 6.88 (broadened d, 1 H, H(5), 7.0–7.4 (m, 8 H, aromatic H); m/e 206 (M^+, 91%), 205 (100), 191 (33), 178 (88), 165 (10), 128 (9), 115 (8); exact mass, 206.107 ± 0.003, theoretical mass, 206.110.

Registry No. 4, 62019-39-0; **4**-*3,4-d*$_2$, 88441-17-2; *endo*-**5**, 67504-58-9; *exo*-**5**, 67504-57-8; *endo*-**5**-*1,6-d*$_2$, 88441-19-4; *exo*-**5**-*1,5-d*$_2$, 88441-20-7; **6**, 88441-21-8; **6**-*6,7-d*$_2$, 88441-22-9; **7**, 23114-34-3; **7**-*1,1-d*$_2$, 88441-23-0; 3-phenyl-1-tetralone, 14944-26-4; 2,2-dideuterio-3-phenyl-1-tetralone, 88441-18-3; 1,2,2-trideuterio-1-deuteroxy-3-phenyltetralin, 88453-15-0.

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