Tetrahedron Vol. 46, No. 11, pp 3823 3840, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00
Pergamon Press plc

RING-STRAIN EFFECTS ON THE EFFICIENCIES AND DEUTERIUM EFFECTS ON THE EFFICIENCIES AND REGIOSELECTIVITIES OF THE DI-π-METHANE REARRANGEMENT OF BICYCLIC SYSTEMS

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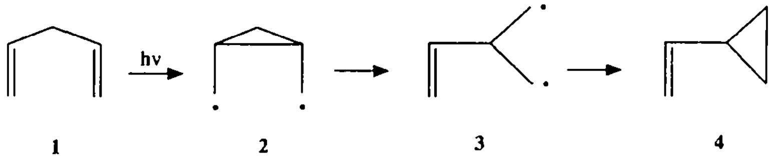
(*Received in Germany* 29 *January* 1990)

Abstract - The protio- and mono-vinyldeuterated benzobicyclo[n.2.2]alkenes (n = 1 to 4) **12** - **13** and **15** - **16** and 1,2-cyclopropabenzobarrelene **14** were synthesized and irradiated under sensitized conditions. The compounds **12** - **15** yielded di-π-methane rearrangement products. **16** was not reactive. The quantum yields for product formation were measured. They increase with ring strain of the bicyclic systems. A kinetic isotope effect on the regiospecifity of the rearrangement was observed in all cases. In addition, an isotope effect on the quantum yields of product formation was observed with **13** and **15**.

INTRODUCTION

The di-π-methane rearrangement was shown to be a very general photochemical reaction. In most cases the reaction proceeds from the excited singlet state in acyclic systems and from the excited triplet state in bicyclic systems.[1]

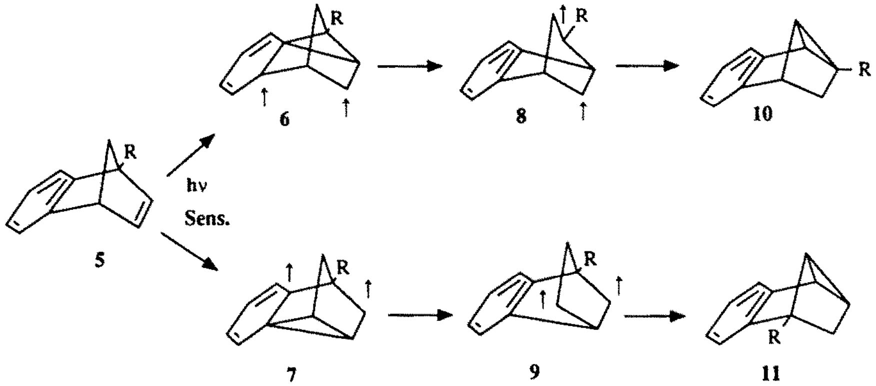
Zimmerman proposed a mechanism for the reaction using valence bond structures and stated that biradicals **2** and **3** (Scheme 1) are approximations of species along the reaction coordinate and are not necessarily intermediates, i. e. energy minima. The participation of biradicals **2** and **3** as intermediates in the course of the di-π-methane rearrangement was discussed by Zimmerman in special cases.[2]



1 **2** **3** **4**

Scheme 1

However Paquette and Bay suggested on the basis of their results on the di-π-methane rearrangement of a large number of bridgehead substituted benzonorbornadienes **5** that cyclopropyldiradicals **6** and **7** may not be intermediates but could be rationalized more succinctly in terms of "a fleeting transition state



Scheme 2

entity" with direct 1,2-aryl-shift forming the biradicals **8** and **9** (Scheme 2).[3] Their interpretation is predominately based upon the observed regiospecifity exerted by bridgehead substituents at the intramolecular competition level, provided there is no reversibility. In addition, the kinetic isotope effects of deuterium at the bridgehead or at the vinyl group were taken as evidence for a 1,2-aryl-shift.[3b,c,e]

In a recent work Hemetsberger et al. investigated the substituent effects of vinyl-substituted benzonorbornadienes and benzobicyclo[2.2.2]octadienes, which are less strained, and found that the efficiencies of the di-π-methane rearrangement were significantly lower with the later ones. It was argued that a funnel for radiationless decay might exist having a geometry close to biradicals **6** and **7**.[4]

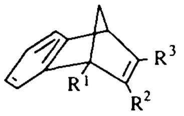
In a theoretical investigation of the triplet di-π-methane rearrangement by Quenemoen, Borden, Davidson and Feller it was found that the biradical **2** appears to be a true intermediate and could be involved in the di-π-methane rearrangement. Its opening to **3** was predicted to be fairly easy, however.[5] In an independent work Jug and Iffert came to the same conclusion.[6]

Kinetic isotope effects were used successfully to probe the role of certain modes of vibrations in thermal reactions.[7] Recently, kinetic isotopic effects are now used in the field of organic photochemistry, as well.[3b,c,e,8]

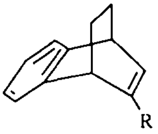
To get more definite information upon the effect of molecular strain on the efficiencies and the involvement of biradicalic species along the reaction coordinate the deuterium effects on the regiospecifity (kinetic isotope effect) and/or on the efficiencies of the di-π-methane rearrangement of the bicyclic systems **12** - **16** were studied. All systems were chosen that way that the di-π-methane rearrangement should start from the excited triplet state by a vinyl-aryl interaction.

SYNTHESIS OF PHOTOCHEMICAL REACTANTS

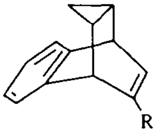
The syntheses of **12a**, **12b** and **12c** were performed according to the procedures described.[3a,b,e] For the synthesis of **12d** 2-benzonorbornanone was treated with deuteromethanol in presence of sodium methoxide three times and was thereafter reduced with lithium aluminumdeuteride. Tosylation and elimination yielded **12d** with a total degree of deuteration of 93.4%. **13a** and **13b** were synthesized in analogy to **12d** starting from 2-benzobicyclo[2.2.2]octenone using lithium aluminumhydride or -deuteride. The degree of deuteration of **13b** was 98.5%. **14a** and **14b** were synthesized from 2-benzobicyclo[2.2.2]octadienone which was transformed to the ketal and treated with diazomethane in the presence of palladium acetate to yield solely the endo-product. After hydrolysis the ketone was transformed as described for **13a** and **13b**. The degree of deuteration of **14b** was 99%. The synthesis of **15a** was performed according to a procedure described by Wilson et al..[9] **15b** was synthesized from **15a** by hydroboration, oxidation and reduction with lithium aluminumdeuteride. After dehydration **15b** was obtained with a degree of deuteration of 99.6%.



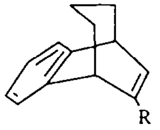
12a: $R^1=R^2=R^3=H$
12b: $R^2=D$, $R^1=R^3=H$
12c: $R^1=D$, $R^2=R^3=H$
12d: $R^1=H$, $R^2=R^3=D$



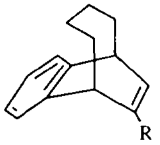
13a: R=H
13b: R=D



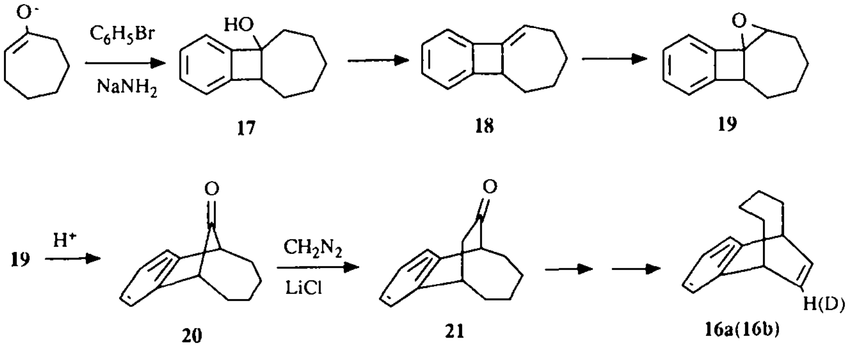
14a: R=H
14b: R=D



15a: R=H
15b: R=D



16a: R=H
16b: R=D



Scheme 3

The synthesis of **16a** and **16b** is outlined in Scheme 3. The enolate of cycloheptanone was treated with benzyne to form the [2+2] cycloadduct **17**.[10] Elimination of water afforded the alkene **18**, which was epoxidized with m-chlorobenzoic acid to yield **19**, which was rearranged to 7,8-benzobicyclo[4.2.1]nonen-9-one **20**.[11] Ring-expansion according to the procedure of Shechter[12] yielded 7,8-benzobicyclo[4.2.2]decen-9-one **21**, which could be transformed to **16a** and **16b** in a total yield of 13%. **16b** was obtained with degree of deuteration of 99.4%.

PHOTOISOMERIZATIONS

The preparative irradiations were either performed in acetone at 310 nm or in benzene solutions containing acetophenone using a 350 nm light source. The concentrations of starting materials were chosen that more than 99% of the light were absorbed by the sensitizer.

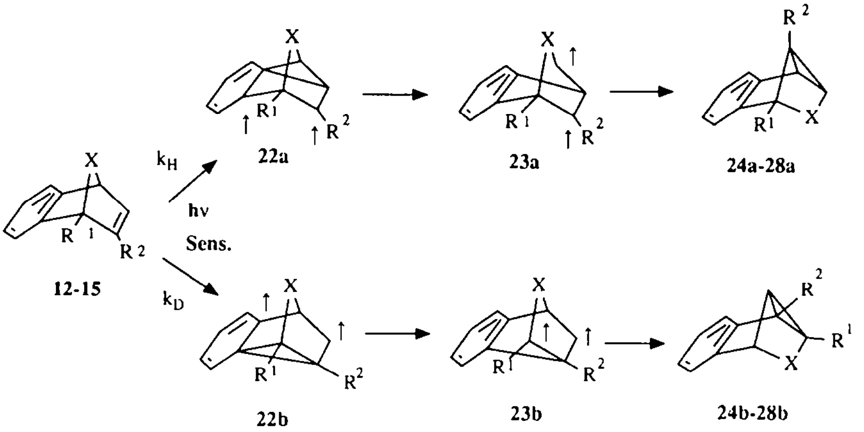
The acetophenone-sensitized irradiation of **12c** yielded the isotopomeric mixture of **24a** and **24b** as described by Paquette and Bay.[3a,b] The ratio of **24a** to **24b** was determined by proton-decoupled ^2H NMR from the ratio of the intensities of the signals at 3.36 ppm C-2 (benzylic) and 1.98 ppm (cyclopropyl) and was found to be 1.25 in agreement with the value of 1.27 reported by these authors. The degree of deuteration of the isotopomeric mixture was determined from the ^1H NMR and was 94.1% corresponding to the degree of deuteration of the starting material.

Irradiation of **12b** was performed in benzene with acetophenone as sensitizer and yielded the mixture of the isotopomers **25a** and **25b** as described by Paquette et al..[3e] The ratio of **25a** to **25b** was determined from the proton-decoupled ^2H NMR from the intensities of the signals at 3.35 ppm C-1 (cyclopropyl) and 2.65 ppm C-2 (benzylic cyclopropyl) and was found to be 0.71. This value agrees well with the 1.31 - 1.37 - the reciprocal value, **25b**/**25a** - reported by Paquette et al.. The degree of deuteration was calculated from the mass spectrum and amounted to 95%.

The irradiation of **13a** was performed either in acetone (E_T = 342,1 kJ/mol) [13] at 310 nm or in benzene with acetophenone as sensitizer (E_T = 309,8 kJ/mol)[13] at 350 nm, but the photoreaction proceeded eight times faster in acetone than in benzene. In addition to the di-π-methane rearrangement product **26** ($R^1 = R^2 = H$) **29** was formed by formal addition of hydrogen to the starting material. The ^1H NMR data of **29** were found identically as reported by Kitahonoki et al..[14] The irradiation was stopped at a conversion of 42%, and the ratio of **26** to **29** was 20:1. The structure of **26** could unequivocally be derived from ^1H NMR (400 MHz) and ^{13}C NMR. The spectroscopic data are presented in the experimental section.

The irradiation of **13b** was performed as described for **13a** in acetone. The ratio of **26a** to **26b** was deduced from the intensities of the signals at 2.73 ppm C-1 (cyclopropyl) and 2.30 ppm C-2 (benzylic cyclopropyl site) from the proton-decoupled ^2H NMR spectrum and was found to be 0.75. The degree of deuteration of the mixture of isotopomers was determined by mass spectroscopy to 98.4%, which is the same value as found for **13b**.

The photoisomerization of **14a** was performed by irradiation with 310 nm Sunlight-Phosphor lamps in acetone in a Rayonet reactor at room temperature. The formation of the di-π-methane rearrangement product **27** (R^1 = R^2 = H) could be observed immediately. After 30 min. the formation of a secondary photoproduct was observed as described earlier.[15] After irradiation for 120 min. the reaction mixture contained 20% starting material, 15% secondary photoproduct and 65% **27**, which was isolated purely using HPLC.



12b, 25a, 25b: X=CH_2, R^1=H, R^2=D

12c, 24a, 26b: X=CH_2, R^1=D, R^2=H

13b, 26a, 26b: X=$(CH_2)_2$, R^1=H, R^2=D

14b, 27a, 27b: X= Δ, R^1=H, R^2=D

15b, 28a, 28b: X=$(CH_2)_3$, R^1=H, R^2=D

Scheme 4

The irradiation of **14b** was performed identically to yield the isotopomeric mixture of **27a** and **27b**. The ratio of **27a** to **27b** was analyzed by proton-decoupled ^2H NMR and ^1H NMR spectroscopy. The ratio of the intensities of the signals at 3.64 ppm C-1 (cyclopropyl) and 2.10 ppm C-7 (benzylic cyclopropyl site) in the ^2H NMR was found to be 0.71, which corresponds to the ratio of **27a** to **27b** in the isotopomeric mixture. In accord with these findings, the ratio of the intensities of these signals in the ^1H NMR was determined to be 1.39. No loss of deuterium occurred in the photorearrangement, since the degree of deuteration was 99.4%, calculated from NMR.

Irradiation of **15a** (R^1 = R^2 = H) in acetone afforded the di-π-methane rearrangement product **28** and **30** the later was formed by hydrogen addition to the double bond of the starting material - in the ratio 7:1. The irradiation was stopped when 35% of the starting material were consumed and polymeric products began to form. The starting material and the photoproducts were separated by HPLC. The ^1H NMR of **30** conforms to the data reported in the literature.[16] The structure of **28** was deduced from the ^1H NMR (400 MHz) and ^{13}C NMR. The data are reported in the experimental section.

The irradiation of **15b** and the separation of the photoproducts were performed as described above. The isotopomeric mixture of **28a** and **28b** was analyzed by proton-decoupled ^{2}H NMR and ^{1}H NMR. From the ^{2}H NMR the ratio of the intensities of the signals at 1.95 ppm C-1 (cyclopropyl) and 2.28 ppm C-7 (benzylic cyclopropyl site) was determined to be 0.89, corresponding to the ratio of **28a** to **28b** in the isotopomeric mixture. In accord, the ratio of the intensities of these signals in the ^{1}H NMR was found to be 1.11. The degree of deuteration was determined from the ^{1}H NMR to 99.5% and corresponds to the degree of deuteration of the starting material.

Compounds **16a** and **16b** failed to rearrange totally either under sensitized or direct irradiations in various solvents.

QUANTUM YIELD MEASUREMENTS

The regiospecifity of the di-π-methane rearrangement exerted by deuterium substitution may be the result of differences in the reactivities along the reaction coordinates. But if aryl-vinyl bridging happens to be reversible, a path for radiationless decay would be open and a change in the efficiencies would result. Knowledge of the quantum yields for the di-π-methane rearrangement of the above systems and the change of the quantum yields with deuterium substitution became desirably.

Table 1. Quantum yields, kinetic isotope effects k_H/k_D (Scheme 4) and isotope effects on quantum yields

compd	solvent	Φ	k_H/k_D	Φ_H/Φ_D
12a	A^a	0.58±0.03^b	-	-
12b	A	0.58±0.03^c	0.71^d	1.00±0.05
12c	A	0.58±0.03	1.25^e	1.00±0.05
12d	A	0.58±0.03	-	1.00±0.05
13a	B^a	0.039±0.002	-	-
13b	B	0.052±0.002	0.76	0.75±0.05
14a	B	0.10±0.01^f	-	-
14b	B	0.10±0.01	0.71	1.00±0.05
15a	B	0.020±0.002	-	-
15b	B	0.024±0.002	0.89	0.84±0.05
16a	B	-	-	-
16b	B	-	-	-

a) A=benzene/acetophenone irradiation at 365 nm, B=acetone irradiation at 300 nm; C=benzene,benzophenone irradiation at 365 nm; b) Lit. 0.81^{3e}; c) Lit. 0.79^{3e}; d) Lit. 0.72-0.76^{3e}; e) Lit. 1.27^{3a,b}; f) Lit. 15.

The quantum yields of the undeuterated compounds were either measured by irradiation with a HBO 200 lamp using a Bausch & Lomb high intensity monochromator and an electronic actinometer[17] calibrated by ferrioxalate actinometry,[18] or taken from literature and are collected in Table 1. For the deuterated compounds relative quantum yields were measured in a Rayonet reactor using a "merry go round" apparatus. To minimize errors in each run three samples of the undeuterated and three of the deuterated compounds were irradiated together. In the following runs the reaction vessels were changed towards each other.

INTERPRETATIVE DISCUSSION

Bicyclic di-π-methane systems rearrange commonly via the excited triplet states.[19] Since systems **12** to **15** rearrange substantially more efficiently in sensitized irradiations than in direct ones, the excited triplet state will be the reactive one. Acetophenone sensitization was only efficient as acetone sensitization in the rearrangement of **12** but was less efficient with the systems **13** to **15**. Consequently, the triplet energies of the benzonorbornadienes **12** are lower than those of the systems **13** to **15**. The triplet energies of **13** to **15** are above 310 kJ/mole.

The first point to be noticed is the strong dependence of the quantum yield on the strain in the bicyclic systems. It was found that the efficiencies of the rearrangements become lower if the systems are less strained. The reason for this observation might stem from the possibility of the more flexible system to acquire a geometry in the proximity of a funnel suited for a jump from the triplet to the ground state hypersurface. Similar cases were reported by Zimmerman for acyclic systems.[19]

To evaluate the results of the observed regiospecifities in terms of a secondary α- or β-kinetic isotope effects, k_H/k_D, it is necessary to define, what processes are actually meant by k_H and k_D. By one definition k_H could be the bridging process on the site of hydrogen substitution and, correspondingly, k_D on the site of deuterium, as can be seen in Scheme 4 by the processes **12-15** to **22a** and **22b**. Alternatively, k_H can be defined as the atomic reorganization process, in which a biradical is formed with a hydrogen atom at the radical center and k_D with a deuterium atom at the radical center. We prefer to adopt the first definition without anticipating any mechanistic statement that the biradicals **22a** and **22b** are true intermediates (Scheme 4).

The participation of the biradicals **23a** and **23b** as intermediates in the course of the rearrangement was discussed by Zimmerman.[2] Adam generated photochemically unsubstituted **23** from an azoalkane[2c] and found that the biradical reacted only to the tricyclic system. If it is assumed that biradicals **22** and **23** are species residing in minima on the triplet hypersurface, the observed isotope effects can be explained. It is known from isotope effects on radical reactions that radicals, which are heavier substituted by deuterium are less easily formed, implying a higher energy barrier for formation of that radical.[21] The first step in the rearrangement leads to the biradicals **22a** and **22b**. If there is a small barrier, the radicals will be formed in unequal amounts, and the biradical will exceed which is not substituted on the radical center. k_D is larger than k_H (Scheme 4) as it is observed for **12b**, **13b**, **14b** and **15b**, but only a small effect should operate on **12c**. In the second step a cyclopropylcarbinyl-homoallyl-rearrangement follows, and the second biradicals will be formed. Again a deuterium effect might operate, but the situation is reversed there. A noticable effect is observed for **12c** which is substituted with deuterium on bridgehead, and k_D is smaller than k_H. The deuterium effect of this step should be minor for **12b**, **13b**, **14b** and **15b**.

Possibly, the geometry of the biradical **22** is similar or equal to the geometry of the species corresponding to the energy minimum on the excited triplet hypersurface in the region of the funnel, which is responsible for the radiationless decay. The rate of the radiationless decay depends on the energy difference in the funnel between the excited and the ground state hypersurface and is small, if the energy gap is large. The energies of the biradical **22** depend on the strain of the system, and the biradicals formed from **12** and **14** will be higher in energy than those of **13**, **15** and **16**.

The quantum yield of product formation depends on the competition of the reaction rate of the process **22** to **23** and the rate of the radiationless decay of **22** to the ground state of the starting material. The largest energy gap is expected for the biradicals formed from **12** and the largest quantum yield for the reaction is observed. Contrary, the gap for the biradical formed from **16** is smallest and the biradical decays completely rendering the system photochemically unreactive.

In addition an isotope effect on the quantum yields was observed for **13** and **15**, which rearrange with low quantum yields, in contrast to **12** and **14**, which rearrange efficiently where no effect was found (Table 1). This effect could be the result of changes in the triplet lifetimes. It is known that deuterated systems exhibit longer triplet lifetimes than unsubstituted systems, caused by a reduced rate of radiationless decay.[22,23] In the cases studied, the same effect might operate, since the deuterated systems have higher quantum yields of product formation than the unsubstituted ones. The effect is small and should be only significant, if the efficiency of the photoreaction is small against the efficiency of radiationless decay, as it is the case for **13** and **15**.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a BRUKER WP 80 (80 MHz), BRUKER WH 250 (250 MHz) and BRUKER AM 400 (400 MHz). The ^{13}C NMR spectra were recorded with a BRUKER WH 90 (22.63 MHz), BRUKER WH 250 (62.86 MHz) and BRUKER AM 400 (100.61 MHz); mass spectra were obtained using a Varian MAT CH-5. High resolution mass spectra were recorded using a Varian MAT 731 (70 eV) spectrometer. The following values were used for calculation of the theoretical values : H=1.0078, C=12.0000, N=14.0031, O=15.9949, F=18.9984 and Cl=34.9689. Analytical and semipreparative separations were performed with a HPLC apparatus consisting of a Waters M 6000 pump, Waters UK 6 injector and LDC UV 254 nm detector.

Synthesis of compounds:

2-Deutero-benzobicyclo[2.2.1]hepten-2-endo-ol (**31**): A sample of 10.0 g (0.063 mol) benzobicyclo[2.2.1]hepten-2-one[24] was dissolved in 30 ml dry ether and added to a suspension of 1.0 g (0.024 mol) $LiAlD_4$ in 30 ml dry ether within 30 min under nitrogen. The reaction mixture was stirred and heated under reflux for 3 h. After cooling, H_2SO_4 (10%) was added. The organic phase was separated, washed with a solution of $NaHCO_3$ and dried. The solvent was removed in vacuo and the residue recrystallized from pentane to yield 9.1 g (0.057 mol) **31**; m.p. 74°C, - 74.5°C undeuterated compound (lit.[24]). ^1H NMR ($CDCl_3$, 80 MHz): 7.05-7.35 ppm (m, 4H, H-arom.), 3.30 and 3.41 (m, 2H, C1-H and C4-H), 2.42 (m, 2H, endo-C7-H), 1.51-2.02 (m, 2H, C3-H), 0.85 (dd, 1H, exo-C7-H); MS (m/z, 70 eV): 161 (M^+, 13%), 117 (19), 116 (100); determination of the degree of deuteration (MS, 30 eV): d_0 = 5.31%, d_1 = 93.53% and d_2 = 1.2%.

2-Deutero-benzobicyclo[2.2.1]heptadiene (**12b**): A sample of 2.0 g (0.012 mol) 2-deutero-benzobicyclo[2.2.1]hepten-2-endo-ol (**31**) and 4g (0.021 mol) p-toluenesulfonyl chloride were dissolved in 25 ml dry $CHCl_3$. The reaction mixture was cooled in an ice bath. 5.6 ml dry pyridine were added within 30 min with stirring and the mixture was kept 1 h at this temperature. After 24 h at room temperature the reaction mixture was poured on a mixture of ice and HCl, and the tosylate was extracted with $CHCl_3$. After washing and drying the organic phase the solvent was removed in vacuo, and the resulting oil used in the next step without further purification. 3.9 g (0.012 mol) tosylate were dissolved in 50 ml dry benzene, and 5.6 g (0.05 mol) K-O-t-butylate and 2 g (0.008 mol) 18-crown-6 were added. The reaction mixture was stirred 3 h at 80°C and after cooling treated with 200 ml water and 200 ml pentane. The organic layer was separated, washed with water and dried with Na_2SO_4 . The solvent was removed in vacuo, and the resulting oil was purified by chromatography on a short column (40 x 15 mm, silica) using pentane as mobile phase. Yield 255 mg colorless oil (1.75 mmol, 15%); ^1H NMR ($CDCl_3$, 80 MHz): 6.92-7.31 ppm (m, 4H, H-arom.), 6.85 (t, 1H, C2-H), 3.95 (q, 2H, C1-H, C4-H), 2.35 (m, 2H, C7-H); MS (m/z, 70 eV): 143 (M^+, 90%), 142 (100); determination of the degree of deuteration (MS, 14 eV): d_0 = 4.9%, d_1 = 94.9% and d_2 = 0.2%.

3,3-Dideutero-5,6-benzobicyclo[2.2.1]hepten-2-one (**32**): A solution of 5.50 g (0.035 mol) 5,6-benzobicyclo[2.2.1]hepten-2-one[24] in 50 ml benzene was added to a solution of 0.5 g (0.02 mol) sodium in 25 ml methanol-d_1 under nitrogen. The reaction mixture was stirred at room temperature for 3 h. 0.5 g NH_4Cl were added, the solution was filtered, and the solvent was removed in vacuo. The residue was dissolved in benzene and the solution was washed with water and dried over Na_2SO_4. The procedure, described above, was repeated three times to improve the degree of deuteration. Yield 4.1 g (0.026 mol, 74%) **32** as a colorless oil; ^1H NMR (80 MHz, $CDCl_3$): 6.90-7.20 ppm (m, 4H, H-arom.), 3.45 (m, 2H, C1-H and C4-H) and 2.15-2.60 (m, 2H, exo/endo- C7-H); MS (m/z, 70 eV): 160 (M^+, 10%), 159 (8), 116 (100); determination of deuteration (MS, 70 eV): d_0 = 1.6%, d_1 = 4.4% and d_2 = 94.0.

2,3,3-Trideutero-5,6-benzobicyclo[2.2.1]hepten-2-ol (**33**): The reduction of the 3,3-dideutero-5,6-benzobicyclo[2.2.1]hepten-2-one (**32**) was performed as described for **31**. 2.0 g (0.0125 mol) of the ketone were treated with 160 mg (4.0 mmol) $LiAlD_4$ to yield 1.9 g (0.012 mol, 94%) **33**; m.p. 74°C; the ^1H NMR spectrum of **33** was identical to the spectrum of **31** with the exception that the multiplet between 1.51-2.02 ppm was missing; MS (m/z, 70 eV): 163 (M^+, 12%), 145 (2), 116 (100); determination of the degree of deuteration (MS, 70 eV): d_0 =1.7%, d_1 =0.2%, d_2 = 6.6% and d_3 = 91.5%.

2,3-Dideutero-5,6-benzobicyclo[2.2.1]heptadiene (**12d**): The diene was prepared by the procedure described for the synthesis of **12b**. 1.5 g (9.26 mmol) 2,3,3-trideutero-5,6-benzobicyclo[2.2.1]hepten-2-ol (**33**) yielded 430 mg (0.03 mmol, 33%) **12d** as a colorless oil; ^1H NMR (80 MHz, $CDCl_3$): 6.90-7.30 ppm (m, 4H, H-arom.), 3.95 (t, 2H, C1-H and C4-H), 2.35 (dd, 2H, exo- and endo-C7-H); MS (m/z, 70 eV): 144 (M^+, 92%), 143 (100); determination of the degree of deuteration (MS, 13.5 eV): d_0 = 4.5%, d_1 = 4.1% and d_2 = 91.4%.

exo/endo-2-Deutero-benzobicyclo[2.2.2]octen-2-ol (**35**): A sample of 2.0 g (12.0 mmol) benzobicyclo[2.2.2]octen-2-one (**34**),[25] dissolved in 20 ml dry ether, was added, to a suspension of 0.17 g (4.0 mmol) $LiAlD_4$ in 20 ml dry ether. The reaction mixture was stirred for 16 h. 5 ml NaOH (10%) were added and after filtration the organic phase was separated, washed with water and dried over Na_2SO_4. The solvent was removed in vacuo to yield 1.8 g (10.0 mmol, 89%). m.p. 87°C; ^1H NMR ($CDCl_3$, 80 MHz): 7.10-7. ppm (m, 4H, H-arom.), 3.10 (m, 2H, C1-H, C4-H), 1.30-2.45 (m, 7H, H-aliphat.); MS (m/z, 70 eV): 175 (M^+, 19%), 131 (20), 130 (100); determination of the degree of deuteration (MS, 30 eV): d_0 = 0.59%, d_1 = 98.14% and d_2 = 1.27%.

2-Deutero-benzobicyclo[2.2.2]octadiene (**13b**): The synthesis of **13b** was performed in the same way as described for **12b**. A sample of 3.0 g (0.017 mol) exo/endo-2-deutero-benzobicyclo[2.2.2]octen-2-ol (**35**) was treated with 6.8 g (0.036 mol) p-toluenesulfonyl chloride and 10 ml dry pyridine in 50 ml $CHCl_3$. The crude tosylate was treated with 10.0 g (0.089 mol) K-O-t-butylate and 4.0 g (0.015 mol) 18-crown-6 in 80 ml dry benzene. Yield 2.05 g (0.013 mol, 74%) colorless oil; ^1H NMR ($CDCl_3$, 80 MHz): 7.05-7.32 ppm (m, 4H, H-arom.), 6.50 (dd, 1H, CH-2), 3.95 ppm (ddd, 2H, C1-H and C4-H), 1.45 (m, 4H, H-aliph.); MS (m/z, 70 eV): 157 (M^+, 11%), 130 (14), 129 (100); determination of deuteration (MS, 15 eV): d_0 = 0.80%, d_1 = 98.5% and d_2 = 0.70%.

6,7-Benzobicyclo[3.2.2]6,8-nonadiene (**15a**): A sample of 9.0 g tricyclo[6.3.2.02,7]trideca-4,12-dien-3,6-diol[9] and 35.1 g p-toluenesulfonyl chloride were dissolved in 250 ml dry $CHCl_3$ and 47 ml dry pyridine were added within 30 min at 0°C. After 1 h at this temperature the mixture was kept at room temperature 24 h. 200 g ice and 150 ml conc. HCl were added, and the ditosylate was extracted with $CHCl_3$. The organic phase was separated, washed with water and dried over Na_2SO_4 . The solvent was removed in vacuo and the residue dissolved in 200 ml dry benzene. 20 g (0.178 mol) K-O-t-butylate were added in small portions. In the course of the addition the solvent starts boiling. The reaction mixture was kept at room temperature 1 h, 200 ml water and 300 ml pentane were added and the organic phase was separated, washed with water and dried over Na_2SO_4. The solvent was removed in vacuo, and the resulting yellow oil was purified by chromatography on silica (column 50x15 mm) using pentane as mobile phase. 4.7 g (0.028 mol) **15a** as colorless oil were obtained. ^1H NMR ($CDCl_3$, 400 MHz): 7.23 ppm (s, 4H, H-arom.), 6.48 (dd, 2H, H-vinyl), 3.50 (ddd, 2H, CH-1 and CH-5), 1.70, 1.55, 1.35 (m, 6H, H-aliphat.); ^{13}C NMR ($CDCl_3$, 100.61 MHz): 23.08 ppm (t, C2 and C4), 26.61 (t, C3), 40.50 (d, C1 and C5), 125.00 and 125.50 (d, C-arom.), 134.30 (d, C-vinyl), 143.45 (s, C-arom.); MS (m/z, 70 eV): 170 (M+, 56%), 142 (66), 141 (100).

exo/endo-6,7-Benzobicyclo[3.2.2]6-nonen-8-ol (**36**): A sample of 1.0g (5.88 mmol) benzobicyclo[3.2.2]6,8-nonadiene (**15a**) was dissolved in 3.5 ml diglyme and 90 mg $NaBH_4$ was added. Within 15 min 0.4 ml BF_3-Et_2O was added and the reaction mixture stirred for 1 h at room temperature. 0.5 ml water were added followed by 0.6 ml NaOH (12%) and 0.6 ml H_2O_2 (30%) at 40°C. The mixture was kept 30 min at room temperature. 50 ml ether were added and the organic phase was separated, washed with a solution of Fe(II)sulfate, three times with water and was dried over Na_2SO_4. The solvent was removed in vacuo to yield 1.0 g (5.32 mmol, 90%) **36** as a crystalline solid; m.p. 92°C; ^{1}H NMR ($CDCl_3$, 80 MHz): 7.00-7.20 (m, 4H, H-arom.) 4.38 (dt, 1H, C8-H), 3.00, (m, 2H, C1-H and C5-H), 1.90-2.70 (m, 2H, exo/endo-C9-H), 1.40-1.85 (m, 7H, exo/endo-C2-H, C3-H and C4-H and O-H); MS /m/z, 70 eV): 189 (M^++1, 7%), 188 (M^+, 60), 144 (100).

6,7-Benzobicyclo[3.2.2]6-nonen-8-one (**37**): A solution of 1.0 g (5.32 mmol) exo/endo-6,7-benzobicyclo[3.2.2]6-nonen-8-ol (**36**) in 25 ml ether was cooled to -15°C, and a solution of 5.4 ml $Na_2Cr_2O_7$ - prepared by dissolving 100 g (0.33 mol) $Na_2Cr_2O_7$ in 300 ml water, addition of 136 g H_2SO_4 (97%) and dilution to 500 ml - was added under stirring. After 20 min 25 ml ether were added. The organic phase was separated, was washed with a solution of $NaHCO_3$ and water and was dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by chromatography on silica (column 280x24 mm, 0.063-0.2 mm) using hexane/ether (80:20) as mobile phase to yield 0.73 g (3.92 mmol, 73%) **37** as a colorless oil; ^{1}H NMR ($CDCl_3$, 80 MHz): 7.00-7.30 ppm (m, 4H, H-arom.), 3.57 (t, 1H, C1-H), 3.30 (m, 1H, C5-H), 2.60 (dd, 2H, exo/endo-C9-H), 1.30-1.95 (m, 6H, C2-H, C3-H and C4-H); MS (m/z, 70 eV): 187 (M^++1, 10%), 186 (M^+, 58), 129 (100).

exo/endo-8-Deutero-6,7-benzobicyclo[3.2.2]6-nonen-8-ol (**38**): A solution of 0.70 g (3.76 mmol) 6,7-benzobicyclo[3.2.2]6-nonen-8-one (**37**) in 12 ml dry ether was added to a suspension of 46 mg (1.15 mmol) $LiAlD_4$ in 25 ml ether. The reaction mixture was stirred and heated under reflux for 2 h. 5 ml NaOH (10%) were added, and the organic phase was separated, washed with water and dried over Na_2SO_4. The solvent was removed in vacuo to yield 0.6 g (3.17 mmol, 84%) of the alcohol as a colorless solid. m.p. 92°C; the ^{1}H NMR was identical to the ^{1}H NMR of **36** except the signal at 4.38 ppm, which is missing. MS (m/z, 70 eV): 190 (M^++1, 8%), 189 (M^+, 50), 144 (100); determination of the degree of deuteration (MS, 70 eV): d_0 = 0.6%, d_1 = 99.3%, d_2 = 0.1%.

8-Deutero-6,7-benzobicyclo[3.2.2]6,8-nonadiene (**15b**): The synthesis was performed identically to that of the undeuterated alkene. A sample of 600 mg (3.21 mmol) 8-deutero-6,7-benzobicyclo[3.2.2]6-nonen-8-ol (**38**) was treated with K-O-t-butylate to yield 190 mg (1.12 mmol, 35%); the ^{1}H NMR spectrum was entirely identical to the spectrum of alkene **15a**. MS (m/z, 70 eV): 172 (M^++1, 8%), 171 (M^+, 52), 142 (100); determination of the degree of deuteration by MS was not possible because of exchange reactions. The degree could be determined from the ^1H NMR-spectrum: d_0 = 0.4%, d_1 = 99.6%.

7,8-Benzobicyclo[4.2.2]7-decen-9-one (**39**): The synthesis of **39** was performed in analogy to a procedure described by Shechter[26]. A solution of 3.0 g (0.016 mol) 7,8-benzobicyclo[4.2.1]7-nonen-9-one[10] in 17 ml dry $CHCl_3$ and 9 ml dry methanol was cooled to 0°C and 0.2 g LiCl were added. An ether solution of diazomethane prepared from N-nitroso-N-methylurea was added, and the reaction mixture was kept at this temperature for 24 h with occasional additions of small quantities of LiCl. Excess of diazomethane was decomposed by formic acid, and the organic solution was washed with water and a solution of $NaHCO_3$ and was dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by chromatography on alumina (column 280x24 mm, 0.063-0.2 mm, basic alumina) using n-hexane/ether (80:20), until the first fraction was eluted. The second fraction was eluted with ether. The first fraction 0.60 g (3.0 mmol, 19%) yielded an exo/endo mixture of spiro[7,8-benzobicyclo[4.2.1]7-decen]-9-oxirane (**40**). The second fraction yielded 1.60 g (8.0 mmol, 50%) 9,10-benzobicyclo[4.2.2]9-decen-7-one (**39**) as colorless liquid; **39**: ^1H NMR ($CDCl_3$, 80 MHz): 7.0-7.2 ppm (m, 4H, H-arom.), 3.55 (dd, 1H, C1-H), 3.25 (m, 1H, C6-H), 2.25-2.60 (m, 2H, exo/endo-C10-H), 1.20-2.10 (C2-H, C3-H and C4-H); $J_{1,2exo} = J_{1,2endo}$ = 6Hz; MS (m/z, 70 eV): 201 (M^++1,12%), 200 (M^+, 63), 129 (100); **40**: ^1H NMR ($CDCl_3$, 80 MHz): 7.20 ppm (s, 4H, H-arom.), 3.06 (dd, 2H, C1-H and C6-H), 2.80 (s, 2H, C10-H), 1.1-2.0 (m, 8H, C2-H, C3-H, C4-H and C5-H); MS (m/z, 70 eV): 201 (M^++1, 8%), 200 (M^+, 50), 170 (100).

exo/endo-7,8-Benzobicyclo[4.2.2]7-decen-9-ol (**41**): A solution of 0.60 g (3.0 mmol) 7,8-benzobicyclo[4.2.2]7-decen-9-one (**39**) in 10 ml dry ether was added to a suspension of 36 mg $LiAlH_4$ in 20 ml dry ether. The reaction mixture was stirred and heated under reflux for 2 h. 5 ml NaOH (10%) were added, the ether phase was separated, washed with water and dried over Na_2SO_4. The solvent was removed in vacuo to yield 0.55 g (2.72 mmol) of the alcohol as a colorless solid; m.p. 104°C; ^1H NMR ($CDCl_3$, 80 MHz): 7.0-7.2 ppm (m, 4H, H-arom.), 4.21 (ddd, 1H, C9-H), 3.15-3.48 (m, 2H, C1-H and C6-H), 2.20-2.90 (m, 2H, exo/endo-C10-H), 1.2-2.0 (m, 9H, C2-H, C3-H, C4-H, C5-H and OH); MS (m/z, 70 eV): 202 (M^+, 2%), 190 (3.5), 96 (14), 57 (100).

7,8-Benzobicyclo[4.2.2]7,9-decadiene (**16a**): The diene was synthesized by the procedure described for 6,7-benzobicyclo[3.2.2]6,8-nonadiene (**15a**). A sample of 0.50 g (2.64 mmol) exo/endo-7,8-benzobicyclo[4.2.2]7-decen-9-ol (**41**) yielded 240 mg (1.30 mmol, 53%) **16a** as a colorless oil; ^1H NMR ($CDCl_3$, 400 MHz): 7.05-7.20 ppm (m, 4H, H-arom.), 6.11 (dd, 2H, C9-H and C10-H), 3.58 (ddd, 2H, C1-H and C6-H), 1.30-1.90 (m, 8H, C2-H, C3-H, C4-H and C5-H); $J_{1,9} = J_{6,10}$ = 6 Hz; ^{13}C NMR ($CDCl_3$, 100.61 MHz): 144.95 ppm (s, q-C-arom), 128.08 (d, C9 and C10), 126.96 and 125.76 (d, t-C-arom.), 40.52 (d, C1 and C6), 37.86 (t, C2 and C5), 24.66 (t, C3 and C4); MS (m/z, 70 eV): 184 (M^+, 40%), 173 (85), 141 (100); MS-high-resolution: found 184.1246; $C_{14}H_{16}$ requires 184.1252.

exo/endo-2-Deutero-7,8-benzobicyclo[4.2.2]7-decen-9-ol (42): The compound was synthesized as described for **41** using $LiAlD_4$. Yield 0.55 g (2.72 mmol,91%); the ^1H NMR spectrum is identical to the spectrum of **41** with the exception that there is no signal at 4.21 ppm. MS (m/z, 70 eV): 203 (M^+, 2%), 191 (18), 58 (100); determination of the degree of deuteration (MS, 20 eV): d_0 =0.6%, d_1 =99.3% and d_2 =0.1%.

9-Deutero-7,8-benzobicyclo[4.2.2]7,9-decadiene (16b): The diene was synthesized as described for the undeuterated compound **16a**. A sample of 0.50 g **42** yielded 0.255 g (1.38 mmol, 56%) **16b** as a colorless oil. The ^1H NMR spectrum was identical to the spectrum of **16a** with the exception that the intensity of the signal at 6.11 ppm was only half; determination of the degree of deuteration was not possible by MS, because of exchange reactions. The degree of deuteration was obtained from ^1H NMR: d_0 = 0.6% and d_1 = 99.4%.

8,8-Ethylenedioxy-5,6-benzotricyclo[3.2.2.0^{2,4}]6-nonene (43): A sample of 2.14 g (0.01 mol) 2,2-ethylenedioxy-5,6-benzobicyclo[2.2.2]5,7-octadiene[27] **44** was dissolved in 50 ml $CHCl_3$, and 0 2 g palladium-(II)-acetate were added. Diazomethane - prepared from 62 g N-nitroso-N-methyl-p-toluenesulfonamide in 100 ml anisol with 30 g KOH in 30 ml water and 200 ml diethyleneglycolmonomethyl ether at 60°C - was carried through two dewar flasks kept at -15°C into the reaction flask by a stream of argon within 2h. In addition, during the reaction time 0.1 g palladium-(II)-acetate was added twice. After an additional hour the reaction mixture was filtered, and the solvent was removed in vacuo and the residue purified by chromatography on silica (column 280x24 mm, 0.063-02 mm) using n-hexane/ether (80:20) as mobile phase. Yield 1.8 g (8.49 mmol, 85%); m.p. 117°C; ^1H NMR ($CDCl_3$, 80 MHz): 6.95-7.20 (m, 4H, H-arom.), 3.85-4.00 (m, 4H, H-ethylendioxy-), 3.30 (dd, 1H, C5-H), 3.22 (d, 1H, C1-H), 2.00 (m, 2H, exo- and endo-C9-H), 1.30 (m, 2H, C2-H and C4-H), 0.90 (m, 1H, exo-C3-H), 0.20 (dd, 1H, endo-C3-H); $J_{1,2} = J_{3,5} = 4$ Hz; Ms (m/z, 70 eV): 228 (M^+, 6.4%), 142 (100).

6,7-Benzotricyclo[3.2.2.0^{2,4}]6-nonen-8-one (45): A sample of 1.80 g (8.49 mmol) 8,8-ethylenedioxy-5,6-benzotricyclo[3.2.2.0^{2,4}]6-nonene (**43**) was dissolved in 50 ml ethanol and treated with 20 ml HCl/H_2O (1:3) at 40°C for 24 h. 200 ml water were added, and the mixture was extracted with three portions of 100 ml ether. The combined ether phases were washed with a solution of $NaHCO_3$ and water and dried with Na_2SO_4. The solvent was removed in vacuo to yield 1.50 g (8.15 mmol, 96%) **45** as a colorless solid. m.p. 65°C; ^1H NMR ($CDCl_3$, 80 MHz): 6.95-7.20 (m, 4H, H-arom.), 3.72 (d, 1H, C1-H), 3.51 (dd, 1H, C5-H), 2.25 (m, 2H, exo- and endo-C9-H), 1.44 (m, 2H, C2-H and C4-H), 0.38 (dd, 1H, exo-C3-H), -0.40 (ddd, 1H, endo-C3-H); MS (m/z, 70 eV): 184 (M^+, 22%), 142 (100);

6,7-Benzotricyclo[3.2.2.0^{2,4}]6-nonen-8-ol (46): A sample of 0.60 g (3.26 mmol) 6,7-benzotricyclo[3.2.2.0^{2,4}]6-nonen-8-one (**45**) was reduced with $LiAlH_4$ as described for the synthesis of exo/endo-7,8-benzobicyclo[4.2.2]7-decen-9-ol (**41**). Yield 0.58 g (3.12 mmol, 96%); m.p. 98°C; ^1H NMR ($CDCl_3$, 80 MHz): 6.95-7.20 (m, 4H, H-arom.), 4.05-4.40 (m, 1H, C8-H), 3.35 (ddd, 1H, C1-H), 3.23 (m, 1H, C5-H), 2.20-2.60 and 0.95-1.65 (m, 5H, exo/endo C9-H, C2-H, C4-H, OH), 0.18 (dd, 1H, exo-C3-H), -0.72 (ddd, 1H, endo-C3-H); MS (m/z, 70 eV): 186 (M^+, 2.3%), 142 (100).

8-Deutero-6,7-benzotricyclo[3.2.2.0^{2,4}]6-nonen-8-ol (47): The synthesis of **47** was performed as described for the undeuterated **46** using $LiAlD_4$. Yield 0.57 g (3.05 mmol, 93%); m.p. 98°C; the ^1H NMR spectrum of **47** was identical with the spectrum of **46** with the exception that the signal 4.05-4.40 ppm was missing. MS (m/z, 70 eV): 187 (M^+, 0.6%), 142 (100); determination of the degree of deuteration (MS, 70 eV): d_0 = 0.5%, d_1 = 99.1%, d_2 = 0.4%.

6,7-Benzotricyclo[3.2.2.0^{2,4}]6,8-nonadiene (14a): The compound was prepared from the alcohol **46** as described for **12b**. A sample of 500 mg (2.69 mmol) **46** and 1.10 g (5.78 mmol) p-toluenesulfonyl chloride was dissolved in 10 ml $CHCl_3$ and 1.7 ml dry pyridine were added at 0°C. The reaction mixture stirred at this temperature for 1 h and was kept at room temperature for another 24 h. After work-up the crude tosylate was dissolved in 25 ml dry benzene, and 0.8 g 18-crown-6 and 2.25 g (20 mmol) K-O-t-butylate were added. The reaction mixture was heated under reflux for 2 h. The purification was performed by chromatography on silica (40x15 mm, 0.063-0.2 mm) using pentane as mobile phase to yield 210 mg (1.25 mmol, 46%) **14a** as colorless oil which crystallized on cooling; m.p. 40°C (43°C[28]). The spectroscopic data are in accord with those reported by Kitahonoki.[28]

from the alcohol **47** as described for the undeuterated compound **14a**. A sample of 500 mg (2.69 mmol) **14b** yielded 230 mg (1.36 mmol, 50%) **14b**; m.p. 41°C; ^1H NMR (80 MHz, $CDCl_3$): 7.05 ppm (s, 4H, H-arom.), 6.75 (dd, 1H, C9-H), 4.00 (ddd, 2H, C1-H and C5-H), 1.40 (dd, 1H, exo-C3-H) and -0.35(ddd, 1H, endo-C3-H); ^{13}C NMR (100.61 MHz, $CDCl_3$): 141.50 ppm (s, q. C-arom.), 139.47 (d, C8 and C9), 125.21 and 123.18 (d, t. C-arom.), 41.38 (d, C1), 41.29 (d, C5), 19.81 (d, C2 and C4) and 15.90 (t, C3); MS (m/z, 70 eV): 170 (M^++1, 10%), 169 (M^+, 87), 168 (100); determination of the degree of deuteration could not be performed by mass spectrometry, because of exchange reactions, but was determined from the integrals in the ^1H NMR: d_0 = 1.0%, d_1 = 99.0%.

Preparative photoisomerizations:

The starting materials were dissolved in dry acetone and the solutions were stirred and irradiated in a quartz vessel, which was purged with N_2 prior and during the reaction and was cooled with tap water in a Rayonet-Photochemical Reactor with 16 Sunlight Phosphor lamps. The progress of the photoreactions was monitored by HPLC.

Irradiation of endo-6,7-benzotricyclo[3.2.2.0^{2,4}]6,8-nonadiene (14a): A solution of 150 mg (0.89 mmol) **14a** in 150 ml acetone was irradiated 15 min and the formation of 8,9-benzotetracyclo[4.2.0.0^{3,5}.0^{2,9}]nonene (**48**) was observed as the only product. Continuation of the irradiation yielded 7,8-benzotricyclo[4.2.0.0^{2,9}]3,7-nonadiene (**49**) as a secondary photoproduct. The irradiation was terminated after 2 h when 80% of the starting material were consumed. The solvent was removed in vacuo, and the residue was separated into three fractions by HPLC (LiChrosorb Si 100, C18, 10μ, 300x15.5 mm) with methanol/water (75:25). The first fraction contained starting material, the second **27** and the third **48**.

The ratio of the starting material and products in the reaction mixture was: **14a**:**27**:**48**=20:65:15.

27: yield 45 mg (0.27 mmol, 30%); ^{1}H NMR (400 MHz, $CDCl_3$): 7.19 ppm (m, 1H, H-arom.), 7.03 (m, 2H, H-arom.), 6.80 (m, 1H, H-arom.), 3.78 (dd, 1H, C6-H), 3.64 (ddd, 1H, C1-H), 2.15 (m, 1H, C5-H), 2.10 (dd, 1H, C9-H), 1.92 (m, 1H, C3-H), 1.85 (ddd, 1H, C2-H), 0.33 (m, 2H, exo- and endo-C4-H). The assignment of the signals could be performed by comparing the spectrum with the ^{1}H NMR spectrum of the deuterated compound **27** and by running a homoskalar correlated 2-D-NMR (COSY) of the deuterated compound. The following coupling constant could be obtained: $J_{1,2}$ = 6.5 Hz, $J_{1,6}$ = 6.0 Hz, $J_{1,9}$ = 7,5 Hz, $J_{2,3}$ = 6.5 Hz, $J_{2,9}$ = 7.5 Hz and $J_{5,6}$ = 6.0 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): 149.92 ppm (q. C-arom.), 125.80, 125.73, 123.18, 121.97 (d, t. C-arom.), 57.39, 49.11, 38.04, 34.92, 34.44 27.87 (d, C1, C2, C3, C5, C6, C9); 18.16 (t, C4); MS (m/z, 70 eV): 169 (M^++1, 22%), 168 (M^+, 74), 167 (100).

Irradiation of 8-deutero-endo-6,7-benzotricyclo[3.2.2.0.^{2,4}]6,8-nonadiene (14b): The irradiation and isolation of the products were performed as described for **14a**. Irradiation of 150 mg (0.89 mmol) yielded 55 mg (0.33 mmol, 36%) of an isotopomeric mixture of 1- and 9-deutero-endo-7,8-benzotetracyclo[4.2.0.0^{2,9}.0^{3,5}]nonene **27a/b**. ^{1}H NMR (400 MHz, $CDCl_3$): the position of the signals was identical as described for the undeuterated compound **14a**. 2.10 ppm (d, 0.417H, C9-H), 3.64 (m, 0.583H, C1-H); ^{2}H NMR (61.42 MHz, CCl_4): 3.64 ppm (s, 0.414D, C1-D), 2.10 (s, 0.586D, C9-D); ^{13}C NMR (100.61 MHz, $CDCl_3$): the spectrum is identical to the spectrum of **14a** with the exception that the signals at 49.01 and 34.42 ppm appeared as triplets. The degree of deuteration could not be determined by MS, because of exchange reactions. It was determined from the intensities of the corresponding ^{1}H NMR signals: d_0 = 0.6%, d_1 = 99.4%.

Irradiation of 6,7-benzobicyclo[3.2.2]6,8-nonadiene (15a): A solution of 200 mg (1.20 mmol) **15a** in 200 ml acetone was irradiated, and the formation of 7,8-benzotricyclo[4.2.0.0^{2,9}]nonene (**28**) was observed as the only product after 15 min. On longer irradiation times the formation of 6,7-benzobicyclo[3.2.2]nonene (**49**) as second photoproduct was observed. The irradiation was terminated when 70% of the starting material was consumed. The composition of the reaction mixture was **15a**:**28**:**49** = 30:50:20. This mixture was separated by HPLC (LiChrosorb Si 100, C18, 10µ, 300x15.5 mm) with methanol/water (75:25). The first fraction contained starting material, the second **28** and the third **49**.

28: 70 mg (0.40 mmol, 33%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.21 ppm (dd, 1H, H-arom.), 7.07 (dd, 2H, H-arom.), 6.96 (m, 1H, H-arom.), 3.56 (m, 1H, C6-H), 2.28 (m, 1H, C9-H), 1.95 (dd, 1H, C1-H), 1.87 (ddd, 1H, exo-C5-H), 1.71 (ddd, 1H, H-aliph.), 1.64 (m, 1H, H-aliph.), 1.25 (m, 2H, H-aliph.) and 1.00 (m, 2H, H-aliph.); $J_{1,2}$ = 7.4, $J_{1,6}$ = 7.4, $J_{1,9}$ = 5.2, $J_{2,9}$ = 6.8, $J_{6,5\text{-endo}}$ = 2.0, $J_{6,5\text{-exo}}$ = 0 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): 150.31 ppm (s, q. C-arom.), 144.51 (s, q. C-arom.), 126.6, 126.3, 124.8, 124.4 (d, t. C-arom.), 38.61 (d, C9), 28.00 (d, C6), 25.70, 17.85, 17.01 (t, C4, C5 and C6), 22.30 (d, C2), 19.40 (d, C1); MS (m/z, 70 eV): 170 (M^+, 78%), 169 (17), 141 (100);

49: 10 mg (0.06 mmol, 5%) m.p. 32°C; ^{1}H NMR (80 MHz, $CDCl_3$): 7.10-7.20 ppm (m, 4H, H-arom.), 3.02 (m, 2H, C1-H and C5-H) and 1.2-2.0 (m, 10H, H-aliph.); MS (m/z, 70 eV): 172 (M^+, 36%), 171 (10), 129 (100);

Irradiation of 8-deutero-6,7-benzobicyclo[3.2.2]6,8-nonadiene (15b): The irradiation and isolation of the products was performed as described for **15a**. Irradiation of 120 mg (0.70 mmol) **15b** in 150 ml acetone yielded the isotopomeric mixture of 1- and 9-deutero-7,8-benzotricyclo[4.2.0.0^{2,9}]nonene **(28a/b)** and 8-deutero-6,7-benzobicyclo[3.2.2]nonene **(50)**

28a/b yield 55 mg (0.32 mmol, 46%) as a colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): 7.21 ppm (dd, 1H, H-arom.), 7.07 (dd, 2H, H-arom.), 6.96 (m, 1H, H-arom.), 3.56 (m, 1H, C6-H), 2.28 (d, 0.475H, C9-H), 1.95 (t, 0.525H, C1-H), 1.87 (ddd, 1H, exo-C5-H), 1.71 (ddd, 1H, H-aliph.), 1.64 (m, 1H, H-aliph.), 1.25 (m, 2H, H-aliph.) and 1.00 (m, 2H, H-aliph.); ^{2}H NMR (61.42 MHz, CDCl$_3$): 2.28 ppm (s, 0.53D, C9-D), 1.95 (s, 0.47D, C1-D); ^{13}C NMR (100.61 MHz, CDCl$_3$): 150.31 ppm (s, q. C-arom.), 144.51 (s, q. C-arom.), 125.78, 125.53, 124.04, 123.61 (d, t. C-arom.), 38.25 (d, C9), 27.77 (d, C6), 25.65, 17.85, 17.01 (t, C4, C5 and C6), 22.07 (d, C2), 19.25 (d, C1); MS (m/z, 70 eV): 172 (M$^+$+1, 8%), 171 (M$^+$, 63), 142 (100).

50: yield 16 mg (0.09 mmol, 13%) m.p. 32°C; ^{1}H NMR (80 MHz, CDCl$_3$): 7.00-7.20 ppm (m, 4H, H-arom.), 3.00 (m, 2H, C6-H and C9-H), 1.20-2.00 (m, 9H, H-aliph.); MS (m/z, 70 eV): 173 (M$^+$, 38%), 172 (9), 130 (100).

Irradiation of 2-deutero-5,6-benzobicyclo[2.2.1]heptadiene (12b): A solution of 120 mg (0.85 mmol) **12b** and 40 mg (0.33 mmol) acetophenone in 50 ml benzene was irradiated 90 min until all starting material was consumed. The solvent was removed in vacuo and the residue dissolved in pentane and filtered through a layer of 15 mm silica. The solvent was removed in vacuo to yield 705 mg (4.93 mmol, 70%) of an isotopomeric mixture of 1- and 2-deutero-3,4-benzotricyclo[2.2.0.0^{2,7}]heptene **(25a/b)** as the only product; ^{1}H NMR (250 MHz, CDCl$_3$): 7.05-7.6 ppm (m, 4H, H-arom.), 3.30-3.55 (m, 1.631H, C1-H and C5-H), 3.00 (dddd, 1H, exo-C6-H), 2.65 (d, 0.429H, C2-H), 2.1 (dd, 1H, C7-H) and 0.9 (dd, 1H, endo-C6-H); $J_{5,6endo}$ = 0 Hz, $J_{5,6exo}$ = 7.6, $J_{5,7}$ = 5.33, $J_{6exo,6endo}$ = 8.9, $J_{1,6exo}$ = 3.26 and $J_{2,7}$ =5.33 obtained by decoupling experiments. ^{2}H NMR (250 MHz, CCl$_4$): 2.65 ppm (s, 0.585D, C2-D), 3.35 (s, 0.415D, C1-D); ^{13}C NMR (250 MHz, CDCl$_3$): 149.3 and 142.4 ppm (s, q. C-arom.), 125.7, 124.7, 123.0 and 119.8 (d, C-arom.), 45.1 (d, C5), 43.2 (d, C2-H), 43.1 (t, C2-D), 29.4 (t, C6), 29.1 (d, C7) and 19.1 (d, C1) 19.0 (t,C1-D); MS (m/z, 70 eV): 143 (M$^+$, 76%), 142 (100); degree of deuteration (MS, 14 eV): d_0 = 5.0%, d_1 = 94.8%, d_2 = 0.2%.

Irradiation of 2-deutero-5,6-benzobicyclo[2.2.2]octadiene (13b): A solution of 500 mg (3.21 mmol) **13b** in 500 ml acetone was irradiated 6 h. The solvent was removed in vacuo and the product mixture separated by HPLC (LiChrosorb Si 60, C18, 5μm, 150x15 mm) using methanol/water (75:25) as mobile phase. The first fraction contained starting material, the second fraction an isotopomeric mixture of 1- and 2-deutero-3,4-benzotricyclo[3.2.0.0^{2,8}]octene **(26a/b)** and the third fraction an exo/endo mixture of 5-deutero-2,3-benzobicyclo[2.2.2]octene **(51)**.

26a/b: yield 205 mg (1.28 mmol, 40%) as a colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): 7.12, 7.02, 6.97 and 6.89 ppm (m, 4H, H-arom.), 3.50 (dd, 1H, C5-H), 2.73

(dd, 0.577H, C1-H), 2.30 (d, 0.435H, C2-H), 2.11 (dddd, 1H, exo-C6-H), 1.70 (m, 2H, endo-C6-H and C8-H), 1.54 (dd, 1H, endo-C7-H) and 1.04 (ddd, 1H, exo-C7-H); ^{2}H NMR (250 MHz, CCl_4): 2.73 ppm (s, 0.431D, C1-D), 2.30 (s, 0.569D, C2-D); ^{13}C NMR (250 MHz, $CDCl_3$): 148.8 and 142.7 ppm (s, q. C-arom.), 126.1, 125.9, 123.6 and 122.8 (d, t. C-arom.), 48.9 (d, C2-H), 48.8 (t, C2-D), 44.2 (d, C6), 38.3 (d, C5), 33.2 (d, C8), 29.3 (d, C1) and 22.6 (t, C7); MS (m/z, 70 eV): 157 (M^+, 30%), 156 (16), 129 (100); degree of deuteration (MS, 14 eV): d_0 = 1.2%, d_1 = 98.4% and d_2 = 0.4%.

Quantum yields:

Method A: Light from an Osram HBO 200 W high intensity mercury lamp was passed through a Bausch and Lomb high intensity monochromator, entrance slit 5.4 and exit slit 3.0 mm, giving a band pass of 20 nm at half peak height. Samples were irradiated in 1 cm quartz cells in an electronic actinometer calibrated by ferrioxalate actinometry. Solutions use acetone as solvent and were degassed 15-30 min prior and during photolysis using deoxygenated nitrogen. The values listed result from the average of at least three measurements. All runs were conducted to a conversion of at least 6% and may be taken to be kinetic.

Method B: Relative quantum yields were obtained by irradiations of the undeuterated and the deuterated compound simultaneously with a merry-go-round apparatus in a Rayonet Photochemical Reactor. Solutions of the undeuterated and deuterated compounds of the same concentrations were prepared in acetone or benzene. 3 ml of these solutions were placed into 3 quartz tubes (1 cm internal diameter) at a time giving a set of six tubes, which were irradiated with Sunlight Phosphor lamps. To minimize errors produced by optical inhomogenity the quartz tubes were interchanged, and a second run was performed.

Analysis was performed by HPLC using internal standards on Shandon Hypersil ODS 3μm, 125x4.6 mm, using methanol/water (80/20) as mobile phase.

The results are listed in the order: starting material: solvent, concentration (mmol/l), method of quantum yield determination, quantum yields of formation: **12b**: benzene containing 39 mmol/l acetophenone, 9.00, B, Φ=0.58±0.05; **12c**: benzene containing 39 mmol/l acetophenone, 9.00, B, Φ=0.58±0.05; **12d**: benzene containing 39 mmol/l acetophenone, 9.00, B, Φ=0.58±0.05; **13b**: acetone, 6.00, A, Φ=0.052±0.002; **14b**: acetone, 6.00, A, Φ=0.10±0.01; **15b**: acetone, 6.00, B, Φ=0.024±0.002.

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