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PHOTOCHEMICAL DEUTERIUM EFFECT ON THE REARRANGEMENT OF TRIPTYCENE

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Abstract-Triptycene monodeuterated at the bridgehead position shows in direct and sensitized irradiation a photochemical isotope effect k_H/k_D=2.2-2.4. From quantum yield of undeuterated, $\Phi_{H,H}$=0.33 and monodeuterated triptycene, $\Phi_{H,D}$=0.24 was concluded that the effect stems from differences in the reaction rates and not from differences in the radiationless deactivations.

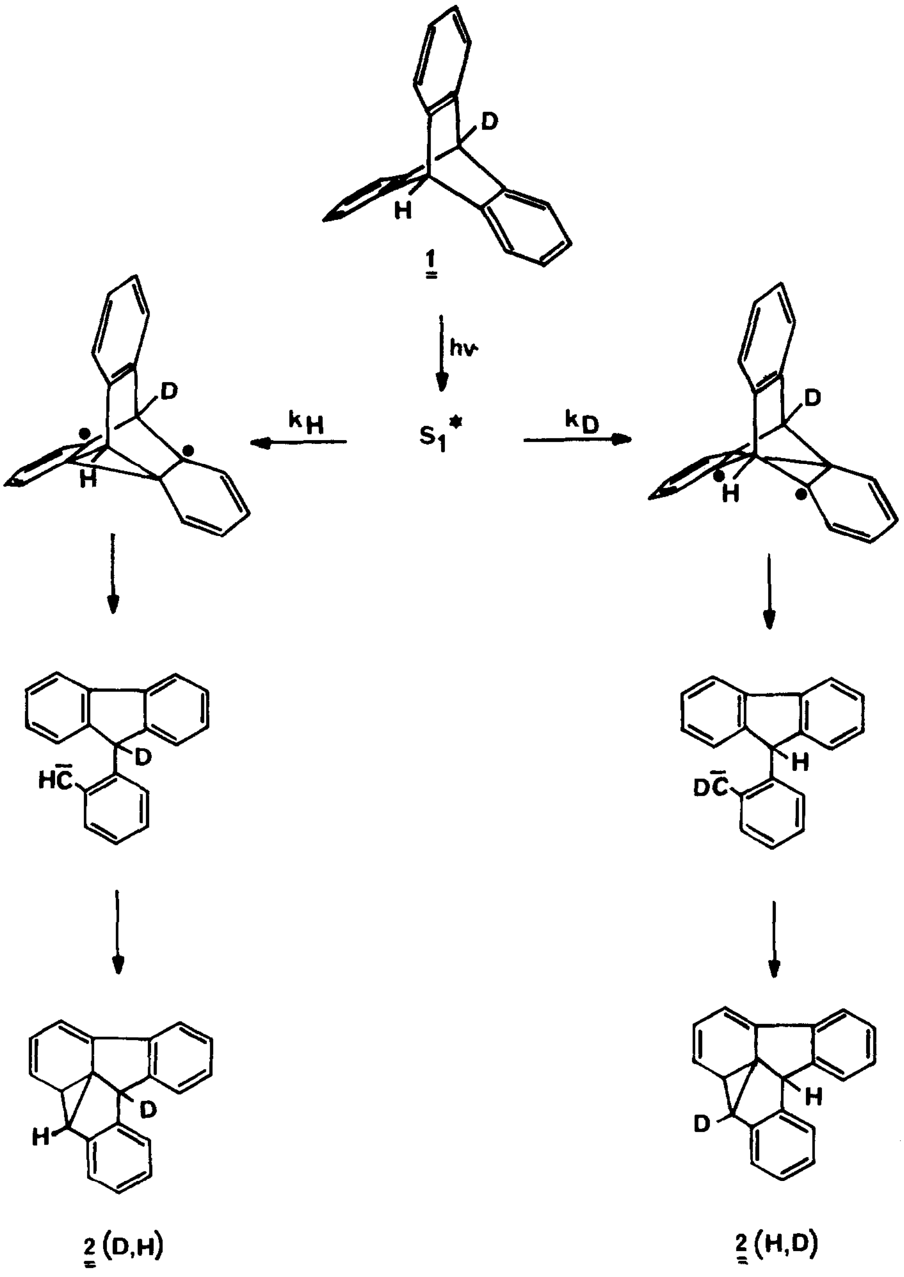
The photorearrangement of triptycene was shown to proceed via the intermediate formation of a carbene, which adds to an aromatic π-bond leading to a norbornadiene derivative.[1] Following the general interest in the control of the regioselectivity of photochemical rearrangements[2] Iwamura et al. investigated the photochemical bridging regioselectivity in bridgehead substituted 9,10-(o-benzeno)-9,10-dihydroanthracenes (triptycenes) and found that bridging was prefered on the site near to the substituent X independent of its ability to donate or accept electrons.[3] An exception to this finding seemed to be alkyl groups, where the bridging selectivity was altered.

We have chosen this system to investigate the photochemical isotope effect on the regioselectivity of bridging (X=D) with the hope to gain insight in the importance of isotopic substitution on the reaction rate. In a previous paper we have reported on a deuterium effect in the photorearrangement of homodibenzobarrelene.[4]

A great number of deuterium isotope effects in photoreactions was reported. In these cases C-H or C-D bonds were broken or at least stretched to an extent that migration of hydrogen or deuterium could occur.[5] Isotope effects of this type can be classified as primary isotope effects. On the other hand examples for photochemical isotope effects corresponding to thermal secondary isotope effects are rare and not well understood.[6] Strong deuterium effects were found for triplet lifetimes of deuterated hydrocarbons. The radiative lifetimes increased and were nearly equal to the maximum radiative lifetime.[7] Contrary to these results, no significant deuterium effect on the singlet lifetimes τ_s and the quantum yields of fluorescence Φ_F of aromatic compounds could be observed.[8] It was concluded that the probability of internal conversion (IC) is much lower than for intersystem crossing (ISC) or fluorescence. In both cases it was argued that Franck-Condon factors are responsible for the results obtained.

The radiationless transitions IC and ISC are conversions of electronic energy into nuclear motion as it is the case with the photoreactions and the distinction between photophysical and photochemical processes is confused.[9] For this reason, we suspected that isotopic substitution at the bridgehead position in triptycene might show an effect on the reaction rate, if the energy hypersurfaces of the electronic excited triptycene and the intermediate - biradical or carbene - are placed properly.

Lacking the possibility to determine singlet lifetimes to gain information on the reaction rates k_r we decided to measure the deuterium isotope effect k_H/k_D directly. This was done by the measurement of the regiospecifity of the rearrangement of triptycene *1* (H,D) deuterated at one bridgehead position.



SCHEME 1. Overall Reaction Mechanism

RESULTS

Syntheses and Photorearrangements

9,10-Benzeno-9-deutero-10-hydroanthracene (triptycene) *1*(D,H) was prepared by benzyne addition to 9-deuteroanthracene,[10] which was obtained from 9-bromoanthracene via the Grignard compound. The deuterium distribution was determined by mass spectroscopy to d_0=2.42%, d_1=92.47% and d_2=5.11%.

Direct irradiation of triptycene *1*(H,H) in diethylether with light of 254 nm yielded exclusively 2,3,5,6-dibenzo-tetracyclo$[5.4.1.0^{4,12}.0^{8,12}]$ 2,5,9,11-dodecatetraene(*2*), which was firstly obtained by Walsh[11] and Turro.[12] No secondary products were formed. The photorearrangement of *1*(H,D) yielded the isotopomeric products *2*(H,D) with deuterium on the cyclopropylring and *2*(H,D), with hydrogen in the benzylic position according to the routes k_H or k_D of the rearrangement. From mass spectra of the isotopomeric mixture the deuterium distribution was obtained: d_0=5.38%, d_1= 88.0% and d_2=6.61%. Again *2*(H,D) and *2*(D,H) proved to be photochemically stable. Acetophenone sensitized runs in benzene of *1*(H,H) and *1*(D,H) at 310 nm yielded the same photoproducts *2*(H,H) and *2*(H,D) plus *2*(D,H) respectively after prolonged periods of irradiation. In these experiments the photoproducts could be shown to be stable, if molecular oxygen was carefully excluded.

The preparative isolation of the photoproducts was achieved by reversed phase HPLC. Control experiments with a 2:1 mixture of *2*(H,D) and *2*(D,H) did not show any deuterium scrambling to occur under the chromatographic conditions.

Determination of the ratio of the isotopomeric compounds 2(D,H) *and 2*(H,D)

The position and the degree of deuterium substitution were determined by the integration differences in the ^{1}H-NMR spectra of labeled and unlabeled compounds. The signals of the cyclopropylhydrogen H_A appeared well separated as a broadened doublet at δ=2.46 ppm, whereas the 9-fluorenylhydrogen H_B showed its resonance signal without any overlap as a broad singlet at δ=4.46 ppm. The three olefine hydrogen atoms of the norcaradien moiety gave rise to a signal without superposition at δ=6.13 ppm with the intensity three. This signal was taken as an internal standard for the evaluation of the isotopic distribution. Control experiments with undeuterated *2* yielded the mean values for the intensity ratios of H_B and H_A, I_B/I_A=1.010 and H_B and $H_{Standard}$, $3I_B/I_{St}$=1.0095

Quantum yield determination

Analytical quantities of *1*(H,H) and *1*(H,D) were irradiated with a HBO 200 lamp through a Bausch and Lomb high intensity monochromator. The light intensity was measured by a unit described by Amrein et al.[12] and was calibrated by ferrioxalate actinometry. The photochemical conversions were monitored by HPLC. Table 2 lists the quantum yields which were obtained by extrapolation to zero conversion. The results obtained are collected in table 2.

Interpretative discussion

The regiospecifity of the photorearrangement caused by deuterium substitution can be easily evaluated from the integral values of the ^{1}H-NMR of the hydrogen atoms H_A and H_B. The ratio of the mole fractions $x_{2(H,D)}/x_{2(D,H)}$ is equal to the ratios of the reaction rates k_H/k_D which is equivalent to the kinetic deuterium isotope effect. Correc-

Table 1

Irradiated compounds	Integral (mm) H_A	H_B	H_{St}	Number of Measurements
1(H,H)	14.82	14.97	44.83	16
1(H,D) dir.	13.46	6.44	41.77	18
1(H,D) sens.	13.46	6.08	47.20	23

tions have to be introduced for undeuterated photoproduct. The following formulas can be deduced with $I'_{St}=I_{St}/3$.

$$x_{2(H,D)}=I_A/I'_{St}-x_{2(H,H)}$$

and

$$x_{2(D,H)}=I_B/I'_{St}-x_{2(H,H)}.$$

It follows

$$k_H/k_D=\frac{I_A-I'_{St}\cdot x_{2(H,H)}}{I_B-I'_{St}\cdot x_{2(H,H)}}.$$

Taking the data of table 1 and inserting $x_{2(H,H)}$ from the deuterium distribution obtained by mass spectroscopy the following values for the deuterium effect can be evaluated.

Direct irradiation:

$$k_H/k_D=2.35\pm0.06$$

Sensitized irradiation:

$$k_H/k_D=2.41\pm0.09$$

As was noted a minor amount of triptycene was dideuterated. We could not localize the position of the second deuterium atom. If we assume at the worst that both bridgehead atoms were deuterated and recalculate k_H/k_D the following values for direct and sensitized irradiations are obtained. k_H/k_D(dir.)= 2.36 and k_H/k_D(sens.)=2.40

Table 2: Quantum yields of product formation in the rearrangement of triptycenes *1*(H,H) and *1*(D,H)

Run[a)]	Sample	Sensitizer	Absorbance[b)]	$\Phi_{appear.}$[c)]
1	*1*(H,H)	-	1.49	0.32
2	*1*(H,H)	-	2.56	0.32
3	*1*(H,H)	-	3.67	0.33
4	*1*(H,D)	-	2.33	0.23
5	*1*(H,H)	Acetophenone[d)]	-[e)]	2.04×10^{-2}
6	*1*(H,H)	Acetophenone[f)]	-[e)]	1.12×10^{-2}

a) in all runs λ(irradiation) was 250 nm, with the exception of run 5 and 6 (315 nm); b) the absorbance was determined at 250 nm; c) all quantum yields were obtained by extrapolation to zero conversion; d) sensitizer concentration 1×10^{-2} mol/l; e)triptycene concentration 5.7×10^{-4} mol/l; f) sensitizer concentration 3.0×10^{-2} mol/l.

The ratio of the quantum yields $\Phi_{H,H}/\Phi_{H,D}$ can be calculated from the values given in table 2 and is found to be 1.37±0.12. The deuterium effect on the quantum yield appears to be much lower than the kinetic isotope effect.

Iwamura found that the excited photoreactive state of *1*(H,H) is probably a singlet state. It was not possible to quench the photoreaction of *1*(H,H) with piperylene and triptycene substituted with an acetyl group at the bridgehead position formed a ketocarbene in the singlet state, which gave a Wolff-rearrangement.

The isotopic effects found in the direct and sensitized irradiations are identical within the experimental error. This implies that the same excited state is reactive in both experiments. Since the quantum yields of acetophenone sensitized irradiations are only about 5 to 10% of those found in direct irradiations and go down with increasing sensitizer concentration, it has to be assumed that the small amount of photorearrangement in the sensitized runs is the consequence of direct light capture by the educt.

The rationalization of the kinetic deuterium effect observed in this work requires a close consideration of the deactivating processes of the excited state. Since no fluorescene could be observed under the experimental conditions, only radiationless processes as IC or ISC will compete with the photoreaction. As a working hypothesis it will be assumed that the deuterium isotope effect is exclusively the result of different probablities of *1*(H,D) in the excited singlet state to pass from the energy hypersurface of the singlet to the hypersurface of an intermediate - biradiacal or carbene - on the site of the hydrogen or the deuterium atom. (Scheme 1) Vibronic mixing of the hypersurfaces of the singlet and the intermediate ought to be the determining factor. Under these assumptions it is possible to connect the quantum yields for *1*(H,H) and *1*(H,D) with the kinetic isotope effect k_H/k_D.

$$\Phi_{H,D} = \frac{k_{H,D}}{k_{H,D}+k_d} \quad \text{and} \quad \Phi_{H,H} = \frac{k_{H,H}}{k_{H,H}+k_{d'}}$$

k_d and $k_{d'}$ are the sums of the rates of all radiationless processes. The ratio $k_H/k_D=2.3$ means that the probability of *1*(H,D) to leave the singlet hypersurface is 2.3 times greater on the hydrogen site than on the deuterium site. Consequently $k_{H,H}=2k_H$ and $k_{H,D}=k_H+k_D$. From the quantum yields the ratios of the rates of radiationless deactivation k_d and k_d' and k_H can be evaluated. The values $k_d/k_H=4.25$ and $k_{d'}/k_H=4.52$ are equal within experimental error.

This agreement indicates that the entire deuterium effect stems from differences in the reaction rates and there is no influence on the radiationless processes in this rearrangement.

Photochemical isotope effects caused by Franck-Condon factors require that vibrations of high frequency are operating and that the electronic energy gap between the excited electronic educt and the primary photochemical product - in this case the intermediate - is high. C-H vibrations belong to the highest frequency vibrations in organic molecules. Consequently, the first requirement is fulfilled. The second requirement makes it necessary to discuss the energies of the possible intermediates. The biradical intermediate ought to be an extremely high energetic species, because of the loss of aromaticity in both benzene rings. A thermochemical estimation puts the energy to 480 kJ/mole above the ground state of the educt. Contrary, the carbene intermediate is only by 334 kJ/mole more energetic. These considerations argue against the biradical and favour the carbene intermediate. Iwamura arrived at similar conclusions by the rationalization of the electronic effects of substituents on the regiospecifity of the photorearrangement. Even the reversed regiospecifity of the photorearrangement of alkyl substituted triptycenes can be explained by the effect of Franck-Condon factors. The photochemical deuterium isotope effect as described here is by no means unique. Other examples were found and are investigated presently. In addition the appearance of an isotope effect can be a valuable mechanistic probe for the primary product forming photochemical step.

EXPERIMENTAL

Proton NMR spectra were determined on Varian T-60 and a Bruker WH-90; Mass spectra were obtained using a Varian MAT-CH-5. The calculations of the degree of deuteration were performed by the method of Budzikiewicz.[14] UV spectra were determined on a Cary 17 spectrometer.

Preparative irradiations were performed in a Rayonet-Photochemical Reactor, RPC 100 of the Southern New England Ultraviolet Company equipped with RPR 2537 Å or RPR 3000 lamps respectively.

Quantum yield irradiations were performed using a microbench apparatus similar to that described by Zimmerman.[15] Light from an Osram HBO 200 W high pressure mercury lamp was passed through a Bausch and Lomb Model 33-86-75 high intensity monochromator, entrance slit 5.4 mm and exit slit 3.0 mm, giving a band pass of 20 nm at half peak height. Wavelength setting will be given below. Samples were irradiated in 1 cm quartz cells in an electronic actinometer calibrated by ferrioxalate actinometry.[16] Solutions used ether as solvent and were degassed 15 min. prior to and during photolysis using deoxygenated nitrogen. After irradiations of the solutions an aliquot of anthracene was added as internal standard and deluted to 25 ml with methanol for analysis with HPLC by reversed phase.

Analytical and semipreparative separations were performed with HPLC apparatus consisting of a Waters M 6000 pump, Waters UK 6 injector and LDC UV III detector at 254 nm. Peak height and peak area determinations were performed with LDC 308 computing integrator.

9-Deuteroanthracene

A solution of 13 g (51 mmol) 9-bromoanthracene in 100 ml dry ether and 2.5 g Grignard magnesium was refluxed under nitrogen for 24 hours. The reaction was started by addition of 0.1 ml ethylbromid. 7.5 g D_2O was added to the reaction mixture and the refluxing continued for 30 minutes. After addition of deluted HCl the product was filtered and recrystallized from toluene. 9.8 g (71%); mp.: 217-218°C; MS: d_0=2.11%, d_1=94.43% and d_2=3.46%; ^{1}H-NMR: ($CDCl_3$) δ=7.3-8.0 (m, 8H); δ=8.3 (s, 1H).

9,10-(o-Benzeno)-9-deutero-10-hydroanthracene 1(D,H).

9-Deuteroanthracene was converted to *1*(D,H) by the method of Friedman.[10] 12.5 g 9-deuteroanthracene yielded 5.2 g (29.5%), which was further purified for photochemical experiments by liquid chromatography. Column: 30 cm, 2 cm ɸ, silica 60, 230 mesh, ASTM, plus 2% fluorescence indicator F_{254}, Merck using n-hexane/CH_2Cl_2=9:1 as mobile phase. A centre cut of the eluting band was isolated and the solvent evaporated in *vacuo* yielding colorless crystalls of *1*(D,H). mp.: 255-256°C: MS: d_0=2.4%, d_1=92.5% and d_2=5.1%; ^{1}H-NMR: ($CDCl_3$) δ=6.4 (s, 1H, bridgehead); δ=6.8-7.5(m, 12H).

Direct irradiation of 9,10-(o-Benzeno)-9-deutero-10-hydroanthracene 1(D,H).

0.305 g *1*(D,H) was desolved in 500 ml dry ether (1.2×10^{-3}M) and irradiated under nitrogen 90 minutes at 254 nm with low pressure mercury lamps in a Rayonet-Reactor to the conversion of 68%. The ether was evaporated in *vacuo* and the photoproduct purified by semipreparative HPLC on silica (LiChrosorb Si 60, 5 µm, Merck) 250x 7.8 mm, n-hexane/Et_2O/isopropanol=99.58/ 0.125/0.025 or LiChrosorb 100, C18, 10 µm; 280x7.8 mm methanol/H_2O=9/1. 102 mg pure 4D-(or 7D-)2,3,5,6-dibenzotetracyclo $[5.4.1.0^{4,12}.0^{8,12}]$ 2,5,9,11-dodecatetraene <u>2</u> was isolated by extraction with CH_2Cl_2; mp.: 137-138°C; ^{1}H-NMR ($CDCl_3$) δ=1.26 (m, 1H-cyclopropyl); 2.47 (m, H-cyclopropyl) and 4.50 (s.,H-benzylic) adding to 1H;

6.13 (m, 3H-olefin.), 7.2-7.9, (m, 8H-arom.). MS: d_o=5.38%, d_1=88.02% and d_2=6.61%. The integral values for the protons H_A and H_B of the NMR are given in tab. 1.

Sensitized irradiations of 1(D,H).
0.287 g (1.13x10^{-3} mol) *1*(D,H) and 0.188 g (1.56x10^{-3} mol) acetophenone, purified by destillation, were desolved in 500 ml benzene and irradiated at 300 nm 100 minutes in a Rayonet-Reactor. The solvent was removed by destillation in *vacuo*, the residual mixture desolved in n-hexane and the product separated and purified by HPLC on LiChrosorb Si 100, 10 µm, C18-phase, 280x7.8 mm, using methanol/H_2O= 9/1 as mobile phase. After extraction 26 mg <u>2</u> as the only product was obtained beside unchanged *1*(D,H). MS: d_o=5.12%, d_1=89.3% and d_2=5.58%. The integral values of the NMR for the protons H_A and H_B are given in tab. 1.

Summary of quantum yield results for the direct irradiations.

The equipment and the procedure described above was used. The wavelength setting was 250 nm. The data are listed as follows. Starting material, absorbance at 254 nm, quanta absorbed, procentual conversion, quantum yield of formation <u>2</u>.

Run 1, *1*(H,H), 1.49, 8.09x10^{-7}mEinstein, 6.17%, Φ=0.310.
Run 2, *1*(H,H), 1.49, 12.37x10^{-7}mEinstein, 9.29%, Φ=0.305.
Run 3, *1*(H,H), 1.49, 16.80x10^{-7}mEinstein, 12.4%, Φ=0.300.
Run 4, *1*(H,H), 2.56, 7.87x10^{-7}mEinstein, 3.50%, Φ=0.311.
Run 5, *1*(H,H), 2.56, 12.07x10^{-7}mEinstein, 5.32%, Φ=0.308.
Run 6, *1*(H,H), 2.56, 15.89x10^{-7}mEinstein, 6.98%, Φ=0.307.
Run 7,. *1*(H,H), 3.67, 8.12x10^{-7}mEinstein, 2.57%, Φ=0.317.
Run 8, *1*(H,H), 3.67, 20.56x10^{-7}mEinstein, 6.14%, Φ=0.299.
Run 9, *1*(H,D), 2.33, 3.70x10^{-7}mEinstein, 1.21%, Φ=0.210.
Run 10, *1*(H,D), 2.33, 7.99x10^{-7}mEinstein, 3.12%, Φ=0.248.
Run 11, *1*(H,D), 2.33, 12.31x10^{-7}mEinstein, 4.25% Φ=0.210.
Run 12, *1*(H,D), 2.33, 16.75x10^{-7}mEinstein, 5.38% Φ=0.205.

Sensitized quantum yield.

Acetophenone was used as sensitizer and benzene as solvent. The concentrations of acetophenone and triptycene were adjusted that >96% of the light was absorbed by the sensitizer at 315 nm. Concentration of triptycene was 5.7x10^{-4}M.

Run 1, acetophenone (1x10^{-2}M), conversion 0.022%, 4.71x10^{-7}mEinstein, Φ= 7.86x10^{-3}.
Run 2, acetophenone (1x10^{-2}M), conversion 0.067%, 5.40x10^{-7}mEinstein, Φ= 20.37x10^{-3}.
Run 3, acetophenone (3x10^{-2}M), conversion 0.034%, 7.22x10^{-7}mEinstein, Φ= 11.2x10^{-3}.

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