Synthesis and Photochemical Properties of 1,3-Di-9-anthryl-2-propanol, 1,3-Di-9-anthrylacetone, and Related Propano-Linked Anthracenes

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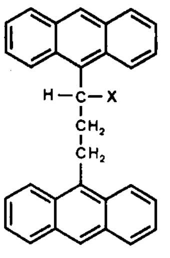
9-Anthryllithium reacts with epichlorohydrin to give 1,3-di-9-anthryl-2-propanol via 3-(9-anthryl)-1-chloro-2-hydroxypropane and 3-(9-anthryl)-1,2-epoxypropane. Oxidation of dianthryl-2-propanol with Dess-Martin reagent gave 1,3-di-9-anthrylacetone. Various other 1,3-bichromophoric anthracenes were synthesized by way of C-methylation of dianthrylacetone, 1,3-di-9-anthryl-1-propanone, and 1,3-di-9-anthrylpropenone. 9-Anthrylacetone, formed as byproduct in the reaction of anthryllithium with epichlorohydrin, was prepared from 9-anthrylacetaldehyde by Grignard reaction with methylmagnesium iodide and subsequent oxidation. The excited-state properties of dianthryl-2-propanol, dianthrylacetone, 1,3-di-9-anthryl-2-methyl-1-propanone, 1,3-di-9-anthryl-2-methyl-2-propanol, diastereomeric 1,3-di-9-anthryl-1-butanols, 1,3-di-9-anthryl-2-butanone, 1,3-di-9-anthryl-1-butanone, and diastereomeric 1,3-di-9-anthryl-2-methyl-1-butanones have been evaluated by fluorescence quantum yields, and by quantum yields for the isomerization by intramolecular $4\pi + 4\pi$ cycloaddition. Dianthryl-2-propanol, 1,3-di-9-anthryl-2-methyl-2-propanol, dianthrylacetone, diastereomeric 1,3-di-9-anthryl-1-butanols, and 1,3-di-9-anthryl-2-butanone isomerize in their excited singlet state with quantum yields of 0.046, 0.021, 0.25, 0.23, and 0.22, respectively. The photochemical isomerization of those 1,3-bichromophoric anthracenes which are characterized by a 9-anthroyl chromophore involves the excited triplet state, and the cyclization quantum yield may be as high as 0.72.

Introduction

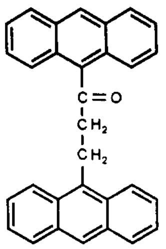
Bichromophoric anthracene derivatives are of photochemical interest because conformation-dependent interactions between the π-systems may be detectable by emission spectroscopy and may be borne out in the mode and efficiency of isomerization by cycloaddition.[1,2] As for the series di-9-anthrylmethane through 1,10-di-9-anthryldecane, the quantum yields for the excited singlet state isomerization by $4\pi + 4\pi$ cycloaddition vary between 0.0004 for the decano linked bichromophore and an optimal value of 0.24 obtained for 1,2-di-9-anthrylethane.[3-6] The quantum yield for the photoisomerization of 1,2-di-9-anthrylethanol (Φ = 0.35) exceeds that of the parent dianthrylethane, and it is conceivable that the enhanced photoreactivity of dianthrylethanol is due to a more favorable ground-state conformation.[7]

The separation of the two chromophores by three carbon atoms facilitates parallel overlap of the anthracene π-systems, and the resultant interplanar distance of about 2.5 Å should be conducive to intramolecular cycloaddition.[7] However, the photochemical cyclomerization of both 1,3-di-9-anthrylpropane (**1a**) and 1,3-di-9-anthryl-1-propanol (**1b**) is less efficient (Φ = 0.14) than that of dianthrylethane.[2,3] Photoexcited 1,3-di-9-anthryl-1-propanone (**2**) does undergo the analogous isomerization with a quantum yield of 0.65,[7] which is the highest quantum yield ever observed for an intramolecular cyclomerization of a bichromophoric anthracene. However, in this case, the photochemistry is governed by the propensity of the conjugated 9-anthroyl chromophore to undergo intersystem crossing, i.e., the isomerization does not proceed in the excited singlet state but involves the triplet state which is characterized by longer lifetime.



1a: X = H

1b: X = OH



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The photochemistry of 1,3-di-9-anthrylalkanones in which the carbonyl group is not conjugated with the aromatic π-system has not previously been studied. Nonconjugated dianthrylalkanones are expected to react in their excited singlet state, since intramolecular triplet sensitization should be inefficient in view of the electron spectral separation of the anthracene and carbonyl chromophores, which facilitates virtually exclusive photoexcitation of the anthracene chromophore.[2]

We have synthesized 1,3-di-9-anthrylacetone and some generically related bichromophoric anthracenes and investigated their photochemical isomerization.

Results and Discussion

Syntheses. The route chosen for the synthesis of dianthrylacetone (**6**) is outlined in Scheme I. Thus, 1,3-di-9-anthryl-2-propanol (**5**) was found to be accessible in a one-pot reaction from 9-anthryllithium (A-Li) and epichlorohydrin. A typical run involving A-Li (12 mmol) and epichlorohydrin (6 mmol) afforded **5** in 36% yield, together with 3-(9-anthryl)-1,2-epoxypropane (**4**; 21% yield). 9-Anthrylacetone (**8**), isolated in about 20% yield, is an undesired byproduct of the reaction. We have established in separate experiments that 9-anthrylacetone is not formed by isomerization of epoxide **4** but derives from 3-(9-anthryl)-1-chloro-2-hydroxypropane (**3**) upon treatment with 9-anthryllithium, presumably by way of elim-

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[1] Bouas-Laurent, H.; Desvergne, J.-P.; Castellan, A. *Pure Appl. Chem.* **1980**, *52*, 2633.

[2] Becker, H.-D. *Pure Appl. Chem.* **1982**, *54*, 1589.

[3] Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Chem. Phys. Lett.* **1980**, *76*, 390.

[4] Livingston, R.; Wei, K. S. *J. Am. Chem. Soc.* **1967**, *89*, 3098.

[5] Bergmark, W. R.; Jones, G., II; Reinhardt, T. E.; Halpern, A. M. *J. Am. Chem. Soc.* **1978**, *100*, 6665.

[6] Becker, H.-D.; Elebring, T.; Sandros, K. *J. Org. Chem.* **1982**, *47*, 1064.

[7] Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1986**, *51*, 2956.

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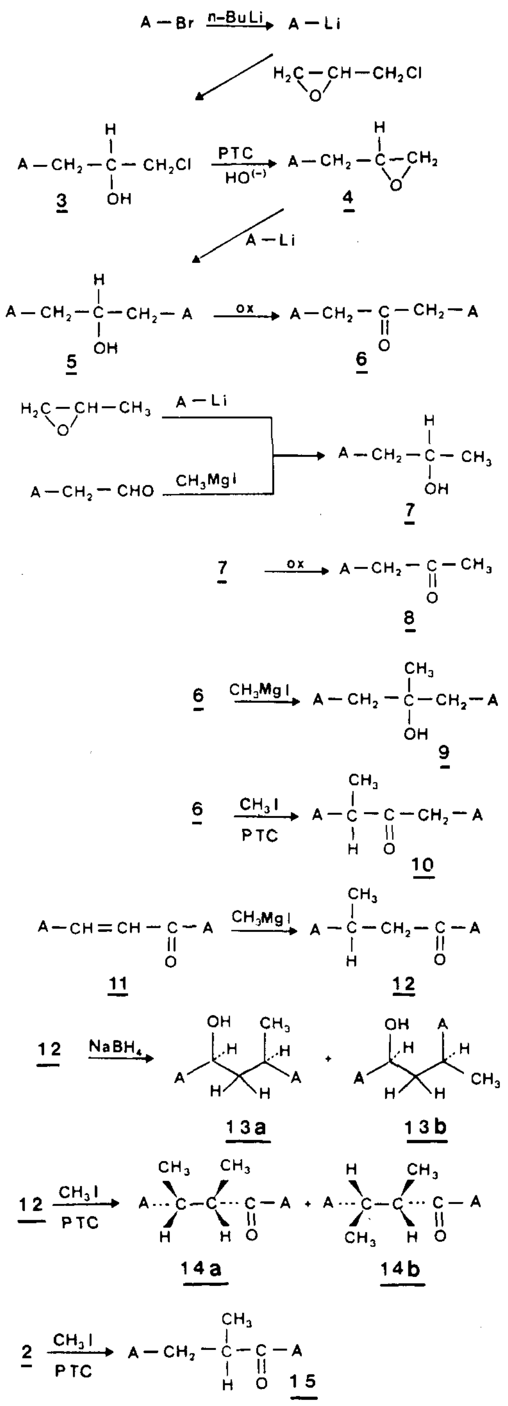
Scheme I[a]



[a] A = 9-anthryl.

ination of HCl. For identification purposes, we have also prepared 9-anthrylacetone by oxidation of 9-anthryl-2-propanol (7), which, in turn, was synthesized both by Grignard reaction of methylmagnesium iodide with 9-anthrylacetaldehyde and by reaction of 9-anthryllithium with propylene oxide.

The formation of 9-anthrylacetone as a byproduct may be responsible for the moderate yield of dianthryl-2-propanol 5 from 9-anthryllithium and epichlorohydrin. Under appropriate reaction conditions (see Experimental Section), the intermediate 3 can be obtained as the main product (62% yield). Phase-transfer-catalyzed (PTC) elimination of HCl from chlorohydrin 3 gives epoxide 4 in 94% yield. Oxidation of dianthryl-2-propanol 5 to give dianthrylacetone 6 in virtually quantitative yield was accomplished with Dess–Martin periodinane.[9]

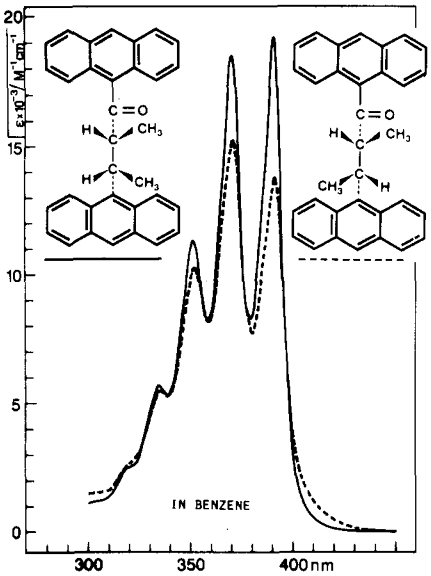


Figure 1. Electronic absorption spectra of diastereomers **14a** (solid curve) and **14b** (dashed curve) in benzene.

Grignard reaction of methylmagnesium iodide with dianthrylacetone afforded the tertiary alcohol **9**. Phase-transfer-catalyzed carbon alkylation of dianthrylacetone with methyl iodide gave 1,3-di-9-anthryl-2-butanone (**10**). The isomeric 1,3-di-9-anthryl-1-butanone (**12**) was prepared by conjugate addition of methylmagnesium iodide to *trans*-1,3-di-9-anthrylpropenone (11). Four additional 1,3-bichromophoric anthracenes were then accessible from 12. Reduction with sodium borohydride gave (1*R*,3*S*/1*S*,3*R*)-1,3-di-9-anthryl-1-butanol (**13a**) and (1*R*,3*R*/1*S*,3*S*)-1,3-di-9-anthryl-1-butanol (**13b**), which were separated by column chromatography on silica gel/toluene. (The configurational assignments are based on the ^{1}H NMR spectroscopic data for their conformationally more rigid photoisomers discussed below.) Phase-transfer-catalyzed alkylation of 12 with methyl iodide gave diastereomeric 1,3-di-9-anthryl-2-methyl-1-butanones **14**, i.e., the 2*R*,3*S*/2*S*,3*R* racemate **14a** and 2*R*,3*R*/2*S*,3*S* racemate **14b**, whose separation also was accomplished by column chromatography on silica gel with toluene as eluant. In this case, assignments of configuration are based on model considerations in conjunction with noticeable differences in their electronic absorption and ^{1}H NMR spectra. Thus, the UV spectrum of **14b** is distinguishable from that of **14a** by broadening and, consequently, lower molar extinction coefficients (see Figure 1), indicating enhanced intramolecular interactions of the two aromatic π-systems. Indeed, only the 2*R*,3*R*/2*S*,3*S* configuration of **14b** allows for a parallel alignment of the two anthracene moieties, without steric interference of the inner peri hydrogen (H-1/H-8) with the methyl group representing C-4 of the butanone moiety (see Figure 2a). Parallel arrangement of the two anthracene ring systems in the 2*R*,3*S*/2*S*,3*R* isomer **14a** is sterically impaired because the C-4 methyl group would be oriented coplanar with the anthracene ring system. Therefore, the 2*R*,3*S*/2*S*,3*R* isomer **14a** should assume a staggered conformation with anti-oriented methyl groups (see Figure 2b). As a ^{1}H NMR consequence, the methyl group at C-2 becomes shielded by both anthracene systems and gives rise to absorption at 0.69 ppm (d, J = 7 Hz), while the C-4 methyl group gets deshielded by the spatially

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[8] Cf.: De Schryver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359.

[9] Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

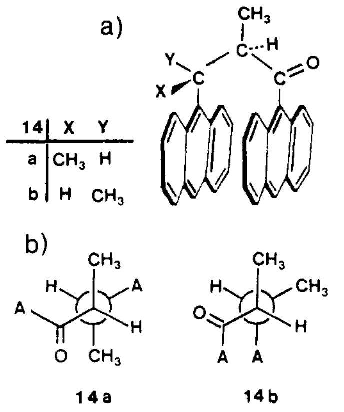


Figure 2. (a) Perspective view of diastereomeric **14a** and **14b** with parallel aligned anthracene ring systems. (b) Newman projections of diastereomeric **14a** and **14b**.

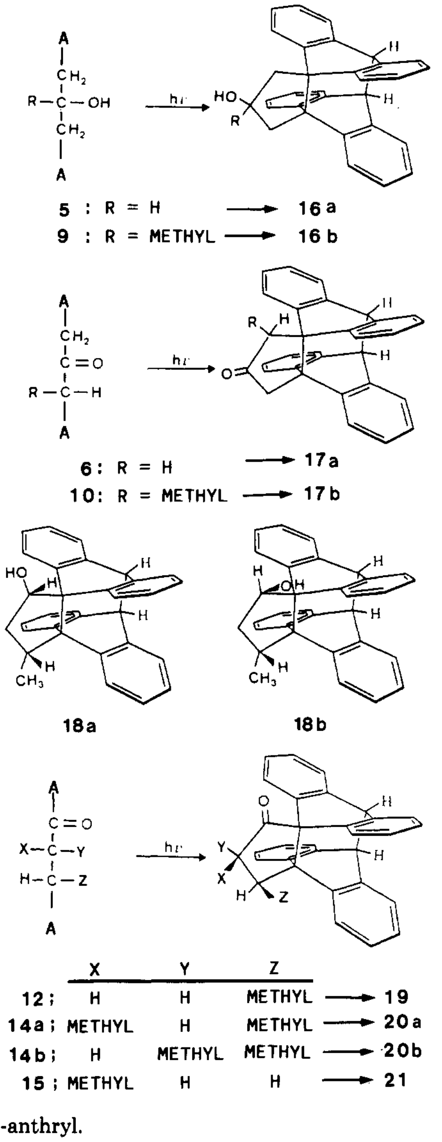
adjacent carbonyl group and appears at 2.02 ppm (d, J = 7 Hz). For the 2R,3R/2S,3S diastereomer **14b**, the chemical shifts of the methyl groups are 1.60 and 1.80 ppm. Model considerations lead us to the conclusion that the staggered conformation in which the methyl group at C-2 and the anthracene at C-3 are anti-oriented should be thermodynamically favored for **14b**. Significantly, it is in this conformation that the parallel alignment of the two aromatic π-systems mentioned above is feasible.

Finally, 1,3-di-9-anthryl-2-methyl-1-propanone (**15**) was prepared by phase-transfer-catalyzed methylation of 1,3-di-9-anthryl-1-propanone (**2**).

Photochemical Properties. Irradiation of 1,3-di-9-anthrylalkanols **5**, **9**, and **13a**/**13b**, as well as 1,3-di-9-anthrylalkanones **6**, **10**, **12**, **14a**/**14b**, and **15**, was found to result in isomerization by $4\pi + 4\pi$ cycloaddition to give the corresponding photoproducts **16**–**21** (see Scheme II). Their structures are supported by their ^{1}H NMR spectra (see Experimental Section), and we have found no UV spectroscopic evidence for the formation of $4\pi + 2\pi$ cyclomers as byproducts. Chemical yields of isolated products generally ranged between 80 and 90%. Significantly, in some cases, the choice of solvent was of importance. For most dianthrylalkanones, dichloromethane was used without problems. Unexpectedly, however, irradiation of some dianthrylalkanols in dichloromethane resulted in the formation of dark-colored decomposition products, while cyclizations in ethyl acetate proceeded smoothly. We deem it conceivable that the decomposition involves some kind of complex between the halogenated solvent and the photoexcited dianthrylalkalol. (The effect of solvents on the photochemistry of dianthrylalkanols remains to be investigated. We are indebted to a referee for constructive comments on this subject.)

The quantum yields of fluorescence and of isomerization, summarized in Table I, reveal characteristic differences between dianthrylalkanols and dianthrylalkanones. Thus, the fluorescence quantum yield of dianthryl-2-propanol **5** (0.48) is virtually identical with that of the parent 1,3-di-9-anthrylpropane (0.47), but the cyclization quantum yield is as low as 0.046. By contrast, dianthrylacetone **6** is characterized by low fluorescence quantum yield (0.009), while its photochemical isomerization by $4\pi + 4\pi$ cycloaddition proceeds with a quantum yield of 0.25. In air-saturated solution, the quantum yield decreases slightly to 0.22, indicating that the reaction involves mainly the excited singlet state, and that the triplet-state contribution to the cyclization is of minor importance. It is conceivable that the observed differences in cyclization efficiency for **5** and **6** are attributable to differences in ground-state conformation. Relative to the electronic absorption spectrum of dianthryl-2-propanol, the spectrum of dianthrylacetone is slightly broadened and bathochromically

Scheme II[a]



[a] A = 9-anthryl.

Table I. Quantum Yields of Fluorescence (Φ_F) in Cyclohexane and Cycloaddition (Φ_R) in Benzene of 1,3-Linked Bichromophoric Anthracenes

	Φ_F	Φ_R
1,3-di-9-anthrylpropane (**1a**)	0.47[a]	0.14[a]
1,3-di-9-anthryl-1-propanol (**1b**)	0.27[b]	0.14[b]
1,3-di-9-anthryl-2-propanol (**5**)	0.48	0.046
1,3-di-9-anthryl-2-methyl-2-propanol (**9**)	0.24	0.021
(1R,3S/1S,3R)-1,3-di-9-anthryl-1-butanol (**13a**)	0.15	0.23
(1R,3R/1S,3S)-1,3-di-9-anthryl-1-butanol (**13b**)	0.07	0.23
1,3-di-9-anthryl-2-propanone (**6**)	0.009	0.25
1,3-di-9-anthryl-2-butanone (**10**)	0.007	0.22
1,3-di-9-anthryl-1-butanone (**12**)	<0.001	0.40[c]
(2R,3S/2S,3R)-1,3-di-9-anthryl-2-methyl-1-butanone (**14a**)	<0.001	0.19[d]
(2R,3R/2S,3S)-1,3-di-9-anthryl-2-methyl-1-butanone (**14b**)	<0.001	0.17[e]
1,3-di-9-anthryl-1-propanone (**2**)	<0.001	0.65[f,g]
1,3-di-9-anthryl-2-methyl-1-propanone (**15**)	<0.001	0.72[h]

[a] In methylcyclohexane; from ref 3. [b] From ref 2. [c] Φ_R = 0.048 in air-saturated solution. [d] No cyclization detectable in air-saturated solution. [e] Φ_R = 0.10 in air-saturated solution. [f] From ref 7 and confirmed in the present work. [g] Φ_R = 0.02 in air-saturated solution. [h] Φ_R = 0.02 in air-saturated solution.

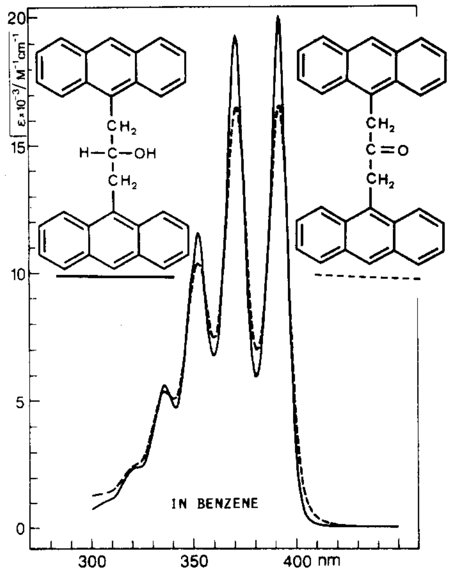


Figure 3. Electronic absorption spectra of 1,3-di-9-anthryl-2-propanol (solid curve) and 1,3-di-9-anthrylacetone (dashed curve) in benzene.

shifted (see Figure 3), indicative of intramolecular π-orbital interaction.

Isomeric 1,3-di-9-anthryl substituted butanols **9** and **13** were found to differ in cyclization quantum efficiency by 1 order of magnitude. The quantum yield for the photochemical isomerization of the 1,3-di-9-anthryl substituted *tert*-butyl alcohol **9** to give **16b** is as low as 0.02, while the isomerization of diastereomeric *sec*-butyl alcohols **13a** and **13b** to give cyclomers **18a** and **18b**, respectively, proceeds in both cases with a quantum yield of 0.23. Diastereomeric 1,3-dianthrylbutanols **13a** and **13b** have virtually identical electronic absorption spectra, suggesting that conformational differences between the two diastereomers are less pronounced than they are between diastereomers **14a**/**14b** discussed above or diastereomeric bis(9-anthrylmethyl) ethers investigated previously.[10]

The formation of cyclomers **18a** and **18b** turned out to be of structural interest insofar as stereochemical differences between the two isomers are borne out in their ^{1}H NMR spectra, and we can tentatively assign configurations to their diastereomeric precursors **13a**/**13b** on the basis of the following arguments. Due to the spatial demand of the methyl group, the conformation of the propano linkage in photoproducts **18a** and **18b** deriving from (1*R*,3*S*/1*S*,3*R*)-butanol **13a** and (1*R*,3*R*/1*S*,3*S*)-butanol **13b**, respectively, should be as shown in the structural formulas. Thus, in both photoisomers, the methyl group should point out of the plane of the aromatic rings, and there will be one aromatic proton each which is deshielded due to the proximity of the hydroxyl group. Inspection of Dreiding molecular models leads to the conclusion that deshielding in the 1*R*,3*S*/1*S*,3*R* diastereomer **18a** should be less effective than in the 1*R*,3*R*/1*S*,3*S* diastereomer **18b**, because only in (1*R*,3*R*/1*S*,3*S*)-**18b** will the quasi-equatorial orientation of the methyl group be associated with the quasi-axial orientation of the hydroxyl group (and its consequential coplanarity with an aromatic ring). Indeed, the ^{1}H NMR spectra of **18a** and **18b** exhibit a downfield doublet each (integrating for one aromatic proton), whose chemical shifts are 7.66 and 8.55 ppm, respectively. Other stereochemical differences between the two photoisomers are evident from the coupling pattern of the methine proton attached to the hydroxyl-substituted carbon. In the spectrum of **18a**, this methine gives rise to a pair of doublets at 5.42 ppm (J = 11.5 and 5.5 Hz), while the corresponding proton in the 1*R*,3*R*/1*S*,3*S* diastereomer **18b** appears as one doublet (J = 3 Hz). Again, we deduce from the Dreiding molecular model of **18b** that the dihedral angle between the methine proton in question and a proton of the adjacent methylene group could be about 90°, so that one of the two coupling constants may be close to 0 Hz.

The excited-state properties of 1,3-di-9-anthryl-2-butanone (**10**) in terms of fluorescence quantum yield (0.007) and cyclization quantum yield (0.22) closely resemble those of dianthrylacetone. Also, the cyclization quantum yield for **10** is not affected by molecular oxygen, indicating the reaction to involve the excited singlet state. By contrast, the photochemistry of 1,3-di-9-anthryl-1-butanone (**12**) is governed by the presence of the 9-anthroyl group, so that **12** isomerizes by 4π + 4π cycloaddition to give **19** in the excited triplet state. The quantum yield for the cyclization of **12** decreases from 0.40 in degassed benzene to 0.048 in air-saturated solution.

As for diastereomeric 1,3-di-9-anthryl-2-methyl-1-butanones **14a**/**14b**, both racemates are virtually nonfluorescent in cyclohexane, as is expected for 9-anthroyl derivatives. Upon irradiation in degassed benzene, both **14a** and **14b** isomerize to give **20a** and **20b** with similar, though comparatively modest, quantum yields of 0.19 and 0.17, respectively. In accordance with a triplet-state isomerization, oxygen efficiently quenches the intramolecular cycloaddition (see Table I) in the case of **14a**, for which we had deduced the staggered anti conformation shown in Figure 2b. To our surprise, however, we find the quantum yield for the photochemical isomerization of **14b** in air-saturated solution to be as high as 0.10. This finding could indicate either that there is a significant singlet-state contribution to the cycloaddition reaction or, more likely, that the intramolecular chemical deactivation of triplet-excited **14b** is very fast due to the favorable ground-state predisposition of the two anthracene π-systems, as we had deduced from its spectroscopic properties discussed above (see Figures 1 and 2a).

The difference in isomerization quantum yields observed for 9-anthroyl derivatives **12** and **14a**/**14b** suggests that steric factors may affect the efficiency of triplet-state intramolecular cycloadditions of 1,3-linked bichromophoric anthracenes. One might conclude, therefore, that the quantum yield of 0.65 previously measured for the isomerization by intramolecular 4π + 4π cycloaddition of photoexcited 1,3-di-9-anthryl-1-propanone (**2**) is singularly high. However, we now find that the quantum yield for the photochemical isomerization by 4π + 4π cycloaddition of 1,3-di-9-anthryl-2-methyl-1-propanone (**15**) to give **21** is even higher, viz., 0.72. Again, we are dealing with a triplet-state isomerization, as the quantum yield for the isomerization of **15** in air-saturated solution is only 0.02. We have ascertained that the photochemical isomerization of **15** to give **21** also can be sensitized by biacetyl.

In summary, the efficiency for the intramolecular deactivation by 4π + 4π cycloaddition of photoexcited propano-linked bichromophoric anthracenes is governed by the molecular geometry of the ground state and substitution pattern of the propano linkage. Optimal quantum yields found for excited-singlet-state reactions are about 0.25. Whenever a 9-anthroyl moiety is present, cycloadditions will then proceed in the excited triplet state, and quantum yields may exceed those of excited-singlet-state reactions. For example, the intramolecular 4π + 4π cy-

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[10] Becker, H.-D.; Andersson, K. *J. Org. Chem.* **1982**, *47*, 354.

cloaddition of 1,3-di-9-anthryl-2-methyl-1-propanone (**15**) proceeds with the record quantum yield of 0.72.

Experimental Section

^{1}H NMR spectra were taken in $CDCl_3$ solution on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Absorption and emission spectra were recorded on a Kontron Uvicon 810 and an Aminco SPF 500 (corrected spectra) spectrometer, respectively. Melting points (uncorrected) were taken on a hot-stage microscope. Elemental analyses were carried out by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark.

Flash chromatographic separations involved a 3.5 cm × 35 cm column. The phase-transfer catalyst Basacrylsalz AN is commercially available from BASF AG, Ludwigshafen, Germany. It is a mixture of dibenzyldimethylammonium chloride (35%), trimethylbenzylammonium chloride (15%), methanol (5%), ethylene glycol (5%), and water (40%).

Actinometry and Preparative Photochemical Cyclizations. Actinometric measurements were made in an optical bench arrangement with a 1000-W mercury/xenon lamp. The excitation wavelength of 366 nm was selected by means of a monochromator. The cyclization quantum yield of 1,2-di-9-anthrylethane (0.22, in air-saturated solution)[4] served as actinometer. Fluorescence quantum yields are based on the fluorescence quantum yield of 9,10-diphenylanthracene (0.83).[11]

Preparative photochemical isomerizations were carried out at 14–20 °C with a 125-W high-pressure mercury lamp (Philips HPK 125 W) in a water-cooled immersion-well apparatus equipped with a liquid-filter sleeve of about 0.5-cm path length. A 2 M aqueous solution of potassium nitrate served as cutoff filter for wavelengths <330 nm. Selective excitation of biacetyl ($\lambda > 420$ nm) was accomplished by means of a filter solution of potassium chromate (380 mg) in water (200 mL).

3-(9-Anthryl)-1-chloro-2-propanol (3). Commercially available *n*-butyllithium (3.75 mL of a 1.6 M solution; 6 mmol) was added over a 5-min period to an ice-cooled solution of 9-bromoanthracene (1.54 g, 6 mmol) in dry ether (50 mL) under argon blanketing. The reaction mixture was stirred at ice-bath temperature for 40 min, and epichlorohydrin (0.47 mL, 0.56 g, 6 mmol) was then added to the yellow suspension. Stirring at ice-bath temperature was continued for 75 min. Subsequent workup by addition of ice water (150 mL) and ether (50 mL), followed by separation of the organic layer, washing, drying, and evaporation of solvent, gave a yellow crystalline residue. Purification by flash chromatography on silica gel/dichloromethane, and subsequent recrystallization from dichloromethane/pentane, gave 1.02 g (62%) of yellow-greenish crystals, mp 96–98 °C. ^{1}H NMR: 8.43 (s, H-10), 8.32–7.44 (m, 8), 4.34 (m, 1), 3.93 (d, J = 6.5 Hz, 2), 3.64 (m, 2), 2.1 (br, OH). Anal. Calcd for $C_{17}H_{15}ClO$: C, 75.41; H, 5.58. Found: C, 75.66; H, 5.69.

3-(9-Anthryl)-1,2-epoxypropane (4). Potassium hydroxide (pellets; 1.2 g) was added to a solution of 3-(9-anthryl)-1-chloro-2-propanol (1.5 g) and phase-transfer catalyst 18-crown-6 (120 mg) in dichloromethane (100 mL). The suspension was stirred under nitrogen for 3 h and subsequently filtered through Celite. Vacuum evaporation of solvent from the filtrate gave a residue, which gave colorless crystals (1.22 g, 94%), mp 119–121 °C (from dichloromethane/hexane) after flash chromatography on silica gel/dichloromethane. ^{1}H NMR: 8.40 (s, H-10), 8.30–7.44 (m, 8). Aliphatic H give rise to an ABMXY spectrum for which the coupling constants were obtained by way of simulation: 3.98 (A, dd, J = 13.0, 4.5 Hz), 3.93 (B, dd, J = 13.0, 5.1 Hz), 3.4 (M, m, J = 5.1, 4.5, 4.4, 2.8 Hz), 2.74 (X, "t", J = 5.0, 4.4 Hz, 2.61 (Y, dd, J = 5.0, 2.8 Hz). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.07; H, 6.18.

1,3-Di-9-anthryl-2-propanol (5). A. From 9-Anthryllithium and Epichlorohydrin. 9-Anthryllithium (12 mmol) was prepared from 9-bromoanthracene (3.08 g, 12 mmol) and *n*-butyllithium (4.8 mL of a 2.5 M solution) in ether (100 mL) at ice-bath temperature under argon. After 40 min, epichlorohydrin (0.5 mL, 6.3 mmol) was added at ice-bath temperature. The reaction mixture was kept at 0 °C for 20 min, then warmed to room temperature, and diluted with benzene (50 mL) to give a clear yellow solution. Upon refluxing under argon, a yellow crystalline precipitate formed within 15 min. Refluxing was continued for an additional 2.25 h. Conventional workup after quenching of the reaction by addition of aqueous ammonium chloride gave a yellow crystalline residue. Washing with warm dichloromethane (30 mL) left 550 mg of virtually pure 1,3-di-9-anthryl-2-propanol undissolved. The filtrate was subjected to flash chromatography on silica gel/dichloromethane to give additional dianthryl-2-propanol (350 mg) and 3-(9-anthryl)-1,2-epoxypropane (310 mg, 21%). (9-Anthrylacetone (15–20% yield), eluted from the column together with dianthryl-2-propanol, is easily separated from **5** due to its much greater solubility in boiling ethanol.) The total yield of **5** (pale greenish-yellow crystals, mp 235–237 °C, after recrystallization from dichloromethane/ethanol) was 36%. The yield of **5** was 50% (based on epichlorohydrin!) when epichlorohydrin (9 mmol) was reacted with excess 9-anthryllithium (27 mmol) in ether (200 mL), and the reaction mixture was refluxed (without addition of benzene) for 20 h.

B. From 9-Anthryllithium and 3-(9-Anthryl)-1,2-epoxypropane. A solution of 3-(9-anthryl)-1,2-epoxypropane (703 mg, 3 mmol) in ether (50 mL) was added to an ice-cooled solution of 9-anthryllithium (prepared from 4.5 mmol of 9-bromoanthracene and *n*-butyllithium) in ether (50 mL). After 2 h at ice-bath temperature, the reaction mixture was refluxed for 17 h. Workup as described under A gave 780 mg (63%) of 1,3-di-9-anthryl-2-propanol, mp 235–236 °C. ^{1}H NMR: 8.38 (s, 2, H-10), 8.9–7.33 (m, 16), 4.69 (m, 1), 4.05 (dd, J = 14.3, 7.7 Hz, 2), 3.88 (dd, J = 14.3, 5.4 Hz, 2), 1.6 (br, OH). Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 90.02; H, 5.89.

1,3-Di-9-anthryl-2-propanone (6). Dess–Martin oxidant[9] (0.74 g, 1.75 mmol) was added to a stirred solution of 1,3-di-9-anthryl-2-propanol (0.412 g, 1 mmol) in anhydrous dichloromethane (100 mL). The reaction mixture was stirred in a stoppered flask for 100 min, then diluted with dichloromethane (75 mL), and poured into 1.3 M aqueous sodium hydroxide (20 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed first with 1.3 M aqueous NaOH (20 mL) and then with water (2 × 50 mL) and finally dried over magnesium sulfate. The pale yellow crystalline residue obtained on vacuum evaporation of solvent was recrystallized from dichloromethane/ethanol. The crystalline product thus obtained (0.423 g) contains about 1 molecule of dichloromethane per 4 molecules of dianthrylacetone (^{1}H NMR analysis). Solvent-free material, mp 270–272 °C, was obtained by dissolving the crude product in dichloromethane, adding hexane, and boiling off the dichloromethane. ^{1}H NMR: 8.35 (s, 2, H-10), 7.97–7.33 (m, 16), 4.69 (s, 4). Anal. Calcd for $C_{31}H_{22}O$: C, 90.70; H, 5.40. Found: C, 90.43; H, 5.45.

1-(9-Anthryl)-2-propanol (7). A. From 9-Anthrylacetaldehyde and Methylmagnesium Iodide. 9-Anthrylacetaldehyde[7] (1.1 g, 5 mmol) was Soxhlet-extracted over a 6-h period into a boiling solution of methylmagnesium iodide (30 mmol) in ether (50–100 mL). Conventional workup by addition of aqueous ammonium chloride and final flash chromatography (silica gel/dichloromethane) gave 1.15 g (97%) of **7** as pale yellow crystals (from dichloromethane/hexane), mp 105–107 °C.

B. From 9-Anthryllithium and Propylene Oxide. A solution of propylene oxide (0.65 mL, 0.54 g, 9.2 mmol) in ether (20 mL) was added at ice-bath temperature to a stirred suspension of 9-anthryllithium (6 mmol; prepared from 6 mmol of 9-bromoanthracene and 3.75 mL of 1.6 M *n*-butyllithium in 50 mL of ether). Conventional workup after 35 min by addition of ice/water, extraction of the aqueous layer with dichloromethane, and vacuum evaporation of solvents from the combined organic layers gave a residue, which was subjected to flash chromatography (silica gel/dichloromethane). The yield of **7**, mp 105–107 °C, was 800 mg (56%). ^{1}H NMR: 8.38 (s, H-10), 8.32 ("d", 2), 8.0 ("d", 2), 7.49 (m, 4), 4.34 (m, methine), 3.80 (m, methylene), 1.49 (br s, OH), 1.41 (d, J = 6 Hz, 6). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.16; H, 6.74.

9-Anthrylacetone (8). Dess–Martin reagent[9] (1.27 g, 3 mmol) was added to a stirred solution of 1-(9-anthryl)-2-propanol (474 mg, 2 mmol) in dichloromethane (25 mL). The solution turned yellow, and after 5 min, a colorless precipitate formed. Filtration

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[11] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; p 103.

through Celite after 25 min gave a pale yellow filtrate, from which part of the solvent was removed by vacuum evaporation. Column chromatography (silica gel/dichloromethane) gave 9-anthrylacetone (420 mg, yield 89%) as pale greenish-yellow needle-shaped crystals (from ether/pentane), mp 112–113 °C (lit.[12] mp 111–112 °C). ^{1}H NMR: 8.45 (s, H-10), 8.16 ("d", 2), 8.03 ("d", 2), 7.5 (m, 4), 4.68 (s, 2), 2.05 (s, 3). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.85; H, 5.95.

1,3-Di-9-anthryl-2-methyl-2-propanol (9). A suspension of dianthrylacetone (498 mg, 1.21 mmol) in benzene (70 mL) was added to a solution of methylmagnesium iodide, prepared from magnesium (290 mg, 11.9 mmol) and methyl iodide (0.87 mL, 14 mmol) in ether (20 mL). The reaction mixture was refluxed for 19 h. Workup involved addition of aqueous ammonium chloride (20%, 100 mL) and ether (50 mL) and gave a suspension, from which crystalline material, consisting of product and unreacted dianthrylacetone, was removed by filtration. Washing of the crystalline residue with toluene (50 mL) dissolved with desired product and left mainly dianthrylacetone undissolved. The organic solutions were combined, washed with water, and dried over magnesium sulfate. The residue obtained on vacuum evaporation of solvents was subjected to flash column chromatography on silica gel/toluene to give 155 mg (30%) of **9** as pale yellow crystals, mp 272–274 °C (from dichloromethane/ethanol). ^{1}H NMR: 8.41 (s, 2, H-10), 8.39–7.37 (m, 16), 4.20 (d, J = 14.5 Hz, 2), 4.14 (d, J = 14.5 Hz, 2), 1.30 (br, OH), 1.18 (s, 3). Anal. Calcd for $C_{32}H_{26}O$: C, 90.11; H, 6.14. Found: C, 89.78; H, 6.19.

1,3-Di-9-anthryl-2-butanone (10). The phase-transfer catalyst Basacrylsalz AN (36 drops) was added dropwise over a period of 2.5 h to a nitrogen-blanketed stirred solution of dianthrylacetone (200 mg) and methyl iodide (5.5 mL) in dichloromethane (125 mL) in the presence of aqueous potassium hydroxide (5 g/10 mL). The reaction mixture was shaken for a total of 3.5 h until the organic layer no longer assumed a red color. Conventional workup and vacuum evaporation of solvent gave a solid yellow residue. It was dissolved in dichloromethane, and the solution was passed through a short column of silica gel on which "phase-transfer iodide" was retained. Subsequent flash chromatography (silica gel/toluene) of the crude product gave 136 mg (66%) of dianthrylbutanone **10** as yellow crystals, mp 277–278 °C (from dichloromethane/ethanol). ^{1}H NMR: 8.13 (s, H-10), 7.99 (s, H-10′), 7.9 (v br, 2), 7.74 (d, J = 8.5 Hz, 2), ca 7.4 (v br signal overlapping sharp signals, 10), 7.1 ("t", J = 8 Hz, 2), 4.83 (q, J = 7 Hz, 1), 4.28 (AB, J = 17 Hz, 2), 1.69 (d, J = 7 Hz, 3). Anal. Calcd for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.43; H, 5.71.

1,3-Di-9-anthryl-1-butanone (12). A suspension of *trans*-1,3-di-9-anthrylpropenone[13] (**11**; 613 mg, 1.5 mmol) in benzene (70 mL) was added over a period of 12 min to a solution of methylmagnesium iodide prepared from magnesium (182 mg, 7.5 mmol) and methyl iodide (1.06 g, 0.47 mL, 7.5 mmol) in ether (20 mL). The yellow reaction mixture, which transiently had turned red, was refluxed for 1 h. Conventional workup after addition of saturated aqueous ammonium chloride gave the crude product as a yellow oil. Flash chromatography on silica gel/dichloromethane gave 575 mg (90%) of almost colorless crystals (from dichloromethane/hexane, or dichloromethane/methanol), mp 180–182 °C. ^{1}H NMR: 8.13 (s, H-10), 7.99 (s, H-10′), 7.87 (br, 2), 7.74–7.0 (m, 14), 4.83 (q, J = 7 Hz, 1), 4.47 (d, J = 17 Hz, 1), 4.38 (J = 17 Hz, 1), 1.69 (d, J = 7 Hz, 3). Anal. Calcd for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.57; H, 5.75.

Reduction of Dianthrylbutanone 12 with Sodium Borohydride To Give 1,3-Di-9-anthrylbutanols 13a and 13b. Sodium borohydride (800 mg) was added to a stirred hot solution of dianthrylbutanone **12** (425 mg, 1 mmol) in a mixture of dioxane (15 mL) and methanol (5 mL). The reaction mixture was refluxed for 2 h, when TLC analysis (silica gel/toluene) showed complete consumption of starting material and the formation of two products. The reaction mixture was then cooled to room temperature, diluted with water (250 mL), and extracted with dichloromethane (90 mL + 25 mL). The organic layer was washed with water to remove dioxane and dried over magnesium sulfate. The pale yellow oily residue obtained on vacuum evaporation of solvent was subjected to flash chromatography on silica gel/toluene to give 150 mg (35%) of the 1*R*,3*S*/1*S*,3*R* racemate **13a** (R_f = 0.29) and 215 mg (50%) of the 1*R*,3*R*/1*S*,3*S* racemate **13b** (R_f = 0.19). Racemate **13a** (mp 166–169 °C) and racemate **13b** (mp 215–216 °C) may be recrystallized from ether/pentane and from dichloromethane/methanol, respectively.

The room-temperature ^{1}H NMR of **13a** exhibits very broad absorption around 7.1 ppm, in addition to the following sharp signals, with typical "aromatic" coupling constants of about 8 Hz: 8.59 (d, 1), 8.44 (d, 1), 8.42 (s, H-10), 8.22 (s, H-10′), 8.10 (d, 1), 8.03 (d, 1), 7.86 (d, 2), 7.52–7.42 (m, 3), 7.33–7.26 (m, 3), 5.53 (m, 1), 5.1 (m, 1), 3.14 (m, 2), 1.95 (br, OH), 1.87 (d, J = 7.4 Hz, 3). At −30 °C, the NMR spectrum changes to the effect that a sharp doublet appears at 9.1 (1 H), and the broad absorption around 7.1 changes to sharp signals at 7.1 ("t", 1), 6.7 ("t", 1), and 6.5 ("d", 1).

The room-temperature ^{1}H NMR spectrum of **13b** exhibits broad absorption around 8.4 ppm (indicating hindered rotation) and sharp signals in the aromatic region with typical "aromatic" coupling constants at 8.37 (s, H-10), 8.34 (s, H-10′), 8.23 (br "d", 1), 7.97 ("d", 4), and 7.35 (m, 8). Aliphatic protons give rise to signals at 6.4 (dd, J = 9.0, 5.0 Hz, 1), 4.74 (m, 1), 3.31 (m, 1), 3.04 (m, 1), 2.0 (v br, OH), and 1.75 (d, J = 7 Hz, 3). At −30 °C, a broad signal appears around 9 ppm, and the broad doublet at 8.23 sharpens. Anal. Calcd for $C_{32}H_{26}O$: C, 90.11; H, 6.14. Found for **13a**: C, 89.76; H, 6.18. Found for **13b**: C, 89.76; H, 6.16.

Alkylation of 1,3-Di-9-anthryl-1-butanone (12) To Give 1,3-Di-9-anthryl-2-methyl-1-butanones 14a and 14b. The phase-transfer catalyst Basacrylsalz AN (18 mL) was added dropwise over a 35-min period to a rapidly stirred mixture of 1,3-di-9-anthryl-1-butanone (500 mg) and methyl iodide (18 mL) in dichloromethane (50 mL), and potassium hydroxide (17.5 g) in water (35 mL) under nitrogen. The organic layer was separated, washed with water, and dried over magnesium sulfate. The "phase-transfer iodide" was retained on the column by passage of the solution through a column of silica gel/dichloromethane. Vacuum evaporation of solvent from the eluate gave a yellow crystalline residue, which was subjected to flash column chromatography on silica gel/toluene. After three consecutive separations, 128 mg (24%) of the 2*R*,3*S*/2*S*,3*R* racemate **14a** (R_f = 0.49) and 180 mg (43%) of the 2*R*,3*R*/2*S*,3*S* racemate **14b** (R_f = 0.38) were obtained. Various (fluorescent!) O-alkylated products were discarded.

14a: pale yellow crystals, mp 264–266 °C (from dichloromethane/hexane, and from dichloromethane/methanol). ^{1}H NMR: 8.76 (d, J = 9 Hz, 1), 8.54 (s, H-10), 8.36 (s, H-10′), 8.37–7.32 (m, 15), 5.44 (m, 1), 4.55 (m, 1), 2.02 (d, J = 7 Hz, 3), 0.69 (d, J = 7 Hz, 3). Anal. Calcd for $C_{33}H_{26}O$: C, 90.38; H, 5.98. Found: C, 90.21; H, 6.11.

14b: pale yellow crystals, mp 202–205 °C (from dichloromethane/hexane, and from dichloromethane/methanol). ^{1}H NMR: 8.72 (d, J = 9 Hz, 1), 8.17 (d?, 1), 8.15 (s, H-10), 8.15 (s, H-10′), 7.92–7.07 (m, 14), 5.14 (m, 1), 4.68 (m, 1), 1.80 (d, J = 7.7 Hz, 3), 1.60 (d, J = 7 Hz, 3). Anal. Calcd for $C_{33}H_{26}O$: C, 90.38; H, 5.98. Found: C, 90.33; H, 6.09.

1,3-Di-9-anthryl-2-methyl-1-propanone (15). The phase-transfer catalyst Basacrylsalz AN (15 mL) was added dropwise over a 35-min period to a rapidly stirred mixture of 1,3-di-9-anthryl-1-propanone (600 mg) and methyl iodide (18 mL) in dichloromethane (60 mL), and potassium hydroxide (18 g) in water (38 mL) under nitrogen. The dichloromethane solution obtained after conventional workup was passed through a short column of silica gel in order to remove phase-transfer catalyst. Vacuum evaporation of solvent from the resulting eluate gave a residue, which was subjected to flash column chromatography on silica gel/toluene to give 317 mg (51%) of **15** as yellow-greenish crystals (from dichloromethane/methanol), mp 209–212 °C. ^{1}H NMR: 8.50 (s, H-10), 8.35 (s, H-10′), 8.14–7.94 (m, 6), 7.7 (v br, 2), 7.49–7.30 (m, 8), 4.35–4.23 (m, 1), 3.97–3.85 (m, 2), 1.19 (d, J = 6.2 Hz, 3). Anal. Calcd for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.55; H, 5.70.

Photochemical Isomerization of Dianthryl-2-propanol 5 To Give 16a. A solution of 1,3-di-9-anthryl-2-propanol (100 mg) in ethyl acetate (125 mL) was irradiated at 15 °C for 1 h. Vacuum evaporation of solvent gave a colorless oily residue, which was

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[13] Becker, H.-D.; Andersson, K. *J. Org. Chem.* **1983**, *48*, 4542.

dissolved in little dichloromethane. Upon dilution with hexane, colorless crystals precipitated. The precipitate was recrystallized from dichloromethane/hexane to give 80 mg of colorless crystals, mp 253–257 °C dec. ^{1}H NMR: 7.20–6.80 (m, 16), 7.16 (m, 1), 4.53 (s, 2 bridgehead H), 2.96 ("t", J = 11.5 Hz, 2), 2.70 (dd, J = 12.4, 5 Hz, 2), 2 (br, OH).

Photochemical Isomerization of 1,3-Di-9-anthryl-2-methyl-2-propanol (9) To Give 16b. The isomerization was carried out analogously to the preceding experiment. Vacuum evaporation of solvent after 1 h of irradiation gave a pale yellow solid residue. It was washed with little ether and recrystallized from dichloromethane/hexane to give colorless needle-shaped crystals, mp 247–250 °C dec. ^{1}H NMR: 7.55 ("d", J = 7 Hz, 2), 7.11–6.81 (m, 14), 4.59 (s, 2 bridgehead H), 3.07 (d, J = 14 Hz, 2), 2.76 (d, J = 14 Hz, 2), 2.1 (s, OH), 1.86 (s, 3).

Photochemical Isomerization of 1,3-Di-9-anthrylacetone To Give 17a. A solution of dianthrylacetone (50 mg) in dichloromethane (120 mL) was irradiated for 10 min at 15 °C. Vacuum evaporation of solvent gave an almost colorless crystalline residue, which was washed with little ether. Recrystallization from dichloromethane/methanol gave 45 mg of colorless crystals. Upon heating, the crystals turn yellow and opaque around 230 °C, and they then undergo phase transformation and melt between 270 and 272 °C, i.e., the melting point of dianthrylacetone. ^{1}H NMR: 7.09–6.83 (m, 16), 4.58 (s, 2 bridgehead H), 3.39 (s, 4).

Photochemical Isomerization of Dianthryl-2-butanone 10 To Give 17b. A solution of **10** (50 mg) in ethyl acetate (120 mL) was irradiated for 12 min as described in the experiment above. Vacuum evaporation of solvent gave a colorless crystalline residue, which was recrystallized from dichloromethane/hexane: yield 40 mg (80%); mp 277–279 °C dec. ^{1}H NMR: 7.15–6.72 (m, 16), 4.54 ("s", 2 bridgehead H), 4.0 (m, 1), 3.8 (dd, J = 16, 2.6 Hz, 1), 3.04 (d, J = 16 Hz, 1), 1.26 (d, J = 6.4 Hz, 3).

Photochemical Isomerization of Diastereomer 13a To Give 18a. A solution of **13a** (50 mg) in ethyl acetate (120 mL) was irradiated under argon at 15 °C for 30 min. Vacuum evaporation of solvent gave a colorless crystalline residue. Recrystallization from dichloromethane/ethanol gave 30 mg of colorless crystals, mp 204–210 °C dec. ^{1}H NMR: 7.66 ("d", J = 7 Hz, 1), 7.32–6.73 (m, 15), 5.42 (dd, J = 11.5, 5.5 Hz, 1), 4.47 ("s", 2 bridgehead H), 3.35 (m, 1), 3.17 ("q" = m, 1), 2.6 (m, 1), 1.85 (br, OH), 1.34 (d, J = 7.4 Hz, 3).

Photochemical Isomerization of Diastereomer 13b To Give 18b. A solution of **13b** (50 mg) in ethyl acetate (120 mL) was irradiated under argon at 15 °C for 20 min. Vacuum evaporation of solvent gave a colorless crystalline residue. Recrystallization from dichloromethane/ethanol gave 25 mg of colorless crystals, mp 203–209 °C dec. ^{1}H NMR: 8.55 ("d", J = 8 Hz, 1), 7.27–6.70 (m, 15), 5.50 (d, J = 3 Hz, 1), 4.42 (s, 2 bridgehead H), 4.1 (m, 1), 3.09 ("t"d, J = 13.5, 3.5 Hz, 1), 2.29 (dd, J = 12.5, 5 Hz, 1), 2.05 (br, OH), 1.36 (d, J = 7.4 Hz, 3).

Photochemical Isomerization of Dianthryl-1-butanone 12 To Give 19. A solution of dianthrylbutanone **12** (100 mg) in dichloromethane (120 mL) was irradiated for 15 min at 18 °C. Vacuum evaporation of solvent gave a pale yellow crystalline residue. It was recrystallized by dissolving it in dichloromethane, adding hexane, and boiling off part of the solvent. The colorless crystals thus obtained (90 mg) melt between 240 and 250 °C dec. ^{1}H NMR: 7.33 (d, J = 7 Hz, 1), 7.05–6.61 (m, 15), 4.54 ("s", 2), 3.5 (m, 1), 3.39 (d, J = 15 Hz, 1), 3.03 (dd, J = 15, 4 Hz, 1), 1.53 (d, J = 6.6 Hz, 3).

Photochemical Isomerization of 14a To Give 20a. A solution of **14a** (52 mg) in dichloromethane (125 mL) was irradiated under nitrogen at 18 °C for 15 min. The solid pale yellow residue obtained on vacuum evaporation of solvent was recrystallized from dichloromethane/hexane to give colorless crystals (43 mg, 83%), mp 260–272 °C dec. ^{1}H NMR: 7.36–6.62 (m, 16), 4.56 ("s", 2 bridgehead H), 3.98–3.85 (m, 1), 3.22–3.07 (m, 1), 1.73 (d, J = 8 Hz, 3), 1.47 (d, J = 7 Hz, 3).

Photochemical Isomerization of 14b To Give 20b. The isomerization was carried out in the same fashion as described in the preceding experiment, to give 47 mg (90%) of colorless crystals, mp 260–272 °C dec. ^{1}H NMR: 7.3–6.5 (m, 16), 4.54 ("s", 2 bridgehead H), 3.44–3.30 (m, 1), 3.07–2.91 (m, 1), 1.51 (d, J = 6.5 Hz, 3), 1.47 (d, J = 7 Hz, 3).

Photochemical Isomerization of 1,3-Di-9-anthryl-2-methyl-1-propanone (15) To Give 21. A. By Direct Excitation. A solution of **15** (50 mg) in dichloromethane (120 mL) was irradiated ($\lambda > 320$ nm) under nitrogen at 18 °C for 5 min. Vacuum evaporation of solvent gave a colorless crystalline residue, which was recrystallized from dichloromethane/hexane: yield 41 mg (82%); mp 255–265 °C dec (phase transition around 208 °C). ^{1}H NMR: 7.15–6.50 (m, 16), 4.59 ("s", 2 bridgehead H), 3.41 (m, 1), 3.0–2.6 (m, 2), 1.56 (d, J = 6.4 Hz, 3).

B. By Biacetyl Sensitization. A solution of **15** (26 mg) and biacetyl (0.7 mL) in benzene (125 mL) was irradiated ($\lambda > 420$ nm) for 6 min. Vacuum evaporation of benzene and biacetyl left an almost colorless crystalline residue, which was recrystallized from dichloromethane/hexane. Yield: 23 mg of colorless crystalline **21**, identical (^{1}H NMR) with the photoproduct obtained by direct excitation.

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