Topochemical Selectivity in Solid-State Photorearrangement: Conformational Control in Photorearrangements of *cis*-1,2-Dibenzoylalkenes

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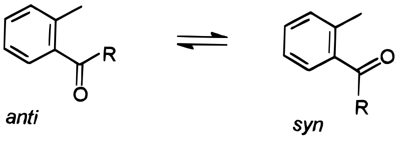
Received June 7, 1995

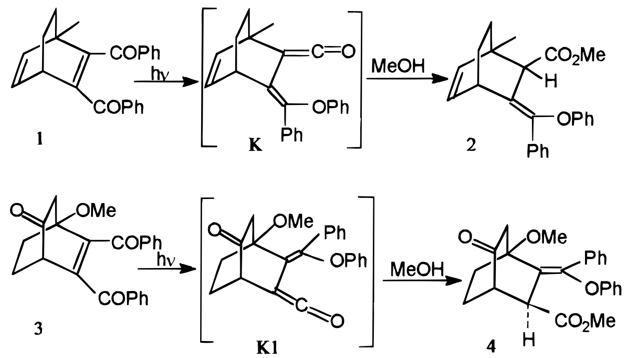
Results from different groups on the photoenolization of *ortho*-alkyl substituted aryl ketones have shown that such molecules exist in a thermal equilibrium of two distinctly different conformers (*syn* and *anti*).[1−3] On excitation, these molecules form two distinct excited states, and intramolecular hydrogen abstraction takes place only from the *syn*-triplet state that is generated by rapid intersystem crossing (ISC). On the other hand, in the case of the *anti* conformer a bond rotation leading to the *syn* form must take place to favor the intramolecular hydrogen abstraction. Although such conformational constraints are widely known to control intramolecular hydrogen abstraction in aryl ketones, examples of analogous conformation specificity in aroyl alkenes have not been explored much in the literature. We report here an example where the regioselectivity of intramolecular carbon to oxygen photo-phenyl migration in *cis*-1,2-dibenzoylalkenes has been found to be controlled by such a conformational constraint.



Results and Discussion

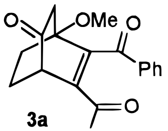
The *cis*-1,2-dibenzoylalkene chromophore is known to undergo a photoinduced intramolecular carbon to oxygen phenyl migration[4a−j] presumably through a singlet n,π* state.[4d,4i,5] Such phenyl migrations have been found to be regioselective in unsymmetrical alkenes. As in 1-phenyl,[4d] 1-pyrazolyl,[4i] and 1-imidazolyl[4j] derivatives of *cis*-1,2-dibenzoylalkene, photo-phenyl migration in 1-methyl-2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**1**) in MeOH takes place from the benzoyl group attached to be more crowded olefinic carbon atom.[4k] On the other hand, such a regioselectivity was totally reversed in the case of **3**[6] (Scheme 1). Although different authors have proposed different explanations for such regioselective photophenyl migrations, the exact reasons have not yet been fully understood. In view of the different results obtained in our irradiation experiments, we decided to carry out the present work.

Scheme 1

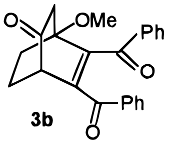


An X-ray crystallographic study (Figure 1) revealed that the conformation of the aroyl groups in **3** is such that they are nonequivalent. Similar nonequivalence in the two *cis*-aroyl groups has been observed in the case of **1**[7] and in the light sensitive crystal form of tetrabenzoylethylene.[4f] Crystals of **3** are monoclinic, space group $P2_1/c$, $a = 11.059(4)$ Å, $b = 14.188(5)$ Å, $c = 11.996(5)$ Å, $\beta = 102.39°$, $Z = 4$. The structure was refined to a final R of 0.047 for 1796 reflections, with $I > 2.5\sigma(I)$. Full crystallographic details will be published separately.[8]

It was rather intriguing that in spite of the apparently favorable geometry in its crystal (Figure 1), photo-phenyl migration in **3** took place from C17 to O3 instead of from C10 to O4 to give the photo-product **4** in methanol (Scheme 1). Since in crystals, organic molecules generally prefer to remain in their stable lowest energy conformation, **3a** (*anti-syn*)[9] was expected to be of the lowest energy in this case, and formation of **4** from the solution phase photochemistry of **3** indicated the presence of another conformer **3b** (*syn-anti*) in the solution phase.



3a
anti-syn



3b
syn-anti

Interestingly, the distance C11−O4 in **3a** (3.237 Å) and the sum of the van der Waals radii of the two interacting atoms (C, 1.70 Å; O, 1.52 Å) were almost equal in the crystal. Hence, following the proposition made by Scheffer and co-workers[10] we reasoned that phenyl migration from **3** in solid state should take place in the expected manner. Thus, when irradiation of **3** in the solid-state

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[†] Department of Organic Chemistry.

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(9) For future reference the conformations at the C5 and C6 benzoyl groups will be referred to as *anti* and *syn* respectively (Figure 1).

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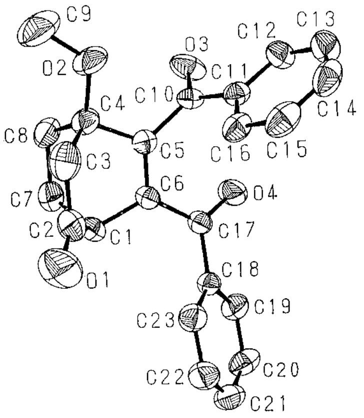
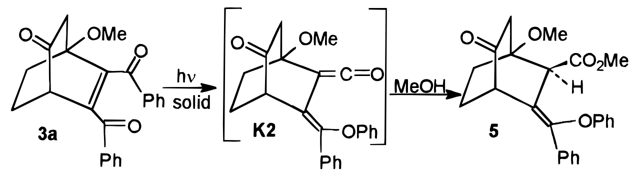


Figure 1. ORTEP diagram for **3**.

Scheme 2



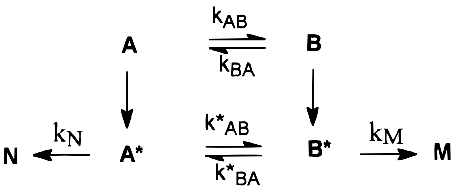
was carried out following a reported procedure,[11] the reaction mixture after 36 h showed a ketene-band at 2103 cm^{-1} in the IR spectrum. Interestingly, the intermediate ketene was found to be fairly stable since complete disappearance of this band took more than 48 h. The ketene was trapped by methanol to give 4-methoxy-6-(phenoxyphenylmethylene)-5-*exo*-carbomethoxybicyclo-[2.2.2]octan-2-one (**5**), mp 41 °C, indicating the structure of the ketene to be **K2** (Scheme 2). The structure of **5** was confirmed from its analytical and spectral data. We could not trace the other ester **4** from the reaction mixture. Exclusive formation of **5** from this reaction clearly indicates that the origin of the solid-state photoreaction of **3**, unlike its solution phase, is only from its conformer **3a**.

To get more information about the effects of molecular conformation on photochemical behavior, the photochemistry of **3** has been investigated in further detail.

When the photoreaction of **3** in MeOH was repeated for 2 h using light of 300 nm, a mixture of esters **4** and **5** (4:1, from NMR) was obtained in 55% yield. From this mixture, **4** could only be partially separated. Along with the earlier reported spectral and analytical data, the structure of **4** was further confirmed from its crystallographic study. The crystals were monoclinic, space group $P2_1/c$, $a = 6.630(3)$ Å; $b = 21.780(6)$ Å; $c = 14.759(5)$ Å; $\beta = 98.35°$; $Z = 4$; $R = 0.064$ for 1323 reflections with $I > 2\sigma(I)$.[8] When the reaction was carried out in aprotic solvents like benzene or acetonitrile, the intermediate ketenes could be identified from the IR band at 2103 cm^{-1}. Treatment of the reaction mixtures with MeOH in both the cases gave a nearly 32% yield of a mixture of esters **4** and **5** (4:1, from NMR). Again from this mixture, **4** could only be partially separated in pure form.

When two conformers yield different photoproducts in solution, the kinetic scheme may be given by Scheme 3.

Scheme 3



The product ratio in such a case is primarily guided by two limiting factors: (i) the activation energies for primary product formation may be more than that of excited state conformational isomerization ($k^*_{AB} \gg k_M$ and k_N); (ii) the activation energy of excited state conformational isomerization may be more than those for primary products formation ($k^*_{AB} \ll k_M$ and k_N).[10,12] In case ii, the ratio of the primary photoproducts will depend upon the population of the excited state conformers A* and B*. Since electronic excitation is much faster than molecular motion, the ground state conformation populations will then ultimately decide the populations in the excited states and hence the ratio of the photoproducts. In the case of **3**, from AM1 calculation the ground state energies of the two conformers **3a** ($\Delta H_f = -59.6$ kcal/mol) and **3b** ($\Delta H_f = -57.0$ kcal/mol) were found to be comparable. Since the major photoproduct from **3** in solution was always found to be from conformer **3b**, case ii did not appear to be the major factor guiding the product ratio. The product ratio in these photoreactions would then be guided by i (Curtin−Hammett principle[13]). This was further supported from the finding that, when the radiation experiment was repeated in benzene and acetonitrile, followed by trapping of the ketenes with methanol, the product ratio (**4**:**5**) was found to be the same as that in MeOH.

The ratio (4:1) of esters **4** and **5** indicated an enhanced photoreactivity for **3b** in comparison to **3a** in solution. This may at least partly be explained in terms of steric assistance in the transition state.[13b] As has been confirmed by the AM1 calculation results, the steric repulsion between adjacent groups in **3b** is expected to elevate its energy in the ground state. Since steric repulsion is more important in the ground state than in the transition state, the activation energy for phototransformation from the higher energy conformer would then be expected to at least partly decrease with reference to that from the lower energy one. Thus the photoreaction from **3b** will be more activated than that from **3a** in the solution phase.

In the crystal structure of **3**, intermolecular hydrogen bonding (2.434 Å) involving the *ortho*-hydrogen atom of the C5-benzoyl group of one molecule (x, y, z) and O1 of another neighboring molecule e.g. C16−H16···O1 ($-x$, $-y$, $-z + 2$) has been observed (Figure 2). Further, the *para*-hydrogen of the C6-benzoyl group of this molecule was also found to be involved in such hydrogen bonding (2.393 Å) with O3 of another neighboring molecule: C21−H21···O3 ($x - 1$, y, z). These interactions appear to have a role, in addition to steric interactions, in preventing the bond rotation in **3a** in the solid state. With no scope for bond rotation obviously, no photoproduct derived from **3b** could be observed in this case. A similar topochemical

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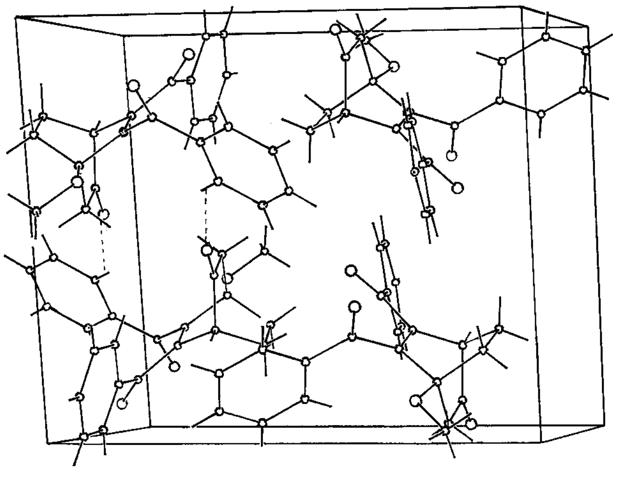
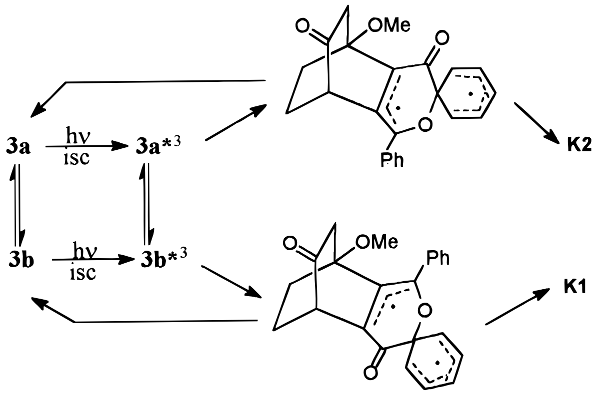


Figure 2. Packing diagram for **3** showing intermolecular H-bonding.

Scheme 4

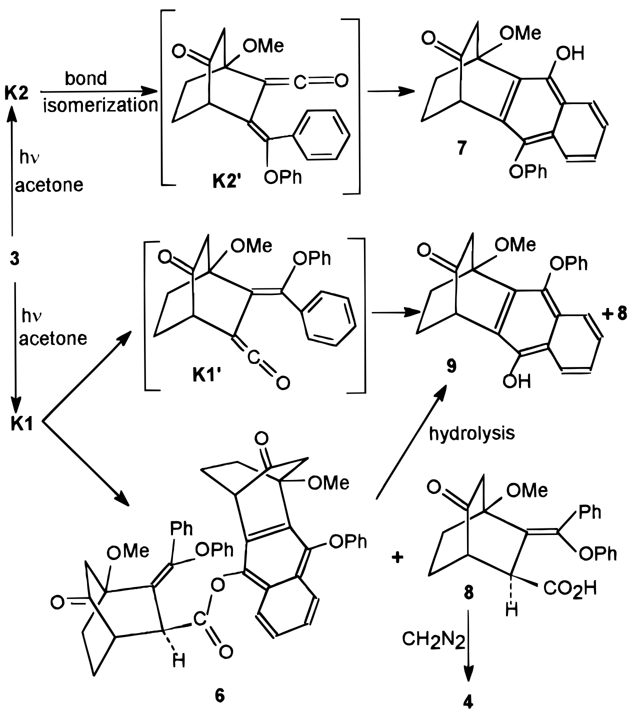


restriction on molecular motion, brought about by the interaction between benzoyl group oxygen atoms and *ortho*-hydrogen atoms of neighboring phenyl groups, has been observed in a solid phase photoreaction by Scheffer, Trotter, and co-workers.[14] The role and existence of such C−H···O hydrogen bond has now become very significant in organic molecular crystallography.[15a,b]

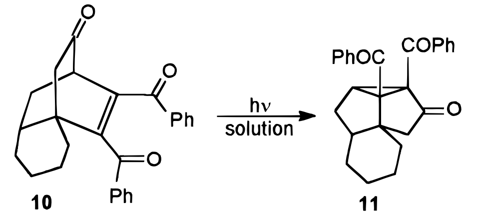
Formation of both **4** ($\phi = 0.06$) and **5** ($\phi = 0.02$) in methanol were found to be quenched by oxygen. From these observations, the processes occurring in solution may be represented by Scheme 4. A rapid intersystem crossing is expected in aryl ketones leading to the triplet states and involvement of such triplet derived biradicals has already been suggested in the bicyclo[2.2.2]octene system.[4g]

Photoproducts from the irradiation experiment in acetone need special mention. The intermediate ketenes **K1** and **K2** appeared to be further sensitized in acetone leading to the isomeric ketenes **K1′** and **K2′** which on further photocyclization then gave anthracene derivative **7** from **K2′** and an ester **6** and an acid **8** from **K1′** (Scheme 5). Esterification of **8** with diazomethane gave **4** that confirmed its structure. The ester **6** was formed from an intermolecular addition of the hydroxyl anthracene derivative **9** to the ketene **K1**. Acid hydrolysis of **6** gave back **9**. Under the reaction condition, **8** could not be separated from the hydrolyzed mixture. Interestingly, when the acetone photolysis was carried out in water **9**, instead of **6**, was isolated along with **7** and **8**.

Scheme 5



Scheme 6



It may be pointed out here that, in an analogous system like **10**, similar irradiation experiments in benzene, acetonitrile, methanol, and acetone gave only an oxa-di-pi-methane (ODPM) product **11** (Scheme 6).[16] Such (ODPM) product could not be isolated from the irradiation experiment of **3** at all. On the otherhand, irradiation experiment with **10** in the solid state gave back the unreacted starting material only. From the above results it appears that the photo reactivity in unsymmetrical *cis*-1,2-dibenzoylalkenes is at least partly controlled by the molecular conformational constraint.

Experimental Section

General Procedures. All melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using tetramethylsilane as internal standard. Silica gel used for column chromatography was of 60−120 mesh. Petroleum ether (PE) used was the fraction of bp 60−80 °C. Solvents were purified according to reported procedures.[17] Spectral grade solvents were used for some of the irradiation experiments and for recording of UV spectra. Irradiation experiments in solution were carried out in a Rayonet photoreactor using 300 nm lamps after purging argon through the solution for 15 min before reaction. A sample of 5,6-dibenzoyl-4-methoxybicyclo[2.2.2]oct-5-en-2-one (**3**), mp 174 °C was prepared by a reported method.[6]

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(15) For some examples, see: (a) Desiraju, G. R. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 63. (b) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747.

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4-Methoxy-6-(phenoxyphenylmethylene)-5-*exo*-carbomethoxybicyclo[2.2.2]octan-2-one (5). An emulsion of **3** (1 g, 2.77 mmol) in distilled water (150 mL) was irradiated using a 450 W medium pressure Hanovia lamp and a Pyrex filter for 36 h with stirring. The photolyzed mixture was extracted with dichloromethane. Removal of the solvent in vacuo gave a thick residue. It was then stirred with methanol for about 6 h. Solvent was removed in vacuo to give a residue that was chromatographed over a silica gel column. Elution with a mixture of 15% ethyl acetate (EA) in PE gave **5** as a white solid, mp 41 °C (230 mg, 21%), which was crystallized with difficulty from a mixture of *n*-pentane and dichloromethane (4:1). IR (KBr) 1720 (C=O) cm^{-1}; ^{1}H NMR (300 MHz) δ 2.18−2.41 (m, 4H), 2.46 (d, J = 18 Hz, 1H), 2.64 (dd, J = 18 Hz and 3 Hz, 1H), 3.35 (s, 3H), 3.45 (m, 1H), 3.55 (s, 3H), 3.95 (d, J = 2 Hz, 1H), 6.7−6.95 (m, 3H), 7.1−7.45 (m, 7H); UV (EtOH) 255 nm (log 3.99); MS *m/e* 392 (M$^+$ for $C_{24}H_{24}O_5$). Anal. Calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.20; H, 6.27. Further elution with a mixture of 40% EA in PE gave 620 mg (62%) of unreacted **3** (mmp 174 °C).

4-Methoxy-5-(phenoxyphenylmethylene)-6-*exo*-carbomethoxybicyclo[2.2.2]octan-2-one (4). In Methanol. A solution of **3** (500 mg, 1.38 mmol) in dry methanol (110 mL) was irradiated using 300 nm lamps for 2 h under an argon atmosphere. The residue obtained after removal of the solvent was chromatographed on a silica gel column. Elution with a mixture of EA in PE (20%) gave white crystals (280 mg, total 55%) of a mixture (4:1 by NMR) of esters **4** and **5**. On recrystallization from a mixture (4:1) of PE and methylene chloride, 160 mg of **4**, mp 180−181 °C (mmp[6] 180−181 °C) was obtained. The other ester **5** could not be separated from the filtrate. Further elution with 40% of EA in PE gave back **3** (160 mg, 32%) mmp 174 °C.

In Benzene. The above-mentioned procedure was repeated to irradiate 500 mg (1.38 mmol) of **3** in benzene (90 mL) for 2 h. The photolyzed mixture was immediately stirred with 50 mL of bidistilled methanol for 15 h. Removal of solvent and chromatography of the residue gave 175 mg (total 32%) of a mixture (4:1) of esters **4** and **5** from which 120 mg of 4, mp 180−181 °C (mmp[6] 180−181 °C) was obtained. Here again the other ester **5** could not be separated from the filtrate. Further elution of the column gave back 310 mg (62%) of **3**, mmp 174 °C.

In Acetonitrile. Repetition of the above procedure with 500 mg (1.38 mmol) of **3** in acetonitrile (100 mL) gave 170 mg (total 31%) of a mixture (4:1) of esters **4** and **5** from which 110 mg of **4**, mmp 180−181 °C only could be recrystallized out. Further elution gave back 300 mg (60%) of unreacted **3**, mmp 174 °C.

Quenching Studies of the Phototransformations in Oxygen. A stock solution of **3** (approximately 2.4 × 10^{-3} M) was prepared in dry MeOH. From this solution 15 mL aliquots were irradiated in the presence of argon and oxygen in a Rayonet photoreactor at 300 nm using a merry-go-round apparatus. The time of irradiation was chosen to bring about 10−15% conversion of the starting material. Comparative phototransformations (%) were calculated from PMR data, and quantum yields for product formations were determined by uranyl oxalate actinometry.[18]

Irradiation of 3 in Acetone. A solution of **3** (500 mg, 1.38 mmol) in spectral grade acetone (115 mL) was irradiated for 3.75 h under an argon atmosphere. This was repeated to irradiate a total of 1 g (2.77 mmol) of compound. **Ester 6**: Removal of the solvent gave a residue which on repeated cooling and scratching in methanol gave a white solid that was filtered and was recrystallized from a mixture (1:4) of methanol and PE to give **6** (180 mg, 18%) mp 266 °C. IR (KBr) 1760, 1735 (C=O), 1655 (C=C−O) cm^{-1}; UV (EtOH) 235 nm (log ϵ 4.97), 270 (4.16); ^{1}H NMR (270 MHz) δ 1.96−2.28 (m, 6H), 2.34−2.7 (m, 3H), 2.57 (s, 3H), 3.15−3.49 (m, 4H), 3.52 (s, 3H), 3.99 (bs, 1H), 4.25 (d, J = 3.5 Hz, 1H), 6.68−7.65 (m, 17H), 7.90−8.03 (m, 2H); ^{13}C NMR δ 21.7, 22.7, 29.4, 34.6, 46.2, 46.5, 46.6, 48.5, 50.9, 52.7, 65.8, 79.0, 79.1, 114.4, 117.1, 117.5, 121.5, 122.6, 122.7, 125.7, 127.0, 127.2, 127.29, 127.32, 128.7, 128.8, 128.82, 129.2, 129.4, 129.5, 129.6, 130.6, 130.7, 130.9, 131.2, 133.4, 138.7, 141.6, 147.8, 155.1, 160.2, 160.3, 209.3, 209.4; MS *m/e* (rel intensity) 720 (M$^+$, 5), 361 (67), 360 (100), 333 (65), 291 (50). Anal. Calcd for $C_{46}H_{40}O_8$: C, 76.65; H, 5.59. Found: C, 76.85; H, 5.81.

1,4-Dihydro-9-phenoxy-4-methoxy-10-hydroxy-1,4-ethanoanthracen-2(3*H*)-one (7). Solvent was removed from the filtrate, and the residue was chromatographed over silica gel. Elution with a mixture of EA (15%) in PE gave a white solid of **7** (270 mg, 27%) mp 198 °C that was recrystallized from a mixture (1:4) of dichloromethane and PE. IR (KBr) 3260 (O−H), 1730 (C=O) cm^{-1}; UV ($CHCl_3$) 245 nm (log ϵ 4.53), 272 (3.65), 280 (3.68), 309 (br 3.83); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 1.6−2.43 (m, 4H), 2.52 (dd, J = 18 Hz and 2 Hz, 1H), 2.88 (d, J = 18 Hz, 1H), 3.63 (s, 3H), 3.88 (t, J = 2.5 Hz, 1H), 6.6−8.4 (m, 9H), 9.71 (s, 1H, exchangeable with D_2O). Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.28; H, 5.28. Further elution of the column with a mixture of 25% EA in PE gave back unreacted **3** (230 mg, 23%) mmp 174 °C.

4-Methoxy-5-(phenoxyphenylmethylene)-6-*exo*-carboxybicyclo[2.2.2]octan-2-one (8). Further elution with 40% mixture of ethyl acetate in PE gave **8** as a white solid (260 mg, 25%), mp 216 °C, that was recrystallized from a mixture (1:4) of dichloromethane and PE. IR (KBr) 3160 (O−H), 1730 (C=O), 1660 (C=C−O) cm^{-1}; UV (EtOH) 251 nm (log ϵ 4.05); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 1.94−2.05 (m, 4H), 2.33 (d, J = 18 Hz, 1H), 2.53 (s, 3H), 2.76 (m, 1H), 3.15 (dd, J = 18 Hz and 3 Hz, 1H), 3.70 (d, J = 3 Hz, 1H), 6.83−7.56 (m, 11H, 1H exchangeable with D_2O). Anal. Calcd for $C_{23}H_{22}O_5$: C, 72.99; H, 5.86. Found: C, 72.34; H, 5.81.

Esterification of 8 to 4. An ether solution of diazomethane was added dropwise to an ether solution of **8** (30 mg). Removal of solvent gave a residue which on recrystallization from a mixture (4:1) of PE and methylene chloride gave white crystals of **4** (27 mg, 89%) mmp 180−181 °C.

1,4-Dihydro-10-phenoxy-4-methoxy-9-hydroxy-1,4-ethanoanthracen-2(3*H*)-one (9). The ester **6** (100 mg, 0.139 mmol) was refluxed with a mixture of glacial acetic acid (4 mL), concd hydrochloric acid (2 mL) and water (1 mL) on an oil bath at 120 °C for 10 h. The reaction mixture was dried in vacuo, and the residue was chromatographed on a silica gel column. Elution with a 15% mixture of EA in PE gave a white solid of **9** (30 mg, 60%), mp 212 °C, that was crystallized from a mixture (1:4) of dichloromethane and PE. IR (KBr) 3420 (O−H), 1720 (C=O) cm^{-1}; UV (EtOH) 222 nm (log ϵ 4.64), 234 (4.65), 273 (3.75), 280 (3.81), 301 (3.85); ^{1}H NMR (200 MHz) δ 1.88−2.17 (m, 4H), 2.48 (d, J = 18 Hz, 2H), 2.65 (d, J = 18 Hz, 1H), 3.51 (s, 3H), 4.13 (t, J = 2.8 Hz, 1H), 5.83 (s, 1H, exchangeable with D_2O), 6.69−7.53 (m, 7H), 7.94−8.13 (m, 1H). Anal. Calcd for $C_{23}H_{22}O_5$: C, 76.64; H, 5.59. Found: C, 76.38; H, 5.92.

Irradiation of 3 in Aqueous Acetone. A solution of **3** (450 mg, 1.25 mmol) in 100 mL of aqueous acetone (70%) was irradiated for 3.5 h under an argon atmosphere. On removal of solvent a thick residue was obtained from which no **6** could be separated. Chromatography of this residue over a silica gel column gave **7** (50 mg, 11%) mmp 198 °C on elution with a 15% mixture of EA in PE. Further elution of the column with a 20% mixture of EA in PE gave **9** (60 mg, 13%), mmp 212 °C. Further elution with a mixture (40%) of EA in PE gave **8** (250 mg, 53%) mmp 216 °C.

Acknowledgment. Financial assistance from D.S.T. is gratefully acknowledged. We thank Professor S. P. Bhattacharyya for helping us with the AM1 calculations.

JO951038A

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