Short-Lived 1,5-Biradicals Formed from Triplet 1-Alkoxy- and 1-(Benzyloxy)-9,10-anthraquinones

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Abstract: The cyclopropylmethyl and (*trans*-2-phenylcyclopropyl)methyl radical clocks were used to estimate the lifetimes of triplet state biradicals formed from substituted 1-alkoxy-9,10-anthraquinones by photoexcitation and subsequent 1,5-hydrogen atom transfer. Irradiation (350 nm) of 1-(cyclopropylmethoxy)-2-methyl-9,10-anthraquinone (**1cp**) in argon-purged methanol generated the primary anthrahydroquinone product (**2**). Upon exposure to air, **2** was rapidly converted to cyclopropanecarboxaldehyde and 1-hydroxy-2-X-9,10-anthraquinone (**3**). In contrast, irradiation of 1-{(*trans*-2-phenylcyclopropyl)methoxy}-2-benzyl-9,10-anthraquinone (**1pcp**) under similar conditions produced only small amounts of **3** and the corresponding aldehyde, *trans*-(2-phenylcyclopropyl)carboxaldehyde. In addition, products resulting from rearrangement of the 1,5-biradical to a homoallylic 1,8-biradical were also obtained. Using the known rate constant for the rearrangement of the phenylcyclopropylmethyl radical to the homoallylic radical and the observed product ratio, lifetimes of approximately 1−2 ns were estimated for 1,5-biradicals from these anthraquinones which are about an order of magnitude shorter than those reported for triplet state biradicals derived from structurally related benzophenones and acetophenones. The short lifetimes of these biradicals are attributed to the facile formation of a zwitterion which results from an intramolecular electron transfer from one radical site, which serves as electron donor, to the other radical site, which is a semianthraquinone and therefore serves as a good electron acceptor. If either the electron-donating or electron-accepting site is absent in the biradical, zwitterion formation is not observed and coupling of the biradical occurs resulting in a longer lifetime.

Introduction

Rearrangements initiated by hydrogen atom abstractions constitute a promising recent synthetic development in organic photochemistry.[1] Considerable effort has been directed toward a better understanding of the factors which control the lifetimes of biradicals generated by this process.[2] Many investigators believe that intersystem crossing of a triplet-generated biradical to its singlet state before coupling determines its lifetime.[3] Lifetimes for a limited number of biradicals, generated by thermal or photochemical means, have been accurately determined by nanosecond and picosecond transient absorption[4] or by more indirect methods such as radical clocks.[5] The paucity of lifetime measurements is primarily a reflection of the short lifetime for the ground states of these species at room temperature.[6]

Our previous studies showed that photoexcited 1-alkoxy- and 1-(benzyloxy)-9,10-anthraquinones (**1**) undergo facile conversion to their corresponding anthrahydroquinones (**2**) in methanol (Scheme 1).[7] This process can be viewed as an intramolecular redox reaction between the anthraquinone and the alkoxy group at the 1-position. Upon exposure to air, the intermediate anthrahydroquinone is rapidly converted to the corresponding carbonyl (**4**) and a substituted 1-hydroxy-9,10-anthraquinone (**3**), which can be recycled. The intermolecular variant to the former reaction has been known for quite some time.[8]

Deuterium isotope effects, substituent effects, and solvent polarity studies support a mechanism in which a biradical is formed by an intramolecular δ-hydrogen atom transfer that occurs in one step, rather than sequential electron and proton transfers.[7a] The biradical presumably decays via an intramolecular electron transfer to a zwitterion. This intermediate would be expected to react with methanol to generate the primary photoproduct (**2**) (Scheme 2). In our preliminary studies, we were surprised to find that acetal **2** is quite labile. Exposure of a methanol solution of this anthrahydroquinone to air during workup resulted not only in the expected oxidation of the anthrahydroquinone to anthraquinone, but in the hydrolysis of the acetal as well. Recently we have shown that this photochemical process can be effectively used in the synthesis of aldehydes and ketones containing acid-sensitive groups.[9]

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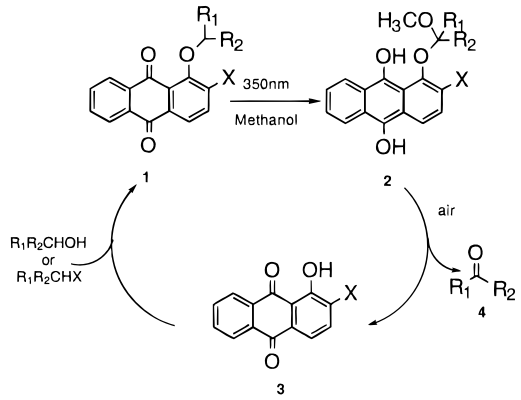
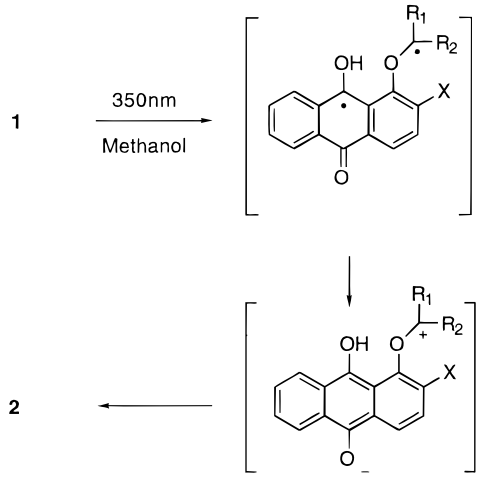
Scheme 1



Scheme 2



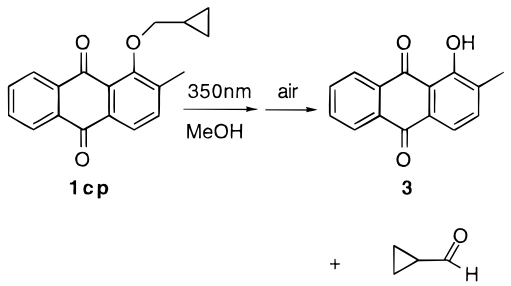
In this paper we estimate the lifetime of the biradical formed by δ-hydrogen abstraction in a substituted anthraquinone using two radical clocks[10,11] that undergo a cyclopropylcarbinyl ring opening to 3-butenyl. We find that the anthraquinone derived biradicals have lifetimes on the order of 1−2 ns, which are approximately one order of magnitude shorter than those derived from analogous benzophenones.[12]

Results and Discussion

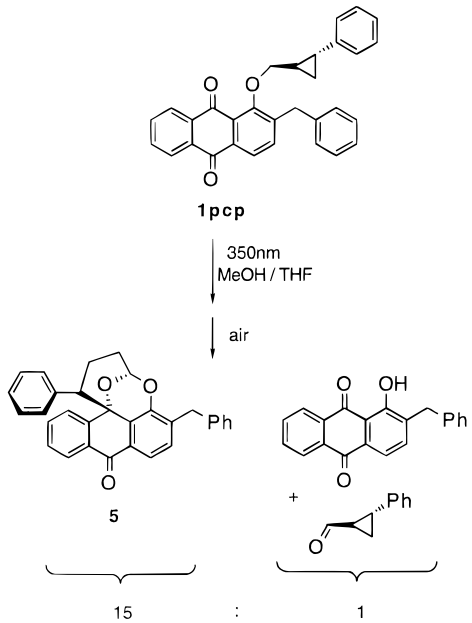
Anthraquinones **1cp** and **1pcp** were prepared to estimate the lifetimes of biradicals that are believed to form as intermediates in the photochemistry of 1-alkoxy-9,10-anthraquinones (**1**). Dilute solutions (0.02 M) of these compounds in methanol or methanol/THF were irradiated (350 nm) under argon. Product formation was monitored by HPLC and ^{1}H NMR and products were isolated by chromatographic techniques. The structures were determined by spectroscopic methods and, in the case of a major product arising from the photolysis of **1pcp**, with X-ray crystallography.

Irradiation (350 nm) of **1cp** in argon-purged methanol resulted in its conversion to 1-hydroxy-2-methyl-9,10-anthraquinone and the corresponding aldehyde, cyclopropanecarboxaldehyde, after exposing the photolysis solution to air (Scheme 3).[9] No peaks were observed in the vinyl region of the ^{1}H NMR spectrum of the reaction mixture. Thus, cyclopropane ring opening of the biradical from **1cp** did not occur to any appreciable extent. Based upon this result, it can be concluded that zwitterion formation occurs appreciably faster than 7×10^7 s^{-1}, the most recent measurement of the rate constant for the ring opening of the cyclopropylmethyl radical.[13]

Scheme 3



Scheme 4



Photolysis of **1pcp** under similar conditions did not bring about photocleavage to produce 2-benzyl-1-hydroxy-9,10-anthraquinone and the corresponding *trans*-(2-phenylcyclopropyl)-carboxaldehyde, δ 9.3 (d, J = 4.5 Hz)[14] to any great extent. Instead, irradiation of **1pcp** gave rise to a number of products, some of which resulted from the opening of the phenylcyclopropane ring. One of these, anthrone (**5**), comprised ca. 60% of the mixture (by NMR integration) and was isolated by preparative HPLC. The structure of **5** was unequivocally determined by X-ray crystallography (Figure 1). ^{1}H NMR analysis of the reaction mixture indicated a 15:1 mixture of **5** and 2-benzyl-1-hydroxy-9,10-anthraquinone. We were unable to isolate any products from this reaction with a *trans* double bond. Since anthrone **5** is a major product in this reaction and its structure requires a precursor with a cis double bond, it appears that most *trans* biradicals derived from **8** revert back to the ground state of **1pcp**.

Scheme 5 displays what we consider to be the most likely pathway for anthrone **5** formation: cyclization of the 1,8-

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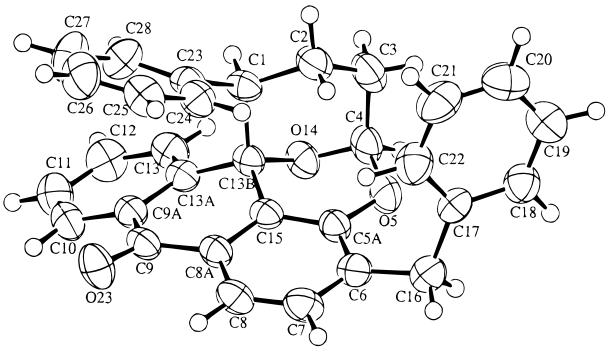
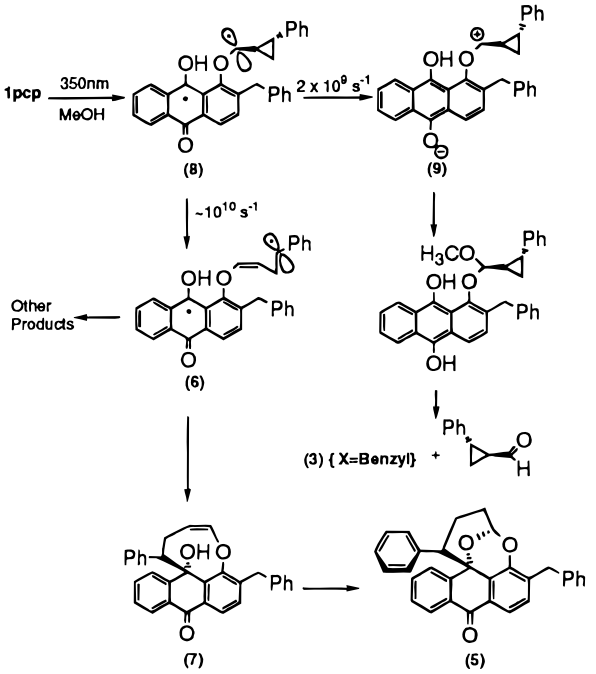


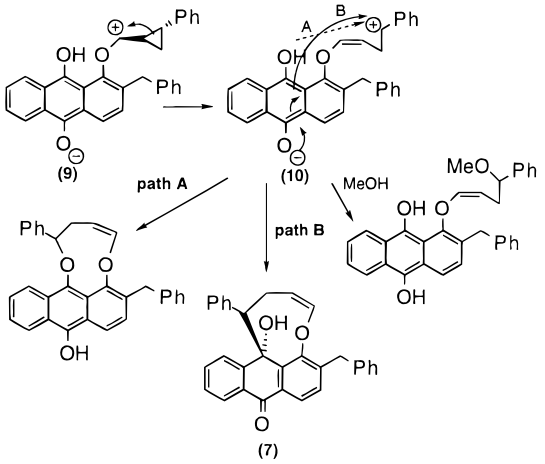
Figure 1. X-ray crystal structure of **5**.

Scheme 5



biradical (**6**), resulting from the rearrangement of the phenylcyclopropylmethyl radical, followed by intramolecular electrophilic addition of the alcohol group to the enol ether (**7**). The precise mechanism of the latter step is uncertain. One possibility is that it is catalyzed by trace amounts of acid present in the methanol.[15] Another possibility is that the alcohol is adding to the double bond via a photoexcited state.[12b,16,17] In either case, the formation of **5** appears to be an intramolecular example of some ionic process. Scheme 5 also illustrates the competing reactions of the 1,5-biradical (**8**) as determined from the observed product ratio. The rate constant for the opening of the *trans*-phenylcyclopropylmethyl radical[11] is 3×10^{11} s^{-1}. Although the biradicals derived from these anthraquinones are oxygen substituted, this substitution should not have a major effect on their rate constants for ring opening.[18] Newcomb and co-workers found that alkyl radicals react with tin hydride at 25 °C about one order of magnitude faster than their α-methoxy-substituted derivatives. They noted that the lower rate constant for the H-atom transfer to the latter is consistent with a smaller BDE value for a C−H bond with an α-methoxy group. Assuming that the aryloxy group in biradical **8** affects the ring-opening reaction to the same extent, that is, decreases the rate

Scheme 6



constant by a factor of 10, this leads to an estimate of $1-2 \times 10^9$ s^{-1} for the decay of biradical **8** to the zwitterion **9**. In an effort to obtain another estimate of this rate constant, we tried to incorporate methoxy- and *tert*-butoxy-substituted cyclopropylmethyl radical clocks into the anthraquinone.[19a] Unfortunately, we were unsuccessful because cyclopropane ring opening occurred when we attempted to couple the radical clock to the anthraquinone.

Since cyclopropylcarbenium cations are known to undergo fast rearrangement as well,[19] a second pathway to **5** is considered in Scheme 6. Rearrangement of the phenylcyclopropylcarbenium ion in zwitterion **9** leads to zwitterion **10**, and three possible reactions of the latter are presented. Several arguments can be made against a mechanism involving cations. First, it is quite possible that the cyclopropane ring in **9** would not even open. Kirmse and co-workers generated a variety of arylcyclopropylcarbenium ions in 2,2,2-fluoroethanol (TFE) solutions of methanol and obtained high yields of ethers that retain the cyclopropane ring.[20] In **9**, the aryloxy group would be expected to stabilize the cyclopropylcarbenium ion somewhat relative to an aryl group, but the phenyl group on the cyclopropane ring would stabilize the ring-opened product. It is not clear what the overall effect of the opposing aryloxy and phenyl groups in **9** is, but ring opening of the cyclopropane should not be a foregone conclusion. If the cyclopropane in zwitterion **9** opens producing zwitterion **10**, three possible reactions of the latter are considered in Scheme 6. Given the conformational requirements for cyclization, it seems unlikely that either path A or path B would be able to compete with the trapping of zwitterion **10** by the solvent methanol. Although the rate constant for the reaction of **10** with methanol is not known, it can be estimated from related systems. Diphenylmethyl cation and cyclopropylphenylmethyl cation have rate constants of 2.8×10^8 and 3.2×10^6 s^{-1}, respectively, in TFE.[20] In the much more nucleophilic methanol, there is a 3-fold increase in the rate constant for carbocation trapping in comparsion to TFE.[20b] Assuming that the stabilizing effect of a cyclopropyl group is about the same as a phenyl group and that an aryloxy group increases the lifetime of a cation by a factor of 10 compared to a phenyl group, this leads to an estimate of 1−10 ns for the lifetime of **10** in methanol making it unlikely that either path A or path B would be able to compete. Also, it should be noted that even

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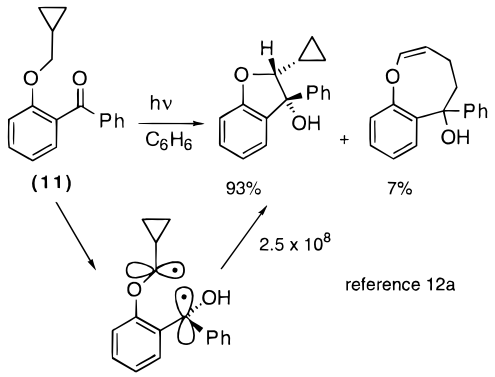
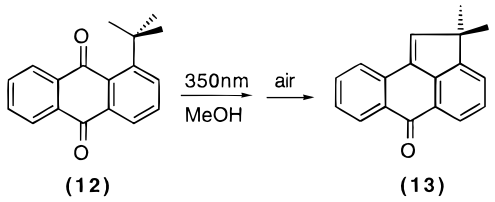
Scheme 7



Scheme 8



if path A or path B were competitive, intramolecular trapping of the homoallylic cation intermediate by the oxygen nucleophile (path A) should supersede or at least compete with carbon−carbon bond formation (path B). Perhaps the strongest argument, though, against a cationic route to anthrone **5** is that zwitterion **9** would have to form with a rate constant of at least 10^{10} s^{-1} to compete with the **8** to **6** rearrangement, or zwitterion **9** would have to form directly from the triplet state of **1pcp** by hydride transfer. Our earlier work has already ruled out a hydride transfer.[7a]

This work shows that the lifetimes of 1,5-biradicals derived from substituted anthraquinones are approximately 10 times shorter than biradical lifetimes in structurally similar acetophenone and benzophenone systems **11** studied by Wagner and coworkers (Scheme 7).[12a] The main reason for this difference is that anthraquinone biradicals undergo an intramolecular electron transfer to a zwitterion faster than they undergo the usual coupling reactions. One radical site in the anthraquinone serves as the electron donor and is converted to an oxygen stabilized carbocation. The other radical site, a semianthraquinone, serves as the electron acceptor, a role which has been well-documented in the literature.[21] If one of the radical sites in a biradical is not a good electron acceptor, coupling of the biradical becomes the principal mode of reaction as shown for **11**. The same fate awaits a biradical that has a good acceptor site but not a good donor site. Photolysis of anthraquinone **12**, which was prepared to make this point, produces **13** in high yield (Scheme 8). Further work toward identifying systems in which the photogenerated biradical can undergo intramolecular electron transfer to the zwitterion is in progress.

Experimental Section

General Methods. All reagents were purchased from Aldrich Chemical Co. and were used as received. Melting points were determined in open capillary tubes with a Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. IR spectra were obtained with a Mattson Galaxy 4020 FT-IR spectrometer. Low-resolution mass spectra were recorded on a Hewlett-Packard 5971A GC/MS. HPLC analyses were made with a Rainin Model 81-NM pump, Rainin C-18 reverse phase column, and Milton Roy 3100 detector using methanol−water mixtures as the eluting solvent. Proton and ^{13}C NMR spectra were recorded on a Bruker 250-MHz AC-E spectrometer.

1-Hydroxy-2-benzyl-9,10-anthraquinone.[22] To a solution of 1.00 g of 1-hydroxy-9,10-anthraquinone (4.46 mmol) in 100 mL of 5% NaOH (1:1 methanol−water) under argon was added 4.3 g of sodium dithionite and the mixture was heated to 70−5 °C for 10 min. Benzaldehyde (44.6 mmol) was added and the mixture was heated at reflux overnight. The red reaction mixture was cooled, poured into a cold 200-mL solution of 2.5% sulfuric acid, and extracted with methylene chloride (3 × 50 mL). The methylene chloride extracts were combined and dried over $CaCl_2$. The solvent was removed in a rotary evaporator under reduced pressure and the residue was chromatographed on silica gel and eluted with 2:1 hexane−CH_2Cl_2. A large yellow band was collected and evaporated to dryness. The solid residue was recrystallized twice from methanol giving yellow crystals: mp 149−152 °C. ^1H NMR (250 MHz, $CDCl_3$): δ 4.09 (s, 2H), 7.19−7.35 (m, 5H), 7.43 (d, $J = 7.5$ Hz, 1H), 7.7−7.8 (m, 4H), 8.22-8.3 (m, 2H), and 13.3 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 188.8, 182.2, 160.6, 139.0, 137.6, 136.9, 134.6, 134.0, 133.7, 133.2, 131.6, 129.1, 128.6, 127.3, 126.9, 126.5, 119.3, 115.6, and 35.6. IR (KBr): 3029, 1667, 1632, 1590, 1432, 1297, 1262, 783, and 714 cm^{-1}.

***trans*-(2-Phenylcyclopropyl)carbinol.** The procedure of Sneen et al.[23] was followed starting from *trans*-2-phenylcyclopropanecarboxylic acid. The product was obtained as a colorless oil by vacuum distillation (83%, bp 68−69 °C {0.2 mm}). ^1H NMR (250 MHz, $CDCl_3$): δ 0.9 (m, 2H), 1.4 (m, 1H), 1.6 (br s, 1H), 1.8 (m, 1H), 3.6 (d AB quartet, 2H), 7.0−7.4 (m, 5H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 142.49, 128.37, 125.85, 125.66, 66.49, 25.29, 21.32, and 13.86. IR (neat): 3350, 3027, 2872, 1605, 1497, 1462, 1092, 1031, 698 cm^{-1}.

1-{(*trans*-2-Phenylcyclopropyl)methoxy}-2-benzyl-9,10-anthraquinone. Neat *trans*-(2-phenylcyclopropyl)carbinol (0.142 g, 0.957 mmol) and DEAD (0.20 g, 1.15 mmol) were consecutively added via a syringe to an argon-purged suspension of 1-hydroxy-2-benzyl-9,10-anthraquinone (0.20 g, 0.638 mmol) and triphenylphosphine (0.25 g, 0.957 mmol) in freshly distilled THF (15 mL). The resulting mixture was stirred for 2 h at room temperature and then heated (50 °C) for 16 h. The solution was cooled to room temperature and then concentrated in vacuo. The crude mixture was purified by chromatography on silica gel (CH_2Cl_2/hexane). An analytically pure sample was obtained by recrystallization from methanol (0.236 g, 83.4%, mp. 117−118 °C). ^1H NMR (250 MHz, $CDCl_3$): δ 1.1 (m, 2H), 1.8 (m, 1H), 1.9 (m,1H), 4.0 (dd, $J = 10.1$ and 7.3 Hz, 1H), 4.1 (dd, $J = 10.1$ and 6.9 Hz, 1H), 4.2 (AB quartet, 2H), 7.0−7.3 (m, 10H), 7.5 (d, $J = 7.95$ Hz, 1H), 7.8 (m, 2H), 8.05 (d, $J = 7.95$ Hz, 1H), and 8.3 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 183.03, 182.59, 157.74, 143.84, 142.24, 139.47, 136.16, 134.84, 134.22, 134.14, 133.51, 132.66, 129.15, 128.72, 128.37, 127.27, 126.65, 126.54, 125.89, 125.74, 125.68, 123.41, 78.60, 36.29, 23.15, 22.06, and 14.16. IR (KBr): 3028, 1670, 1325, 1275, 960, 716, and 700 cm^{-1}. Anal. Calcd for $C_{31}H_{24}O_3$: C, 83.76; H, 5.44. Found: C, 84.17; H, 5.76.

1-(Cyclopropylmethoxy)-2-methyl-9,10-anthraquinone.[9] Yellow needles were obtained by recrystallization from cyclohexane: mp 116−117 °C. ^1H NMR (250 MHz, $CDCl_3$): δ 0.4 (m, 2H), 0.65 (m, 2H), 1.04 (m, 1H), 2.43 (s, 3H), 3.8 (d, $J = 7.2$ Hz, 2H), 7.6 (d, $J = 7.8$ Hz, 1H), 7.75 (m, 2H), 8.0 (d, $J = 7.8$ Hz, 1H), and 8.2 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 183.2, 182.7, 158.0, 141.3, 136.3, 134.8, 134.0, 133.8, 133.4, 132.7, 127.2, 126.6, 125.6, 123.2, 79.0, 17.1, 11.2, and 3.3. IR (KBr): 3000, 1671, 1582, 1324, 1273, 1246, 1050, 972, and 714 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.68; H, 5.62.

Irradiation of 1pcp. A ∼0.013 M solution of *trans*-1-{(2-phenylcyclopropyl)methoxy}-2-benzyl-9,10-anthraquinone (236 mg) in HPLC grade methanol/THF (5:1, 40 mL) was vigorously degassed under argon for 15 min and irradiated for 2.5 h in a Rayonet (350 nm). ^1H NMR and HPLC were used to monitor the course of the reaction. After the reaction had gone to completion, the solvent was removed in

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a rotary evaporator and the residue (~60% **5** by ^{1}H NMR integration) was separated using preparative HPLC. The major product was further purified by recrystallization in methanol (53 mg, 22.5%). [1*R*-(1α,4*β*,-13a*β*)]-1,2,3,4-Tetrahydro-1-phenyl-6-(phenylmethyl)-9*H*-4,13b-epoxyanthra[1, 9-*bc*]oxocin-9-one **(5)**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.85 (br dq, J = 17.5 and 3.5 Hz, 1H), 2.08 (ddd, J = 17.5, 13 and 5.5 Hz, 1H), 2.24 (m, 2H), 3.25 (dd, J = 13, and 3.5 Hz, 1H), 4.08 (s, 2H), 6.0 (br d, J = 7.0 Hz, 2H), 6.10 (t, 1H), 6.86 (dd, J = 7.2 and 7.5 Hz, 2H), 7.06 (dt, J = 1.0 and 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.21 (m, 1H), 7.25 (m, 4H), 7.36 (dd, J = 7.5 and 1.0 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.66 (ddd, J = 7.5, 7.0, and 1.0 Hz, 1H), 7.70 (dd, J = 7.5 Hz and 1.0 Hz, 1H), and 7.94 (d, J = 7.5 Hz, 1H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 181.77, 149.97, 143.12, 139.97, 137.64, 132.57, 132.40, 131.52, 130.92, 130.01, 129.22, 128.90, 128.44, 127.97, 127.52, 127.43, 126.17, 125.73, 123.72, 121.79, 117.34, 96.18, 74.09, 56.97, 35.93, 32.87, and 22.20. IR (neat): 2922, 1672, 1588, 1441, 1302, 1283, 1246, 1125, and 1032 cm^{-1}. HRMS (EI) calcd for $C_{31}H_{24}O_3$ 444.1725, found 444.1744.

Crystal Structure of 5. X-ray crystallography was performed on a 0.17 × 0.25 × 0.45 mm crystal with Mo Kα radiation (λ = 0.71073 Å) on a Rigaku MSC-AFC6S. Unit cell dimensions (triclinic, space group P $\bar{1}$,No. 2) are as follows: a = 8.888(4) Å, b = 18.204(5) Å, c = 7.888(4) Å, α = 95.78(3)°, β = 114.53(4)°, γ = 96.39(3)°, V = 1138.5(8) Å^3, Z = 2, D = 1.297 g/cm^3. Data were collected at 293 K using the θ−2θ scan technique. A total of 4299 reflections were collected, of which 4017 were unique. The structure was solved by the direct methods program SHELXS-86[24] with full-matrix least-squares refinement on F^2 (R = 0.0478 and R_w = 0.0962).

Irradiation of 1cp.[9] A solution of 1-(cyclopropylmethoxy)-2-methyl-9,10-anthraquinone (102 mg) in approximately 75 mL of HPLC grade methanol and under argon was irradiated for 2 h in a Rayonet (350 nm). Workup provided 1-hydroxy-2-methyl-9,10-anthraquinone (68.5 mg, 82.4%) and cyclopropanecarboxaldehyde (16.2 mg, 68%)**:** ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.9−1.0 (d, 4H), 1.9 (m, 1H), and 8.9 (d, 1H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 201.6, 22.6, and 7.3.

2-Carboxy-2′-(1,1-dimethylethyl)benzophenone. To a mixture of Mg (0.341 g, 14.0 mmol) and 10 mL of anhydrous ether under argon was added approximately one-third of a solution of 85% *o*-bromo-*tert*-butylbenzene[25] (1.99 g, 7.94 mmol) in 10 mL of anhydrous ether. Once the reaction was initiated, the remaining bromide was added slowly to maintain a steady reflux (20 min). After the addition, the reaction mixture was heated at reflux for 30 min, cooled in an ice bath, and added to a solution of freshly sublimed phthalic anhydride (1.40 g, 9.46 mmol) in 50 mL of anhydrous ether. A solid separated immediately and the reaction mixture was heated to reflux for 1.25 h. Aqueous HCl (6.0 M, 25 mL), previously cooled in an ice bath, was slowly added to the reaction mixture and the ether layer was separated. The aqueous layer was extracted with 25 mL of ether. The ether extracts were combined and washed with 90 mL of saturated aqueous $NaHCO_3$. The ether layer containing isopropenylbenzene was discarded. The aqueous $NaHCO_3$ extract was acidified with 25 mL of concentrated HCl resulting in the separation of the above acid as a viscous liquid. The acid was extracted into CH_2Cl_2 (3 × 25 mL) and isolated from the solution after drying ($CaCl_2$) and removal of solvent under reduced pressure in a rotary evaporator. The residue (1.24 g) solidified upon standing and was recrystallized from aqueous ethanol giving 765 mg (34%) of the desired acid as colorless plates: mp 171−2 °C; ^{1}H NMR (250 MHz, acetone-d_6): δ 1.41 (s, 9H) and 7.24−7.77 (m, 9H). ^{13}C NMR (250 MHz, acetone-d_6): δ 199.5, 169.8, 149.9, 139.9, 139.4, 135.4, 132.4, 131.4, 130.8, 130.5, 130.3, 129.3, 128.0, 125.6, 36.6, and 32.1. IR (KBr): 3300−2500, 1698, 1673, 1296, 1255, 930, 765, and 638 cm^{-1}.

1-(1,1-Dimethylethyl)-9,10-anthracenedione (12). A solution of 2-carboxy-2′-(1,1-dimethylethyl)benzophenone (500 mg, 1.89 mmol) in 5.0 mL of concentrated H_2SO_4 was heated at 70−75 °C for 1.5 h, cooled, and poured over approximately 50 g of ice water. The mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the extracts were combined and dried over $CaCl_2$. After the solvent was removed in a rotary evaporator under reduced pressure, the yellow residue was chromatographed on silica gel. Elution with hexane−CH_2Cl_2 (5:3) gave a single yellow band which contained 368 mg (80%) of **12**. An analytically pure sample was obtained by recrystallization from heptane which gave the desired **AQ** as yellow needles: mp 103−104 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.54 (s, 9H) and 7.59−8.26 (m, 7H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 188.3, 183.6, 153.6, 136.7, 136.0, 135.4, 134.1, 133.7, 133.0, 132.5, 132.2, 126.9, 126.2, 126.0, 37.1, and 31.5. IR (KBr): 1678, 1580, 1304, 1262, 964, 852, 808, and 710 cm^{-1}. MS, *m/e* (rel intensity) 264 (59), 247 (100), 231 (41), 222 (65), 202 (19), 165 (22), 152 (16), and 117 (14). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.08; H, 6.06.

Irradiation of 12. A solution of 1-(1,1-dimethylethyl)-9,10-anthracenedione (56 mg, 0.014 M) in methanol (15 mL) was deoxygenated with argon and irradiated for 3 h in a Rayonet (350 nm). HPLC analysis of the reaction mixture indicated almost 60% conversion of **12**. Three products were observed by HPLC, with one comprising the major amount (~85%). The solvent was removed under reduced pressure to give a yellow oil, which was separated by preparative HPLC (eluent, methanol): **12** (21 mg) and **13** (25 mg, 77%) as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.6 (s, 6H), 7.15 (s, 1H), 7.5 (dd, J = 7.6 and 7.4 Hz, 1H), 7.55 (dt, J = 1.4 and 7.3 Hz, 1H), 7.6 (dtd, J = 8, 7.3, and 1.4 Hz, 1H), 7.7 (dt, J = 1.46 and 7.65 Hz, 1H), 8.0 (dd, J = 7.64 and 1.5 Hz, 1H), 8.1 (dd, J = 7.66 and 0.6 Hz, 1H), and 8.5 (dd, J = 7.9 and 1.5 Hz, 1H). ^{13}C NMR (250 MHz, $CDCl_3$): δ 179.77, 151.52, 144.25, 143.94, 132.49, 132.34, 131.30, 128.77, 128.42, 127.11, 126.82, 125.31, 124.78, 124.73, 123.65, 51.83, and 24.24. IR: 3059, 2963, 2926, 2861, 1652, 1599, 1581, 1462, 1300, 1262, 1159, 777, 748, and 702 cm^{-1}. MS, *m/e* (rel intensity) 246 (75), 231 (100), 202 (55), and 101 (22). HRMS (EI) calcd for $C_{18}H_{14}O$ 246.1045, found 246.1042.

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Supporting Information Available: Crystallographic summary for **5** including tables of crystal data and structure refinement, bond lengths and angles, least-squares planes, atomic coordinates, and stereoviews for **5** (12 pages). See any current masthead for ordering and Internet access instructions.

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