Photochemistry of 1-Alkoxy- and 1-(Benzyloxy)-9,10-anthraquinones in Methanol: A Facile Process for the Preparation of Aldehydes and Ketones†

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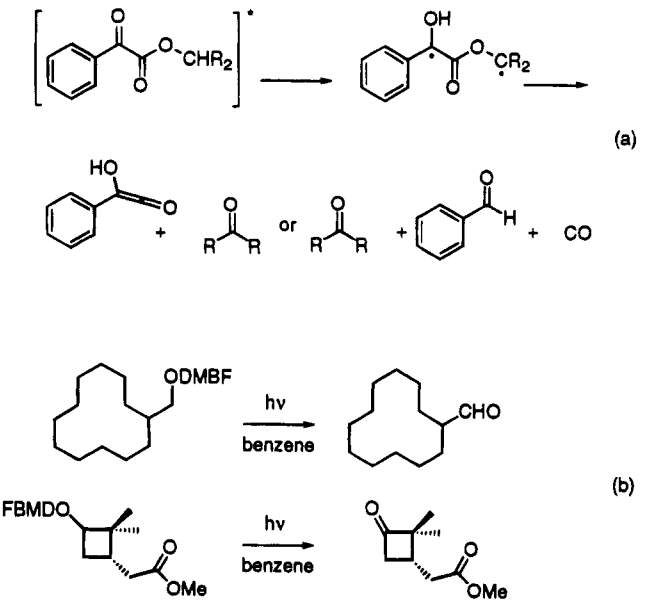
The facile production of acid sensitive aldehydes and ketones via photochemical intramolecular δ-hydrogen atom transfer in 1-alkoxy- and 1-(benzyloxy)-9,10-anthraquinones (**1**) was investigated. Irradiation of **1** in argon purged methanol generates the primary photoproducts, 1-(RCH(OMe)O)- and 1-(ArCH(OMe)O)-9,10-anthrahydroquinones (**2**), respectively. Upon exposure to air, the intermediate anthrahydroquinone is rapidly converted to the corresponding aldehyde and 1-hydroxy-9,10-anthraquinone (**3**), which can be recycled. Aldehydes containing an acetal or ketal were prepared in high yields using this photoprocess. Apparent rate constants for the photodemethylation of 1-methoxy-2-X-9,10-anthraquinones (X = H, Me, Et, Pr, Bu, i-Bu, and benzyl) were measured and found to vary by a factor of 10 separating the slowest anthraquinone (X = H) and the fastest (X = benzyl), indicating a strong dependency upon the size of the substituent at the 2-position. These rate constants are ascribed to equilibrium populations of conformers in the geometry required for reaction in the n,π* triplet state.

Introduction

A variety of methods have been reported for the preparation of aldehydes.[1] The most prevalent examples of these involve oxidation of primary alcohols using chromium(VI).[2] Although these procedures are often very effective, copious amounts of chromium oxidants must be employed which is undesirable given their cost and toxicity.[3] Catalytic amounts of chromium oxidants have been employed to compensate for these shortcomings.[4] Problems, however, still persist in these methods such as catalyst construction and overoxidation to the carboxylic acid. The aforementioned limitations make the development of new synthetic methods for the preparation of aldehydes desirable.

Photochemically induced reactions of α-keto acids and esters have been shown to generate carbonyl byproducts.[5] Initially, α-keto acids and their derivatives were used as photochemically-removable protecting groups in a variety of technologies including bioorganic and stereolithography techniques.[6] Recently, however, their ability to produce carbonyl compounds has been investigated. Sciano reported that direct (366 nm) irradiation of alkyl benzoylformates in the absence of oxygen produces carbonyl compounds. The mechanism for this transformation involves a 1,5-hydrogen abstraction from the n,π* triplet state of the benzoylformate (Scheme 1a).[7]

Scheme 1



Product studies suggest that several competing reactions are involved in the decay of the biradical leading to mixtures which are highly absorbing (ketene, benzaldehyde, and carbon monoxide). Pirrung and Tepper have recently exploited the photochemistry of substituted benzoylformate esters for the preparation of several aldehydes and ketones.[8] Two notable examples are presented in Scheme 1b. Cyclododecylmethyl (2,4-dimethoxybenzoyl)formate (DMBF) upon UV irradiation in benzene forms cyclododecanecarboxaldehyde in 64% yield. Similarly, irradiation of the DMBF ester of a pinene-derived cyclobutanol in benzene produced methyl 2,2-dimethyl-3-oxocyclobutaneacetate in 66% yield. Irradiation of the DMBF esters in a benzene–methanol

† This paper is dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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(1) (a) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1992; p 1495. (b) Smith, M. B. *Organic Synthesis;* McGraw-Hill, Inc.: New York, 1994; p 1595.

(2) (a) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis*; Plenum Press: New York, 1984; p 343. (b) Haines, A. H. *Methods for the Oxidation of Organic Compounds*; Academic Press: London, 1985. (c) Piancatelli, C.; Scettri, A.; D'Auria, M. *Synthesis* **1982**, 245.

(3) (a) Burrows, D. *Chromium Metabolism and Toxicity*; CRC Press: Boca Raton, 1983; p 172. (b) *IARC Monogr.* **1980**, *23*, 205. (c) *IARC Monogr.* **1973**, *2*, 100.

(4) Muzart, J. *Chem. Rev.* **1992**, *92*, 113.

(5) Huyser, E. S.; Neckers, D. C. *J. Org. Chem.* **1964**, *29*, 276.

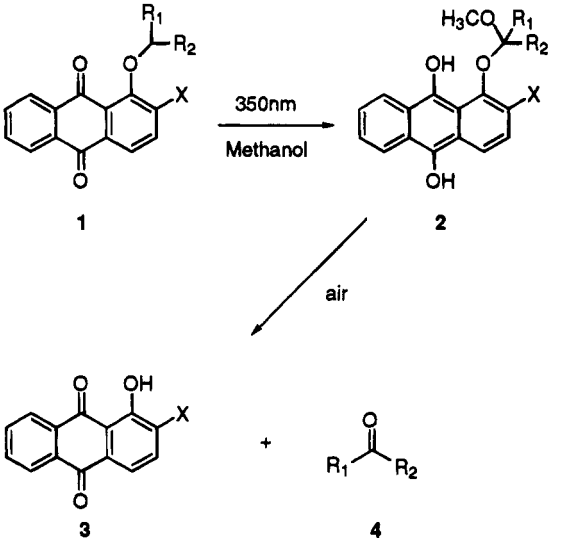
(6) Pillai, V. N. R. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1987; Vol. 9, pp 225–323.

(7) Encinas, M. V.; Lissi, E. A.; Zanocco, A.; Stewart, L. C.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 386–391.

(8) Pirrung, M. C.; Tepper, R. J. *J. Org. Chem.* **1995**, *60*, 2461–2465.

0022-3263/95/1960-6852$09.00/0

Scheme 2



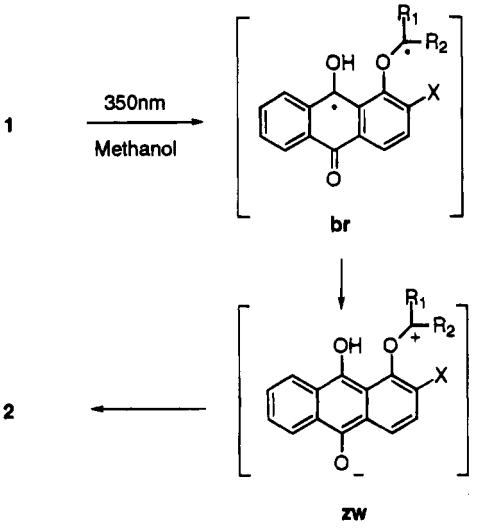
solution produces a mandelate ester derived from the trapping of an intermediate hydroxyketene.

In 1991, we reported that photoexcited 1-alkoxy- and 1-(benzyloxy)-9,10-anthraquinones **1** undergo facile conversion to their corresponding anthrahydroquinones (**2**) in methanol (Scheme 2).[9] This process can be viewed as an intramolecular redox reaction between the anthraquinone and the alkoxy group at the 1-position. The intermolecular variant to this reaction has been known for quite some time.[10] Upon exposure to air, the intermediate anthrahydroquinone is rapidly converted to the corresponding carbonyl and 1-hydroxy-9,10-anthraquinone (**3**), which can be recycled.

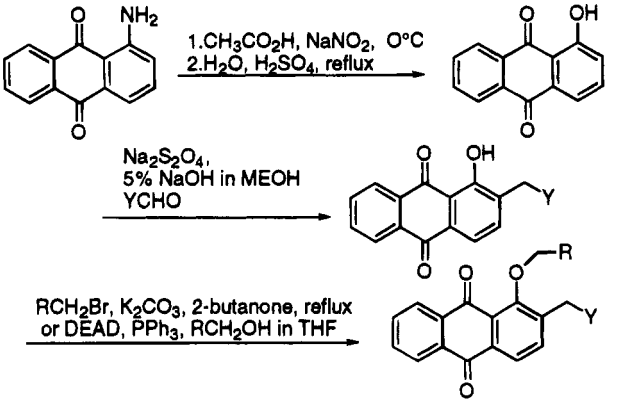
Deuterium isotope effects, substituent effects, and solvent polarity studies support a mechanism in which a biradical intermediate (br) is formed by an intramolecular δ-hydrogen atom transfer that occurs in one step, rather than sequential electron and proton transfers (Scheme 3).[9a] The biradical presumably decays via an intramolecular electron transfer to a zwitterion (zw). This intermediate would be expected to react with methanol to generate the primary photoproduct **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 also in the hydrolysis of the acetal. In this paper we exploit this photochemical transformation for the purpose of preparing aldehydes and ketones, some of which contain acid-sensitive groups such as acetals and ketals. This method provides a number of advantages over current routes: expensive oxidizing agents are not necessary (oxidizing source is air), the anthraquinone is recyclable, and photoactivation can be performed using visible light at ambient temperatures. The photoprocess is also highly chemoselective—olefins and acetals are not affected and overoxidation of the aldehyde is not observed.

Scheme 3



Scheme 4



Results and Discussion

Variation of Alkyl Size at the 2-Position in the Anthraquinone. Anthraquinones **5a–g** were prepared by addition of the corresponding aliphatic or aryl aldehyde to the reduced form of 1-hydroxy-9,10-anthraquinone under basic conditions[11] as shown in Scheme 4, followed by coupling with dimethyl sulfate.

These anthraquinones were prepared to probe the effect of different alkyl groups at the 2-position on the rate of photodemethylation of 1-methoxy-9,10-anthraquinones. Dilute solutions (0.020 mM) of these compounds in methanol were irradiated simultaneously using a merry-go-round apparatus with a 300-W tungsten lamp at the center.[12] Aliquots were removed at regular intervals and analyzed by HPLC. Plots of $\ln\{[\mathbf{5}]_0/[\mathbf{5}]_t\}$ versus time (s), as shown in Figure 1 for **5a**, are linear. The relative slopes from these plots, k_{dis}, which are apparent rate constants, can serve as a quantitative measure of these substitutent effects. The data show good correlation between alkyl size (steric bulk) and k_{dis} which varies by a factor of 10 separating the slowest anthraquinone **5a** and the fastest anthraquinone **5g** containing a benzyl group at the 2-position (see Table 1).

The dependence of the photodemethylation rate upon the size of the substituent at the 2-position suggests that

(9) (a) Blankespoor, R. L.; DeJong, R. L.; Dykstra, R.; Hamstra, D. A.; Rozema, D. B.; VanMeurs, D. P.; Vink, P. *J. Am. Chem. Soc.* **1991**, *113*, 3507–3513. (b) Blankespoor, R. L.; Hsung, R.; Schutt, D. L. *J. Org. Chem.* **1988**, *53*, 2877.

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(11) (a) Marschalk, C.; Koenig, F.; Oursoussoff, N. *Bull Soc. Chim. Fr.* **1936**, *3*, 1545–1575. (b) Zembower, D. E.; Kam, C-M.; Powers, J. C.; Zalkow, L. H. *J. Med. Chem.* **1992**, *35*, 1597–1605.

(12) Moses, F. G.; Liu, R. S. H.; Monroe, B. H. *Mol. Photochem.* **1969**, 245.

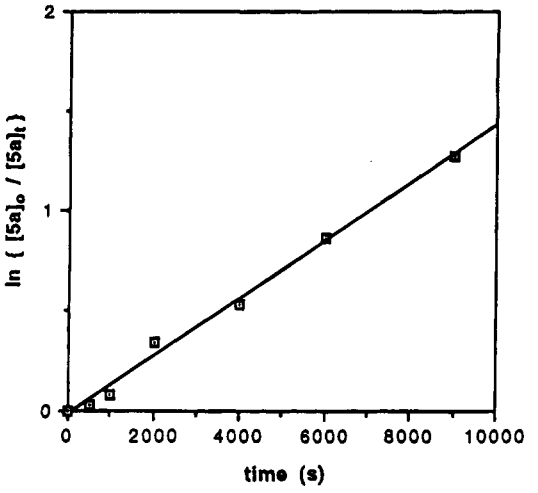
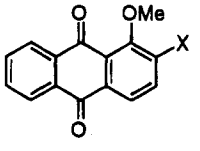


Figure 1. Plot of $\ln\{[\mathbf{5a}]_o/[\mathbf{5a}]_t\}$ versus time from the photolysis of 0.20 mM **5a** in methanol using visible light. R = 0.994.

Table 1. Apparent Rate Constants for the Disappearance of 5 during Photolysis in Methanol

Anthraquinone (5)	$k_{dis} \times 10^4$ s^{-1}
5a	0.239
5b	1.45
5c	1.69
5d	1.94
5e	1.72
5f	2.05
5g	2.66

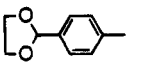
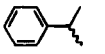
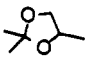
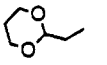
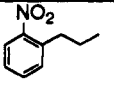


5a: X=H
5b: X=CH_3
5c: X=CH_2CH_3
5d: X=$CH_2CH_2CH_3$
5e: X=$CH_2CH_2CH_2CH_3$
5f: X=$CH_2CH(CH_3)_2$
5g: X=CH_2Ph

conformational factors play an important role in the rate-determining step. It seems likely that the observed differences in k_{dis} reflect the relative populations of conformations that require minimal bond rotation in order to reach the transition state in accord with the Winstein–Holness principle.[13] The ramifications of conformational equilibrium in the kinetics of intramolecular excited state reactions and decay have been thoroughly reviewed elsewhere.[14]

Preparation of Carbonyl Compounds. A variety of anthraquinones was required to examine the synthetic potential of this process. These compounds were prepared by a conventional route involving coupling of 1-hydroxy-2-(CH_2Y)-9,10-anthraquinones to the corresponding alkyl halide or alcohol, according to the method outlined in Scheme 4.[15] Yields for the synthesis of **1** are presented in Table 2. In most cases, coupling to form **1** occurs in greater than 70% yield (not optimized).

Table 2. Synthesis of 2-Substituted 1-Alkoxy- and 1-(Benzyloxy)-9,10-anthraquinones (1)

1	R_1	R_2	X	% Yield (1)
1a		H	Benzyl	78
1b		H	Butyl	76
1c		H	Butyl	54
1d		H	Butyl	75
1e		H	Butyl	71
1f		H	Butyl	73
1g		H	Methyl	68
1h		H	Methyl	78
1i		H	Methyl	80
1j		CH_3	Methyl	64
1k	R_1,R_2 = -$(CH_2)_5$-		Methyl	59

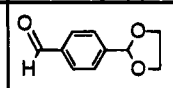
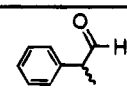
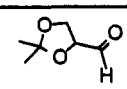
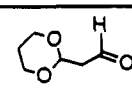
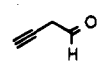
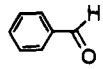
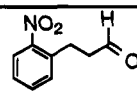
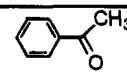
Irradiation of ~0.02 M methanol solutions of **1** under argon, followed by exposure to air, resulted in the formation of the corresponding carbonyl and 1-hydroxy-2-(CH_2X)-9,10-anthraquinone (**3**) in high chemical yield. The photoproducts were separated by chromatographic techniques. Isolated yields for the two photoproducts are presented in Table 3. In all cases, compound **3** was subsequently recycled. The identity of the carbonyl was established, when applicable, by comparison of its spectral data (^{1}H NMR, ^{13}C NMR, and IR) with an authentic sample prepared by an independent method.

As shown in Table 3, activated 1-(benzyloxy)-9,10-anthraquinones were converted to substituted and unsubstituted benzaldehydes and acetophenone in excellent yields. Irradiation of anthraquinones **1a**, **1g**, and **1j** in

(13) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562.
(14) (a) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. (b) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461–467. (c) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491. (d) Wagner, P. J.; Meador, M. A.; Park, B.-S. *J. Am. Chem. Soc.* **1990**, *112*, 5199–5211.

(15) (a) Mitsunobu, O. *Synthesis* **1981**, 1–28. (b) Hughes, D. L. *Org. React.* **1992**, *42*, 335.
(16) (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (b) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275. (c) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1989**, *54*, 2681.

Table 3. Isolated Yields of Products from the Photolysis of 1 in Methanol Using Visible Light

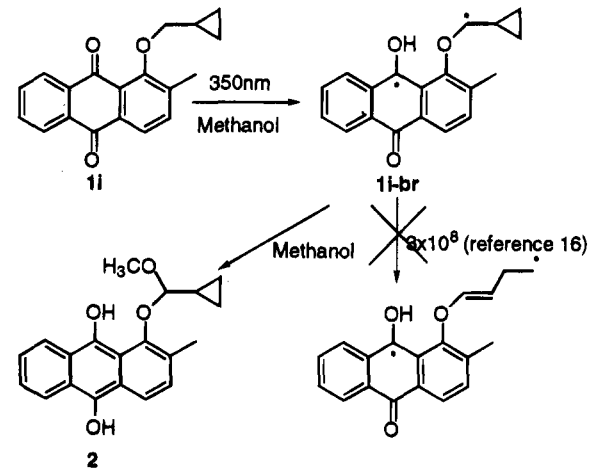
1	Carbonyl (4)	(3-X)	Yield (4)	Yield (3)
1a		Benzyl	79%	77%
1b		Butyl	70%	81%
1c		Butyl	75%	84%
1d		Butyl	52%	77%
1e		Butyl	54%	86%
1f		Butyl	63%	81%
1g		Methyl	81%	76%
1h		Methyl	83%	82%
1i		Methyl	68%	82%
1j		Methyl	78%	83%
1k		Methyl	58%	77%

methanol resulted in nearly quantitative yields of **2**. Upon exposure to air and subsequent purification, 4-(1,3-dioxolan-2-yl)benzaldehyde, benzaldehyde, and acetophenone, respectively, were obtained in approximately 80% yield. Anthraquinones with saturated primary and secondary alkoxy groups at the 1-position were also converted to their corresponding carbonyl compounds and 1-hydroxy-2-X-9,10-anthraquinone in high yields. In most cases, the aldehydes and ketones can be obtained relatively pure in approximately 70% yield following chromatographic separation.

Anthraquinones **1a**, **1c**, **1d**, **1e**, and **1f** were prepared to investigate the utility of this method for the generation of aldehydes containing acid sensitive groups. In all cases studied, the acid sensitive moiety was unaffected by the photoprocess. Ring opening of the dioxolane and dioxane was not observed by ^{1}H NMR. For example, irradiation of **1c** produced 2,3-*O*-isopropylideneglyceraldehyde (**4c**) in 75% isolated yield. Irradiation of **1e** and **1f** produced the β,γ-unsaturated aldehydes, 3-butenal and 3-butynal, respectively. Isolation of these aldehydes was accomplished by preparatory GC. For 3-butynal, partial thermal rearrangement to 2,3-butadienal occurred on the column at 110 °C.

Given the likelihood of a biradical intermediate in the photochemistry of 1-alkoxy-9,10-anthraquinone (**1**), anthraquinone **1i** was prepared to estimate the lifetime of the biradical (Scheme 5).

Scheme 5



Irradiation (350 nm) of anthraquinone **1i** in methanol and under argon resulted in the conversion to 1-hydroxy-2-methyl-9,10-anthraquinone and the corresponding aldehyde, cyclopropanecarboxaldehyde (**4i**), after exposing the photolysis solution to air. There was no observation by ^{1}H NMR of vinyl hydrogens in this photoconversion. Thus, cyclopropane ring opening in **1i** did not occur to any appreciable extent. It can be concluded based on this result that the rate constant for primary photoproduct formation is on the order of 1×10^9 s^{-1} (lower limit). Further work aimed at establishing the rate constant for this photochemical process is underway using faster radical clocks.[17]

Conclusion

These results show that this photochemical process can be used in the synthesis of aldehydes and ketones containing acid sensitive groups. In addition to its low cost and environmental benefits, this method is superior to some other currently used routes particularly because the anthraquinone template can be recycled and long wavelength radiation can be used. To date most chromium(VI) oxidations are performed in acidic medium or under acid catalysis which precludes these methods for the generation of acid sensitive compounds.[18] Collin's reagent (chromium trioxide/pyridine complex) overcomes the acidity problem; however, a high oxidant to substrate ratio (6:1) is generally required, which is undesirable given chromium's toxicity.[19]

We are now extending this method to the preparation of chiral aldehydes by asymmetric induction of a chiral auxiliary at the 2-position. Efforts are also underway to incorporate this synthetically useful photoreaction onto a solid state support. This should allow for direct access of the aldehyde without the use of purification techniques. Details of these ongoing studies will be forthcoming.

Experimental Section

All reagents were purchased from Aldrich Chemical Co. and used as received. Melting points were determined in open capillary tubes with a Hoover capillary melting point ap-

(17) Blankespoor, R. L.; Peelen, T. J.; Smart, R. P. Paper in preparation.
(18) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 270.
(19) (a) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000. (b) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5927.

paratus 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. 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-9,10-anthraquinone. This compound was prepared from 1-amino-9,10-anthraquinone using a modified procedure of Dimroth.[20] To a 1 L, three-necked flask equipped with a mechanical stirrer, dropping funnel, and thermometer were added 22.3 g (0.100 mol) of 1-amino-9,10-anthraquinone and 300 mL of acetic acid. Concentrated sulfuric acid (90 mL) was added, and the mixture was heated to 70 °C. A small amount of insoluble material was removed by filtering the warm solution through a glass funnel. The filtrate was cooled in an ice–salt bath and a solution of 9.0 g (0.13 mol) of sodium nitrite in 50 mL of water was added over 30 min while the reaction mixture was kept at 5 °C. After stirring an additional 20 min, 3 g of urea was added to quench any unreacted nitrous acid, and the cold solution was added over 30 min to a refluxing solution of 150 mL of concd sulfuric acid in 600 mL of water. The reaction was heated at reflux until nitrogen evolution ceased and then cooled in an ice bath. The yellow-orange crystals were collected by vacuum filtration and sublimed at 150 °C/0.20 Torr. Recrystallization from heptane–toluene gave 15.5 g (70%) of 1-hydroxy-9,10-anthraquinone as yellow needles: mp 195–6 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 7.28 (d, J = 8 Hz, 1H), 7.66 (t, J = 8 Hz, 1H), 7.78–7.82 (m, 3H), 8.23–8.29 (m, 2H), and 12.6 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 116.1, 119.5, 124.3, 126.0, 127.4, 133.2, 133.4, 133.6, 134.1, 134.6, 136.7, 162.5, 182.3, and 188.6.

General Preparation of 1-Hydroxy-2-X-9,10-anthraquinone (3). A literature procedure was used to synthesize these compounds.[11b] To a solution of 1.0 g of 1-hydroxy-9,10-anthraquinone (4.46 mmol) in 100 mL of 5% NaOH in 1:1 methanol–water under argon was added 4.3 g of sodium dithionite, and the mixture was heated to 70–75 °C for 10 min. XCHO (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.

1-Hydroxy-2-butyl-9,10-anthraquinone. Yellow solid: mp 118–119 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 0.96 (t, J = 7.7 Hz, 3H), 1.41 (sextet, J = 7.6 Hz, 2H), 1.62 (m, 2H), 2.8 (t, J = 7.7 Hz, 2H), 7.54 (d, J = 7.72 Hz, 1H), 7.7–7.73 (m, 3H), 8.16–8.21 (m, 2H), and 13 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 13.9, 22.6, 29.6, 31.1, 115.2, 119.2, 126.7, 127.1, 131.1, 133.2, 133.7, 133.8, 134.4, 136.2, 139.3, 160.8, 182.1, and 188.8. IR (KBr): 2956, 2929, 2863, 1667, 1632, 1590, 1432, 1354, 1297, 1266, 795, and 714 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.03; H, 5.86.

1-Hydroxy-2-benzyl-9,10-anthraquinone. Yellow solid: 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, 3H), 8.22–8.3 (m, 2H), and 13.3 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 35.6, 115.6, 119.3, 126.5, 126.9, 127.3, 128.6, 129.1, 131.6, 133.2, 133.7, 134.0, 134.6, 136.9, 137.6, 139.0, 160.6, 182.2, and 188.8. IR (KBr): 3029, 1667, 1632, 1590, 1432, 1297, 1262, 783, and 714 cm^{-1}.

1-Hydroxy-2-ethyl-9,10-anthraquinone. Yellow crystals: mp 155 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 1.23 (t, J = 7.5 Hz, 3H), 2.8 (q, J = 7.5 Hz, 2H), 7.5 (d, J = 7.8 Hz, 1H), 7.8 (m, 3H), 8.3 (m, 2H), and 13 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 14, 23, 115, 119, 127(2), 131, 133(2), 134(2), 136, 141, 161, 183, and 189. IR (KBr): 2967, 1671, 1632, 1590, 1439, 1362, 1289, 1262, 1239, 776, and 710 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18 H, 4.79. Found: C, 75.93; H, 5.03.

1-Hydroxy-2-(2-methylpropyl)-9,10-anthraquinone. Yellow crystals: mp 109–110 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 0.9–1.0 (d, J = 6.6 Hz, 6H), 2.1 (m, 1H), 2.7 (d, J = 7.2 Hz, 2H), 7.5 (d, J = 7.7 Hz, 1H), 7.7–7.8 (m, 3H), 8.3 (m, 2H), and 13 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 23, 28, 39, 115, 119, 127(2), 133(2), 134(2), 136, 138, 139, 161, 183, and 188. IR (KBr): 2956, 1671, 1628, 1594, 1358, 1297, 1266, 783, and 710 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.20; H, 5.90.

1-Hydroxy-2-propyl-9,10-anthraquinone. Yellow crystals: mp 130 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 1.0 (t, J = 7.3 Hz, 3H), 1.7 (br sextet, J = 7.4 Hz, 2H), 2.7 (t, J = 7.35 Hz, 2H), 7.5 (d, J = 7.9 Hz, 1H), 7.7–7.8 (m, 3H), 8.2 (m, 2H), and 13 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 14, 22, 32, 115, 119, 127(2), 131, 133(2), 134(2), 136, 139, 161, 182, and 189. IR (KBr): 2964, 2937, 1671, 1632, 1590, 1432, 1358, 1297, 1262, 1235, and 710 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68 H, 5.30. Found: C, 76.73; H, 5.76.

General Preparation of 1a–c,e,f,j,k. Neat RCH_2OH (0.277 mmol) and DEAD (0.323 mmol) were consecutively added via a syringe to an argon-purged suspension of **3** (0.185 mmol) and triphenylphosphine (0.231 mmol) in freshly distilled THF (5 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 silica gel column chromatography. An analytically pure sample was obtained by recrystallization.

1-[[[4-(1,3-Dioxolan-2-yl)]benzyl]oxy]-2-benzyl-9,10-anthraquinone (1a). Yellow prisms by recrystallization from heptane: mp 145–46 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 4.0–4.2 (m, 4H), 4.05 (s, 2H), 5.0 (s, 2H), 5.85 (s, 1H), 7.1–7.3 (m, 5H), 7.55 (d, J = 7.95 Hz, 1H), 7.5–7.6 (m, 4H), 7.8 (m, 2H), 8.1 (d, J = 7.95 Hz, 1H), and 8.3 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 36.2, 65.3, 75.8, 103.6, 123.7, 126.0, 126.5, 126.6, 126.7, 127.3, 128.4, 128.7, 129.1, 132.6, 133.5, 134.2, 134.2, 134.8, 136.3, 138.0, 138.1, 139.4, 143.9, 157.4, 182.6, and 182.9. IR (KBr): 2894, 1667, 1582, 1324, 1266, 1080, 976, 814, and 714 cm^{-1}. Anal. Calcd for $C_{31}H_{24}O_5$: C, 78.14; H, 5.08. Found: C, 78.23; H, 5.17.

1-(2-Phenylpropanoxy)-2-butyl-9,10-anthraquinone (1b). Yellow needles and prisms by recrystallization twice from methanol: mp 69.5–71 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 0.9 (t, J = 7.2 Hz, 3H), 1.3 (m, 2H), 1.6–1.4 (m, 2H), 1.5 (d, J = 8 Hz, 3H), 2.55 (m, 2H), 3.5 (m, 1H), 4.1–3.9 (dd, J = 8.54, 8.21 Hz, 1H), 4.1–3.9 (dd, J = 8.54, 7.1 Hz, 1H), 7.3 (m, 5H), 7.6 (d, J = 7.9 Hz, 1H), 7.75 (m, 2H), 8.05 (d, J = 7.9 Hz, 1H), and 8.3 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 14, 18, 22, 30, 32, 41, 80, 123, 126, 127(3), 128(3), 133(3), 134(2), 135, 146, 161, 183(2). IR (KBr): 2964, 2929, 1675, 1578, 1323, 1273, 1250, 972, and 718 cm^{-1}. Anal. Calcd for $C_{27}H_{26}O_5$: C, 81.38; H, 6.58. Found: C, 81.48; H, 6.50.

1-[[4-(2,2-Dimethyl-1,3-dioxolanyl)]methoxy]-2-butyl-9,10-anthraquinone (1c). Yellow needles by recrystallization from hexane: mp 78–80 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 0.9 (t, J = 7.23 Hz, 3H), 1.3–1.5 (m, 2H), 1.48 (s, 3H), 1.5 (s, 3H), 1.6–1.7 (m, 2H), 2.8 (m, 2H), 4.05 (dAB quartet, J = 5.47, 14.66 Hz, 2H), 4.25 (dAB quartet, J = 6.45, 31.5 Hz, 2H), 4.7 (m, 1H), 7.6 (d, J = 7.96 Hz, 1H), 7.8 (m, 2H), 8.1 (d, J = 7.96 Hz, 1H), and 8.25 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 182.9, 182.6, 157.1, 145.5, 135.6, 134.7, 134.0, 133.6, 133.4, 132.6, 127.1, 126.5, 125.7, 123.6, 109.4, 74.6, 74.3, 66.5, 32.3, 29.9, 26.7, 25.3, 22.7, and 13.9. IR (KBr): 2956, 2937, 1671, 1324, 1277, 1239, 1050, and 714 cm^{-1}. Anal. Calcd for $C_{24}H_{26}O_5$: C, 73.08; H, 6.64. Found: C, 72.86; H, 6.88.

1-[2-(1,3-Dioxan-2-yl)ethoxy]-2-butyl-9,10-anthraquinone (1d). Yellow needles by recrystallization from methanol: mp 110–111 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 0.9 (t, J = 7.25 Hz, 3H), 1.3–1.5 (m, 2H), 1.6–1.7 (m, 2H), 2.0–2.2 (m, 2H), 2.3 (m, 2H), 2.8 (m, 2H), 3.85 (dt, J = 2.4, 12.2 Hz, 2H), 4.05 (t, J = 6.3 Hz, 2H), 4.2 (br dd, J = 5.07, 10.7 Hz, 2H), 5.0 (t, J = 5.36 Hz, 1H), 7.6 (d, J = 7.93 Hz, 1H), 7.8 (m, 2H), 8.1

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(d, J = 7.93 Hz, 1H), and 8.25 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 183.2, 182.7, 157.7, 145.6, 135.6, 134.9, 134.1, 133.7, 133.4, 132.7, 127.3, 126.6, 125.8, 123.5, 88.1, 70.1, 67.0, 35.9, 32.3, 30.0, 25.9, 22.7, and 14.0. IR (KBr): 2964, 2925, 1675, 1324, 1277, 1250, 1138, 1050, 1011, and 718 cm^{-1}. Anal. Calcd for $C_{24}H_{26}O_5$: C, 73.08; H, 6.64. Found: C, 72.83; H, 6.39.

1-(3-Butenoxy)-2-butyl-9,10-anthraquinone (1e). Yellow platelets by recrystallization twice from methanol: mp 85–86 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.9 (t, J = 7.3 Hz, 3H), 1.4 (m, 2H), 1.6 (m, 2H), 2.8 (m, 4H), 4.1 (t, J = 6.7 Hz, 2H), 5.15 (br d, J = 10.2 Hz, 1H), 5.25 (ddd, J = 17.1, 1.7, 1.5, 1H), 6.0 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H), 7.6 (d, J = 7.94 Hz, 1H), 7.75 (m, 2H), 8.1 (d, J = 7.9 Hz, 1H), and 8.25 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 13.9, 22.7, 30.2, 32.4, 34.8, 73.8, 117.1, 123.4, 125.8, 126.6, 127.2, 132.7, 133.4, 133.8, 134.0, 134.7, 134.9, 135.6, 145.6, 157.8, 182.8, and 183.2. IR (KBr): 2956, 2933, 1671, 1578, 1324, 1273, 1246, 1057, and 714 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.97; H, 6.82.

1-(3-Butynoxy)-2-butyl-9,10-anthraquinone (1f). Yellow needles by recrystallization twice from methanol: mp 93–95 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 1.4 (m, 2H), 1.6 (m, 2H), 2.1 (t, J = 2.7 Hz, 1H), 2.8 (m, 2H), 2.9 (dt, J = 2.7, 6.8 Hz, 2H), 4.1 (t, J = 6.83 Hz, 2H), 7.6 (d, J = 7.96 Hz, 1H), 7.75 (m, 2H), 8.1 (d, J = 7.96 Hz, 1H), and 8.25 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 13.9, 20.3, 22.7, 32.5, 34.8, 69.8, 72.1, 82.2, 123.7, 125.7, 126.6, 127.2, 132.7, 133.5, 133.8, 134.1, 134.8, 135.6, 145.6, 157.1, 182.7, and 183.1. IR (KBr): 3280, 2954, 2123, 1668, 1323, 1273, 1246, and 714 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.07. Found: C, 79.26; H, 6.06.

1-(Benzyloxy)-2-methyl-9,10-anthraquinone (1g). A mixture of 26 mg (0.109 mmol) of 1-hydroxy-2-methyl-9,10-anthraquinone, benzyl bromide (650 mg), and K_2CO_3 (1 g, 7.25 mmol) in 45 mL of 2-butanone was heated to reflux for 19 h. After cooling, the mixture was diluted with 35 mL of H_2O and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated on the rotary evaporator. The resulting yellow solid was recrystallized from heptane, giving 24.2 mg (68%) of yellow needles: mp 150–151 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.05 (s, 2H), 7.34–7.47 (m, 3H), 7.60–7.64 (m, 3H), 7.72–7.83 (m, 2H), 8.07–8.10 (d, 1H), and 8.24–8.33 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 17.2, 76.3, 120.5, 123.6, 125.9, 126.6, 127.3, 128.3, 128.6, 132.7, 133.5, 133.9, 134.1, 134.9, 136.5, 137.0, 141.1, 157.7, 182.7, and 183.2. IR (Nujol): 1670, 1325, 1276, 1242, 1192, 1160, 1045, 1013, 975, 915, 850, 760, 725, and 696 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.68; H, 5.03.

1-[[3-(*o*-Nitrophenyl)propyl]oxy]-2-methyl-9,10-anthraquinone (1h). A mixture of 46 mg (0.193 mmol) of 1-hydroxy-2-methyl-9,10-anthraquinone, *o*-(3-iodopropyl)-nitrobenzene (354 mg, 1.22 mmol), and K_2CO_3 (533 mg, 3.86 mmol) in 10 mL of 2-butanone was heated to reflux for 15 h. The reaction mixture was cooled, filtered, and concentrated on the rotary evaporator. The crude mixture was purified by silica gel column chromatography (benzene/hexane). The resulting yellow solid was recrystallized from heptane/toluene, giving 60.2 mg (78%) of yellow needles: mp 162–163 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.27 (m, 2H), 2.43 (s, 3H), 3.19–3.26 (m, 2H), 4.06 (t, 2H), 7.34–7.41 (m, 1H), 7.51–7.61 (m, 3H), 7.70–7.81 (m, 2H), 7.92 (dd, 1H), 8.02–8.05 (d, 1H), and 8.19–8.29 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 17, 30, 31, 73, 123, 125, 126, 127(2), 132, 133(4), 134(2), 135, 136, 137, 141, 150, 158, and 183(2). IR (Nujol): 1562, 1460, 1176, 1155, 1130, 1090, 1055, 950, 927, 906, 870, 829, 783, 760, 74, 710, 690, 652, 638, 625, and 611 cm^{-1}. Anal. Calcd for $C_{24}H_{19}NO_5$: C, 71.81; H, 4.77; N, 3.49. Found: C, 71.69; H, 5.03; N, 3.49.

1-(Cyclopropylmethoxy)-2-methyl-9,10-anthraquinone (1i). Yellow needles by recrystallization from cyclohexane: mp 116–117 °C. ^{1}H 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 3.3, 11.2, 17.1, 79.0, 123.2, 125.6, 126.6, 127.2, 132.7, 133.4, 133.8, 134.0, 134.8, 136.3, 141.3, 158.0, 182.7, and 183.2. 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.

1-(1-Phenylethoxy)-2-methyl-9,10-anthraquinone (1j). Yellow solid: mp 114–115 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.8 (d, J = 6.5 Hz, 3H), 2.1 (s, 3H), 5.2 (q, J = 6.5 Hz, 1H), 7.4–7.2 (m, 5H), 7.5 (d, J = 7.85 Hz, 1H), 7.7 (m, 2H), 7.9 (d, J = 7.85 Hz, 1H), and 8.3 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 17.9, 21.4, 82.7, 119.2, 123.0, 125.9, 126.6, 127.3, 128.3, 132.7, 133.4, 133.9, 134.0, 135.0, 136.2, 137.8, 141.4, 141.8, 156.6, 183.0, and 183.2. IR (KBr): 1667, 1578, 1324, 1273, 1057, and 710 cm^{-1}. Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.80; H, 5.33.

1-Cyclohexoxy-2-methyl-9,10-anthraquinone (1k). Yellow needles by recrystallization from heptane: mp 126 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.2 (m, 3H), 1.6 (m, 3H), 1.8 (m, 2H), 2.2 (m, 2H), 2.4 (s, 3H), 4.1 (m, 1H), 7.6 (d, J = 7.8 Hz, 1H), 7.7 (m, 2H), 8.0 (d, J = 7.8 Hz, 1H), and 8.2 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$): 18.1, 24.6, 25.5, 32.8, 83.9, 122.7, 125.8, 126.5, 127.3, 132.7, 133.3, 133.9, 134.0, 135.0, 136.1, 141.7, 157.0, 182.9, and 183.2. IR (KBr): 2933, 2856, 1675, 1578, 1320, 1273, 1246, 1050, and 714 cm^{-1}. Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29. Found: C, 78.85; H, 6.24.

1-Methoxy-2-methyl-9,10-anthraquinone (5b). Prepared by the method of Savard and Brassard: yellow needles, mp 164–165 °C (lit.[21] mp 166–67 °C). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.00; H, 5.08.

1-Methoxy-2-ethyl-9,10-anthraquinone (5c). Yellow needles by recrystallization from heptane: mp 140–41 °C. ^{1}H NMR (250 MHz, $CDCl_3$): 1.25 (t, 3H), 2.75–2.84 (m, 2H), 3.92 (s, 3H), 7.6 (d, 1H), 7.7–7.75 (m, 2H), 8.05 (d, 1H), and 8.17–8.25 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 14, 23, 62, 124, 125, 127(2), 133(2), 134(2), 135, 136, 147, 159, and 183(2). IR (KBr): 2967, 1671, 1590, 1439, 1358, 1293, 776, and 710 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.86; H, 5.18.

1-Methoxy-2-propyl-9,10-anthraquinone (5d). Yellow needles by recrystallization from heptane: mp 130–31 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.0 (t, J = 7.3 Hz, 3H), 1.7 (m, 2H), 2.75 (t, 2H), 3.92 (s, 3H), 7.6 (d, J = 7.94 Hz, 1H), 7.7–7.75 (m, 2H), 8.05 (d, J = 7.94 Hz, 1H), 8.2 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 14, 23, 32, 61, 123, 125, 127(2), 132, 133, 134(2), 135, 136, 145, 159, 183, and 184. IR (KBr): 2967, 2871, 1675, 1582, 1324, 1162, 1050, 965, and 714 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.73; H, 5.76.

1-Methoxy-2-butyl-9,10-anthraquinone (5e). Yellow needles by recrystallization from heptane: mp 95–97 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (t, 3H), 1.34–1.48 (m, 2H), 1.63 (m, 2H), 2.78 (t, 2H), 3.94 (s, 3H), 7.6 (d, 1H), 7.7–7.8 (m, 2H), 8.05 (d, 1H), and 8.25 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 14, 23, 30, 32, 62, 123, 125, 127(2), 132, 133, 134(2), 135, 136, 146, 159, 183, and 184. IR (KBr): 2956, 2870, 1675, 1582, 1323, 1277, 1050, 965, and 714 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.79; H, 5.96.

1-Methoxy-2-(2-methylpropyl)-9,10-anthraquinone (5f). Yellow needles by recrystallization from heptane: mp 100 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.95 (d, J = 7.0 Hz, 6H), 1.96–2.04 (m, 1H), 2.63–2.66 (d, J = 7.2 Hz, 2H), 3.93 (s, 3H), 7.6 (d, J = 7.9 Hz, 1H), 7.7–7.8 (m, 2H), 8.05 (d, J = 7.9 Hz, 1H), and 8.22–8.29 (m, 2H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 23, 29, 39, 62, 123, 125, 127(2), 132, 133, 134(2), 135, 136, 144, 159, 183(2). IR (KBr): 3310, 2956, 2867, 1675, 1582, 1486, 1324, 1273, 1058, 956, and 714 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.5; H, 6.01.

1-Methoxy-2-benzyl-9,10-anthraquinone (5g). Yellow needles: mp 139–140 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.30–8.19 (m, 2H), 8.07 (d, J = 7.5 Hz, 1H), 7.7–7.8 (m, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.13–7.34 (m, 5H), 4.16 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 36.17, 61.98, 123.51, 126.51, 126.66, 127.22, 128.68, 129.04, 129.05, 132.59, 133.53, 134.16, 134.20, 134.73, 136.24, 139.43, 143.57, 158.95, 182.52,

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and 182.93. IR (KBr): 1674, 1323, 1277, 713 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.71; H, 5.17.

General Photolysis Procedure. A ~0.02 M solution of **1** (60–100 mg) in 50–70 mL of HPLC grade methanol or a methanol/THF (depending upon solubility) was vigorously degassed under argon for 15 min and irradiated for 2 h in a Rayonet (350 nm). ^1H NMR and HPLC were used to monitor the course of the reaction. Once the reaction had gone to completion, the solvent was removed in a rotary evaporator and the residue was chromatographed on basic alumina or silica gel.

Irradiation of 1-[[[4-(1,3-Dioxolan-2-yl)]benzyl]oxy]-2-benzyl-9,10-anthraquinone (1a). A solution of 1-[[[4-(1,3-dioxolan-2-yl)]benzyl]oxy]-2-benzyl-9,10-anthraquinone (66.2 mg) in approximately 45 mL of HPLC grade methanol/THF (2:1) and under argon was irradiated for 3 h in a Rayonet (350 nm). Workup gave 19.6 mg of 4-(1,3-dioxolan-2-yl)benzaldehyde **(4a)** (79%) and 33.5 mg of 1-hydroxy-2-benzyl-9,10-anthraquinone (77%). 4-(1,3-Dioxolan-2-yl)benzaldehyde:[22] ^1H NMR (250 MHz, $CDCl_3$) δ 4.05 (m, 4H), 5.95 (s, 1H), 7.63 (d, 2H), 7.91 (d, 2H), and 10.02 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 65, 103, 127, 130, 137, 144, and 192.

Irradiation of 1-(2-Phenylpropoxy)-2-butyl-9,10-anthraquinone (1b). A solution of 1-(2-phenylpropoxy)-2-butyl-9,10-anthraquinone (114 mg) in 60 mL of argon purged HPLC grade methanol/acetonitrile (5:1) was irradiated for 4 h in a Rayonet (350 nm). Workup of the photoreaction gave 26.8 mg of 2-phenylpropanal **(4b)** (70%) and 65 mg of 1-hydroxy-2-butyl-9,10-anthraquinone (81%). 2-Phenylpropanal:[23] ^1H NMR (250 MHz, $CDCl_3$) δ 1.4 (d, J = 7.1 Hz, 3H), 3.6 (dq, J = 1.5, 7.1 Hz, 1H), 7.4–7.2 (m, 5H), and 9.7 (d, J = 1.5 Hz, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 201.1, 137.8, 129.1, 128.4, 127.6, 53.0, and 14.6. IR (film): 2979, 1729, 1497, 1455, 1023, 760, and 698 cm^{-1}.

Irradiation of 1-[[4-(2,2-Dimethyl-1,3-dioxolanyl)]-methoxy]-2-butyl-9,10-anthraquinone (1c). A solution of 1-[[4-(2,2-dimethyl-1,3-dioxolanyl)]methoxy]-2-butyl-9,10-anthraquinone (83 mg) in approximately 60 mL of HPLC grade methanol and under argon was irradiated for 4 h in a Rayonet (350 nm). Workup gave 20.4 mg of 2,3-*O*-isopropylideneglyceraldehyde[24] **(4c)** (75%) and 49.6 mg of 1-hydroxy-2-butyl-9,10-anthraquinone (84%). 2,3-*O*-Isopropylideneglyceraldehyde **(4c)**: ^1H NMR (250 MHz, $CDCl_3$) δ 1.40 (br s, 3H), 1.42 (br s, 3H), 4.1 (dd, J = 8.82, 4.9 Hz, 1H), 4.2 (dd, J = 8.82, 7.4 Hz, 1H), 4.4 (ddd, J = 7.4, 4.9, 1.9 Hz, 1H), and 9.7 (d, J = 1.9 Hz, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 25.1, 26.2, 65.5, 79.8, 111.2, and 201.8. IR (film): 2820, 1725, 1380, and 840 cm^{-1}.

Irradiation of 1-[[2-(1,3-Dioxan-2-yl)]ethoxy]-2-butyl-9,10-anthraquinone (1d). A solution of 1-[[2-(1,3-dioxan-2-yl)]ethoxy]-2-butyl-9,10-anthraquinone (119 mg) in approximately 90 mL of HPLC grade methanol and under argon was irradiated for 8 h in a Rayonet (350 nm). The solvent was removed in a rotary evaporator, and the residue was chromatographed on silica gel. Elution with petroleum ether–ether gave 19.8 mg of 1,3-dioxane-2-acetaldehyde **(4d)** (52%) and 62.4 mg of 1-hydroxy-2-butyl-9,10-anthraquinone (77%). 1,3-Dioxane-2-acetaldehyde **(4d)**: bp: 75–77 °C (lit.[25] bp: 74–76 °C), ^1H NMR (250 MHz, $CDCl_3$) δ 2.05 (m, 1H), 2.1 (m, 1H), 2.6 (dd, J = 4.7, 2.4 Hz, 2H), 3.8 (m, 2H), 4.1 (m, 2H), 5.0 (t, J = 4.7 Hz, 1H), and 9.8 (t, J = 2.4 Hz, 1H). IR (film): 3000, 2730, 1725, 1140, and 1050 cm^{-1}.

Irradiation of 1-(3-Butenoxy)-2-butyl-9,10-anthraquinone (1e). A solution of 1-(3-butenoxy)-2-butyl-9,10-anthraquinone (61.2 mg) in approximately 15 mL of HPLC grade methanol and under argon was irradiated for 3.5 h in a Rayonet (350 nm). The solvent was removed by fractional distillation, and the residue was chromatographed on a preparative silica gel TLC plate. Developing with methylene chloride/hexane (1:2) gave 43 mg of 1-hydroxy-2-butyl-9,10-anthraquinone (85%). The aldehyde, 3-butenal, was obtained by injecting the crude reaction mixture through a preparatory GC (Gow Mac). The yield for 3-butenal (54%) was determined by ^1H NMR integration. 3-Butenal[26] **(4e)**: ^1H NMR (250 MHz, $CDCl_3$) δ 3.2 (ddd, J = 6.9, 1.8, 1.5 Hz, 2H), 5.2 (bqd, J = 1.43, 17.1 Hz, 1H), 5.3 (bqd, J = 1.3, 10.3 Hz, 1H), 5.9 (tdd, J = 6.91, 10.37, 17.1 Hz, 1H), and 9.7 (t, J = 1.9 Hz, 1H).

Irradiation of 1-(3-Butynoxy)-2-butyl-9,10-anthraquinone (1f). A solution of 1-(3-butynoxy)-2-butyl-9,10-anthraquinone (132 mg) in approximately 40 mL of HPLC grade methanol and under argon was irradiated for 5.25 h in a Rayonet (350 nm). The solvent was removed by fractional distillation, and the residue was chromatographed on a preparative silica gel TLC plate. Developing with petroleum ether/ether (2:1) gave 89.6 mg of 1-hydroxy-2-butyl-9,10-anthraquinone (81%). The aldehyde, 3-butynal, was obtained in the same manner as 3-butenal. Partial thermal rearrangement to 2,3-butadienal occurred during isolation. The yield for 3-butynal (63%) was determined by ^1H NMR integration. 3-Butynal[27] **(4f)**: ^1H NMR (250 MHz, $CDCl_3$) δ 2.30 (t, J = 2.74 Hz, 1H), 3.3 (dd, J = 2.7, 1.6 Hz, 2H), and 9.65 (t, J = 1.6 Hz, 1H). 2,3-Butadienal:[28] ^1H NMR (250 MHz, $CDCl_3$) δ 5.4 (d, J = 6.2 Hz, 2H), 5.9 (dt, J = 7.0, 6.2 Hz, 1H), and 9.55 (d, J = 7.07 Hz, 1H).

Irradiation of 1-(Benzyloxy)-2-methyl-9,10-anthraquinone (1g). A solution of 1-(benzyloxy)-2-methyl-9,10-anthraquinone (91.3 mg) in approximately 45 mL of HPLC grade methanol/THF (5:1) and under argon was irradiated for 1 h in a Rayonet (350 nm). The methanol was removed in a rotary evaporator, and the residue was chromatographed on silica gel. Elution with hexane–CH_2Cl_2 (1:1) gave 24 mg of benzaldehyde **(4g)** (81.3%) and 59.8 mg of 1-hydroxy-2-methyl-9,10-anthraquinone (76.4%). The aldehyde gave spectra data identical in all respects with that of a commercially available sample. Bp: 176–178 °C (lit.[23] bp: 178 °C), ^1H NMR (250 MHz, $CDCl_3$) δ 7.7–7.5 (m, 3H), 7.83 (m, 2H), and 10 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ 192.4, 136.4, 134.4, 129.7, and 128.9. IR (film): 2820, 2739.8, 1709, 1605, 1211.7, 833.5, and 748 cm^{-1}.

Irradiation of 1-[3-(*o*-Nitrophenyl)propyl]-2-methyl-9,10-anthraquinone (1h). A solution of 1-[3-(*o*-nitrophenyl)-propyl]-2-methyl-9,10-anthraquinone (124 mg) in approximately 400 mL of HPLC grade methanol and under argon was irradiated for 46 h with a 300-W tungsten lamp. The methanol was removed in a rotary evaporator, and the residue was chromatographed on silica gel. Elution with hexane–benzene gave 1-hydroxy-2-methyl-9,10-anthraquinone (60.2 mg, 82%). Elution with hexane–toluene–ethyl acetate (70:20:10) gave 50 mg (83%) of 3-(*o*-nitrophenyl)propanal **(4h)**: ^1H NMR (250 MHz, $CDCl_3$) δ 2.32–2.70 (m, 4H), 7.20–7.32 (m, 4H), and 9.7 (s, 1H). IR (film): 3035, 2815, 2720, 1711, 1605, 1511, 1440, 1345, 1167, 1060, 960, 858, 790, 740, 708, and 660 cm^{-1}.

Irradiation of 1-(Cyclopropylmethoxy)-2-methyl-9,10-anthraquinone (1i). 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 16.2 mg of cyclopropanecarboxaldehyde **(4i)** (68%) and 68.5 mg of 1-hydroxy-2-methyl-9,10-anthraquinone (82.4%). Cyclopropanecarboxaldehyde **(4i)**: ^1H 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 7.3, 22.6, and 201.6.

Irradiation of 1-(1-Phenylethoxy)-2-methyl-9,10-anthraquinone (1j). A solution of 1-(1-phenylethoxy)-2-methyl-

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9,10-anthraquinone (97.2 mg) in 30 mL of HPLC grade methanol and under argon was irradiated for 2 h in a Rayonet (350 nm). The solvent was removed under reduced pressure, and the residue was chromatographed on a prep TLC plate [methylene chloride/hexane (1:2)]. 1-Hydroxy-2-methyl-9,10-anthraquinone and acetophenone was obtained in 83.1% (56.2 mg) and 78% (26.7 mg), respectively. Both products were identical to authentic samples. Acetophenone **(4j)**: bp 199 °C (lit. 202 °C).[23]

Irradiation of 1-Cyclohexoxy-2-methyl-9,10-anthraquinone (1k). A solution of 1-cyclohexoxy-2-methyl-9,10-anthraquinone (64 mg) in approximately 15 mL of HPLC grade methanol and under argon was irradiated for 6.25 h in a Rayonet (350 nm). The methanol was removed in a rotary evaporator, and the residue was chromatographed on silica gel. Elution with petroleum ether–ether (2:1) gave 1-hydroxy-2-methyl-9,10-anthraquinone (36.7 mg, 77.1%) and cyclohexanone (11.3 mg, 57.6%). Both products were identical to authentic samples. Cyclohexanone **(4k)**: bp 154 °C (lit. 155 °C).[23]

Measurement of Apparent Rate Constants (k_{dis}). Samples were irradiated simultaneously in a merry-go-round apparatus using a 300-W tungsten light source. Aliquots were removed at various times, and sample concentrations were determined by HPLC at a wavelength of 254 nm. Plots of $\ln\{[AQ]_0/[AQ]_t\}$ versus time (AQ = reactant anthraquinone) were linear and the slopes correspond to the apparent rate constants for the disappearance of AQ (k_{dis}).

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