JOC Article
pubs.acs.org/joc

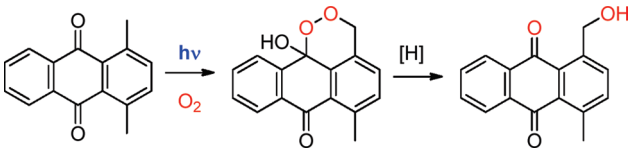
Photochemical Hydroxylation of 1-Methyl-9,10-anthraquinones: Synthesis of 9′-Hydroxyaloesaponarin II

Salwa Elkazaz and Paul B. Jones*

Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27106

jonespb@wfu.edu

Received October 19, 2009

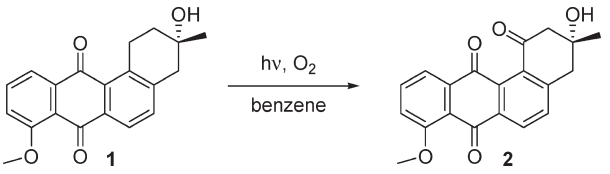


Photolysis of 1-methyl-9,10-anthraquinones in the presence of oxygen yields endoperoxides that can be reduced to produce 1-hydroxymethyl-9,10-anthraquinones. The reaction proceeds in a fashion similar to that of other *o*-alkylphenones which yield either a 1,4-diradical or a "photoenol" upon irradiation. Anthraquinones undergo photochemistry at a wavelength where the endoperoxide is transparent, allowing its isolation. A singlet oxygen quencher had no effect on the rate of formation of the endoperoxide. The photochemical hydroxylation has been used in a total synthesis of a naturally occurring polyketide, 9′-hydroxyaloesaponarin II.

Introduction

Anthraquinones are powerful photo-oxidants that absorb UV-A and blue light.[1−5] Quinones can oxidize material by photoinduced electron transfer (PET) or hydrogen abstraction.[6−8] The reduced form of 9,10-anthraquinones, 9,10-dihydroxyanthracenes, rapidly oxidize to the corresponding 9,10-anthraquinone in the presence of O_2 (air).[9] Singlet excited anthraquinones undergo ISC to the T1 (lowest triplet) excited state with a quantum yield near 1.0.[10] Oxygen quenches the T1 state of most anthraquinones at a diffusion-controlled rate.[11] Anthraquinone photochemistry is rich; anthraquinones are efficient H atom and electron acceptors and are useful triplet sensitizers.[12−15]

SCHEME 1

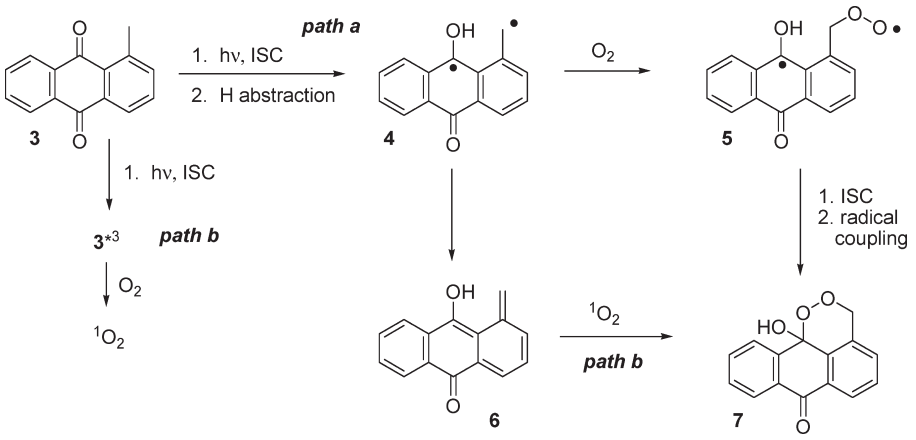


Like most aryl ketones, triplet-excited 9,10-anthraquinones readily abstract H from groups *ortho* to the carbonyl.[16−28] Such hydrogen abstractions have significant

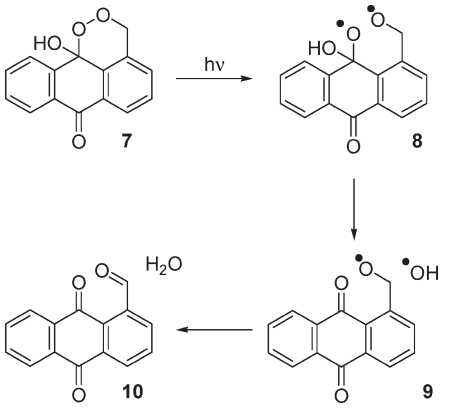
(1) Aquino, A. M.; Abelt, C. J.; Berger, K. L.; Darragh, C. M.; Kelley, S. E.; Cossette, M. V. *J. Am. Chem. Soc.* **1990**, *112*, 5819–5824.
(2) Gan, H.; Whitten, D. G. *J. Am. Chem. Soc.* **1993**, *115*, 8031–8037.
(3) Yoshida, Z.; Takabayashi, F. *Tetrahedron* **1967**, *24*, 933–943.
(4) Kuboyama, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 329–333.
(5) Rontani, J. F.; Giusti, G. *J. Photochem. Photobiol. A* **1990**, *53*, 69–75.
(6) Gorner, H. *Photochem. Photobiol.* **2003**, *77*, 171–179.
(7) Grummt, U. W.; Friedrich, M. *Z. Chem.* **1985**, *25*, 434–435.
(8) Gritsan, N. P.; Khmelinski, I. V.; Usov, O. M. *J. Am. Chem. Soc.* **1991**, *113*, 9615–9620.
(9) Blankespoor, R. L.; Smart, R. P.; Batts, E. D.; Kiste, A. A.; Lew, R. E.; Van der Vliet, M. E. *J. Org. Chem.* **1995**, *60*, 6852–6859.
(10) Pritchina, E. A.; Gritsan, N. P.; Burdzinski, G. T.; Platz, M. S. *J. Phys. Chem. A* **2007**, *111*, 10483–10489.
(11) Nunez Montoya, S. C.; Comini, L. R.; Sarmiento, M.; Becerra, C.; Albesa, I.; Argueello, G. A.; Cabrera, J. L. *J. Photochem. Photobiol. B* **2005**, *78*, 77–83.
(12) Rontani, J. F.; Raphel, D.; Aubert, C. *J. Photochem. Photobiol. A* **1993**, *72*, 189–193.
(13) Rontani, J. F.; Giusti, G. *Tetrahedron Lett.* **1988**, *29*, 1923–1926.
(14) Nakayama, T.; Miki, S.; Shin, H.; Hamanoue, K. *Recent Res. Dev. Photochem. Photobiol.* **2002**, *6*, 63–78.
(15) Geimer, J.; Beckert, D. *Chem. Phys. Lett.* **1998**, *288*, 449–458.
(16) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83–91.
(17) Breslow, R.; Kitabatake, S.; Rothbard, J. *J. Am. Chem. Soc.* **1978**, *100*, 8156–8160.
(18) Blankespoor, R. L.; De Jong, R. L.; Dykstra, R.; Hamstra, D. A.; Rozema, D. B.; VanMeurs, D. P.; Vink, P. *J. Am. Chem. Soc.* **1991**, *113*, 3507–3513.
(19) Nakayama, T.; Honma, C.; Miki, S.; Hamanoue, K. *Chem. Phys. Lett.* **1993**, *213*, 581–585.
(20) Kang, H.; Rokita, S. E. *Nucleic Acids Res.* **1996**, *24*, 3896–3902.
(21) Kaliappan, K. P.; Ravikumar, V. *J. Org. Chem.* **2007**, *72*, 6116–6126.
(22) Kesenheimer, C.; Groth, U. *Org. Lett.* **2006**, *8*, 2507–2510.
(23) Motoyoshiya, J.; Masue, Y.; Iwayama, G.; Yoshioka, S.; Nishii, Y.; Aoyama, H. *Synthesis* **2004**, 2099–2102.
(24) Krohn, K.; Sohrab, M. H.; Flörke, U. *Tetrahedron: Asymmetry* **2004**, *15*, 713–718.

Published on Web 12/14/2009 DOI: 10.1021/jo902247v

SCHEME 2



SCHEME 3



synthetic utility. The rate of the reaction is fastest if the hydrogen is transferred through a six-membered transition state but is an efficient process even when the transfer is through a five- or seven-membered transition state. In some molecules, with the proper conformation, hydrogen can be transferred between remote locations. The hydrogen transfer produces a 1,*x* biradical which can then undergo a variety of reactions including cyclization, oxidation, and fragmentation.[18−31]

Quinones and anthraquinones are found in a number of natural products including the angucyclinones.[24−26,32−42] Syntheses of angucyclinones have often taken advantage of the photo-oxidizing ability of the anthraquinone chromophore to install a carbonyl on an alkyl substituent *ortho* to one of the quinone carbonyls (e.g., **1** to **2**, Scheme 1). The reaction is dependent on molecular oxygen and reliably oxidizes only a methylene *ortho* to the carbonyl.

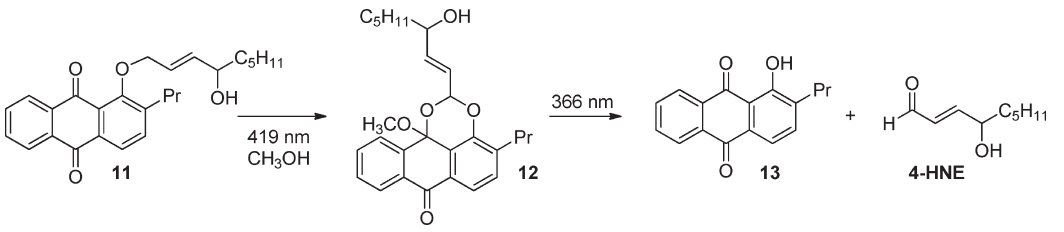
Two possible mechanisms by which an anthraquinone can oxidize an alkyl group *ortho* to the carbonyl have been proposed (Scheme 2).[43−46] The more probable pathway is that the excited quinone (**3**) abstracts hydrogen through a 6-membered transition state to afford a 1,4-diradical (**4**, path a). The diradical would be trapped by molecular oxygen to give a 1,6-peroxodiradical (**5**). Cyclization of this diradical would afford endoperoxide **7**. Alternatively, triplet anthraquinone (**3**) could sensitize the production of singlet oxygen which then might react by cycloaddition to a photoenol (**6**, path b) to give **7**. This route should be less likely as it requires two short-lived species, a photoenol and singlet oxygen, to interact.

Continued photolysis of **7** (Scheme 3) could result in homolytic cleavage of the peroxide O−O bond, producing a diradical (**8**) which could expel hydroxyl radical via β-fragmentation to reform the quinone (**9**). The hydroxyl radical could then abstract hydrogen from the alkyl group to produce the final oxidized product (**10**). Generally, photochemical degradation of the endoperoxide leads to many products and polymeric material, but it has been known to give a single product in good yield.[43]

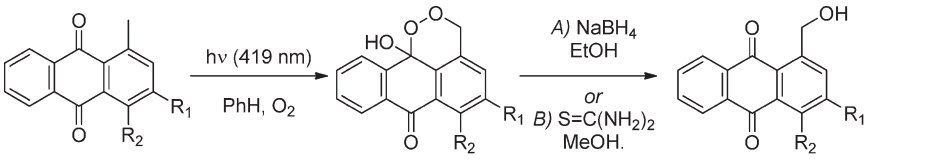
The outcome of photolysis of 1-substituted anthraquinones can be wavelength dependent (Scheme 4).[47] Photolysis

(25) Krohn, K.; Khanbabaee, K.; Micheel *Liebigs Ann. Chem.* **1995**, 1529–1537.
(26) Krohn, K.; Ballwanz, F.; Baltus, W. *Liebigs Ann. Chem.* **1993**, 911–913.
(27) Ito, Y.; Takahashi, H.; Hasegawa, J.-y.; Turro, N. J. *Tetrahedron* **2009**, *65*, 677–689.
(28) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405–422.
(29) Smart, R. P.; Peelen, T. J.; Blankespoor, R. L.; Ward, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 461–465.
(30) Brinson, R. G.; Hubbard, S. C.; Zuidema, D. R.; Jones, P. B. *J. Photochem. Photobiol., A* **2005**, *175*, 118–128.
(31) Wagner, P. J.; Meador, M. A.; Park, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5199–5211.
(32) Krohn, K.; Agocs, A.; Baeuerlein, C. *J. Carbohydr. Chem.* **2003**, *22*, 579–592.
(33) Kalogerakis, A.; Groth, U. *Synlett* **2003**, 1886–1888.
(34) Landells, J. S.; Larsen, D. S.; Simpson, J. *Tetrahedron Lett.* **2003**, *44*, 5193–5196.
(35) Kalogerakis, A.; Groth, U. *Org. Lett.* **2003**, *5*, 843–844.
(36) Krohn, K.; Droege, W.; Hintze, F. *An. Quim.* **1995**, *91*, 388–393.
(37) Krohn, K.; Khanbabaee, K. *Liebigs Ann. Chem.* **1994**, 1109–1112.
(38) Krohn, K.; Khanbabaee, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 99–100.
(39) Moore, H. W.; Czerniak, R. *Med. Res. Rev.* **1981**, *1*, 249–280.
(40) Fotso, S.; Mahmud, T.; Zabriskie, T. M.; Santosa, D. A.; Sulastri; Proteau, P. J. *J. Nat. Prod.* **2008**, *71*, 61–65.
(41) Kalinovskaya, N. I.; Kalinovsky, A. I.; Romanenko, L. A.; Pushilin, M. A.; Dmitrenok, P. S.; Kuznetsova, T. A. *Nat. Prod. Commun.* **2008**, *3*, 1611–1616.
(42) Potterat, O.; Puder, C.; Wagner, K.; Bolek, W.; Vettermann, R.; Kauschke, S. G. *J. Nat. Prod.* **2007**, *70*, 1934–1938.
(43) Konosonoks, A.; Wright, P. J.; Tsao, M.-L.; Pika, J.; Novak, K.; Mandel, S. M.; Krause Bauer, J. A.; Bohne, C.; Gudmundsdottir, A. D. *J. Org. Chem.* **2005**, *70*, 2763–2770.
(44) Fekarurhobo, G. K.; Obomanu, F. G.; Carless, H. A. J. *J. Chem. Soc. Niger.* **2002**, *27*, 24–25.
(45) Yoshioka, M.; Nishizawa, K.; Suzuki, J.; Iwata, Y.; Kumakura, S.; Hasegawa, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3097–3101.
(46) Saito, M.; Kamei, Y.; Kuribara, K.; Yoshioka, M.; Hasegawa, T. *J. Org. Chem.* **1998**, *63*, 9013–9018.

SCHEME 4



SCHEME 5

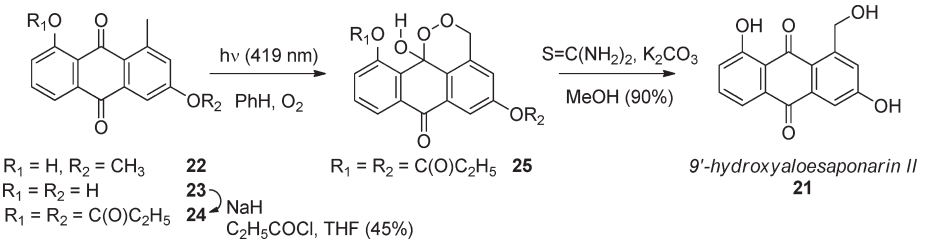


$R_1 = R_2 = H$ **3**
$R_1 = CH_3$, $R_2 = H$ **14**
$R_1 = H$, $R_2 = CH_3$ **15**

$R_1 = R_2 = H$ **7**,
$R_1 = CH_3$, $R_2 = H$ **16**
$R_1 = H$, $R_2 = CH_3$ **17**

$R_1 = R_2 = H$ **18**, 70%^{B}, 65%^{A}
$R_1 = CH_3$, $R_2 = H$ **19**, 55%^{B}, 65%^{A}
$R_1 = H$, $R_2 = CH_3$ **20**, 70%^{B}, 55%^{A}

SCHEME 6



$R_1 = H$, $R_2 = CH_3$ **22**
$R_1 = R_2 = H$ **23**
$R_1 = R_2 = C(O)C_2H_5$ **24**

$R_1 = R_2 = C(O)C_2H_5$ **25**

9′-hydroxyaloesaponarin II **21**

of a caged 4-hydroxy-2-nonenal (4-HNE), **11**, resulted in high yields of 4-HNE when 366 nm light was used but fairly low yields when 419 nm light was employed. The most abundant product at the longer wavelength was acetal **12**, which could be converted cleanly to 4-HNE by irradiation with 366 nm light. Apparently, during photolysis at 366 nm, acetal **12** was formed but was converted to 4-HNE and **13** by a second photoreaction. With the loss of the anthraquinone chromophore, **12** did not absorb at longer wavelengths and, therefore, no secondary photoreaction could occur when longer wavelength light was used.

The photochemical formation of endoperoxides such as **7** from *o*-alkylphenones is known.[43−46] However, yields of endoperoxide are generally poor. Secondary photochemistry of the endoperoxide is a possible explanation for the observed low yields. We speculated that using a chromophore, such as anthraquinone, that absorbs at longer wavelength may allow selective excitation of the initial chromophore which would provide a means to isolate the endoperoxide. Once isolated, the endoperoxide could then be reduced (or further elaborated) under milder conditions than photolysis in order to avoid excessive degradation, allowing the endoperoxide to be a synthetically useful intermediate. A series of 1-methyl-9,10-anthraquinones was thus prepared and their photochemistry investigated.

Results and Discussion

Photolysis of 1-methyl-9,10-anthraquinones using 419 nm light gave the corresponding endoperoxides relatively cleanly (Scheme 5). Irradiation of **3** in O_2-saturated benzene gave an adduct in good yield. The adduct produced ^{1}H NMR and MS data consistent with endoperoxide **7**. The endoperoxide was reasonably stable but decomposed upon any attempt at purification. In solution or in the presence of sunlight **7** would decompose, with common byproducts being an aldehyde (such as **10**) or alcohol (such as **18**), though neither were obtained in good yield in this manner and significant amounts of unidentified material accumulated over time.

In contrast, treatment of the endoperoxides with either $NaBH_4$ or thiourea reduced the peroxide to an alcohol in good yield.[48] Thiourea was a milder reagent, but in some cases a small amount of aldehyde (e.g., **10**) was obtained. In experiments with $NaBH_4$ no aldehyde was observed, presumably due to its reduction. However, the reduction was very sensitive to the amount of $NaBH_4$ used. If too much $NaBH_4$ was used, the quinone was also reduced, lowering yields. In the end, thiourea was found to be a superior reagent, despite a small amount of material being lost as the aldehyde ($< 10\%$).

As expected, the photochemical hydroxylation was selective toward the *ortho* methyl (**14** to **19**). The reaction also cleanly hydroxylated a single *ortho* methyl even when two were present (**15** to **20**). The latter reaction is consistent with an endoperoxide intermediate; the endoperoxide (**17**) chromophore does not absorb blue light well, and so no further hydrogen abstraction occurs once the endoperoxide is

(47) Brinson, R. G.; Jones, P. B. *Org. Lett.* **2004**, *6*, 3767–3770.

(48) Balci, M. *Chem. Rev.* **1981**, *81*, 91–108.

formed. The anthraquinone chromophore is not regenerated until the endoperoxide is reduced, which occurs after photolysis is stopped. Thus, the procedure allows oxidation of a single *ortho* methyl even where other oxidizable methyls are present.

The mechanism of the photo-oxidation was probed by attempting to quench the reaction with dibutyl sulfide, a known $^1O_2$ quencher.[49] The sulfide had no effect on the rate of formation of **7** by photolysis of **3**. This observation rules out path b (Scheme 2). Therefore, the most likely mechanism for the reaction is trapping of an intermediate 1,4-diradical by molecular oxygen (path a) .

The reaction sequence described above could easily be carried out in a one-pot reaction. The anthraquinone was dissolved in benzene, O_2 was bubbled through the solution for 15 min, and then, with a continuous flow of O_2, the solution was photolyzed until TLC indicated complete consumption of the anthraquinone. The oxygen purge was then removed and the reaction mixture diluted with ethanol and either $NaBH_4$ or thiourea added. Typically, the reduction was complete in less than 1 h when $NaBH_4$ was used and in a few hours when thiourea was the reducing agent, though stirring overnight did not reduce yields. Solvent was removed and the product purified by chromatography.

The scope of the reaction was examined by using the photochemical hydroxylation to synthesize 9′-hydroxyaloesaponarin II, **21**, a naturally occurring polyketide.[50−52] Aloesaponarin II (**23**) was prepared following a literature synthesis.[53] Neither **23** nor a related structure, methyl ether **22**,[53] gave any hydroxylation products when irradiated in the presence of oxygen for 6 h. Both **22** and **23** were recovered unchanged after photolysis. As expected, hydrogen abstraction from the *ortho* OH was faster than that from the *ortho* methyl, allowing the *ortho*-OH to serve as an internal quencher.

Acylation of both phenolic groups in **23** with propionyl chloride gave dipropionate **24** (Scheme 6). Irradiation of **24** gave endoperoxide **25**. Treatment of **25** with thiourea and K_2CO_3 in methanol reduced the peroxide and cleaved the propionate protecting groups to give **21** in 90% yield over two steps.

Conclusion

An easy, one-pot hydroxylation of 1-alkyl-9,10-anthraquinones has been developed. The photoinduced hydroxylation proceeds through an isolable endoperoxide produced when an intermediate 1,4-diradical is trapped by molecular oxygen. Singlet oxygen is not involved in the oxidation. When the wavelength of excitation is sufficiently long, the endoperoxide is isolable and relatively stable. This may be a general method for the isolation of endoperoxide adducts of photochemically produced diradicals. The method tolerates the presence of acylated oxygen groups on the quinone rings but not an unprotected *ortho* phenol. The photochemical hydroxylation developed was used in the first synthesis of 9′-hydroxyaloesaponarin II.

Experimental Section

General Procedure for Photochemical Hydroxylation. A 0.003 M solution of the 1-methyl-9,10-anthraquinone derivative in benzene was prepared. Oxygen was bubbled through the solution for 20 min and then while the solution was irradiated at 419 nm. The reaction was followed by TLC until the starting anthraquinone was completely consumed. The solution was concentrated immediately in vacuo in the dark. The crude endoperoxide thus obtained was then reduced using one of the methods listed below. *Safety note: peroxides are unstable and can explode. On the scale prepared, none of the endoperoxides described above exhibited such behavior, but caution should be exercised when repeating these procedures.*

Method A. The crude endoperoxide was dissolved in ethanol and cooled to 0 °C and 0.5 equiv of $NaBH_4$ added. The resulting mixture was not allowed to stir more than 30 min. It was important not to stir the reaction longer as continued exposure to the $NaBH_4$ caused significant product degradation. The reaction was quenched with a dilute solution of aq HCl which was then extracted 3× with EtOAc. The combined organic layers were washed with 2 × 30 mL portions of brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude 1-hydroxymethyl-9,10-anthraquinone was purified by column chromatography over silica gel.

Method B. The crude endoperoxide was dissolved in ethanol and 5 equiv of thiourea added to the solution. The progress of the reaction was monitored by TLC and was usually found to be complete in 30 min. However, stirring for 12 h or more in the dark did not cause degradation of the product. In the case of **22**, 5 equiv of K_2CO_3 was also added. The reaction mixture was added to brine and extracted with 3 × 20 mL EtOAc. The combined organic layers were washed with (2 × 30 mL) portions of 1 N HCl, satd aq K_2CO_3, and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography over silica gel with hexane/EtOAc (3:1) to afford the corresponding anthraquinone-1-methanol derivative as a pale yellow or yellow solid.

Endoperoxide 7. The crude endoperoxide was obtained by evaporation of solvent following photolysis. The endoperoxide decomposed on all attempts at purification, but a ^1H NMR and MS could be obtained on the crude product. ^1H NMR (300 MHz, $CDCl_3$) δ 4.39 (1H, bs), 5.21 (1H, d, J = 15.3), 5.61 (1H, d, J = 15.3), 7.35 (1H, d, J = 9), 7.59 (3H, m), 7.71 (1H, m), 8.05 (1H, d, J = 9), 8.20 (1H, m).

1-(Hydroxymethyl)anthracene-9,10-dione (18).[54] *Method A:* 69.7 mg/65%. *Method B:* 37.5 mg/70%. mp 155−156 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (1H, t, J = 7.4), 5.03 (2H, d, J = 7.4), 7.77 (4H, m), 8.28 (2H, m), 8.36 (1H, dd, J = 1.5, 6.07); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.0, 125.9, 126.4, 126.6, 130.3, 131.7, 133.1, 133.2, 133.22, 133.24, 134.1, 134.6, 142.7, 182.0, 185.2; HRMS calcd for $C_{15}H_{10}O_3Na^+$ 261.0522 [M + Na^+], found 261.0519.

1-(Hydroxymethyl)-3-methylanthracene-9,10-dione (19). *Method A:* 7 mg/65%. *Method B:* 8.8 mg/55%. mp 162−163 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (3H, s), 3.87 (1H, t, J = 7.3), 4.97 (2H, d, J = 7.2), 7.65 (1H, m), 7.78 (2H, t, J = 4.4), 8.16 (1H, m), 8.26 (2H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.8, 29.73 65.1, 126.9, 127.4, 128.0, 129.1, 132.8, 134.0, 134.2, 135.2, 136.7, 143.8, 145.7, 183.4, 186.0; HRMS calcd for $C_{16}H_{12}O_3Na^+$ 275.0678 [M + Na^+], found 275.0678.

(49) Gu, C. L.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 6060–6063.
(50) Cui, H. X.; Shaaban, K. A.; Schiebel, M.; Qin, S.; Laatsch, H. *World J. Microbiol. Biotechnol.* **2008**, *24*, 419–421.
(51) Cui, H.; Shaaban, K. A.; Qin, S. *World J. Microbiol. Biotechnol.* **2006**, *22*, 1377–1379.
(52) Kalaitzis, J. A.; Moore, B. S. *J. Nat. Prod.* **2004**, *67*, 1419–1422.
(53) Roberge, G.; Brassard, P. *Synthesis* **1979**, 148–150.
(54) Ramanathan, V.; Tilak, B. D.; Venkataraman, K. *Proc. Indian Acad. Sci., Sect.* **1953**, *38A*, 161–175.

1-(Hydroxymethyl)-4-methylanthracene-9,10-dione (20). *Method A:* 17.6 mg/55%. *Method B:* 9 mg/70%. mp 164−165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.86 (3H, s), 3.90 (1H, bs), 4.93 (1H, d, J = 5.1), 7.66 (1H, d, J = 7.9), 7.69 (1H, d, J = 7.9), 7.76 (2H, m), 8.2 (2H, m); ^{13}C NMR (500 MHz, $CDCl_3$) δ 24.2, 30.0 65.8, 110.0, 127.1, 127.2, 133.4, 134.0, 134.5, 135.6, 138.2, 138.98, 142.4, 142.6, 185.2, 185.8; HRMS calcd for $C_{16}H_{12}O_3Na^+$ 275.0678 [M + Na^+], found 275.0678.

3,8-Dihydroxy-1-(hydroxymethyl)anthracene-9,10-dione (9-Hydroxyaloesaponarin II) (21).[50−52] *Method B:* 13 mg/90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (1H, t, J = 7.4), 5.03 (2H, d, J = 7.4), 7.77 (4H, m), 8.28 (2H, m), 8.36 (1H, dd, J = 1.5, 6.07); ^{13}C NMR (300 MHz, $CDCl_3$) δ 62.0, 111.8, 116.4, 118.4, 118.6, 120.9, 124.3, 132.5, 136.0, 136.9, 151.4, 161.4, 163.1, 182.4, 189.2.

Acknowledgment. This work was supported by the NSF (CHE-0514576). We thank Dr. Marcus Wright for assistance with NMR spectroscopy.

Supporting Information Available: Experimental procedures for the synthesis of 1-methyl-9,10-anthraquinones and spectral data for all relevant compounds. This material is available free of charge via the Internet at http://pubs.acs.org.