Journal of Photochemistry and Photobiology A: Chemistry 204 (2009) 13–18

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

2-(1′-Hydroxyethyl)-anthraquinone as a photolabile protecting group for carboxylic acids

Ming-Guang Ren, Nai-Min Bi, Mao Mao, Qin-Hua Song*

Department of Chemistry, University of Science and Technology of China, Hefei, 230026, Anhui, PR China

ARTICLE INFO

Article history:
Received 28 August 2008
Received in revised form
23 December 2008
Accepted 11 February 2009
Available online 21 February 2009

Keywords:
Photolabile protecting groups
Carboxylic acids
Photochemistry

ABSTRACT

Using anthraquinone 2-yl ethyl (Aqe) as a photolabile protecting group for carboxylic acids, five caged compounds, Aqe esters of *p*-methoxybenzoic acid (**1a**), *o*-methylbenzoic acid (**1b**), benzoic acid (**1c**), *p*-nitrobenzoic acid (**1d**) and *N*-acetyl-L-tryptophan (**1e**), have been prepared, and their photochemistry was investigated. Upon 350 nm light irradiation, three caged compounds **1a–c** in methanol solutions can efficiently release the corresponding carboxylic acids, their quantum yields ranging from 0.12 to 0.08. The intramolecular triplet–triplet energy transfer and the intramolecular electron transfer between triplet anthraquinone and the caged acids may occur, leading to a low efficiency of caged compounds **1d** and **1e**, respectively. Furthermore, based on quenching experiments, HPLC and spectral analysis, the mechanism of the uncaging reaction was suggested.

1. Introduction

Photolabile protecting groups (PPGs) for various functional groups have great potential in both synthetic [1] and biological chemistry [2]. First reported [3] in the 1960s, the use of photolabile protecting groups did not attract much attention until first use by Kaplan et al. [4] to solve biological problems, such as the rapid release of biologically active compounds from photolabile precursors. They demonstrated that 2-nitrobenzyl ATP and the α-methylated derivative, which are the so-called 'caged' ATP, could be used as photoreactive triggers for biochemical processes, thereby opening up a very productive area of research in the photoliberation of biomolecules.

Carboxylic acids are one of the most common functional groups to be 'caged' by photolabile protecting groups. A number of new protecting groups have been introduced, and some of them have excellent photolabile properties, including 1-acyl-7-nitroindolines [5], 6-bromo-7-hydroxycoumarin-4-yl methyl (Bhc) [6], *p*-hydroxyphenacyl [7], 8-bromo-7-hydroxyquinoline (BHQ) [8], 2-(dimethylamino)-5-nitrophenyl [9], ketoprofenate [10], 7-*N*,*N*-diethylaminocoumarin [11], 3-nitro-2-naphthalanenemethanol [12], α-keto amides [13] and α-carboxy nitrobenzyl [14,15].

The photochemistry of anthraquinones has been extensively investigated due to its widespread use as photosensitizers. Anthraquinone derivatives were also used as photolabile protecting groups for alcohols [16], aldehydes [17,18] and ketones [18]. 2-Methylene-9,10-anthraquinone (Maq) ester was used as a carboxyl protective group in peptide synthesis, and mild reducing agents can convert the ester to its corresponding hydroquinone, which underwent cleavage to the peptide [19]. Blankespoor et al. [20] demonstrated that electrochemical reduction can be used as an alternative method for deprotection of Maq esters of carboxyl acids used in the synthesis of peptides.

In this paper, we reported that anthraquinone ethyl (Aqe) esters were used as PPGs for carboxylic acids. Five carboxylic acid-protected compounds **1a–e** have been prepared, and their uncaging efficiencies were measured. Furthermore, the uncaging mechanism was investigated, and some new insights into photochemistry of anthraquinone were gained.

2. Materials and methods

2.1. General methods

2-(1-Bromo-ethyl)-anthraquinone was prepared using 2-ethylanthraquinone as a starting material. Other materials were purchased from commercial suppliers. Solvents of technical quality were distilled prior to use. ^{1}H and ^{13}C NMR spectra were obtained at 300 K, using a Bruker AV300 spectrometer. Chemical shifts are given in ppm using tetramethylsilane (TMS) as the internal reference. ^{1}H NMR spectra were run at 300 MHz and ^{13}C-NMR spectra were recorded at 75 MHz. FT-IR spectra were carried out on a Bruker Vector22 Infrared Spectrometer. UV–vis absorption

* Corresponding author. Tel.: +86 551 3607524; fax: +86 551 3601592.
E-mail address: qhsong@ustc.edu.cn (Q.-H. Song).

1010-6030/$ – see front matter.
doi:10.1016/j.jphotochem.2009.02.006

spectra were recorded with a Shimadzu UV-2401PC spectrometer. Mass spectra were obtained with a Micromass GCF TOF mass spectrometer. HPLC analysis was performed on a HP Agilent (1100 series) HPLC system with a C-18 reverse phase column (5 μL × 4.6 mm × 2.5 cm).

2.2. Measurements of quantum efficiency

To measure uncaging quantum efficiency of the caged compounds, 0.1 mM methanol solution of the caged compounds were prepared in quartz cuvettes with a Teflon stopper, bubbled with high pure nitrogen for 15 min, and then irradiated with 350 nm UV light from a fluorescence spectrometer with a 20 nm slit. After each period of irradiation, a 50 μL aliquot of the solution was taken out for analysis by HPLC. Photoproducts were identified by co-injection with known samples. The progress curves were plotted by mono-exponential decay. Quantum efficiencies (Q_{u1}) were calculated according to a published method [21,22] using $Q_{u1} = (I\sigma t_{90\%})^{-1}$, where I is the irradiation intensity in ein cm^{-2} min^{-1} and calculated with the equation $I = I_0\ (1 - 10^{-A350})$, σ is the decadic extinction coefficient (10^3 times ε, the molar extinction coefficient) in cm^2 mol^{-1}, and $t_{90\%}$ is the irradiation time in minutes for 90% conversion to product. The intensity of 350 nm light from a fluorescence spectrometer with 20 nm slit, I_0 was measured by using potassium ferrioxalate actinometry [23]. The caged compounds and the corresponding acid were monitored at 250 nm.

2.3. Characterization and synthesis of caged compounds

2-(1′-Bromo-ethyl)-anthraquinone: 2-ethylanthraquinone (5 g, 21 mmol), NBS (3 g, 21 mmol) and azobisisobutyronitrile (AIBN) (0.5 g, 3 mmol) was dissolved in CCl_4 (30 mL), and refluxed for 7 h. 2-(1′-Bromo-ethyl)-anthraquinone was separated by filtrating and the crude product was purified by recrystallizing in ethanol and gave the desired product (4.4 g, 65.4%) [24]; m.p. 156–158 °C.

N-acetyl-L-tryptophan: L-tryptophan (615 mg, 3 mmol) and triethylamine (0.4 ml) were dissolved in 5 mL water, and then added 0.6 mL (6 mmol) acetic anhydride. The mixture is stirred at room temperature for 2 h, and modulating pH with hydrochloric acid to 2–3, giving desired product as a white solid (571 mg, 77.3%); m.p. 195–200 °C; ^{1}H NMR (300 MHz, methanol–d_4) δ = 1.93 (s, 3H), 3.18 (dd, 1H, *H*CHCHCOOH), 3.34 (s, 1H, C*H*COOH), 3.37 (dd, 1H, HC*H*CHCOOH), 7.13–7.58 (m, 5H, H_{Ar}); IR (KBr): nu(tilde) (cm^{-1}) = 3395, 1720, 1636, 1550, 746; TOFMS (EI) calcd for (M^+) $C_{13}H_{14}O_3N_2$: 246.1004, found = 246.1008.

4-Methoxybenzoic acid 1-(anthraquinone-2-yl)-ethyl ester **1a**: *p*-methoxybenzoic acid (305 mg, 2 mmol) and $KHCO_3$ (300 mg, 3 mmol) added to a flask, and after vacuum drying 15 min, 5 ml DMF was added, and the mixture was heated until the $KHCO_3$ dissolved completely, and then 2-(1-bromo-ethyl)-anthraquinone (630 mg, 2 mmol) added to the system. The solution refluxed 2 h and the 2-(1-bromo-ethyl)-anthraquinone reacted completely. The solvent was removed in a rotatory evaporator. Ethyl acetate (30 ml) was added to the residue with stirring. The solution was washed with 30 ml saturated $NaHCO_3$ and 3× 30 ml of water, dried over $MgSO_4$, filtrated, removed the solvent in vacuo. The crude product obtained was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5) to give **1a** (603 mg, 78.1%); R_f = 0.28 (ethyl acetate/petroleum ether, 1:6); m.p. 115–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.73 (d, 3H, CHC*H*$_3$), 3.87 (s, 3H, OC*H*$_3$), 6.21 (q, 1H, C*H*CH$_3$), 6.94–8.30 (m, 11H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = (182.9, 182.7) (*C*=O), 165.5, 163.7, 148.9, 134.2, 134.2, 133.9, 133.6, 132.9, 131.9, 131.6, 127.9, 127.3, 124.5, 122.4, 113.8, 71.9 (*C*HCH$_3$), 55.5 (O–*C*H$_3$), 22.5 (CH*C*H$_3$); IR (KBr): nu(tilde) (cm^{-1}) = 1711, 1673, 1605, 711; TOFMS (EI) calcd for (M^+) $C_{24}H_{18}O_5$: 386.1154, found = 386.1160.

2-Methylbenzoic acid 1-(anthraquinone-2-yl)-ethyl ester **1b**: Using *o*-methylbenzoic acid (312 mg, 2.26 mmol) instead of *p*-methoxybenzoic acid, 2-(1-bromo-ethyl)-anthraquinone (630 mg, 2 mmol), the same procedure was performed, and **1b** (476 mg, 63.9%) was obtained. R_f = 0.52 (ethyl acetate/petroleum ether, 1:6); m.p. 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.74 (d, 3H, CHC*H*$_3$), 2.60 (s, 3H, PhC*H*$_3$), 6.22 (q, 1H, C*H*CH$_3$), 7.24–8.40 (m, 11H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = (183.0, 182.8) (C=O), 166.6 (O–C=O), 148.8, 140.6, 134.2, 134.2, 133.9, 133.6, 133.0, 132.4, 131.9, 131.7, 130.8, 129.3, 127.3, 125.9, 124.6, 72.1 (*C*HCH$_3$), 22.5 (PhC*H*$_3$), 21.9 (CHC*H*$_3$); IR (KBr): nu(tilde) (cm^{-1}) = 1720, 1676, 1591, 1327, 1286, 1254, 1073, 743, 710; TOFMS (EI) calcd for (M^+) $C_{24}H_{18}O_4$: 370.1205, found = 370.1207.

Benzoic acid 1-(anthraquinone-2-yl)-ethyl ester **1c**: Using benzoic acid (124 mg, 1 mmol), 2-(1-bromo-ethyl)-anthraquinone (260 mg, 0.82 mmol), the same procedure was performed, and **1c** (256 mg, 72.7%) was obtained. R_f = 0.467 (ethyl acetate/petroleum ether, 1:6); m.p. 122–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.76 (d, 3H, J = 6.9, CHC*H*$_3$), 6.25 (q, 1H, J = 6.6, C*H*CH$_3$), 7.45–8.30 (m, 12H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = (182.9, 182.7) (*C*=O), 165.7 (O–*C*=O), 148.6, 134.2, 134.2, 133.9, 133.5, 133.3, 133.0, 131.6, 130.0, 129.8, 128.6, 127.9, 127.3, 124.6, 72.3 (*C*HCH$_3$), 22.4 (CH*C*H$_3$); IR (KBr): nu(tilde) (cm^{-1}) = 1718, 1674, 1590, 1290, 1267, 1098, 710; TOFMS (EI) calcd for (M^+) $C_{23}H_{16}O_4$: 356.1049, found = 356.1048.

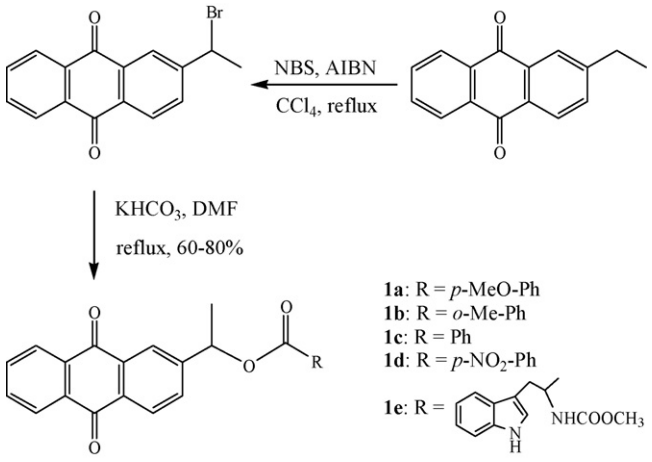
p-Nitrobenzoic acid 1-(anthraquinone-2-yl)-ethyl ester **1d**: Using *p*-nitrobenzoic acid (338 mg, 2.2 mmol), 2-(1-bromo-ethyl)-anthraquinone (630 mg, 2 mmol), the same procedure was performed, and **1d** (640 mg, 79.8%) was obtained. R_f = 0.25 (ethyl acetate/petroleum ether, 1:6); m.p. 160–165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.79 (d, 3H, CHC*H*$_3$), 6.29 (q, 1H, C*H*CH$_3$), 7.79-8.38 (m, 11H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = (182.9, 182.6) (C=O), 163.9 (O–*C*=O), 150.8, 147.7, 135.4, 134.4 134.3, 134.0, 133.5, 133.3, 131.7, 130.9, 128.1, 127.4, 124.6, 123.7, 73.5 (*C*HCH$_3$), 22.2 (CHC*H*$_3$); IR (KBr): nu(tilde) (cm^{-1}) = 1730, 1672, 1603, 1590, 1525, 1288, 1267, 717; TOFMS (EI) calcd for (M^+) $C_{23}H_{15}O_6N$: 401.0899, found = 401.0899.

N-acetyl-L-tryptophan 1-(anthraquinone-2-yl)-ethyl ester **1e**: *N*-acetyl-L-tryptophan(634 mg, 2.57 mmol) and 2-(1-bromo-ethyl)-anthraquinone (903 mg, 2.83 mmol). The crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:5) giving **1e** (888 mg, 71.3%). R_f = 0.167 (ethyl acetate/petroleum ether, 1:1); m.p. 160–165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.55 (d, 3H, J = 6.6, CHC*H*$_3$), 1.99 (s, 3H, C*H*$_3$C = O), 3.27 (d, 2H, J = 6.0, CHC*H*$_2$), 5.03 (q, 1H, J = 6.6, C*H*CH$_3$), 5.94–6.02 (m, 2H, *CHNH*), 6.77–8.33 (m, 12H, H_{Ar}); ^{13}C NMR (75 MHZ, $CDCl_3$) δ = (182.9, 182.8, 171.6, 170.0) (*C*=O), 147.6, 136.2, 134.4, 134.3, 133.7, 133.6, 133.5, 133.0, 131.7, 127.8, 127.6, 127.4, 127.3, 124.7, 122.9, 122.3, 118.6, 111.4, 109.8, 72.9 (*C*HCH$_3$), 53.4 (CHNH), 27.9 (*C*H$_2$CH), 23.3 (*C*H$_3$C=O), 22.1 (*C*H$_3$C—O); IR (KBr): nu(tilde) (cm^{-1}) = 3406, 1737, 1674, 1593, 1287; TOFMS (EI) calcd for (M^+) $C_{29}H_{24}O_5N_2$: 480.1685, found = 480.1684.

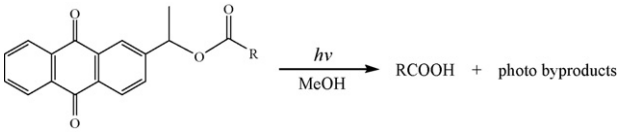
3. Results and discussion

3.1. Synthesis of caged compounds

Five caged compounds were synthesized from the 2-ethylanthraquinone via the routes depicted in Scheme 1. In short, 2-ethylanthraquinone together with NBS and AIBN were dissolved and refluxed in CCl_4 and refluxed for 7 h, giving 2-(1-bromo-ethyl)-anthraquinone. *N*-Acetyl-L-tryptophan was prepared by L-tryptophan with acetic anhydride and little triethylamine in water at room temperature. The five caged compounds were obtained by refluxing in DMF with 2-(1-bromo-ethyl)-anthraquinone and benzoic acid (BA), *o*-methylbenzoic acid (MBA),



Scheme 1.



Scheme 2.

p-methoxybenzoic acid (MOBA), *p*-nitrobenzoic acid (NBA) and *N*-acetyl-L-tryptophan (Trp), respectively.

3.2. Photolysis properties of caged compounds

Methanol solutions of 1×10^{-4} M compounds **1a–e** were prepared in quartz cuvettes with a Teflon stopper. Sample solutions were bubbled with high pure nitrogen for 15 min, and irradiated with 350 nm light from a fluorescence spectrometer with a 20 nm slit. Through HPLC analysis of the photolysis system and co-injection of known solutions, the released carboxylic acid, the photoproduct 2-ethylanthraquinone were confirmed (Scheme 2). A representative set of HPLC chromatograms for the compound **1a** is depicted in Fig. 1, and shows that the caged compound **1a** with a retention time of 10.0 min, 2.1 min for *p*-methoxybenzoic acid, a small amount of the photoreduction product 2-ethylanthraquinone with the retention time 9.0 min and two unknown photoproducts with retention times 3.3 and 3.7 min. With increasing irradiation time, a decrease in concentration of **1a** and an increase in the peak intensity of *p*-methoxybenzoic acid can be clearly observed in Fig. 1.

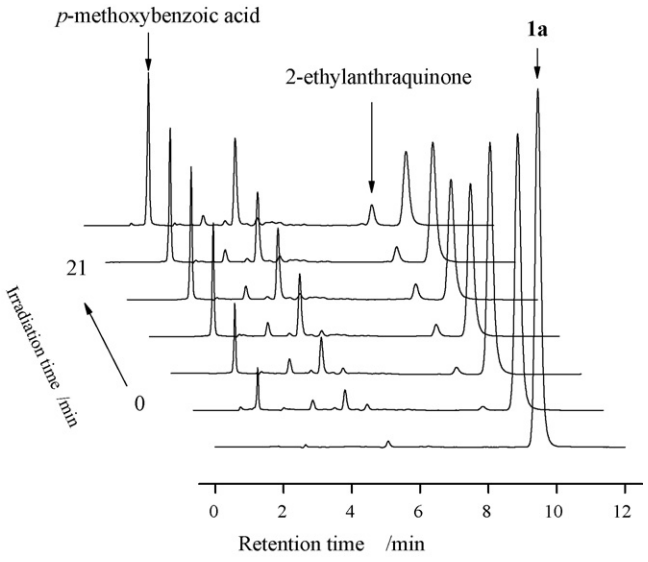


Fig. 1. Sequential recordings at 250 nm of the HPLC analysis of the crude product of **1a** in methanol solution upon 350 nm irradiation. Retention times are 2.1 min for the released *p*-methoxybenzoic acid, 10.0 min for **1a** and 9.0 min for 2-ethylanthraquinone.

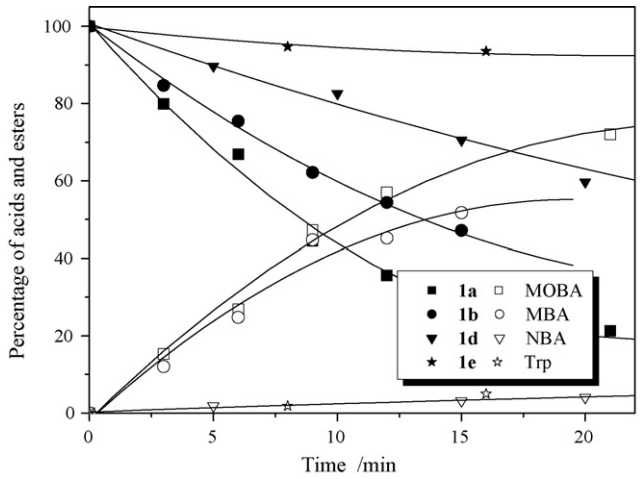


Fig. 2. Release of benzoic acids and remaining caged compounds after different irradiation times monitored by HPLC. Irradiation of 0.1 mM solution of **1a–e** in methanol with 350 nm light. Solid lines through solid symbols are least-squares fits of simple decaying exponentials.

Concentrations of caged compounds and the releasing acids were determined by comparing to standard solutions by HPLC, and the concentrations have been normalized and reported as a percentage. Relative high conversions rates were observed for caged compounds with the exception of **1d**. Comparing the time courses for these reactions shown in Fig. 2, HPLC analysis of aliquots taken at periodic interval shows that in these caged compounds **1a** disappears the most rapidly, and **1e** is the slowest, and data were listed in Table 1. Acid-releasing quantum yields decrease in order of **1a–e**, ranging from 0.125 to 0.006. Three caged compounds **1a–c** have sufficiently high uncaging quantum yields for application to caging chemistry. In order to compare with the uncaging efficiency of Maq ester, Maq ester of *p*-methoxybenzoic acid was synthesized. Under the same condition, the Maq ester disappears rapidly, $\Phi_{dis} = 0.223$, but gave a lower quantum yield of acid release than **1a–c**, $\Phi_{rel} = 0.05$.

3.3. Mechanisms of photochemical deprotection of caged compounds

To investigate the uncaging mechanism, a quenching experiment of the caged compound **1a** by 1,3-cyclopentadiene ($E_T = 243$ kJ mol^{-1} [23]) was performed, and demonstrated the

Table 1
Selected photophysical and photochemical properties.

Caged compounds	λ_{max} [a] (ε[b])	ε_{350} [b]	Φ_{dis} [c]	Φ_{rel} [d]	Conv. (%)
1a	326 (5860)	1820	0.143	0.125	87
1b	324 (5440)	1740	0.088	0.084	95
1c	325 (6100)	1740	0.080	0.077	96
1d	325 (5780)	1840	0.047	0.006	14
1e	326 (6500)	1980	0.007	0.006	90

[a] Absorption spectra were abtained from its methanol solution.
[b] Extinction coefficients (cm^{-1} M^{-1}).
[c] Quantum yields of disappearance of caged compounds under 350 nm light.
[d] Quantum yields of release of corresponding acid under 350 nm light.

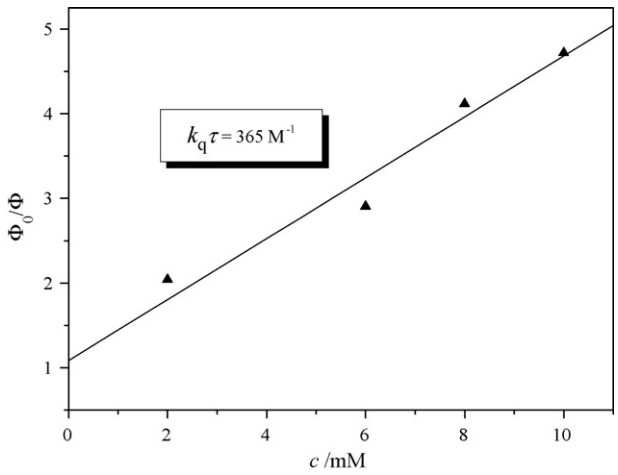


Fig. 3. Stern–Volmer plot of related quantum yields versus concentrations of 1,3-cyclopentadiene for the photolysis of **1a** in methanol solution at 350 nm light.

uncaging reaction undergo triplet excited state of anthraquinone moiety (E_T = 261 kJ mol^{-1} [23]). Stern–Volmer plot for the photolysis of **1a** in methanol at 350 nm gives a fit straight line, and its slope is $k_q\tau$ = 365 M^{-1}, shown in Fig. 3.

Furthermore, the absorption and fluorescence emission spectra of the caged compound **1a** in methanol were measured at different irradiation times. With increasing irradiation time, large changes in these spectra were observed (Fig. 4a for absorption spectra, Fig. 5a for fluorescence spectra). However, in contrast to large changes in methanol, the spectral changes for photolysis of **1a** in CH_3CN–H_2O (1:1) solvent mixture are small (Fig. 4b). The decaying efficiency of **1a** in CH_3CN–H_2O solvent mixture also shows a very low value, being about one-tenth of that in methanol.

Recently, a detailed study on photoredox chemistry of anthraquinones was reported [25]. Proposed mechanisms of intramolecular photoredox reaction were suggested for 2-methylanthraquinone derivatives in aqueous solution, and in the presence of a hydrogen donor such as alcohols, simple photoreduction via initial hydrogen abstraction dominates. Anthraquinone-2-yl methyl acetate was found to be photoinert in deaerated water–acetonitrile solvent mixture, that is, no intramolecular photoredox reaction occurs for the system. Our spectral data also support this conclusion. No notable increase in absorbance at above 350 nm was observed on UV/vis absorption spectra of photolysis of **1a** in 50% CH_3CN aqueous solution. This implies that the intramolecular photoredox reaction or the simple photoreduction occurs in a very low efficiency.

Furthermore, fluorescence spectra of the photolysis recorded after irradiation for different times support the formation of the 9,10-dihydroxyanthracene via the simple photoreduction. The triplet excited state of the anthraquinone moiety abstracts a hydrogen atom from alcohols to form the semianthraquinone radical, and the semianthraquinone radical can further abstract a hydrogen atom to form the dihydroxyanthracene, which has a strong fluorescence emission. After each two-minute irradiation at 350 nm UV light, an increase in the intensity of the fluorescence emission was observed, shown in Fig. 5a. These changes in CH_3CN–H_2O (1:1) solvent mixture are very small. The spectral changes for compound **1a** are accord with its efficiencies of uncaging reaction in two kinds of solvents. Further investigation showed that the rate of uncaging reaction has related with the hydrogen-donating ability of the solvent, or with the formation rate of anthrahydroquinone. In addition, after the methanol solution of **1a** in a cuvette was irradiated for 6 min, its absorption spectrum was recorded. Sequentially, the Teflon stopper of the cuvette was opened, and absorption spectra of this solution in air return gradually to that of **1a**, shown in Fig. 5b. This phenomenon implies that the photoreduction of anthraquinone under 350 nm light forms anthrahydroquinone, and then the anthrahydroquinone is oxidized to anthraquinone in air. These show clearly that the uncaging reaction includes the photochemical reduction of anthraquinone moiety of caged compounds.

Further investigation showed that the photochemical reduction of anthraquinone should occur before releasing corresponding acids. The methanol solution of **1a** was first irradiated for 8 min at 350 nm light and taken out 50 μl for analysis, and then irradiated for 8 min at 430 nm light, where it is not absorbed by anthraquinone. HPLC analysis showed that the concentration of carboxylic acid for adding irradiation at 430 nm light was 40% higher than that of only irradiation at 350 nm in the photolysis system. This implies that photochemical release of carboxylic acid occurs after photoreduction of the anthraquinone moiety. Thus, the low efficiency of release of the carbonyl acid would derive from low efficiency of the photoreduction for the anthraquinone moiety in 50% CH_3CN aqueous solution.

Maq esters of carboxyl acids were used as carboxyl protective groups, and the esters can release the corresponding acid under chemical reduction [19] with a mild regent or electrochemical reduction [20]. This supports that caged compounds with 2-(1′-hydroxy-ethyl)-anthraquinone as a photolabile protecting group for carboxyl acids release the corresponding acids undergoing the photochemical reduction to convert the anthraquinone to anthrahydroquinone moiety. The anthrahydroquinone, which has more wide absorption region than anthraquinone (Figs. 4a and 5b), would undergo spontaneously a heterolytic cleavage of alkyl-oxygen bond [19] or absorb a photon leading to this bond fission and form a carbocation or rapid tautomerization to **3**, which further tau-

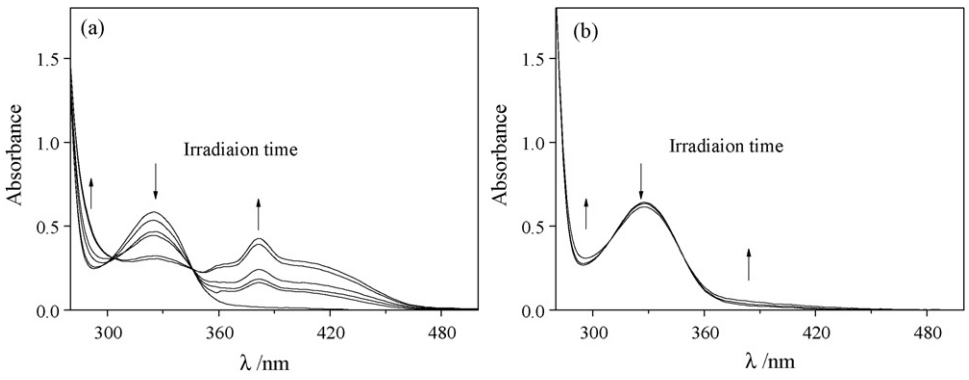


Fig. 4. Absorption spectra of **1a** in methanol solution (0.1 mM) (a) and water–acetonitrile (1:1) mixture (0.1 mM) (b) recorded at different irradiation times upon 350 nm light.

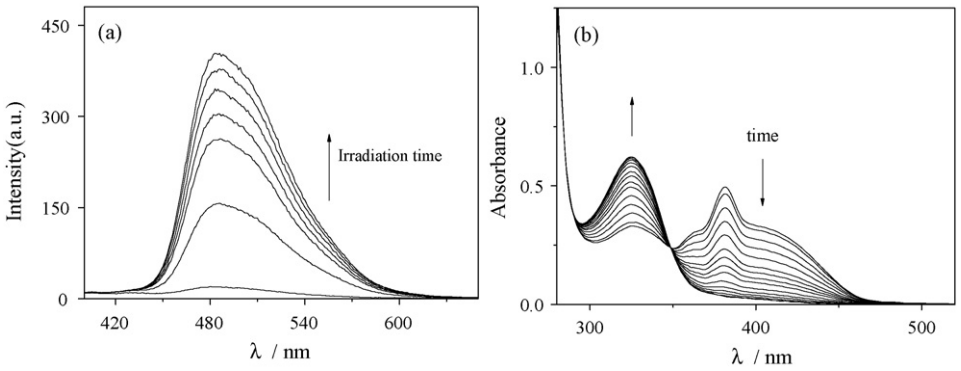
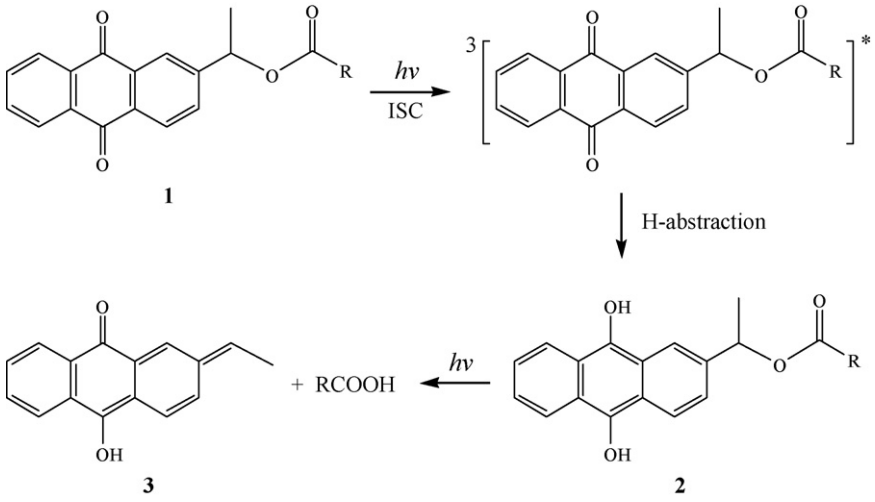


Fig. 5. (a) Fluorescence emission spectra recorded after irradiation for different times; (b) absorption spectra recorded at different times of the solution standing upon air, after irradiation for 6 min, of **1a** in methanol solution (0.1 mM) with 350 nm UV light.



Scheme 3.

tomerizes to give 2-ethylanthraquinone. This proposed mechanism is shown in Scheme 3.

According to the proposed mechanism, the low acid-releasing efficiency of Maq-locked *p*-methoxybenzoic acid may derive from a less stable carbocation from alkyl-oxygen fission than that from **1a**, or undergoes an acyl-oxygen fission leading to a non-acid release.

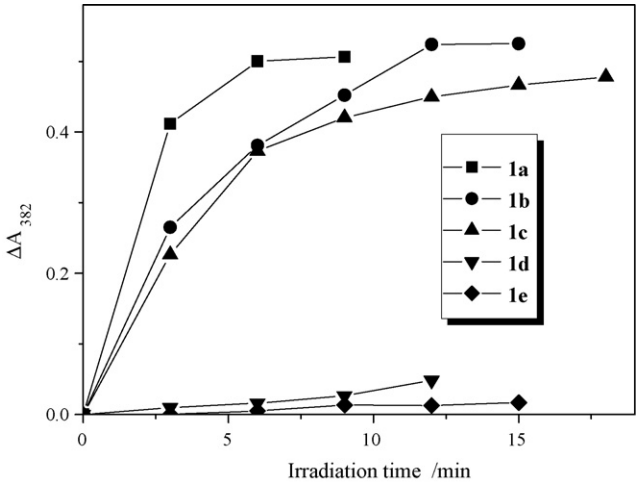


Fig. 6. Dependence of changes in absorbance at 382 nm of 0.1 mM methanol solutions of **1a**–**e** on irradiation time under 350 nm light.

For the difference in uncaging efficiency for **1a**–**e**, UV/vis absorption spectra of **1a**–**e** methane solutions were recorded after irradiation for different times. Their change rates in absorbance at 382 nm show that **1a** is the fastest, the slowest for **1d**, shown in Fig. 6, and this is in agreement with their uncaging efficiencies. This implied that the photoreduction is the step controlling the uncaging efficiency. Thus, competitions with the photoreduction, such as intramolecular triplet–triplet (T–T) energy transfer for **1d** or electron transfer for **1e** between triplet anthraquinone and caged-acid units, would lead to a decrease in the efficiency of photoreduction, giving a low uncaging efficiency. Another case leading to low efficiency for **1d** cannot be ignored, that is 4-nitrobenzoic acid absorbing 350 nm light (molar extinction coefficient ε_{350} = 2000 for 2-ethylanthraquinone, and 200 for *p*-nitrobenzoic acid).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20672106 and 30470444).

References

[1] C.G. Bochet, J. Chem. Soc., Perkin Trans. 1 (2002) 125–142.
[2] M.C. Pirrung, Chem. Rev. 97 (1997) 473–488.
[3] J.A. Barltrop, P.J. Plant, P. Schofield, J. Chem. Soc., Chem. Commun. (1966) 822–823.
[4] J.H. Kaplan, B. Forbush III, J.F. Hoffman, Biochemistry 17 (1978) 1929–1935.
[5] G. Papageorgiou, D.C. Ogden, A. Barth, J.E.T. Corrie, J. Am. Chem. Soc. 121 (1999) 6503–6504.

[6] T. Furuta, S.S.-H. Wang, J.L. Dantzker, T.M. Dore, W.J. Bybee, E.M. Callaway, W. Denk, R.Y. Tsien, Proc. Natl. Acad. Sci. U.S.A. 96 (1999) 1193–2000.
[7] R.S. Givens, J.F.W. Weber, P.G. Conrad, G. Orosz, S.L. Donahue, S.A. Thayer, J. Am. Chem. Soc. 122 (2000) 2687–2697.
[8] O.D. Fedoryak, T.M. Dore, Org. Lett. 4 (2002) 3419–3422.
[9] A. Banerjee, C. Grewer, L. Ramakrishnan, J. Jager, A. Gameiro, H.G.A. Breitinger, K.R. Gee, B.K. Carpenter, G.P. Hess, J. Org. Chem. 68 (2003) 8361–8367.
[10] M. Lukeman, J.C. Scaiano, J. Am. Chem. Soc. 127 (2005) 7698–7699.
[11] V.R. Shembekar, Y. Chen, B.K. Carpenter, G.P. Hess, Biochemistry 44 (2005) 7107–7114.
[12] A.K. Singh, P.K. Khade, Tetrahedron 61 (2005) 10007–10012.
[13] C. Ma, M.G. Steinmetz, E.J. Kopatz, R.J. Rathore, Org. Chem. 70 (2005) 4431–4442.
[14] C. Grewer, J. Jager, B.K. Carpenter, G.P. Hess, Biochemistry 39 (2000) 2063–2070.
[15] M.A. Ashraf, A.G. Russell, C.W. Wharton, J.S. Snaith, Tetrahedron 63 (2007) 568–593.
[16] T. Furuta, Y. Hirayama, M. Iwamura, Org. Lett. 3 (2001) 1809–1812.
[17] R.G. Brinson, P.B. Jones, Org. Lett. 6 (2004) 3767–3770.
[18] J.Y. Yu, W.J. Tang, H.B. Wang, Q.H. Song, J. Photochem. Photobiol. A: Chem. 185 (2007) 101–105.
[19] D.S. Kemp, J. Reczek, Tetrahedron Lett. 18 (1977) 1031–1034.
[20] R.L. Blankespoor, A.N.K. Lau, L.L. Miller, J. Org. Chem. 49 (1984) 4441–4446.
[21] R. Livingston, in: G.H. Brown (Ed.), Techniques of Chemistry, vol. 3, Wiley, New York, 1971, pp. 13–44.
[22] S.R. Adams, J.P.Y. Kao, G. Grynkiewicz, A. Minta, R.Y. Tsien, J. Am. Chem. Soc. 110 (1988) 3212–3220.
[23] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, second ed., Marcel Dekker Inc., New York, 1993.
[24] G. Manecke, W. Storck, Chem. Ber. 94 (1961) 3239–3250.
[25] Y.Y. Hou, P. Wan, Photochem. Photobiol. Sci. 7 (2008) 588–596.