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Short communication

Anthraquinon-2-ylethyl-1′,2′-diol (Aqe-diol) as a new photolabile protecting group for aldehydes and ketones

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Abstract

A new photolabile protecting group for aldehydes and ketones, 2-(1,2-dihydroxyethyl) anthraquinone (Aqe-diol) and four caged compounds have been prepared and their photochemistry investigated. Upon 350 nm light irradiation, the caged compounds **2a-d** in CH_3CN–H_2O solution can efficiently release the carbonyl compounds (conversion rate 60–90%), and their uncaging quantum efficiencies were measured, ranging from 0.03 to 0.09. On the basis of HPLC analysis and quenching experiments, a mechanism of the uncaging reaction was suggested.

Keywords: Photolabile protecting groups; 2-(1,2-Dihydroxyethyl) anthraquinone; Aldehydes and ketones; Photochemistry

1. Introduction

Photoremovable protecting groups (PRPGs) have been found extensive applications in both synthetic and biological chemistry in the past decades [1,2]. The properties of high temporal and spatial resolution afforded by light make the PRPGs particularly useful as "caging" groups in cell biology [3–5]. Many photolabile protecting groups have been applied to protect carboxylic acids, amines, phosphates, and alcohols, including 2-nitrobenzyl, benzoin, 7-nitroindoline, phenacyls, coumarinylmethyl, and anthraquinon-2-ylmethoxycarbonyl [1,2]. However, reports on photolabile protecting groups for aldehydes and ketones are scarce. This is surprising since such functional groups are commonly found in organic synthesis and many bioactive effector molecules. A thorough search of the literature indicated that such groups for aldehydes and ketones which have been reported thus far, other than the *o*-nitrobenzyl-type [6–9], are dithiane [10,11] and 6-bromo-4-(1,2-dihydroxyethyl)-7-hydroxycoumarin (Bhc-diol) [12]. However, significant disadvantages limit the extensive use of dithianyl and *o*-nitrobenzyl. In such system the sensitizer was included as a separate additive, so the probability of encounter between the excited sensitizer and caged substrate is the limiting factor of the rate (and thus quantum yield) of photorelease. The drawbacks of *o*-nitrobenzyl-type cages are their toxicity and strongly light-absorption byproducts, which are incompatible with the biological system investigated.

In a recent report [13], the anthraquinone-2-ylmethoxycarbonyl (Aqmoc) was found to offer a unique property as a potential phototrigger for alcohols. In this work, an interesting modification was made to evaluate whether 2-(1,2-dihydroxyethyl) anthraquinone (Aqe-diol) can serve as a photolabile protecting group for aldehydes and ketones. Since our goal is to develop novel caging groups with desirable photoreactivity that could be applied to caging chemistry, we focused our attention on the properties in aqueous solution. In addition, a higher efficiency of photolysis at around 350 nm would be favorable for caged compounds to release a sufficient quantity of biological messengers, thereby avoiding the short-wavelength light to result in undesired cell damage. Thus, upon 350 nm light irradiation, the photolysis of the resulting caged compounds (**2a-d**) in 50% CH_3CN-phosphate buffered aqueous solutions was performed, and gave efficient releases of aldehydes and ketones.

2. Materials and methods

2.1. General methods

2-(1-Hydroxyethyl) anthraquinone was prepared by literature methods [14] using 2-ethylanthraquinone as a starting material.

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Other materials were purchased from commercial suppliers. Solvents of technical quality were distilled prior to use. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AV 300 spectrometer operating at 300 and 75 MHz, respectively. IR spectra were measured on a Bruker Vector22 Infrared 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 C-18 reverse phase columns. UV spectra were obtained on a Shimadzu UV-2401PC UV–vis spectrometer.

2.2. Measurements of quantum efficiency

To measure uncaging quantum efficiency of the caged compounds, aqueous solutions containing 50% CH_3CN (2 mL, 0.1 mM, phosphate buffer pH 7.3) 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 10-nm slit. After each period of irradiation, a 20 μL aliquot of the solution was removed for analysis by HPLC, using an external standard method to determine concentrations of components. The progress curves were plotted by single-exponential decay. Quantum efficiencies (Q_{u1}) were calculated according to a published method, $Q_{u1} = (I\sigma t_{90\%})^{-1}$ [15,16], where I is the irradiation intensity in einstein cm^{-2} min^{-1}, 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 10-nm slit, I was measured by using potassium ferrioxalate actinometry [17]. The disappearance of the caged compounds and release of benzaldehyde, acetophenone and 4-cyanobenzaldehyde were monitored at 270 nm.

2.3. Characterization and synthesis of all compounds

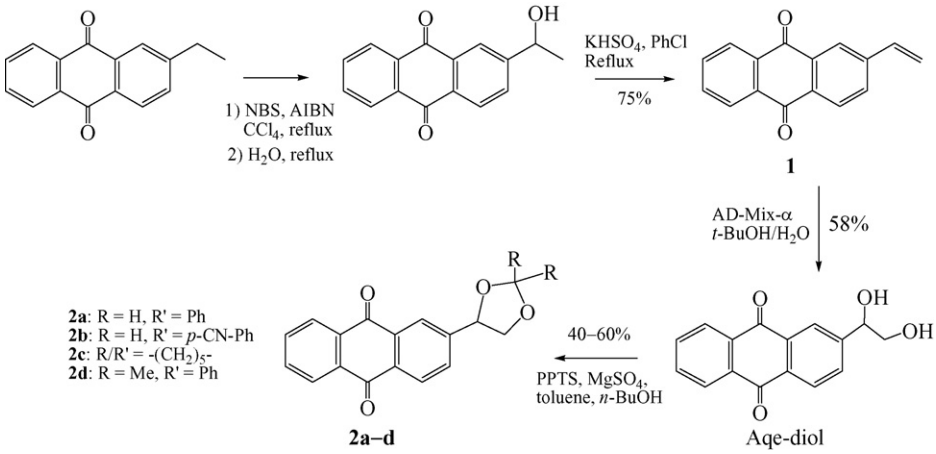
2-Vinylanthraquinone **1**: 2-(1-hydroxyethyl) anthraquinone (100 mg, 0.4 mmol), and potassium bisulfate (180 mg, 9.4 mmol) was dissolved in chlorobenzene (15 mL), and reflux for 3 h. After the mixture was washed with water until neutral, the organic layer was dried and concentrated and the resulting crude product was purified by flash chromatography through silica gel ($CHCl_3$/petroleum ether, 1:1) to give the 2-vinylanthraquinone (73 mg, 75%). $R_f = 0.46$ ($CHCl_3$/Petroleum ether, 1:1); mp 173–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.52$–5.55 (d, $J = 10.9$ Hz, 1H, CH_2), 6.01–6.07 (d, $J = 17.6$ Hz, 1H, CH_2), 6.81–6.91 (dd, $J = 10.9$ Hz, $J = 17.6$ Hz, 1H, $CHCH_2$), 7.79–7.81 (m, 3H, H_{Ar}), 8.28–8.33 (m, 4H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 183.33$ (C=O), 182.83 (C=O), 143.42 (*C*$CHCH_2$), 135.54, 134.30, 134.14, 133.94, 133.80, 133.73, 132.71, 131.54, 128.95, 127.38, 127.35, 125.95, 118.49 (CH_2); IR (KBr): nu(tilde) (cm^{-1}) = 1616 s, 1589 s, 1325 s, 1292 s, 929 m, 708 m; TOFMS (EI) calcd for (M^+) $C_{16}H_{10}O_2$: 234.2494, found 234.2487.

2-(1,2-Dihydroxyethyl) anthraquinone (Aqe-diol): 2-vinylanthraquinone (70 mg, 0.3 mmol) and AD-mix-α (0.45 g) were dissolved in *t*-BuOH/H_2O (1:1, 5 mL). The mixture is stirred at room temperature for 3 h. The reaction is then quenched with 150 mg of sodium sulfite and stirred for 10 min. *t*-BuOH was removed under vacuum and the residue was extracted with EtOAc (3 × 25 mL).The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under vacuum and the resulting crude product was washed with petroleum ether to afford the desired product as white solid (50 mg, 58%). $R_f = 0.36$ (ethyl acetate/petroleum ether, 5:1) mp 169–171 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 3.49$–3.63 (m, 2H, CH_2OH), 4.73–4.77 (*t*, $J = 5.6$ Hz, 1H, C*H*OH), 7.88–7.96 (m, 3H, H_{Ar},), 8.16–8.22 (m, 4H, H_{Ar}); ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 182.62$ (C=O), 182.28 (C=O), 150.75 (*C*CHOH), 134.45, 134.40, 133.00, 132.98, 132.60, 132.40, 131.77, 126.68, 126.62, 126.50, 124.46, 72.92 (CHOH), 66.62 (CH_2OH); IR (KBr): nu(tilde) (cm^{-1}) = 3489 s, 2045 m, 1672 s, 1591 s, 1328 s, 1296 s, 712 m; TOFMS (EI) calcd for (M^+) $C_{16}H_{12}O_4$: 268.0736, found 268.0713.

2-(2-Phenyl-[1,3]dioxolan-4-yl) anthraquinone **2a**: benzaldehyde (25 μL, 0.25 mmol) in 10 μL of 1-butanol was refluxed with a mixture of Aqe-diol (30 mg, 0.12 mmol), pyridinium *p*-toluenesulfonate (PPTS) (32 mg, 0.12 mmol), and anhydrous $MgSO_4$ (100 mg) in anhydrous toluene (4 mL). **2a** (26 mg, 61%) was obtained as mixtures of two diastereomers. $R_f = 0.33$, 0.34 (ethyl acetate/petroleum ether, 1:10); mp 118–120 °C. ^{1}H NMR(300 MHz, $CDCl_3$): δ = [3.87–3.92 (*t*, 1H, $CHCH_2$), 3.99–4.04 (q, 1H, $CHCH_2$)], [4.47–4.52 (*t*, 1H, $CHCH_2$), 4.62–4.67 (q, 1H, $CHCH_2$)], 5.36–5.42 (m, 1H, C*H*CH_2), [6.06 (s, 1H, CH_2OCH), 6.27 (s, 1H, CH_2OCH)], 7.42–7.46 (m, 3H, H_{Ar}), 7.56–7.61 (m, 2H, H_{Ar}), 7.80–7.83 (m, 3H, H_{Ar}), 8.31–8.33 (m, 4H, HAR); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (183.08, 183.04) (C=O), 182.80 (C=O), (146.71, 146.52) (*C*$CHCH_2$), 137.94, 137.03, (134.38, 134.35), 134.28, 134.02, 133.88, 133.7, 133.39, (131.85, 131.51), (129.75, 129.56), (128.70, 128.65), (128.10, 128.07), (127.47, 127.43), 126.84, 126.55, 125.14, 124.73, (105.27, 105.21) (CH_2OCH), (78.06, 77.39) ($CHCH_2$), (72.58, 72.20) (C*H*CH_2); IR (KBr): nu(tilde) (cm^{-1}) = 1672 s, 1591 s, 1324 s, 1290 s, 1061 s, 713 s; TOFMS (EI) calcd for (M^+) $C_{23}H_{16}O_4$: 356.1049, found 356.1060.

4-[4-(9, 10-Dioxo-9, 10-dihydroanthracen-2-yl)-[1, 3]dioxolan-2-yl]benzonitrile **2b**: using cyanobenzaldehyde (40 mg, 0.30 mmol) instead of benzaldehyde, the same procedure was performed, **2b** (23 mg, 53%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.97$–4.02 (q, 1H, $CHCH_2$), 4.50–4.55 (q, 1H, $CHCH_2$), 5.40–5.44 (t, 1H, C*H*CH_2), 6.09 (s, 1H, CH_2OCH), 7.70–7.83 (m, 7H, H_{Ar}), 8.27–8.33 (m, 4H, H_{Ar}); IR (KBr): nu(tilde) (cm^{-1}) = 2234 s, 1672 s, 1590 s, 1329 s, 1289 s, 1077 s, 837 s, 713 s.

2-(1,4-Dioxa-spiro[4,5]dec-2-yl) anthraquinone **2c**: using cyclohexanone (30 μL, 0.30 mmol), the same procedure was performed, and **2c** (23 mg, 55%) was obtained. $R_f = 0.39$ (ethyl acetate/petroleum ether, 1:10); mp 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.45$–1.86 (m, 10H, $(CH_2)_5$), 3.72–3.77 (t, 1H, $CHCH_2$), 4.40–4.45 (q, 1H, $CHCH_2$), 5.22–5.27 (t, 1H, C*H*CH_2), 7.79–7.85 (m, 3H, H_{Ar}), 8.27–8.33 (m, 4H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 183.13$ (C=O), 182.93 (C=O),



Scheme 1.

146.94 (*C*CHCH$_2$), 134.32, 134.25, 133.77, 133.67, 133.19, 131.63, 127.93, 127.40 (2C), 124.88, 111.33 (CH$_2$O*C*), 76.98 (*C*HCH$_2$), 71.12 (CH*C*H$_2$), 36.20, 35.51, 25.28, 24.13, 24.04; IR (KBr): nu(tilde) (cm^{-1}) = 1675 s, 1596 s, 1331 s, 1291 s, 712 m; TOFMS (EI) calcd for (M$^+$) $C_{22}H_{20}O_4$: 348.1362, found 348.1364.

2-(2-Methyl-2-phenyl-[1,3]dioxolan-4-yl) anthraquinone **2d**: Using acetophenone (30 μL, 0.30 mmol), the same procedure was performed, **2d** (18 mg, 40%) was obtained as mixtures of two diastereomers. R_f = 0.28, 0.29 (ethyl acetate/petroleum ether, 1:10); mp 123–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = [1.78 (s, 3H, CC*H*$_3$), 1.86 (s, 3H, CC*H*$_3$)], [3.61–3.67 (t, 1H, CHC*H*$_2$), 3.85–3.89 (q, 1H, CHC*H*$_2$)], [4.20–4.25 (t, 1H, CHC*H*$_2$), 4.50–4.55 (q, 1H, C*H*CH$_2$)], [5.07–5.11 (t, 1H, C*H*CH$_2$), 5.36–5.41 (q, 1H, C*H*CH$_2$)], 7.36–7.40 (m, 3H, H$_{Ar}$), 7.36–7.58 (t, 2H, H$_{Ar}$), 7.79–7.83 (t, 2H, H$_{Ar}$), 7.82–7.83 (m, 1H, H$_{Ar}$), 8.29–8.36 (m, 4H, HAR); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (183.10, 183.00) (C=O), (182.94, 182.87) (C=O), 147.23, 145.65, 143.85, 143.03, 134.34, (134.28, 134.24), 133.85, (133.68, 133.63), (133.27, 133.20), 131.96, 131.76, 128.54, (128.30, 128.21), (128.02, 127.89), 127.43, 125.41, (125.27, 125.18), 125.04, (111.06, 110.90) (*C*CH$_3$), (77.37, 76.96), (*C*HCH$_2$), (71.75, 71.55) (CH*C*H$_2$), (28.70, 28.20) (CH$_3$); IR (KBr): nu(tilde) (cm^{-1}) = 1673 s, 1592 s, 1327 s, 1289 s, 1024 m, 706 m; TOFMS (EI) calcd for (M$^+$) $C_{24}H_{18}O_4$: 370.1205, found 370.1194.

3. Results and discussion

3.1. Synthesis of caged compounds

Four caged compounds were synthesized from the 2-ethylanthraquinone via the routes depicted in Scheme 1. In brief, 2-(1-hydroxyethyl) anthraquinone, which was prepared by conventional methods, together with potassium bisulfate, was dissolved and refluxed in chlorobenzene to give 2-vinylanthraquinone **1**. The Aqe-diol was prepared by dihydroxylation of 2-vinylanthraquinone with AD-mix-α in *t*-BuOH/water. Aqe-diol acetals and ketals were obtained by refluxing in toluene with benzaldehyde, cyanobenzaldehyde, cyclohexanone and acetophenone, respectively, in the presence of pyridinium *p*-toluenesulfonate and anhydrous $MgSO_4$.

3.2. Photolysis properties of *2a-d*

To examine photochemical properties of the caged compounds, their aqueous solutions containing 50% CH_3CN (2 mL, 0.1 mM, phosphate buffer pH 7.3) were irradiated with a 350 nm light beam from a fluorescence spectrometer. Analysis of the photolysis system by HPLC and co-injection of standards confirmed that the carbonyl compounds are released as disappearance of the caged compounds upon 350 nm light irradiation. A representative set of HPLC chromatograms showing the simultaneous disappearance of the compound **2d** is depicted in Fig. 1. The reaction of the compound **2d** with retention times of 8.4 and 9.1 min for a mixture of two diastereomers, generates products acetophenone, **A** and **B** with retention times of 3.3, 2.6 and 2.5 min, respectively, and some side products with retention times 4.9, 5.1 and 5.4 min. No Aqe-diol wth a retention time of 3.1 min was detected in the residues of the photolysis of all caged compounds. A control experiment shows that Aqe-diol

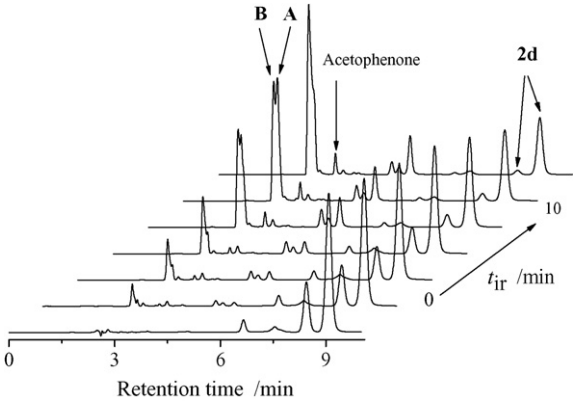


Fig. 1. Sequential recordings at 270 nm of the HPLC analysis of the crude product of **2d** in a 50% CH_3CN–H_2O solution upon 350 nm irradiation. Retention times are 3.3 min for the released acetophenone, 8.4 and 9.1 min for a mixture of diastereomers of **2d**.

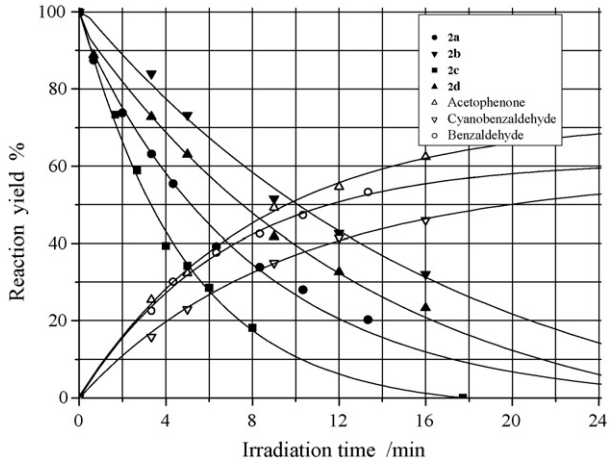


Fig. 2. Time course of photolysis of Aqe-diol protected aldehydes and ketones in a 50% CH_3CN–H_2O solution at 350 nm. Concentrations were determined by HPLC and are the averages of three runs. For comparison, the concentrations have been normalized and reported as a percentage. Solid lines through solid symbols are least-squares fits of first decaying exponentials, which gave time constants τ = 7.9, 17.1, 4.9 and 13.3 min for **2a**, **2b**, **2c** and **2d**, respectively.

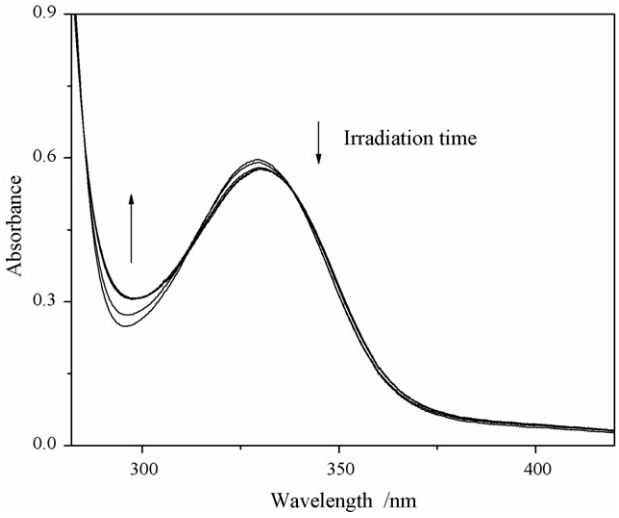


Fig. 3. Absorption spectra of **2c** in a 50% CH_3CN–H_2O solution (0.1 mM) upon 350 nm irradiation from 0 to 8 min with the same fluorescence spectrometer.

under 350 nm light disappears rapidly to generate only photoproducts **A** and **B**. This implies that photolysis of the caged compounds undergoes the formation of Aqe-diol as an intermediate. In addition, photoproduct **B** is an oxide of **A**, for product **A** exposed under air for a short time converts completely into **B**. Thus, product **A** would be a hydroanthraquinone derivative, which can be oxidated by oxygen to an anthraquinone derivative, **B** [18,19].

Fig. 2 shows that the time courses for the consumption of the starting materials follow single exponential decay, suggesting that the photolysis reactions proceeded without remarkable interference by photo byproducts. Comparing the time courses for these reactions, obtained from HPLC analysis of aliquots taken at periodic intervals shows that the Aqu-diol-protected cyclohexanone **2c** disappeaars most rapidly among four compounds, and the slowest for **2b**, the Aqe-diol protected cyanobenzaldehyde, accompanying release of the carbonyl compounds in high conversion rate, 60–90%. To further estimate uncaging efficiency of the compounds, the quantum yields of the starting materials disappearing were measured and listed in Table 1.

As an indication of the efficiency of photolysis, the value of the single-photon uncaging quantum efficiency Q_{u1} should be high enough to be useful for biological applications. Previous investigations revealed that such values of the Bhc-diol [12] and 8-bromo-7-hydroxyquinoline [20] were sufficiently high (0.030–0.057 and 0.005–0.29, respectively) for application to caging chemistry. In our system, the quantum efficiency Q_{u1} of disappearance of the caged compounds were determined, and their values range from 0.03 to 0.09, showing a favorable property as a promising phototrigger for aldehydes and ketones.

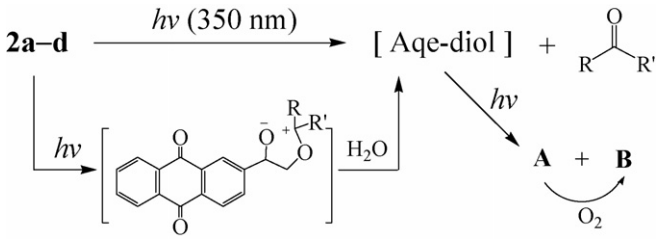
Table 1
Quantum efficiencies for disappearances of the caged compounds **2a-d**[a]

Caged compounds	Q_{u1} (mol einstein^{-1})
2a	0.044
2b	0.031
2c	0.088
2d	0.038

[a] Measurements in 50% CH_3CN–H_2O solutions (0.05 M phosphate buffer pH 7.3) upon 350 nm light irradiation.

Fig. 3 shows the absorption spectrum of the caged compound **2c** before and after photolysis. In contrast to a remarkable decrease at 330 nm and a rather increase at around 380 nm in the photolysis of Aqmoc-protected alcohols [13], the photolysis of **2c** reveals small changes in absorbance at both 330 nm and 380 nm and a notable increase at about 300 nm. The peak at 330 nm is the n-π^* transition of the anthraquinone chromophore. This implies that the anthraquinone chromophore is not destroyed in the uncaging reaction, and regeneration of the carbonyl compounds results in an increase in absorbance at about 300 nm. Thus, the intact anthraquinone moiety in the system gives an added benefit in the biological application.

Furthermore, a solvent effect of the photolysis of the caged compounds shows the uncaging reaction occurs easily under the simulated physiological condition. For example, photolysis of **2c** in CH_3CN gave only the byproducts like photolysis of **2b**, in which generates byproducts with retention time at around 5 min (Fig. 1). With adding water to the solution, in which ratios of water are 25% and 50%, a gradual decrease in the byproducts and the corresponding increase in the photoproducts of Aqe-diol, **A** and **B** were observed. This result implies that increasing polarity of solvent would accelerate the uncaging reaction, consistent with the reaction undergoing a possible zwitterionic intermediate suggested by Dore and co-workers [12]. On the basis of studies of the coumarin-caged phosphates, carboxylate and sulfonates, Bendig and co-workers proposed a photo S_N1 reaction (solvent-assisted photoheterolysis) mechanism [21]. Hence, using a similar zwitterionic intermediate suggested, the uncaging reaction occurs only in the presence of water, and is accelerated with increasing polarity of solvent, can be illuminated shown in Scheme 2.



Scheme 2.

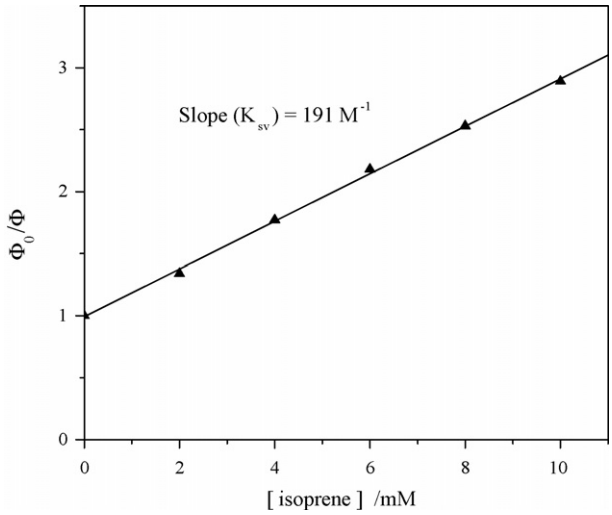


Fig. 4. Stern–Volmer plot for the photolysis of **2c** in a 50% CH_3CN–H_2O solution at 350 nm.

Quenching experiments for the uncaging reaction of the caged compound **2c** by isoprene ($E_T = 251\,kJ\,mol^{-1}$ [17]) demonstrated the uncaging reaction undergo triplet excited state of anthraquinone moiety ($E_T = 261\,kJ\,mol^{-1}$ [17]). Stern–Volmer plot for the photolysis of **2c** in 50% THF–H_2O at 350 nm give a good fit straight line, and its slope is $k_q\tau = 191\,M^{-1}$ (Fig. 4). Assuming the quenching reaction occurs at diffusion control, $k_q = k_{diff} \sim 10^{10}\,s^{-1}\,M^{-1}$, the lifetime of the triplet excited state was estimated to be 19.1 ns, with which the photolysis rate constant is obtained to be $4.6 \times 10^6\,s^{-1}$. The results are similar to Furuta et al.'s observation [13] from Aqmoc-proctected alcohols.

In addition, the hydrolytic stability of the caged compounds was examined, for which is often a key issue in biological applications. No notable decomposition of the caged compounds was observed after 2 days at the room temperature in the dark in 50% CH_3CN–H_2O solutions. Thus, the caged compounds **2a-d** show reasonably good hydrolytic stabilities.

4. Conclusions

Four Aqe-diol protected compounds (**2a-d**) were synthesized and characterized. From the results presented in this paper, the Aqe-diol can be used as an efficient phototrigger for carbonyl compounds. Despite the lower solubility in pure H_2O limits its application to cell biology, the idea of the modification based on efficient photoremovable protecting groups for alcohols allows us to develop new useful diol-type photolabile protecting groups for bioactive aldehydes and ketones.

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