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Mechanism of the photochemical transformation of naphthalene in water

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Abstract

Upon irradiation in air-saturated aqueous solution, naphthalene is mainly converted into 7-hydroxy-1,4-naphthoquinone, 2-formylcinnamaldehyde and 2-carboxycinnamaldehyde. The quantum yield of photolysis is equal to 0.0025±0.0005. Naphthalene is likely to be phototransformed via monophotonic ionization that occurs with a quantum yield equal to 0.02. The radical cations formed after the electron ejection can deprotonate or react with water yielding radicals that are oxidized by molecular oxygen. Finally, 2-formylcinnamaldehyde and 2-carboxycinnamaldehyde are yielded. The production of 7-hydroxy-1,4-naphthoquinone is consistent with the intermediary formation of photolabile 1,4-naphtoquinone. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Naphthalene; Phototransformation; Photoionization; Water

1. Introduction

Naphthalene is a high production volume chemical which is found as pollutant of the environment. Numerous studies were undertaken to promote the oxidation of this compound. Several oxidant systems were used such as Fe^{2+}/H_2O_2 [1], Fe/mercaptobenzoate/O_2 [2], $PdCl_2$/acetic acid/SiO_2 [3] or UO_2^{2+} [4]. By these thermally or photochemically induced reactions, a large number of products are formed including naphthols, 2-formylcinnamaldehyde, 2-carboxyhydroxycinnamic acid, 1,4-naphthoquinone, phthalic or salicylic acids.

In a simpler way, naphthalene can be also degraded photochemically through direct absorption. When irradiated on SiO_2 or Al_2O_3 under an atmosphere of air, naphthalene is converted into phthalic acid [5]. To our knowledge, the products of naphthalene photolysis in water were not studied. However, transient species were examined and several kinetic data were reported. Laser-flash photolysis experiments (laser KrF, λ_{exc}=248 nm) revealed that photoionization takes place along with the intersystem crossing [6]. The ionization process that yields the naphthalene radical cation and the solvated electrons was found to be biphotonic within the energy pulse range 5–40 mJ/pulse. The naphthalene radical cations can be also generated via SO_4^--oxidation of naphthalene [6]. Their reactivity with a series of nucleophiles was studied. The rate constant with water is equal to 4.0×10^4 M^{-1} s^{-1}. Under continuous irradiations, the quantum yield of naphthalene disappearance was evaluated as 0.0015±0.0001 at 313 nm [7]. It was shown that the photolysis is faster in simulated sea water than in distilled water [8]. This rate enhancement that was not observed with NaBr and NaI was found to be correlated with the NaCl concentration.

When we take all together these results, the mechanism of naphthalene photolysis in water looks very unclear. The enhancing effect of chloride ions on the consumption rate may be explained by the quenching of the naphthalene radical cations; however, the formation of these latter species in steady-state irradiations with low intensity light sources is possible if the photoionization is mono and not biphotonic as reported. We may also propose an oxidation of naphthalene by singlet oxygen as an alternative reaction pathway, since it is known that naphthalene sensitizes the formation of this species [9]. Such a reaction was assumed to occur in the case of 1-methylnaphthalene [10].

The goal of the present work was to determine the nature of the naphthalene photoproducts in water and to elucidate the mechanism of the photochemical transformation. Steady-state irradiations were performed at λ>290 nm in order to better approach the natural conditions. Laser-flash photolysis experiments were also undertaken for a better knowledge of the primary processes.

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2. Experimental

2.1. Materials

Naphthalene (Eastman, scintillation grade) was recrystallized from methanol. 1,4-Naphthoquinone, potassium peroxodisulfate and rose bengal were purchased from Aldrich and used as received. Water was purified with a Milli-Q device (Millipore).

2.2. Methods

The irradiations at 313 and 546 nm were carried out using a high-pressure mercury lamp (200 W) equipped with a Bausch and Lomb monochromator. Potassium ferrioxalate was used as chemical actinometer. For analytical runs, naphthalene solutions were irradiated in a device equipped with six sunlamps emitting within the range 280–350 nm with a maximum of emission located at 310 nm. Pyrex-glass was used to cut off wavelengths shorter than 290 nm. Solutions containing naphthalene and peroxodisulfate were irradiated at 253.7 nm in a quartz reactor using a germicidal lamp. In order to avoid the evaporation of naphthalene, solutions were irradiated in well-closed reactors, cooled at 10°C by circulating water, and quickly analyzed. Transient absorption experiments were carried out on a nanosecond laser-flash photolysis spectrometer from Applied Photophysics (LKS.60) with laser excitation at 266 nm from Quanta Ray GCR130-1 Nd:YAG. Experimental details have been described elsewhere [11]. For the quantum yield measurements the system $[Co(NH_3)_5Br](Br)_2$ and NaBr (5×10^{-2} M) was used as chemical actinometer. The formation of Br_2^- was monitored at 380 nm; at this wavelength, the product $\epsilon \times \phi$ is equal to 2880 $M^{-1}\ l\ cm^{-1}$ [12]. UV spectra were recorded on a Cary 3 (Varian) spectrophotometer. ^1H NMR spectra were taken on a Brucker AC400 spectrometer. The LC–MS/MS analyzes were performed with a Thermo Separation Product gradient pump P400 equipped with a 25 cm×4.6 mm column packed with a 5 µm Alltima C_{18} reversed-phase material (Alltech). The following gradient was used for elution: from 0 to 5 min, the mixture was H_2O–MeOH (50–50, v/v), then the content of MeOH was increased reaching 90% at 10 min. The eluent was delivered at 1.0 ml/min. The MS system consisted of a Finnigan MAT LCQ ion-trap mass spectrometer equipped with an atmospheric pressure chemical ionization source (APCI). Nitrogen was used as sheath gas at 80 ml/min and helium as auxiliary gas at 10 ml/min. Vaporiser and capillary temperatures were set at 450°C and 150°C, respectively, and corona discharge at 5 µA. The MS operated in positive ionization mode. Analytical HPLC was carried out on a Waters apparatus equipped with a photodiode array detector (model 996) using a conventional C_{18} reverse phase column. The eluent was a mixture of H_2O and H_3PO_4 (0.1%)–MeOH. The following gradient was used: 50% MeOH from 0 to 5 min, then increase of MeOH content up to 90% at 10 min.

2.3. Identification of photoproducts

2.3.1. A solution of 1,4-naphthoquinone (2.3 $\times10^{-4}$ M) was irradiated with polychromatic lamps for 11 min until the almost complete disappearance of the starting material. The reactional mixture was evaporated to dryness and then analyzed by NMR and LC–MS. Only one product was found.

7-Hydroxy-1,4-naphthoquinone (I): ^1H NMR ($CDCl_3$, ppm) 8.04 (d, 1H, *J*=8.6 Hz), 7.46 (d, 1H, *J*=2.6 Hz), 7.18 (dd, 1H, *J*=8.6 and 2.6 Hz), 6.95 (s, 2H); LC–APCI–MS mass at *m*/*z*=175 corresponding to $[M+H]^+$, product ion mass (MS/MS) at *m*/*z*=147 corresponding to $[M–CO+H]^+$.

2.3.2. Four 25 ml portions of naphthalene (1×10^{-4} M) and $K_2S_2O_8$ (1×10^{-3} M) were irradiated at 253.7 nm for 2 min. Products were extracted with diethylether and analyzed by NMR and LC–MS. Two new photoproducts were found along with (I).

2-Formylcinnamaldehyde (II): ^1H NMR ($CDCl_3$, ppm) 10.24 (s, 1H), 9.82 (d, 1H, *J*=7.8 Hz), 8.59 (d, 1H, *J*=16 Hz), 6.69 (dd, 1H, *J*=16 and 7.8 Hz); ^1H NMR (CD_3OD, ppm) 10.45 (s, 1H), 9.94 (d, 1H, *J*=7.7 Hz), 8.85 (d, 1H, *J*=16 Hz), 7.7 (m, 4H), 6.94 (dd, 1H, *J*=16 and 7.8 Hz); LC–APCI–MS mass at *m*/*z*=161 corresponding to $[M+H]^+$, product ion mass (MS/MS) at *m*/*z*=133 corresponding to $[M–CO+H]^+$.

2-Carboxycinnamaldehyde (III): ^1H NMR ($CDCl_3$, ppm) 10.19 (s, 1H), 9.73 (d, 1H, *J*=7.8 Hz), 8.19 (d, 1H, *J*=16 Hz), 6.37 (dd, 1H, *J*=16 and 7.8 Hz); ^1H NMR (CD_3OD, ppm) 9.88 (d, 1H, *J*=7.7 Hz), 8.41 (d, 1H, *J*=16 Hz), 8-7 ppm (aromatic resonances), 6.89 (dd, 1H, *J*=16 and 7.8 Hz); LC–APCI–MS mass at *m*/*z*=177 corresponding to $[M+H]^+$.

3. Results and discussion

3.1. Steady-state irradiations

The quantum yield of photolysis at 313 nm was found to be equal to 0.0025±0.005, which is in good agreement with the value previously reported [7]. Fig. 1 shows the typical chromatogram of an air-saturated solution of naphthalene irradiated at 313 nm until a conversion extent of 25%. The absorption spectra of the three main photoproducts are given in the insert of Fig. 1. In order to identify these photoproducts, we undertook complementary experiments.

At first, we photolyzed 1,4-naphthoquinone using the polychromatic lamps. (I) was found as a major photoproduct. It was assigned to 7-hydroxy-1,4-naphthoquinone on the basis of mass spectrometry and ^1H NMR data.

Then, naphthalene (1.0×10^{-4} M) was irradiated at 253.7 nm in the presence of $K_2S_2O_8$ (1.0×10^{-3}). Products (I), (II) and (III) were found as in the case of the direct

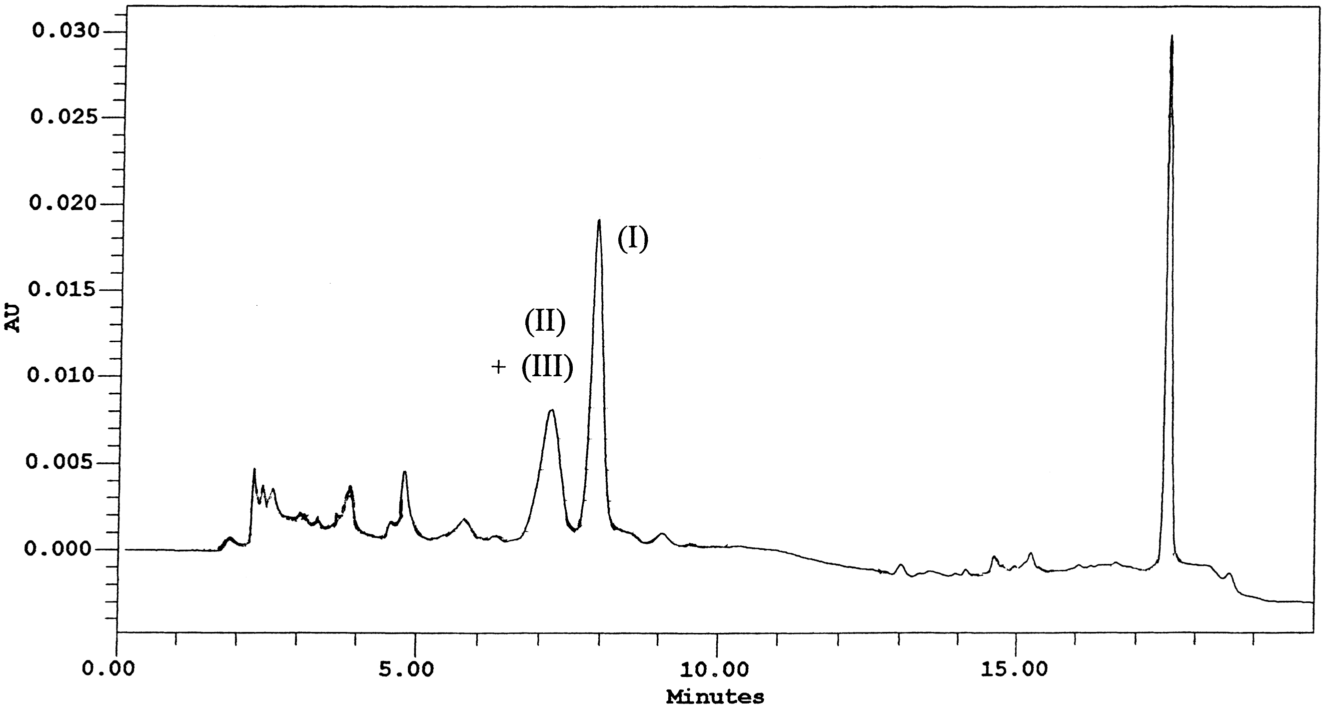
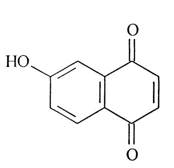
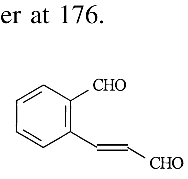


Fig. 1. HPLC chromatogram of an air-saturated solution of naphthalene (10^{-4} M) irradiated at 313 nm. Detection wavelength set at 275 nm.

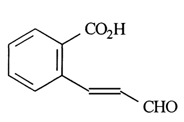
photolysis, but in larger amounts. After being extracted with diethylether, the mixture of products was analyzed by mass-spectrometry and ^{1}H NMR in $CDCl_3$ and CD_3OD. NMR spectra confirmed the presence of 7-hydroxy-1,4-naphthoquinone and revealed the presence of two other molecules exhibiting very close signals. Both of them had two vinylic hydrogens in trans position as indicated by the high coupling constant (J=16 Hz). One of the compounds had two aldehydic hydrogens (9.82 and 10.24 ppm in $CDCl_3$), the proton at 9.82 ppm being coupled with one of the vinylic hydrogen. Referring to published data [4], this compound can be assigned to 2-formylcinnamaldehyde. The other compound exhibited also two resonances in the same region (9.73 and 10.19 ppm in $CDCl_3$), but only the doublet at 9.83 ppm corresponded to an aldehydic proton. As expected for an exchangeable proton, the singlet at 10.19 ppm was removed when $CDCl_3$ was replaced by CD_3OD. This other product was assigned to 2-carboxycinnamaldehyde. In accordance with these assignments, we found by LC–MS one mass at m/z=160 and another at 176.



(I)



(II)



(III)

In order to determine whether naphthalene reacts with singlet oxygen, this latter species was produced using rose bengal as sensitizer. Air-saturated solutions containing rose bengal (2×10^{-6} M) and naphthalene (1×10^{-4} M) were buffered at pH=7 with phosphates and irradiated at 546 nm. No consumption of naphthalene was observed after several hours of irradiation indicating that naphthalene does not react with singlet oxygen.

3.2. Formation of hydrated electrons

By nanosecond laser-flash photolysis, several transient can be observed [6]: the triplet excited state (λ_{max}=420 nm), the radical cations (λ_{max}=685 nm), and the hydrated electrons which exhibit a very broad absorption band with a maximum around 720 nm. We focused our work on the photoionization process in order to determine whether this process was exclusively biphotonic or mixed mono- and biphotonic. Absorbances were measured at 630 nm. At this wavelength, both the naphthalene radical cation and the hydrated electron absorb. However, the kinetic decay of the two species are very different. The solvated electrons disappear by reaction with oxygen ($k=5.8\times10^6$ s^{-1}) in the first µs following the pulse end. On the other hand, the naphthalene radical cations are long-lived species [6]. The absorbance corresponding to the hydrated electrons (A_{he}) can be, therefore, obtained by subtracting the absorbance measured 0.6 µs from that extrapolated at the end of pulse. As shown in Fig. 2, A_{he} increases in a quadratic mode with the energy pulse (P) reflecting a dominant biphotonic formation. However, the linear plot of the ratio A_{he}/P against P gives an intercept of 0.0015±0.0003 showing that monophotonic ionization also occurs (see inset of Fig. 2). Using an appropriate actinometry, we deduced that this value of A_{he}/P is related to $\epsilon_{he}\times\phi_{he}=310\pm60$ M^{-1} l cm^{-1}. Hence, taking for

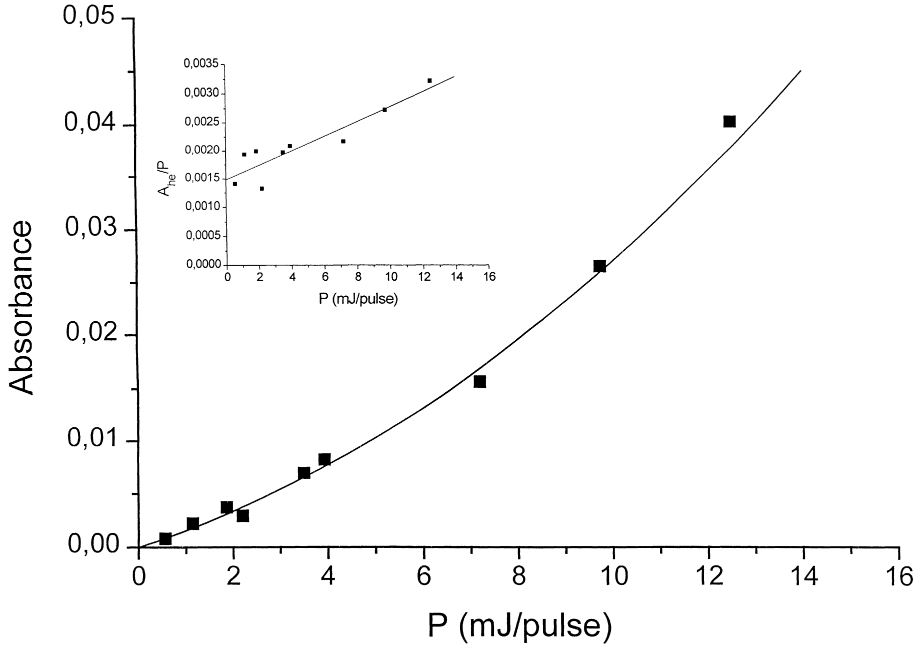


Fig. 2. Plot of A_{he} at 630 nm against the energy pulse P. Inset: Plot of A_{he}/P against P.

ϵ_{he}, the extinction coefficient of the hydrated electrons at 630 nm, the value of 15 700 $M^{-1}\,l\,cm^{-1}$, we obtained that the quantum yield of the monophotonic formation of the hydrated electrons, ϕ_{he}, was equal to 0.020±0.004.

3.3. Influence of N_3^-

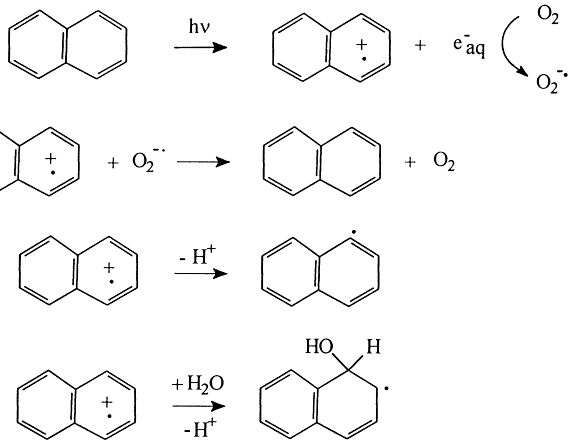
When naphthalene (10^{-4} M) is irradiated in the presence of N_3^- (10^{-2} M), the quantum yield of photolysis is reduced by about 60% and the photoproducts (I), (II) and (III) are not formed. By monitoring the fluorescence decay, we found that the lifetime of the singlet is shorter in the presence than in the absence of azide ions. The rate constant decay (K_{obs}) is equal to $2.7\times10^7\,s^{-1}$ in the absence of N_3^- and to $5.6\times10^7\,s^{-1}$ in the presence of N_3^- (10^{-2} M). This result shows that N_3^- is able to trap the singlet excited state and explains the inhibiting effect N_3^- on the quantum yield of naphthalene photolysis. However, the drastic inhibiting effect on the photoproducts has another ground.

3.4. Proposed mechanism

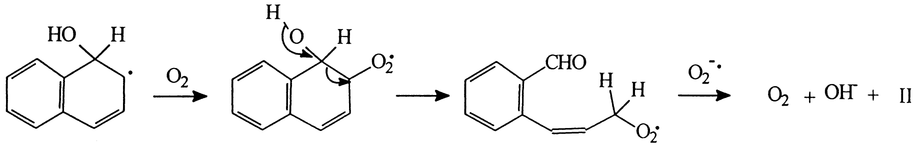
Upon irradiation in air-saturated aqueous solution, naphthalene is photooxidized into 2-formylcinnamaldehyde, 2-carboxycinnamaldehyde and 7-hydroxy-1,4-naphthoquinone. We show that the same photoproducts are formed when naphthalene is oxidized by SO_4^- radicals, i.e. in conditions where the radicals' cations were proved to be formed [6]. Besides, we show that the photoionization process is not only biphotonic as previously reported [6] but mixed mono- and biphotonic, the quantum yield of the monophotonic photoejection being equal to 0.02. This value is higher than that of the quantum yield of naphthalene disappearance (around 0.0025). All these results leads us to propose that the products observed in steady-state irradiation arise from the radical cations produced after monophotonic ionization.

The involvement of the triplet excited state in the reaction is unlikely: in the presence of oxygen, the triplet is known to produce singlet oxygen but no reaction between naphthalene and singlet oxygen is detected.

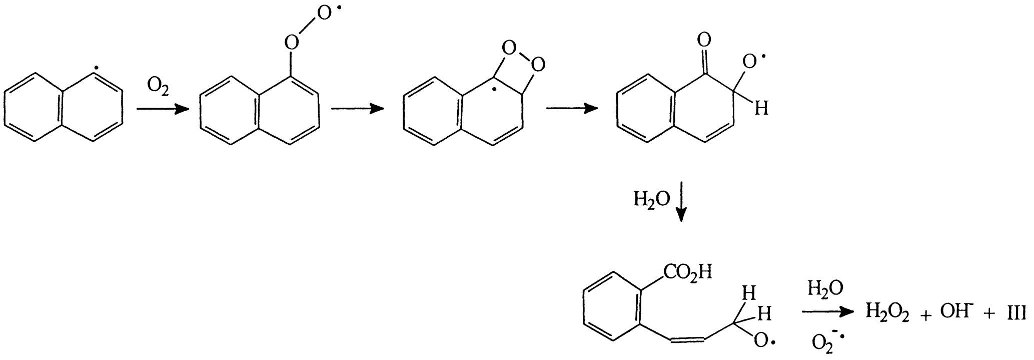
In aerated medium, the ejected electrons are trapped by oxygen. The low efficiency of the naphthalene phototransformation compared to the photoionization can be explained by a reaction between the radical cations and the superoxide anions giving back naphthalene and oxygen (Scheme 1).



Scheme 1.



Scheme 2.



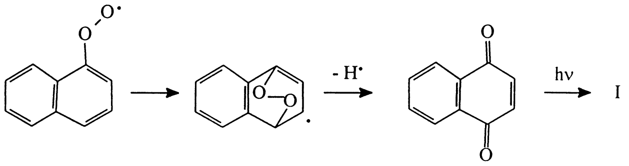
Scheme 3.

Once formed, the radical cations can either react with water (k=4×10^4 M^{-1} s^{-1}) [6] or deprotonate (see Scheme 1). In both cases, oxidable radicals are produced, and several reaction pathways can explain the formation of (II) and (III) (see Schemes 2 and 3). The inhibiting effect of azide ions on the production of (I), (II) and (III) is likely to result from the reaction of the radical cations with N_3^- (k=4.2×10^9 M^{-1} s^{-1} [6]).

On the other hand, (I) is likely to be produced by the secondary photolysis of 1,4-naphthoquinone (Scheme 4). In accordance, we show that 1,4-naphthoquinone is very efficiently photolyzed into (I). 1,4-Naphthoquinone is not detected upon irradiation of naphthalene in water whereas this compound is generally observed upon thermally induced oxidations. We can therefore assume that 1,4-naphthoquinone is produced via photoionization but cannot accumulate as a result of a fast photolysis.

4. Conclusion

The products formed by photolysis of naphthalene in water were determined and the mechanism of the reaction clarified. Naphthalene is mainly phototransformed via monophotonic ionization. 2-Formylcinnamaldehyde and 2-carboxycinnamaldehyde are formed through the oxidation of the radicals arising after deprotonation or hydrolysis of the naphthalene radical cations. 7-Hydroxy-1,4-naphthoquinone is detected as main photoproduct. It is likely to result from the photolysis of 1,4-naphthoquinone that may be involved as photolabile intermediate [12].



Scheme 4.

Acknowledgements

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