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Competing processes in the photochemistry of picolines and their *N*-methyl salts: photoinduced charge transfer, phototransposition and photohydration

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Abstract Photochemical reactivity of a series of picolines and their *N*-methylated salts has been investigated by preparative irradiations and UV–vis spectroscopy. Understanding competing photochemical processes and knowledge of their relative efficiencies is important in the application of pyridines as photocages or in the synthesis of complex polycycles. Contrary to previous reports for the gas phase, picolines are not reactive in the phototransposition, presumably due to protonation of the pyridine nitrogen in the excited state. Deuterium exchange was observed upon irradiation in CD_3CN–D_2O, but it was rationalized by photoionization and radical formation. On the other hand, *N*-methylated picoline salts are not protonated upon excitation. They undergo photohydration and phototransposition ($\Phi_R = 0.01$–0.06). Upon irradiation of iodides, azabicyclic [3.1.0] hydration products were obtained. A difference in product distribution was observed between iodides and perchlorates, due to photoelimination of perchloric acid leading to the thermal aziridine ring opening. Moreover, excitation of iodide derivatives gives rise to change transfer transition forming iodide radicals that eventually give I_3^- with the quantum efficiency $\Phi_R = 0.015$–0.02.

Keywords Pyridine · Pyridinium salt · Excited state proton transfer · Excited state charge transfer · Phototransposition · Photohydration

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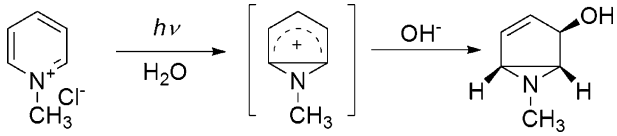
Introduction

Pyridine and pyridinium derivatives are important in various biological processes. For example, pyridinium salts are present in the structure in NAD^+ and $NADP^+$ cofactors, which are essential for the functioning of all living cells. Since pyridines and pyridinium derivatives are photochemically reactive, [1, 2] in principle, excitation by light allows for the activation or deactivation of biochemical processes involving NAD^+ and $NADP^+$ cofactors. Furthermore, biologically important molecules from the family of vitamin B_6 and its derivatives are methylpyridines (also known as picolines), which are also prone to photochemical reactions [3].

Interest in pyridine photochemistry was initiated by the discovery of photochemical rearrangements giving Dewar-type products [4]. Later, in a seminal paper by Kaplan et al. [5], photochemical rearrangement of pyridinium salts was reported. Under basic conditions, pyridinium salt **1** undergoes rearrangement and hydration to azabicyclo[3.1.0] derivative **3**, via a cationic intermediate **2** (Eq. 1) [5, 6]. It is a relatively simple reaction that delivers complex heterocyclic structures with well-defined stereochemistry. Thus, Mariano et al. extended the scope of the pyridinium salts photorearrangement and reported on acid- [7] or base-induced ring opening of the photochemically formed aza-heterocycles, [8] whereas Simpson et al. [9] and Burger et al. [10] used the photorearrangement as the key step in the synthesis of natural compounds.



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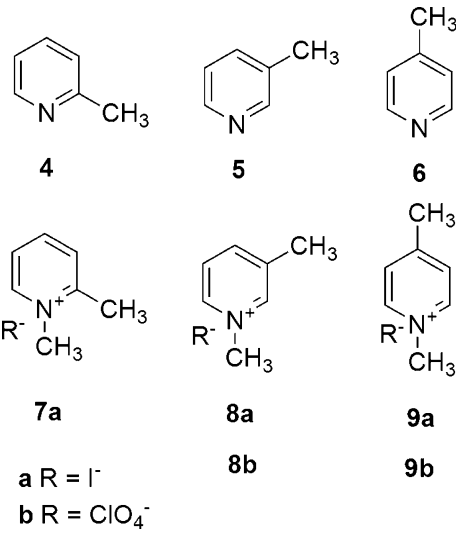
Pyridinium photochemistry has been used in the development of photocages. Falvey et al. developed photocages for alcohols and esters by applying single electron transfer (SET) photochemistry of pyridinium salts in the presence of pyrene and heterocyclic electron donors, [11] or ruthenium(II) sensitizers [12]. Boncella et al. studied *N*-methylpicolinium triflate photocages for aliphatic amines [13]. Furthermore, photocages were developed wherein the electron donor and pyridinium salt were in the same molecule [14]. Photodecaging of carboxylic acids was accomplished by use of golden nanoparticles and pyridinium salts, [15] whereas carboxylic acids, amino acids, and phosphates can be photodeprotected from pyridinium photocages in the presence of cumarine and BODIPY derivatives [16]. Recently, Falvey et al. reported a simple approach for photodecaging of carboxylic acids by use of visible light, based on charge transfer transition in pyridinium iodide salts [17]. Consequently, a deeper understanding of photochemical transformation of pyridine and pyridinium derivatives is of great relevance and could redirect future studies in the life sciences.

Herein, we report a general investigation of photochemical reactivity in a series of α-, β-, and γ-picolines **4–6**, their methyl iodide, and perchlorate salts **7–9**. The investigation is conducted to probe for anticipated competing photochemical reactions including excited state proton transfer (ESPT), charge transfer, photohydration, and photorearrangement. Irradiations of **7–9** were conducted under different conditions, and photoproduct formation studied by NMR and UV–vis spectroscopy. The current investigation indicates occurrence of two competing photochemical processes, charge transfer and photorearrangement, neither of which should be neglected in the applications of pyridines photochemistry. Moreover, we observe an interesting effect of the counterion and the *meta* effect of the methyl group to the photochemical reactivity.



Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Spectrometer at 300, 400, or 600 MHz. Picoline isomers **4–6** were purchased from the usual commercial sources and were purified by distillation. Pyridinium iodide and perchlorate salts **7–9** were prepared according to the known procedures [8, 18]. Experimental procedures for the preparation of **7–9** and the corresponding NMR and UV–vis spectra are in the supporting information. Solvents used for the photochemical experiments were of HPLC grade. UV–vis spectra were recorded on a PG T80/T80 + spectrometer, and fluorescence on a Cary Eclipse Varian spectrometer. MS spectra were obtained on a HPLC–MS–MS Agilent 1200 series, 6410.

Irradiation experiments in NMR tubes

Irradiation experiments were conducted in a Luzchem photochemical reactor equipped with eight lamps (one lamp 8 W, output at 254 nm).

Picoline isomers **4–6** (1.0–2.4 mg) were dissolved in a mixture of CD_3CN (1 mL) and D_2O (100 μL) in quartz NMR tubes ($c = 1.91–2.34 \times 10^{-2}$ M). The solutions were irradiated in a Luzchem reactor at 254 nm over 5 min-2 h. After different irradiation times, NMR spectra were recorded.

Pyridinium salts **7–9** (1.5–2.6 mg) were dissolved in a mixture of CD_3CN (500 μL) and D_2O (50 μL) in quartz NMR tubes ($c = 1.2–2.0 \times 10^{-2}$ M). The solutions were irradiated in a Luzchem reactor at 254 nm, and, after certain irradiation intervals, NMR spectra were recorded.

In the preparative irradiation experiments, pyridinium salt **8a** (376 mg, 0.04 M) was dissolved in aqueous KOH solution (40 mL, 0.05 M). A quartz tube was filled with the solution, purged with Ar for 30 min and sealed. After 8 h irradiation, the solution was extracted with diethyl ether, ethyl acetate, and CH_2Cl_2. The collected extracts were dried over Na_2CO_3, filtered, and the solvent was removed on a rotary evaporator (without heating) to afford the residue that was analyzed by ^{1}H NMR.

UV–vis experiments

A solution of **7a**, **8a**, or **9a** in CH_3CN–H_2O (10:1, 3 mL) was divided into three quartz cells for fluorescence spectroscopy. The first solution was purged with Ar, the second with O_2, and the third was not purged. The absorbances of the solutions at 234 nm were adjusted to 0.75 ($c \approx 5 \times 10^{-5}$ M). The solutions were irradiated in a Luzchem reactor at 254 nm in certain time intervals (2 min-2 h), and after each irradiation UV–vis spectra were recorded.

Alternatively, to the solutions of **7a–9a** in CH_3CN ($c \approx 5 \times 10^{-5}$ M), different amounts of H_2O were added (corresponding to the volumetric ratio of 1, 5, 10, 20, and 50 %). The solutions were irradiated at the same time in a Luzchem reactor at 254 nm. After certain irradiation intervals (2 min-2 h) UV–vis spectra were recorded.

Measurements of reaction quantum efficiencies

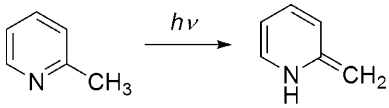
Quantum efficiency for the hydration of **7a–9a** was measured by a valerophenone actinometer ($\Phi_{254} = 0.65 \pm 0.03$) [19, 20]. For the actinometer, a solution of valerophenone in CD_3CN–D_2O (10:1) $c = 1.4 \times 10^{-2}$ M) was used. Solutions of **7a–9a** in CD_3CN–D_2O (10:1) were prepared with the same concentration ($c = 1.4 \times 10^{-2}$ M, $A_{254} > 2$). Quartz NMR tubes were filled with the solutions, the solutions were purged with N_2 15 min and the tubes were sealed. The solutions were irradiated in a Luzchem reactor with four lamps at 254 nm 15 min (valerophenone) or 2 h (**7a–9a**). After the irradiation, NMR spectra were taken. From the conversion of reactant to photoproducts, quantum yields were calculated (for the equations to calculate Φ, see the supporting information). The measurements were performed in triplicate.

Quantum efficiency for the formation of I_3^- from **7a–9a** was measured by a KI/KIO_3 actinometer KI/KIO_3 ($\Phi_{254} = 0.74$), [19, 21]. For the actinometer, a fresh solution of KIO_3 in borate buffer (0.01 M, pH 9.25) was prepared, and then, a solution of KI (0.6 M) in the borate solution of KIO_3. Fresh solutions of **7a–9a** in CH_3CN–H_2O (10:1) were prepared in cells for fluorescence spectroscopy in the concentration range corresponding to $A_{265} \approx 0.5$ ($c \approx 1 \times 10^{-4}$ M). The volume in cells was 2.5 mL, and the room temperature varied from 17 to 22 °C. The solutions were purged with N_2 15 min (or were not purged). Prior to the irradiations, the UV–vis spectra were recorded. The solutions were irradiated in a Luzchem reactor with one lamp at 254 nm 0.5, 1, and 2 min. During the irradiations the cells were kept at a constant distance from the lamp and were covered by a dark paper at three sides to ensure photon flux to the cell only from the front face. Concentration of I_3^- was calculated from the absorbance increase at 352 nm, whereas decomposition of **7a–9a** was obtained from the decrease of absorbance at 235 or 228 nm (for the equations to calculate Φ, see the supporting information). The measurements were performed in triplicate.

Results and discussion

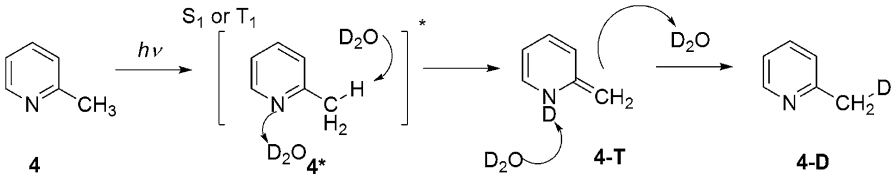
Absorption spectra of picolines **4–6** have an absorption band at $\approx$263 nm (253 nm for **6**) populating S_1 state, which is not fluorescent. Attempts to record fluorescence spectra failed. Pyridinium iodide salts exhibit two absorption bands, at 265 nm (255 nm for **9a**), corresponding to the pyridinium excitation, and at $\approx$235 nm corresponding to a charge transfer transition due to the presence of iodide [17] (see Figs. S1–S4 in the supporting information). Similar to **4–6**, **7a–9a** are not fluorescent.

All irradiation experiments were performed by use of lamps with the output at 254 nm. Electronically excited states are often characterized by different acid–base properties compared to the corresponding ground states [22]. Thus, pyridine derivatives become more basic upon excitation to S_1 (pK_a $S_0 = 5.5$, pK_a $S_1 = 12.7$) [23]. Moreover, phototautomerization of **4** was investigated by computational methods indicating that excitation to S_1 or T_1 lowers the activation barrier for the formation of **4-T** (Eq. 2) [24].



4 **4-T** (2)

Upon electronic excitation, the pyridine nitrogen in picolines is anticipated to become more basic, whereas the methyl group may behave as a carbon photoacid leading to the formation of **4-T**, as shown in Scheme 1. Subsequent thermal tautomerization of **4-T** to **4** should lead to the regiospecific deuterium incorporation in the methyl group in compound **4-D**. Similarly, it is anticipated that pyridinium



Scheme 1 Plausible ESPT reactivity of **4**

Scheme 2 Plausible ESPT reactivity of **7**

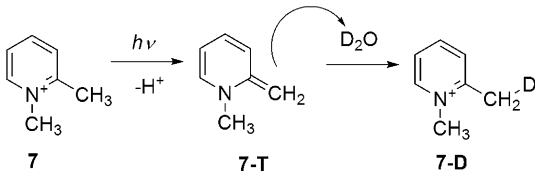
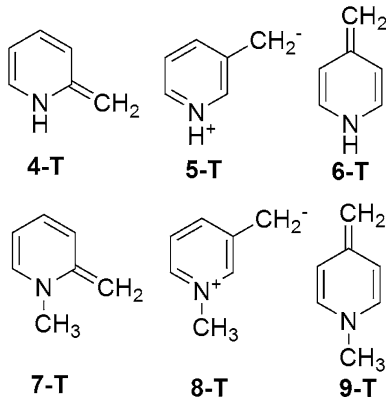


Fig. 1 Anticipated intermediates in the ESPT photochemistry of **4–9**



salts **7–9** behave as carbon photoacids. For example, deprotonation of **7** is anticipated to give **7-T** that should upon thermal protonation in D_2O give **7-D** with the regiospecificaly deuterated methyl group (Scheme 2). It is plausible that *meta* and *para* derivatives undergo similar photoreactions via the corresponding intermediates **5-T**–**9-T** (Fig. 1).

Anticipated ESPT reactivity and phototautomerization of **4–9** was probed by irradiations in CD_3CN–D_2O. After the irradiation, the position and the extent of deuteration was examined by NMR and MS, respectively. It should be noted that protonation (deuteration) of pyridine nitrogen cannot be probed in such a way. Interestingly, after the irradiation of **4–7**, no deuterium incorporation in the methyl group was observed, but it took place in the aromatic ring. Results are compiled in Table 1. The plausible mechanism for deuteration of the aromatic ring may be electrophilic aromatic substitution in S_1, or a radical-cation mechanism similar to

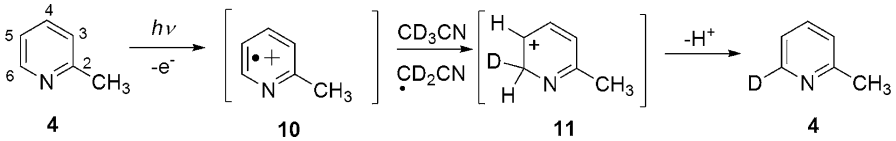
Table 1 Deuterium content in **4–6** after irradiation in CD_3CN–D_2O[a]

Comp.	%D (C-atom)[b]	% (Ion)
4	23 (C3), 23 (C4), 27 (C5), 37 (C6)	25 (M^++1), 38 (M^++2), 24 (M^++3)
5	15 (C2), 20 (C4), 17 (C5), 17 (C6)	93 (M^++1), 6 (M^++2), 1 (M^++3)
6	73 (C2,6), 63 (C3,5)	15 (M^++1), 33 (M^++2), 44 (M^++3)

[a] Irradiation at 254 nm for 2 h in CD_3CN–D_2O, performed in a quartz NMR tube

[b] Obtained by integration of signals in ^{1}H NMR spectra. The numeration of C-atoms follows IUPAC guidelines, as shown in one example on Scheme 3

[c] Obtained from MS



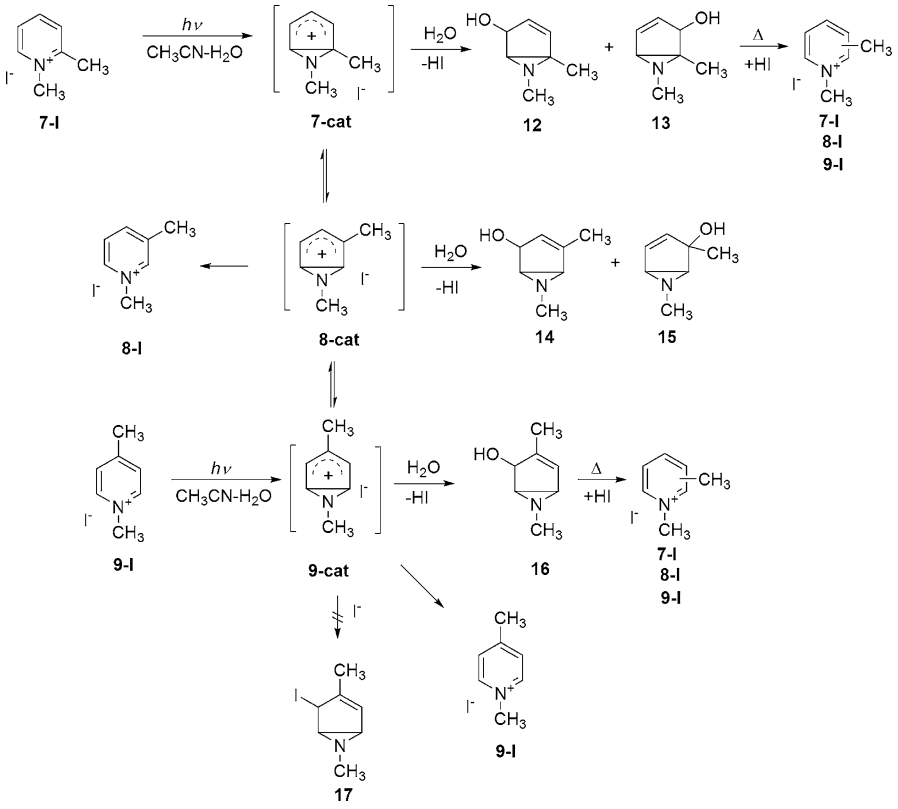
Scheme 3 Plausible mechanism for D-exchange in **4** upon irradiation in CD_3CN–D_2O

the one proposed for the deuteration of pyrroles and similar aza-heterocycles [25]. In such a mechanism, picolines are first oxidized to the corresponding radical-cations **10** that undergo D-abstraction from CD_3CN to give cations **11** and eventually yield D-incorporated molecules (Scheme 3). Very low efficiency of D-incorporation is in line with such a mechanism. Namely, photoionization of pyridine should take place with low efficiency due to its relatively high oxidation potential (in CH_3CN, $E_{ox} = 1.82$ V $_{vs.\ Ag/AgCl}$) [26].

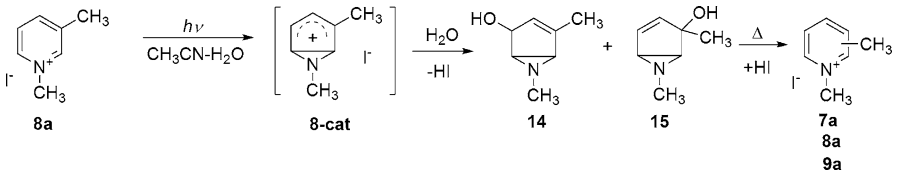
In addition to deuteration of **4–6**, no other photochemical processes were observed. In particular, phototransposition products were not formed, contrary to the previous report by Pavlik et al. [27] on phototransposition of picolines in gas phase. Obviously, photochemical reactivity in gas phase and protic solution differ significantly, presumably due to the protonation of pyridine nitrogen in S_1 [23].

Contrary to picolines, irradiation of the pyridinium derivatives **7–9** did not give rise to deuterated compounds, but gave H_2O-adducts and rearranged products. In addition, during the irradiations of **7a–9a**, the color of the solution changed from transparent to yellow, indicating formation of I_3^- [28]. Therefore, we examined two processes separately, photochemical formation of I_3^- by UV–vis spectroscopy and formation of H_2O-adducts by irradiation in quartz NMR tubes and recording NMR spectra.

Upon irradiation of **7a–9a** in NMR tubes, a new set of signals between 3 and 6 ppm in ^{1}H NMR spectra was observed. Conversion to these primary photoproducts after 2 h irradiation was $\approx$10 % for **7a** and **9a**, whereas for the *meta* isomer **8a**



Scheme 4 Competing photohydration and phototransposition of **7a** and **9a**



Scheme 5 Photohydration of **8a**

it was ≈50 %. From **7a** or **9a**, in addition to primary products formed in yields lower than 10 %, competing phototransposition took place, giving mixtures of all three isomers **7a**–**9a** (Scheme 4). Our observation is in agreement with a preceding theoretical report that photolysis of *meta*-alkylated pyridinium salts takes place without nitrogen migration [29]. Attempts to isolate the primary photoproducts after preparative irradiations in CH_3CN–H_2O failed. In the isolation process, the primary products rearranged in a transposition reaction giving mixtures of **7a**–**9a**. Similarly, upon heating of a NMR tube containing only starting molecule **8a** and primary products **14** and **15**, a mixture of **7a**–**9a** was obtained (Scheme 5).

In principle, primary photoproducts could be associated to the hydration products **12**–**16**, or iodide adducts such as **17** (Scheme 4). Similarity of the signals in ^{1}H NMR to H_2O-adducts described in precedent literature [5] encouraged us to assign the primary products to **12**–**16**. To verify this assignment, the irradiation of **8a** has been conducted under basic conditions, the same as in the report by Kaplan et al. [5] where I-adducts are not expected due to the presence of a large excess of the better nucleophile, OH^-. Indeed, the same products were obtained in the irradiation of neutral and basic solution, indicating that the primary products are correctly assigned to H_2O-adducts. Additional evidence that the primary products are H_2O-adducts came from the lack of their formation upon irradiation in neat CH_3CN. Prolonged irradiation resulted only in the inefficient phototranspositon. Note that **12**–**16** have in principle different diastereomeric forms. Since we did not manage to separate the H_2O-adducts, we were not able to assign their stereochemistry. However, it is known that nucleophile attacks the azabicyclic [3.1.0] cation stereospecifically, *anti*- to the aziridine ring, as shown, for example, in Eq. (1) [5, 7–10].

Efficiency of the photohydration was determined by use of a valerophenone actinometer [19, 20]. Results are compiled in Table 2. It is interesting to note that photohydration of *meta*- isomer **8a** takes place about 2–3 times more efficiently than for the *ortho* or *para* isomers. This result represents one more example of a *meta*-effect in photochemistry [30, 31]. The observation is probably due to the positive inductive effect of the methyl substituent that stabilizes the cationic intermediate, more pronounced in **8-cat** then in **7-cat** or **9-cat**. Our observation of meta-effect is also in agreement with precedent theoretical investigation [29].

Photochemical reactivity of iodide salts **7a**–**9a** in charge transfer reactions was investigated by recording UV–vis spectra during the irradiation, where formation of I_3^- species was clearly observed. For example, Fig. 2 shows the changes in spectra upon irradiation of **8a**, where a decrease of absorbance at 235 and 265 nm indicate a disappearance of I^- and pyridinium chromophores, whereas an increase of absorbance at 290 and 360 nm indicates formation of I_3^-. In particular, the absorption band at 235 nm corresponds to a charge transfer transition [32]. It is clearly demonstrated by UV–vis spectra at different H_2O content where the absorption band shifts hypsochromically with the increase of solvent polarity (See Fig. S4 in the supporting information). Thus, upon excitation, an electron is transferred from I^- to the pyridinium forming a radical pair. Escape of the iodine radicals from the cage leads to the formation of I_2 and I_3^- (Scheme 6). However, by ^{1}H NMR we did not detect the presence of any bispyridine or reduction product,

Table 2 Quantum yield of photohydration (Φ_{H2O}) of **7a**–**9a**[a]

Compound	Φ_{H2O}
7a	0.027 ± 0.003
8a	0.06 ± 0.02
9a	0.014 ± 0.003

[a] Determined by use of a valerophenone actinometer (Φ_{254} = 0.65 ± 0.03) [19, 20]

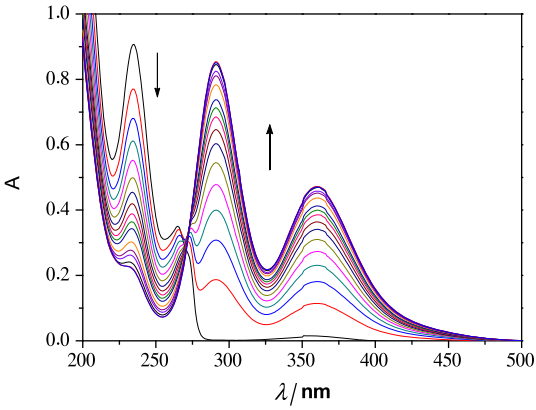
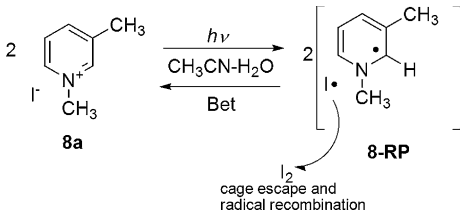


Fig. 2 Changes in the UV–vis spectra of 8a upon irradiation in CH_3CN–H_2O (9:1). The irradiation was performed at 254 nm and the spectra were recorded in the irradiation intervals of 0.5–5 min



Scheme 6 Charge transfer transition in **8a** leading to the formation of I_3^-

indicating that the recombination of pyridyl radicals does not take place or leads to the formation of high molecular weight products.

Whereas charge transfer transition and formation of I_3^- are important in the application of pyridinium salts as photocages, [17] it is an energy wasting process in the synthetic applications. Therefore, we determined quantum efficiency for the chromophore disappearance and formation of I_3^- from **7a** to **9a** by use of a KI/KIO_3 actinometer (Table 3) [20, 21]. Moreover, we investigated the influence of solvent polarity and presence of O_2 to the reaction efficiency. Irradiations were performed in N_2-purged, air-saturated and O_2-purged solutions where we examined the efficiency of the iodine formation, as well as the decay of the

Table 3 Quantum efficiency for the compound degradation (Φ_d) and I_3^- formation (Φ_I) for **7a**–**9a** in N_2-purged and air-saturated solutions[a]

Compound	Φ_d^b	Φ_d^c	Φ_I^b	Φ_I^c
7a	0.075 ± 0.005	0.14 ± 0.04	0.02 ± 0.01	0.015 ± 0.05
8a	0.10 ± 0.01	0.10 ± 0.05	0.02 ± 0.01	0.015 ± 0.05
9a	0.07 ± 0.01	0.10 ± 0.03	0.02 ± 0.01	0.018 ± 0.06

[a] Irradiated at 254 nm and determined by use of a KI/KIO_3 actinometer ($\Phi_{254} = 0.74$) [20, 21]

[b] N_2-purged solution

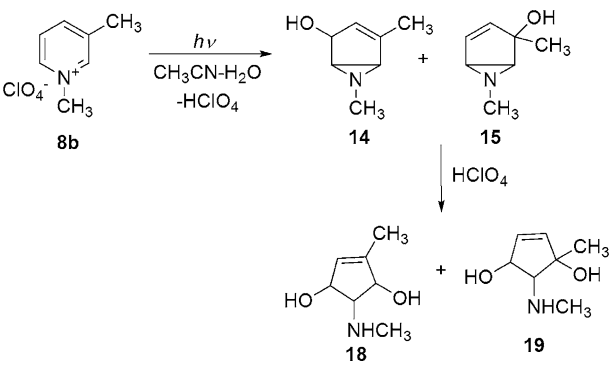
[c] Air-saturated solution

photochemically formed I_3^-. Results in Table 3 and Fig. S7 in the supporting information indicate that I_3^- is formed with similar efficiency when the solution contained O_2, suggesting that no quenching or negligible quenching of the excited state took place.

Monitoring of the absorbance of **8a** after the irradiation at 254 nm indicates that some intermediates or primary products formed in the photochemical reaction are not stable. Their decay was monitored over 1 h wherein we observed slower kinetics in the presence of O_2 than in the Ar-purged solution (see Fig. S8 in the supporting information). However, we were not able to isolate intermediates in the charge-transfer photochemistry or get more confident spectroscopic proofs for their structure.

Efficiency of the I_3^- formation was also tested at different H_2O contents and different **8a** substrate concentrations. Whereas in the tested substrate concentration range no significant influence to the reaction efficiency was observed, H_2O concentration affected the charge transfer transition and the efficiency for the I_3^- formation. At higher H_2O concentration the efficiency of the I_3^- formation decreases (see Fig. S9 in the supporting information), presumably due to competing photohydration. Thus, at higher H_2O concentration, disappearance of the substrate was more efficient.

Irradiation of pyridine iodide salts at 254 nm gives rise to the charge transfer transition and formation of iodine. On the contrary, perchlorate has a high oxidation potential rendering such a transfer energetically impossible. Therefore, we performed photochemical experiments with pyridinium iodide and perchlorate isomers to probe for the counter-ion effect. Interestingly, NMR spectra after the irradiation indicate formation of different products than from the iodide salts. Again, attempts to isolate the products failed. However, the observed difference can be associated to acid-catalyzed aziridine opening by photorelease of a strong acid, $HClO_4$, as shown in Scheme 7. ^{1}H NMR spectrum after irradiation of **8b** showed th presence of two compounds in approximate ratio 1:1 with characteristic signals clearly corresponding to **18** and **19**, in agreement with precedent literature [7].



Scheme 7 Photohydration of **8b** followed by aziridine ring opening

Conclusions

Photochemical reactivity of a series of picolines and their *N*-methylated salts has been investigated. Picolines are not reactive in phototransposition, probably due to protonation of pyridine nitrogen in the excited state. Deuterium exchange was observed upon irradiation in $CD_3CN–D_2O$, presumably due to photoionization and radical formation. On the other hand, *N*-methylated picoline salts are not protonated upon excitation. They undergo photohydration and phototransposition. A difference in reactivity was observed between perchlorate and iodide salts. Upon irradiation of iodides, azabicyclic[3.1.0] hydration products were obtained, whereas due to photoelimination of perchloric acid thermal aziridine ring opening takes place. Excitation of iodide pyridinium salts gives rise to change transfer transition forming iodide radicals that eventually give I_3^-. Revealing the photochemical reactivity of these simple chromophores is of significant importance in the application of these molecules as photocages or in the synthesis of complex polycycles.

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