Photochemistry of *N*-(pyrimidin-2-one-4-yl)pyridinium derivatives. The ring contraction of pyrimidinone into imidazolinone

Grażyna Wenska, Bohdan Skalski, Stefan Paszyc, and Zofia Gdaniec

Abstract: Photochemical reactions ($\lambda > 300$ nm) of *N*-(1-methylpyrimidin-2-one)- and *N*-(1,5-dimethylpyrimidin-2-one)pyridinium chlorides were studied in deoxygenated aqueous solution at various pH's. Only the former compound was found to be reactive under these conditions to give pyrimidine ring contraction photoproducts 1-methyl-4-imidazolin-2-one and 1-methyl-4-imidazolin-2-one-5-carboxyaldehyde, with pH-dependent chemical yields. The photochemical pyrimidine ring contraction reaction does not occur for other photochemically reactive pyrimidin-2-ones bearing 3-methylimidazolium-1,1,2,4-triazol-1-yl, or imidazol-1-yl as substituents at the C-4 position. The suggested mechanism of the reaction involves the addition of water to the pyrimidinone part of the *N*-(1-methylpyrimidin-2-one)pyridinium salt in the excited triplet state as the primary photochemical step. Addition of alcohol to the pyridinium ring was found to be the major reaction under irradiation of *N*-(1-methylpyrimidin-2-one-4-yl)pyridinium chloride in methanol.

Key words: photochemistry, *N*-(pyrimidin-2-one-4-yl)pyridinium compounds, pyrimidine ring contraction, 1-substituted-4-imidazolin-2-ones, 4-imidazolin-2-one-5-carboxyaldehydes.

Résumé : Opérant à divers pH, dans des solutions désoxygénées, on a étudié les réactions photochimiques ($\lambda >$ 300 nm) des chlorures de *N*-(1-méthylpyrimidin-2-one)- et de *N*-(1,5-diméthylpyrimidin-2-one)pyridinium. On a trouvé que, dans ces conditions, le premier composé est le seul à fournir des photoproduits résultant d'une contraction du noyau pyrimidine, soit la 1-méthyl-4-imidazolin-2-one et le 1-méthyl-4-imidazolin-2-one 5-carboxyaldéhyde avec des rendements qui varient avec le pH. La réaction photochimique de contraction du noyau pyrimidine ne se produit pas avec les autres pyrimidin-2-ones photochimiquement réactives portant des substituants 3-méthylimidazolium-1,1,2,4-triazol-1-yle ou imidazol-1-yle en position C-4. Le mécanisme suggéré pour la réaction implique que, dans l'étape photochimique primaire, il y a addition d'eau à la portion pyrimidinone du sel *N*-(1-méthylpyrimidin-2-one)pyridinium dans l'état excité triplet. Lors de l'irradiation du chlorure de *N*-(1-méthylpyrimidin-2-one-4-yl)pyridinium dans le méthanol, on observe que l'addition d'alcool est la réaction principale.

Mots clés : photochimie, composés *N*-(pyrimidin-2-one-4-yl)pyridinium, contraction du noyau pyrimidine, 4-imidazolin-2-ones substituées en position 1, 4-imidazolin-2-one-5-carboxaldéhydes.

[Traduit par la rédaction)

Introduction

Common purine and pyrimidine nucleosides such as guanosine, inosine, thymidine, and uridine can be easily and efficiently converted to the corresponding, fluorescent *N*-(purin-6-yl)- and *N*-(pyrimidin-2-one-4-yl)pyridinium chlorides (1). Some of these derivatives can be incorporated into synthetic oligodeoxynucleotides and used for further, postsynthetic modifications (2, 3). Both purinyl- and pyrimidynyl-pyridinium compounds exhibit significant absorption in the near-UV region ($\lambda > 300$ nm) where common nucleic acid bases are transparent (4) and thus provide the opportunity for their selective excitation in oligonucleotide chains. The photophysical and photochemical properties of *N*-(purin-6-yl)pyridinium salts have been studied extensively over the last several years (5, 6). Some of them were shown to be useful as fluorescent markers in nucleic acids (2, 7) or as efficient acceptors in photochemically induced electron transfer processes (6, 8). In contrast to the purine derivatives, the pyrimidinyl-pyridinium salts have received little attention so far. As a continuation of our interest in this group of modified nucleobases we reported previously on the photophysical properties of pyridinium salts derived from uridine and thymidine (9). It was shown that the lowest energy electronic transition in these compounds is

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This paper is dedicated to Professor David Shugar on the occasion of his 80th birthday.

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Fig. 1. Changes in the UV spectra of an aqueous solution of **1***a* during irradiation with near-UV light (λ > 300 nm).

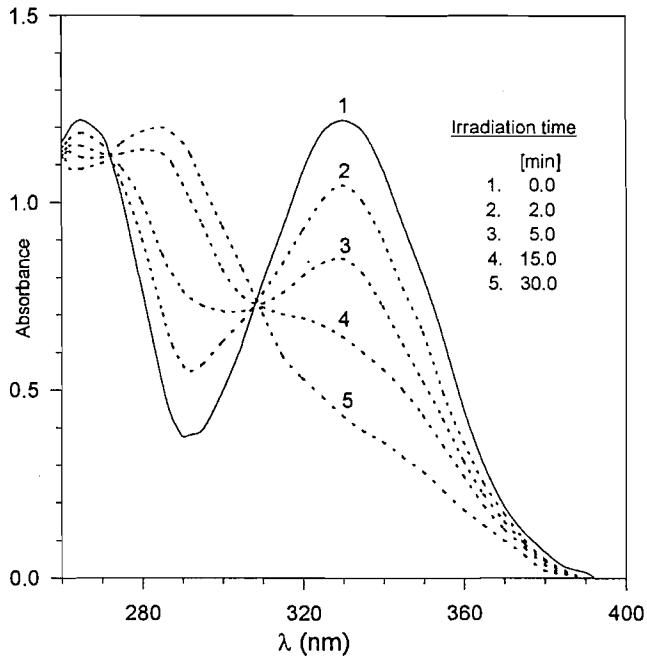
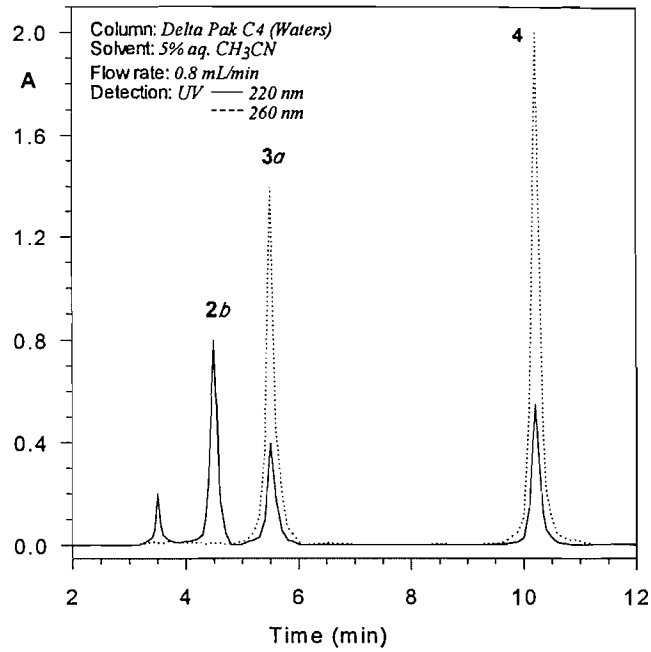
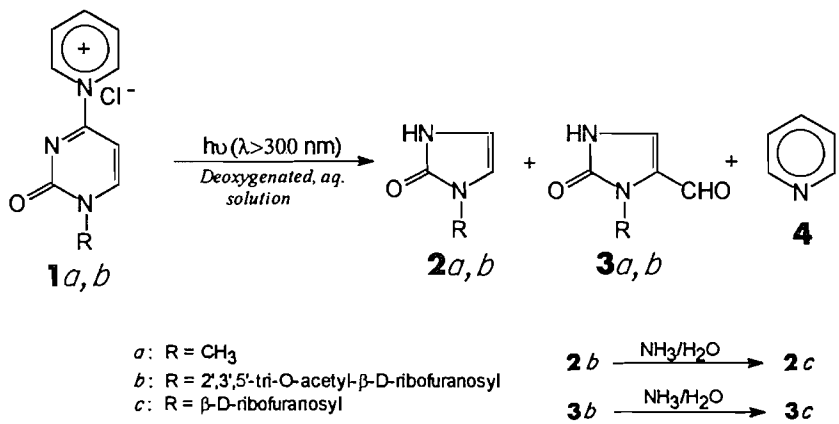


Fig. 2. HPLC of an irradiated solution of **1***a*.



Scheme 1.



associated with a significant charge shift from the pyrimidinyl to the pyridinium moiety, and that the short-lived excited singlet state is deactivated mainly via a nonradiative process.

In the present work we report on the photochemical reactivity of pyridinium salts **1***a*,*b* derived from 1-methyluracil and tri-*O*-acetyluridine as well as structurally related compounds bearing heterocyclic substituents other than pyridine at the C-4 position of the pyrimidine ring.

Results and discussion

Photochemistry of 1*a*,*b* in aqueous solutions

An aqueous solution of **1***a* was irradiated with near-UV light (λ > 300 nm) in the absence of oxygen. As seen in Fig. 1, irradiation results in a gradual disappearance of the absorption band with a maximum at λ = 330 nm, characteristic of *N*-(pyrimidin-2-one-4-yl)pyridinium cations (9), with concomitant formation of a new absorption band at λ = 280 nm. HPLC analysis of the irradiated solution (Fig. 2) revealed the presence of three main photoproducts: **2***a*, **3***a*, and **4**, besides the unreacted starting material. Photoproduct **4** was identified as pyridine whereas the structures of **2***a* and **3***a* were assigned as 1-methyl-4-imidazolin-2-one and 1-methyl-4-imidazolin-2-one-5-carboxyaldehyde, respectively (Scheme 1), based on their spectral and elemental analysis data (vide infra). The chemical yields of the imidazolinone photoproducts depend on the pH of the irradiated solutions (cf. Table 1). The aldehyde **3***a* is the major product when irradiation is performed in water (pH 6.5) and the ratio **3***a*/**2***a* increases significantly when the irradiation of **1***a* is performed in slightly basic solution (0.002 M sodium bicarbonate, pH ~8.2). Because of the chemical instability of pyrimidynyl-pyridinium salts at pH > 9 (due to base-induced pyridinium ring opening (1)), the irradiation of **1***a* was not carried out in more basic solution. Prolonged irradiation of **1***a* reduces the yield of **3***a* (Table 1). In a separate experiment it was found that **3***a* undergoes slow degradation under irradiation with Pyrex filtered light; however, **2***a* was not found among the photoproducts.

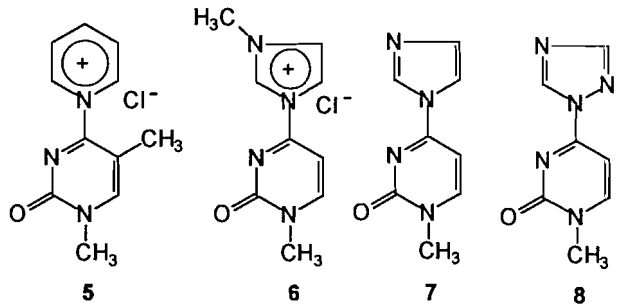
In the case of pyridinium salt **1***b* derived from 2',3',5'-tri-*O*-acetyluridine, which is less resistant towards bases than **1***a*,

Table 1. Chemical yields (%) of photoproducts **2–4**.[a]

Irradiated compound	Solvent (pH)	Conversion (%)	2	3	4
1*a*	0.002 M $HClO_4$ (2.6)	69	*a*: 42	*a*: 20	95
1*a*	Water (6.5)	80	*a*: 20	*a*: 43	100
1*a*	Phosphate buffer (6.5)	86	*a*: 25	*a*: 31	100
1*a*	0.002 M $NaHCO_3$ (8.2)	60	*a*: trace	*a*: 71	70
1*b*	Water (6.5)	61	*b*: 38	*b*: 34	100
1*b*	0.002 M $NaHCO_3$ (8.2)	90	*b*: trace	*b*: 59	65

[a]The yields are determined by HPLC and are given relative to the amount of **1** that reacted.

Scheme 2.



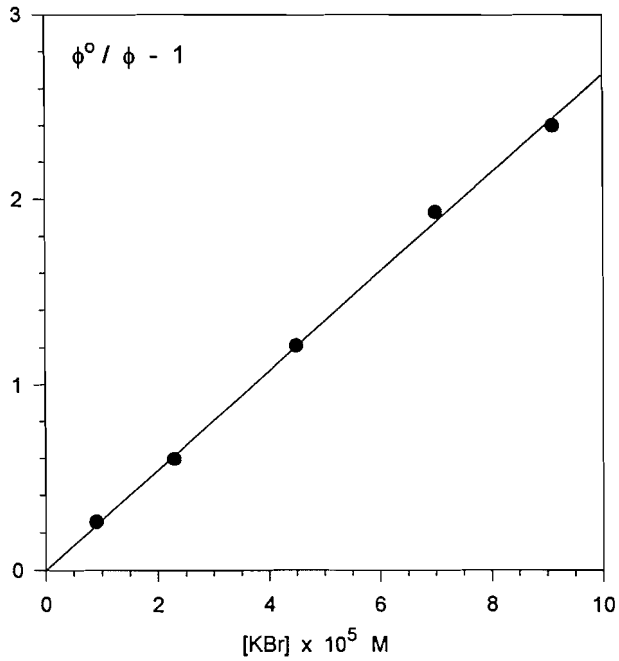
irradiation was performed in aqueous solution at pH 6.5. The expected photoproducts **2***b* and **3***b* were obtained in moderate yields (Scheme 1, Table 1). During the work-up of the irradiated solution of **1***b* in a preparative scale experiment, both photoproducts, **2***b* and **3***b*, were found to undergo partial deacetylation. Therefore they were fully deprotected and characterized as **2***c* and **3***c* (cf. Scheme 1 and Experimental).

The susceptibility to photochemical ring contraction has also been tested for the structurally related *N*-(1,5-dimethylpyrimidin-2-one-4-yl)pyridinium chloride, **5**, and compounds **6**, **7**, and **8** (Scheme 2) bearing 3-methylimidazolium-1, imidazol-1-yl, and 1,2,4-triazol-1-yl substituents at the C-4 position of the pyrimidine ring, respectively. Under the irradiation conditions used for the transformation of **1***a*, compound **5** appeared to be photochemically stable and the estimated quantum yield of its disappearance did not exceed 10^{-4}, whereas in the case of photochemically reactive **6**, **7**, and **8**, no appropriate ring contraction products (**2***a* and **3***a*) could be detected (HPLC) in photolyzed solutions.

The mechanism of the photochemical ring contraction of **1***a,b* is not yet completely clear, but we propose that the addition of a water molecule to the pyrimidinone part of the molecule in the excited triplet state is the primary photochemical event and is followed by a dark transformation of the resulting, unstable, intermediate into **2***a,b* and **3***a,b*. The following observations support the above suggestion.

(*i*) Pyridinium salts **1***a,b* are essentially stable ($\varphi < 10^{-4}$) during irradiation in dry acetonitrile under otherwise identical conditions.

Fig. 3. Stern–Volmer plot for quenching of the photochemical reaction of **1***a* by NaBr.



(*ii*) The photochemical reaction of **1***a* in water is quenched efficiently by bromide ions. Figure 3 shows the relevant Stern–Volmer plot. From the slope of this plot ($K_{sv} = k_q\tau$ = 26 600 $dm^3\ mol^{-1}$) an approximate value of 2.6×10^{-5} s for the lifetime of the reactive species is obtained, assuming $k_q \approx k_{diff} \approx 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$. This value is three orders of magnitude greater than the lifetime of the excited singlet state of **1***a* ($\tau = 0.8$ ns (9)), indicating the involvement of an excited triplet state in the photochemical reaction. The lifetimes of triplet excited pyridinium cations in the purine series have been reported to be in the microsecond region (8).

(*iii*) The quantum yield of disappearance of **1***a* remains constant ($\varphi = 0.05 \pm 0.01$) over the entire pH range studied (pH

Table 2. ^{1}H NMR[a] spectral assignments of photoproducts **3***a*, **3***c*, and **2***c*.

Proton	**3***a*	**3***c*	**2***c*
H-5	—	—	6.63 (d, $J_{4,5}$ = 3.1 Hz)
Formyl H	9.18 (s)	9.16 (s)	—
H-4	7.56 (s)	7.68 (s)	6.50 (d)
N-CH_3	3.42 (s)	—	—
Ribose H-1′	—	6.15 (d, $J_{1',2'}$ = 6.0 Hz)	5.56 (d, $J_{1',2'}$ = 6.0 Hz)
H-2′	—	4.30 (dd, $J_{2',3'}$ = 5.0 Hz)	4.21 (m)
H-3′	—	4.78 (t, $J_{3',4'}$ = 5.1 Hz)	4.37 (m)
H-4′	—	4.00 (m, $J_{4',5'}$ = 5.6 Hz)	4.05 (m)
H-5′, H—5′	—	3.83–3.67 (m)	3.69 (m)

[a]Spectra measured in D_2O.

Table 3. ^{13}C NMR[a] spectral assignments of photoproducts **3***a*, **3***c*, and **2***c*.

Carbon	**3***a*	**3***c*	**2***c*
C-2	155.6	155.0	155.0
C-4	129.3	132.1	111.1
C-5	125.6	124.3	109.9
Formyl C	181.5	180.4	—
CH_3	29.7	—	—
C-1′	—	88.2	86.4
C-2′	—	71.9	73.7
C-3′	—	70.7	71.1
C-4′	—	84.9	85.1
C-5′	—	62.5	62.2

[a]Spectra measured in D_2O.

2.0–8.5) whereas, as mentioned above (cf. Table 1), the relative amounts of **2***a* and **3***a* are pH dependent. This suggests that the formation of these two photoproducts occurs via pH-controlled transformations of a common, thermally unstable, intermediate formed by the initial photoaddition of water to **1***a*.

Examples of photochemically induced transformations of pyrimidines into imidazoles have been reported (10–13). Pyrimidine 1-oxides give low yields of 5-acetyl imidazoles (10) via oxazirines. 5-Diazouracil undergoes ring contraction to 4-imidazoline-2-one-carboxylate via a carbene-type intermediate upon irradiation in methanol saturated with HCl (11, 12). The synthetic procedures leading to imidazolin-2-one-4- and 5-carboxylic acids and carboxylates have been reported (12, 14); however, to our knowledge, the synthesis of aldehydes **3***a,b* has not been previously described.

Identification of photoproducts 2*a,c* and 3*a,c*

The structure of photoproduct **2***a* was established mainly on the basis of its ^{1}H NMR spectrum and an elemental analysis, and was confirmed by comparison of its spectral data and chromatographic (HPLC) mobility with those of an authentic sample synthesized according to a known procedure (15). The ^{1}H NMR spectrum of **2***a* measured in D_2O shows two doublets at 6.51 and 6.38 ppm (J = 3.1 Hz) corresponding to HC=CH protons of the imidazole ring. Two sets of signals having similar chemical shifts and coupling constants appear in the spectrum of **2***c*, which is the nucleoside analog of **2***a*. The remaining resonances in the ^{1}H NMR spectrum of **2***c* correspond to ribose protons. The ^{1}H and ^{13}C NMR signals of **2***c*, as well as those of other photoproducts, were assigned based on chemical shift arguments and by analysis of homo (^{1}H–^{1}H) and hetero (^{1}H–^{13}C) two-dimensional COSY spectra. These assignments are presented in Tables 2 and 3. Contrary to aldehydes **3***a,c* but in agreement with the proposed structures, imidazolin-2-ones **2***a,c* do not show UV absorptions at λ > 240 nm.

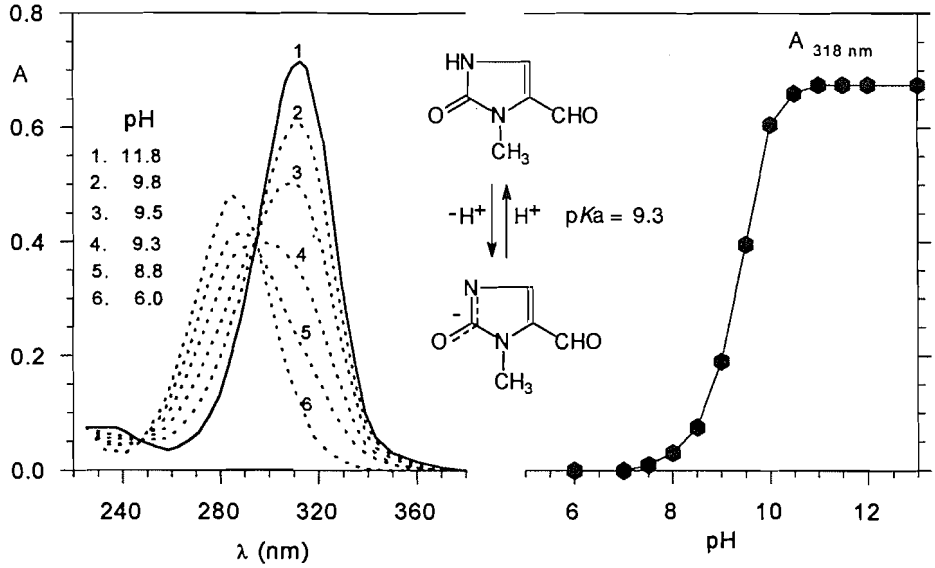
The proposed structures of photoproducts **3***a* and **3***c* are consistent with both their ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **3***a* consists of two singlets at 9.18 and 7.56 ppm corresponding to CHO and H-4 protons, respectively, and one singlet at 3.42 ppm, corresponding to NCH_3 protons (Scheme 2, Table 2). An unequivocal assignment of the site of attachment of the formyl group was deduced from the results of a long-range ^{1}H–^{13}C heteronuclear chemical shift correlation experiment. In the 2-D spectrum both quaternary carbon atoms (δ = 155.6 ppm and δ = 125.6 ppm) show cross peaks with N-CH_3 protons. This observation clearly points to the 5-carboxyaldehyde, **3***a*, and excludes the isomeric 1-methyl-4-imidazolin-2-one-4-carboxyaldehyde structure. As might be expected, the UV absorption spectra of **3***a* and **3***c* are pH dependent owing to their ground state prototropic equilibria (cf. Fig. 4). The relevant ground state ionization constants, pK, obtained from the spectrophotometric titration curves are equal to 9.3 and 8.8 for **3***a* and **3***c*, respectively. Upon prolonged storage in the presence of atmospheric oxygen in aqueous solution, **3***a* undergoes a slow oxidation to 1-methyl-4-imidazolin-2-one-5-carboxylic acid, which has been identified by comparison (HPLC and UV spectra) with an authentic sample prepared by condensation of *N*-methylurea with tartaric acid in fuming sulfuric acid (14). It has been shown that the UV spectra are of diagnostic value in distinguishing between the isomeric imidazolin-2-ones having carboxylic substituents located at the C-4 or C-5 positions of the imidazole ring (14).

It is interesting to note that a positional isomer of **3***c* having an aldehyde function at C-4 is an aglycone of the naturally occurring antibiotic nikkomycin X (16).

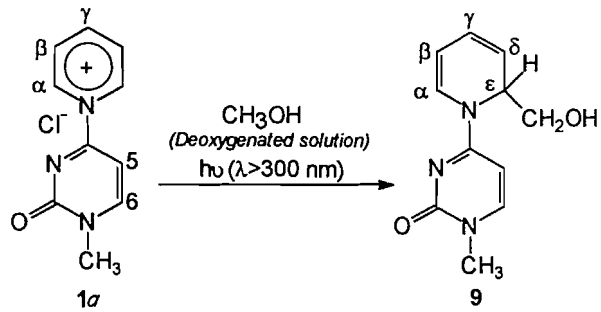
The photochemistry of 1*a* in methanol

The addition of a solvent molecule is the main reaction during the irradiation (λ > 300 nm) of **1***a* in deoxygenated methanol.

Fig. 4. The pH dependence of the UV absorption spectrum and the relevant spectrophotometric titration curve for the ground state prototropic equilibrium of **3***a*.



Scheme 3.



The addition occurs at the C-α position of the pyridinium residue leading to the dihydropyridine-type adduct **9** (Scheme 3). The quantum yield for conversion of substrate is 0.01. The mechanism of the reaction is most likely similar to that previously reported for the photochemical addition of electron donors such as alcohols, ethers, and amines to various *N*-alkyl-, *N*-alkenyl-, and *N*-heteroaromatic-pyridinium salts (17). The respective dihydropyridine-type photoadducts are formed by the initial electron transfer from the donor to the excited pyridinium salts, followed by coupling of the resulting radicals (17).

Identification of photoproduct 9

As is characteristic of the dihydropyridine structure, photoproduct **9** exhibits an intense absorption in the UV spectrum with a maximum at 335 nm (18). In the ^{1}H NMR spectrum of **9** recorded at room temperature, pyridine α and ε protons give rise to very broad signals at 6.51 and 5.67 ppm, respectively (Scheme 3, and Experimental). Lowering the temperature to 253 K results in sharpening of the signals and reveals their multiplet structure. This behaviour of the ^{1}H NMR spectrum is due to hindered rotation around the inter-ring bond caused by the presence of the *ortho* hydroxymethylene group in photoadduct **9**.

Experimental

General

^{1}H and ^{13}C NMR

Varian Unity 300 (300 MHz for ^{1}H); solvents: D_2O or $CDCl_3$ with dioxane or TMS as an internal reference, respectively; all chemical shifts converted to TMS scale (dioxane ^{1}H δ = 3.71 ppm; dioxane ^{13}C δ = 67.4 ppm).

UV

Perkin–Elmer Lambda-17 spectrophotometer.

Elemental analysis

Perkin–Elmer 2400 CHN analyzer.

Thin-layer chromatography (TLC)

Silica gel 60 F_{254} plates (Merck); solvent systems: A: $CHCl_3$–CH_3OH (5:1; v/v); B: $CHCl_3$–CH_3OH (10:1; v/v).

HPLC

Waters 600E; detection: Waters 991 photodiode-array UV–VIS detector; columns: Nova Pak C-18, 8 × 100 mm and Delta Pak C-4, 4.9 × 250 mm (analytical) and Nova Pak C-18, 25 × 100 mm (semipreparative); mobile phases: A: water; B: 50% acetonitrile, 50% water; C: 0.1 M ammonium acetate; D: 50% 0.1 M ammonium acetate, 50% acetonitrile.

Pyridinium salts **1***a, b* and **5**, and 4-substituted pyrimidin-2-ones **6–8** were synthesized as described previously (1*b, d*). 1-Methyl-4-imidazolin-2-one (15) and 1-methyl-4-imidazolin-2-one-5-carboxylic acid (14) were synthesized according to published procedures.

Analytical scale irradiations

The samples of aqueous solutions ($c = 1.6 \times 10^{-3}$ M) of **1***a, b* and **5–8** were placed in a 1 cm path length cell, deoxygenated, and irradiated on an optical bench with a high-pressure mercury lamp (HBO 200, Narva) through a Pyrex filter. Progress

of the reaction was monitored by UV spectroscopy and HPLC. The analytical HPLC was performed on a C-18 column eluted with 100%A (6 min) – 90%C/10%D (1 min) – 50%C/50%D (4 min) in the case of **1***a*, and a C-4 column eluted isocratically with a mixture of 70%C/30%D in the case of **1***b*. The results of chromatographic analyses obtained for the irradiations of **1***a, b* in aqueous solutions are collected in Table 1. The reaction quantum yields, φ, were measured for 313 nm excitation (Zeiss interference filter) using 2-hexanone as an actinometer (19).

General procedure for preparative irradiations

A concentrated aqueous solution (20 mL) containing 3.2 mmol of **1***a, b* was added to 2000 mL of the appropriate solvent (water, 0.002 M sodium bicarbonate, or methanol). Portions (60 mL) of the solutions ($c = 1.6 \times 10^{-3}$ M) were irradiated under an argon atmosphere with an immersion high-pressure mercury lamp (Original Hanau) through a Pyrex filter. The photolyzed solutions were collected and concentrated under reduced pressure. Irradiations were continued up to ca. 70% conversion of the substrate. Chemical yields of the photoproducts are given relative to the amount of substrate that reacted.

Isolation of photoproducts 2*a* and 3*a*

Photoproduct **2***a* was isolated from the irradiated aqueous solution of **1***a* by preparative HPLC (90%A/10%B). Fractions containing **2***a* were evaporated to give 37 mg of colourless solid (17% yield). UV (H_2O), λ_{max}: <220 nm. The ^{1}H NMR spectrum of the photoproduct is in agreement with that reported for 1-methyl-4-imidazolin-2-one (15).

Preparative scale synthesis of **3***a* was performed by irradiation of **1***a* in 0.002 M aqueous sodium bicarbonate. The desired photoproduct was separated from the irradiated mixture by preparative TLC using solvent system A and then subjected to further purification by means of preparative HPLC (90%A/10%B). Evaporation of the solvent gave 155 mg of colorless solid (55% yield). UV (H_2O), λ_{max} (nm) (ε (M^{-1}, cm^{-1})): 286.5 (13 300), (pH 1) 287 (13 600), (pH 12) 312.5 (20 300). ^{1}H and ^{13}C NMR data: Tables 2 and 3. Anal. calcd. for $C_5H_6N_2O_2$: C 47.62, N 22.21, H 4.79; found: C 47.01, N 22.09, H 4.71.

Isolation of photoproducts 2*c* and 3*c*

Leaving the irradiated solutions of **1***c* for several days at room temperature resulted in a partial deacetylation of photoproducts **2***b* and **3***b*, as indicated by HPLC and ^{1}H NMR analyses. Treatment of the mixture with diluted aqueous ammonia over 24 h at room temperature gave the fully deprotected nucleosides **2***c* and **3***c*, which were separated by preparative HPLC (0.005 M aqueous $HClO_4$). The appropriate fractions were collected, neutralized with Dowex-1 resin (HCO_3^-), and evaporated to dryness to give **2***c* (135 mg, 28% yield) and **3***c* (164 mg, 30% yield) as white powders.

2*c*: UV (H_2O), λ_{max}: <220 nm. ^{1}H and ^{13}C NMR data: Tables 2 and 3. Anal. calcd. for $C_8H_{12}N_2O_5$: C 44.45, H 5.59, N 12.96; found: C 44.37, H 5.54, N 12.87.

3*c*: UV (H_2O), λ_{max} (nm) (ε (M^{-1}, cm^{-1})): 283 (13 000), (pH 1) 283 (13 000), (pH 12) 311.5 (21 000). ^{1}H and ^{13}C NMR data: Tables 2 and 3. Anal. calcd. for $C_9H_{12}N_2O_6$: C 44.27, H 4.95, N 11.47; found: C 44.03, H 4.85, N 11.35.

Isolation of photoproduct 9

HPLC analysis (conditions as for irradiation of **1***a* in water) of the methanolic solution of **1***a* irradiated to 68% conversion revealed the presence of only one major photoproduct. Preparative TLC of the concentrated, irradiated solution using solvent system B followed by further purification on HPLC (75%A/25%B) gave an analytically pure sample (83 mg) of **9**, a white solid. Yield: 17% on the isolated product (50%–HPLC). UV (H_2O), λ_{max} (nm) (ε (M^{-1}, cm^{-1})): 283 (4060), 335 (13 900). ^{1}H NMR ($CDCl_3$, 293 K) δ ppm: 7.41 (d, J = 7.3 Hz, 1, H-6), 6.51 (br s, 1, H-α), 6.08 (dd, 1, H-γ), 6.01 (d, J = 7.3 Hz, H-5), 5.67 (br s, 1, H-ε), 5.61 (m, 1, H-δ), 5.51 (m, 1, H-β), 3.71–3.66 (m, 2, CH_2), 3.48 (br s, 1, OH), 3.48 (s, 3, N-CH_3). ^{1}H NMR ($CDCl_3$, 253 K) δ ppm: 7.47 (d, J = 7.3 Hz, 1, H-6), 6.49 (d, J = 7.47 Hz, 1, H-α), 6.10 (dd, 1, H-γ), 6.03 (d, J = 7.3 Hz, H-5), 5.73 (m, 1, H-ε), 5.62 (m, 1, H-δ), 5.56 (m, 1, H-β), 3.84 (s br, 1, OH), 3.71 (m, 2, CH_2) , 3.50 (s, 3, N-CH_3). ^{13}C NMR ($CDCl_3$, 293 K) δ ppm: 163.23 (C-4), 156.15 (C-2), 146.92 (C-6), 123.98 (C-α), 123.06 (C-γ), 121.12 (C-δ), 109.00 (C-β), 92.19 (C-5), 63.64 (CH_2), 54.16 (C-ε), 37.93 (N-CH_3). Anal. calcd. for $C_{11}H_{13}N_3O_2$: C 60.26, H 5.98, N 19.16; found: C 60.08, H 5.90, N 19.07.

Acknowledgements

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