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Photochemistry of *N*-alkylsuccinimide in methanol and ethanol: An experimental and calculated investigation

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Abstract

The photochemistry of *N*-R-succinimide (R = H, Me, Et) in methanol and ethanol was investigated. Two kinds of photo-reduction products, i.e. 5-alkoxy-*N*-R-2-pyrrolidinone (**2**) and 5-(1-hydroxyalkyl)-5-alkoxy-*N*-R-2-pyrrolidinone (**3**) (alkoxy: MeO and EtO, R: Me and Et) have been identified. The formation of **2** relates to a continuous two-step H-abstraction, which is rare in the photolysis of common ketones. However, in the case of succinimide, a new pinacolic product, 5,5′-dihydroxy-5,5′-bis(2-pyrrolidinone) (**4**), was found for the first time. DFT calculations have been carried out in order to study the aggregation behaviors of succinimide during the photochemical process. The strong tendency to form succinimide dimer (**1c**–**1c**) via reciprocal intermolecular hydrogen-bonds is in good explanation for the generation of product **4**.

Keywords: Photolysis; Succinimide; DFT; Dimer; Monomer

1. Introduction

Photochemistry of *N*-alkyl cyclic imides has ever received considerable attention [1–5]. The inter- and intra-molecular photoreactions such as reduction [6], addition [7–9], Norrish type I [10] and type II [11,12] reactions of *N*-alkyl cyclic imides have been reported. Although the photochemical properties of phthalimides were extensively investigated [13–17], the photolysis of succinimides in alcohol has been rather ignored. In our recent investigation of succinimides, photochemical properties varied from that of phthalimides [5] were found.

In this paper, the photolysis of *N*-R-succinimide (**1a**: R = Me, **1b**: R = Et, **1c**: R = H) in methanol and ethanol were investigated and the reaction mechanisms were discussed.

2. Results and discussion

The UV spectra presented in Fig. 1 show the maximum absorptions of the succinimides around 210 nm, which can be attributed to the $\pi \rightarrow \pi^*$ transition of the carbonyl group. Fig. 1 also shows shoulder peaks near 245 nm (249 nm, $\varepsilon = 86$ for **1a**; 244 nm, $\varepsilon = 91$ for **1c**), assigned to the $n \rightarrow \pi^*$ transition of cyclic imides [18]. Therefore, 254 nm UV light emitted from the low-pressure mercury lamp is effective for the $n \rightarrow \pi^*$ transition of these succinimides (Fig. 2).

2.1. Photolysis of *N*-alkylsuccinimides *1a*, *1b* in methanol and ethanol

Upon the exposure of 254 nm UV light, **1a** or **1b** in methanol or ethanol produces two kinds of 2-pyrrolidinone derivatives (Scheme 1), 5-alkoxy-*N*-R-2-pyrrolidinone (**2**) and 5-(1-hydroxyalkyl)-5-alkoxy-*N*-R-2-pyrrolidinone (**3**). The molecular structures of two representative products 5-(1-hydroxymethyl)-5-methoxy-*N*-methyl-2-pyrrolidinone (**3a**) and 5-(1-hydroxyethyl)-5-ethoxy-*N*-methyl-2-pyrrolidinone (**3a′**) have been unequivocally determined by X-ray diffraction analysis. Comparative data on photoproducts **2a**–**3b′** are summarized in Table 1.

The photo-induced reaction between *N*-alkylsuccinimide and the solvents (methanol and ethanol) is most reasonably explained in the following mechanism shown in Scheme 2.

Upon the excitation, the excited singlet state of **1** transfers to its excited triplet state via intersystem crossing as most of the ketones do. The formed excited triplet state of **1** undergoes α-H abstraction from the solvent to form a short-lived radical pair

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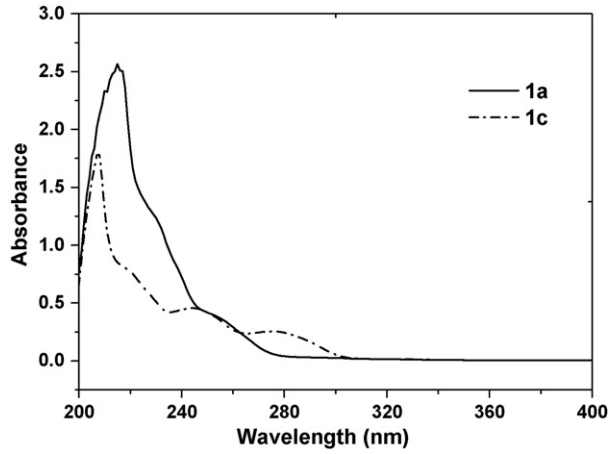
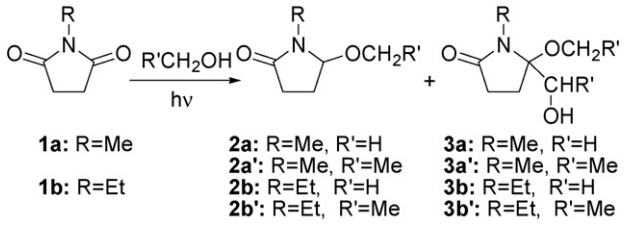


Fig. 1. Absorption spectra of 5×10^{-3} M of **1a** and **1c** in methanol.



Scheme 1.

Table 1
Chemical yields of photoproducts of **1a** and **1b** in alcohol

Product	mp (°C)	Yield (%)
2a (R: Me, R′: H)	Liquid	26
3a (R: Me, R′: H)	79–81	57
2a′ (R: Me, R′: Me)	Liquid	21
3a′ (R: Me, R′: Me)	122–124	55
2b (R: Et, R′: H)	Liquid	24
3b (R: Et, R′: H)	Liquid	60
2b′ (R: Et, R′: Me)	Liquid	20
3b′ (R: Et, R′: Me)	84–86	58

consisting of **5** and a hydroxylalkyl radial, which undergo two pathways: (1) the hydroxylalkyl radical escapes out of the solvent cage and the radical **5** abstracts another α-hydrogen atom from the surrounding solvent to produce intermediate **6**. The resulted **6** is an unstable α-hydroxyamine which condenses with the solvent alcohol easily to generate the final product **2**; (2) a radical coupling process between **5** and the hydroxyalkyl radical generates another unstable intermediate **7**, which is followed by a similar condensation as **6** to give **3**. Obviously, the two pathways are inter-competing processes. The former performs an out-of-cage route, which results in the H-abstraction product. Whereas the latter occurs in solvent cage which results in the radical coupling product. It is obvious that the radical coupling process is energy preferential, which can easy explain the photolysis results, i.e. the yields of compounds **3** (55–60%) are two times higher than those of compounds **2** (20–26%). The UV changes of the photolysis of **1a** were shown in Fig. 3. With the increase of irradiation time, the absorption shoulders of **1a** at 244 nm gradually disappears, which means that the $n \rightarrow \pi^*$ transition of **1** is sensitive to the 254 nm UV light, and the disappearance of the shoulder peak implies that **1a** was gradually transformed into transparent products. In the later measurement, photoproducts **2** and **3** are turned out of being transparent above 235 nm, which agrees well with the UV tracing result.

2.2. Photolysis of succinimides *1c* in methanol and ethanol

In the photolysis of succinimide **1c**, an unexpected snow-like product **4** was formed and precipitated in situ. The molecular structure of **4** has also been unequivocally characterized by X-ray crystallography (Fig. 4). The photochemical reaction of **1c** in methanol or ethanol was described in Scheme 3. The comparative data on photoproducts **2c**–**3c′** are summarized in Table 2.

Besides a similar $n \rightarrow \pi^*$ band (244 nm, $\varepsilon = 91$) to that of **1a**, another absorption band was observed at 276 nm ($\varepsilon = 51$) in the case of **1c** (Fig. 1). Unlike the $n \rightarrow \pi^*$ band, upon irradiation, this new band shows a rapid decay at the first stage (before 1.5 h) then a slow decay (Fig. 3). In the photolysis of **1a** and **1b**, similar bicyclic products to **4** were not detected. Furthermore, the yield of **4** enhances with the increasing concentration of substrate **1c**. All these phenomena imply that during the photolysis, **1c** not only exists at different forms, but also undergoes a different mechanism.

2.3. Theoretical calculation of *1c*

In order to explain the above phenomena and investigate the intermolecular interactions of the succinimide, density

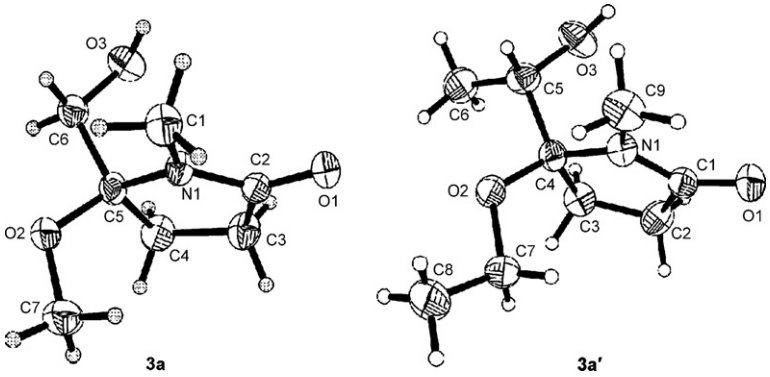
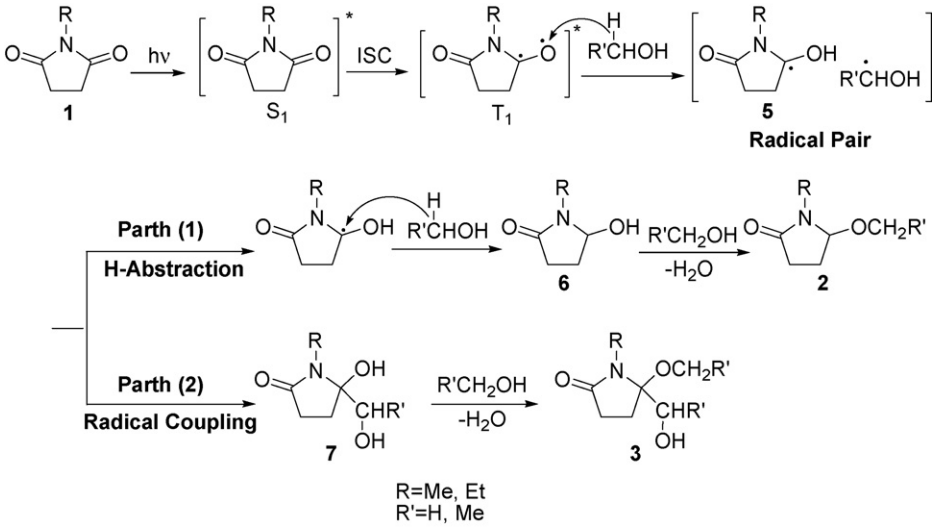


Fig. 2. Perspective view of the crystallographic structures of compounds **3a** and **3a′** [19].



Scheme 2.

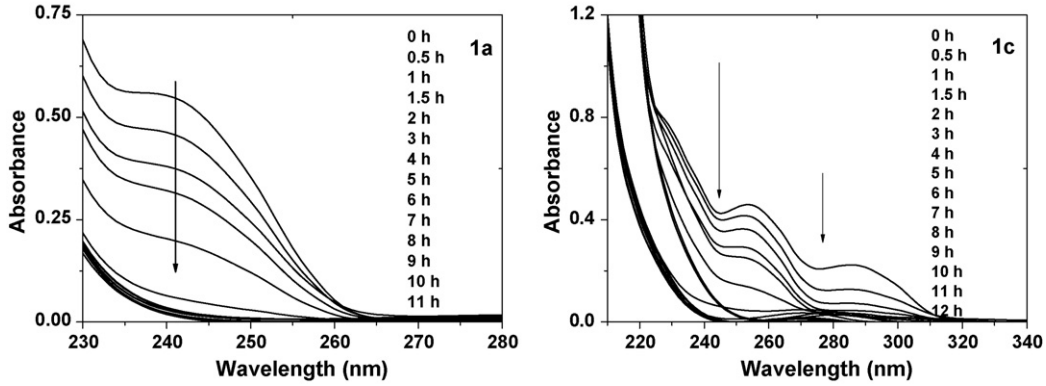


Fig. 3. UV traces of **1a** and **1c** photolyzed in methanol. Both photolyzed in 0.1 M solution, UV detected after being diluted to 5×10^{-3} M.

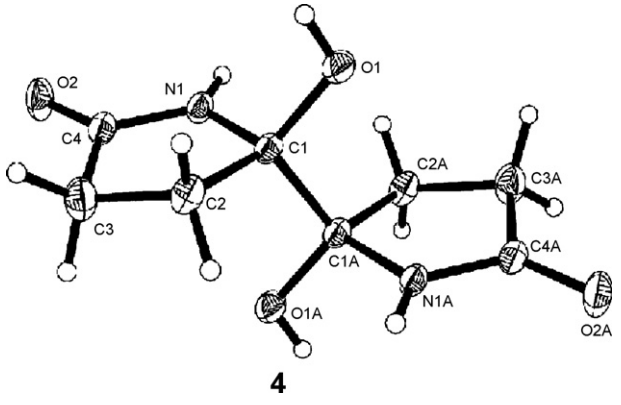
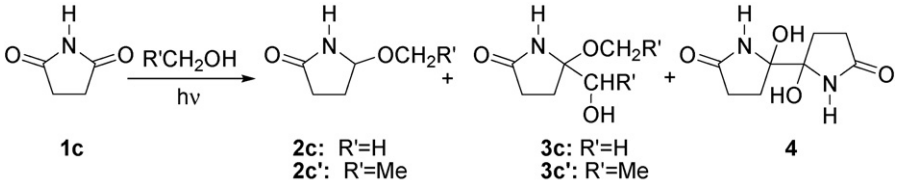


Fig. 4. Perspective view of the crystallographic structures of compounds **4**.

functional theory (DFT) calculations were carried out within Gaussian 03 package [20]. Geometry optimizations were calculated using 6-31+G(d,p) basis set at the B3LYP level of theory. Further energy (*E*) calculations were performed on the 6-31+G(d,p)-optimized structures utilizing higher level basis sets as shown in Table 3. Then, the zero point energy (ZPE) was calculated at B3LYP/6-31+G(d,p) level for energy corrections.

The calculated results show that succinimide adopts a planar conformation. It has a very strong tendency to form dimers (**1c**–**1c**) through reciprocal intermolecular hydrogen bonds between N–H and O=C groups, which is consistent with the reported crystal structure of **1c**. [21] In the hydrogen-bonded dimer, the length of C–N bond is 1.374 Å, which is between the corresponding values of the ketone (1.392 Å) and the enol



Scheme 3.

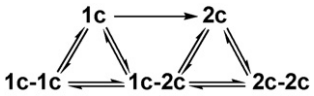
Table 2
Chemical yields of photoproducts of **1c** in alcohol

Product	mp (°C)	Yield (%)
2c (R′: H)	62–64	40
3c[a] (R′: H)	NA	Minor
2c′ (R′: Me)	50–51	38
3c′[a] (R′: Me)	NA	Minor
4	230 (decomp.)	20.8[b], 11.6[c]

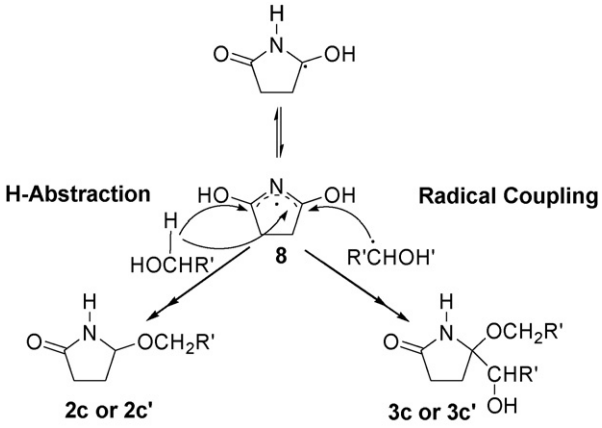
[a] Only identified by GC–MS, not obtained from column chromatography.
[b] Photolysis in methanol.
[c] Photolysis in ethanol.

(1.289 Å) forms. This change in bond length indicates that **1c** is slightly enolized in the dimer form, which increases the intermolecular interaction via the doublet N–H···O hydrogen bonds. Therefore, the reciprocal hydrogen bonds stabilize the dimer form, narrowing the $n \rightarrow \pi^*$ energy gap between the excited triplet state and the ground state. As a result, red shift took place in the dimer form. Owing to the equilibrium of different forms of succinimide, two bands at 244 and 276 nm, respectively, assigned to the monomer and the dimer are observed in the UV spectrum of **1c** (see Fig. 1).

Based on the calculated binding energies (BE), the hydrogen-bonded **1c–2c** complex is more stable than the **1c–1c** dimer [22]. The relatively less stability of **1c–1c** dimer may arise from the secondary electrostatic interactions between the non-hydrogen-bonded (spectator) oxygen in one molecule and the hydrogen-bonded oxygen in the other. The spectator oxygen of **1c** is expected to destabilize the hydrogen-bonded array as shown in Fig. 5. The transformations among **1c**, **2c** and their corresponding hydrogen-bonded complexes are presented in Scheme 4.



Scheme 4.



Scheme 5.

Table 3
Calculated energies (E + ZEP) and binding energies (BE)

Basis sets	E + ZEP (kJ mol^{-1})			BE (kJ mol^{-1})		
	1c–1c	**1c–2c**	**2c–2c**	**1c–1c**	**1c–2c**	**2c–2c**
6-31+G(d,p)	−1893564.2	−1999747.2	−2105928.2	−43.0	−46.3	−48.9
6-311+G(d,p)	−1894011.9	−2000208.8	−2106405.0	−42.6	−45.7	−48.1
6-311++G(d,p)	−1894012.6	−2000209.6	−2106406.0	−42.8	−45.7	−48.0

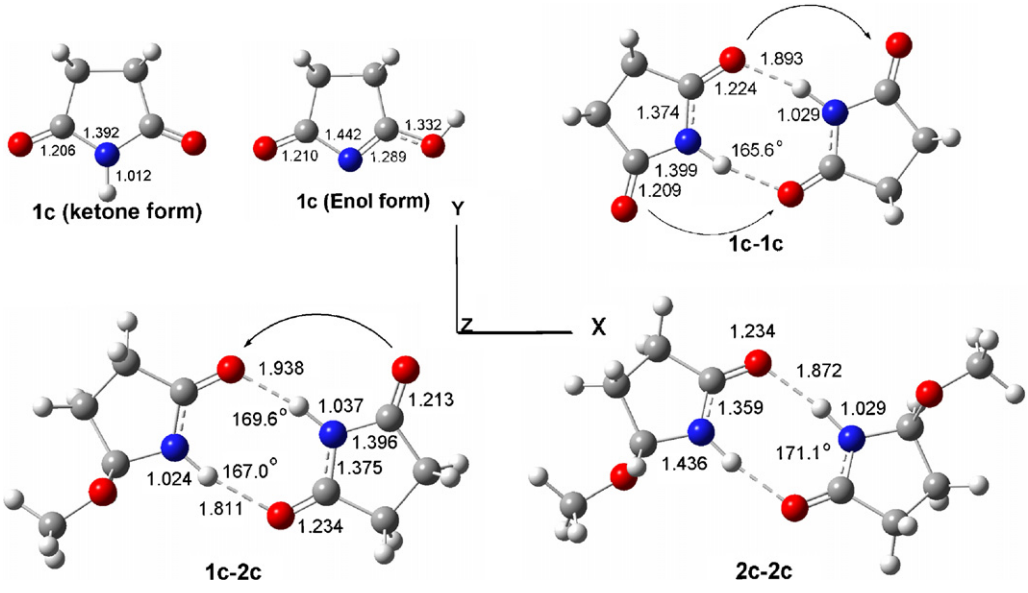
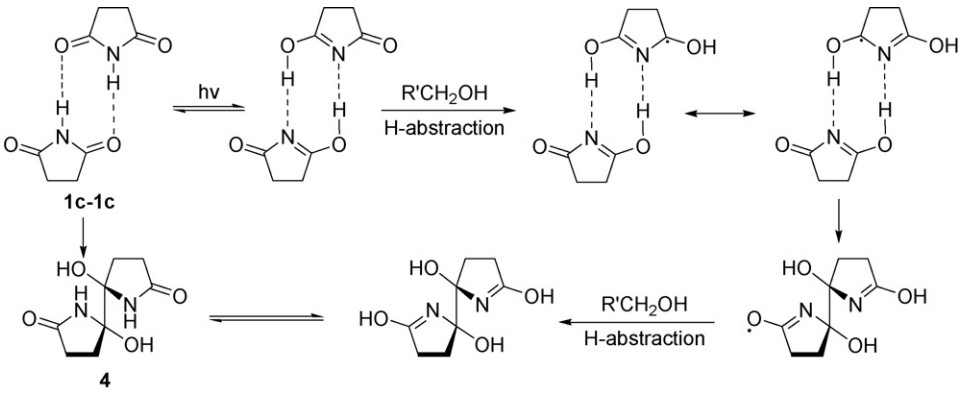


Fig. 5. The 6-31+G(d,p)-optimized structures (bond length in Å).



Scheme 6.

Before irradiation, succinimides exist at two equilibrium forms: monomer and dimer. In the first stage of photolysis, **1c**–**1c** dimers sharply decrease with irradiation due to the high concentration of substrate. Meanwhile, the **1c**–**2c** complexes are slowly formed with the generation of **2c**. But the decrease of **1c**–**1c** makes the main contribution to the absorption decay at 276 nm. Subsequently, the **1c**–**2c** complexes gradually make more contribution with the increased concentration of **2c** and the intrinsic relative stronger association, as a result of which the UV shows a slow decay at this band. Finally, along with the conversion of **1c**, the absolute amount of hydrogen-bonded complexes containing **1c** (**1c**–**1c** and **1c**–**2c**) gradually decreases and disappears. The transparent products (at 244 and 276 nm) **2c** and **2c**–**2c** dimers predominate in the reaction mixture. The overall trend of hydrogen-bonded interactions is in excellent agreement with the UV changes.

Based on the computation results and the above analysis, the photolysis of **1c** may start from two different forms of succinimide: solvated monomer and dimer. The generation of product **2c** (or **2c**′) and **3c** (or **3c**′) may undergo a route similar to **1a** and **1b**. However, the yield of **3** is markedly decreased. One reason might be the competition of the formation of pinacolic product **4**. In addition, as shown in Scheme 5, the isomerization from ketone to enol form stabilizes radical **8** due to the efficient electron delocalization to its resonance system. The lifetime of radical **8** is markedly prolonged, which offers it enough time to escape from the solvent cage. Therefore, the radical coupling reaction to form **3** is greatly inhibited, but the out-of-cage H-abstraction becomes dominant in the competition between the two pathways.

The formation of **4** in alcohol may be related to the succinimide dimer. It is reasonable to deduce on the theoretical calculation that the hydrogen-bond-stabilized dimer of **1c**–**1c** results in the formation of in-cage coupling product **4**. The further investigation is in progress (Scheme 6).

3. Conclusion

The photochemical behavior of succinimides in alcohol was investigated. Three kinds of photoproducts were obtained, which provides a new method for preparation of pyrrolidinone derivatives. Theoretical calculations at DFT level were carried out in exploring conformation and intermolecular interactions of succinimide during the photoreaction, which aids in proposing and rationalizing two pathways that start, respectively, from the dimer and the monomer. In addition, it was found that the photoreaction is catalyzed by the acid.

4. Experimental and computational methods

4.1. Materials

N-Methylsuccinimide (**1a**, mp 69–71 °C, lit 71 °C [23]) and *N*-ethylsuccinimide (**1b**, mp 45–46 °C, lit 46 °C [24]) were prepared by the reaction of corresponding alkylamine and succinic anhydride according to the literature procedure [25]. Succinimide **1c** was commercially available and recrystallized from ethanol. All solvents for the photoreactions and analyses are purified by standard methods.

4.2. Instrumentation and experimental methods

Melting points were taken on a Yanagimoto MP-500 apparatus (uncorrected). FT-IR spectra were taken on a BIO-RAD FTS 3000 Infrared Spectrometer and UV spectra on a HP 8453 UV–vis spectrophotometer in CH_3OH. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz) and elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. The GC and MS spectra were performed by a Trace DSQ GC–MS spectrometer. pH were monitored in the corresponding methanol solution with adscititious water (V_{MeOH}:V_{Water} = 4:1) by a PHS-3C detector. Photoproducts were separated by column chromatography.

Preparative irradiations were conducted in a 110 ml quartz tube reactor by using a 20 W low-pressure mercury lamp. All of the irradiation results were traced by GC–MS.

4.3. Preparative photolysis of succinimides (*1a*–*1c*)

4.3.1. General procedure for preparative photolysis of *N*-alkylsuccinimides (*1a* and *1b*) in alcohol

To 0.01 mol of *N*-alkylsuccinimide in a quartz tube was added 100 ml of alcohol. The sample, de-aerated by nitrogen purging for 0.5 h, was irradiated under a low-pressure mercury lamp for

proper time. GC–MS detection showed the photolysis was carried to 100% conversion. After removal of the solvent under reduced pressure, photoproducts **2** and **3** were isolated by column chromatography with petroleum ether and ethyl acetate (gradient elution) as an eluent.

4.3.1.1. 5-Methoxy-1-methylpyrrolidin-2-one (2a). **1a** irradiated in methanol for 20 h, yield 26%; IR (KBr) ν (cm^{-1}) 3420 (m), 2939 (w), 1683 (s), 1456 (w), 1403 (w), 1290 (w), 1080 (m), 890 (w); MS: *m/z* (relative intensity): 129 (M^+, 1.9), 128 (2.7), 100 (2.4), 98 (100), 74 (7.0), 72 (2.9), 71 (5.0), 70 (7.6). 68 (10.2), 55 (7.2), 42 (29.2); ^{1}H NMR ($CDCl_3$) δ: 4.82 (dd, 1H, J_1 = 1.6 Hz, J_2 = 6.4 Hz), 3.25 (s, 3H), 2.83 (s, 3H), 2.46 (m, 1H), 2.27 (m, 1H), 2.13 (m, 1H), 1.96 (m, 1H).

4.3.1.2. 5-Methoxy-5-hydroxymethyl-1-methylpyrrolidin-2-one (3a). **1a** irradiated in methanol for 20 h, yield 57%; colorless crystal, mp 79–81 °C; IR (KBr) ν (cm^{-1}) 3309 (m), 2962 (w), 1675 (s), 1459 (w), 1191 (w), 1088 (m), 929 (w), 666 (w); MS: *m/z* (relative intensity): 159 (M^+, 0.1), 128 (100), 109 (7.7), 100 (34.6), 98 (40.2), 70 (13.7), 68 (47.8), 56 (14.0), 55 (19.7), 42 (32.9); ^{1}H NMR (CD_3OD) δ: 3.61 (d, 1H, J = 11.6 Hz), 3.57 (s, 1H), 3.42 (d, 1H, J = 11.6 Hz), 3.08 (s, 3H), 2.69 (s, 3H), 2.49–2.33 (m, 2H), 2.24 (m, 1H), 2.07 (m, 1H); ^{13}C NMR (CD_3OD) δ: 176.9, 96.1, 63.0, 47.7, 29.4, 23.3, 22.8; Anal. Calcd. for $C_7H_{13}NO_3$: C, 52.83; H, 8.18; N, 8.81; found: C, 53.43; H, 7.85; N, 8.87.

4.3.1.3. 5-Ethoxy-1-methylpyrrolidin-2-one (2a′). **1a** irradiated in ethanol for 23 h, yield 21%; IR (KBr) ν (cm^{-1}) 3410 (m), 3129 (m), 2992 (m), 1689 (s), 1429 (m), 1101 (m); MS: *m/z* (relative intensity): 143 (M^+, 4.2), 114 (5.0), 98 (100), 70 (4.3), 68 (4.9), 56 (1.1), 55 (1.8), 42 (10.6); ^{1}H NMR (CD_3CN) δ: 4.85 (dd, 1H, J_1 = 1.6 Hz, J_2 = 6.4 Hz), 3.43 (m, 2H, J = 7.2 Hz), 2.92 (s, 3H), 1.94–2.51 (m, 4H), 1.11 (t, 3H, J = 7.2 Hz).

4.3.1.4. 5-Ethoxy-5-(1-hydroxyethyl)-1-methylpyrrolidin-2-one (3a′). **1a** irradiated in ethanol for 23 h, yield 55%; colorless crystal, mp 122–124 °C; IR (KBr) ν (cm^{-1}) 3363 (m), 2978 (m), 1677 (s), 1448 (m), 1394 (m), 1261 (m), 1170 (w), 1076 (m), 670 (w); MS: *m/z* (relative intensity): 187 (M^+, 0.2), 142 (83.1), 123 (7.2), 114 (100), 98 (17.0), 86 (16.7), 68 (10.9), 58 (12.3), 45 (9.3), 42 (9.9); ^{1}H NMR (CD_3CN) δ: 3.87 (m, 1H), 3.36 (m, 1H), 3.05 (m, 1H), 2.88 (s, 1H), 2.60 (s, 3H), 2.37–2.11 (m, 3H), 1.90 (m, 1H), 1.15 (t, 3H, J = 7.2 Hz), 0.97 (d, 3H, J = 6.4 Hz); ^{13}C NMR (CD_3CN) δ: 175.7, 98.0, 71.3, 57.5, 30.1, 25.4, 21.8, 16.8, 15.6; Anal. Calcd. for $C_9H_{17}NO_3$: C, 57.75; H, 9.09; N, 7.49; found: C, 57.60; H, 9.12; N, 7.21.

4.3.1.5. 5-Methoxy-1-ethylpyrrolidin-2-one (2b). **1b** irradiated in methanol for 17 h, yield 24%; IR (KBr) ν (cm^{-1}) 3481 (m), 2978 (m), 2938 (m), 1696 (s), 1458 (m), 1423 (m), 1281 (m), 1253 (w), 1077 (m), 889 (w); MS: *m/z* (relative intensity): 143 (M^+, 8.4), 142 (4.3), 128 (1.2), 114 (2.8), 112 (100), 96 (9.8), 88 (7.5), 84 (34.8), 72 (11.6), 71 (11.6), 56 (11.2), 55 (6.4), 41 (26.1); ^{1}H NMR ($CDCl_3$) δ: 4.92 (dd, 1H, J_1 = 1.2 Hz, J_2 = 6.4 Hz), 3.49 (m, 1H), 3.22 (s, 3H), 3.12 (m, 1H), 2.45 (m, 1H), 2.26 (m, 1H), 2.08 (m, 1H), 1.94 (m, 1H), 1.10 (t, 3H, J = 8.4 Hz).

4.3.1.6. 5-Methoxy-5-hydroxymethyl-1-ethylpyrrolidin-2-one (3b). **1b** irradiated in methanol for 17 h, yield 60%; IR (KBr) ν (cm^{-1}) 3391 (m), 2941 (w), 1673 (s), 1456 (w), 1417 (m), 1356 (w), 1185 (w), 1090 (m), 927 (w), 667 (w); MS: *m/z* (relative intensity): 173 (M^+, 0.1), 142 (100), 123 (5.2), 114 (21.0), 112 (20.9), 98 (4.7), 86 (8.4), 84 (12.7), 82 (28.8), 55 (8.8), 41 (10.1); ^{1}H NMR (CD_3CN) δ: 3.54 (q, 1H, J = 6.4 Hz), 3.43 (q, 1H, J = 6.4 Hz), 3.13 (m, 2H), 3.12 (s, 1H), 3.03 (s, 3H), 2.38–2.12 (m, 3H), 1.95 (m, 1H), 1.09 (t, 3H, J = 6.4 Hz); ^{13}C NMR (CD_3CN) δ: 175.3, 95.9, 64.2, 48.2, 33.4, 29.2, 23.5, 13.1; Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.49; H, 8.67; N, 8.09; found: C, 55.60; H, 8.90; N, 7.78.

4.3.1.7. 5-Ethoxy-1-ethylpyrrolidin-2-one (2b′). **1b** irradiated in ethanol for 17 h, yield 20%; IR (KBr) ν (cm^{-1}) 3456 (m), 3019 (m), 2988 (m), 1701 (s), 1456 (m), 1101 (m); MS: *m/z* (relative intensity): 157 (M^+, 0.6), 128 (3.9), 112 (100), 98 (6.2), 85 (5.53), 84 (26.4), 72 (5.8), 68 (9.7), 57 (10.1), 41 (14.6); ^{1}H NMR (CD_3CN) δ: 4.91 (m, 1H), 3.53 (m, 2H), 3.24 (m, 2H), 1.92–2.58 (m, 4H), 1.09–1.26 (m, 6H).

4.3.1.8. 5-Ethoxy-5-(1-hydroxyethyl)-1-ethylpyrrolidin-2-one (3b′). **1b** irradiated in ethanol for 17 h, yield 58%; colorless crystal, mp 84–86 °C; IR (KBr) ν (cm^{-1}) 3296 (m), 2978 (m), 1675 (s), 1458 (m), 1417 (m), 1289 (w), 1173 (w), 1125 (m), 1082 (m), 1037 (m), 692 (w); MS: *m/z* (relative intensity): 201 (M^+, 1.2), 156 (87.0), 128 (100), 112 (9.9), 100 (23.0), 84 (6.8), 72 (7.9), 56 (5.3), 55 (9.0); ^{1}H NMR (CD_3CN) δ: 3.81 (m, 1H), 3.34 (m, 1H), 3.14 (q, 2H, J = 7.2 Hz), 3.07 (m, 1H), 2.96 (s, 1H), 2.33–2.12 (m, 3H), 1.83 (m, 1H), 1.14–1.09 (m, 9H); ^{13}C NMR (CD_3CN) δ: 176.3, 99.0, 68.8, 57.5, 34.4, 30.2, 21.9, 17.6, 15.5, 14.0; Anal. Calcd. for $C_{10}H_{19}NO_3$: C, 59.70; H, 9.45; N, 6.97; found: C, 59.96; H, 9.38; N, 7.23.

4.3.2. General procedure for reparative photolysis of succinimide (1c) in alcohol

To 0.01 mol of succinimide (**1c**) in a quartz tube was added 100 ml of alcohol. The sample, de-aerated by nitrogen purging for 0.5 h, was irradiated under a low-pressure mercury lamp for proper time. A white solid was precipitated from the solution. After staying for a day and filtration, a white solid **4** was obtained. GC–MS study on the residual solution showed that the photolysis was carried to 100% conversion. After removal of the solvent under reduced pressure, photoproduct **2** was isolated by column chromatography with petroleum ether and ethyl acetate (gradient elution) as an eluent. Unfortunately, compound **3** was not obtained due to the minor amount and was only identified by GC–MS.

4.3.2.1. 5-Methoxypyrrolidin-2-one (2c). **1c** irradiated in methanol for 27 h, yield 40%; colorless crystal, mp 62–64 °C, lit value 60–62 °C [26]; IR (KBr) ν (cm^{-1}) 3186 (s), 3111 (m), 2934 (m), 1696 (s), 1458 (m), 1284 (s), 1253 (s), 1101 (s), 1059 (s), 806 (m), 763 (m), 657 (m); MS: *m/z* (relative intensity): 115

(M^+, 3.4), 86 (1.7), 84 (100), 72 (2.4), 71 (5.6), 60 (29.2), 56 (12.2), 55 (7.6); ^{1}H NMR ($CDCl_3$) δ: 6.85 (s, 1H), 4.87 (d, 1H, J = 5.6 Hz), 3.28 (s, 3H), 2.48 (m, 1H), 2.32–2.17 (m, 2H), 2.07 (t, 1H, J = 10.8 Hz); ^{13}C NMR ($CDCl_3$) δ: 179.5, 87.1, 54.4, 28.4, 28.1.

4.3.2.2. 5-Methoxy-5-hydroxymethylpyrrolidin-2-one (3c). **1c** irradiated in methanol for 27 h, MS: *m/z* (relative intensity): 145 (M^+, 2.6), 114 (100), 84 (51.7), 72 (12.4), 55 (5.6), 45 (10.2).

4.3.2.3. 2,2′-Dihydroxy-2,2′-bipyrrolidine-5,5′,-dione (4). **1c** irradiated in methanol for 27 h, yield 20.8%; white solid, mp 230 °C (decomp.); IR (KBr) ν (cm^{-1}) 3275 (m), 3196 (m), 1672 (s), 1222 (w), 1174 (w), 1141 (w), 1096 (m), 805 (w), 641 (w); ^{1}H NMR (DMSO-d_6) δ: 7.82 (s, 2H), 5.61 (s, 2H), 2.43–2.19 (m, 4H), 2.06 (m, 2H), 1.72 (m, 2H); ^{13}C NMR (DMSO-d_6) δ: 176.5, 91.2, 30.9, 30.6; Anal. Calcd. for $C_8H_{12}N_2O_4$: C, 48.00; H, 6.00; N, 14.00; found: C, 48.18; H, 6.45; N, 13.79.

4.3.2.4. 5-Ethoxypyrrolidin-2-one (2c′). **1c** irradiated in ethanol for 25 h, yield 38%; colorless crystal, mp 50–51 °C, lit value 48–53 °C [27]; IR (KBr) ν (cm^{-1}) 3190 (s), 3112 (m), 2976 (s), 2876 (w), 2931 (w), 1701 (s), 1459 (m), 1251 (s), 1120 (m), 1094 (m), 1066 (s), 805 (m), 761 (m), 655 (m); MS: *m/z* (relative intensity): 129 (M^+, 1.2), 114 (15.0), 100 (3.1), 85 (7.0), 84 (100), 74 (5.7), 72 (1.8), 56 (8.4), 55 (7.2); ^{1}H NMR ($CDCl_3$) δ: 7.35 (s, 1H), 4.94 (d, 1H, J = 6.0 Hz), 3.53 (m, 1H), 3.40 (m, 1H), 2.32–2.15 (m, 2H), 2.04 (m, 1H), 1.19 (m, 3H).

4.3.2.5. 5-Ethoxy-5-(1-hydroxyethyl)-pyrrolidin-2-one (3c′). **1c** irradiated in ethanol for 25 h, MS: *m/z* (relative intensity): 173 (M^+, 1.2), 128 (100), 100 (86.0), 110 (5.7), 84 (29.0), 72 (12.4), 55 (9.6), 45 (15.2).

4.4. Computational methods

The calculations were performed using the Gaussian 03 series of programs. Full geometry optimization were done at the DFT levels, in which the hybrid functional B3LYP was carried out with constraint. Different basis sets of 6-31+G(d,p), 6-311+G(d,p) and 6-311++G(d,p) were utilized in calculations. The vibrational frequency and zero point energies (ZPE) were then computed with the 6-31+G(d,p) methods. The binding energies for the **1c**–**1c**, **1c**–**2c** and **2c**–**2c** complexes were calculated by the following equation:

$$\mathrm{BE} = [\mathrm{E} + \mathrm{ZPE}]_\mathrm{H} - \sum [\mathrm{E} + \mathrm{ZPE}]_\mathrm{M} \quad (1)$$

where H is the hydrogen-bonded complex and M is the monomer.

Supplementary material

CCDC 297875, 251724 and 297876 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 336033).

References

[1] M.K. Hargreaves, J.G. Pritchard, H.R. Dave, Chem. Rev. 70 (1970) 439–469.
[2] K. Maruyama, T. Ishitoku, Y. Kubo, J. Org. Chem. 46 (1981) 27–34.
[3] P.H. Mazzocchi, L. Klingler, J. Am. Chem. Soc. 106 (1984) 7567–7572.
[4] P.H. Mazzocchi, S. Minamikawa, P. Wilson, J. Org. Chem. 44 (1979) 1186–1188.
[5] Y. Kanaoka, K. Sakai, R. Murata, Y. Hatanaka, Heterocycles 3 (1975) 719.
[6] C. Somich, P.H. Mazzocchi, H.L. Ammon, J. Org. Chem. 52 (1987) 3614–3619.
[7] Y. Kanaoka, K. Yoshida, Y. Hatanaka, J. Org. Chem. 44 (1979) 664–666.
[8] K. Maruyama, Y. Kubo, J. Org. Chem. 42 (1977) 3215–3216.
[9] K. Maruyama, T. Ishitoku, Y. Kubo, J. Am. Chem. Soc. 101 (1979) 3670–3671.
[10] Y. Kanaoka, K. Koyama, Tetrahedron Lett. 13 (1972) 4517–4520.
[11] Y. Sato, H. Nakai, H. Ogiwara, T.M.Y. Migita, Y. Kanaoka, Tetrahedron Lett. 14 (1973) 4565–4568.
[12] P.H. Mazzocchi, M.J. Bowen, N.K. Narain, J. Am. Chem. Soc. 99 (1977) 7063–7064.
[13] K. Maruyama, Y. Kubo, M. Machida, K. Oda, Y. Kanaoka, K. Fukuyama, J. Org. Chem. 43 (1978) 2303–2304.
[14] K. Maruyama, Y. Kubo, J. Am. Chem. Soc. 100 (1978) 7772–7773.
[15] Y. Sato, H. Nakai, T. Mizoguchi, Y. Hatanaka, Y. Kanaoka, J. Am. Chem. Soc. 98 (1976) 2349–2351.
[16] U.C. Yoon, S.W. Oh, J.H. Lee, J.H. Park, K.T. Kang, P.S. Mariano, J. Org. Chem. 66 (2001) 939–943.
[17] Y. Kanaoka, K. Koyama, J.L. Flippen, I.L. Karle, B. Witkop, J. Am. Chem. Soc. 96 (1974) 4719–4721.
[18] Y. Kanaoka, Y. Hatanaka, J. Org. Chem. 41 (1976) 400–401.
[19] G.C. Ma, H.M. Liu, W.Q. Zhang, Acta Cryst. E 60 (2004) o1541–o1542.
[20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision B. 05, Gaussian Inc., Pittsburgh, PA, 2003.
[21] R. Mason, Acta Cryst. 9 (1956) 405–410.
[22] W.L. Jorgensen, D.L. Severance, J. Am. Chem. Soc. 113 (1991) 209–216.
[23] A.R. Doumaux, D.J. Trecker Jr., J. Org. Chem. 35 (1970) 2121–2125.
[24] N.A. Kalinina, I.I. Migunova, V.I. Lovchikov, Russ. J. Appl. Chem. 72 (1999) 291–297.
[25] P.J. Voorstad, J.M. Chapman, G.H. Cocolas, S.D. Wyrick, I.H. Hall, J. Med. Chem. 28 (1985) 9–12.
[26] X.T. Phan, P.J. Shannon, J. Org. Chem. 48 (1983) 5164–5170.
[27] J.C. Hubert, J.B.P.A. Wijnberg, W.N. Speckamp, Tetrahedron 31 (1975) 1437–1514.