

COMMUNICATION

LASER FLASH PHOTOLYSIS STUDY ON THE PHOTOCYCLIZATION OF *N*-(*O*-HALOBENZYL) IMIDAZOLE

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In connection with our interest on the photochemical properties of heteroaryl halides, which are currently the subject of heterocyclic ring formation and haloarene degradation, we have studied the photochemistry of the haloarene linked to *N*-heteroarene compounds. Imidazo[5,1-*a*]isoindole was synthesized from *N*-(*o*-chlorobenzyl)imidazole¹ or *N*-(*o*-bromobenzyl)imidazole² in acidic aqueous solution or acetonitrile via the intramolecular photocyclization (Table 1). This type of reaction provides the synthetic methods for 5- and 6-membered polyheteroatomic heterocyclic ring compounds.

However, the reaction mechanism for the intramolecular photocyclization of haloarene tethered heteroarenes has not yet been established. Grimshaw *et al.* suggested a mechanism for homolytic carbon-halogen bond fission assisted by radical complexation to explain their results in the photocyclization of 5-(2-

Table 1. The yield of the photoreaction of *N*-(*o*-halobenzyl)imidazole in acetonitrile.

X	Time(min)	yield(%)	
		1	2
Cl	15	40	trace
Br	20	20	< 5

chlorophenyl)-1,3-diphenylpyrazole.³ They also reported the detection of acyclohexadienyl intermediate involved in the above reaction.⁴ Park *et al.* reported several transient intermediates involved in the laser flash photolysis of *N*-(*o*-halobenzyl) pyridinium⁵ and *N*-benzyl-2-halopyridinium salts.⁶

Thus we performed the laser flash photolysis study on the photocyclization reaction of *N*-(*o*-chlorobenzyl)imidazole to identify the intermediate species involved in the reaction. Here, we report on the preliminary results in the photocyclization reaction of *N*-(*o*-halobenzyl)imidazole through the detection of reaction intermediates.

Details of the experimental procedure can be found elsewhere.⁶ When the argon-saturated acetonitrile solution of *N*-(*o*-chlorobenzyl)imidazole was irradiated by 266 nm laser pulse (*ca.* 6 ns), three transient species were observed at about 260, 280, and 350 nm, respectively (Fig. 1). Among those transient species observed at 5 μ s delay after the laser pulse, only two absorption bands at 260 and 280 nm remained when we recorded the transient absorption spectrum at 300 μ s delay.

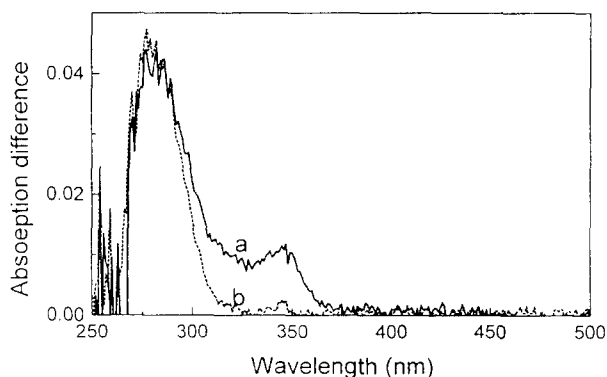


Figure 1. Transient absorption spectra observed in the laser flash photolysis of *N*-(*o*-chlorobenzyl)imidazole (3.2×10^{-3} M) in acetonitrile under argon. (a) measured at 5 μ s after laser pulse; (b) measured at 300 μ s after the laser pulse.

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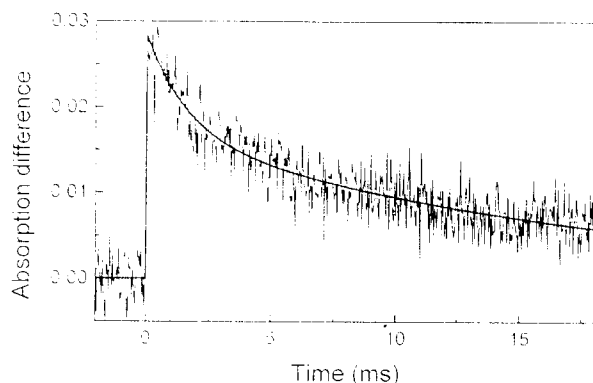


Figure 2. The temporal profile of the transient at 260 nm in the photolysis of *N*-(*o*-chlorobenzyl)imidazole (3.2×10^{-3} M) in acetonitrile.

The temporal profile of the transient species at 260 nm is shown in Figure 2. As we used a flow type cuvette, there was an interference in absorption decay from the reaction product which was flowing out of the reaction cell. The measured lifetimes of the decay components were 1.6 and 16.8 ms, respectively. Here, the component of 16.8 ms is regarded as to come from the product because the absorption wavelength is the same as that of product and the decay rate corresponds to the flow rate of the sample solution. Thus the lifetime of 260 nm transient species was determined to be 1.6 ms. This value is similar to that of the phenyl radical observed in the flash photolysis of *N*-(*o*-chlorobenzyl) pyridinium salts.⁵ Furthermore, this transient was quenched by the addition of *t*-butyl- α -phenylnitron which is known as a radical scavenger.⁵⁷ On the basis of the above results, the transient species at 260 nm is assigned as a phenyl radical.

The temporal profile of the transient species at 280 nm was also recorded. There is a rise component corresponding to the rise time of 91 μ s (a in Fig. 3). The presence of the rise component in the temporal profile at 280 nm indicates that a precursor such as the triplet state of reactant is involved in the formation of this transient species. The 280 nm transient species was also quenched by the addition of the *t*-butyl- α -phenylnitron (b in Fig. 3), which indicates that this transient species is a radical rather than the molecular triplet state. As the lifetime of the 280 nm transient (530 μ s) is different from that of 260 nm transient, the transient species at 280 nm is assigned as a conjugated radical of imidazo[5,1-*a*]isoindole. As the conjugated radical of imidazo[5,1-*a*]isoindole is less conjugated (one less double bond) than the conjugated 2,3-dihydrohexadienylpyridinium π radical (310 nm),⁷ shorter wavelength absorption

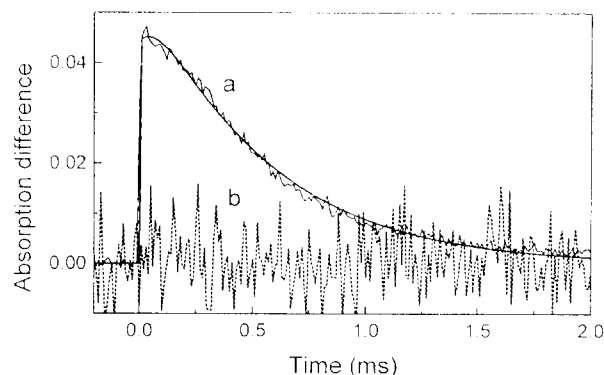
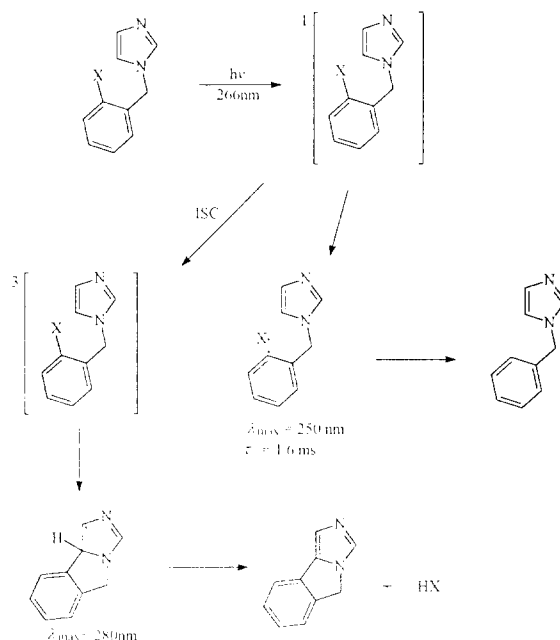


Figure 3. The temporal profile of the transient at 280 nm in the photolysis of *N*-(*o*-chlorobenzyl)imidazole (3.2×10^{-3} M) in acetonitrile. (a) sample only; (b) *t*-butyl- α -phenylnitron added

is expected compared with the conjugated 2,3-dihydrohexadienylpyridinium π radical.

The temporal profile of a transient at about 350 nm are shown in Figure 4. There were two decay components whose lifetimes correspond to 14 μ s and 321 μ s, respectively. The former is assigned as that of chlorine anion radical because the lifetime and absorption wavelength are same as that of halogen anion radical.^{5,6} The second species is regarded as a benzyl radical because the same transient species in absorption wavelength and decay time was observed in the laser flash photolysis of benzyl bromide in acetonitrile.



Scheme 1

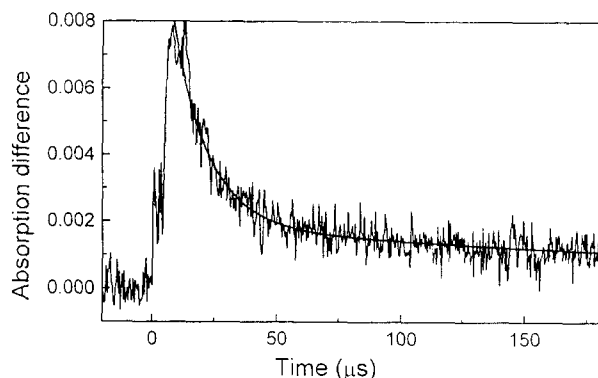


Figure 4. The temporal profile of a transient at 350 nm in the photolysis of *N*-(*o*-chlorobenzyl)imidazole (3.2×10^{-3} M) in acetonitrile.

On the basis of the above observations, we propose the following reaction mechanism (Scheme 1). The excited singlet state of *N*-(*o*-chlorobenzyl)imidazole is populated by the absorption of photons. Then the singlet state proceeds to triplet state *via* intersystem crossing or a phenyl radical *via* homolytic cleavage of aryl-halogen bond. The phenyl radical can proceed to the photoreduced product, *N*-benzyl imidazole. The triplet state is converted to a conjugated radical by arylation of arene moiety to the haloarene moiety through a π -complex between chlorine and arene moieties. The photocyclized product, an isoindole, is formed by hydrogen ejection of the conjugated radical.

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