Photochemistry of 2-(Methoxycarbonyl)phenyl Azide in Solution at Room Temperature: A Time-resolved Infrared Study

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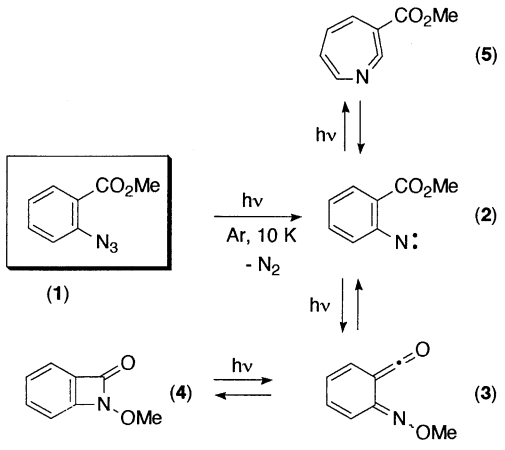
Time-resolved infrared studies of intermediates generated by photolysis of the title azide in solution at room temperature demonstrated that 3-(methoxycarbonyl)azacycloheptatetraene was the sole intermediate at least in the μs time scale, which is in sharp contrast with that observed in the photolysis in argon matrix at 10 K. Substituent effects on the reactivity of the dehydroazepine toward diethylamine are also discussed.

There is considerable interest in the photochemistry of aryl azides[1] since these compounds are utilized both as photoaffinity labels[1,2] and photoresists.[1,3] However the complete picture of the chemical reactions initiated by the elimination of nitrogen has only recently begun to unfold. Matrix isolation has been proven to be a powerful tool for investigating intermediates involved in the photochemistry of phenyl azide.[4] Photolysis of phenyl azide generates singlet phenylnitrene, which is in equilibrium with the strained rearranged product, didehydroazepine.

In the matrix, didehydroazepine was found to have a strong infrared absorption at ca.1885 cm^{-1}. In solution, the didehydroazepine intermediate can be trapped in the presence of amine to produce, for example, 2-amino-*3H*-azepine. Time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis and fast infrared spectroscopy, has been a powerful technique for the investigation of reactive intermediates in solution at room temperature, particularly of metal carbonyl complexes.[5]

The combination of matrix isolation studies and TRIR has been sucessfully applied to simple aryl azides.[6] However, substituted aryl azides have been shown to have a rich photochemistry and in this paper we have used TRIR to elucidate



the solution photochemistry of 2-(methoxycarbonyl)phenyl azide (**1**) in solution at room temperature. On photolysis in a matrix at 10K, **1** produces the unstable intermediates: 1-(methoxycarbonyl)phenylnitrene (**2**, 1757 cm^{-1}: $\nu_{C=O}$), imino ketene (**3**, 2088, 2118 cm^{-1}: $\nu_{C=C=O}$), azetinone (**4**, 1857 cm^{-1}: $\nu_{C=O}$), together with the expected ring expanded didehydroazepine (**5**, 1887: $\nu_{C=C=N}$, 1734 cm^{-1}: $\nu_{C=O}$).[7] Thus, it is quite intriguing to determine whether **1** generates similar diverse intermediates in solution at room temperature. Furthermore, kinetic data will probe the effect of substituents at the ortho position on the reactivity of the expected didehydroazepine, which is largely unknown.

The FTIR spectrum of **1** (3.3×10^{-3} mol. dm^{-3}) in n-heptane solution is shown in Figure 1a. Figure 1b shows the TRIR spectrum (probed from ca.1800 to 2200 cm^{-1}), 1 μs after the laser flash (XeCl excimer laser, 308 nm, 20 ns, 10 mJ per pulse). It is clear that the strong parent absorptions due to the azide group are bleached and a strong band at 1883 cm^{-1} is produced. This product band is assigned to didehydroazepine (**5**) by comparison with results from matrix isolation[7] and previous TRIR studies.[6] The lifetime of didehydroazepine can be determined by monitoring the time dependence of its infrared absorption band. Under the laser irradiation conditions described above, the didehydroazepine absorption decay follows a first-order rate law with a lifetime of 0.3 ms (Figure 2a). Further confirmation of the assignment of the intermediate comes from verification of its rapid reaction with amines. Irradiation of **1** in n-heptane solution containing diethylamine (DEA) also gives the 1883 cm^{-1} band of the dehydroazepine, but under these conditions it decays away in a few μs (Figure 2b). The decay is pseudo first order in the presence of DEA (5.4×10^{-3} mol. dm^{-3}), $k_{obs}=6.6\ (\pm0.5)\times10^5\ s^{-1}$. From this we estimate the rate constant for the reaction of didehydroazepine with DEA, (k_{DEA}) to be $1.2(\pm0.5)\times10^8\ mol^{-1}\ dm^3\ s^{-1}$.

It is interesting to compare this rate constant with those of the analogous reaction of didehydroazepines bearing a series of substituents at the 5-position.[6] In general, the rate constant for this reaction increases with the increasing electron-withdrawing power of the substituent. The rate constant for **5** is some 20 times greater than that of "parent" didehydroazepine ($k_{DEA}=6.5\times10^6\ mol^{-1}\ dm^3\ s^{-1}$) and similar with that of the 5-acetyl derivative ($k_{DEA}=2.8\times10^8\ mol^{-1}\ dm^3\ s^{-1}$), indicating that electronic effects play a more important role than steric ones. Similar observations were made by Sundberg[8] employing UV flash photolysis in the study of 2-substituted phenyl azides. The reactions of intermediates generated from o-methylphenyl azides with DEA were slower by a factor of 500 than for phenyl azides, whilst those generated from o-trifluoromethylphenyl azide were faster than the unsubstituted compound by a factor of 20. However it is often difficult to assign with certainity the structure of an intermediate detected solely by UV spectroscopy, owing to

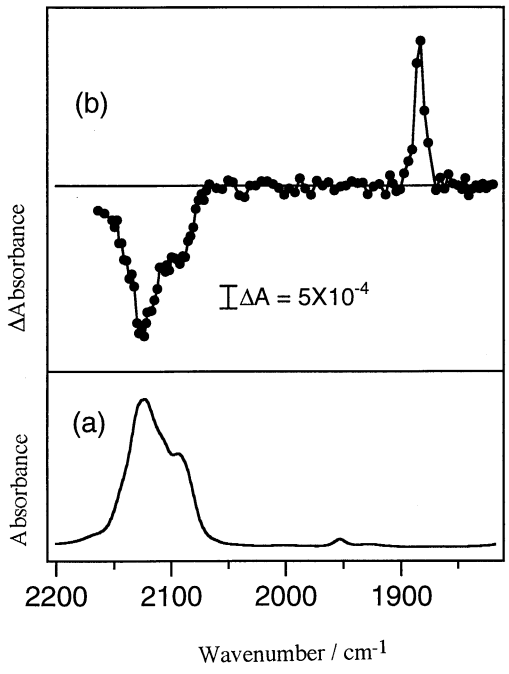


Figure 1. (a) FTIR spectrum of **1** in n-heptane. (b) Transient IR spectrum recorded after 1 μs after irradiation (308 nm).

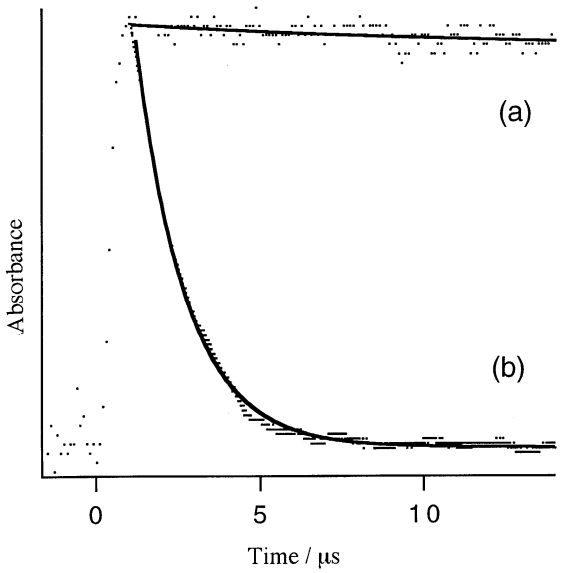


Figure 2. The time dependence of the transient IR signal monitored at 1883 cm^{-1} in (a) absence and (b) presence of diethylamine.

their broad featureless bands. Sundberg assigned the intermediate to azirine and/or azacycloheptatrienylidene.[8] Although o-methyl- and o-trifluoromethylphenyl azides have not been studied by TRIR, other TRIR results suggest that the intermediate reacting with DEA is didehydroazepine since no evidence for azirine formation was obtained for a range of substiuted phenyl azides.[4] Furthermore the trends in reactivity of Sundberg's intermediate towards DEA are still accounted for following this reassignment.

The rather insensitive nature of the attack of DEA on the heterocumulenic double bond of didehydroazepines to steric factor can be explained in terms of this bond having a bent structure, which is due to its incorporation into the seven-membered ring. This fact is evident from the appearance of the stretching vibration of this bond at a notably lower frequency (1883 cm^{-1}) compared with the usual value for the bond when it is not constrained in a ring.

In matrix isolation experiments, the imino ketene (**3**) and azetinone (**4**) were produced following irradiation of **1**.[7] We can clearly state that we observe no detectable signal due to azetinone at ca. 1857 cm^{-1} at least in the μs time scale. The question whether there is any signal due to imino ketene is more difficult since its IR bands overlap with the strong azide vibrations of the parent compound. Ketene IR bands are strong and have been previously detected by TRIR.[9] The bleach of the parent absorption bands match exactly the FTIR profile (Figure 1). We interpret this to mean that there is no detectable signal due to imino ketene at ca. 2088 and 2118 cm^{-1}.

Thus, we have shown that photochemistry of **1** is significantly different in room temperature n-heptane solution compared with Ar matrices at 10 K. Under matrix conditions, these intermediates are in the photoequilibrium and this suggests that they are produced from secondary photolysis. Two-laser, two-color irradiation and/or laser-jet techniques might allow us to probe multiphoton chemistry of **1** in solution. Alternatively, it may be that some of these intermediates decay in the ns time region.

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