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Full Paper

Singlet Photoreactivity of 3-Methyl-2-phenyl-2H-azirine

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Irradiation of 3-methyl-2-phenyl-2*H*-azirine (1) at 254 nm in argon matrices results in ylide **6**. Similarly, laser flash photolysis ($\lambda = 266$ nm) of azirine **1** in acetonitrile yields ylide **6**, which has a transient absorption with λ_{max} at ~340 nm and a lifetime of 14 µs. Density functional theory calculations were preformed to support the characterisation of ylide **6** in solution and argon matrices. Irradiation of azirine **1** above 300 nm has previously been reported (*J. Org. Chem.* **2014**, 79, 653) to yield triplet vinylnitrene in solution and ketenimine in cryogenic argon matrices. Thus, the photochemistry of azirine **1** is dependent on the irradiation wavelength.

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Introduction

2*H*-Azirines are strained molecules and thus highly reactive. Their reactivity has been captured in various synthesis-related applications.^[1] The photochemistry of 2*H*-azirine derivatives is also driven by relieving the steric strain via opening the cyclic structure.^[2–4] Intriguingly, the photoreactivity results in the breaking of both C–C and C–N bonds to form ylides and vinylnitrene intermediates, respectively (Scheme 1). It has been theorised that the nature of the substituents on 2*H*-azirine controls whether either C–C or C–N bond breakage is favoured upon exposure to light.^[2,5] For example, it has been postulated that electron-withdrawing groups on the azirine moiety facilitate C–N bond cleavage.^[6] However, it has also been hypothesised that the substituents on the azirine ring can act as intramolecular sensitisers to form the triplet excited state of the azirine, which breaks apart to form vinylnitrene, whereas direct excitation of the azirine chromophore results in C–C bond cleavage.^[7] The ylides obtained from 2*H*-azirine derivatives



Scheme 1. Photolysis of 2*H*-azirine resulting in either C–C or C–N bond cleavage.

are typically long-lived intermediates that can be trapped in 1,3-dipolar additions.^[8,9]

We reported earlier that laser flash photolysis of 3-methyl-2-phenyl-2H-azirine (1) using 308-nm laser irradiation yields triplet vinylnitrene 2 ($\lambda_{max} \sim 440 \text{ nm}$) in solution (Scheme 2). Quenching studies demonstrate that triplet vinylnitrene 2 is formed from a triplet precursor or T_1 of **1**. Triplet vinylnitrene 2 has a lifetime of a few microseconds and decays by intersystem crossing to reform azirine 1.^[7] Vinylnitrene 2 displays characteristic reactivity towards a triplet biradical in solution as it can be intercepted by oxygen and bromine radicals. In comparison, photolysis of 1 through a Pyrex filter in argon matrices does not yield triplet vinylnitrene 2, but rather ketenimine 3 (Scheme 2). We theorised that at cryogenic temperatures, triplet vinylnitrene 2 intersystem crosses to form ketenimine 3 and that the intersystem crossing is facilitated by the 1,3-biradical character of vinylnitrene 2, which makes rotation around its vinyl bond feasible. The only triplet vinylnitrenes that have been stable enough to be directly detected at cryogenic temperatures are cyclic vinylnitrenes. Rotation around their vinyl bond does not occur and thus they cannot intersystem cross to form ketenimine products.^[10,11]

We also reported that laser flash photolysis of 2-methyl-3-phenyl-2*H*-azirine (**4**), which is an isomer of **1**, with 308-nm irradiation at ambient temperature results in the formation of ylide **5**, and irradiation of **4** through a Pyrex filter at cryogenic temperatures in argon matrices also resulted in ylide **5** (Scheme 3).^[7] Because the azirine moiety is not conjugated with the phenyl chromophore in **1**, unlike in **4**, we proposed that intramolecular sensitisation from the phenyl group to the azirine moiety in **1** forms the triplet excited state of the azirine moiety, which cleaves to form triplet vinylnitrene **2**. In contrast, because the azirine moiety in **4** is conjugated with the phenyl ring, it is



Scheme 2. Proposed mechanism of the photoreactivity of azirine 1 in solution and cryogenic matrices with irradiation at >300 nm.^[7]



Scheme 3. Photoreactivity of azirine 4 in solution and cryogenic matrices.^[7]



Scheme 4. Photoreactivity of azirine **1** in solution (irradiation at 266 nm) and cryogenic matrices (irradiation at 254 nm).

not possible to selectively excite these two different chromophores to control the reactivity.

In this paper, we describe the photoreactivity of 1 upon irradiation at 254 nm and at ambient temperature in acetonitrile and argon matrices at cryogenic temperatures to obtain ylide **6** (Scheme 4). We used density functional theory (DFT) calculations to characterise the obtained ylide **6**.

Results

Laser Flash Photolysis

We used laser flash photolysis to identify the intermediate formed upon photolysis of 1 with 266-nm irradiation (Nd:YAG laser, 3 ns).^[12,13] A transient with λ_{max} at 340 nm was produced. This absorption was assigned to ylide 6 based on comparison with the calculated spectrum of 6. Time-dependent DFT (TD-DFT) calculations generated the largest electronic transition for ylide 6 at 329 nm (f = 0.501, Fig. 1b), which fits well with the observed spectrum. The decay of the absorption at 340 nm can be fitted to a mono-exponential function with a rate constant of $7.3 \times 10^4 \,\text{s}^{-1}$ or a lifetime of $\sim \! 14 \,\mu\text{s}$. The lifetime of ylide **6** is not affected by oxygen, thereby supporting that 6 is formed on the singlet surface of azirine 1. The lifetime of ylide 6 is in the order of microseconds, similarly to the lifetime of ylide 7, which decays by intramolecular reaction.^[14] In contrast, ylides **8**, which decay by intermolecular reaction, are much longer lived (Scheme 5).^[15] Our previous studies showed that laser flash photolysis of azirine 1 with 308-nm irradiation forms triplet vinylnitrene 2 (Scheme 1),



Fig. 1. (a) Transient spectra obtained by laser flash photolysis of **1** with a 266-nm laser in acetonitrile. (b) TD-DFT calculated electronic transition for ylide **6**. (c) Kinetic trace obtained at 340 nm.



Scheme 5. Intra- versus intermolecular reactivity of ylides in solution.^[7,14,15]

which has a transient absorption spectrum with λ_{max} at ~440 nm.^[7] Thus, the photochemistry of azirine **1** in solution is dependent on the irradiation wavelength, with irradiation at shorter wavelengths yielding ylide **6** and irradiation at longer wavelengths yielding triplet vinylnitrene **2**.

Matrix Isolation of 1

The photochemistry of azirine 1 in argon matrices at 14 K was investigated to identify its reactivity upon irradiation with short wavelength light at cryogenic temperatures. Azirine 1 was deposited onto argon matrices by passing the vapor over a sample of pure azirine in flowing argon and depositing the resulting sample on a 14-K cryogenic surface. The resulting matrix was irradiated at 254 nm for a total of 16 h, and infrared spectra were recorded at different time intervals. The photolysis of 1 at 254 nm resulted in a reduction of the characteristic infrared bands of azirine 1. Concurrently with the depletion of these bands, the growth of new absorption bands was observed at 1947, 1934, 1926, 1469, 1413, 1025, 1020, 876, 756, 691, 689, 621, 533, and 499 cm⁻¹. The intensities of all these new bands showed similar increases with further irradiation, indicating that they could be assigned to one intermediate. These bands were assigned to ylide 6 based on comparisons with its calculated spectrum (Figs 2 and 3). All the computed vibrational infrared frequencies were adjusted by a scaling factor of 0.9613.^[16]

The C=N=C stretching of the ylide is calculated to be 2001 cm⁻¹ (calculated intensity $I_{calc} = 445$), and scaling by 0.9613 places it at 1924 cm⁻¹, which fits well with the bands observed at 1947, 1934, and 1926 cm⁻¹. The observation of multiple bands in the matrix is most likely due to ylide 6 being trapped in different matrix sites. The C=C stretching of the phenyl ring is calculated to be at 1648 cm⁻¹ ($I_{calc} = 48$), which scaling places at $1584 \,\mathrm{cm}^{-1}$. This band is not visible as it is overlaps with the intense parent bands. However, the difference spectrum clearly shows the formation of a band at $1600 \,\mathrm{cm}^{-1}$, which is assigned to the C=C phenyl stretching. The experimentally observed bands at 1501 and 1469 cm⁻¹ are in excellent agreement with the calculated data for coupled phenyl ring and C=N=C moiety stretching; the calculated bands are observed at $1542 \text{ and } 1519 \text{ cm}^{-1}$ and scaled to be at 1482 and 1460 cm^{-1} , respectively. The bands at 1025 and 1020 cm⁻¹ are assigned to C-H wagging of the methyl group coupled with twisting of the C=N=C bond, and the calculated band is at 1058 cm^{-1} and scaled to be at 1017 cm^{-1} . As above, the multiplicity of this band is due to the presence of different matrix sites. Furthermore, the band at 691 cm^{-1} is assigned to C–H wagging and is calculated to be at 699 cm^{-1} and scaled to be at 672 cm^{-1} . We assign the bands at 876 and 621 cm⁻¹ to the twisting of the C=N=C group, which are calculated to be at 893 cm^{-1} and 634 cm^{-1} and scaled

to be at 859 and 610 cm^{-1} respectively. Finally, we also observed C=N=C bending at 533 cm⁻¹, which is calculated to be at 558 cm⁻¹ and scaled to be at 537 cm⁻¹.

Therefore, the matrix isolation experiments demonstrate that the photolysis of azirine **1** at cryogenic temperatures with 254-nm light yields ylide **6**. In contrast, in a previous study, we previously showed that irradiation of azirine **1** in argon matrices through a Pyrex filter selectively yields ketenimine **3**.^[7] Furthermore, irradiation of azirine **1** with a 254-nm light without the filter that cuts off the lines above 300 nm (see Supplementary Material) results in the concurrent formation of ylide **6** and ketenimine **3** (Fig. S1, Supplementary Material). Thus, it is unlikely that ketenimine **3** and ylide **6** can be interconverted photochemically.

Product Studies

Irradiation of azirine 1 in acetonitrile at 254 nm resulted in the formation of one major product according to gas chromatography and gas chromatography–mass spectrometry analyses, and we identified this compound as isoindole **10** (Scheme 6). Our results agree with the findings of Padwa et al. who reported that azirine **11**, which is a derivative of azirine **1**, forms isoindole **12** upon irradiation at 248 nm (Scheme 7).^[9]

Theoretical Calculations

We performed DFT calculations using *Gaussian09* at the B3LYP level of theory with the 6-31+G(d) basis set to aid in the characterisation of ylide **6**.^[17–19] The optimised ground-state structures of azirine **1** and ylide **6** are shown in Fig. 4. TD-DFT calculations placed the first excited state (S₁) of **1** at 106 kcal mol⁻¹ (1 kcal = 4.184 kJ) above its ground state (S₀) (Fig. 5).

In addition, stationary points on the singlet surface of azirine 1 for forming ylide 6 were calculated, and the results are displayed in Fig. 5. The transition state barrier for azirine 1 to form ylide 6 was located 41 kcal mol⁻¹ above the S₀ of 1. It can be speculated that the formation of ylide 6 proceeds either by involving a vibrationally hot S₀ of 1 or by conical intersection of S₁ of 1. The calculated transitions state barrier for ring closure of ylide 6 to form 9 is located 28 kcal mol⁻¹ above the S₀ of 1. Furthermore, the calculated transition state barrier for H-atom shift in compound 9 to yield aromatic indole 10 is 13 kcal mol⁻¹. Thus, formation of ylide 6 from azirine 1 is feasible on its singlet surface at cryogenic temperatures, whereas in solution, ylide 6 reacts further to form indole 10 at ambient temperature.

Discussion

Irradiation of azirine **1** with short-wavelength light in both solution (266 nm) and argon matrices (254 nm) yields ylide **6**. The identity of ylide **6** was confirmed by infrared spectroscopy in matrices and transient UV absorption in solution, and the spectroscopic characterisation was further supported by DFT calculations. Furthermore, ylide **6** has been previously prepared by photolysis of diazo compound **13**. Specifically, photolysis of **13** generated carbene **14** that upon trapping with acetonitrile subsequently yielded ylide **6** (Scheme 8).^[20] There is good agreement between the transient spectra of ylide **6** obtained by irradiation of azirine **1** at 266 nm and by irradiation of diazo compound **13** at 308 nm in acetonitrile.

Nitrile ylides, such as ylide **6**, can exist in different configurations, as shown in Scheme 9. The structures of propargylic, allenic, and carbenic ylides have been characterised theoretically and experimentally using spectroscopy.^[21–25] These ylide forms are resonance hybrid structures, and their relative importance will



Fig. 2. Comparison of infrared spectra obtained before (black curve) and after (red curve) irradiation of 1 in an argon matrix at 254 nm.



Fig. 3. Experimental infrared spectral profiles of azirine 1 in argon matrices (a) before and (b) after photolysis for 16 h at 254 nm (red curves). For comparison, the calculated and scaled infrared spectra of ylide 6 are also shown (blue curves). The positive bands are formed upon irradiation, and the negative bands are due to depletion of azirine 1.



Scheme 6. Product obtained following irradiation of azirine **1** in acetonitrile at 254 nm.



Scheme 7. Irradiation of azirine 11 to yield isoindole 12.



Fig. 4. Optimised ground-state structures of azirine 1 and ylide 6 calculated at the B3LYP level of theory using the 6-31+G(d) basis set.

be reflected in their spectroscopic characterisations. In addition, X-ray structural analyses have been obtained for several stable propargylic and allenic ylides.^[26] As ylide **6** has C=N=C stretches at 1947, 1934, and 1926 cm⁻¹, and the lengths of its allenic bonds

in PhCH=N=CCH₂ are calculated as 1.29 and 1.22 Å, respectively, the structure of ylide **6** is best described as allenic. This is as expected because electronegative substitution on the trigonal carbon atom favours propargylic ylide structures, whereas carbenic ylides are stabilised by electron-donating groups.

The reactivity of azirine is summarised in Scheme 10. The scheme shows that irradiating with light at <300 nm results in formation of ylide 6, which is stable in argon matrices but reacts to form isoindole 10 in solution. In comparison, irradiation of azirine 1 with light at >300 nm results in the formation of triplet vinylnitrene 2, which intersystem crosses to reform azirine 1 in solution but intersystem crosses to form ketenimine 3 in matrices.

The reactivity of azirine **1** is similar to that reported for azirine **15**, which also displays wavelength-dependent photochemistry.^[14,27] Azirine **15** has an acetophenone moiety that serves as a built-in triplet sensitiser, and irradiation with light at >300 nm is absorbed by the acetophenone chromophore. The latter chromophore intersystem crosses effectively to its triplet excited state and transfers its energy to the azirine moiety to form triplet vinylnitrene **16** in solution and ketenimine **17** in cryogenic matrices (Scheme 11). Nevertheless, the triplet reactivity of azirine **15** can be bypassed by directly exciting the azirine chromophore using short-wavelength irradiation. Thus, irradiation of azirine **15** at 266 nm yields ylide **7** both in matrices and solution, presumably because the azirine moiety in **15** absorbs light directly.

Ylides 6 and 7 have lifetimes of ~ 14 and $\sim 6 \,\mu$ s, respectively, as they presumably decay by intramolecular rearrangement in solution, whereas in cryogenic argon matrices, these ylides are stable. In comparison, vinylnitrene 2 has a lifetime of $\sim 7 \,\mu$ s in acetonitrile and is therefore longer lived than vinylnitrene 16, which has a lifetime of $\sim 3 \,\mu$ s in acetonitrile. Thus, we theorise that the carbonyl group in vinylnitrene 16 may further enhance its intersystem crossing to form products.

The photoreactivity of azirines **1** and **16** in argon matrices mirrors the findings of Inui et al. on the photoreactivity of 2-(1-naphthyl)-2*H*-azirine derivatives in argon matrices.^[6,28,29] Short-wavelength irradiation yields the corresponding ylides and longer-wavelength irradiation yields ketenimines, presumably through the formation of triplet vinylnitrene intermediates. Thus, we theorise that the naphthalene moiety serves as a triplet sensitiser for such azirines (Scheme 12).

There are reports on the photolysis of non-conjugated azirines, in which irradiation at short wavelengths results in the formation of the corresponding ylides.^[9,30] Similarly, there are reports on the irradiation of non-conjugated azirine derivatives with light at >300 nm that yields the corresponding ketenimines in cryogenic matrices.^[5,7,31] However, the photoreactivity of these azirines has not been studied as a function of irradiation wavelength.

Conclusion

The photochemistry of azirine 1 is wavelength dependent. Irradiation of azirine 1 with light at <300 nm in solution and in cryogenic matrices yields ylide 6 through singlet reactivity, whereas irradiation with light at >300 nm yields triplet vinylnitrene 2 in solution and ketenimine 3 in matrices through triplet reactivity. Thus, the photochemistry of non-conjugated azirines can be tailored to instigate either C–C cleavage by direct excitation of the azirine moiety or C–N cleavage through intramolecular sensitisation. Understanding the wavelength dependence of the



Fig. 5. Calculated stationary points on the singlet surface of azirine 1. The energy of S_1 was obtained by TD-DFT calculations, whereas the other surface state energies were obtained by optimisation calculations. All energies are given in kcal mol⁻¹.



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Scheme 8. Photolysis of diazo compound 13 in acetonitrile to yield ylide 6.



Scheme 9. Electron configuration of nitrile ylides.

photochemistry of non-conjugated azirines facilitates their usage in synthesis-related applications.

Experimental

Molecular Modelling

All geometries were optimised at the B3LYP level of theory using the 6-31+G(d) basis set, as implemented in *Gaussian09*.^[17–19] The transition states were confirmed to have one imaginary vibrational frequency by analytical determination of the second derivatives of the energy with respect to the internal coordinates. Intrinsic reaction coordinate calculations were used to confirm that the located transition states corresponded to the attributed reactant and product.^[32,33] Absorption spectra were calculated using TD-DFT.^[34–36]

Laser Flash Photolysis

Laser flash photolysis was carried out using a Nd:YAG laser (266 nm, 3 ns).^[12,13] In a typical experiment, a stock solution of 1 was prepared in spectroscopic-grade acetonitrile such that the solutions had an absorbance of 0.3–0.6 at 266 nm. Typically, $\sim 1 \text{ mL}$ of the stock solution was placed in a 10 mm × 10 mm quartz cuvette, which was 48 mm long, and then purged with either argon or oxygen for 5 min.

Matrix Isolation

Matrix isolation studies were performed in cryogenic argon matrixes at 14 K using conventional equipments.^[37]

Preparation of 1

Synthesis of (2-Azido-1-iodopropyl)benzene

(2-Azido-1-iodopropyl)benzene was prepared from *trans*propenylbenzene, as we have published earlier,^[7] using the method previously described by Bader and Hansen.^[38]

 λ_{max} (CDCl₃)/cm⁻¹ 2984, 2099, 1451, 1259. δ_{H} (CDCl₃, 400 MHz) 7.50–7.29 (10H, m), 5.00 (1H, d, *J* 8), 4.94 (1H, d, *J* 8), 4.0–3.9 (1H, m), 3.88–3.81 (1H, m), 1.54 (3H, d, *J* 4), 1.25 (3H, d, *J* 8). δ_{C} (CDCl₃, 100 MHz) 140.7, 140.4, 128.9, 128.7, 128.5, 128.4, 128.1, 63.7, 63.2, 37.4, 36.3, 19.8, 18.4. *m/z* (electron impact (EI)) 91 (100 %, [C₇H₇]⁺), 217, 127, 117, 105, 77, 65.

Synthesis of (2-Azidoprop-1-en-1-yl)benzene

(2-Azido-1-iodopropyl)benzene was converted into (2-azidoprop-1-en-1-yl)benzene as described earlier. The ¹Hand ¹³C-NMR spectra of (*Z*)- and (*E*)-(2-azidoprop-1-en-yl) benzene were in agreement with those previously published.^[7]

 $\begin{array}{l} \lambda_{max} \ ({\rm CDCl_3})/{\rm cm^{-1}} \ 2121, \ 2099, \ 2055, \ 1646, \ 1597, \ 1572, \\ 1492, \ 1265. \ (Z)-(2-azidoprop-1-en-yl)benzene: \ \delta_{\rm H} \ ({\rm CDCl_3}, \\ 400 \ {\rm MHz}) \ 7.56-7.15 \ (5{\rm H}, \ {\rm m}), \ 5.62 \ (1{\rm H}, \ {\rm br} \ {\rm s}), \ 2.20 \ (3{\rm H}, \ {\rm s}). \ \delta_{\rm C} \\ ({\rm CDCl_3}, \ 100 \ {\rm MHz}) \ 135.3, \ 131.1, \ 128.5, \ 128.2, \ 126.6, \ 115.7, \\ 19.8. \ (E)-(2-azidoprop-1-en-yl)benzene: \ \delta_{\rm H} \ ({\rm CDCl_3}, 400 \ {\rm MHz}) \\ 7.35-7.17 \ (5{\rm H}, \ {\rm m}), \ 6.18 \ (1{\rm H}, \ {\rm br} \ {\rm s}), \ 2.06 \ (3{\rm H}, \ {\rm s}). \ \delta_{\rm C} \ ({\rm CDCl_3}, \\ 100 \ {\rm MHz}) \ 136.1, \ 135.4, \ 128.6, \ 128.4, \ 126.6, \ 115.9, \ 15.6. \end{array}$

Photolysis of (2-Azidoprop-1-en-1-yl)benzene to Yield Azirine **1**

(2-Azidoprop-1-en-1-yl)benzene was converted into azirine 1 as described earlier.^[7,39] The spectroscopic characterisation of 1 matched previously published data.^[7,39]

 $\lambda_{max}~(CDCl_3)/cm^{-1}$ 3029, 1764, 1668, 1598, 1495, 1454, 1261, 913, 766. $\delta_{\rm H}~(CDCl_3, 400~MHz)$ 7.31–7.21 (3H, m), 7.07–7.05 (2H, d), 2.89 (1H, s), 2.52 (3H, s). $\delta_{\rm C}~(CDCl_3, 100~MHz)$ 164.5, 141.2, 128.3, 126.8, 125.6, 33.4, 12.9. m/z~(EI) 130 (100 %, $[\rm M-H]^+)$, 131, 90, 89, 77, 65.

Photolysis of Azirine 1

Azirine 1 (1 mg, 7.6 mmol) was dissolved in [D3]acetonitrile (1 mL) and placed in a quartz cuvette. The resulting solution was purged with argon for 10 min and photolysed with 254-nm



Scheme 10. Wavelength-dependent photochemistry of azirine 1. ISC, Intersystem crossing.



Scheme 11. Wavelength-dependent photochemistry of azirine 15.



Scheme 12. Wavelength-dependent photochemistry of 2-(1-naphthyl)-2*H*-azirine derivatives. mercury pen-ray lamps. The progress of the reaction was monitored by gas chromatography–mass spectrometry, which showed formation of isoindole 10. m/z (EI) 131, 130, 105, 63.

Supplementary Material

Cartesian coordinates and energies of **1**, **6**, **9**, and **10**, ¹H and ¹³C NMR spectra of **1** and 2-azidoprop-1-en-1-yl)benzene, and IR spectra of **1** argon matrix before and after irradiation are available on the Journal's website.

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