Journal of Molecular Structure xxx (2018) 1–8

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Wavelength-dependent photochemistry of 2-azidovinylbenzene and 2-phenyl-2*H*-azirine

Onyinye Osisioma, Mrinal Chakraborty, Bruce S. Ault, Anna D. Gudmundsdottir*

Department of Chemistry, University of Cincinnati, PO Box 210172, Cincinnati OH 45221, USA

ARTICLE INFO

Article history:
Received 31 December 2017
Received in revised form
30 March 2018
Accepted 10 April 2018
Available online xxx

Keywords:
Azirine
Vinyl azide
Argon matrix
Wavelength-dependent photochemistry
Laser flash photolysis
Density functional theory calculation

ABSTRACT

Irradiation of 2-azidovinylbenzene (**1**) in a cryogenic argon matrix with a 254 nm bandpass filter results in 2-phenyl-2*H*-azirine (**2**) as the major product, some ketenimine **5**, and a small amount of *cis*-**1**, whereas irradiation of vinyl azide **1** with light above 300 nm forms only azirine **2** and ketenimine **5**. Prolonged irradiation of azirine **2** through a 254 nm bandpass filter produces ylide **3** selectively. Laser flash photolysis with excitation at 308 nm demonstrated that azirine **2** forms triplet vinylnitrene **4** ($\lambda \sim 440$ nm), whereas vinyl azide **1** does not exhibit transient absorption on a nanosecond timescale. DFT calculations (B3LYP/6-31 + G(d)) were used to aid the characterization of the photoproducts and to support the proposed formation mechanisms.

1. Introduction

Wavelength dependent photochemistry is fascinating because by simply using a different wavelength of light, the same reagent can be transformed into distinct products. The origin of wavelength dependent photochemistry is the excitation of separate chromophores in a reagent, resulting in the population of different excited states that react distinctively. It is also possible that excitation at different wavelengths can lead to the formation of different excited states of the same chromophore. Such examples are rare, as higher excited states generally undergo efficient internal conversion to the lowest excited state, as according to Kasha's rule, but a number of exceptions have been reported, such as azulene [1], naphthyl azides [2], and diazirines [3].

The photochemistry of nonconjugated aromatic azirine derivatives is extraordinary, as short wavelength irradiation leads to cleavage of the C—C bond of the azirine ring to form ylides, whereas longer wavelength irradiation results in the C—N bond breaking to form triplet vinylnitrenes [4,5]. For example, short wavelength irradiation of 3-methyl-2-phenyl-2*H*-azirine in an argon matrix yields the corresponding ylide, whereas longer wavelength irradiation forms the corresponding ketenimine (Scheme 1) [6,7]. We theorized that breakage of the C—C bond occurs following direct absorption by the azirine moiety. In contrast, longer wavelength irradiation selectively excites the phenyl moiety, which intersystem crosses to its triplet excited state, and subsequent energy transfer to the triplet excited state of the azirine chromophore results in cleavage of the C—N bond to form triplet vinylnitrene. However, as triplet vinylnitrene was not observed directly, it was theorized that the vinylnitrene intersystem crosses efficiently to form ketenimine. The hypothesis that the phenyl group serves as a triplet sensitizer was further supported by the fact that the photochemistry of 2-methyl-3-phenyl-2*H*-azirine, in which C═N is conjugated with the phenyl ring, does not display a wavelength dependence. In this case, the ylide is formed, regardless of the irradiation wavelength, as it is not possible to selectively irradiate the phenyl group of this molecule, and thus only singlet reactivity is observed (Scheme 2).

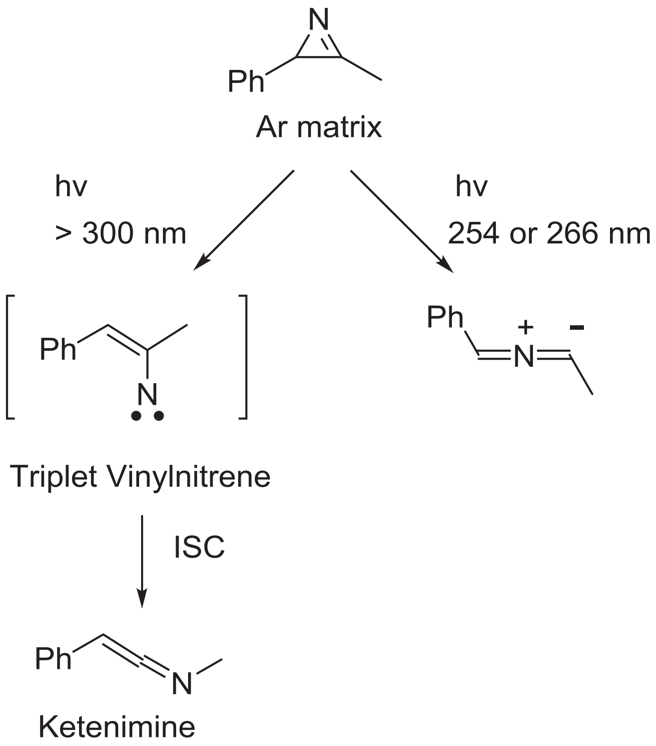
In this article, we report the photochemistry of 2-azidovinylbenzene (**1**) and 2-phenyl-2*H*-azirine (**2**) in cryogenic argon matrices as a function of irradiation wavelength. Because the phenyl chromophore is in conjugation with the vinyl azide moiety in **1**, but is not conjugated with the C═N moiety in azirine **2**, it is possible to compare their photochemistry to determine whether vinyl azide **1** reacts on its singlet or triplet surface upon direct irradiation. The photochemistry of azirine **2** is strongly wavelength

---

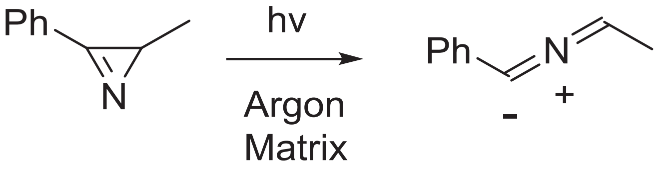
* Corresponding author.
E-mail address: Anna.Gudmundsdottir@uc.edu (A.D. Gudmundsdottir).

https://doi.org/10.1016/j.molstruc.2018.04.042
0022-2860/© 2018 Published by Elsevier B.V.

Please cite this article in press as: O. Osisioma, et al., Wavelength-dependent photochemistry of 2-azidovinylbenzene and 2-phenyl-2*H*-azirine, Journal of Molecular Structure (2018), https://doi.org/10.1016/j.molstruc.2018.04.042



Scheme 1. Photolysis of 3-methyl-2-phenyl-2*H*-azirine in argon matrices.



Scheme 2. Photolysis of 2-methyl-3-phenyl-2*H*-azirine in argon matrices.

dependent, whereas the reactivity of vinyl azide **1** is relatively less affected by the irradiation wavelength.

2. Experimental

2.1. Synthesis of 1

Vinyl azide **1** was synthesized according to a published procedure [8]. A catalytic amount of $CuSO_4$ (80 mg, 0.50 mmol) was added to NaN_3 (390 mg, 6.0 mmol) and dissolved in methanol (15 mL). *Trans*-2-phenylvinylboronic acid (0.739 g, 5.0 mmol) was added to the solution, and the resulting mixture was stirred until thin layer chromatography (TLC) showed complete depletion of the starting material and formation of a new product. The solvent was removed under vacuum and the resulting oil was dissolved in petroleum ether. After washing with water, the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum, providing vinyl azide **1** as an oil (0.4048 g, 2.79 mmol, 56% yield). Characterization of vinyl azide **1** by IR and ^1H NMR spectroscopy agreed well with the data reported in the literature [9]. ^1H NMR ($CDCl_3$, 400 MHz): 6.18 (d, $J = 16$ Hz, 1H), 6.83 (d, $J = 16$ Hz, 1H), 7.2–7.3 (m, 5H) ppm. IR ($CDCl_3$): 2108, 1636, 1260, 1019, 930, 798, 747, 692 cm^{-1}.

2.2. Matrix isolation

Matrix isolation was performed using conventional equipment [10]. Vinyl azide **1** was deposited onto a CsI cold window cooled to 20 K by a CTI closed-cycle refrigerator. A stream of argon was passed over the volatile oil under vacuum to entrap vinyl azide **1** into the argon matrix. In two different sets of experiments, the argon matrix was irradiated over short time intervals with a medium-pressure short-arc 200 W mercury arc lamp through a Pyrex filter (>300 nm) or a 254 nm bandpass filter, which transmitted light between wavelengths of 233–271 nm. Infrared spectra were recorded at a resolution of 1 cm^{-1} using a PerkinElmer Spectrum One FTIR spectrometer during and after matrix deposition and intermittently during irradiation.

2.3. Laser flash photolysis

Laser flash photolysis was carried out using an excimer laser (308 nm, 17 ns) [11]. In a typical experiment, a stock solution of vinyl azide **1** or azirine **2** was prepared in spectroscopic-grade acetonitrile, such that the solution had an absorbance of 0.3–0.6 at 308 nm.

2.4. Photolysis of 1

Vinyl azide **1** was dissolved in chloroform-d_1 in a Pyrex NMR tube sealed with a rubber septum, and argon was bubbled through the solution for 17 min. The resulting solution was irradiated with 10 light-emitting diodes (LEDs; 450 ± 5 nm) in parallel alignment, each with a constant current of 2 mA and a voltage drop of 3.2–3.8 V across each diode. After irradiation for 17 min, ^1H NMR spectroscopy of the reaction mixture showed the formation of azirine **2** (76%) and remaining starting material (24%).

Preparative preparation of azirine 2. Vinyl azide **1** (17 mg, 0.12 mmol) was dissolved in chloroform-d_1 (0.6 mL, 7.49 mmol) and purged with argon for 5 min in a Pyrex NMR tube, which was sealed with a rubber septa cap and irradiated with a mercury-argon lamp for 40 min ^1H NMR spectroscopy verified the formation of azirine **2** (51% yields) [12].^1H NMR ($CDCl_3$, 400 MHz): 9.99 (d, $J = 2$ Hz, 1H), 7.2 (m, 5H), 2.72 (d, $J = 2$ Hz, 1H) ppm.

2.5. Calculations

The geometries were optimized at the B3LYP level of theory with the 6-31+G(d) basis set, as implemented in the Gaussian09 program [13–15]. The transition states were confirmed to have one imaginary vibrational frequency, and intrinsic reaction coordinate calculations were used to verify that the transition states corresponded to the attributed reactant and product [16,17]. To obtain the calculated absorption spectra for the excited states and intermediates, time-dependent density functional theory (TD-DFT) calculations were conducted at the same level of theory with the same basis set.

3. Results

3.1. Photolysis of vinyl azide 1 in solution

A solution of vinyl azide **1** in chloroform,-d_1 was exposed to 450 ± 5 nm LED light for 17 min ^1H NMR spectroscopy revealed the formation of azirine **2** (76%) and remaining starting material (Scheme 3).

Please cite this article in press as: O. Osisioma, et al., Wavelength-dependent photochemistry of 2-azidovinylbenzene and 2-phenyl-2*H*-azirine, Journal of Molecular Structure (2018), https://doi.org/10.1016/j.molstruc.2018.04.042