Triplet vinylnitrenes

UPASANA BANERJEE, KOSALA THENNA-HEWA and
ANNA D. GUDMUNDSDOTTIR

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221, USA
e-mail: gudmunad@ucmail.uc.edu

I. INTRODUCTION

Organic azides are one of the more adaptable functional groups in synthetic chemistry because they react easily with both electrophiles and nucleophiles to form new C−N bonds[1]. The dipolar character of organic azides makes them suitable for cycloaddition to alkynes and

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

olefins, which has been used in numerous syntheses[2–8]. The quest for sustainable chemistry has inspired interest in using sunlight[9, 10], a natural resource, or energy-efficient light-emitting diodes (LEDs) for synthetic applications. Although most organic azides do not absorb visible light, transition metal photocatalysts can be used to realize visible-light-driven photochemical transformations[11]. For example, photocatalytic sensitization of aryl and vinyl azides has been successfully used for selective C−N bond formation[12, 13]. Generally, the photochemistry of organic azides has been of limited synthetic utility, as their reactivity is complex and depends on multiple factors, such as molecular structure and whether excitation occurs directly or with sensitizers[14–20]. Upon excitation, organic azides can form products in a concerted manner or form nitrene intermediates, and their reactivity depends on their electron configuration and substituents. This chapter focuses on the formation and characterization of triplet vinylnitrenes from various precursors and their intriguing reactivity, with emphasis on identifying the factors that control the reactivity, both in solution and in cryogenic matrices. A better understanding of the reactivity of vinylnitrenes will make it possible to use them in synthetic applications. It should, however, be noted that this chapter is biased toward the authors' own research on triplet vinylnitrene intermediates.

II. ARYLNITRENES

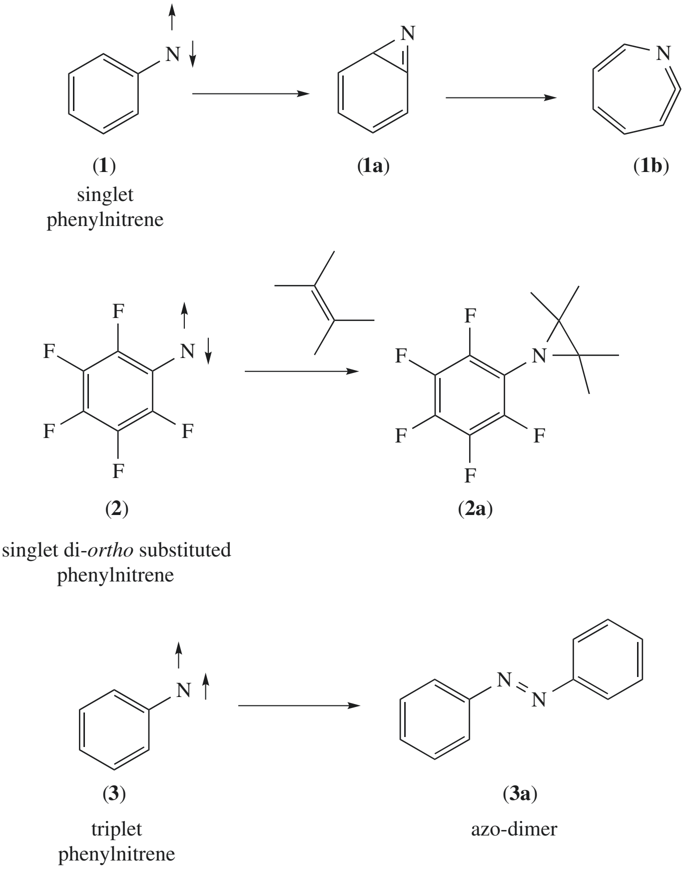
Generally, nitrenes are electron-deficient short-lived intermediates that can be stabilized by electron-donating substituents[15, 16, 21–23]. The formation of arylnitrenes and their reactivity have been studied extensively. For example, singlet arylnitrenes are highly reactive and insert into themselves to yield unimolecular reactivity, as shown in Scheme 1. Arylnitrenium ions generated from singlet nitrenes are also well documented[24–27]. However, singlet arylnitrenes with at least two ortho substituents are sufficiently long-lived to insert into surrounding bonds, which makes them useful in applications such as polymer cross-linking and surface modification.[21, 23, 28–36] In contrast, triplet arylnitrenes are long-lived intermediates in solution[37–39], which do not react with the solvent but mainly decay to form azo-dimers (Scheme 1). Triplet arylnitrenes are stable at cryogenic temperatures and can be directly detected spectroscopically[40]. Because they are thermally stable at cryogenic temperatures, triplet arylnitrenes are sufficiently long-lived to have a rich photochemistry.

The most common method for forming singlet arylnitrenes is to activate aryl azides with heat or UV light, resulting in the extrusion of molecular N_2 and the formation of singlet arylnitrenes. In comparison, triplet arylnitrenes can be formed by triplet-sensitized irradiation of aryl azides. In addition, triplet arylnitrenes can be formed at cryogenic temperatures by direct irradiation of aryl azides, as the intersystem crossing of singlet arylnitrenes to their triplet configurations competes effectively with the unimolecular reactivity at low temperatures. The characterization and reactivity of arylnitrenes have been reviewed in several recent articles and book chapters[16, 19–22, 37, 41–45].

III. ALKYLNITRENES

Alkylnitrenes, like arylnitrenes, are stabilized by electron-donating alkyl groups, and they have been detected and characterized in solution and at cryogenic temperatures[46–48]. In solution, alkylnitrenes are long-lived intermediates that decay to form the corresponding azo products (Scheme 2), and thus, they exhibit similar behavior to triplet arylnitrenes[49–51]. Furthermore, we demonstrated that the azo dimers are formed by dimerization of two alkylnitrenes, rather than a triplet alkylnitrene reacting with its azido precursor to form a tetrazete followed by nitrogen loss[52]. Electron spin resonance (ESR) spectroscopy reveals, as expected, that the unpaired electrons of triplet alkylnitrenes are localized on the nitrogen atoms[19, 20, 50]. Triplet alkylnitrenes are mainly formed by triplet-sensitized photolysis of alkyl azides[51–53]. A significant

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



(**1**)
singlet
phenylnitrene

(**1a**)

(**1b**)

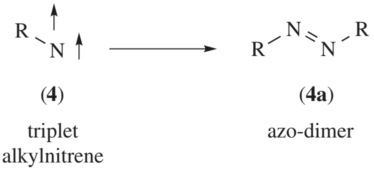
(**2**)
singlet di-*ortho* substituted
phenylnitrene

(**2a**)

(**3**)
triplet
phenylnitrene

(**3a**)
azo-dimer

SCHEME 1. Reactivity of singlet and triplet arylnitrenes.



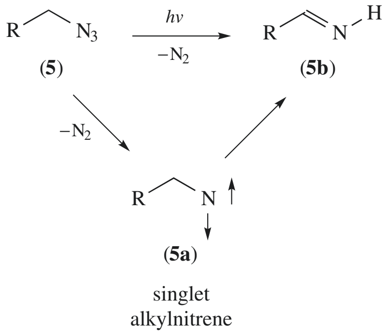
(**4**)
triplet
alkylnitrene

(**4a**)
azo-dimer

SCHEME 2. Reactivity of triplet alkylnitrenes.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

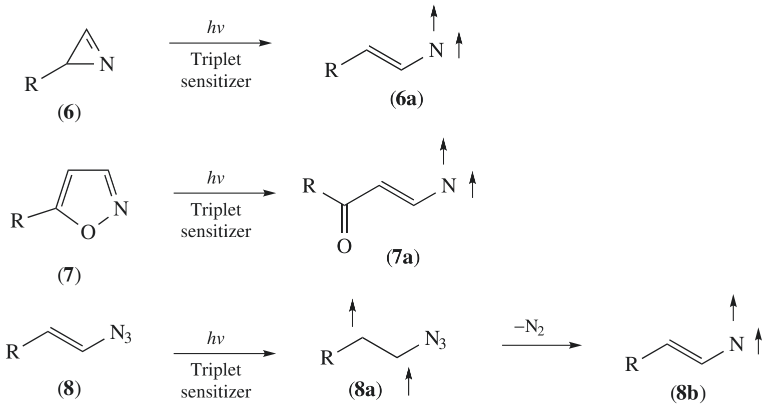
difference between the reactivities of aryl- and alkyl-nitrenes is that triplet alkylnitrenes cannot be formed by intersystem crossing of singlet alkylnitrenes, as direct photolysis of alkyl azides at cryogenic temperatures generally does not yield triplet alkylnitrenes[54–56], although a few exceptions have been reported[57–59]. Direct irradiation of alkyl azides in solution does not yield triplet alkylnitrenes, either because alkyl azides undergo concerted rearrangement in the singlet excited state or because alkylnitrenes react faster than they intersystem cross to form their triplet counterparts (Scheme 3)[57,60].



SCHEME 3. Direct irradiation of alkyl azides.

IV. VINYLNITRENES

Although triplet vinylnitrenes have an electron-donating substituent, they display very different reactivity from triplet alkyl- and aryl-nitrenes, as they are generally short-lived intermediates that have a lifetime of a few microseconds in solution and decay by intersystem crossing[61]. Their reactivity in solution and cryogenic matrices is discussed in more detail in the following sections. Triplet vinylnitrenes can be formed by photolysis of azirines, isoxazoles, and vinyl azides (Scheme 4); however, photolysis of these precursors does not yield triplet vinylnitrenes



SCHEME 4. 2*H*-Azirines, isoxazoles, and vinyl azides as precursors to triplet vinylnitrenes.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

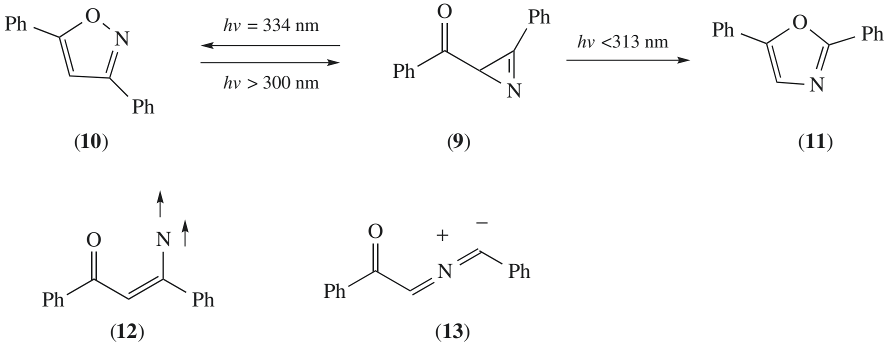
without the involvement of a triplet sensitizer. Thus, if direct irradiation of these precursors yields the corresponding singlet vinylnitrenes, it can be concluded that they react faster to form products than they intersystem cross to their triplet configurations. It is, however, just as possible that the singlet excited states of these precursors react in a concerted manner to form products, rather than forming singlet vinylnitrenes.

Most reported intramolecular sensitizations of azirine derivatives that successfully yield triplet vinylnitrenes have been carried out with acetophenone or naphthalene as the sensitizer moiety (triplet energies of 74 and 61 kcal mol^{-1}, respectively)[62,63]. Similarly, intramolecular sensitizations of vinyl azide derivatives with an acetophenone or naphthoquinone (58 kcal mol^{-1})[64] sensitizer have effectively yielded triplet vinylnitrenes. However, other triplet sensitizers may also be useful. The energy gap between the triplet and singlet configurations of vinylnitrenes will be discussed in Section C.

A. Formation, Characterization, and Reactivity of Triplet Vinylnitrenes in Solution

1. Triplet Vinylnitrenes from 2H-Azirines

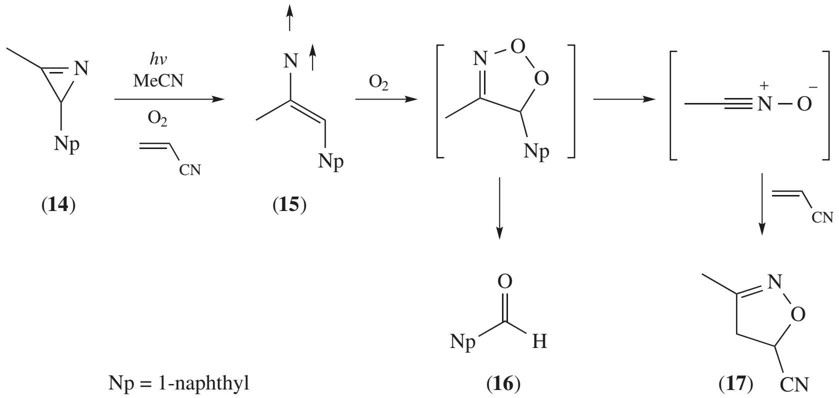
Singh and coworkers showed that azirine (**9**), which has an adjacent carbonyl group, can be converted photochemically into isoxazole (**10**) with 334 nm irradiation, whereas short-wavelength irradiation resulted in the formation of oxazole (**11**) (Scheme 5)[65,66]. Furthermore, irradiation of isoxazole (**10**) resulted in conversion into azirine (**9**). The authors theorized that the interconversion of azirine (**9**) and isoxazole (**10**) occurs through triplet vinylnitrene intermediate (**12**), whereas transformation of azirine (**9**) into oxazole (**11**) occurs through ylide (**13**)[65].



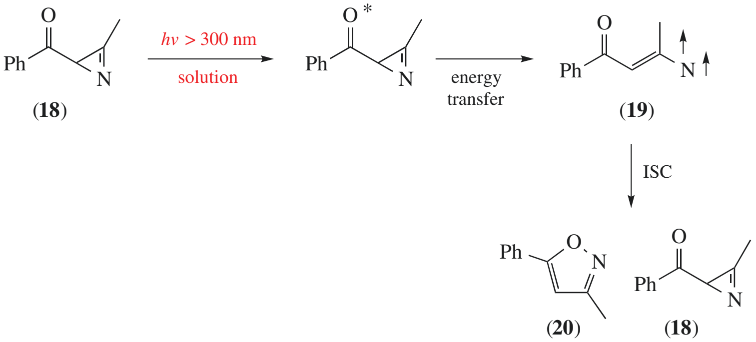
SCHEME 5. Photoreactivity of azirine (**9**) as a function of irradiation wavelength.

One of the challenges in identifying reactivity attributable to the formation of triplet vinylnitrenes is that vinylnitrenes intersystem cross to re-form the starting materials, unless they have an intramolecular trapping agent such as a carbonyl group. For example, Inui and Murata did not observe any new products during the photolysis of azirine (**14**) in the presence of acrylonitrile in argon-saturated acetonitrile, presumably because azirine (**14**) yields triplet vinylnitrene (**15**), which decays by intersystem crossing to re-form azirine (**14**)[67–69]. In contrast, photolysis of **14** in oxygen-saturated acetonitrile resulted in the formation of products **16** and **17**, which the authors attributed to trapping of triplet vinylnitrene (**15**), as shown in Scheme 6.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



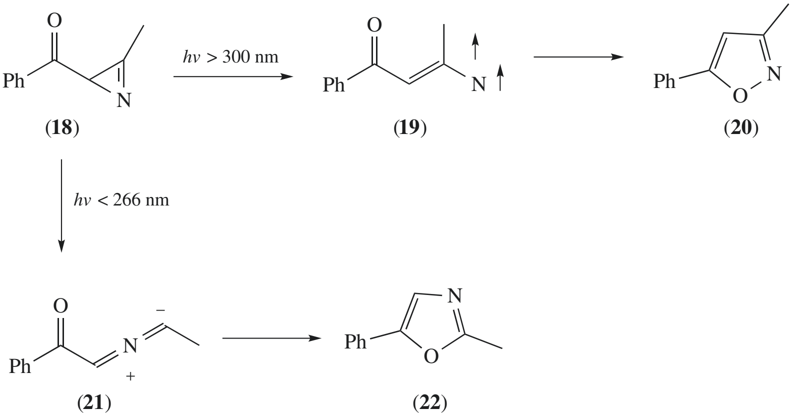
SCHEME 6. Photoreactivity of azirine (**14**) in oxygen-saturated acetonitrile.



SCHEME 7. Proposed mechanism for forming triplet vinylnitrene (**19**) from azirine (**18**).

Because it is difficult to determine whether irradiation of azirine derivatives results in the formation of triplet vinylnitrenes based on product studies, we have relied on laser flash photolysis to identify triplet vinylnitrenes in solution. The first direct detection of a vinylnitrene in solution was realized by laser flash photolysis of azirine (**18**), which has an acetophenone moiety as a built-in triplet sensitizer (Scheme 7)[61]. Irradiation at longer wavelengths (>300 nm) allows selective excitation of the ketone chromophore in **18**. The triplet excited state of the ketone undergoes energy transfer to form the triplet excited state of the azirine, which undergoes cleavage of the C–N bond to form triplet vinylnitrene (**19**) (Scheme 8). In contrast to triplet alkyl- and aryl-nitrenes, vinylnitrene (**19**) has a lifetime of only a few microseconds in both acetonitrile and methanol solutions, and it is efficiently quenched with oxygen[70]. Triplet vinylnitrene (**19**) is short-lived because it intersystem crosses effectively to form isoxazole (**20**) and to re-form azirine (**18**). Furthermore, irradiation of azirine (**18**) at shorter wavelengths results in ylide (**21**), which is formed upon direct excitation of the azirine chromophore, followed by cleavage of the C–C bond (Scheme 8)[71].

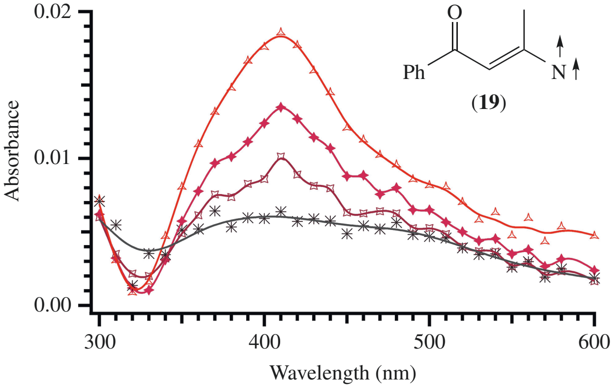
PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



SCHEME 8. Wavelength-dependent photoreactivity of azirine (**18**).

Ylide (**21**), which has a lifetime of 6 μs in acetonitrile, decays to form oxazole (**22**), and, as expected, its lifetime is not affected by oxygen. Singh and coworkers showed that the photochemistry of azirine (**18**) is wavelength dependent[65], with short-wavelength irradiation yielding oxazole (**22**) and longer wavelength irradiation resulting in isoxazole (**20**). Using laser flash photolysis, we established that isoxazole (**20**) is formed through triplet vinylnitrene (**19**), whereas oxazole (**22**) originates from ylide (**21**) (Figure 1)[61].

The photoreactivity of azirine (**23**) further confirmed the wavelength dependency of the photochemistry of azirines in solution (Scheme 9)[70]. Laser flash photolysis of azirine (**23**) with a



(a)

FIGURE 1. Transient absorption spectra obtained by laser flash photolysis of azirine (**18**) with (a) a 308 nm laser and (b) a 266 nm laser collected between (A) 0.19 and 1.3 μs (red trace) and (B) 18 and 39 μs (black trace) after the laser pulse. Adapted with permission from Ref. 61. © 2011 American Chemical Society.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

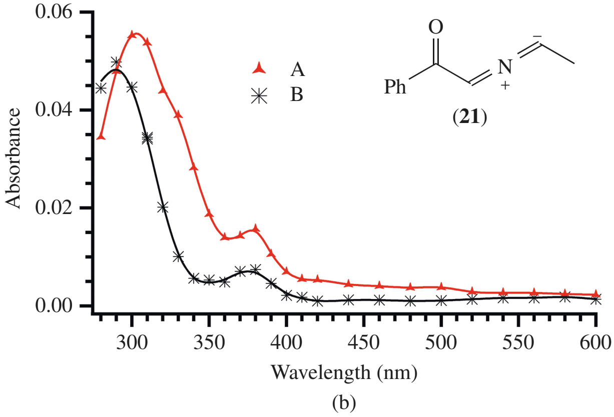
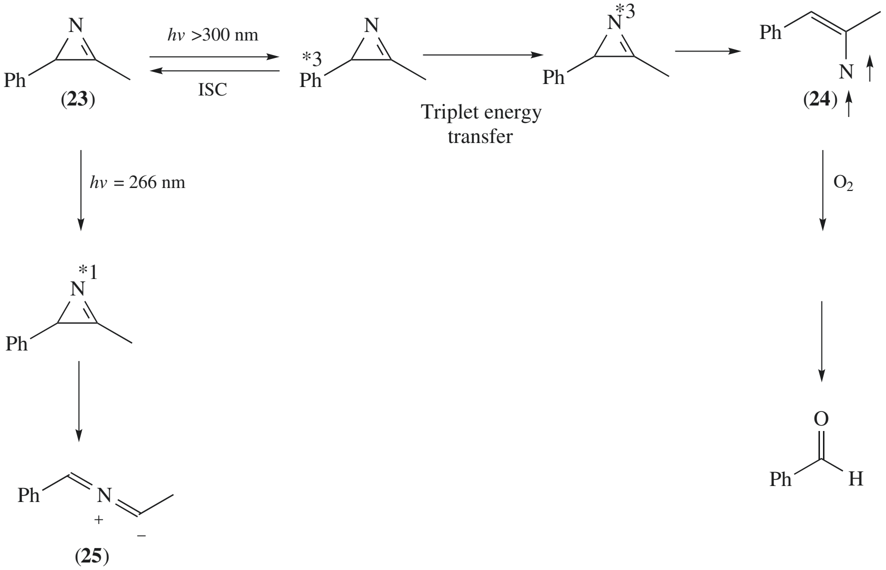


FIGURE 1. (*continued*)



SCHEME 9. Wavelength-dependent photochemistry of azirine (**23**).

308 nm laser resulted in transient absorption owing to the formation of triplet vinylnitrene (**24**), which has λ_{max} at 440 nm and a lifetime of ~7 μs in acetonitrile (Figure 2). Quenching studies supported the assignment of this transient absorption to triplet vinylnitrene (**24**), as the precursor to triplet vinylnitrene (**24**) was quenched by isoprene. In contrast, laser flash photolysis of azirine (**23**) with a 266 nm laser resulted in a different transient spectrum with λ_{max} at ~340 nm, which was assigned to ylide (**25**) (Figure 3). The lifetime of ylide (**25**) was determined to be only 14 μs. Photolysis of azirine (**23**) in acetonitrile through a Pyrex filter does

---

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

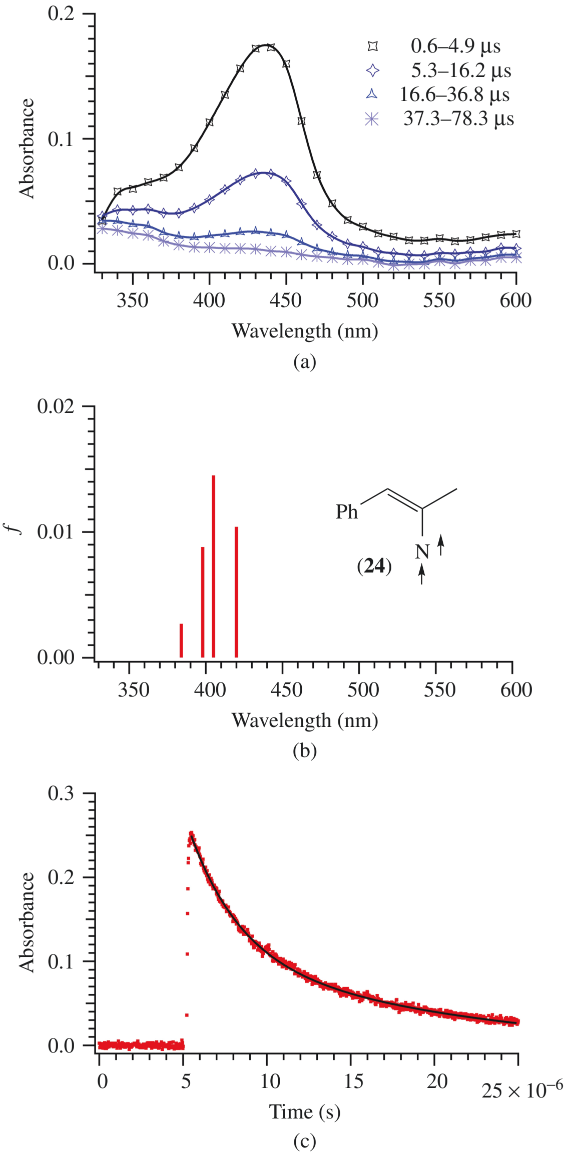


FIGURE 2. (a) Transient absorption spectra obtained by laser flash photolysis of azirine (**23**) in acetonitrile with a 308 nm laser. (b) TD-DFT calculated electronic transitions for triplet vinylnitrene (**24**). (c) Kinetic trace obtained at 460 nm. Adapted with permission from Ref. 70. © 2014 American Chemical Society.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

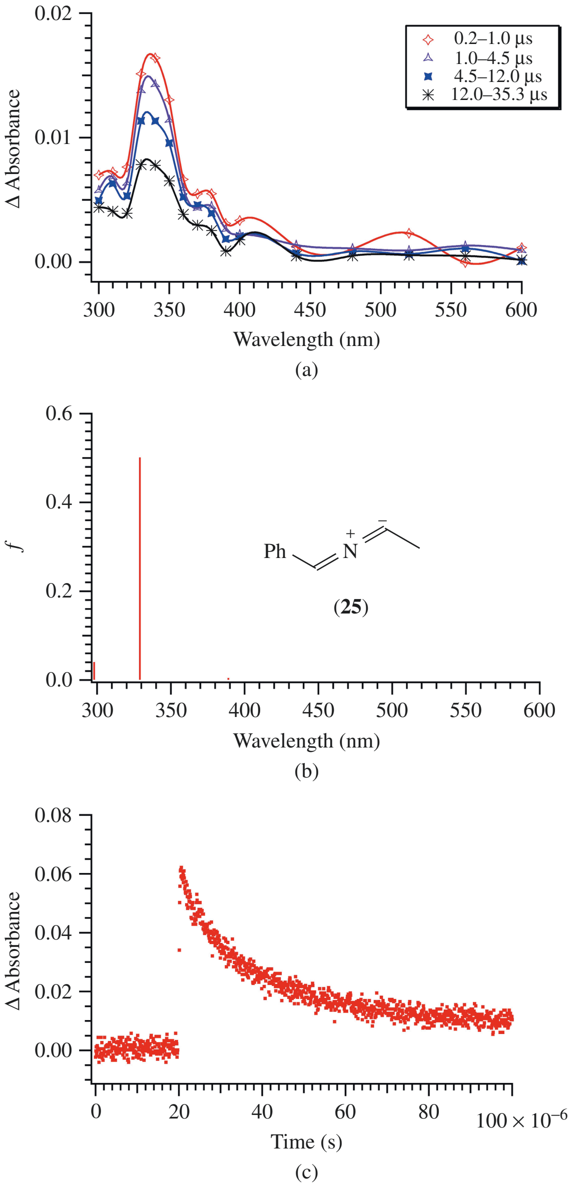
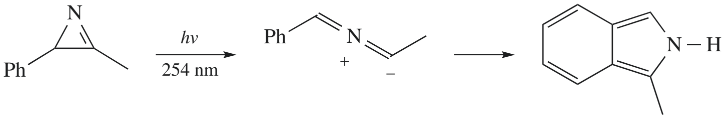


FIGURE 3. (a) Transient absorption spectra obtained by laser flash photolysis of azirine (**23**) in acetonitrile with a 266 nm laser. (b) TD-DFT calculated electronic transitions for ylide (**25**). (c) Kinetic trace obtained at 340 nm. Reproduced from Ref. 71 with permission of CSIRO Publishing.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

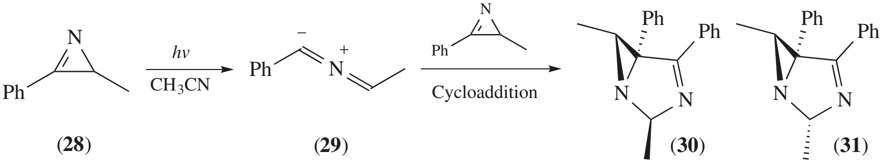
not yield any products owing to intersystem crossing of triplet vinylnitrene (**24**) to re-form azirine (**23**), although triplet vinylnitrene (**24**) can be trapped with molecular oxygen to form benzaldehyde (Scheme 9). In contrast, irradiation of azirine (**23**) at 254 nm results in the formation of heterocycle (**26**) through ylide (**25**) (Scheme 10)[70, 72, 73]. Because laser flash photolysis of azirine (**23**) confirmed that the reactivity under longer wavelength irradiation occurs on the triplet surface, we theorized that the phenyl chromophore acts as a triplet sensitizer, as it is not in conjugation with the azirine moiety. In more detail, at longer wavelengths, it is possible to selectively excite the phenyl chromophore in azirine (**23**), which intersystem crosses to its triplet configuration and transfers its energy to the azirine moiety. In contrast, at shorter wavelengths, the azirine chromophore must absorb directly to form ylide (**25**).



(**23**) (**25**) (**26**)

SCHEME 10. Products formed by irradiation of azirine (**23**) at 254 nm.

To further support this notion, we investigated the photochemistry of azirine (**28**), an isomer of azirine (**23**) in which the phenyl and azirine moieties are in conjugation (Scheme 11)[70]. The photochemistry of azirine (**28**) is not wavelength dependent, and laser flash photolysis demonstrated that excitation of azirine (**28**) results in the formation of ylide (**29**) (Figure 4). In addition, ylide (**29**) is long-lived, as it does not decay by unimolecular reactivity, as observed for ylide (**25**), but rather by cycloaddition to azirine (**28**) to form heterocycles (**30**) and (**31**)[70, 72, 73].



(**28**) (**29**) (**30**) (**31**)

SCHEME 11. Photoreactivity of phenyl-conjugated azirine (**28**).

2. Triplet vinylnitrenes from isoxazoles

Further, we verified with laser flash photolysis that both azirine (**9**) and isoxazole (**10**) serve as precursors to triplet vinylnitrene (**12**) (Scheme 12)[74]. Laser flash photolysis of isoxazole (**10**) in argon-saturated solution showed the formation of triplet vinylnitrene (**12**), which has a broad absorption band with λ_{max} at 440 nm ($\tau \sim 1.8\ \mu s$). Similarly, laser flash photolysis of azirine (**9**) in argon-saturated acetonitrile resulted in the formation of triplet vinylnitrene (**12**), and also ylide (**13**) (λ_{max} at 440 nm, $\tau = 13\ \mu s$).

This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

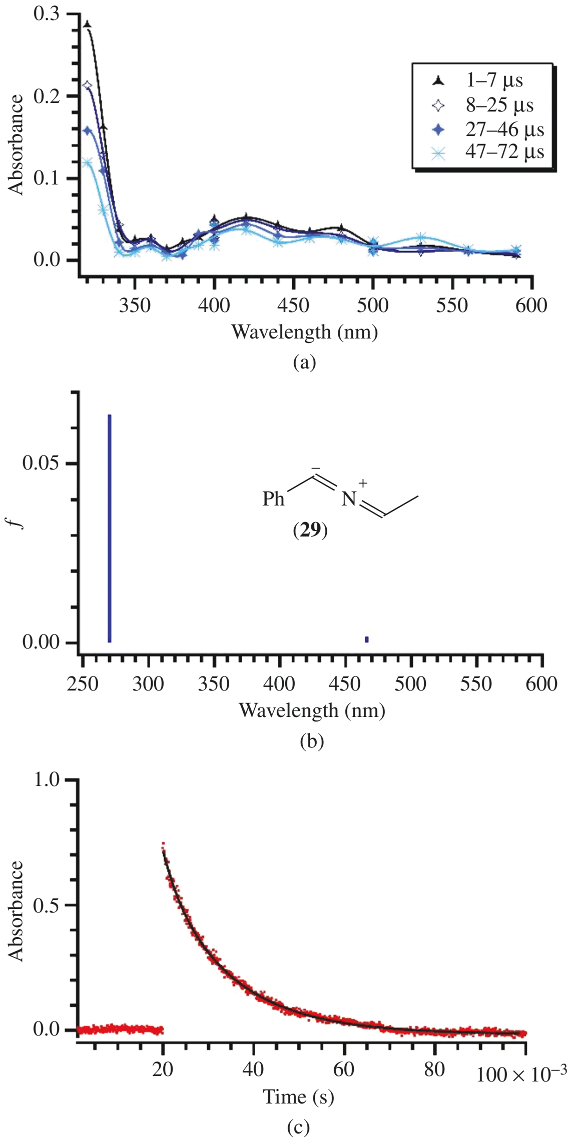
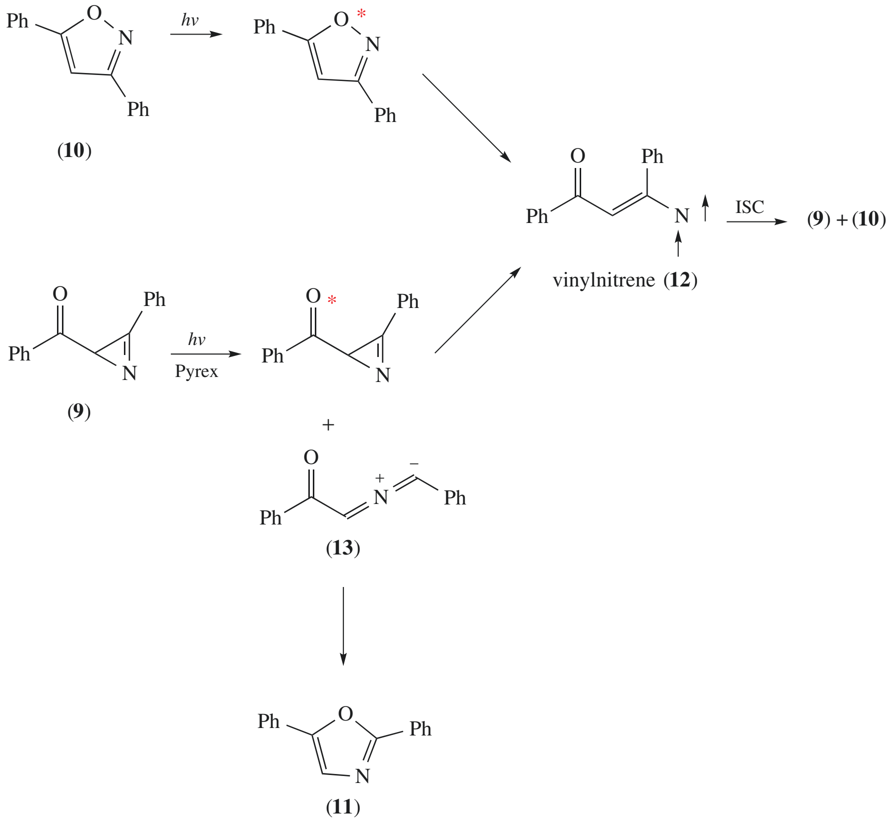
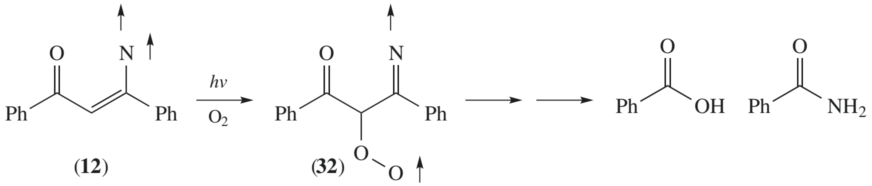


FIGURE 4. (a) Transient absorption spectra of ylide (**29**) obtained by laser flash photolysis of azirine (**28**) in acetonitrile with a 308 nm laser. (b) TD-DFT calculated electronic transitions for ylide (**29**). (c) Kinetic trace obtained at 320 nm. Adapted with permission from Ref. 70. © 2014 American Chemical Society.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



SCHEME 12. Proposed mechanism for forming vinylnitrene (**12**) from azirine (**9**) and isoxazole (**10**).



SCHEME 13. Reactivity of vinylnitrene (**12**) in oxygen-saturated solution.

Photolysis of azirine (**9**) in oxygen-saturated chloroform enabled trapping of triplet vinylnitrene (**12**) to form small amounts of benzoic acid and benzamide (Scheme 13) in addition to isoxazole (**10**) and oxazole (**11**). Similarly, irradiation of isoxazole (**10**) in oxygen-saturated chloroform-*d* yielded small amounts of benzoic acid and benzamide in addition to azirine (**9**). Furthermore, laser flash photolysis of azirine (**9**) and isoxazole (**10**) in oxygen-saturated solution (Figure 5) allowed the direct detection of peroxide radical (**32**) (λ_{max} at 360 nm,

---

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

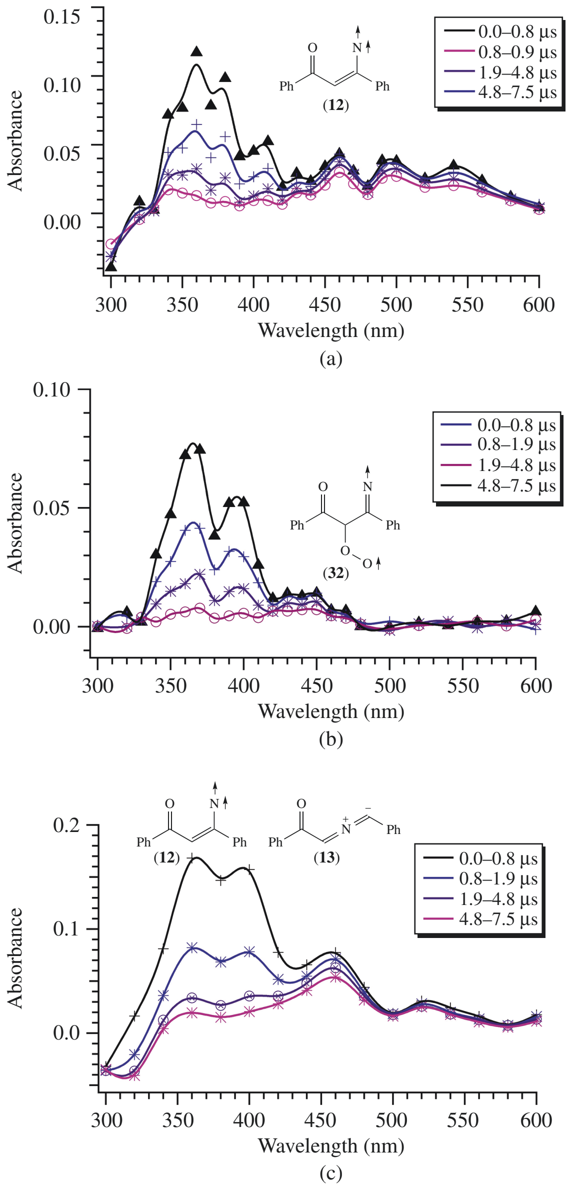


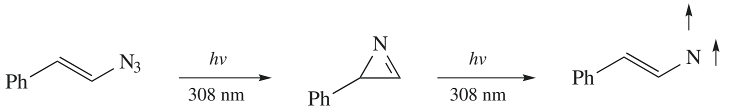
FIGURE 5. Transient absorption spectra obtained by laser flash photolysis of isoxazole (**10**) in (a) argon-saturated and (b) oxygen-saturated acetonitrile. (c) Transient absorption spectra obtained by laser flash photolysis of azirine (**9**) in argon-saturated methanol with a 308 nm laser. Adapted with permission from Ref. 74. © 2013 American Chemical Society.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

$\tau \sim 0.7\ \mu s$). The rate constant for the reaction of vinylnitrene (**12**) with oxygen was determined to be $2 \times 10^9\ M^{-1}\ s^{-1}$. As vinylnitrene (**12**) has significant radical character on the β-carbon atom, it reacts with oxygen much more efficiently than is typically observed for triplet alkyl- or aryl-nitrenes[74]. In comparison, triplet alkylnitrenes have been reported to react with oxygen with a rate constant of $\sim 5 \times 10^4\ M^{-1}\ s^{-1}$, whereas triplet arylnitrenes react faster, with reported rates constants between 10^5 and $10^7\ M^{-1}\ s^{-1}$[38, 50, 75].

3. Vinylnitrenes from vinyl azides

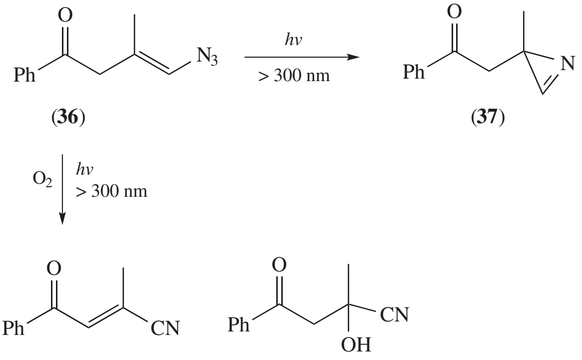
a. Direct photolysis of simple vinyl azides. We investigated the solution photochemistry of vinyl azide (**33**), in which the vinyl azido chromophore is in conjugation with the phenyl moiety, and found that it forms azirine (**34**) (Scheme 14), as reported earlier by Isomura and coworkers[76] Laser flash photolysis of vinyl azide (**33**) did not yield any transient absorption on the nanosecond timescale[77]. In contrast, laser flash photolysis of azirine (**34**) resulted in transient absorption that was assigned to the formation of triplet vinylnitrene (**35**). Thus, it was concluded that vinyl azide (**33**) reacts on its singlet surface to form azirine (**34**).



(**33**) (**34**) (**35**)

SCHEME 14. Photoreactivity of vinyl azide (**33**).

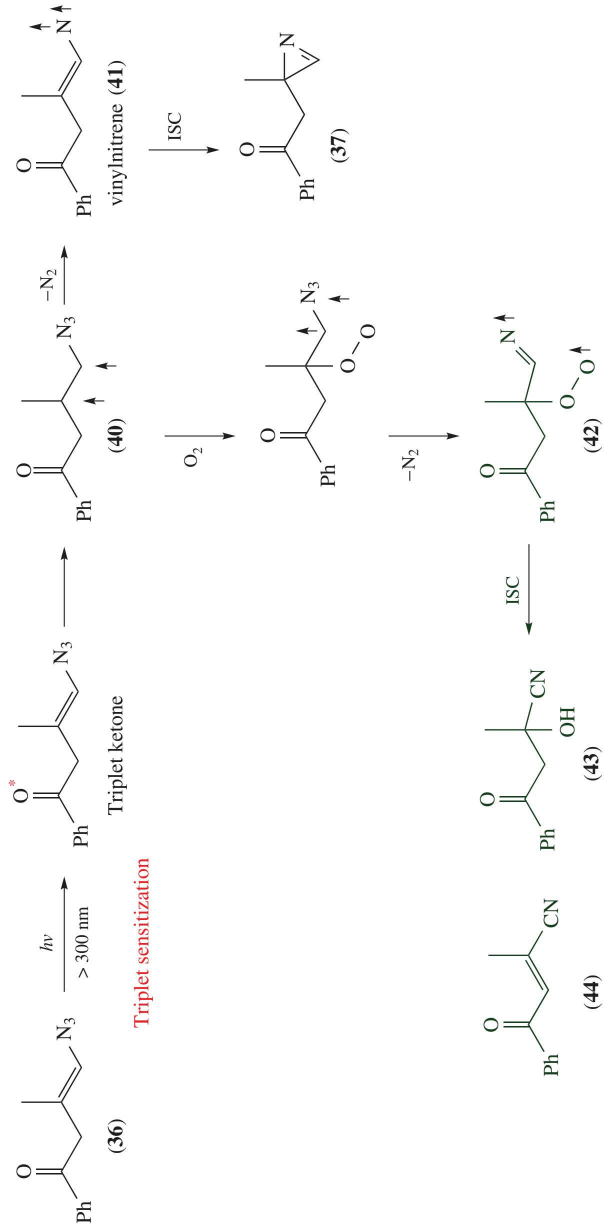
b. Sensitized photolysis of flexible vinyl azides. Because direct photolysis of vinyl azide (**33**) does not yield any reactivity from its triplet excited state, we prepared vinyl azide (**36**), which has a built-in triplet acetophenone sensitizer (Scheme 15)[78]. Irradiation of vinyl azide (**36**) in argon-saturated solution resulted in quantitative formation of azirine (**37**), whereas in oxygen-saturated solution, cyanides (**38**) and (**39**) were formed. With the aid of laser flash photolysis and density functional theory (DFT) calculations, it was determined that excitation of vinyl azide (**36**) results in the formation of the triplet excited state of its ketone chromophore, which undergoes energy transfer to form triplet biradical **40** (Scheme 16



(**36**) (**37**) (**38**) (**39**)

SCHEME 15. Photoreactivity of flexible vinyl azide (**36**).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



SCHEME 16. Proposed mechanism for the photoreactivity of vinyl azide (**36**).

This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

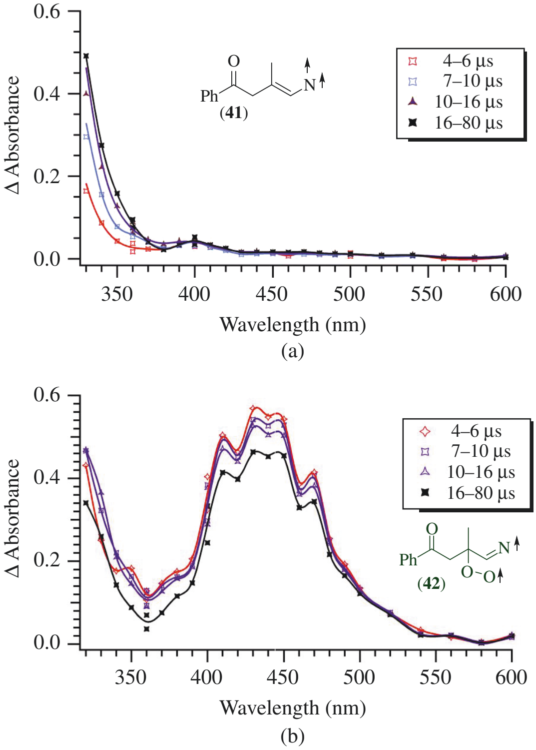
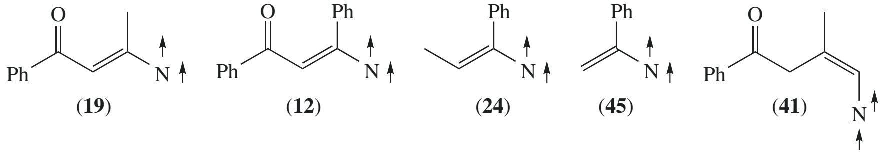


FIGURE 6. Transient absorption spectra obtained by laser flash photolysis of vinyl azide (**36**) in (a) argon- and (b) oxygen-saturated acetonitrile with a 308 nm laser. Adapted with permission from Ref. 78. © 2014 American Chemical Society.

and Figure 6). Biradical **40** decays by expelling molecular N_2 to form triplet vinylnitrene (**41**), which has a broad absorption band between 310 and 330 nm. The rate constant for forming vinylnitrene (**41**) from biradical **40** is $3.0 \times 10^5\ s^{-1}$ ($\tau = 3.3\ \mu s$) in methanol, but the lifetime of vinylnitrene (**41**), which is limited by intersystem crossing to azirine (**37**), is considerable longer (on the order of 1 ms). In comparison, laser flash photolysis in oxygen-saturated solution resulted in a different transient spectrum because biradical **40** was efficiently intercepted by molecular oxygen to form peroxide biradical **42** (λ_{max} at ~420 nm). The rate constant for forming peroxide biradical **42** is $4.9 \times 10^6\ s^{-1}$ ($\tau = 204$ ns) in oxygen-saturated methanol, whereas its decay rate constant is $1.9 \times 10^5\ s^{-1}$ ($\tau = 5.2\ \mu s$). Thus, product studies and laser flash photolysis of vinyl azide (**36**) highlighted that triplet vinylnitrene can be formed by intermolecular sensitization of vinyl azides. However, the precursor to the triplet vinylnitrene is effectively trapped by molecular oxygen to form the peroxide biradical following extrusion of molecular N_2[78].

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

c. Triplet-sensitized photolysis of cyclic vinyl azides. As vinylnitrenes can be trapped by molecular oxygen in solution to form new C−O bonds, they are expected to have significant 1,3-biradical character, and thus, rotation around the vinyl bond must be possible at ambient temperature. DFT calculations also predict that triplet vinylnitrenes have significant 1,3-biradical character, and therefore, the rotational barrier around the vinyl bond in triplet vinylnitrenes is much less than that around the vinyl bond of ground state vinyl azides. The calculated rotational barriers for several vinylnitrenes are shown in Scheme 17. Furthermore, because triplet vinylnitrenes decay by efficient intersystem crossing to form new C−N or C−O bonds, yielding azirine or isoxazole derivatives, it is anticipated that rotation around the flexible vinyl bond is necessary to access conformers that are well set up for intersystem crossing to singlet products. We theorized that triplet vinylnitrenes decay by intersystem crossing because they are flexible, and thus, we were prompted to studied cyclic vinyl azides, which are not flexible.

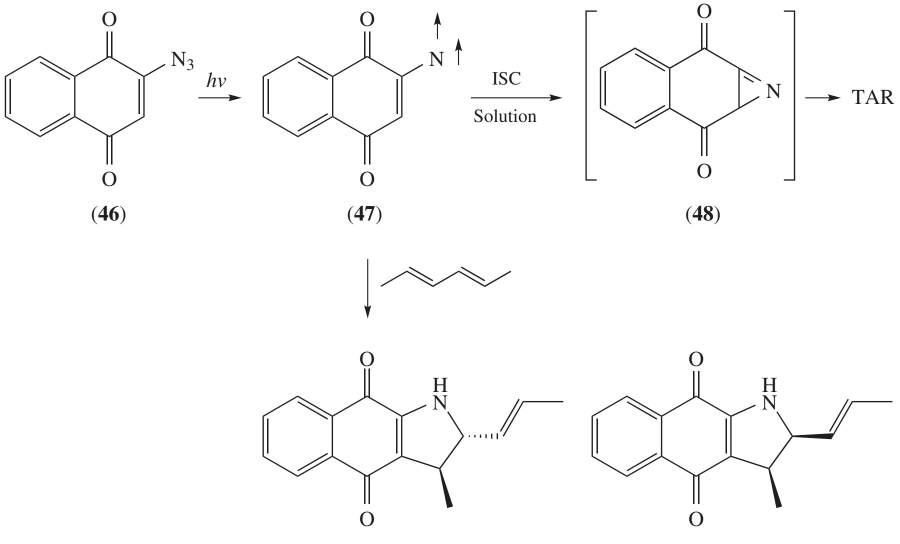


(**19**) (**12**) (**24**) (**45**) (**41**)

Calculated rotational barrier (kcal/mol) around the vinyl bond (DFT/B3LYP/6–31 + G(d))

(**19**)	(**12**)	(**24**)	(**45**)	(**41**)
11	8	10	11	>14

SCHEME 17. Calculated rotational barriers for vinylnitrenes.



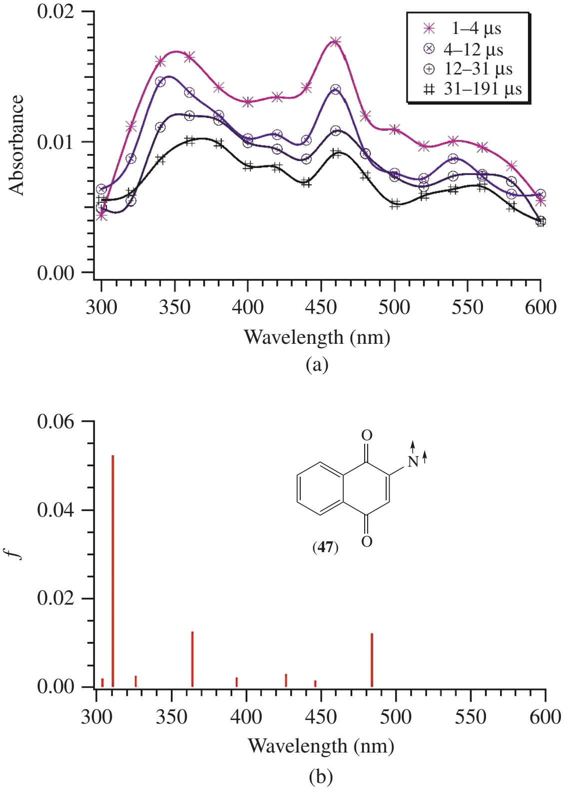
(**46**) (**47**) (**48**) (**49**) (**50**)

SCHEME 18. Photochemistry of cyclic vinyl azide (**46**).

PATAI'S Chemistry of Functional Groups, Online 2009−2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

We prepared vinyl azide (**46**), which is part of a bicyclic structure and has a built-in triplet sensitizer (naphthoquinone), and studied its photochemistry (Scheme 18)[79]. Upon irradiation, vinyl azide (**46**) forms polymeric tar, but products **49** and **50** can be formed by trapping with dienes. We theorized that vinyl azide (**46**) forms triplet vinylnitrene (**47**) in solution. Vinylnitrene (**47**) then intersystem crosses to azirine (**48**), which is not stable and polymerizes. Furthermore, laser flash photolysis of vinyl azide (**46**) yielded triplet vinylnitrene (**47**), which has a broad absorption band and a lifetime of ~22 μs in argon-saturated acetonitrile (Figure 7). We concluded that, despite its cyclic structure, vinylnitrene (**47**) is flexible enough at ambient temperature to decay by intersystem crossing, although it can be trapped in bimolecular reactions[79, 80].

To further explore the effect of flexibility on the reactivity of vinylnitrenes, we investigated vinyl azide (**51**), which has a built-in triplet sensitizer (acetophenone) and is part of a bicyclic structure, similar to vinyl azide (**46**) (Scheme 19). However, owing to its smaller ring structure, vinyl azide (**51**) is more strained than vinyl azide (**46**)[81]. Laser flash photolysis of vinyl azide (**51**) yielded triplet vinylnitrene (**52**), which has a broad absorption band from 300 to

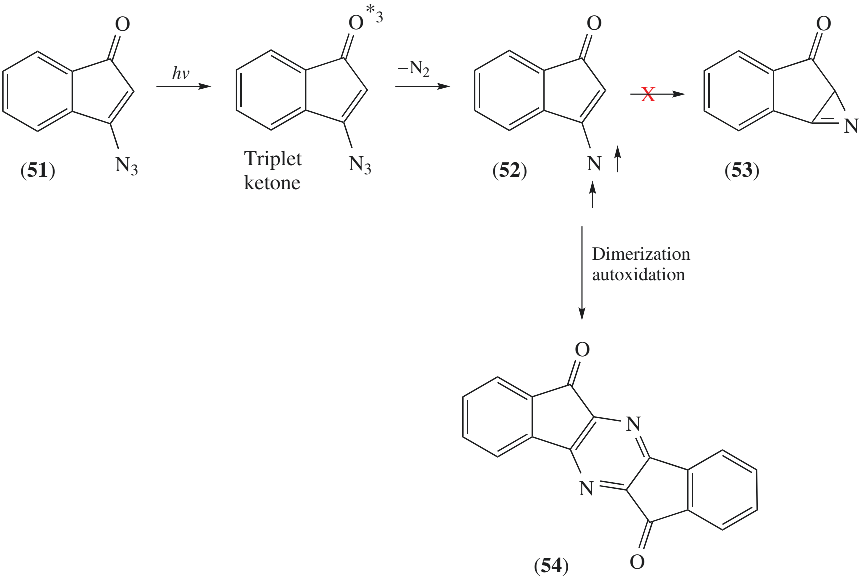


(a)

(b)

FIGURE 7. (a) Transient absorption spectra obtained by laser flash photolysis of vinyl azide (**46**) in argon-saturated acetonitrile with a 308 nm laser. (b) TD-DFT calculated electronic transitions for triplet vinylnitrene (**47**). Adapted with permission from Ref. 79. © 2015 American Chemical Society.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



SCHEME 19. Photoreactivity of vinyl azide (**51**).

520 nm with λ_{max} at 340 and 480 nm (Figure 8). Interestingly, vinylnitrene (**52**) did not decay by intersystem crossing to form azirine (**53**), but selectively dimerized to form **54**. The steric strain of the molecular structure prevents triplet vinylnitrene (**52**) from decaying by intersystem crossing to form azirine (**53**) because azirine (**53**) is higher in energy than triplet vinylnitrene (**52**). Additionally, because vinyl azide (**51**) is highly conjugated, it absorbs visible light, and irradiation with a 405 nm LED is sufficient for quantitative transformation of vinyl azide (**51**) to dimer (**54**) (Figure 9).

B. Formation, Characterization, and Reactivity of Triplet Vinylnitrenes in Cryogenic Matrices

Until recently, there have been no reports on the direct detection of triplet vinylnitrenes in cryogenic matrices, presumably because vinylnitrenes intersystem cross to products, similar to the behavior observed in solution[79,81]. However, as cyclic vinylnitrenes (**47**) and (**52**) are stable at cryogenic temperatures, their physical properties and photoreactivity can be explored at cryogenic temperatures.

1. ESR and IR spectroscopy of cyclic triplet vinylnitrenes in cryogenic matrices

ESR spectroscopy revealed that triplet vinylnitrene (**47**) is thermally stable in methyltetrahydrofuran (mTHF) matrices up to at least ~100 K (Figure 10). The zero-field splitting parameters

---

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

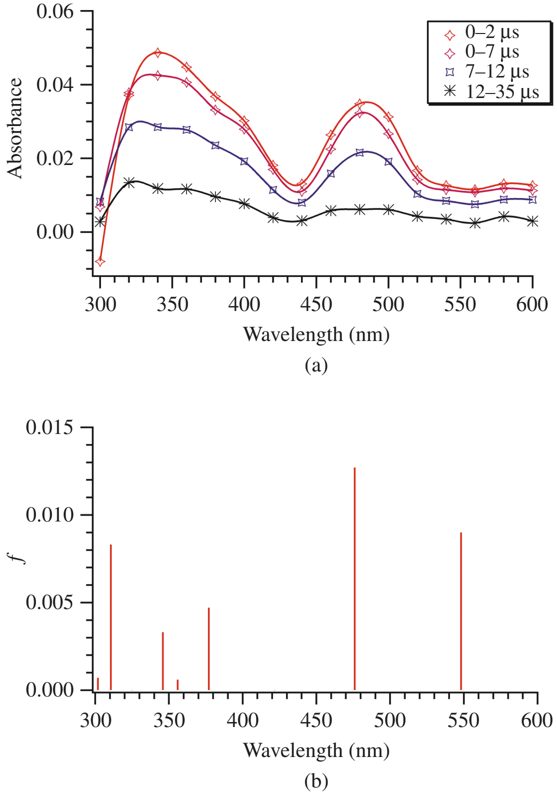


FIGURE 8. (a) Transient absorption spectra obtained by laser flash photolysis of vinyl azide (**51**) in acetonitrile with 308 nm laser. (b) TD-DFT calculated electronic transitions for triplet vinylnitrene (**52**). Adapted with permission from Ref. 81. © 2016 American Chemical Society.

obtained for triplet vinylnitrene (**47**) ($D/hc = 0.729\ \mathrm{cm}^{-1}$ and $E/hc = 0.0048\ \mathrm{cm}^{-1}$) highlighted its significant 1,3-biradical character. The zero-field splitting parameters for triplet vinylnitrene (**52**) are $D/hc = 0.460\ \mathrm{cm}^{-1}$ and $E/hc = 0.005\ \mathrm{cm}^{-1}$, indicating that it has more 1,3-biradical character than triplet vinylnitrene (**47**) (Figure 11).

Wentrup and coworkers have shown that, generally, there is a linear correlation between the calculated spin densities of triplet nitrenes and the measured zero-field splitting parameters (Figure 12)[82–84]. The calculated spin densities on the nitrogen and vinylic β-carbon atoms of triplet vinylnitrenes (**47**) (1.42) and (**52**) (1.29) obey the same trend.

Photolysis of vinyl azides (**46**) and (**51**) in argon matrices at 8 and 10 K also resulted in the formation of triplet vinylnitrenes (**47**) and (**52**), respectively. Because vinylnitrenes (**46**) and (**52**) are stable at cryogenic temperatures, they can absorb light and react further. Upon excitation, vinylnitrene (**47**) undergoes α-cleavage to form cyanide (**55**) (Scheme 20 and

This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

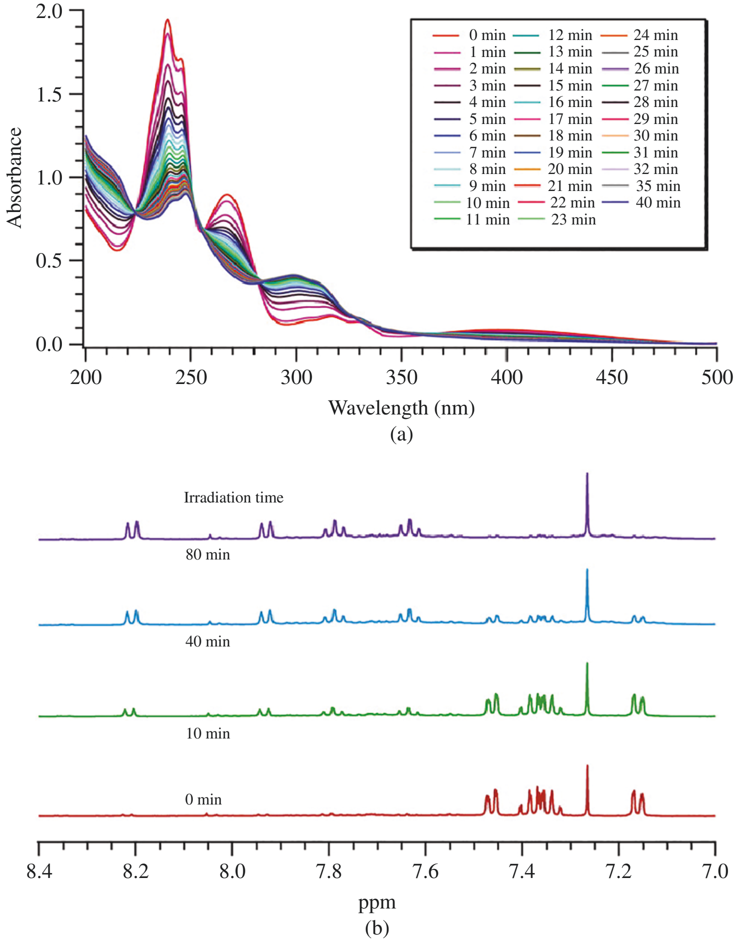


FIGURE 9. (a) UV and (b) NMR spectra of vinyl azide (**51**) as a function of irradiation time with a 405 nm LED. Adapted with permission from Ref. 81. © 2016 American Chemical Society.

Figure 13), whereas vinylnitrene (**52**) undergoes secondary photolysis through both α- and β-cleavage to form products **56** and **57** (Scheme 21 and Figure 14). Thus, vinylnitrene (**52**) is more reactive than vinylnitrene (**47**) because it is more strained.

2. Irradiation of flexible vinyl azides in cryogenic matrices

In contrast, irradiation of noncyclic vinyl azides in argon matrices does not yield triplet vinylnitrene intermediates. For example, Lopes and coworkers studied the photoreactivity of vinyl

This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

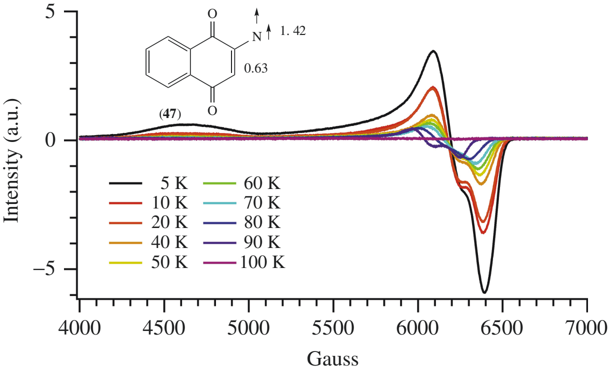


FIGURE 10. ESR spectra obtained by irradiating **46** in mTHF as a function of temperature. Microwave frequency: 9.398896 GHz; $H_0 = 3353.5$ G. $X_2 = 6008$ G; $Y_2 = 6224$ G; $Z_1 \sim 4500$ G; $\Delta m_s = 2$–1685 G. $D/hc = 0.7292\ \text{cm}^{-1}$; $E/hc = 0.0048\ \text{cm}^{-1}$. Adapted with permission from Ref. 79. © 2015 American Chemical Society.

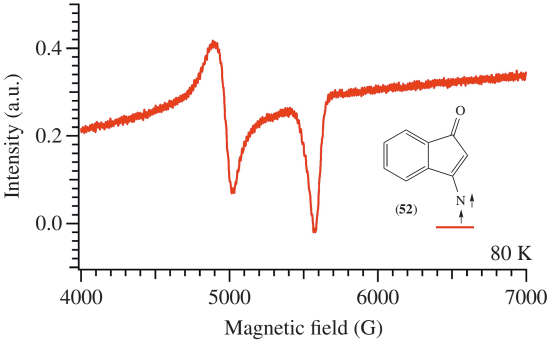


FIGURE 11. ESR spectrum obtained by irradiating **51** in mTHF at 80 K. Adapted with permission from Ref. 81. © 2016 American Chemical Society.

azide (**58**) in argon matrices and demonstrated that it yields ketenimine (**59**) and azirine (**60**) (Scheme 22)[86]. The authors theorized that ketenimine (**59**) is formed from Curtius rearrangement of the vinyl azide and that azirine (**60**) is formed through singlet reactivity. Furthermore, upon prolonged irradiation, azirine (**60**) is converted into oxazole (**62**), presumably through ylide (**61**), although it was not observed directly in the matrix[86].

Similarly, irradiation of vinyl azide (**33**) in argon matrices yields ketenimine (**63**) and azirine (**34**) through singlet reactivity (Scheme 23)[77]. Short-wavelength irradiation of azirine (**34**) results in the formation of ylide (**64**). Thus, vinyl azides (**33**) and (**58**) do not yield any products that can be attributed to the formation of triplet vinylnitrenes.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

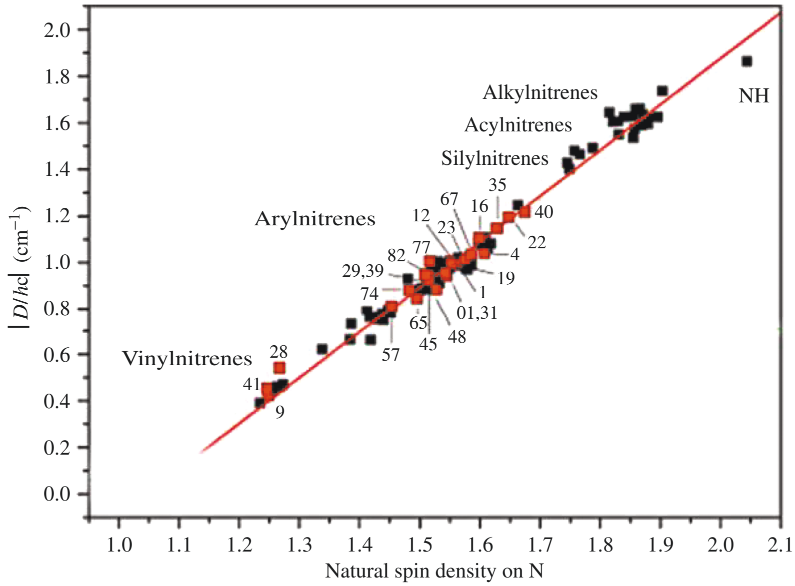


FIGURE 12. Correlation between the ESR zero-field splitting parameter *D*/*hc* (cm^{-1}) and the natural spin density ρ on the nitrene–N. Legend: **1**, phenylnitrene; **4**, 2-pyridylnitrene; **9**, ring-opened cyanobutadienylnitrene from 2-pyridylnitrene; **12**, 3-pyridylnitrene; **22**, 4-pyridylnitrene; **23**, 2-pyrazinylnitrene; **28**, ring-opened vinylnitrene from 2-pyrazinylnitrene; **31**, 3-isoquinolylnitrene; **32**, ring-opened nitrene from 3-isoquinolylnitrene; **35**, 2-quinazolinylnitrene; **40**, 2-pyrimidinylnitrene; **41**, ring-opened vinylnitrene from 2-pyrimidinylnitrene; **45**, phenanthridinylnitrene; **48**, ring-opened arylnitrene from phenanthridinylnitrene; **57**, phenanthrylnitrene; **65**, 1-isoquinolylnitrene; **67**, 2-quinolylnitrene; **74**, 4-quinolylnitrene; **81**, 2-quinoxalinylnitrene; **82**, 2-naphthylnitrene; **77**, 4-biphenylylnitrene. Further details can be obtained from the publications by Wentrup and coworkers[82–84]. Reproduced with permission from Ref. 41. © 2017 American Chemical Society.

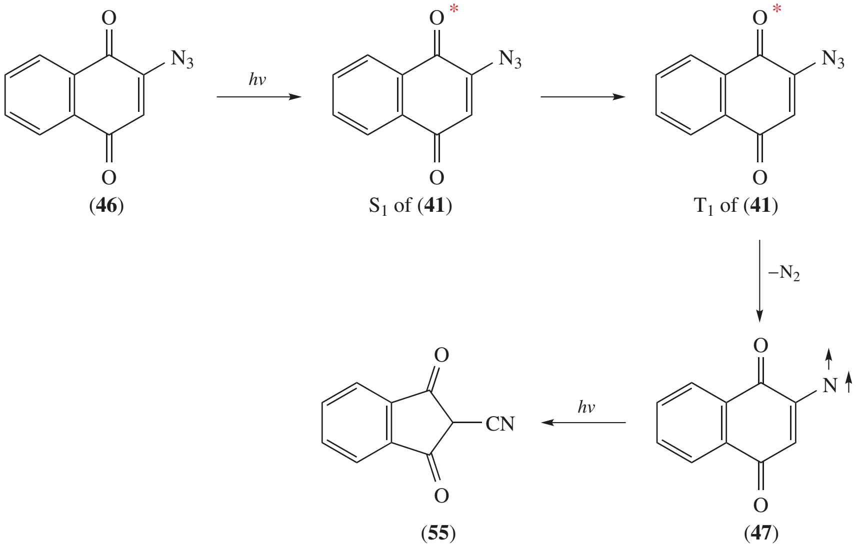
3. Irradiation of azirines in cryogenic matrices

Inui and Murata demonstrated that naphthyl-substituted azirine (**14**) shows wavelength-dependent photochemistry in cryogenic matrices, similar to the behavior observed in solution[67]. Short-wavelength irradiation leads to selective C–C bond cleavage to form corresponding ylide (**65**), whereas irradiation above 366 nm yields ketenimine (**67**). Photolysis of azirine (**14**) in argon matrices with oxygen suppressed the formation of ketenimine (**67**), as well as the formation of aldehyde (**16**) and acetonitrile oxide (**66**), which must originate from trapping of the corresponding triplet vinylnitrene (**15**) (Scheme 24).

Similarly, we showed that long-wavelength irradiation of azirine (**18**) in cryogenic argon matrices does not yield triplet vinylnitrene (**19**) but ketenimine (**68**), presumably through intersystem crossing of triplet vinylnitrene (**19**) (Scheme 25). In comparison, short-wavelength irradiation of azirine (**18**) in argon matrices results in the formation of ylide (**21**). The photochemical behavior of azirine (**23**) in matrices mirrors that of azirine

---

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



SCHEME 20. Photoreactivity of vinyl azide (**46**) in cryogenic argon matrices.

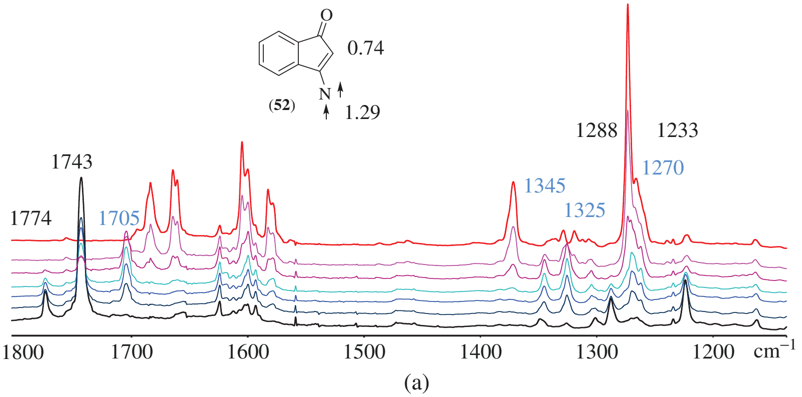
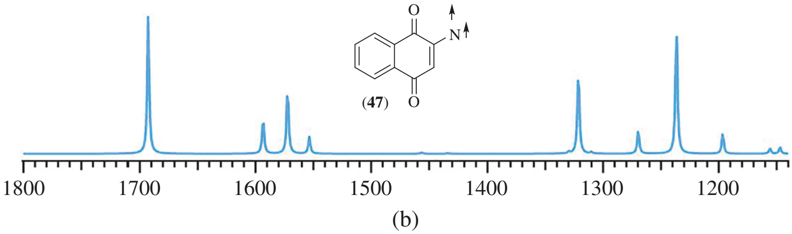


FIGURE 13. (a) IR spectra obtained before (red) and after (blue to black) irradiation of vinyl azide (**46**) in an argon matrix at 8 K. Calculated IR spectra at the B3LYP/6-31 + G(d) level for (b) triplet vinylnitrene (**47**) and (c) cyanide (**55**) after scaling by 0.9613[85]. Reproduced with permission from Ref. 79. © 2015 American Chemical Society.

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



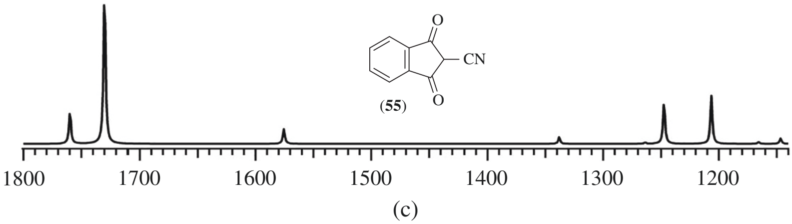
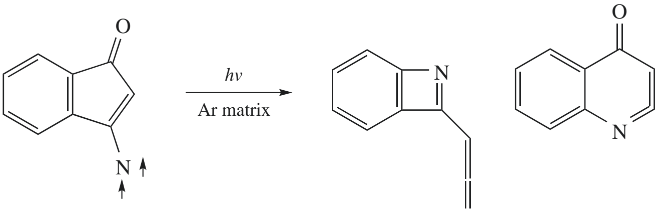


FIGURE 13. (*continued*)



(**52**) (**56**) (**57**)

SCHEME 21. Cryogenic reactivity of vinyl azide (**52**).

(**18**) (Scheme 26). Long-wavelength irradiation gives ketenimine (**69**) and short-wavelength irradiation ylide (**25**). Furthermore, irradiation of azirine (**28**), in which the aryl moiety is in conjugation with the azirine chromophore, in matrices only yields ylide (**29**) (Scheme 27). Thus, irradiation of azirines (**18**), (**23**), and (**28**) in matrices reflects their reactivities in solution, except that the triplet vinylnitrenes can intersystem cross to form ketenimines rather than re-forming the starting materials.

Fausto and coworkers studied the photochemistry of azirine esters (**70a**) and (**70b**), with and without a chloro substituent[87, 88]. Upon irradiation, both (**70a**) and (**70b**) were found to form the corresponding ketenimine (**71**) and ylide (**72**) as products (Scheme 28).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

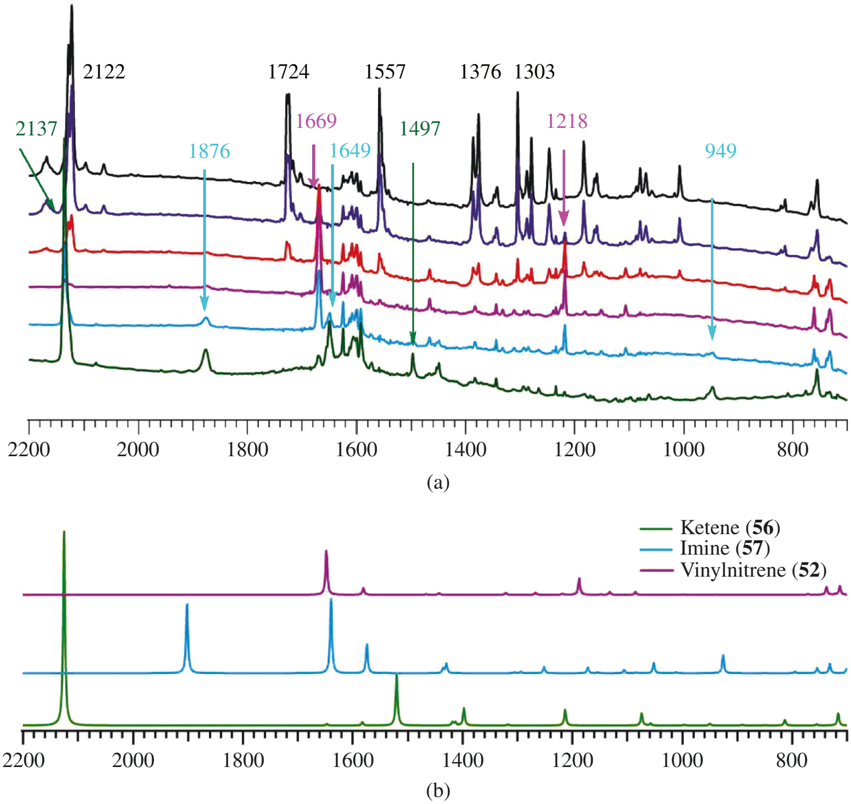


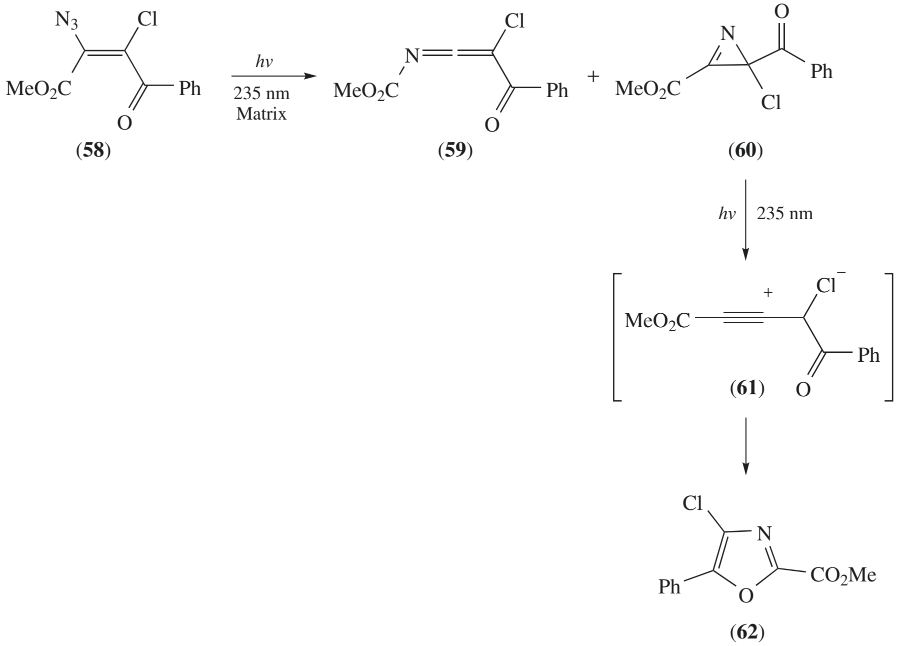
FIGURE 14. (a) IR spectra obtained before and after irradiation of vinyl azide (**51**) in an argon matrix at 10 K. (b) Calculated IR spectra of triplet vinylnitrene (**52**), ketene (56), and ketenimine (57) after scaling by 0.9613[85]. Reproduced with permission from Ref. 81. © 2016 American Chemical Society.

4. Irradiation of isoxazoles in cryogenic matrices

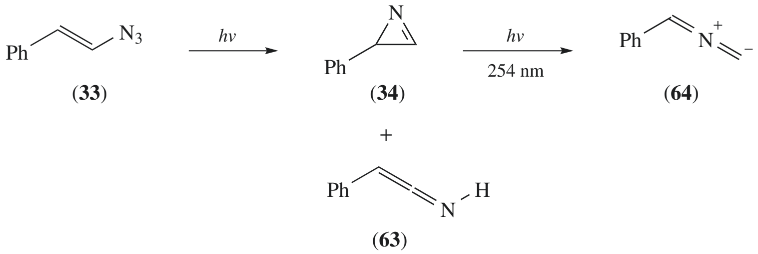
The photochemistry of isoxazole derivatives has also been studied in cryogenic matrices. For example, Fausto and coworkers showed that short-wavelength irradiation of isoxazoles (**73**) and (**79**) yields both azirine and ketenimine products (Schemes 29 and 30)[87, 88].

The photoreactivity of 1,2-benzisoxazole derivatives was also studied by Fausto and coworkers (Scheme 31)[89, 90] Interestingly, irradiation of benzisoxazole (**88**) at 280 nm resulted in the formation of ketenimine (**90**) and spiro-2*H*-azirine (**91**), presumably through vinylnitrene intermediate (**89**). Irradiation with light above 400 nm converted ketenimine (**90**) and azirine (**91**) into cyano phenol (**92**).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

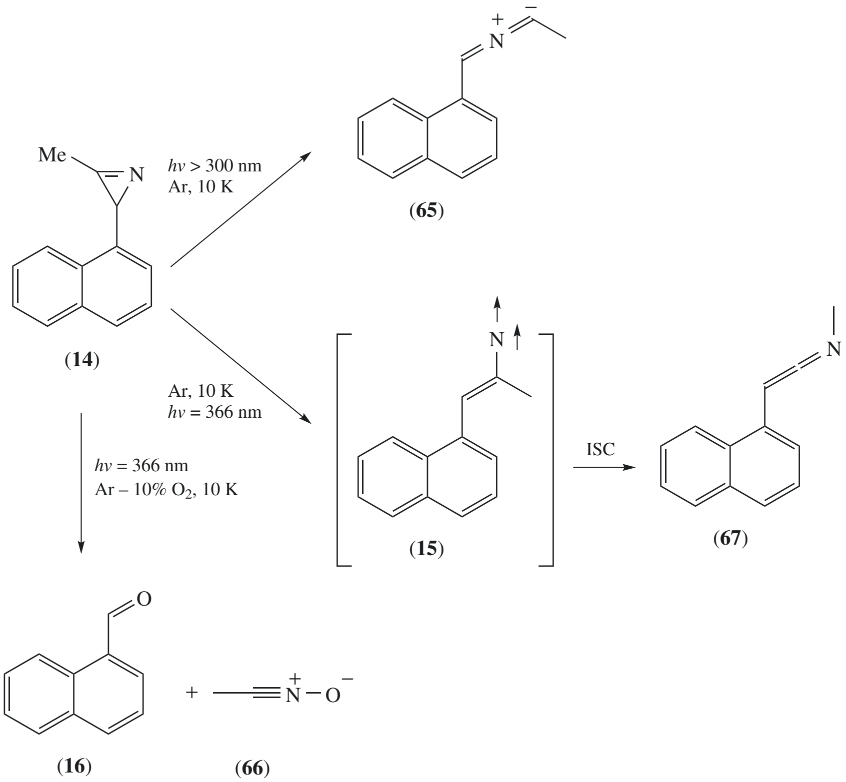


SCHEME 22. Cryogenic photoreactivity of vinyl azide (**58**).

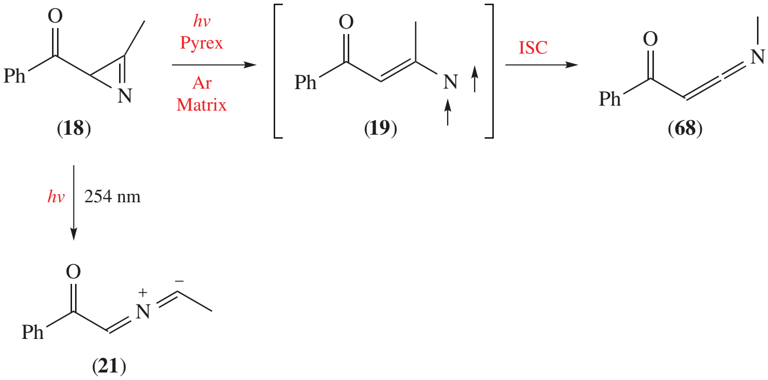


SCHEME 23. Cryogenic photoreactivity of vinyl azide (**33**).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

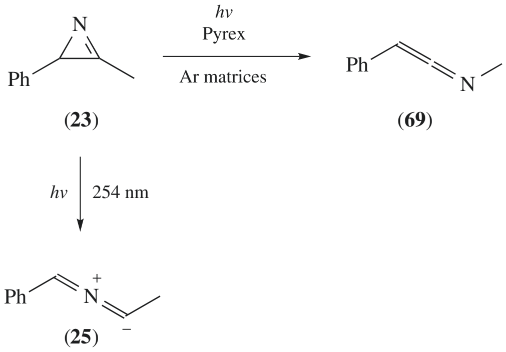


SCHEME 24. Photoreactivity of azirine (**14**) in argon and argon–oxygen matrices.

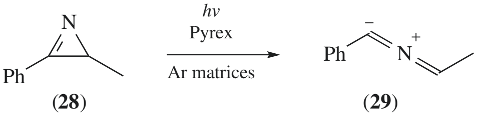


SCHEME 25. Cryogenic photoreactivity of azirine (**18**).

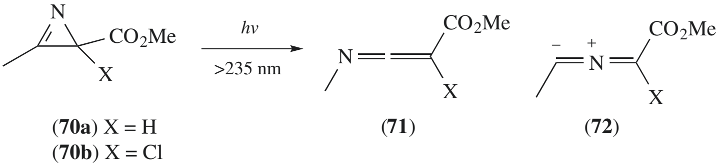
PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



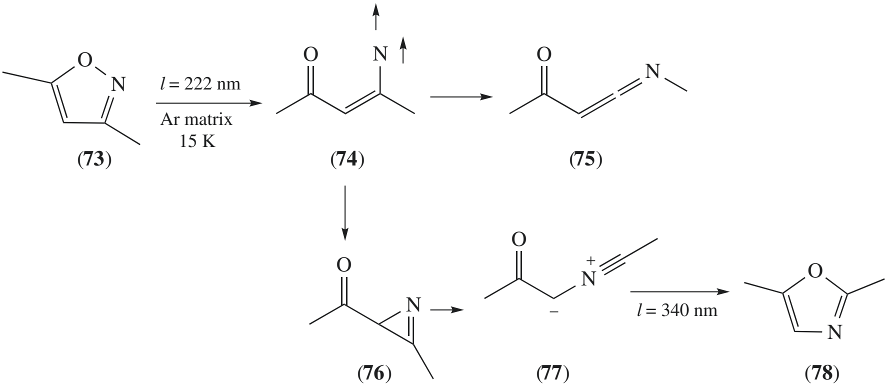
SCHEME 26. Cryogenic photoreactivity of azirine (**23**).



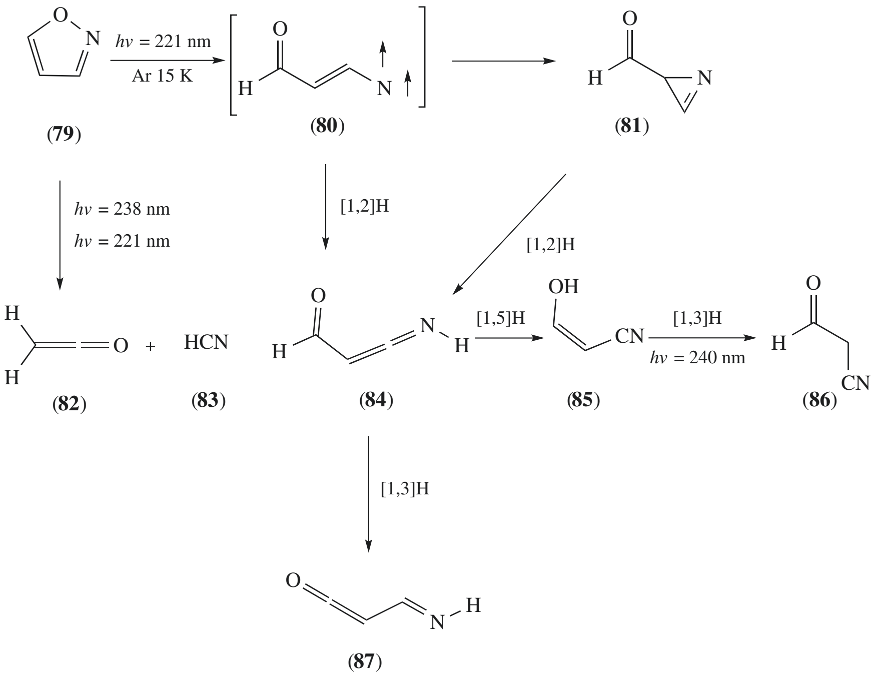
SCHEME 27. Cryogenic photoreactivity of azirine (**28**).



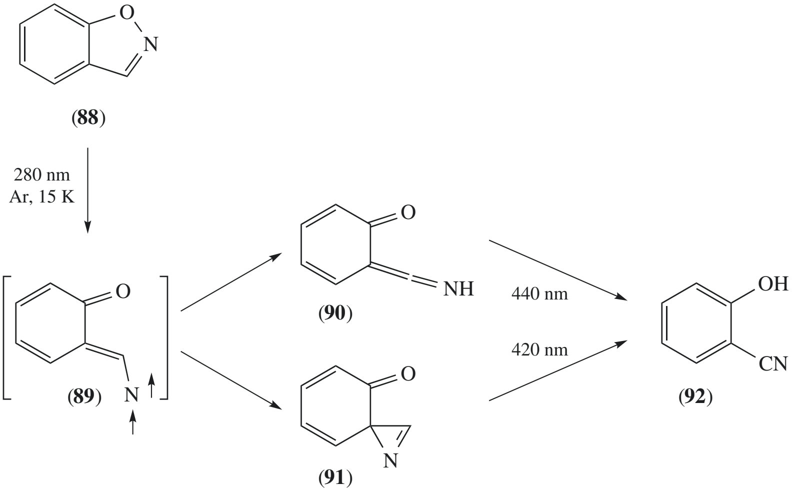
SCHEME 28. Cryogenic photoreactivity of azirines (**70a**) and (**70b**).



SCHEME 29. Cryogenic photoreactivity of isoxazole (**73**).

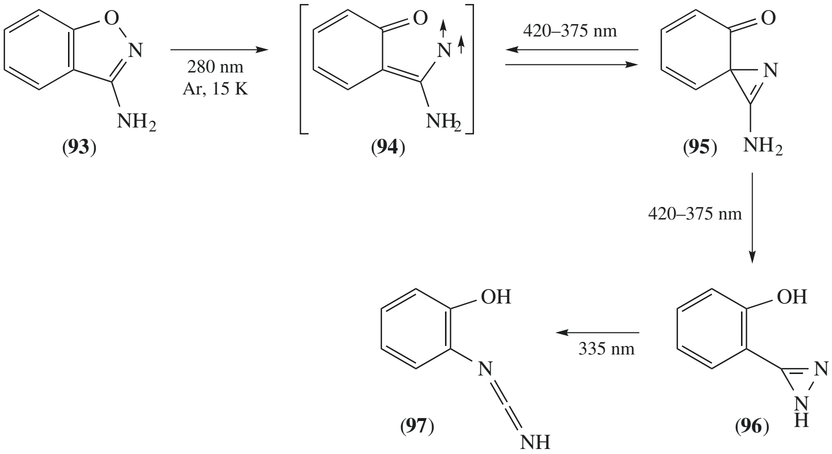


SCHEME 30. Cryogenic photoreactivity of isoxazole (**79**).



SCHEME 31. Cryogenic photoreactivity of isoxazole (**88**).

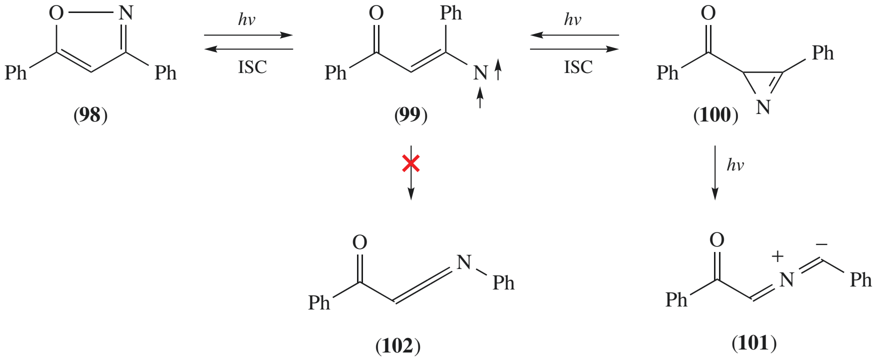
PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925



SCHEME 32. Cryogenic photoreactivity of isoxazole (**93**).

Benzisoxazole (**93**), an amino-substituted derivative of **88**, selectively formed spiroazirine (**95**) under irradiation at 280 nm, presumably through vinylnitrene (**94**) (Scheme 32). Upon subsequent irradiation of azirine (**95**) at a higher wavelength, some of **95** isomerized back to benzisoxazole (**93**) with concurrent formation of azirine (**95**). Irradiation of azirine (**95**) at 335 nm yielded ketenimine (**97**).

We studied the photoreactivity of isoxazole (**98**) in argon matrices and found that irradiation with a xenon lamp resulted in the formation of azirine (**100**) instead of ketenimine (**102**), which was the product predicted by previous cryogenic matrix isolation studies of isoxazole photochemistry[91]. The α-phenyl substituent in vinylnitrene (**99**) is thought to lower the rotational barrier and facilitate intersystem crossing to azirine (**100**) rather than ketenimine (**102**) (Scheme 33).



SCHEME 33. Cryogenic photoreactivity of isoxazole (**98**).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

C. Theoretical Calculations

In this section we only briefly describe calculations performed on vinylnitrenes that we have studied experimentally, although several theoretical papers on vinylnitrenes have been published[23,41,45,92–99]. DFT calculations can be used to better understand the physical properties of triplet vinylnitrenes and to aid in determining their reactivity. For example, Figure 15 displays the calculated stationary points on the triplet surface of vinyl azide (**46**) for formation of triplet vinylnitrene (**47**). These results demonstrate that the transition state barrier for forming triplet vinylnitrene (**47**) from the lowest triplet excited state of vinyl azide (**46**) is only a few kilocalories per mole, and thus, formation of triplet vinylnitrene (**47**) from the triplet excited state of vinyl azide (**46**) should be easily accessible[79]. DFT calculations can be used to verify that vinylnitrene formation is feasible from the triplet precursors, but they cannot be used to determine whether intersystem crossing to the triplet surface of the precursors is feasible.

DFT calculations also allow straightforward estimations of the spin densities of triplet vinylnitrenes and thus the extent of their 1,3-biradical character. Furthermore, as described earlier, the calculated spin densities are correlated with the *D*/*hc* values measured for triplet vinylnitrenes, which makes it feasible to approximate the 1,3-character of vinylnitrenes for which ESR spectra cannot be recorded because they are not stable at cryogenic temperatures. Furthermore, the rotational barrier around the vinyl bond in triplet vinylnitrenes can easily be estimated with DFT calculations, although the accuracy of the calculated rotational barriers has not been verified (Scheme 17).

In addition, DFT calculations (B3LYP/6-31+G(d)) can be used to estimate the energy gap between the open-shell singlet and triplet configurations of triplet vinylnitrenes by optimizing the singlet vinylnitrenes using the broken-symmetry method with guess = mix as a keyword, as featured in Gaussian09 (Table 1)[79,81]. Using this method, the energy gaps between

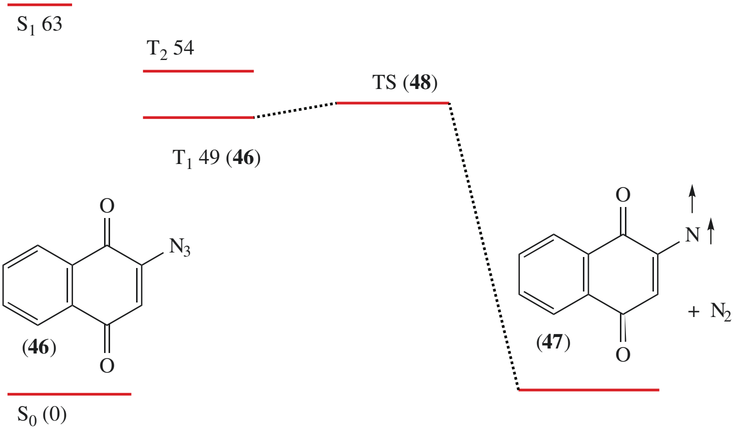


FIGURE 15. Calculated stationary points on the triplet surface of (**46**). The energies of the first singlet excited state (S1 = 63), first triplet excited state (T_1 = 49), and second excited triplet state (T_2 = 54) of **46** were obtained from TD-DFT calculations, whereas the energies of the ground state (S_0 = 0), T1 (**46**), transition state (TS = 48), and triplet vinylnitrene (**47**) were obtained by optimization calculations. Energies are in kcal mol^{-1}. Reproduced with permission from Ref. 79. © 2015 American Chemical Society.

This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

TABLE 1. Calculated energies of singlet and triplet configurations of vinylnitrenes (**52**) and (**47**)

B3LYP/6-31 + G(d)				CASSCF(12,12)/cc-pVDZ		CASPT(12,12)/cc-pVDZ //CASSCF(12,12)/cc-pVDZ	
State	*E* (au)	S^2	Rel *E*	*E* (au)	Rel *E*	*E* (au)	Rel *E*
Vinylnitrene (***52***)							
$^3A''$	−475.865	2.05	0.0	−473.155	0.0	−474.444	0.0
$^1A''$	−475.837	1.01	17.5	−473.139	10.3	−474.428	10.1
$^1A'$	−475.81		34.2	−473.077	49	−474.373	44.2
Vinylnitrene (***47***)							
				CASSCF(14,14)/cc-pVDZ		CASPT(14,14)/cc-pVDZ //CASSCF(14,14)/cc-pVD	
$^3A''$	−589.198	2.06	0.0	−585.935	0.0	−587.484	0.0
$^1A''$	−589.173	1.01	16.1	−585.909	16.4	−587.464	13
$1A'$				−585.861	46.6	−587.417	42.3

Relative energies in kcal mol^{-1}, not corrected for ZPE differences.
Source: Reproduced with permission from Ref. 81. © 2016 American Chemical Society.

the open-shell singlet and triplet configuration of vinylnitrenes (**47**) and (**52**) were estimated to be 16.1 and 17.5 kcal mol^{-1}, respectively. However, more sophisticated calculations using CASSCF and CASPT2 theories have demonstrated that the DFT calculations overestimate the energy gap.

CASPT calculations demonstrate that the singlet–triplet energy gap for triplet vinylnitrene (**47**) is 13.0 kcal mol^{-1}, which is somewhat smaller than that reported for phenylnitrene (14.9 kcal mol^{-1})[100]. Interestingly, CASPT calculations reveal that the singlet–triplet energy gap for vinylnitrene (**52**) is only 10 kcal mol^{-1} when considering the open-shell singlet state, which is smaller than that for triplet vinylnitrene (**47**). Despite this low energy gap, vinylnitrene (**52**) is less reactive than vinylnitrene (**47**) in solution because it decays by dimerization but not vinylnitrene (**47**). Thus, it can be theorized that the energy gap between the singlet and triplet configurations of vinylnitrenes is affected by substituents and can be used to control the reactivity.

V. CONCLUSION

Triplet vinylnitrenes can be formed in solution and cryogenic matrices through triplet sensitization. The 1,3-biradical character of triplet vinylnitrenes makes them flexible, and they mainly react by intersystem crossing to form products. Triplet vinylnitrenes that are part of a bicyclic structure are stable at cryogenic temperatures, whereas more flexible triplet vinylnitrenes intersystem cross to ground-state products. Because triplet vinylnitrenes can be designed to undergo bimolecular reactions, a better understanding of how their reactivity can be controlled will reveal their potential for use in synthetic applications. Furthermore, because triplet vinylnitrenes can be rendered stable at cryogenic temperature they have the potential to be used as building blocks for high-spin assemblies.

VI. ACKNOWLEDGMENTS

We acknowledge the National Science Foundation (CHE-1800140 and CHE-1464694) and the Ohio Supercomputer Centre for generous support to study the reactivity of triplet

---

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

vinylnitrenes. A.D.G. thanks Dr K. Kristinsson for his technical support. K.T.H. acknowledges the Schubert Fellowship Award from the Chemistry Department at the University of Cincinnati. U.B. expresses gratitude for Doctoral Enhancement and Laws Fellowships from the Chemistry Department at the University of Cincinnati.

VII. REFERENCES

1. S. Bräse, C. Gil, K. Knepper and V. Zimmermann, *Angew. Chem., Int. Ed.*, **44**, 5188 (2005).
2. J. Fu, G. Zanoni, E. A. Anderson and X. Bi, *Chem. Soc. Rev.*, **46**, 7208 (2017).
3. S. Xie, S. A. Lopez, O. Ramström, M. Yan and K. N. Houk, *J. Am. Chem. Soc.*, **137**, 2958 (2015).
4. H. D. Agnew, R. D. Rohde, S. W. Millward, A. Nag, W.-S. Yeo, J. E. Hein, S. M. Pitram, A. A. Tariq, V. M. Burns, R. J. Krom, V. V. Fokin, K. B. Sharpless and J. R. Heath, *Angew. Chem., Int. Ed.*, **48**, 4944 (2009).
5. C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem.*, **67**, 3057 (2002).
6. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, **41**, 2596 (2002).
7. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, **40**, 2004 (2001).
8. R. Huisgen, *Angew. Chem., Int. Ed.*, **2**, 565 (1963).
9. S. Protti, D. Ravelli, M. Fagnoni and A. Albini, *Chem. Commun.*, **7351** (2009).
10. A. Albini and M. Fagnoni (Eds.), *Handbook of Synthetic Photochemistry*, Wiley-VCH, Weinheim, 2010.
11. D. M. Schultz and T. P. Yoon, *Science*, **343**, 985 (2014).
12. X. Huang, R. D. Webster, K. Harms and E. Meggers, *J. Am. Chem. Soc.*, **138**, 12636 (2016).
13. E. P. Farney and T. P. Yoon, *Angew. Chem., Int. Ed.*, **53**, 793 (2014).
14. N. P. Gritsan, in *Nitrenes and Nitrenium Ions* (Eds. D. E. Falvey and A. D. Gudmundsdottir) Chap. 12, Wiley, Hoboken, NJ, 2013, p. 481.
15. N. Gritsan and M. Platz, in Organic Azides*:* Synthesis and Applications (Eds. S. Bräse and K. Banert), Wiley, Chichester, 2010, p. 311.
16. M. S. Platz, in *Reactive Intermediates* (Eds. R. A. Moss, M. S. Platz and M. Jones, Jr.) Chap. 11, Wiley, Hoboken, NJ, 2004, p. 501.
17. G. Bucher, *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed., CRC Press LLC, Boca Raton, FL, 2004, p. 44/1.
18. M. S. Platz, *Acc. Chem. Res.*, **28**, 487 (1995).
19. E. F. V. Scriven and K. Turnbull, *Chem. Rev.*, **88**, 297 (1988).
20. E. F. V. Scriven and Editor, Azides and Nitrenes*:* Reactivity and Utility, Academic Press, Inc., 1984.
21. J. Wang, G. Burdzinski and M. S. Platz, in *Nitrenes and Nitrenium Ions* (Eds. D. E. Falvey and A. D. Gudmundsdottir), Wiley, Hoboken, NJ, 2013, p. 1.
22. N. P. Gritsan and M. S. Platz, *Chem. Rev.*, **106**, 3844 (2006).
23. W. T. Borden, N. P. Gritsan, C. M. Hadad, W. L. Karney, C. R. Kemnitz and M. S. Platz, *Acc. Chem. Res.*, **33**, 765 (2000).
24. Y. Zhang, M. Chakraborty, C. G. Cerda-Smith, R. N. Bratton, N. E. Maurer, E. M. Senser and M. Novak, *J. Org. Chem.*, **78**, 6992 (2013).
25. M. Novak and M. Chakraborty, *J. Phys. Org. Chem.*, **24**, 960 (2011).
26. M. Chakraborty, K. J. Jin, S. A. Glover and M. Novak, *J. Org. Chem.*, **75**, 5296 (2010).
27. M. Chakraborty, K. J. Jin, S. C. Brewer, H.-L. Peng, M. S. Platz and M. Novak, *Org. Lett.*, **11**, 4862 (2009).
28. M. R. Cline, S. M. Mandel and M. S. Platz, *Biochemistry*, **46**, 1981 (2007).
29. S. Mandel, J. Liu, C. M. Hadad and M. S. Platz, *J. Phys. Chem. A*, **109**, 2816 (2005).
30. M.-L. Tsao and M. S. Platz, *J. Am. Chem. Soc.*, **125**, 12014 (2003).
31. N. P. Gritsan, I. Likhotvorik, M.-L. Tsao, N. Celebi, M. S. Platz, W. L. Karney, C. R. Kemnitz and W. T. Borden, *J. Am. Chem. Soc.*, **123**, 1425 (2001).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

32. N. P. Gritsan, A. D. Gudmundsdottir, D. Tigelaar, Z. Zhu, W. L. Karney, C. M. Hadad and M. S. Platz, *J. Am. Chem. Soc.*, **123**, 1951 (2001).
33. N. P. Gritsan, A. D. Gudmundsdottir, D. Tigelaar and M. S. Platz, *J. Phys. Chem. A*, **103**, 3458 (1999).
34. H. Zhai and M. S. Platz, *J. Phys. Org. Chem.*, **10**, 22 (1997).
35. A. Marcinek and M. S. Platz, *J. Phys. Chem.*, **97**, 12674 (1993).
36. E. Leyva, M. J. T. Young and M. S. Platz, *J. Am. Chem. Soc.*, **108**, 8307 (1986).
37. N. P. Gritsan and M. S. Platz, *Adv. Phys. Org. Chem.*, **36**, 255 (2001).
38. T. Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, **109**, 7803 (1987).
39. E. Leyva, M. S. Platz, G. Persy and J. Wirz, *J. Am. Chem. Soc.*, **108**, 3783 (1986).
40. J. C. Hayes and R. S. Sheridan, *J. Am. Chem. Soc.*, **112**, 5879 (1990).
41. C. Wentrup, *Chem. Rev.*, **117**, 4562 (2017).
42. J. S. Poole, *Top. Heterocycl. Chem.*, **111** (2017).
43. C. Wentrup, in *Nitrenes and Nitrenium Ions* (Eds. D. E. Falvey and A. D. Gudmundsdottir) Chap. 8, Wiley, Hoboken, NJ, 2013, p. 273.
44. C. Wentrup, *Acc. Chem. Res.*, **44**, 393 (2011).
45. N. P. Gritsan, M. S. Platz and W. T. Borden, *Mol. Supramol. Photochem.*, **13**, 235 (2005).
46. S. Muthukrishnan, R. A. A. U. Ranaweera and A. D. Gudmundsdottir, in *Nitrenes and Nitrenium Ions* (Eds. D. E. Falvey and A. D. Gudmundsdottir) Chap. 5, Vol. 6, Wiley , Hoboken, NJ, 2013, p. 167.
47. R. A. Abramovitch, in *Organic Reactive Intermediates* (Ed. S. P. Mcmanus) Chap. 3, Vol. 26, Academic Press, Inc., New York, NY, 1973, p. 127.
48. R. A. Abramovitch and E. P. Kyba, in *The Chemistry of the Azido Group* (Ed. S. Patai) Chap. 5, Wiley, London, 1971, p. 221.
49. J. Sankaranarayanan, L. N. Bort, S. M. Mandel, P. Chen, J. A. Krause, E. E. Brooks, P. Tsang and A. D. Gudmundsdottir, *Org. Lett.*, **10**, 937 (2008).
50. P. N. D. Singh, S. M. Mandel, J. Sankaranarayanan, S. Muthukrishnan, M. Chang, R. M. Robinson, P. M. Lahti, B. S. Ault and A. D. Gudmundsdóttir, *J. Am. Chem. Soc.*, **129**, 16263 (2007).
51. P. N. D. Singh, S. M. Mandel, R. M. Robinson, Z. Zhu, R. Franz, B. S. Ault and A. D. Gudmundsdóttir, *J. Org. Chem.*, **68**, 7951 (2003).
52. S. Muthukrishnan, S. M. Mandel, J. C. Hackett, P. N. D. Singh, C. M. Hadad, J. A. Krause and A. D. Gudmundsdóttir, *J. Org. Chem.*, **72**, 2757 (2007).
53. S. M. Mandel, J. A. Krause Bauer and A. D. Gudmundsdottir, *Org. Lett.*, **3**, 523 (2001).
54. I. R. Dunkin and P. C. P. Thomson, *Tetrahedron Lett.*, **21**, 3813 (1980).
55. M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **56**, 333 (1975).
56. D. E. Milligan, *J. Chem. Phys.*, **35**, 1491 (1961).
57. N. P. Gritsan, I. Likhotvorik, Z. Zhu and M. S. Platz, *J. Phys. Chem. A*, **105**, 3039 (2001).
58. J. G. Radziszewski, J. W. Downing, C. Wentrup, P. Kaszynski, M. Jawdosiuk, P. Kovacic and J. Michl, *J. Am. Chem. Soc.*, **107**, 2799 (1985).
59. J. G. Radziszewski, J. W. Downing, C. Wentrup, P. Kaszynski, M. Jawdosiuk, P. Kovacic and J. Michl, *J. Am. Chem. Soc.*, **106**, 7996 (1984).
60. R. F. Klima and A. D. Gudmundsdottir, *J. Photochem. Photobiol. A*, **162** (2004).
61. S. Rajam, R. S. Murthy, A. V. Jadhav, Q. Li, C. Keller, C. Carra, T. C. S. Pace, C. Bohne, B. S. Ault and A. D. Gudmundsdottir, *J. Org. Chem.*, **76**, 9934 (2011).
62. S. K. Ghoshal, S. K. Sarkar and G. S. Kastha, *Bull. Chem. Soc. Jpn.*, **54**, 3556 (1981).
63. D. F. Evans, *J. Chem. Soc.*, **1351** (1957).
64. G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).
65. B. Singh, A. Zweig and J. B. Gallivan, *J. Am. Chem. Soc.*, **94**, 1199 (1972).
66. B. Singh and E. F. Ullman, *J. Am. Chem. Soc.*, **89**, 6911 (1967).
67. H. Inui and S. Murata, *J. Am. Chem. Soc.*, **127**, 2628 (2005).
68. H. Inui and S. Murata, *Chem. Phys. Lett.*, **359**, 267 (2002).
69. H. Inui and S. Murata, *Chem. Lett.*, **832** (2001).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925

70. X. Zhang, S. K. Sarkar, G. K. Weragoda, S. Rajam, B. S. Ault and A. D. Gudmundsdottir, *J. Org. Chem.*, **79**, 653 (2014).
71. G. K. Weragoda, A. Das, S. K. Sarkar, H. D. M. Sriyarathne, X. Zhang, B. S. Ault and A. D. Gudmundsdottir, *Aust. J. Chem.*, **70**, 413 (2017).
72. N. Gakis, M. Märky, H. J. Hansen and H. Schmid, *HeIv. Chim. Acta*, **55**, 748 (1972).
73. A. Padwa, J. Smolanoff and S. I. Wetmore, *J. Chem. Soc., Chem. Commun.*, **409** (1972).
74. D. W. Gamage, Q. Li, R. A. A. U. Ranaweera, S. K. Sarkar, G. K. Weragoda, P. L. Carr and A. D. Gudmundsdottir, *J. Org. Chem.*, **78**, 11349 (2013).
75. E. A. Pritchina and N. P. Gritsan, *J. Photochem. Photobiol. A*, **43**, 165 (1988).
76. K. Isomura, M. Okada and H. Taniguchi, *Tetrahedron Lett.*, **10**, 4073 (1969).
77. O. Osisioma, M. Chakraborty, B. S. Ault and A. D. Gudmundsdottir, *J. Mol. Struct.*, **1174**, 94 (2018).
78. S. Rajam, A. V. Jadhav, Q. Li, S. K. Sarkar, P. N. D. Singh, A. Rohr, T. C. S. Pace, R. Li, J. A. Krause, C. Bohne, B. S. Ault and A. D. Gudmundsdottir, *J. Org. Chem.*, **79**, 9325 (2014).
79. S. K. Sarkar, A. Sawai, K. Kanahara, C. Wentrup, M. Abe and A. D. Gudmundsdottir, *J. Am. Chem. Soc.*, **137**, 4207 (2015).
80. Y. Naruta, T. Yokota, N. Nagai and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, **972** (1986).
81. S. K. Sarkar, O. Osisioma, W. L. Karney, M. Abe and A. D. Gudmundsdottir, *J. Am. Chem. Soc.*, **138**, 14905 (2016).
82. S. Torker, D. Kvaskoff and C. Wentrup, *J. Org. Chem.*, **79**, 1758 (2014).
83. D. Kvaskoff, P. Bednarek, L. George, K. Waich and C. Wentrup, *J. Org. Chem.*, **71**, 4049 (2006).
84. C. Wentrup and D. Kvaskoff, *Aust. J. Chem.*, **66**, 286 (2013).
85. J. B. Foresman and Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Inc, Pittsburgh, PA, 1996.
86. S. Lopes, C. M. Nunes, A. Gómez-Zavaglia, T. M. V. D. Pinho, E. Melo and R. Fausto, *Tetrahedron*, **67**, 7794 (2011).
87. A. Gómez-Zavaglia, A. Kaczor, A. L. Cardoso, T. Melo and R. Fausto, *J. Mol. Struct.*, **834**, 262 (2007).
88. A. Kaczor, A. Gómez-Zavaglia, A. L. Cardoso, T. M. V. D. Pinho, E. Melo and R. Fausto, *J. Phys. Chem. A*, **110**, 10742 (2006).
89. C. M. Nunes, S. M. V. Pinto, I. Reva and R. Fausto, *Eur. J. Org. Chem.*, **2016**, 4152 (2016).
90. C. Nunes, S. Pinto, I. Reva and R. Fausto, *Tetrahedron Lett.*, **57**, 5038 (2016).
91. H. D. M. Sriyarathne, K. R. S. Thenna-Hewa, T. Scott and A. D. Gudmundsdottir, *Aust. J. Chem.*, **68**, 1707 (2015).
92. J. Cao, *J. Chem. Phys.*, **142**, 244302/1 (2015).
93. M. T. Nguyen, T. D. Hang, N. P. Gritsan and V. G. Kiselev, *J. Phys. Chem. A*, **119**, 12906 (2015).
94. Y. Liu, P. Guan, Y. Wang, L. Liu and J. Cao, *J. Phys. Chem. A*, **119**, 67 (2015).
95. S. Vyas, A. H. Winter and C. M. Hadad, in *Nitrenes and Nitrenium Ions* (Eds. R. A. Moss, M. S. Platz and M. Jones, Jr.), Wiley, Hoboken, NJ, 2013.
96. P. G. Wenthold, *J. Org. Chem.*, **77**, 208 (2012).
97. C. M. Nunes, I. Reva, T. M. V. D. Pinho, E. Melo, R. Fausto, T. Solomek and T. Bally, *J. Am. Chem. Soc.*, **133**, 18911 (2011).
98. S. E. Worthington and C. J. Cramer, *J. Phys. Org. Chem.*, **10**, 755 (1997).
99. V. Parasuk and C. J. Cramer, *Chem. Phys. Lett.*, **260**, 7 (1996).
100. N. R. Wijeratne, M. D. Fonte, A. Ronemus, P. J. Wyss, D. Tahmassebi and P. G. Wenthold, *J. Phys. Chem. A*, **113**, 9467 (2009).

PATAI'S Chemistry of Functional Groups, Online 2009–2017 John Wiley & Sons, Ltd.
This article is © 2017 John Wiley & Sons, Ltd.
This article was published in *PATAI's Chemistry of Functional Groups* in 2017 by John Wiley & Sons, Ltd.
DOI: 10.1002/9780470682531.pat0925