RECENT ADVANCES IN THE PHOTOCHEMISTRY OF THE CARBON-NITROGEN DOUBLE BOND

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ABSTRACT

The excited states of imines were shown not to be reactive intermediates in the photoreduction of a series of benzaldehyde N-alkylimines. Instead, ketyl radicals were clearly implicated as the active reducing agent. These ketyl radicals were derived from carbonyl compounds present in the reaction mixture as an impurity, an added sensitizer, or as a photogenerated species. The lack of reactivity of the excited state of simple imines suggests that the excited states undergo a very efficient non-radiative decay to ground state thereby precluding hydrogen abstraction. This facile energy deactivation is a consequence of rotation about the C—N double bond (i.e. syn-anti photoisomerization). In rigid systems, this mode of energy dissipation would not be available and these molecules would have maximum opportunity to undergo reaction from an electronically excited state. In this regard, the photocycloaddition of arylazirenes with electron deficient olefins to give Δ'-pyrrolines has been examined in mechanistic detail. The formation of the adduct was interpreted as proceeding by way of irreversible opening of the azirene ring to form a nitrile ylide intermediate which is then trapped by a suitable dipolarophile. Irradiation of a number of substituted arylazirenes in an inert solvent gives 1,3-diazabicyclo-[3.1.0]hex-3-enes as primary photoproducts. The formation of these dimers can be rationalized by 1,3-dipolar addition of the initially generated nitrile ylide on to a ground state azirene molecule. Support for this conclusion was obtained by a study of the variation of the quantum yield for adduct formation as a function of the concentration of added dipolarophile. The study shows that the amount of adduct formed is dependent on the initial concentration of arylazirene and on the activity of the dipolarophile.
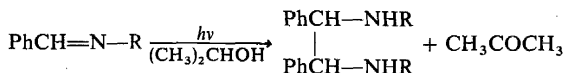
INTRODUCTION

One of the most active areas of organic photochemistry has been the study of systems which possess a carbonyl group[1-4]. As a result of these studies the photochemical transformations of organic molecules containing this functional group have been categorized into a number of primary photochemical processes[5]. This state of affairs contrasts sharply with the present status of the structurally related imine system, the photochemistry of which is mainly qualitative with relatively little available in the way of quantum yield data and kinetic studies. Even though the photochemistry of the C—N double bond

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has not been the subject of mechanistic studies, a considerable number of diverse reports have accumulated in the literature without critical review. Irradiation may lead to isomerization[6, 7], prototropy[8], rearrangement[9–14], addition[15–17], oxidation[18], hydrolysis[19], cyclization[20–22], photoreduction[23–32], and photoalkylation[33–36]. Of these processes, photoreduction is the most widely observed but, in many respects, the least fully investigated. A comparison of the photoreduction of the imine group with the extensively studied aryl ketone system could be of practical and theoretical interest. The elegant studies of Hammond[37], Cohen[38], Pitts[39] and others have indicated that intra- and intermolecular hydrogen abstraction processes in carbonyl photochemistry can be a most useful probe into the nature and reactivity of the excited state. This comparison and our interest in the chemical consequences of electronic excitation of the C—N double bond prompted a study of the photochemistry of aryl *N*-alkylimines.
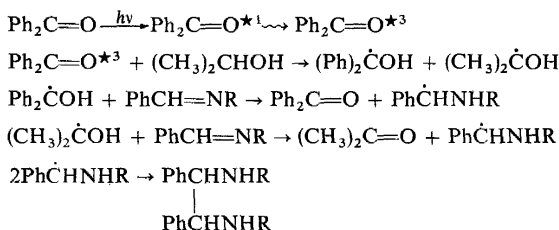
The feasibility of a formal comparison of the photochemistry of these two functional groups requires first a consideration of the spectroscopic properties of the imine system. The ultra-violet absorption spectra of non-conjugated imines generally show a band of modest intensity ($\varepsilon \sim 100$) in the 235-mμ region which is considered to be due to an n–$\pi^\star$ transition[40]. Its carbonyl counterpart is found at longer wavelength with a lower band intensity[41]. With aryl alkyl ketones the carbonyl n–$\pi^\star$ band is bathochromically shifted with enhancement of band intensity. On the other hand, aryl *N*-alkylamines do not generally show a distinct band that can be attributed to an n–$\pi^\star$ transition, since this band is often obscured by the intense π–$\pi^\star$ absorption. However, the long-wavelength tail of a conjugated imine such as benzalaniline has been interpreted to be partially due to an n–$\pi^\star$ transition[41]. Irradiation at this long-wavelength tail assures that at least the lowest energy singlet (and possibly the lowest triplet) of aryl *N*-alkylamines possesses an n–$\pi^\star$ configuration. The interest in n–$\pi^\star$ states stems from the fact that in carbonyl group photochemistry they have been designated as the reactive state in hydrogen abstraction and other types of reaction[42]. Extending this reasoning, some workers[43, 44] have suggested that the n–$\pi^\star$ excited state of the imine is the reactive state in photoreduction. Our studies[24] on the photoreduction of benzaldehyde *N*-alkylimines disclosed a number of disquieting features which altered this conception of the reaction.

We have found that the irradiation of a series of benzaldehyde *N*-alkylimines in alcoholic solvent affords dihydro-photodimers. Although the reaction bears analogy to aryl ketone photoreduction, the available data indicate that the reaction is quite different mechanistically in that it appears

$$PhCH{=}N{-}R \xrightarrow[\text{(CH}_3)_2\text{CHOH}]{hv} \begin{array}{c} PhCH{-}NHR \\ | \\ PhCH{-}NHR \end{array} + CH_3COCH_3$$

not to involve the excited state of the imine as an intermediate in the reduction. We have been able to demonstrate that the reaction proceeds via an α-amino radical, formed by hydrogen atom transfer to the imine from a ketyl radical. The ketyl radical is derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species (see Scheme I).

Scheme I

$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^{\star 1} \rightsquigarrow Ph_2C{=}O^{\star 3}$$

$$Ph_2C{=}O^{\star 3} + (CH_3)_2CHOH \rightarrow (Ph)_2\dot{C}OH + (CH_3)_2\dot{C}OH$$

$$Ph_2\dot{C}OH + PhCH{=}NR \rightarrow Ph_2C{=}O + Ph\dot{C}HNHR$$

$$(CH_3)_2\dot{C}OH + PhCH{=}NR \rightarrow (CH_3)_2C{=}O + Ph\dot{C}HNHR$$

$$2Ph\dot{C}HNHR \rightarrow \underset{\underset{PhCHNHR}{\mid}}{PhCHNHR}$$

A number of related reports have subsequently appeared in the literature showing that reactions apparently involving sensitization by benzophenone in hydrogen-donating solvents proceed, in fact, via formation of ketyl radicals[45]. The term 'chemical sensitization' was suggested to distinguish between such cases and sensitization involving excitation-energy transfer[25].

The lack of reactivity of the excited state of simple imines suggests that the excited states undergo a very efficient non-radiative decay to ground state thereby precluding hydrogen abstraction. This facile energy deactivation may be a consequence of rotation about the C—N double bond (i.e. syn ⇄
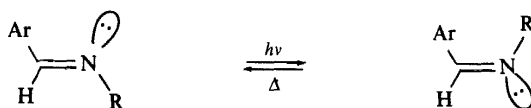
anti photoisomerization). In fact, we have recently demonstrated that syn-anti photoisomerization provides the major route for deactivation of the excited state of an oxime-*O*-methyl ether[46]. In rigid systems, this mode of energy dissipation would not be available and these cyclic imines would have maximum opportunity to undergo reaction from an electronically excited state.

OBSERVATIONS ON THE SCOPE OF THE PHOTOCYCLOADDITION OF ARYLAZIRENES

In order to evaluate the effect of incorporating a C—N double bond into a cyclic system, we have studied the photochemistry of a number of aryl-azirenes. When phenylazirene (**1**) was irradiated in the presence of methyl acrylate a good yield (80 per cent) of a 1:1 adduct was obtained. The adduct could be assigned structure **2a** on the basis of unambiguous spectral evidence.


2a: R = CO_2CH_3
2b: R = CN
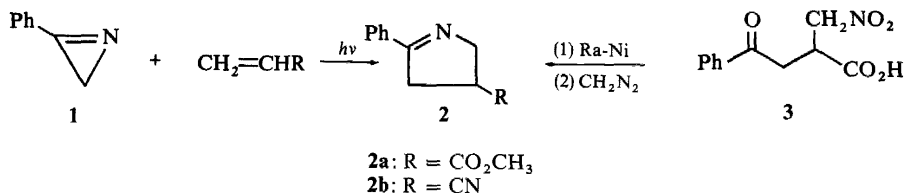
Structure **2a** was further confirmed by its unequivocal synthesis from 3-benzoyl-2-nitromethylpropionic acid (**3**) by Raney nickel (W2) reduction followed by esterification with diazomethane. Similarly, when acrylonitrile or tetracyanoethylene was used as substrate, Δ^1-pyrroline **2b** and 2-phenyl-3,3,4,4-tetracyano-Δ^1-pyrroline (**2c**) were formed in high yield.

The photochemical reaction of 2,3-diphenylazirene (**4**) with electron-deficient olefins was also investigated. Under standard irradiation conditions the reaction of **4** and methyl methacrylate afforded a mixture of 2,5-diphenyl-4-methyl-4-carbomethoxy-Δ^1-pyrrolines **5** (40 per cent) and **6** (60 per cent).
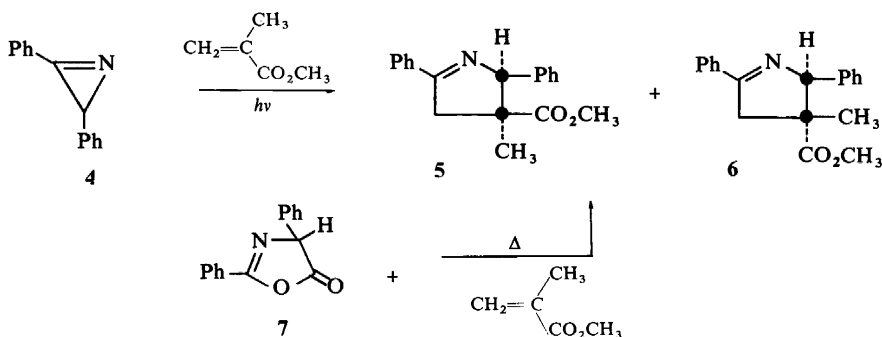

The stereochemical relationship of photoadducts **5** and **6** is apparent from the spectral data. The same two adducts were prepared by heating 2,4-diphenyl-Δ^2-oxazoline-5-one (**7**) with methyl methacrylate in xylene. Similar cyclo-additions using tetracyanoethylene, acrylonitrile and methyl acrylonitrile as substrates furnished related photoadducts in high yield. The photoaddition of diphenylazirene with methyl propiolate or dimethylacetylene dicarboxylate produced pyrroles **8** and **9** in good yield.
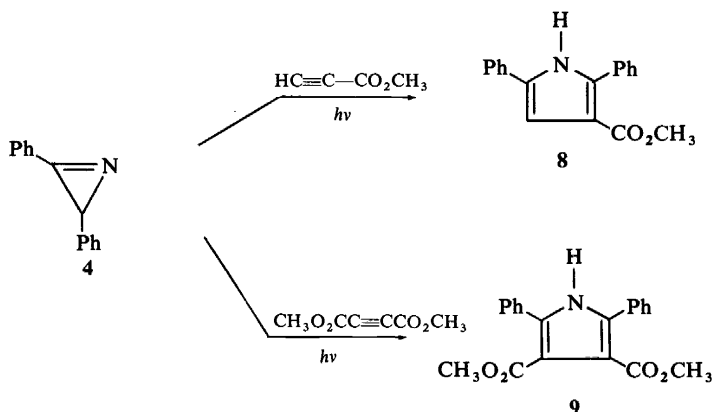

Irradiation of a mixture of **4** and methyl acrylate led to an especially clean photoaddition process giving 2,5-diphenyl-*cis*-4-carbomethoxy-Δ^1-pyrroline

(10) as the only photoadduct. In contrast, heating 7 with methyl acrylate afforded the isomeric *trans*-pyrroline 11.
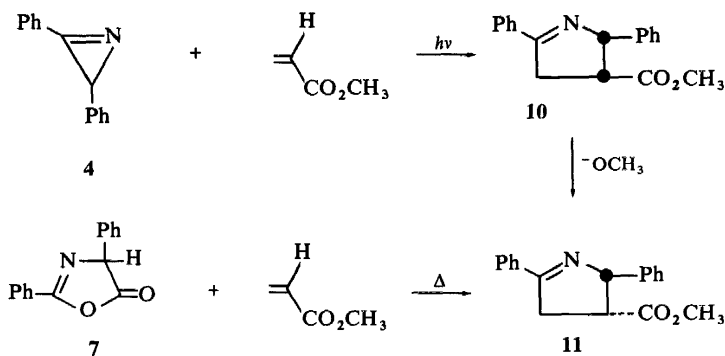
Control experiments demonstrated that 10 was stable to the thermal conditions. Proof of the *cis* relationship of the groups in 10 was obtained by base-catalysed epimerization of 10 to 11. The difference in product stereochemistry from the reactions of 4 and 7 with methyl acrylate suggests the absence of a common intermediate. Irradiation of arylazirenes 12, 13, and 14 with acrylonitrile in benzene was also found to give Δ^1-pyrrolines as major products.
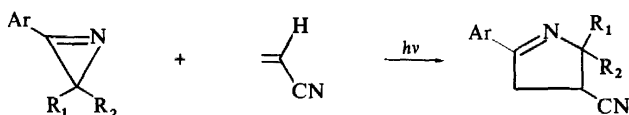

12: Ar = Naphthyl, $R_1 = R_2 = H$
13: Ar = Ph, $R_1 = CH_3$; $R_2 = H$
14: Ar = Ph, $R_1 = R_2 = CH_3$

MECHANISM OF CYCLOADDUCT FORMATION

The photocycloaddition of arylazirenes with electron-deficient olefins to produce Δ^1-pyrrolines can be rationalized by the assumption that the electronically excited state of the azirene opens to give a nitrile ylide intermediate 15. As a 1,3-dipole, 15 can be intercepted with suitable dipolarophiles to form five-membered rings[47].
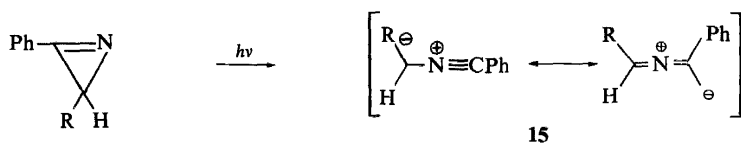

The 1,3-dipolar cycloaddition of azlactones such as 7 has been suggested to proceed by tautomerization to a mesoionic oxazolium 5-oxide (16) which

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then combines with the dipolarophile[48]. This is consistent with the difference in product stereochemistry found in the reactions of **4** and **7** with methyl acrylate. Formation of the less thermodynamically stable *cis*-Δ^1-pyrroline **10** from the irradiation of **4** may be the result of preferred geometrical or
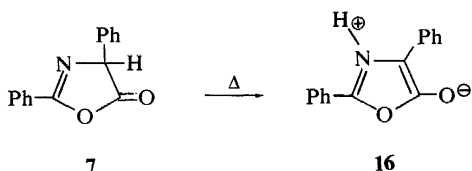

electronic factors operative in the transition state for cycloaddition. The orientation of the groups in the Δ^1-pyrrolines is similar to that observed by Huisgen in related 1,3-dipolar additions (i.e. the base-induced elimination of HCl from imidoyl chloride **17**)[49, 50]. This orientation is the opposite of that expected on the basis of the nitrilium resonance formula **18**. It is also interesting to note that Huisgen has reported that diarylazirenes do not undergo thermal cycloaddition with dipolarophiles[51].
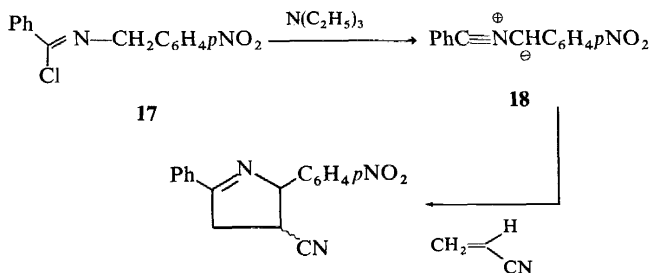

All the cycloadditions of octet-stabilized 1,3-dipoles examined so far have been shown to undergo stereospecific *cis*-addition[50]. In order to determine whether the nitrile ylide (**15**) generated from the photolysis of diphenylazirene behaves similarly, we have studied the irradiation of **4** with fumaric and maleic esters. The results obtained show that the addition of **15** to the *cis*

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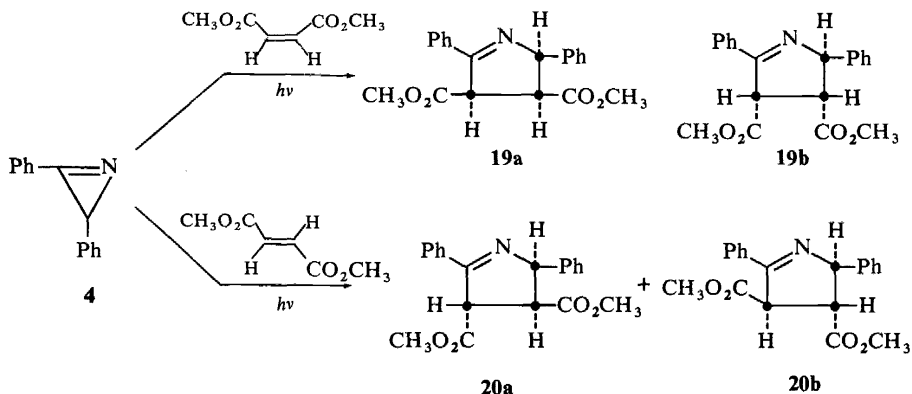
and *trans* dipolarophiles is totally stereospecific yielding the diastereo-isomeric Δ^1-pyrrolines **19a, b** and **20a, b**. All of these compounds can be dehydrogenated to the same pyrrole (**9**). Dimethylphenylazirene (**14**) also reacts stereospecifically with the fumaric and maleic esters, producing the respective adducts (**21, 22**) nearly quantitatively with no admixtures of their diastereoisomers.
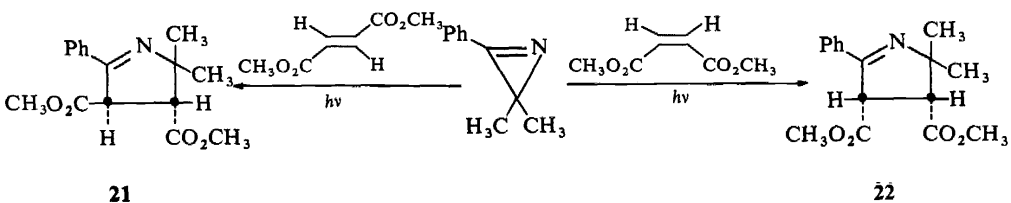
When the irradiation of diphenylazirene was carried out in cyclohexane or with olefins of low dipolarophilic activity (such as methyl β-methylcrotonate), no photoadduct was obtained, but instead tetraphenylpyrazine (**23**) was isolated on extended photolysis. Hassner and Levy have also reported the formation of tetraphenylpyrazine (40 per cent) from the irradiation of α-azido-*trans*-stilbene[52].
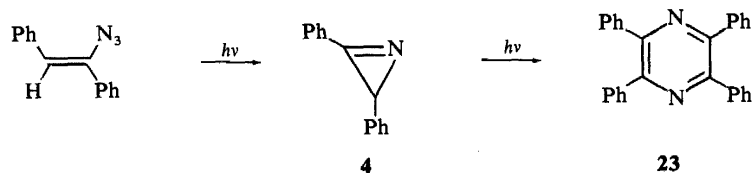
On the basis of the data obtained in our studies, we wish to suggest that the dimerization proceeds by addition of the nitrile ylide **15** to ground-state azirene with the formation of a 1,3-diazabicyclo[3.1.0]hex-3-ene intermediate. On further irradiation this species is converted to tetraphenylpyrazine.

These conclusions are confirmed by a study of the variation of the quantum yield of adduct formation as a function of the concentration of added di-polarophile at 3130 Å. The results of the quantum yield measurements in degassed pentane solution are given in *Figures 1* and *2*.

Although a good linear relationship is found between the inverse of the quantum yield for adduct formation and the inverse of concentration of dipolarophile, the slope of the line varies both with the structure of the dipolarophile and the concentration of diphenylazirene used. At infinite concentration of dipolarophile, the quantum yield for cycloaddition is 0.8, showing that the major pathway from the excited state of azirene involves bond rupture and formation of nitrile ylide **15**. The photoaddition reactions of **4** could not be quenched by standard triplet quenchers nor could they be sensitized by triplet donors. These results suggest that the reaction originates from the excited singlet manifold of **4**. The plots shown in *Figures 1* and *2* are consistent with the mechanism shown in Scheme II, where Ao denotes diphenylazirene, NY is nitrile ylide (**15**), and O is dipolarophile.
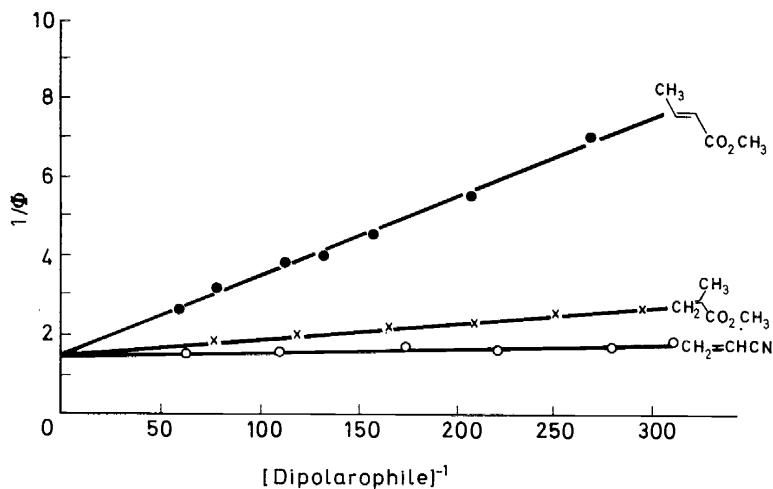
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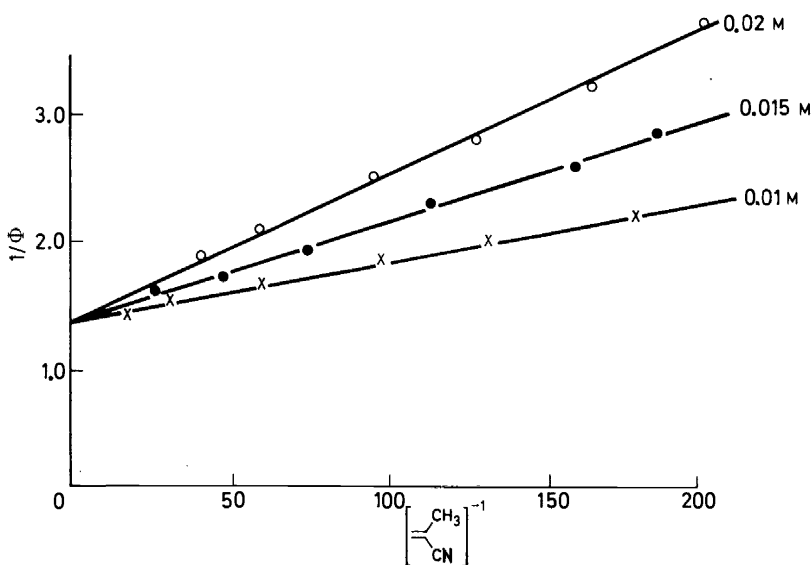Figure 1. Plot of (quantum yield of cycloaddition)$^{-1}$ against [dipolarophile]$^{-1}$.
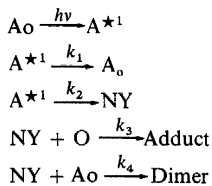

Figure 2. Plot of (quantum yield of cycloaddition)$^{-1}$ against [α-methylacrylonitrile]$^{-1}$ as a function of diphenylazirene concentration.

Scheme II

$$Ao \xrightarrow{h\nu} A\star^1$$
$$A\star^1 \xrightarrow{k_1} A_o$$
$$A\star^1 \xrightarrow{k_2} NY$$
$$NY + O \xrightarrow{k_3} Adduct$$
$$NY + Ao \xrightarrow{k_4} Dimer$$

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By making the usual steady state assumption, we can write

$$\frac{1}{\Phi_{adduct}} = \frac{1}{\tau k_2}\left[1 + \frac{k_4[Ao]}{k_3[O]}\right]$$

where τ is the excited singlet lifetime. According to this mechanistic scheme, the slope of the plot should be dependent on both the initial concentration of diphenylazirene as well as the magnitude of k_3. Quantitatively, if $k_3 \gg k_4[Ao]$, then little variation in slope is to be expected as the concentration of **4** is increased. This is so with acrylonitrile, an olefin of high dipolarophilic activity. In cases where k_3 and $k_4[Ao]$ have similar values (such as with methyl acrylonitrile) the slope of the plot will depend on the concentration of diphenylazirene.

From the slope and intercept of the Stern–Volmer analysis for adduct formation with a given dipolarophile and at a fixed azirene concentration, we find that

$$slope/intercept = k_{4'}/k_3 \qquad \text{where} \quad k_{4'} = k_4[Ao]$$

For the case of methyl methacrylate, $k_{4'}/k_3 = \frac{1}{6}$. This value indicates that the rate constant for cycloaddition of **15** with methyl methacrylate is six times greater than the rate of its reaction with ground state azirene. Since $k_{4'}$ is constant for a given azirene series, we can estimate the relative reactivity of various dipolarophiles toward the photochemically generated nitrile ylide by determining the magnitude of their slopes and intercepts in a Stern–Volmer plot.

$$\frac{[k_{4'}/k_{3A}]\ \text{Olefin}\#\,A}{[k_{4'}/k_{3B}]\ \text{Olefin}\#\,B} = \frac{k_{3B}}{k_{3A}} = k_{rel.}$$

Another approach was also used to secure a quantitative measure of the relative reactivity of various dipolarophiles toward nitrile ylide **15**. Generation of **15** by photolysis of **4** in the presence of a mixture of dipolarophiles creates a competitive system from which the ratio of relative rates, $k_{rel.} = k_{3B}/k_{3A}$ may be obtained by standard treatment of the kinetic data. The required data for the calculation of $k_{rel.}$ are the initial concentration of each of the competing dipolarophiles and the concentration of each at a subsequent stage in the reaction. In principle these data may be determined either directly by measuring the amount of dipolarophile remaining or indirectly

$$k_{rel.} = \frac{k\ \text{Olefin}\#\,B}{k\ \text{Olefin}\#\,A} = \frac{\log([O_B]\,i/[O_B]\,f)}{\log([O_A]\,i/[O_A]\,f)}$$

from a knowledge of the concentration of reaction products. The agreement between the $k_{rel.}$ values determined by the Stern–Volmer technique and those determined by the direct competition method is excellent (see *Table 1*).

Table 2 gives a list of the relative rate constants for the cycloaddition of various dipolarophiles with nitrile ylide **15**. To facilitate comparison, all the k_3 values are related to that for methyl crotonate, which is taken as unity. The data presented in *Table 2* show that the rate of cycloaddition is dramatically

affected by steric factors. Sterically congested dipolarophiles react so sluggishly that their very small rate constants cannot be measured satisfactorily. Introduction of a methyl group into the α- or β-position of an acrylic ester results in a significant diminution in rate. Also, *trans*-substituted dipolarophiles undergo cycloaddition at a much faster rate than the corresponding *cis* isomers. These same phenomena have been reported by Huisgen for related 1,3-dipolar cycloaddition reactions[50].

Table 1. Relative reactivity of dipolarophiles toward nitrile ylide **15** determined by the Stern–Volmer and direct competition methods

	Stern–Volmer technique	Direct competition
α-Methyl methacrylate	8.5	9
α-Methyl acrylonitrile	3.6	3.6
Methyl crotonate	1	1

Table 2. Relative reactivity of a series of olefins toward nitrile ylide **15**

Dipolarophile	Relative rate	Dipolarophile	Relative rate
Methyl crotonate	1	Acrylonitrile	180
Diphenylazirene	2.5	Dimethylacetylene dicarboxylate	540
α-Methyl acrylonitrile	3.6	*cis*-Dicyanoethylene	2 300
α-Methyl methacrylate	9	Diethyl fumarate	56 000
Diethyl maleate	135	Dimethyl fumarate	84 000
Methyl acrylate	160	*trans*-Dicyanoethylene	189 000
Dimethyl maleate	166		

The above discussion has indicated that the photocycloaddition of diphenylazirene (**4**) with a variety of dipolarophiles proceeds by way of irreversible ring opening of **4** to form a nitrile ylide intermediate (**15**). The reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**17**) with triethylamine in the presence of a dipolarophile has also been shown to proceed by way of a nitrile ylide intermediate (**18**). In order to secure additional information on

Table 3. Relative reactivities of olefins toward the nitrile ylides generated from diphenylazirene (**4**) and *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**17**)

Olefin	Diphenylazirene	Imidoyl chloride
	Slow set	
Methyl crotonate	1	1
Methyl methacrylate	9	10
Diethyl maleate	135	51
Dimethyl maleate	166	61
	Fast set	
Diethyl fumarate	1	1
Dimethyl fumarate	1.5	1.3
Fumaronitrile	3.3	3.1

whether an electronically relaxed nitrile ylide intermediate is involved in the photocycloaddition reaction, we have compared olefin reactivities toward **15** generated by photolysis of **4** with the reactivities of the same olefins toward ylide **18**. We expect that the *p*-nitro group present in **18** will not appreciably affect the reactivity of this species. The results are given in *Table 3*. Especially noteworthy is the near identity of the relative reactivities of all the olefins examined toward both nitrile ylides. These results would lead one to conclude that similar species are involved in the product-forming step in both systems; the most reasonable intermediate common to both systems is a vibrationally and electronically relaxed nitrile ylide.

## FORMATION AND PHOTOCHEMISTRY OF THE 1,3-DIAZABICYCLO[3.1.0]HEX-3-ENE SYSTEM

The Stern–Volmer plots shown in *Figures 1* and *2* make it clear that the dimerization of diphenylazirene proceeds by reaction of the nitrile ylide **15** with diphenylazirene. Further support for this contention was obtained by irradiating diphenylazirene in an inert solvent for shorter periods of time. Photolysis of **4** in cyclohexane afforded *endo* (**24**) and *exo*-2,4,5,6-tetraphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**25**) as well as tetraphenylpyrazine (**23**).
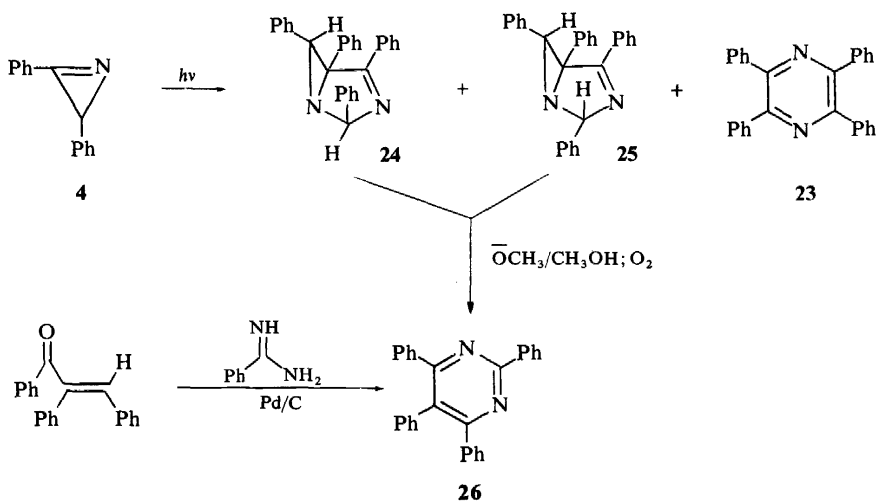

Chemical confirmation of these structures was obtained by treating **24** and/or **25** with sodium methoxide in methanol in the presence of oxygen to give tetraphenylpyrimidine (**26**). Compound **26** was independently synthesized by treating 1,2-diphenylacrylophenone with benzamidine followed by oxidation over palladium on charcoal.

The formation of products **24** and **25** can be interpreted in terms of 1,3-dipolar addition of nitrile ylide **15** on to diphenylazirene. On further irradiation, dimers **24** and **25** are converted to tetraphenylpyrazine (**23**). This latter transformation has been shown to proceed by ring opening of the diazabicyclic system to enediimine **27** which thermally cyclizes to *cis*-dihydropyrazine

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28. Oxidation of **28** during work-up nicely rationalizes the formation of tetraphenylpyrazine (**23**).
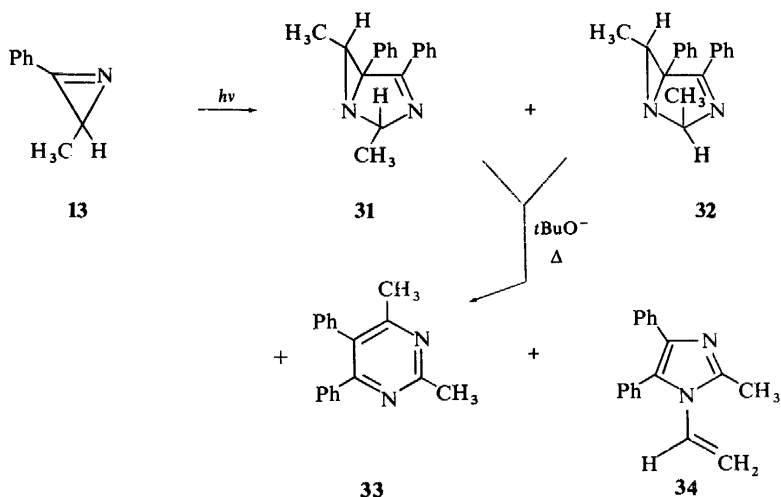

24 (and/or 25)   27   28
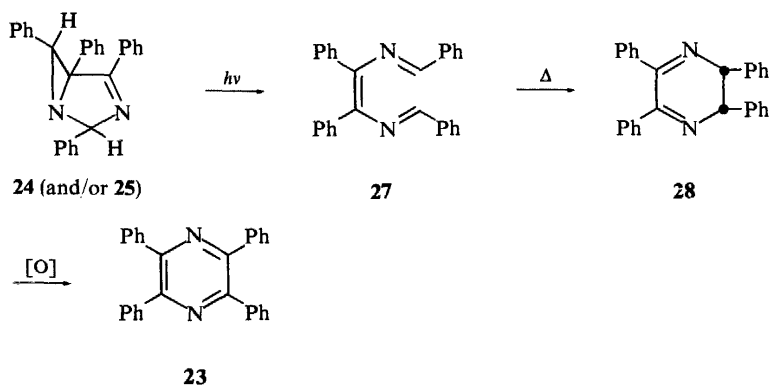
Woerner, Reimlinger and Arnold[53, 54] had previously reported that irradiation of 2-phenylazirene (**1**) results in the formation of 4-phenyl-3-phenylimino-1-azabicyclo[2.1.0]pentane (**29**). We have found that irradiation of **1** produces a dimer consistent with that described by these workers to which we assign an alternate structure, 4,5-diphenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene (**30**), based on the data and an independent synthesis. Again,
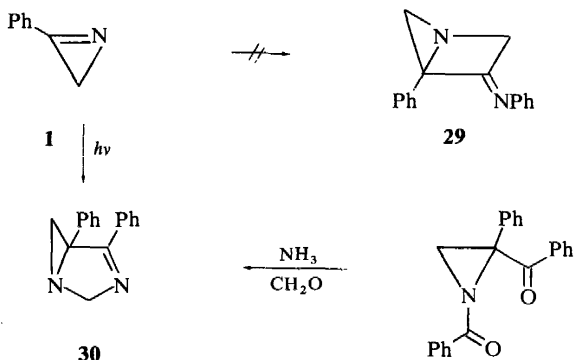
the formation of the dimer can be interpreted in terms of 1,3-dipolar addition of the initially generated nitrile ylide on to phenylazirene.
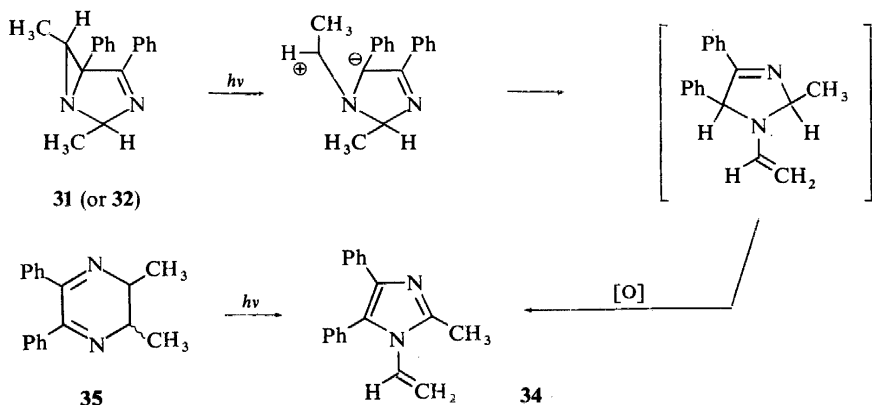
When 3-methyl-2-phenylazirene (**13**) was irradiated in cyclohexane at room temperature, a 3:1 mixture of diazabicyclohexenes **31** and **32** was obtained in 45 per cent yield. The structure of the dimers rests firmly on spectroscopic and chemical evidence. Chemical confirmation was obtained by treating **31** and/or **32** with potassium tert-butoxide in refluxing toluene to give 2,4-dimethyl-5,6-diphenylpyrimidine **33**. In addition to dimers **31** and **32**, pyrimidine **33** (8 per cent) and N-vinyl-3-methyl-4,5-diphenylimidazole **34** (12 per cent) were also isolated from the irradiation of **13**.

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Ph—C=N
H₃C H

13

hv →

H₃C H
Ph Ph
N H N
CH₃

31

+

tBuO⁻
Δ

H₃C H
Ph Ph
N CH₃ N
H

32

+

CH₃
Ph
Ph N CH₃

33

+

Ph
N
Ph N CH₃
H CH₂

34

Imidazole **34** was independently synthesized by irradiating 2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine (**35**) in cyclohexane according to the procedure of Beak and Miesel[9]. These workers had previously demonstrated that 2,3-dihydropyrazines rearrange to imidazoles upon photolysis.

Compounds **33** and **34** were shown to be secondary photoproducts derived from further irradiation of diazabicyclohexenes **31** and **32**. The photoconversion of **31** (and/or **32**) into **34** may be formulated as proceeding via an azomethine ylide formed by cleavage of the aziridine C—C bond[13, 14]. Proton transfer followed by oxidation of the transient N-vinylimidazoline readily accounts for the formation of **34**. The isolation of pyrimidine **33** from the photolysis of **31** (and/or **32**) can be attributed to cleavage of the aziridine C—N bond followed by loss of hydrogen.

H₃C H
Ph Ph
N N
H₃C H

31 (or 32)

hv →

CH₃
H⊕ Ph Ph
N⊖ N
H₃C H

→

Ph
Ph—C=N
CH₃
N
H H
H CH₂

Ph
Ph N CH₃
H₃C CH₃

35

hv →

Ph
N
Ph N CH₃
H CH₂ **34**

← [O]

Further evidence for the mechanism of the photodimerization of arylazirenes was derived by irradiating an equimolar mixture of 2-phenyl- and 2,3-diphenylazirene. At 3130 Å the extinction coefficient for diphenylazirene is

about twenty times that of phenylazirene, so that *ca.* 95 per cent of the light is absorbed by diphenylazirene in the above experiment. Under these conditions a mixture of two 1:1 adducts was isolated and subsequently identified as *endo-* and *exo-*2,4,5-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (36 or 37).
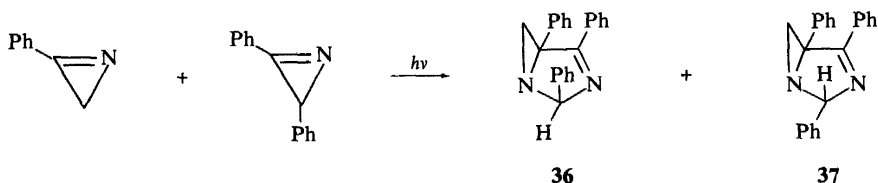
Upon treatment with sodium methoxide in methanol, 36 and/or 37 afforded 2,4,5-triphenylpyrimidine 38. Compound 38 was prepared independently by the reaction of α-phenylacrylophenone with benzamidine followed by oxidation over palladium on charcoal. The above structural assignments were further confirmed by an independent synthesis of 36 and 37 from 1,2-dibenzoyl-2-phenylaziridine, benzaldehyde and ammonia.
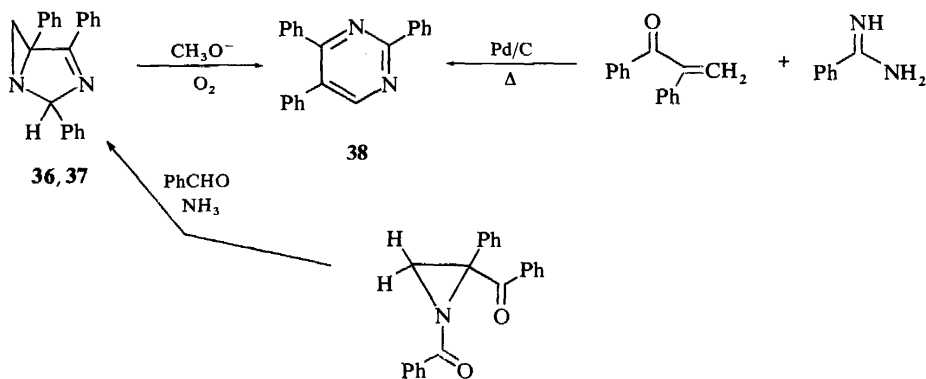

The formation of 36 and 37 can be most economically rationalized in terms of 1,3-dipolar addition of the initially generated nitrile ylide on to phenylazirene.
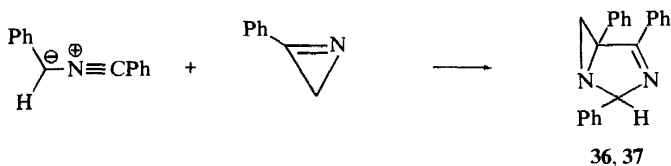
On further irradiation (in cyclohexane) 36 and 37 are converted to triphenylpyrimidine (38) in low yield. When the irradiation of 36 (or 37) was carried out in methanol, two new compounds were formed in addition to 38. These

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structures have been assigned as *N*-methoxymethyl-2,4,5-triphenyl-2,3-dihydroimidazole (**39**) and *N*-methoxymethyl-2,4,5-triphenylimidazole (**40**). The latter two products can be attributed to the addition of methanol to the azomethine ylide formed on irradiation of **36** (or **37**).

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

40
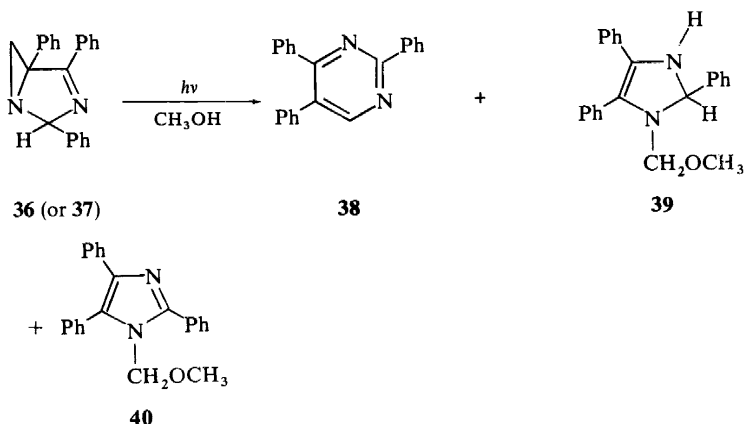
CONCLUSION

The foregoing examples have been considered in order to provide at least a partial indication of the intriguing transformations that small ring cyclic imines undergo upon electronic excitation. Clearly much more remains to be done on the photochemical behaviour of imine derivatives. Mechanistic parameters such as solvent, substituent, wavelength and temperature effects, and structure/property correlations remain to be explored. Considerable work in this area has been carried out by many investigators, and it may be safely anticipated that significant and new findings in imine photochemistry will be forthcoming in the future.

ACKNOWLEDGEMENT

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