Photochemistry of the Carbon–Nitrogen Double Bond

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Contents

I. 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. Although the light-induced reactions of carbon-nitrogen double bond compounds have been the subject of investigation since the late nineteenth century, this area of photochemistry has only recently been exposed to the wealth of techniques now available to the modern investigator. As a result, our knowledge of the photochemistry of the C–N double bond is mainly qualitative with relatively little available in the way of quantum yield data and kinetic studies. Likewise, emission spectroscopy, a powerful tool for elucidating the nature of lowest excited states, has been employed only sparingly on the substrates to be discussed. Even though the photochemistry of the C–N double bond has not been the subject of extensive mechanistic studies, a considerable number of diverse reports have accumulated in the literature without critical review. Irradiation may lead to isomerization, prototropy, rearrangement, cycloaddition, oxidation, hydrolysis, cyclization, photoreduction, and photoalkylation. The large number of known photochemical reactions associated with the C–N double bond has commonly been treated as a group of separate entities; only recently have attempts been made to classify them in some fashion.[6,7] The present manuscript, which covers the literature through December 1975, provides a summary of the photochemical transformations of C–N double bond systems and attempts to relate the excited state behavior of these systems to that of C–O and C–C double bond analogs. In this report we review all C–N double bond processes including electronic absorption phenomenon, luminescence, nonradiative decay, energy transfer, and chemical reaction. The emphasis is on critical evaluation of all published material and enough data are presented to establish strong generalities.

II. Spectroscopy

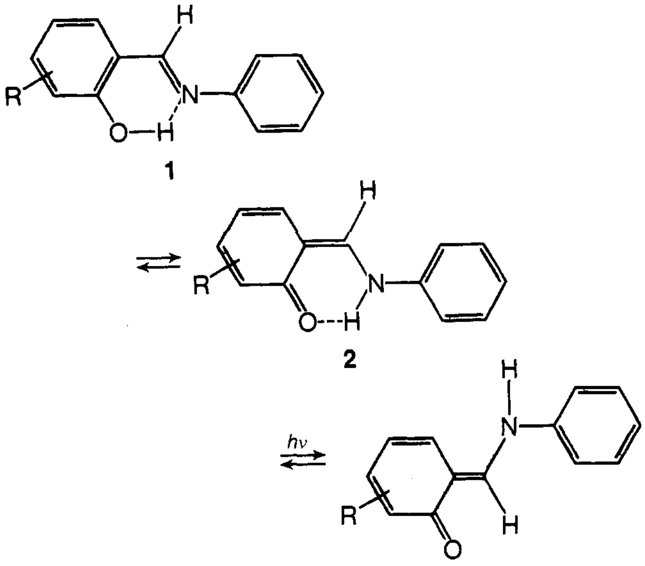
An isolated azomethine group gives rise to two absorption peaks in the ultraviolet region of the spectrum. The band at 2400 Å has been assigned to a $n-\pi^*$ transition because its molar absorptivity is about 2×10^2, and it shows a bathochromic shift on decreasing the polarity of the solvent.[9–14] The band at 1800 Å has a higher molar absorptivity of about 10^4, shows a hypsochromic shift, and has been designated as a $\pi-\pi^*$ transition.[15] Protonation of the nonbonded electrons on the nitrogen atom causes the weak band to be replaced by a strong absorption, presumably due to a $\pi-\pi^*$ transition.[10] Since the azomethine group is a weak chromophore and is located in the far-ultraviolet, its effect is easily submerged if other chromophoric groups are present in the molecule. Thus, in some of the steroidal azomethines, the band is partially submerged in end absorption and appears merely as an inflection.[16]

The conjugation of the azomethine chromophore with olefinic or aryl groups changes the spectrum considerably, since rather weak bands due to $n-\pi^*$ transitions are now submerged by strong absorption associated with $\pi-\pi^*$ transitions. Often bands still appear in the 230-nm region, but their intensities ($\epsilon \sim 10^4$) leave little room for confusion. Further bands or inflections may be observed at longer wavelengths, and these have been attributed, in some cases, to $n-\pi^*$ components.[17] The long-wavelength absorption of *N*-benzylidenealkylamines is the subject of conflicting reports. In some cases[11,13] inflections in the 280-nm region have been observed; in others these have not been noted.[18,19] Benzophenone imine is reported to have a strong absorption at 260 nm ($\epsilon \sim 10^4$) and a weaker one at 340 nm (ϵ 125) in absolute alcohol.[20] The long-wavelength absorption band is generally thought to be derived from population of a $n-\pi^*$ state. Irradiation at this long-wavelength tail assures that at least the lowest energy singlet (and possibly the lowest triplet) of aryl *N*-alkylimines possesses an $n-\pi^*$ configuration. The interest in $n-\pi^*$ states stems from the fact that in carbonyl photochemistry they have been designated as the reactive state in hydrogen abstraction and photocycloaddition reactions,[21] although some exceptions have begun to appear in the literature.[22-24]

III. Photochromism

Photochromism is the phenomenon of a reversible change in color brought about by exposure to electromagnetic radiation. In photochromic substances absorption of radiation leads to a photochemically stable but thermodynamically metastable state B from which it may revert to the original state A by absorption either of light of a different wavelength or of thermal energy. Three conditions are necessary for a material to be photochromic; the state B should be moderately stable, it should absorb radiation in a different region of the spectrum to A, and the radiation or thermally induced change B → A should occur. A great number of C–N-containing double-bond compounds exhibit photochromism both in solution and in the solid state. A list of such compounds includes anils, hydrazones, osazones, and semicarbazones. In some cases the reactions responsible for the color change are known, but for several reactions the mechanism is totally unknown.

Schiff bases having a hydroxyl group ortho to the C=N bond on the benzaldehyde ring are known to give rise to crystals which change their color from yellow to red upon exposure to light.[25–28] The process is reversible; heating in the dark or irradiation within the new absorption band reverts the system to the initial state. The importance of an *o*-hydroxy group was confirmed by the absence of photochromy when benzaldehyde or *p*-hydroxybenzaldehyde was condensed with aniline, or when the *o*-hydroxy group was methylated. Many of the ring-substituted anils exist in two polymorphic forms, one of which is photochromic and the other thermochromic. These observations have been interpreted by postulating a two-step molecular rearrangement. Compound **1** is the stable anil which is in tautomeric equilibrium with **2**. Thermochromism involves a shift in this equilibrium toward **2**. Photochromism accompanies the cis–trans isomerization of **2** into **3** through rotation about the C=C double bond. The thermal activation energy for the reverse (color-fading) reaction is that required for the thermal trans–cis isomerization. The long-wavelength absorption at 540–580 nm in the photochromic colored species is assigned to the $n-\pi^*$ transition in the quinoid isomer **3** where the oxygen atom is no longer involved in hydrogen bonding.[29–33] The reason for the different behavior of the two polymorphs lies in their crystal structures. In the photochromic form the molecules are nonplanar and there are no close intermolecular contacts normal to the ring. Consequently, the activation energy for the cis–trans isomerization step is not much higher than in the free molecule. In the thermochromic form the molecules are planar with intermolecular spacing normal to the rings of only 3.3 Å. This close contact increases the activation energy and also stabilizes the quinoidal form **2** through intermolecular (dipole–dipole or hydrogen-bonding) interactions.



1

2

3

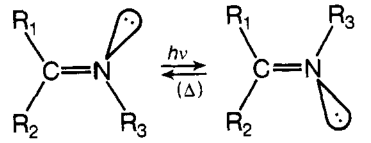
With C–N double-bond-containing compounds other than anils, the knowledge of the photochromism is often rudimentary; in many cases all that is known is that a particular compound undergoes a color change. Many interesting examples of photochromic reactions, a great number of which directly account for color changes of dyestuffs, have been reviewed elsewhere.[34]

IV. Syn–Anti Photoisomerization

The thermal[39–45] and photo-[46–69] interconversions of the syn and anti isomers of imines are a subject of long-standing interest. The mechanism for the thermal interconversion of imine diastereomers is currently the subject of considerable debate[70–79] and has been considered in terms of either a planar inversion mechanism or a rotation mechanism. The rotation or torsion mechanism involves a twisting about the C–N double bond. In order to bring about this change in geometry, there must be a reduction in the double bond character of the imine bond in the transition state relative to the ground state. The C=N—C bond angle remains constant at 120 °C on proceeding through the transition state, as does the sp^2 conjugation of the lone pair of electrons on nitrogen. The inversion mechanism, on the other hand, is characterized by an increase in the angle of the C=N—C bond from approximately 120 °C in the ground state to 180 °C in the transition state. The double-bond character of the imine bond remains intact in the transition state, as the lone pair of electrons on nitrogen rehybridizes from sp^2 to sp. With this mechanism, the nonbonding electrons on nitrogen become available as p electrons for conjugative interaction with other π-electron systems attached to the nitrogen atom in the transition state. Evidence obtained from studies of substituent effects (steric and electronic) suggests that most simple imines interconvert by the inversion mechanism,[80] although some of the results obtained have been considered to be inconclusive.[70–72] Lehn has recently reported that heteroatoms present in the substituents of alkyl- and aryl-substituted imines may appreciably perturb the C–N double bond and lower the barrier to torsion below that of inversion.[70] Some support for this view is provided by the calculations of Raban.[81]

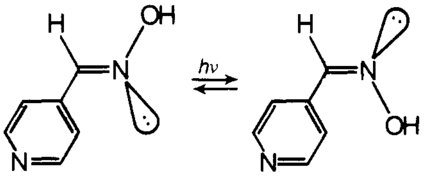
Recent investigations into the factors influencing the ease of thermal isomerization about the C–N double bond have shown that the interconversion barrier is remarkably sensitive to the attached substituent groups.[39,40] For example, among imino compounds derived from benzophenone, changes in groups attached to nitrogen produce a range of rates of uncatalyzed isomerizations of greater than 14 powers of 10.[39,43] Attempts to elucidate the mechanisms (lateral shift, rotational, or intermediate possibilities) of individual thermal imine isomerizations continue to challenge the ingenuity of various research groups and provide fuel for controversy.[73–79]

The mechanism by which the syn and anti isomers of imines are interconverted in the excited state is even more complicated. Whether isomerization about the C–N double bond proceeds by rotation or linear inversion remains to be clarified. A major complication with the photochemical studies is that the thermal barrier between the two diastereomers of most imines is sufficiently low that the photochemically induced shift in the configurational equilibrium is only temporary at ambient temperatures and is frequently followed by a rapid, thermal relaxation which reestablishes the initial configurational equilibrium between the syn and anti isomers.



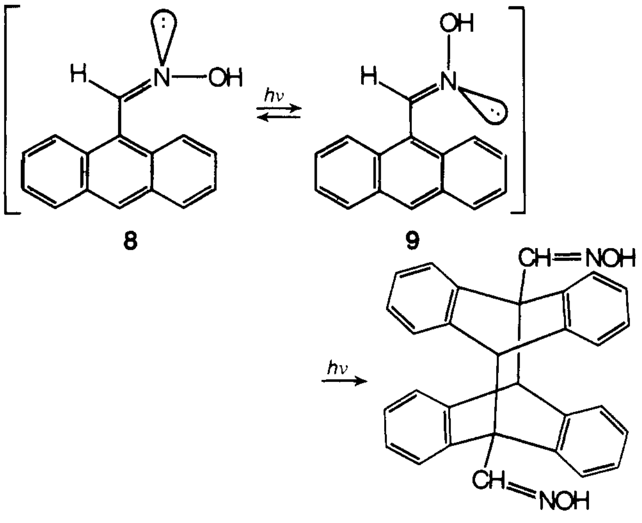
4 **5**

Even before the turn of the century, evidence was available which showed that ultraviolet light causes the rearrangement in oximes from one geometric isomer to the other.[46] Sporadic studies of this reaction have since been undertaken.[47–52] Its use for the chemical synthesis of the pharmacologically active isomer has been described for *trans*-isonicotinaldehyde oxime.[52]



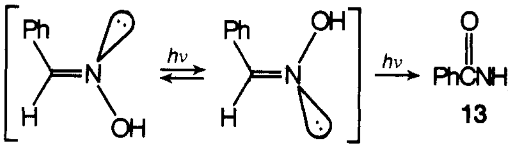
6 7

In addition to undergoing syn-anti photoisomerization, oximes are known to afford other products on electronic excitation. For example, Calas and co-workers observed that the oxime of 9-anthraldehyde not only photoisomerized but also underwent a competing [4 + 4] cyclodimerization.[53] These workers did not pursue the more mechanistic features of the photoisomerization process.



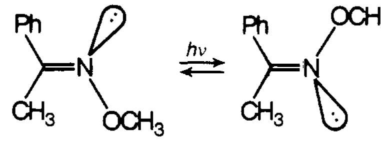
8 9 10

In 1963, deMayo's group found that aryl aldoximes undergo a photoinduced Beckmann rearrangement in competition with photoisomerization.[50] Benzaldoxime, for instance, gave benzamide on irradiation through quartz. The major route for energy degradation, however, was syn-anti isomerism.[51] These workers noted that the photoisomerization process could be induced by a variety of triplet sensitizers. Direct irradiation of benzaldoxime led to isomerism with high quantum efficiency ($\Phi \sim 0.4$). The composition of the calculated sensitized photostationary state was found to be in fair agreement with the experimentally found value. This led deMayo and co-workers to suggest that the isomerization induced by direct irradiation also passed through a triplet state.



11 12 13

Padwa and Albrecht have investigated the solution-phase syn-anti photoisomerization of oxime ethers in order to clarify the mechanistic details of the C–N double bond photoisomerization.[67,82,83] The great configurational stability of oxime ethers at room temperature stands in striking contrast to the behavior of *N*-aryl- and -alkylimines.[39] These oximes ethers are attractive candidates for mechanistic photostudies since the presence of the alkoxyl group drastically reduces the rate of thermal interconversion ($k < 10^{-13}$ at 60 °C) and allows mechanistic studies to be carried out at ambient temperatures. The irradiative conversion of oxime ethers into their geometrical isomers was first described by Ciusa in 1907[84] and has been studied more recently by other workers.[85] The results obtained by Padwa and Albrecht with oxime ethers **14** and **15** are of fundamental interest by virtue of the superficial parallels to and mechanistic differences from the corresponding situation in olefin photochemistry.



14 (syn) **15** (anti)

Irradiation of degassed pentane solutions of syn (or anti) oxime ethers (**14** or **15**) at 2537 Å led to a photostationary state ratio (syn/anti) of 2.20 over a wide concentration range (0.01–0.30 M). The quantum yield for syn → anti isomerization at 2537 Å was 0.30 in the 4–5% reaction range, while that for anti → syn was 0.27. The photostationary state obtained in the direct irradiation is that given below.

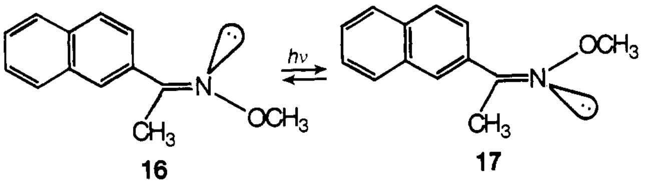
$$\frac{[\text{syn}]}{[\text{anti}]} = \frac{\epsilon_{\text{anti}}[\Phi_{\text{anti}\rightarrow\text{syn}}]}{\epsilon_{\text{syn}}[\Phi_{\text{syn}\rightarrow\text{anti}}]}$$

The photostationary state was calculated to be 2.40, which was found to be essentially identical with the experimental limits of the observed value.

Photoisomerization about the C–N double bond of the oxime ethers was also induced by triplet excitation. Various sensitizers with known triplet energies were employed to reach a sensitized photostationary state. The plot obtained showed several features comparable to those found in the study of stilbenes, namely (1) a high-energy region in which the stationary state ratio is ca. 1.5, (2) a gradual increase in the syn/anti ratio from 72 down to 58 kcal of triplet energy, and (3) a sharp decrease from 59 down to 54 kcal. The latter two observations could be satisfactorily explained by nonvertical excitation of the acceptor. The triplet energy of both isomers were determined as anti ($E_t \sim 58$ kcal/mol) and syn ($E_t \sim 72$ kcal/mol) by assuming that the syn energy level is the cause of the asymptotic behavior of the plot and the anti energy level is located at the maximum syn/anti ratio. The authors point out that the predicted photostationary state values ($\Phi_{A\rightarrow S}/\Phi_{S\rightarrow A}$) in these triplet-sensitized experiments are not in agreement with the photostationary state values actually obtained. This was attributed to the fact that the rate constants for quenching the sensitizer triplets by the two oxime ethers were not the same.

The fact that the sum of the triplet-sensitized quantum yields, $\Phi_{S\rightarrow A} + \Phi_{A\rightarrow S}$, was less than unity indicates that the triplet states of the oxime ethers include radiationless decay processes which proceed by paths not involving syn-anti isomerization. The data obtained show that syn-anti isomerization of the oxime ethers can be induced by direct irradiation as well as by triplet sensitization. A double sensitization experiment using the oxime ethers and *trans*-stilbene indicated that triplet energy transfer occurs from the oxime ethers to *trans*-stilbene. Since the direct irradiation could not be quenched with high concentrations of piperylene, it was suggested that the electronically excited singlet state is the reactive state in the direct isomerization. The sum of the quantum yields, $\Phi_{S\rightarrow A} + \Phi_{A\rightarrow S}$, in the direct irradiation was observed to be less than unity. This suggests that deactivation of the singlet state of the oxime ether also includes radiationless decay processes which proceed by paths not involving syn-anti isomerization. The source of inefficiency may be related to energy-degrading processes within a twisted excited state or may involve relaxation of planar excited states in competition with decay of the twisted form. The conclusion derived from this mechanistic study is that, although radiationless paths which maintain geometric integrity are important to a degree, syn-anti isomerization provides the major route for deactivation of the excited imine state.

Additional information on the reactivity of the excited state(s) involved in the syn–anti photoisomerization reaction was obtained by studying the photochemistry of the related naphthyl-substituted oxime ether.[83] Irradiation of degassed pentane solutions of syn (or anti) oxime ethers (**16** or **17**) at 3130 Å led to photostationary states whose composition varied from 64% syn at [oxime ether] = 0.003 M to 42% syn at [oxime ether] = 1.35 M. The data obtained indicate that the final photostationary state composition is dependent on both the temperature maintained and the concentration and solvent used during the course of the irradiation. The results showed that high oxime ether concentrations enhance the fraction of the anti isomer in the photostationary state. High temperatures, however, tended to diminish the fraction of the thermodynamically more stable anti form. Since no evidence for ground-state complexing could be found by UV, IR, or NMR spectroscopy, the observed variation in the photostationary state was attributed to interactions between excited- and ground-state molecules. The data obtained were consistent with the involvement of an excimer which is capable of inducing syn–anti isomerization and whose "decay ratio" differs from that of the excited monomer. The mechanism proposed to explain the data involves excitation of the oxime ether (X_0 = syn or anti oxime ether) to its spectroscopic singlet state followed by formation of a twisted excited state (P*). The spectroscopic singlet state can decay (k_d), fluoresce (k_f), or undergo collisional interaction with a ground-state molecule (k_2) to produce an excimer. The excimer's decay ratio differs from that of monomer (P* or possibly X^{*1}) and leads to preferential formation of the thermodynamically more stable anti isomer (A_0).



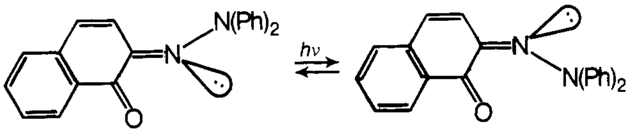
16 **17**

$$X_0 \xrightarrow{h\nu} X^{*1}$$
$$X^{*1} \xrightarrow{k_f} X_0 + h\nu^1$$
$$X^{*1} \xrightarrow{k_d} X_0$$
$$X^{*1} \xrightarrow{k_1} P^*$$
$$X^{*1} + X_0 \xrightarrow{k_2} [X\text{–}X]^{*1}$$
$$[X\text{–}X]^{*1} \xrightarrow{k_3} \alpha S_0 + \beta A_0$$
$$P^* \xrightarrow{k_4} S_0$$
$$P^* \xrightarrow{k_5} A_0$$
$$P^* + X_0 \xrightarrow{k_6} \alpha' S_0 + \beta' A_0$$
$$X^{*1} + C_0 \xrightarrow{k_7} [X\text{–}C_0]^{*1}$$
$$[X\text{–}C_0]^{*1} \xrightarrow{k_8} C_0 + \alpha'' S_0 + \beta'' A_0$$

In this scheme α and β represent partitioning factors and C_0 represents 1,3-cyclohexadiene. This rationale was reinforced by the observation that the fluorescence emission spectra of the oxime ethers are subject to concentration quenching. A new emission component in the fluorescence spectrum of the oxime ether appeared as the concentration was increased. The variation of the photostationary state composition as a function of temperature was attributed to the dissociation of the excimer with re-formation of the excited monomer at higher temperatures. The equilibrium associated with excimer formation and its corresponding "decay ratio" is expected to be influenced by the nature of the solvent system used. Excimers have also been reported to play an important role in the photoisomerization of certain olefinic systems.[86-88] In these cases it was found that a high olefin concentration enhances the fraction of the trans isomer in the photostationary state. This is analogous to the results outlined in the above oxime ether system.

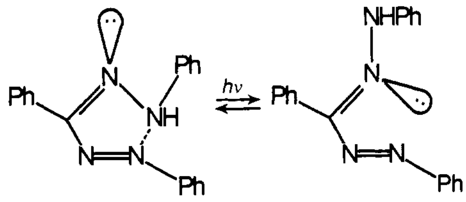
Quenching experiments using 1,3-cyclohexadiene as a singlet quencher were also carried out. The anti isomer was found to be more sensitive to fluorescence quenching than the corresponding syn form. The authors point out that chemical quenching is only one-quarter as efficient as fluorescence quenching.[83] Two possibilities were proposed to account for the variation in fluorescence vs. chemical quenching observed with the oxime ether system. One rationale involves the partial involvement of a short-lived unquenchable precursor to photoisomerization. This could be an upper excited state or a nonquenchable upper vibrational level of the first excited state. The diminished 1,3-cyclohexadiene quenching of the isomerization reaction would then reflect a combination of partial quenching of isomerization from the vibrationally equilibrated S_1 state and zero quenching of reaction from the upper vibrational levels of S_1 or an upper excited state. The other possibility which could account for the difference between fluorescence and chemical quenching assumed the involvement of an exciplex in the quenching reaction. In order to explain the preferred fluorescence quenching, the authors suggested that exciplex decay results in the partial isomerization of the oxime ether. The overall effect would then be less efficient chemical quenching than fluorescence quenching.

Photochemical syn–anti isomerization of hydrazones has also been reported in the literature.[54-57,89,90] The quinonoid system, 1,2-naphthoquinone 2-diphenylhydrazone (**18**), gave rise to remarkably large spectral changes; a wavelength shift of the absorption peak of 100 nm was reported.[89]



18 **19**

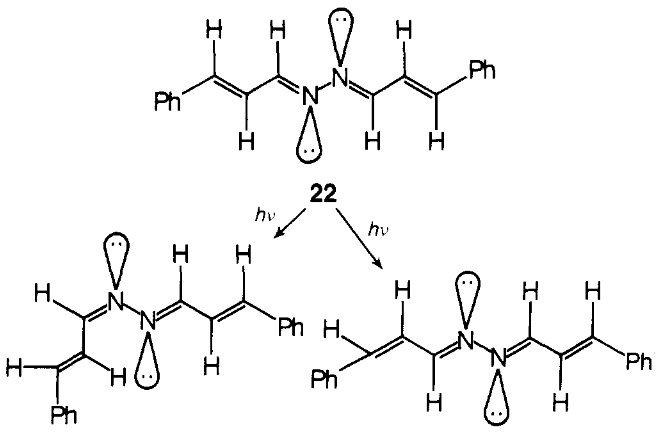
Triphenylformazone (**20**) undergoes a rearrangement which is thought to be a syn–anti photoisomerization about the C–N double bond. A benzene solution of this compound changes color from red to yellow upon irradiation with visible light.[54-57] A quantum yield of about 0.02 was measured for this process.



20 **21**

The all-trans form of cinnamaldehyde azine (**22**) is converted to two different mono cis isomers on irradiation.[91] One of these is believed to have a *Z* configuration with respect to the C–N double bond.

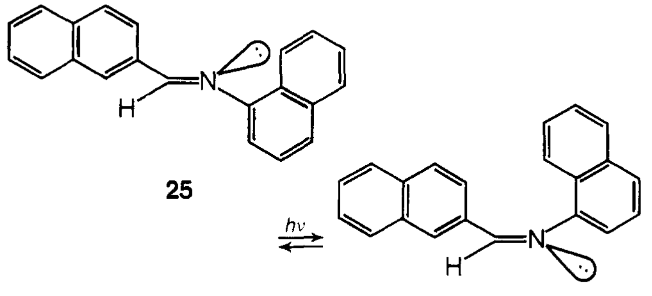
The photochemical interconversion of the syn and anti isomers of Schiff bases is of recent origin.[63] Initial reports appeared in the literature claiming that the geometric isomers could be separated. Soon afterwards, however, other authors stated that they were unable to repeat the experiment or that the isomerism in question was a case of dimorphism.[6] In 1957, Fischer and Frei, working at temperatures below −100 °C, were able to detect distinct changes in the absorption spectra of *N*-benzylideneaniline, *N*-(α-naphthylidene)-α-naphthylamine, and related compounds.[58] These spectroscopic changes were found to be



22

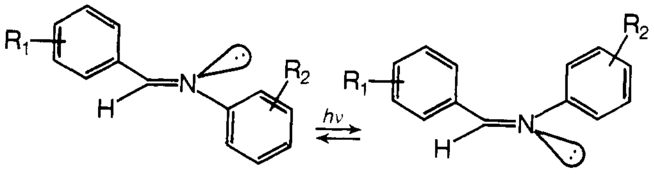
23 **24**

reversed on warming to room temperature. The thermal relaxation was measured in the range −70 to −40 °C and was estimated to have an activation energy of 16–17 kcal/mol, which should be compared with the values of 23 and 42 kcal/mol which apply to the isoelectronic molecules azobenzene and stilbene, respectively. The spectral changes observed with the naphthylimine system were attributed to the formation of the thermally unstable *Z* isomer (**26**) which isomerized to the thermodynamically more stable *E* isomer on warming. *N*-Benzohydrylideneaniline (**27**) showed no spectral changes on irradiation since this molecule has no distinguishable stereoisomers. This was taken as additional proof for the interpretation of syn–anti photoisomerization.



25 **26**

Wettermark and co-workers were able to demonstrate the syn–anti photoisomerization with other substituted *N*-benzylideneanilines, even at room temperature.[59,60] At 25 °C the thermal relaxation proceeds with a half-life of about one second. More recent work showed that the rate constant for the thermal relaxation of photoisomerized aromatic Schiff bases follows the bond order about the C–N double bond.[92,93]

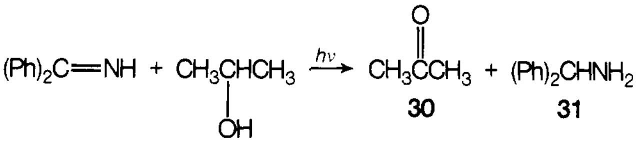


27 **28**

The above results clearly indicate that the thermal barrier between the two diastereomers of most imines is sufficiently low that the photochemically induced shift in the configurational equilibrium is only temporary at ambient temperatures and is frequently followed by a rapid, thermal relaxation which reestablishes the initial configurational equilibrium between the syn and anti isomers.[94] Photoisomerization about the C–N double bond is undoubtedly a major path responsible for the high rate and efficiency of radiationless decay of the excited state of simple imines and accounts for the lack of photoreactivity of a large number of systems possessing a C–N double bond.

V. Photoreduction

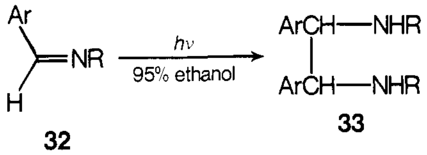
Among the most common reactions of compounds containing the carbonyl chromophore, upon irradiation in solvents containing readily abstractable hydrogens, is photoreduction.[1-5] The photoreduction of benzophenone and related ketones occurs readily via abstraction of hydrogen from alcohols and other hydrogen donors by the excited carbonyl compound. Although the photochemical reactions of compounds containing a carbon–nitrogen double bond have received less attention than those containing a carbon–oxygen double bond, reactions analogous to the photoreduction of the carbonyl group have been observed.[95-122] The mechanism initially proposed to account for the photoreduction was one in which the n–π* excited state of the imine was suggested to be the reactive state in the hydrogen abstraction step.[103] Thus, the photochemical reduction of benzophenone imine in 2-propanol to benzhydrylamine[103] was proposed to occur by a mechanism similar to the photochemical reduction of benzophenone.[123]



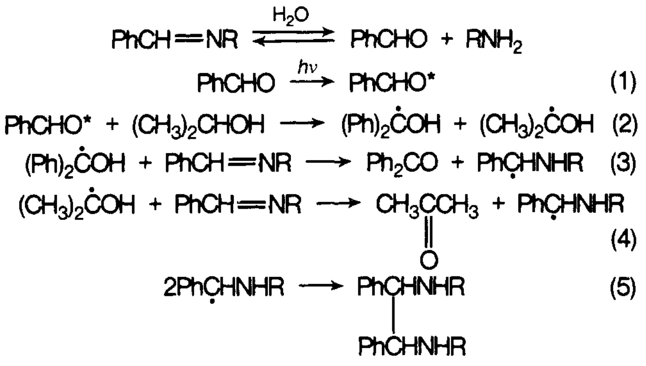
$$(Ph)_2C{=}NH + CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow{h\nu} CH_3\overset{O}{\overset{\|}{C}}CH_3 + (Ph)_2CHNH_2$$

29 **30** **31**

Later work by Padwa[96] and Fischer[97] showed that imine photoreductions do not involve the excited states of the imines at all, but are the result of a most interesting set of circumstances which serve to illustrate the hazards and complicating features in photochemistry. These workers found that the irradiation of a series of benzaldehyde *N*-alkylimines in alcoholic solvents afforded dihydro photodimers.[96] Although the reaction bears analogy to aryl ketone photoreduction, the data obtained indicated that the reaction is quite different mechanistically in that it did not involve the excited states of the imine as intermediates in the reduction. Considerable information was accumulated for the photoreduction process. The more readily derived facts follow. (1) While direct irradiation of benzaldehyde *N*-alkylimines proceeded readily in 95% ethanol, the imine is not photoreduced in 2-propanol, a solvent which is very effective in photoreducing benzophenone.[124] Photoreduction proceeded readily, however, when 2-propanol was diluted with water and led to dihydro dimer **33** and acetone. (2) In marked contrast to the substituent effects noted in the aryl ketone system, imine photoreductions proceeded smoothly without apparent effect by substituents on the aromatic ring. (3) Excitation with 2537-Å light did not result in photoreduction, whereas with 3130-Å light, smooth photoreduction occurred. (4) Benzophenone's phosphorescence is not quenched by the imine even though the reaction was sensitized by benzophenone. (5) Examination of the quantum efficiency of a number of triplet sensitizers in effecting imine photoreduction revealed a correlation with the ability of the sensitizer itself to photoreduce in the alcoholic medium. (6) High-energy sensitizers that do not themselves photoreduce in alcohol are ineffective as sensitizers. These observations when taken together suggest that the photoreduction does not involve an excited state of the imine, but rather is brought about by one or more of the intermediates of the ketone photoreduction. The photoreaction was represented by the sequence of reactions described below, starting with abstraction of hydrogen from the carbinol carbon by the lowest excited triplet state of the sensi-



32 **33**



$$PhCH{=}NR \overset{H_2O}{\rightleftharpoons} PhCHO + RNH_2$$

$$PhCHO \xrightarrow{h\nu} PhCHO^* \qquad (1)$$

$$PhCHO^* + (CH_3)_2CHOH \longrightarrow (Ph)_2\dot{C}OH + (CH_3)_2\dot{C}OH \qquad (2)$$

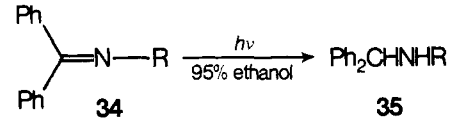
$$(Ph)_2\dot{C}OH + PhCH{=}NR \longrightarrow Ph_2CO + Ph\underset{\cdot}{C}HNHR \qquad (3)$$

$$(CH_3)_2\dot{C}OH + PhCH{=}NR \longrightarrow CH_3\underset{\underset{O}{\|}}{C}CH_3 + Ph\underset{\cdot}{C}HNHR \qquad (4)$$

$$2Ph\underset{\cdot}{C}HNHR \longrightarrow \begin{array}{c} PhCHNHR \\ | \\ PhCHNHR \end{array} \qquad (5)$$

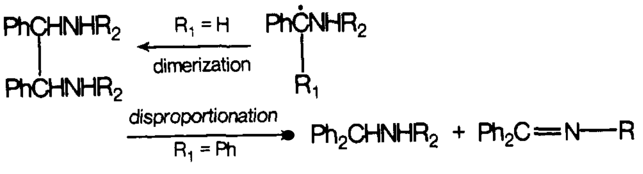
tizer. It should be noted that this scheme involves radical intermediates similar to those proposed by Cohen in the photoreduction of aromatic ketones using amines as hydrogen sources.[125] For that case the reverse of reaction 4 was suggested as an important step.

It is interesting to note that photoreduction of the closely related benzophenone *N*-benzylimine system (**34**) gave the corresponding amine (**35**) as opposed to a dihydro photodimer. This



34 **35**

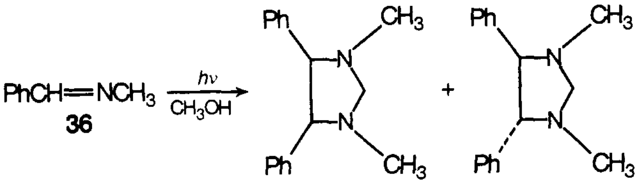
result is readily accommodated in the proposed mechanistic framework. The tendency of the imino radicals to either dimerize or to disproportionate is reflected not only in the photoreduction sequence, but also in the reduction of the imines by reaction with



$$\begin{array}{c} PhCHNHR_2 \\ | \\ PhCHNHR_2 \end{array} \xleftarrow[\text{dimerization}]{R_1 = H} \begin{array}{c} Ph\dot{C}NHR_2 \\ | \\ R_1 \end{array} \xrightarrow[R_1 = Ph]{\text{disproportionation}} Ph_2CHNHR_2 + Ph_2C{=}N{-}R$$

ketyl radicals generated by chemical means. This effect parallels the well-documented increase in disproportionation to coupling ratios of free radicals as they change from primary to tertiary.[126]

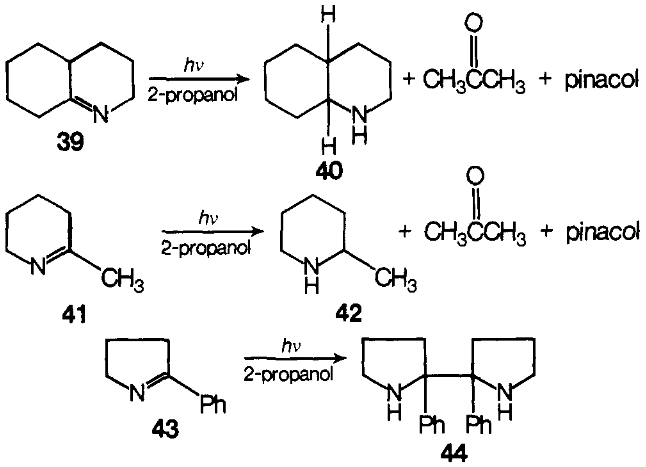
Other examples of imine photoreductions reported in the literature may be best described by a scheme similar to that outlined above.[102-106] Cerutti and Schmid claimed that the irradiation of benzaldehyde *N*-methylimine (**36**) in methanol gave a mixture of *dl*- and *meso*-1,3-dimethyl-4,5-diphenylimidazolidine (**37** and **38**) as primary photoproducts.[101] The best mechanistic



36 **37** **38**

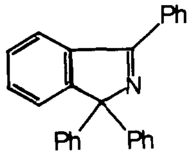
interpretation for this transformation, however, involves initial formation of a dihydro dimer followed by condensation with the formaldehyde formed from methanol. A number of related reports have appeared in the literature showing that reactions apparently involving sensitization by carbonyl compounds in hydrogen-donating solvents proceed, in fact, via formation of ketyl radicals.[127-131] The term "chemical sensitization" was suggested to distinguish between such cases and sensitization involving excitation-energy transfer.[97]

There are several possible reasons for the low reactivity of excited imines toward hydrogen abstraction reactions. First, the rate of hydrogen abstractions by the excited imine may be slow, as postulated by Fischer.[97] Alternatively, it may be that the rate of radiationless decay of the excited imine is much faster than hydrogen abstraction. Padwa and co-workers[96] have postulated the latter explanation and have further suggested that twisting about the C–N double bond is responsible for this rapid radiationless decay. The result of such twisting, (i.e., syn-anti isomerization) is a known photochemical reaction of the C–N double bond and has been discussed in some detail in part IV of this review article. Recently Hornback and co-workers reported on the photochemical reductions of some cyclic imines in 2-propanol.[132] The incorporation of the C–N double bond into a ring system should prevent twisting as a deactivation mechanism and should allow observation of photoprocesses normally obscured by syn-anti isomerization. Irradiation of $\Delta^{1,9}$-octahydroquinoline (**39**) in 2-propanol gave *trans*-decahydroquinoline (**40**) while 2-methyl-Δ^1-piperideine (**41**) gave 2-methylpiperidine (**42**). Photolysis of the related five-ring system (i.e., 2-phenyl-Δ^1-pyrroline (**43**)) gave 2,2′-diphenyl-2,2′-bipyrrolidine (**44**) as the only photoproduct. Comparison of **43** with an acyclic model compound, *N*-benzylidenecyclohexylamine, revealed that the cyclic imine did not show an enhanced reactivity toward photoreduction. The results indicated that imines with C–N double bonds in a five- or six-membered ring, like acyclic imines, are much less reactive toward photochemical hydrogen abstraction than are carbonyl compounds. The chemical sensitization route was eliminated as a possible reaction path for these systems. The low reactivity of **43** toward hydrogen abstraction was suggested to be due to factors other than rapid radiationless decay by twisting. Other possible explanations for this low reactivity include a slow rate of hydrogen abstraction, or other rapid decay processes.

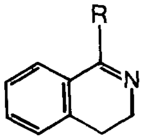


39 **40** **41** **42** **43** **44**

Ohta and Tokumura have also examined the photochemistry of C–N double bond systems which are restricted in cyclic rings and report that these imines are unreactive toward hydrogen atom abstraction.[111] For example, 1,3,3-triphenylisoindolenine (**45**) and 1-methyl-, 1-benzyl-, and 1-phenyl-3,4-dihydroisoquinoline (**46**) were found to be quite stable upon irradiation in hydrogen donor solvents. These workers report that these cyclic imines phosphoresce at 77 K in both EPA and methylcyclohexane. The results showed that the triplet states of the imines lie 53–61 kcal/mol above their ground states with lifetimes ranging from 0.1 to 0.8 s. The triplet lifetimes were found to be longer in the more polar rigid glass and are consistent with a π–π^* state as the lowest lying triplet state. When **45** was irra-



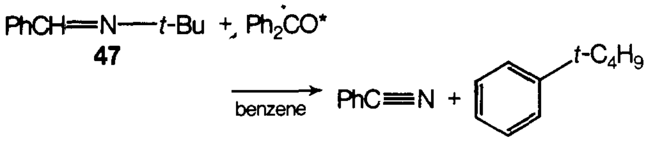
45

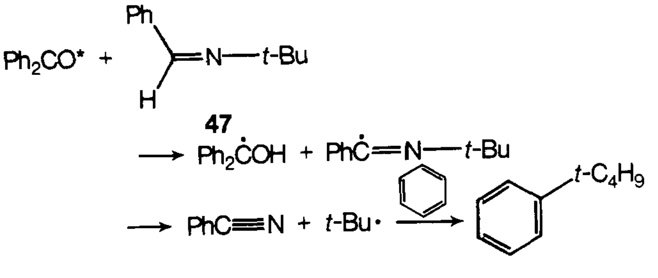


46, R = CH_3, CH_2Ph, Ph

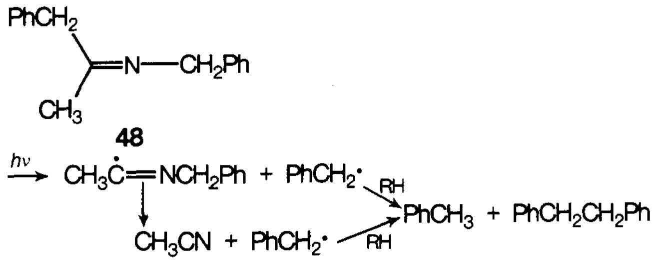
diated in the presence of *trans*-piperylene, under conditions where all the light was absorbed by **45**, a photostationary state equilibration of piperylene was achieved. Comparison of the photostationary state ratio with Hammond's earlier results[133] revealed that the triplet energy of **45** lies in the range of 55–58 kcal/mol, which is in satisfactory agreement with the emission results. The unreactive nature of the excited imine system was attributed to the high π–π^* character of the triplet state.

These same Japanese workers have studied the photochemical reactions of benzaldimines using poor hydrogen atom donors as solvent.[134] Irradiation of a mixture of *N*-benzylidene-*tert*-butylamine (**47**) and benzophenone in benzene afforded benzonitrile and *tert*-butylbenzene as the major photoproducts. In this case, no dihydro photodimer was detected. Similar irradiation of *p*-methoxy- or *p*-chlorobenzylidene-*tert*-butylamine and benzophenone gave *p*-methoxy- or *p*-chlorobenzonitrile. In the absence of the triplet sensitizer, no detectable quantities of the aromatic nitrile could be found, thus indicating the action of the benzophenone to be responsible for the formation of the nitrile. The above reactions were rationalized in terms of an excited benzophenone triplet abstracting the imidoyl hydrogen atom from **47** to give an imidoyl radical which subsequently undergoes decomposition to benzonitrile and a *tert*-butyl radical. The latter radical reacts with benzene to afford *tert*-butylbenzene.



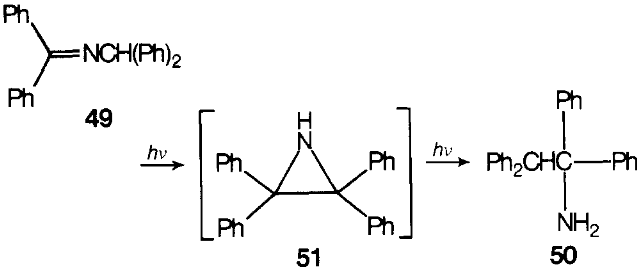


A closely related fragmentation occurred on irradiation of *N*-(1-phenyl-2-propylidene)benzylamine (**48**).[135] Photolysis of this imine afforded acetonitrile, bibenzyl, and toluene as the major photoproducts. The formation of these compounds was



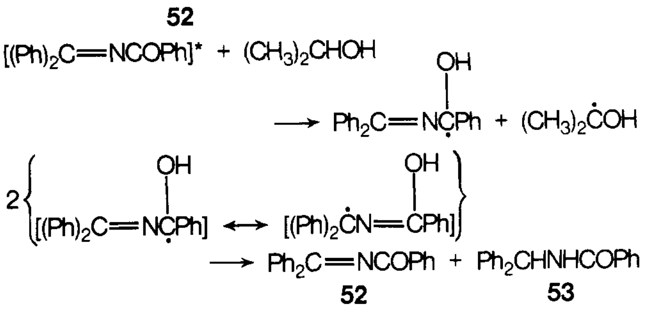
attributed to an α-cleavage reaction of the excited imine state to a benzyl and imidoyl radical. This fragmentation is analogous to the Norrish type I reaction of excited carbonyl compounds. The initially formed imidoyl radical was suggested to undergo subsequent decomposition to acetonitrile and a benzyl radical which could then abstract hydrogen or couple to give toluene and bibenzyl. An alternate path for cleavage of the excited imine into a benzyl and imino radical, $PhCH_2(CH_3)C{=}N\cdot$, and subsequent decomposition of the imino radical into acetonitrile and a benzyl radical was rejected by the finding that the irradiation of *N*-benzylidenebenzylamine in benzene did not show any evidence for such a cleavage. These results indicate that the excited states of certain imines undergo cleavage with sufficiently large rates to compete with other deactivation processes. In this case, the excitation energy can be dissipated by α-cleavage as well as by syn-anti isomerization. The observed fragmentation is undoubtedly related to the low bond dissociation energy associated with the benzylimine chromophore.

A rather unusual reaction was reported to occur on irradiation of benzophenone *N*-benzhydrylimine (**49**).[110] Photolysis of this



compound in 95% ethanol gave 1,1,2,2-tetraphenylethylamine (**50**) as the major photoproduct (22%). The formation of this product was suggested to proceed through the intermediacy of aziridine **51**. Obviously further work needs to be done before this mechanism can be accepted.

Recently, Okada, Nozaki, Toshima, and co-workers reported that the photoreduction of *N*-(α-phenylbenzylidene)benzamide (**52**) in 2-propanol proceeds via an electronically excited triplet state (i.e., intramolecular chemical sensitization), in contrast with other diarylketimine photoreductions.[112–117] Similar results were reported by Fraser-Reid and co-workers with related compounds.[118]



$$(Ph)_2C{=}NCOPh \xrightarrow{h\nu} [(Ph)_2C{=}NCOPh]^*$$

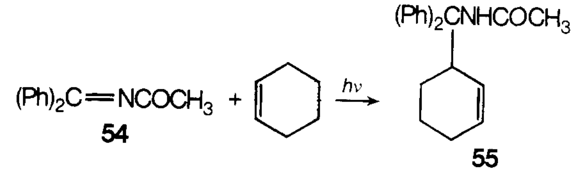
52

$$[(Ph)_2C{=}NCOPh]^* + (CH_3)_2CHOH \longrightarrow Ph_2C{=}N\overset{OH}{\dot{C}}Ph + (CH_3)_2\dot{C}OH$$

$$2\left\{[(Ph)_2C{=}N\overset{OH}{\dot{C}}Ph] \longleftrightarrow [(Ph)_2\dot{C}N{=}\overset{OH}{C}Ph]\right\} \longrightarrow Ph_2C{=}NCOPh + Ph_2CHNHCOPh$$

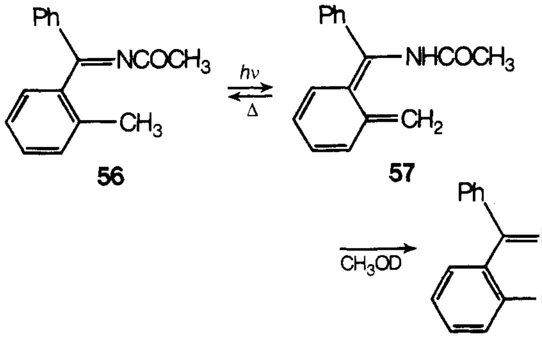
52 **53**

The Japanese workers also reported that the excited triplet state of *N*-acyldiphenylmethylenimine (**54**) can abstract the allylic hydrogens of cyclic and acyclic olefins and produce photochemical addition products (i.e., **55**). The photoreduction and addition reactions were completely quenched by piperylene and were markedly retarded by diphenyl sulfide, a good radical scavenger. The yield of photoadduct **55** was enhanced when benzophenone or acetophenone was used as a triplet sensitizer. The mechanism proposed to account for these observations involves excitation of the ketimine followed by intersystem crossing and hydrogen atom abstraction from the solvent by the triplet state.[112–117]



55

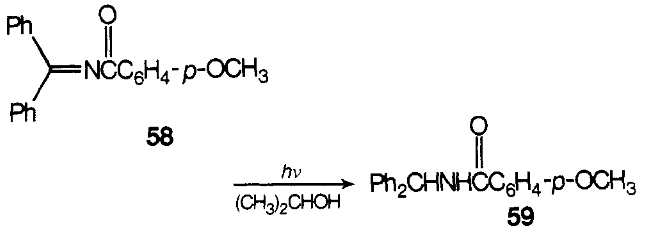
Further support for the involvement of the triplet state in these systems was obtained by studying the photochemistry of several *o*-alkyl aromatic imines (**56**).[115–117] Irradiation of **56** was reported to result in an isomerization to an enamide derivative (**57**) by a path similar to that observed with the related *o*-alkylbenzophenone system.[136,137] On the basis of these observations it would appear as though the mechanism for the reduction of



56 **57**

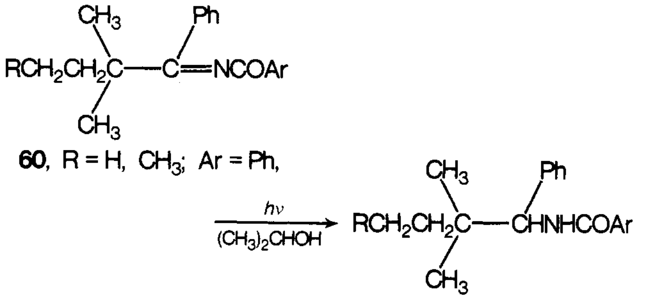
N-acylimines is quite different from that followed by N-alkylimines. This difference is undoubtedly related to the presence of the carbonyl group in the N-acylimine system. These N-acylimines are formally aza analogs of α,β-unsaturated ketones.

More recent work by Padwa and co-workers[119,120] has shown that the irradiation N-diphenylmethylene-p-anisamide (**58**) in 2-propanol afforded N-benzhydryl-p-methoxybenzamide (**59**) and acetone in quantitative yield. The quantum yield in 2-propanol was extremely low ($\Phi \sim 10^{-6}$) but increased substantially when benzophenone or acetophenone was used as the sensitizer ($\Phi \sim 2 \times 10^{-3}$). The quantum yield was enhanced when small quantities of water were added to the reaction mixture. Furthermore, high-energy sensitizers such as triphenylene, which do not undergo photoreduction in alcohol, were ineffective as sensitizers. These observations when taken together suggest that photoreduction of **58** in 2-propanol does not involve the excited triplet state of the imine but is brought about by one or more of the intermediates of the ketone photoreduction. The ability of piperylene and diphenyl sulfide to retard the formation of **59** is perfectly consistent with the "chemical sensitization" scheme.



58 **59**

This situation does not hold, however, when cyclohexene is used as the solvent. Toshima and co-workers have presented convincing evidence demonstrating the involvement of the electronically excited triplet state of N-acyldiphenylmethyleneimine in the photochemical addition to cyclic and acyclic olefins.[113] Padwa and Koehn have also found that the irradiation of a series of N-(α-alkylbenzylidene)benzamides (**60**) in hydrogen-donating solvents results in reduction of the carbon–nitrogen double bond.[120] The photoreduction was shown to involve an electronically excited state and did not occur by the chemical sensitization path encountered with simple N-alkylimines. Sensitization and emission studies showed that the reaction is derived from an n–π* triplet state. The failure of the imine nitrogen to initiate Norrish type II reactions in these systems suggests that the intermolecular hydrogen abstraction by the excited N-acylketimine occurs on the oxygen atom of the carbonyl group rather than on the nitrogen atom of the imine chromophore. Stern–Volmer quenching plots showed that the rates of hydrogen abstraction of the triplet states of the N-acylketimines are low compared with those of aryl ketones. The low quantum efficiency of the photoreduction was attributed to both a low bimolecular hydrogen abstraction rate ($k_r = 1 \times 10^3$ l. mol^{-1} sec^{-1}) and a fast rate of triplet decay. The results indicate that the photoreduction of the N-acylimine system can proceed by both "chemical sensitization" and by hydrogen abstraction from the triplet state.[117,120] The specific route followed appears to be a function of the substituent groups present about the 2-azaenone chromophore.

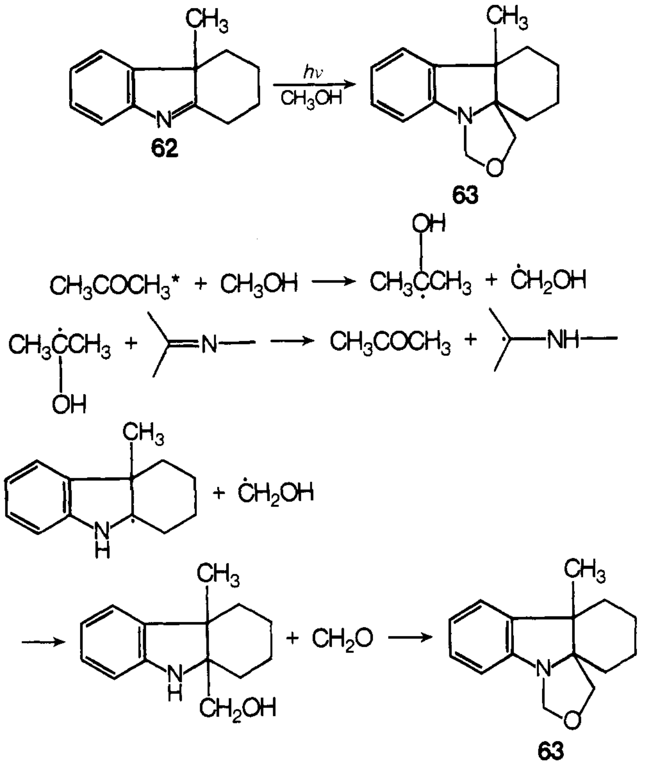


60, R = H, CH_3; Ar = Ph,

61, R = H, CH_3; Ar = Ph,

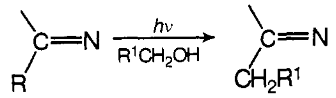
VI. Photoalkylation

A large number of seemingly unrelated imine photoalkylations reported in the literature can now be correlated into a general reaction mechanism[107] which is very similar to the photoreduction scheme discussed in the previous section. For example, the photoalkylation of indolenes (**62**)[101] in a methanol-acetone solvent may be rationalized in the fashion shown below.

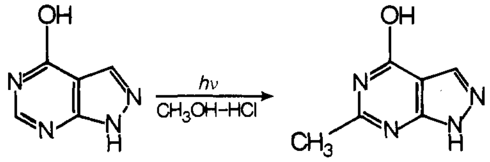


62 **63** **63**

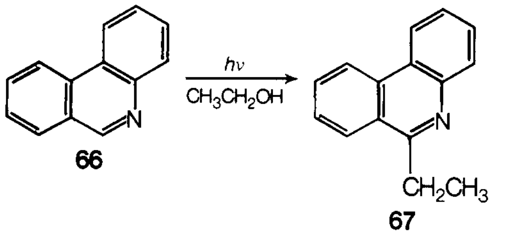
The photoalkylation reaction of many C–N double bond containing systems can be generalized by the following equation.



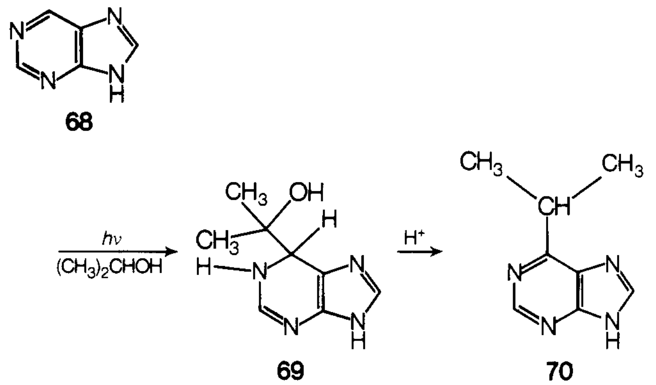
In most cases, R = H, but examples where R = alkyl[107] and R = Cl[107] are also known. Several of the examples reported in the literature are described below.[107,138-143]



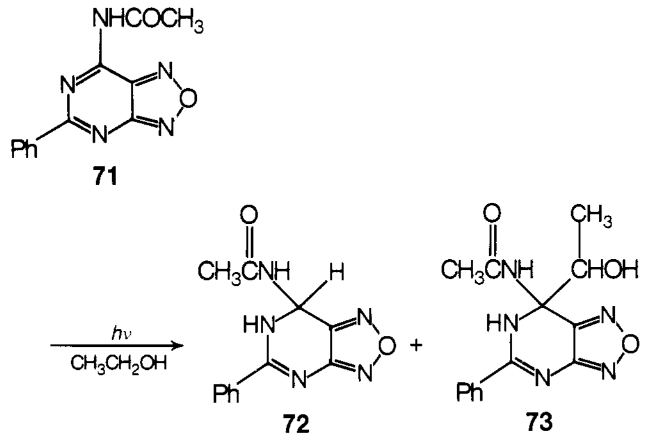
64 **65**



66 **67**

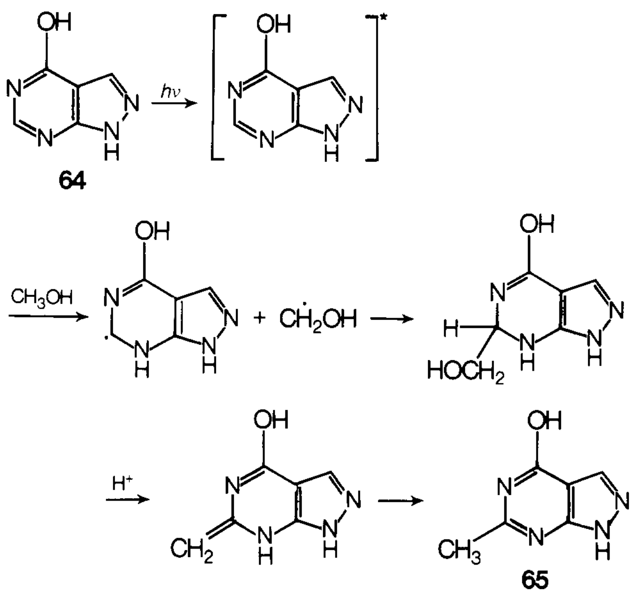


68 **69** **70**



71 **72** **73**

SCHEME I



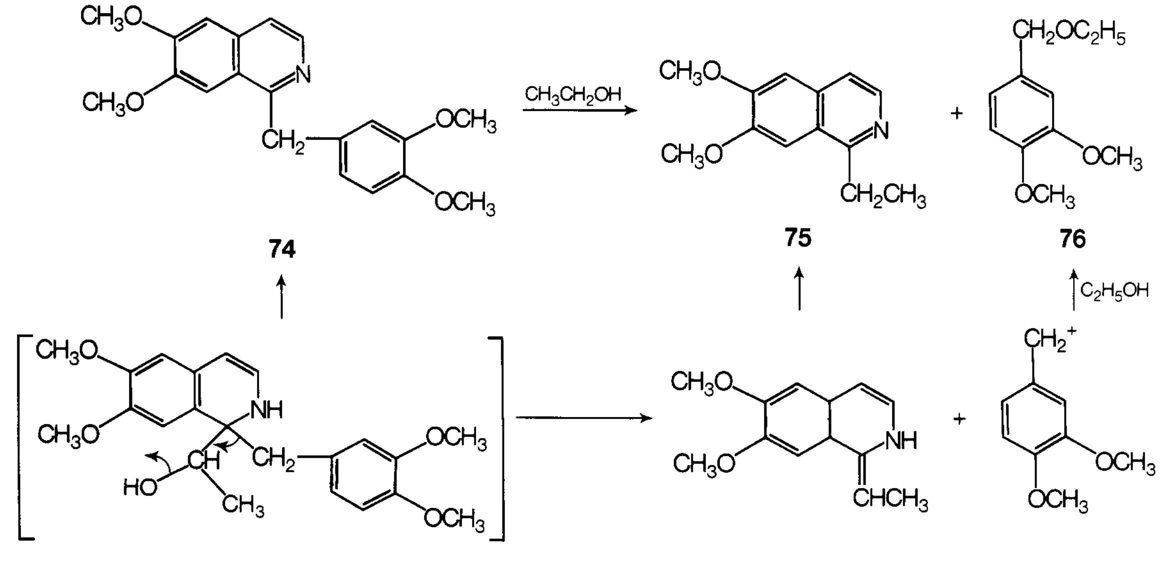
64 **65**

Absorption spectrum changes generally similar to those seen in the purine reaction have been observed after irradiation of deoxygenated ethanol solutions of many heterocyclic molecules, including pyridine, pyrazine, pyrimidine, benzimidazole, benzoxazole, quinoline, isoquinoline, quinoxaline, 1,4,5-triazanaphthalene, and phenazine.[140] It would appear that the photoalkylation of alcohols to heteroaromatic molecules is a very general reaction. The results can best be explained by an initial hydrogen abstraction process followed by coupling and elimination of water. Scheme I outlines the suggested mechanism, using pyrimidine **64** as a model system. Elimination of water cannot occur with pyrimidine **71** and in this case the initial coupled product (i.e., **73**) was isolated. A similar reaction scheme occurs with indolene **62.** The hydrogen abstraction step may proceed via the "chemical sensitization" route (i.e., **62** → **63**) or may involve an electronically excited state of the heterocyclic molecule.

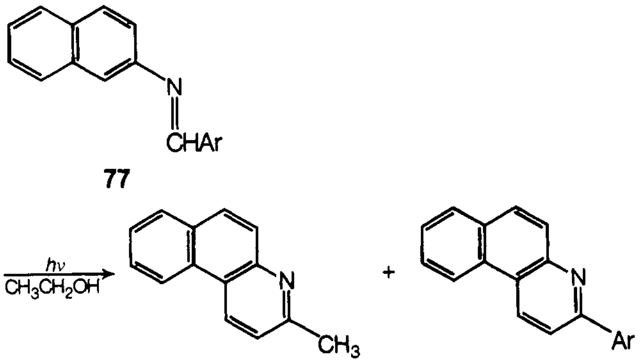
Additional evidence for the above scheme was obtained by the isolation of products **75** and **76,** which are those expected of ionic type reactions, from the irradiation of papaverine (**74**) in acidic ethanol[107] (Scheme II).

A wide variety of photoalkylation reactions of imines and nitrogen heteroaromatics reported in the literature[144-165] conform to the general mechanism outlined in Scheme II. The photoreactions of flavins provide an intramolecular counterpart of these hydrogen abstractions.[166] Imine photoalkylation has also been suggested to lead to products involving rearrangement of the abstracted hydrogen prior to coupling. One example of this is shown below and involves the complex photoconversion of naphthylimine **77** to quinoline derivatives **78** and **79.**[144] The first step was suggested to involve hydrogen abstraction from the

SCHEME II



74 **75** **76**



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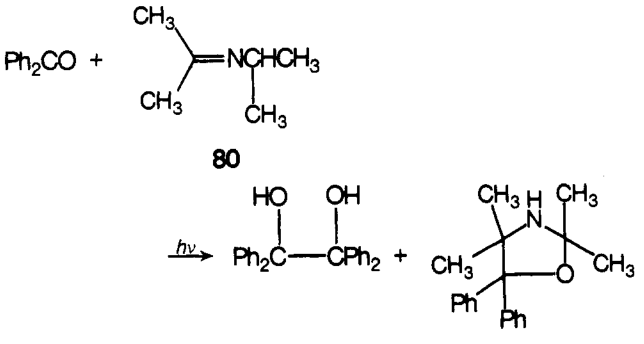
78

79

alcohol by the excited imine (or by "chemical sensitization") followed by a 1,2-hydrogen shift from nitrogen to carbon prior to coupling.[107]

Another interesting example of the photoalkylation reaction involves the formation of oxazolidines from the photolysis of aryl ketones and aliphatic imines.[167] Irradiation of benzophenone and isopropylidineisopropylamine (**80**) in benzene gave 2,2,4,4-tetramethyl-5,5-diphenyloxazolidine (46%) and benzopinacol (50%) as the two major photoproducts. The oxazolidine was formed by initial abstraction of a hydrogen from imine **80** by triplet benzophenone. The 2-azallyl radical formed undergoes mixed coupling. The initially produced hydroxy imine was proposed to undergo cyclization under the reaction conditions. Support for this path was made on the basis of deuterium-labeling experiments. Irradiation of isopropylideneisopropylamine containing 80% deuterium in the allylic methyl positions gave oxazolidene **81** which had the deuterium equally distributed between the methyls at C-2 and C-4. As was pointed out in an earlier section, the ketyl radical usually delivers a hydrogen atom to the C–N double bond of an arylimine and the resulting α-aminoalkyl radical gives product by coupling or disproportionation. In the above case, however, the α-aminoalkyl radical formed would not benefit from aryl stabilization, and consequently reduction of the imine double bond does not compete favorably with the cross-coupling reaction.



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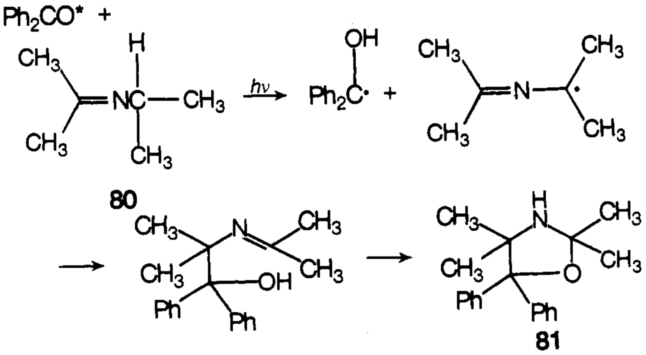
81



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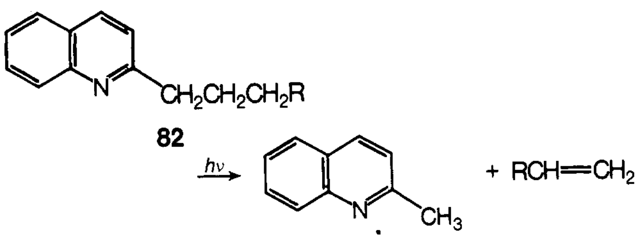
81

VII. Photoelimination

Studies of the photochemistry of ketones that possess a hydrogen-bearing γ carbon have shown that two major reaction pathways are available. The first involves a photoelimination reaction, commonly called the Norrish type II cleavage,[168] to yield olefins and smaller carbonyl compounds, and the second involves the formation of cyclobutanols.[169] Both reactions are intramolecular with little or no detectable side reactions and have been visualized as arising from a common biradical intermediate formed by internal hydrogen abstraction from the n-π^* excited state. Stermitz has recently reported that 2-substituted quinolines bearing a hydrogen γ to the C=N undergo photoelimination in a similar manner to the well-known Norrish type II cleavage of carbonyl compounds.[170-172] The rate of elimination of a series of 2-substituted quinolines followed the expected order of ease of abstraction of the γ-hydrogen. The photoreactive state was defined as a n-π^* singlet since the photoelimination was not sensitized by benzophenone, was not quenched by piperylene, and did not proceed in acidic solution.[172] Those compounds which were found to undergo photoelimination also exhibited a McLafferty rearrangement ion as the base peak in the mass spectrum. The decrease in quantum yields of photoelimination in the presence of oxygen led Stermitz to favor a diradical mechanism for the photoelimination. Also, the low quantum yield of photoelimination is consistent with the diradical undergoing considerable reverse hydrogen transfer.



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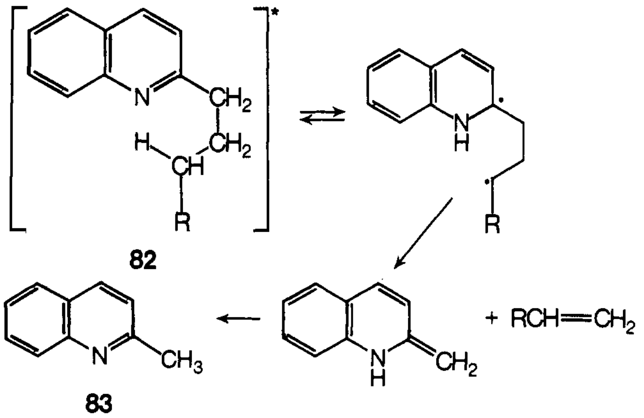

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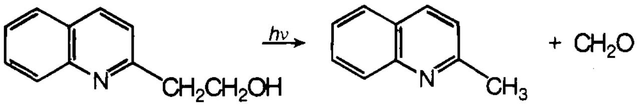
83

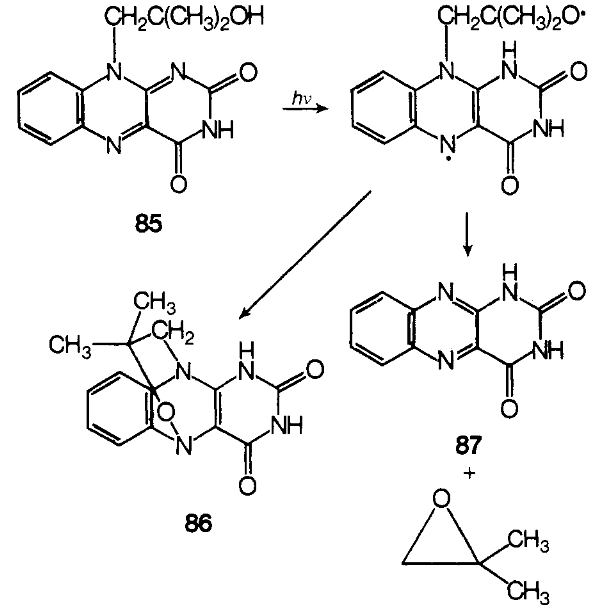
The photoelimination of 2-(2-hydroxyethyl)quinoline (**84**) is an interesting case since abstraction of a hydroxylic hydrogen atom is rarely seen in carbonyl group photochemistry. Moreover, the high quantum yield observed with this system (Φ = 0.11), when compared to the 2-alkyl-substituted quinoline system (Φ = 0.0087), was unexpected.[172] A possible explanation for the high quantum efficiency may reside in the strong intramolecular hydrogen bond from the OH to the quinoline nitrogen atom which eventually results in a proton transfer in the excited state.



84

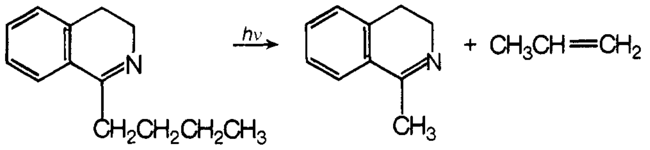
83

SCHEME III

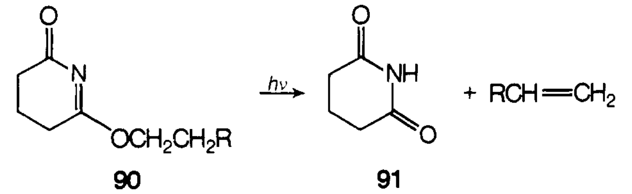


Another example of a system which undergoes internal hydrogen atom transfer from a hydroxyl group was reported by Moore and Baylor.[173] These authors found that irradiation of isoalloxazine **85** resulted in the formation of two photoproducts. Both products were rationalized in terms of an initial hydrogen transfer according to the mechanism outlined in Scheme III.

A number of other examples of photoelimination have appeared in the literature.[173–175] Ogata has reported that substituted dihydroisoquinolines undergo an analogous reaction[173] to that observed in the quinoline series. Koch and co-workers have observed photochemical reactions of keto imino ethers which resemble the Norrish type II reactions of ketones.[174] Sensitization and quenching studies showed that the type II reaction of **90** occurs predominantly via the n–π* singlet state.

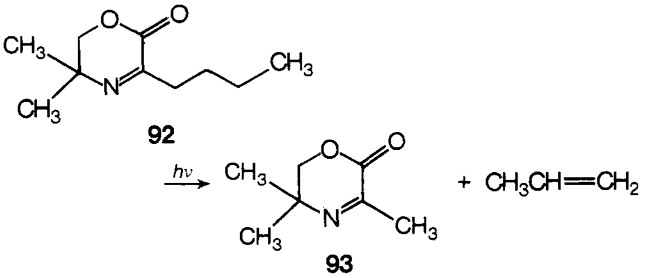


88 **89**



90 **91**

Irradiation of oxazinone **92** also results in a reaction which resembles the Norrish type II cleavage.[175] In this case, however, the quantum yield of product formation was concentration dependent. If the photoreaction of **92** occurred by a type II elimination path, the quantum yield of formation of **93** should be independent of the concentration of starting material. This observation led Koch to consider a chemical sensitization path to explain the formation of **93**.



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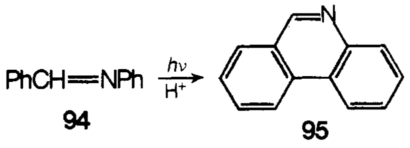
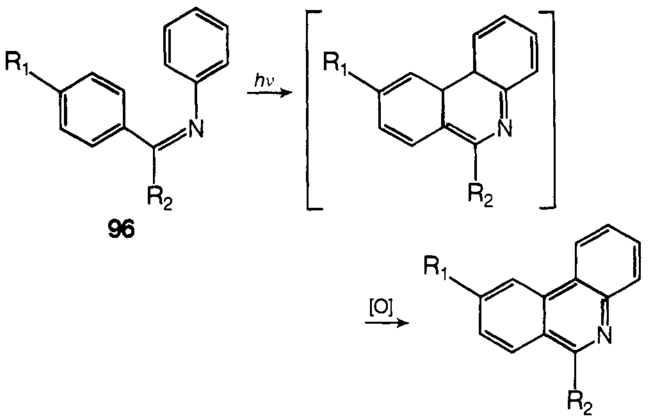
VIII. Photocyclization

The study of the cyclization of polynuclear aromatic hydrocarbon-substituted ethylenes has attracted considerable attention over the past several years. Reviews on the photocyclization of stilbene analogs are available and provide a most comprehensive and useful source of references for the subject.[176–178] Stilbene-type cyclizations have also been reported for compounds which contain a C–N double bond.[178–191] The oxidative photocyclization of *N*-benzylideneaniline (**94**) to phenanthridine (**95**) was reported to proceed only in the presence of strong acid.[179,180,183]



94 **95**

Acetophenone anils undergo a similar reaction to form related heterocycles.[183] Other Schiff bases were observed to undergo smooth photocyclization in neutral solution containing an oxidant (I_2 or O_2).



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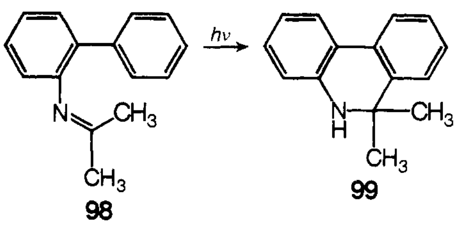
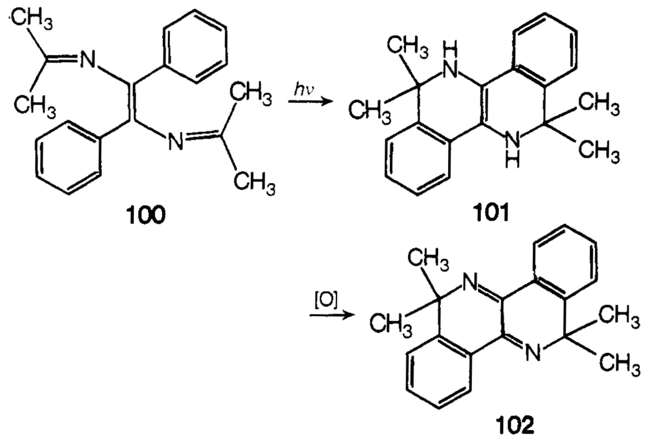
Swenton and co-workers have shown that *N*-(2-propylidene)-2-aminobiphenyls undergo an analogous nonoxidative photocyclization in high yield.[187] The low quantum efficiencies observed with these photocyclizations may be attributed to a very facile syn–anti photoisomerization, thereby reducing the quantum yield of cyclization.



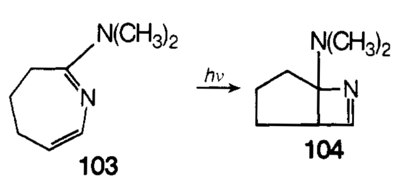
98 **99**

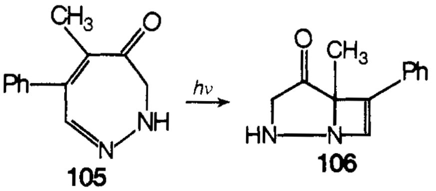
The photoinduced cyclization of trans enediimine **100** to the diazachrysene derivative **102** is of interest in this connection. The intermediate dihydro derivative **101** is presumably formed by a double cyclization of the azahexatriene type.[188]

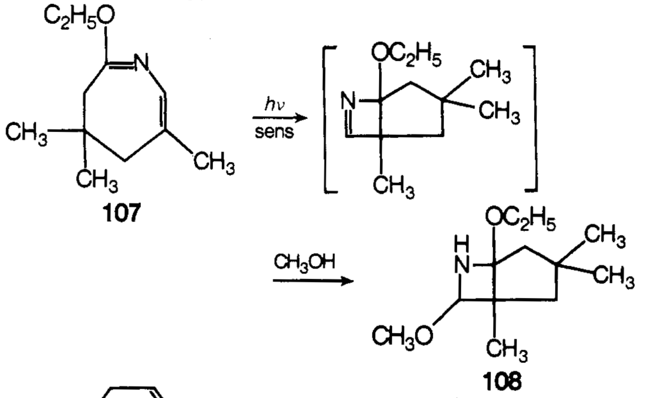
Electrocyclic processes in six- and seven-membered heterocycles which contain C–N double bonds have been the subject of a number of studies.[192–205] While many of these reports have little novelty, the synthetic applications of these photoreactions have been exploited, particularly in the alkaloid

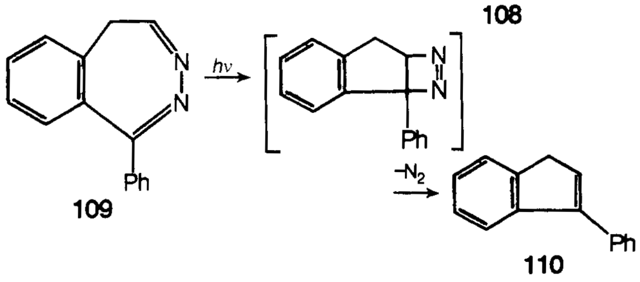


field. A number of examples of this type of photocyclization are shown below.

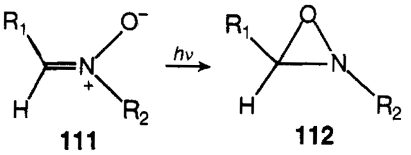




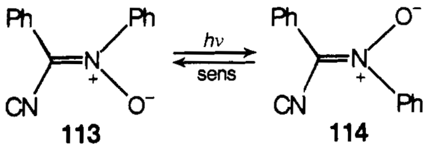




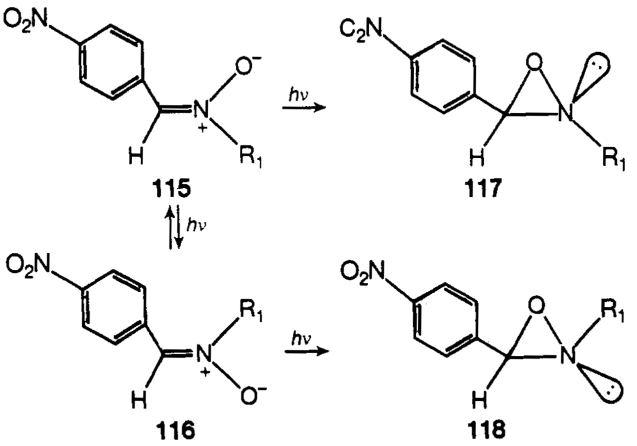
Interest continues to be shown in the photocyclization of nitrones and *N*-oxides, and in particular in the role of an oxaziridine as the intermediate. An extensive review has appeared dealing with the photochemical cyclizations of nitrones and aromatic *N*-oxides and will be of use to all workers in the field.[206] This article has yielded a fairly clear understanding of the chemical processes involved. It now seems that the initial photochemical reaction of most nitrones is cyclization to the corresponding oxaziridine. This fact was not recognized at first because many oxaziridines are highly unstable and rearrange to the corresponding amides as soon as they are formed. In general, oxaziridines with aryl substituents in both the 2 and 3 positions are too unstable thermally to be isolated.[207] Another reason for failure to isolate the oxaziridines is that they are often unstable to light and rearrange to amides or to other products on prolonged irradiation.



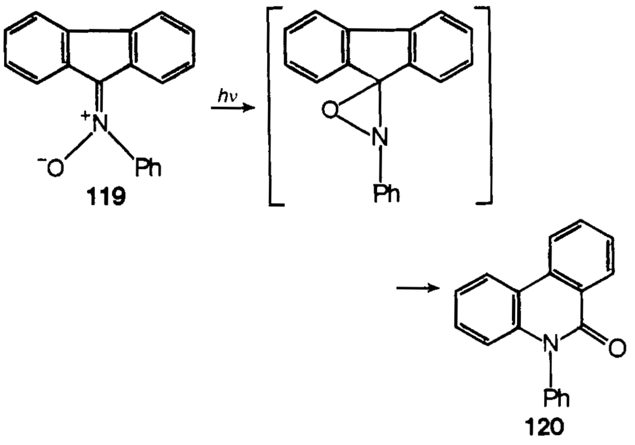
Photolytic oxaziridine formation is a reaction of the singlet state of nitrones.[208] Deliberate excitation of either *cis-* or *trans*-α-cyano-α,*N*-diphenylnitrone to the triplet state by means of a sensitizer causes only cis–trans isomerization.[208] The photoequilibrium established is different from the thermal equilibrium, thus indicating that the photochemical isomerization is caused by triplet–triplet energy transfer. No oxaziridine is formed from the triplet state.



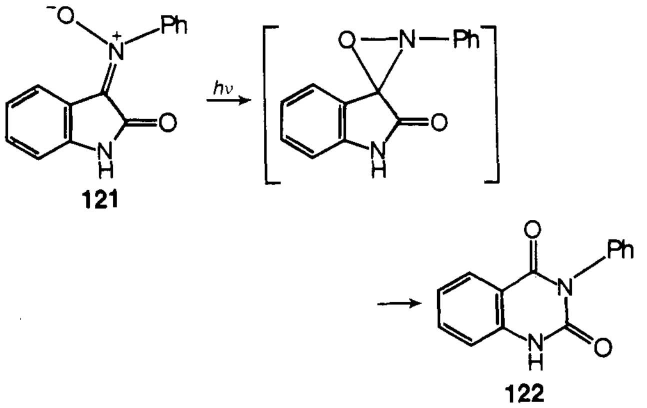
The photocyclization of a series of trans nitrones at −60 °C was found to undergo a stereospecific rearrangement to the corresponding *trans*-oxaziridines. In certain cases, however, the irradiation gave rise to a mixture of *cis-* and *trans*-oxaziridines. Further study showed that the mixture arose from a rapidly established photostationary state of the nitrone.[209] These observations are consistent with predictions based on orbital-symmetry considerations.



In some cases, amides are the products isolated when nitrones are irradiated.[210,211] Several examples of this rearrangement are described below. In at least one case, the prod-



ucts which result from the photolysis of the oxaziridines (i.e., **124**) are identical with those obtained from the corresponding nitrone (i.e., **123**).[212]



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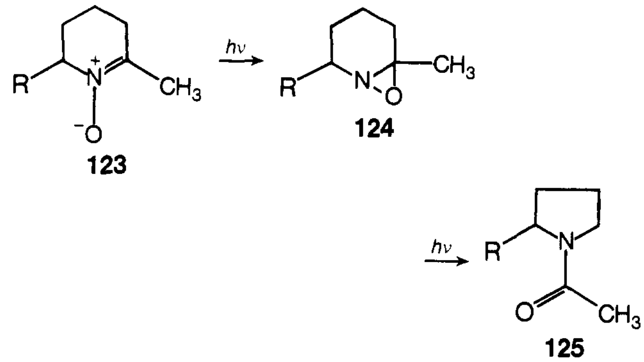
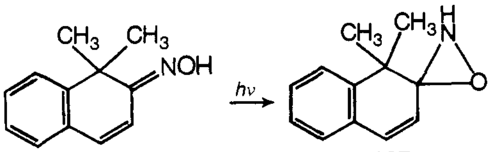


123

124

125

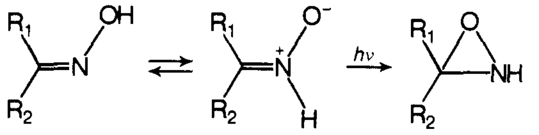
Aldoximes and ketoximes have also been shown to undergo light-induced rearrangements.[50,213-216] The early reports described the rearrangements to amides, and oxaziridines were suggested as intermediates. This was more recently demonstrated by Oine and Mukai who succeeded in obtaining the oxaziridine **127** by photolysis of oxime **126**.



126

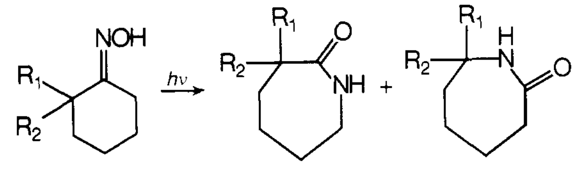
127

Similar results were obtained by Izawa, de Mayo, and Tabata[215] who observed that α-p-anisaldoxime, upon irradiation at −88 °C, was transformed into an oxaziridine. The most likely state(s) leading to oxaziridine formation in the irradiation of oximes was assumed to be the π–π^* singlet or triplet. Quenching experiments with piperylene or oxygen actually showed that the reaction took place from a singlet state.[126] Labeling with ^{18}O indicated the overall oxygen rearrangement to be intramolecular.[215] The similarity of this photochemical oxaziridine formation to the one observed with nitrones can be rationalized by assuming that the immediate precursor of the oxaziridine **130** is the prototropic tautomer **129** rather than the oxime itself. This assumption is supported by the fact that the quantum yields for oxaziridine formation in the oxime series are much lower than in the nitrone series.[215]



128 **129** **130**

The photorearrangement of acyclic and cyclic oximes to amides and lactams has been postulated to proceed via an oxaziridine intermediate.[217-227] Both thermal and photochemical pathways may well be involved in the ring cleavage of the transient oxaziridine.

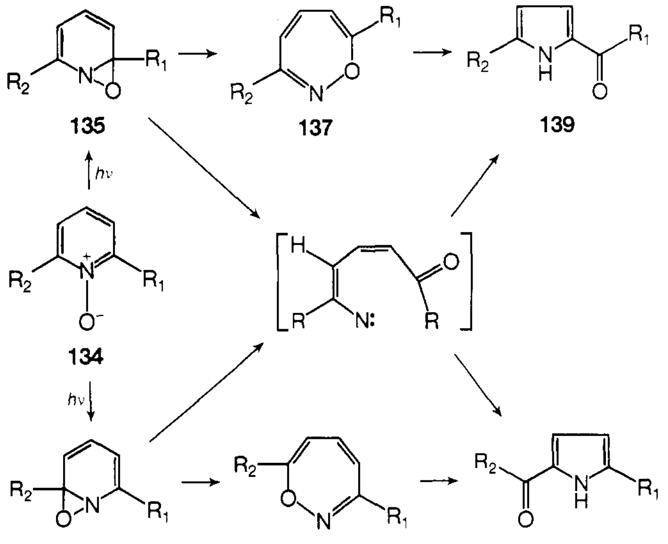


131 **132** **133**

The synthetic potential of the photo-Beckmann reaction is illustrated by the conversion of 2,2,6,6-tetramethylcyclohexanone oxime into the caprolactam in 60% yield;[217] in the normal Beckmann rearrangement, the yield of lactam decreases on α-substitution, and in the case of the tetramethylcyclohexanone, no lactam is obtained.

The irradiation of heteroaromatic *N*-oxides has attracted considerable attention, and many examples of the photorearrangement of mono- and polycyclic compounds have been reported.[206] The product distribution in the light induced reactions of aromatic amine *N*-oxides at first glance seems rather confusing. However, by distinguishing between observed primary photoproducts and secondary thermal products derived from the former, a much simpler pattern appears, which accounts for the great majority of observed products. The initial step in these transformations has been proposed to involve the formation of an oxaziridine intermediate.[228-237] All attempts, however, to observe oxaziridines in the photolysis of aromatic *N*-oxides have been unsuccessful. This may indicate that oxaziridines are formed with so much thermal energy that they immediately break down into other products.

In the pyridine *N*-oxide series (**134**) several rearranged products have been observed. Streith and Sigwalt[232] have proposed that the first step in these rearrangements is the formation of oxaziridines (**135** and **136**). The oxaziridines were then depicted as undergoing valence-tautomerization to 1,2-oxazepines (**137** and **138**). Further rearrangement of these species would account for the formation of the pyrrole derivatives (**139** and/or **140**). Alternatively, the oxaziridine (**135** or **136**) could fragment to give an intermediate nitrene, which upon ring closure and tautomerization would give the observed pyrroles.

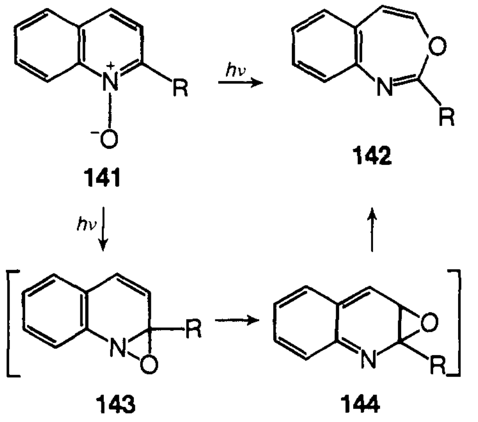


135 **137** **139**

134

136 **138** **140**

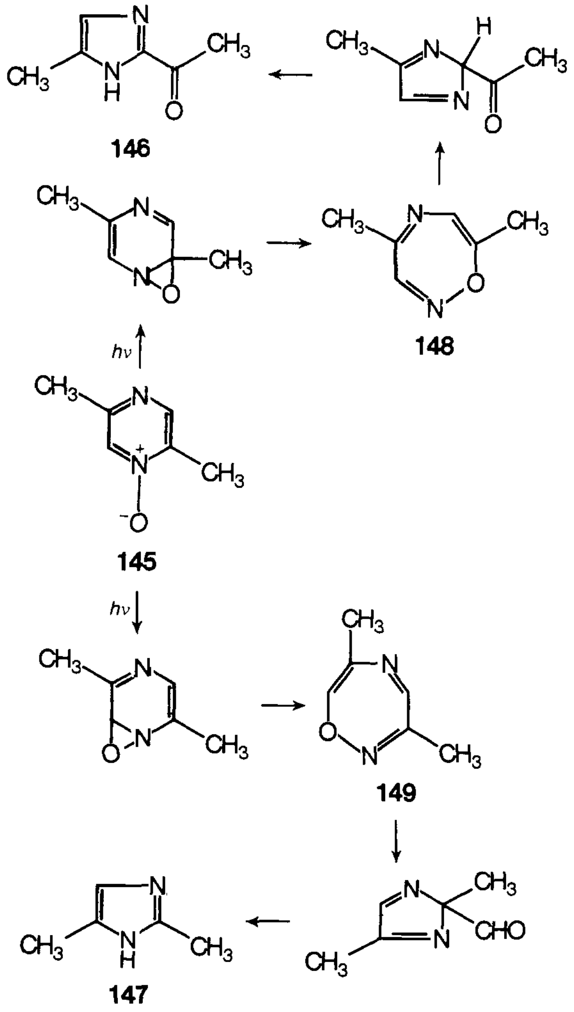
Heteroaromatic *N*-oxides will also undergo ring expansion to seven-membered rings. This type of process is known to take place in the quinoline, isoquinoline, phenanthridine, quinoxaline, and quinazoline series and is illustrated for the conversion of quinoline *N*-oxide (**141**) to benzo-1,3-oxazepine (**142**).[238] This transformation is believed to involve the initial formation of oxaziridine **143** followed by a symmetry-allowed thermal [1,5]-sigmatropic shift to **144** which undergoes ring opening to **142**.[206] The benzo-1,3-oxazepines are very reactive toward water, and frequently their hydrolysis products are isolated.



141 **142** **143** **144**

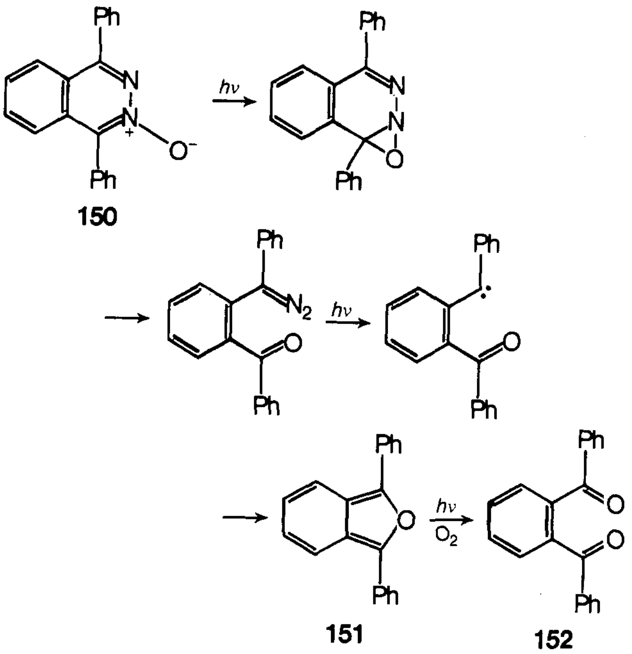
Irradiations of compounds containing more than one heterocyclic nitrogen or *N*-oxide function appear to proceed as expected on the basis of the simpler systems. For example, irradiation of 2,5-dimethylpyrazine *N*-oxide (**145**) in benzene has been reported to give 2-acetyl-4(5)-methylimidazole (**146**) and 2,4(5)-dimethylimidazole (**147**). It has been suggested that the imidazoles arise from rearrangement of the 1,2-oxadiazepines **148** and **149** which could, in turn, be formed from **145**[239] (Scheme IV).

SCHEME IV



146 **148** **145** **149** **147**

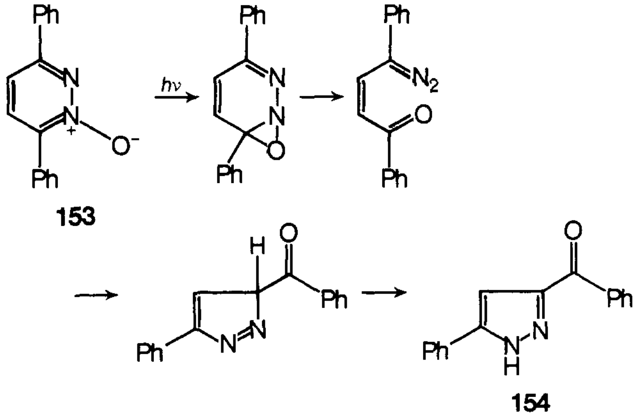
SCHEME V



150 **151** **152**

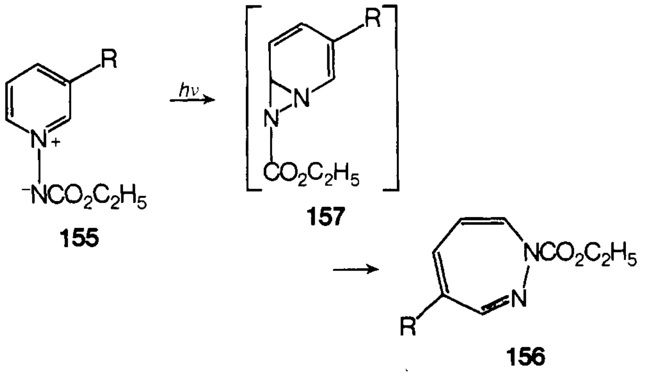
An oxaziridine intermediate has also been postulated to account for the reaction which results from the irradiation of phthalazine *N*-oxides (**150**) in acetone.[235] In the absence of oxygen, nitrogen is evolved, and only one product, 1,3-diphenylisobenzofuran (**151**), is initially formed. Continued photolysis yields several compounds of which phthalazine and 1,2-dibenzoylbenzene (**152**) have been identified. From the proposed mechanism outlined in Scheme V, it is seen that the first steps are consistent with the general mechanism previously outlined.

The photolysis of the closely related 3,6-diphenylpyridazine *N*-oxide (**153**) has also been investigated.[240] Ring contraction to 3-benzoyl-5-phenylpyrazole (**154**) is observed, and the intermediacy of a diazo compound is again suggested. The formation of an intense yellow color (λ 410 nm), and the appearance of an absorption at 2070 cm^{-1} in the IR spectrum of the irradiated pyridazine *N*-oxide, strongly indicates that a diazo compound is also involved in this transformation.[240]



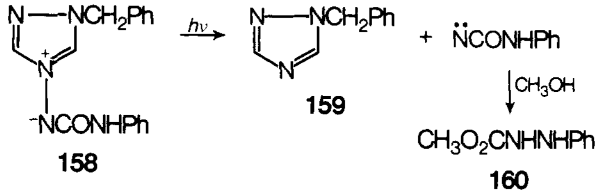
153 **154**

The photochemistry of pyridinium ylides and related systems has received considerable attention in recent years[241-258] and bears close similarity to the photochemistry of heteroaromatic *N*-oxides. The photocyclization of *N*-aminopyridinium ylides (**155**) to the corresponding diazepines (**156**) is believed to go through a diaziridine intermediate[254] (**157**). This type of reaction appears to be general for compounds related to **155** and provides access to new diazepines. In many reactions of this type, a competing process is photolytic N-N bond cleavage in the ylide giving rise to the parent pyridine and a nitrene. In the presence of triplet



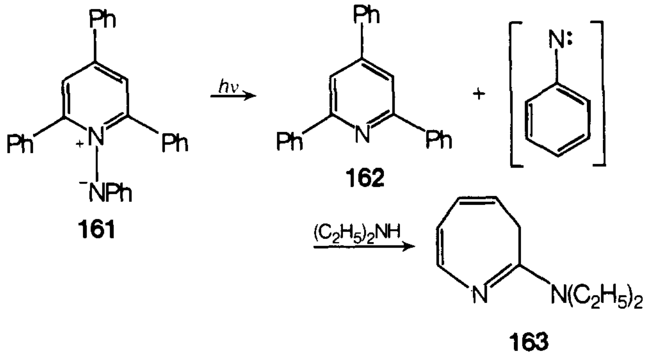
155 **157** **156**

sensitizers, a notable increase in N–N bond cleavage has been observed,[250] thus supporting a singlet pathway for the formation of the diazepine and a triplet pathway for the competing cleavage. No rearrangement is observed on irradiation of a series of 4-imino-1,2,4-triazolium ylides (**158**).[257] Instead, N–N bond cleavage occurs resulting in a 1,2,4-triazole and a nitrene which can be trapped with methanol.



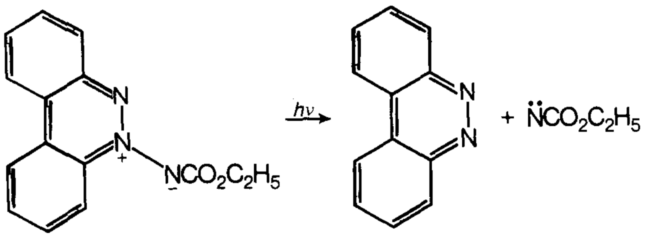
158 **159** **160**

Further evidence for nitrene intermediates in these reactions is provided by the photolysis of **161** in diethylamine. In addition to pyridine **162**, minor amounts of 2-diethylamino-3*H*-azepine (**163**) were isolated.[246]

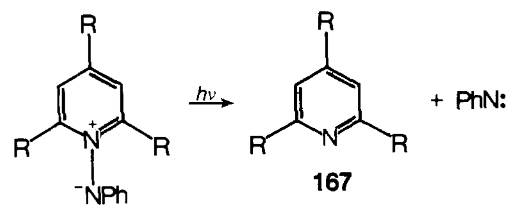


161 **162** **163**

Other examples of the photodecomposition of pyridinium ylides to give pyridine and a nitrene include a series of *N*-iminobenzocinnolinium ylides (**164**)[252] and certain *N*-(2-methyl-4,6-diphenyl-1-pyridinioanilides (**166**).[253]

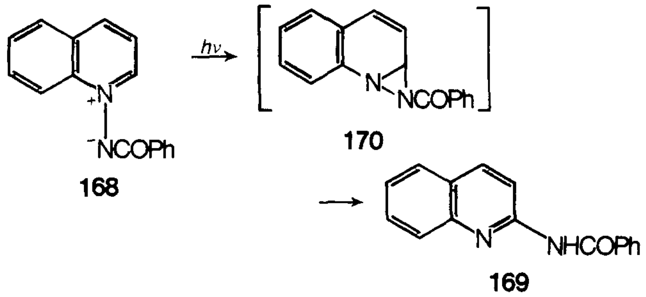


164 **165**



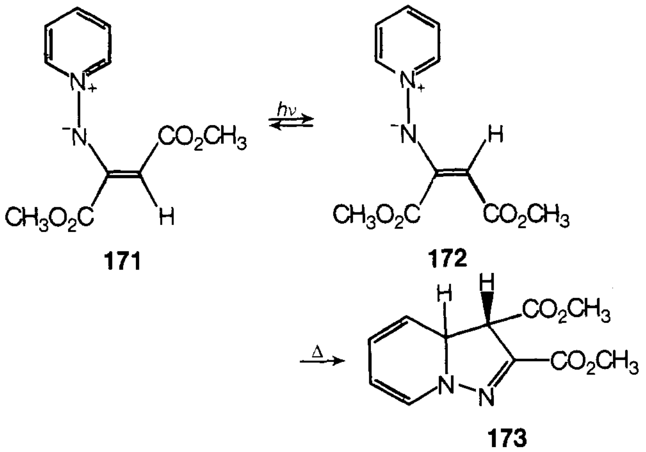
166 **167**

With *N*-benzoyliminoquinolinium (**168**) and isoquinolinium ylides, rearrangement takes place to give, not the diazepine, but the corresponding benzamidoquinoline (**169**) and benzamidoisoquinoline.[251] This reaction presumably occurs by an alternative N–N bond cleavage of the diaziridine intermediate.



168 **170** **169**

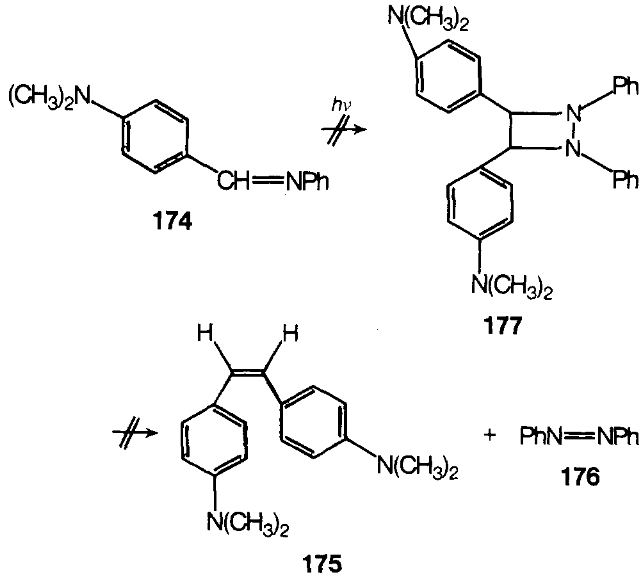
A particularly interesting example of pyridinium ylide photochemistry was found with ylide **171**. This system is converted into the bicyclic **173** by what appears to be a 1,5-dipolar cyclization.[258] The process is actually the result of a photochemically induced trans–cis isomeriztion followed by a thermal disrotatory cyclization.



171 **172** **173**

IX. Photocycloaddition

Although [2 + 2] photocycloaddition of π bonds to carbon–oxygen[259] and carbon–carbon double bonds[260] are common, synthetically useful reactions, similar cycloadditions to the



174 **177** **175** **176**

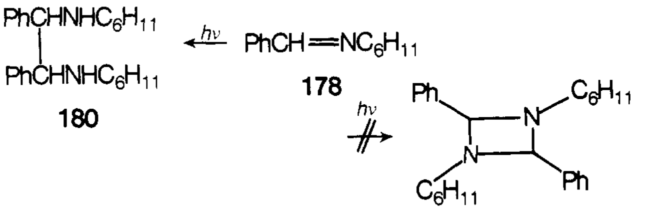
carbon–nitrogen double bond are less frequently encountered. The first apparent example of such a reaction was reported by Searles and Clasen in 1965.[261] These authors claimed that the irradiation of *N*-(4-dimethylaminobenzylidene)aniline (**174**) gave *cis*-4,4'-bis(dimethylamino)stilbene (**175**) and azobenzene (**176**) via an unstable 1,2-diazetidine intermediate (**177**).

This photochemical reaction was reinvestigated by Ohta and Tokumaru[262] who found that they were unable to reproduce the earlier results. The Japanese workers studied the reaction under a variety of experimental conditions and showed that the reported products were not produced. The only products that could be obtained were 4-dimethylaminobenzaldehyde and aniline. Imine **174** did not hydrolyze in the dark, and thus the hydrolysis appears

$$\mathrm{ArCH{=}NPh} + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{ArCHO} + \mathrm{PhNH_2}$$

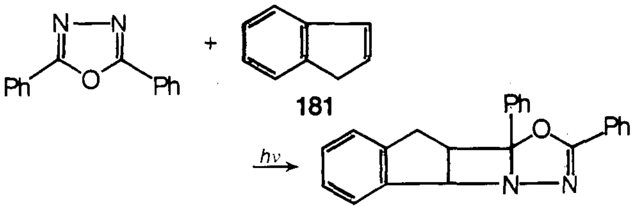
to be promoted by irradiation as was observed by Furey and Kan for benzylideneaniline.[263] The Japanese workers also found that imine **174** exhibits phosphorescence in an EPA glass at 77 K with maxima at 435 and 455 nm and with a lifetime of 0.4 s. No fluorescence was detected at 77 K or at room temperature. This result indicates that the triplet state of **174** lies 63 kcal/mol above the ground state. The long lifetime observed suggests that the triplet state is abundant in π–π* or charge-transfer character.

The photodimer of benzaldehyde *N*-cyclohexylimine (**178**) was originally reported to be a 1,3-diazetidine[105] (**179**) but was subsequently shown by Padwa and co-workers to be a reductive dimer, *N,N'*-dicyclohexyl-1,2-diphenyl-1,2-diaminoethane[96] (**180**).



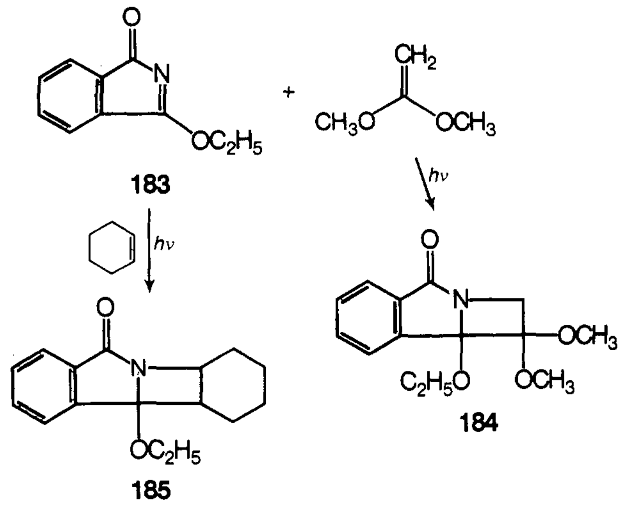
180 178 179

The first example of the photocycloaddition of olefins to C–N double bonds involved the photoaddition of 2,5-diphenyl-2,3,4-oxadiazole to indene and furan.[264]

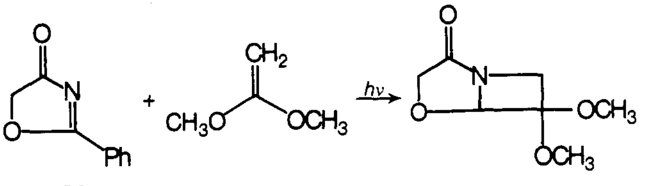


181 182

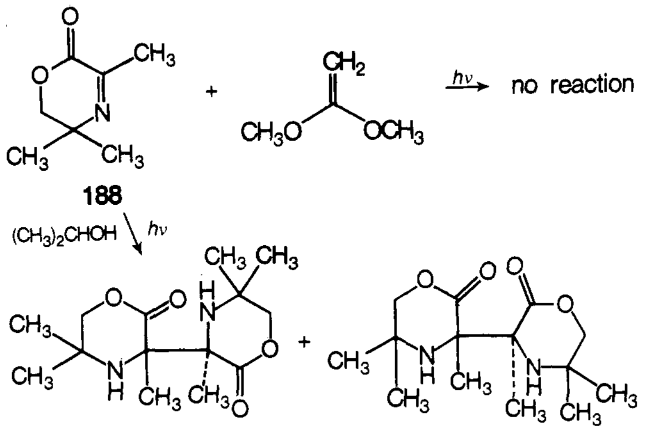
In 1972 Koch and Howard reported on the [2 + 2] photocycloaddition of olefins to C–N double bonds.[265] Irradiation of 3-ethoxyisoindolone (**183**) with 1,1-dimethoxyethylene resulted in regiospecific cycloaddition and afforded cycloadduct **184.** Similar results were obtained when cyclohexene was used as the olefin. With an electron-deficient olefin, such as fumaronitrile, 3-ethoxyisoindolone showed no tendency to undergo [2 + 2] cycloaddition. Koch also found that 2-phenyl-2-oxazolin-4-one (**186**) undergoes [2 + 2] photocycloaddition with 1,1-dimethoxyethylene to give cycloadduct **187.**[266] Again the photoaddition proceeded with high regiospecificity. The authors concluded that molecules which are reactive in the [2 + 2] photocycloaddition with carbon–nitrogen double bonds have low-energy π–π* states, and those which are unreactive have low-energy n–π* states.[175] Thus, the failure of oxazinone **188** to undergo [2 + 2] cycloaddition with 1,1-dimethoxyethylene was attributed to a low lying n–π* state in **188.** Support for this contention was obtained by carrying out the irradiation of **188** in 2-propanol. The formation of the reductive dimers (**189** and **190**) was ascribed to hydrogen abstraction from solvent by the low-lying n–π* triplet state of **188.**



183 184 185

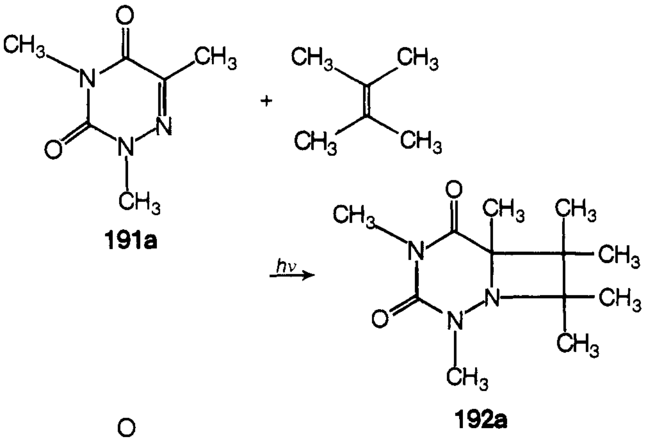


186 187

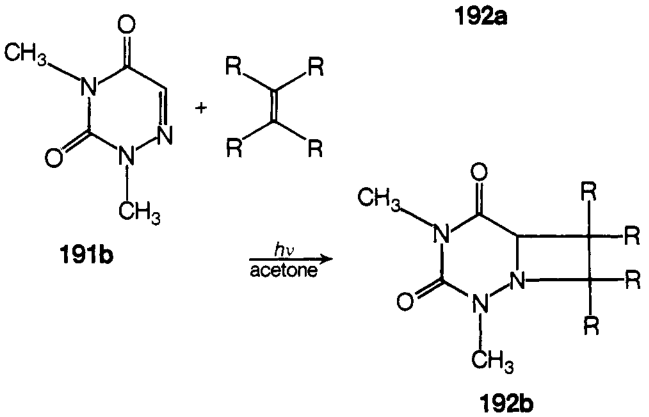


188 189 190

The acetone-sensitized cycloaddition of 1,3-dimethyl-6-azathymine (**191a**) *and 1,3-dimethyl-6-azauracil* (**191b**) *to olefins* has been studied by Swenton and Hyatt.[267,268] With azauracil **191b**, high yields of cycloadducts were formed with ethylene, tetramethylene, isobutylene, ethyl vinyl ether, vinyl acetate, and isopropenyl acetate. Photosensitized cycloaddition studies of azathymine **191a** with tetramethylene and vinyl acetate indicate that the photochemical reactivity of **191a** and **191b** are very similar. The authors discussed the structural features present in **191a** and **191b** which permitted facile cycloaddition to the generally unreactive imine linkage.[268] One possibility considered is that the carbon–nitrogen double bond is present in a six-membered ring. This should tend to minimize deactivation processes arising from bond rotations and nitrogen inversion mechanisms. However, this condition alone is not sufficient for imine photoreactivity, since attempted cycloadditions to cyclic imines lacking the carbonyl group were not successful.[268] The authors point out that it may be necessary for a conjugated electron-withdrawing group to be attached to the C–N double bond in order for cycloaddition to proceed. Obviously further work must be done before these points can be clarified.



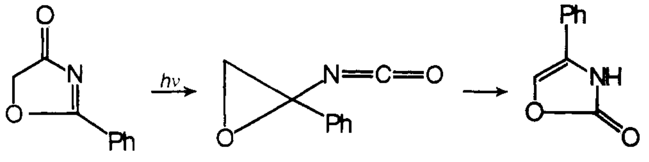
191a **192a**



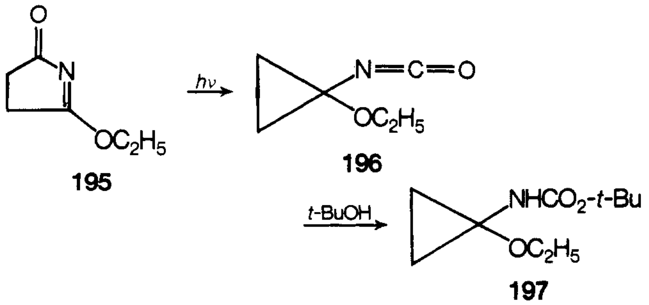
191b **192b**

X. Photofragmentation

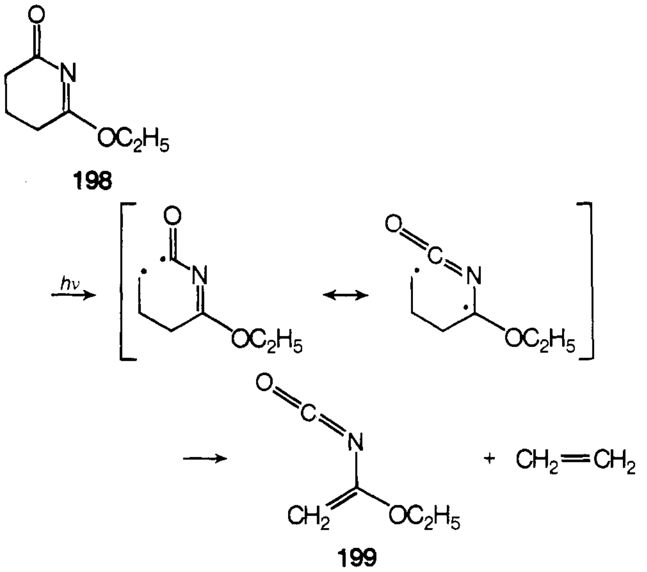
The Norrish type I reaction or α-cleavage is a common photochemical reaction of carbonyl compounds.[168] The photochemical type I cleavage of cyclic keto imino ethers, which structurally resemble 2-cyclopentenone and 2-cyclohexenone, has recently been described.[174] In these examples, α-cleavage was found to occur to the complete exclusion of photodimerization or cycloaddition to olefins. For example, irradiation of a benzene solution of 2-phenyl-2-oxazolin-4-one (**186**) gave 4-phenyl-4-oxazolin-2-one (**194**) as the major photoproduct. When the irradiation of **195** was carried out in *tert*-butyl alcohol, 2-methyl-2-propyl *N*-(ethoxycyclopropyl)carbamate **197** was formed in high yield.[174] Photolysis of **195** in tetrahydrofuran gave cyclopropyl isocyanate **196**. When the irradiation of **195** was carried out in the presence of dimethoxyethylene, no photocycloaddition to the C–O or C–N double bonds occurred. This result is in contrast to the reported [2 + 2] cycloadditions of olefins to the C–N double bonds of the structurally related molecules, 3-ethoxyisoindolone (**183**)[265] and 2-phenyl-2-oxazolin-4-one (**186**).[266] The above photoreactions were rationalized by a Norrish type I mechanism. Subsequent collapse of the initially produced 1,3-diradical will yield an isocyanate (i.e., **196**) which could be trapped with *tert*-butyl alcohol (to give **197**) or undergo an acid-catalyzed rearrangement (to give **194**). Evidence was presented which showed that **195** reacts from the n–π^* singlet state.[174] Usually, α-cleavage is an uncommon reaction of α,β-unsaturated ketones structurally related to **186** and **195**. Photodimerization and photocycloaddition are generally the observed reactions. The difference in reactivity of **186** and **195** compared with cyclic α,β-unsaturated ketones is apparently a matter of energetics. The n–π^* singlet energies of **186** and **195** are considerably higher than n–π^* singlet energies of α,β-unsaturated ketones. Hence, sufficient energy is available along the reaction coordinate for α-cleavage, and this mode of reactivity is then competitive with the various modes of energy dissipation available to the excited state. Photolysis of the homologous 6-ethoxy-4,5-dihydro-2(3*H*)-pyridone (**198**) system gave ethoxyvinyl isocyanate (**199**) via a similar path.[174]



186 **193** **194**



195 **196** **197**

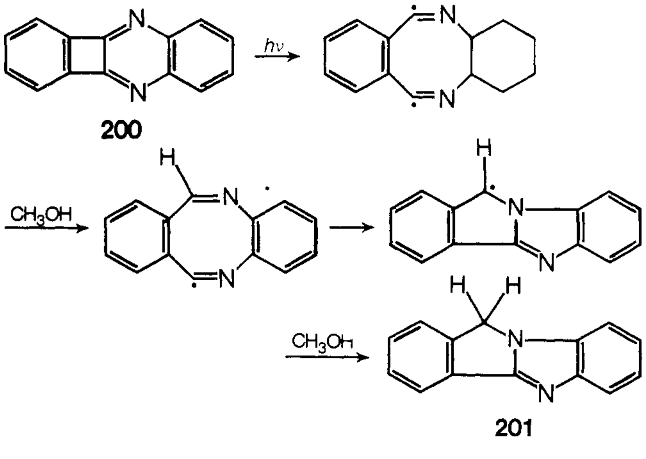


198 **199**

A wide variety of photoreactions appears to be initiated by cleavage of a bond adjacent to the C–N double bond. These processes are analogous to the Norrish type I cleavage reactions. There seems to be only limited information on the nature of the excited states in these reactions. Some appear to be sensitized by triplet energy transfer agents; however, characterization of the intermediates has generally not been done. Clearly more work is needed to determine the nature of the reacting species.

One interesting case involves the photochemistry of benzo[3,4]cyclobuta[1,2-*b*]quinoxaline (**200**). Irradiation of **200**

SCHEME VI

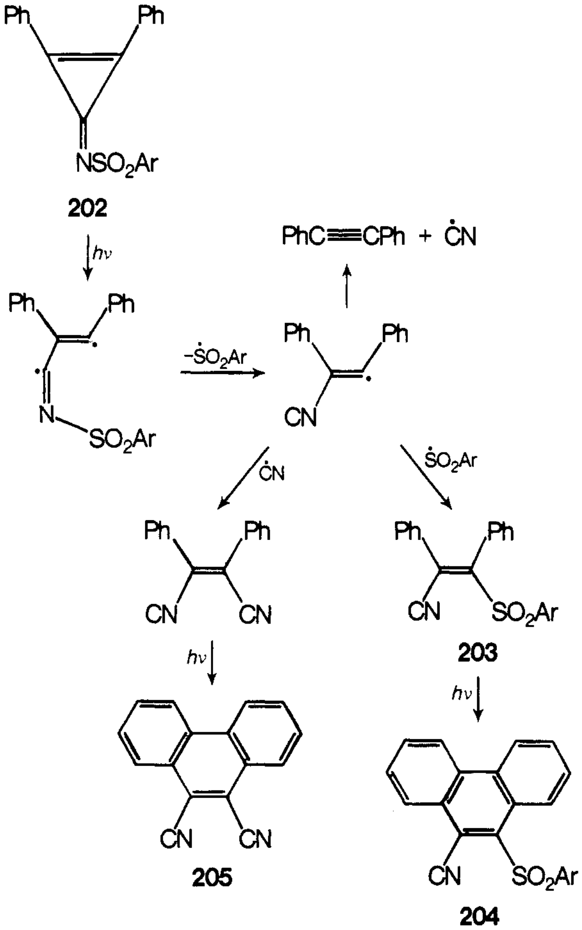


200 **201**

in methanol through Pyrex led to an 80% yield of 11*H*-isoindolo[2,1-*a*]benzimidazole (**201**).[269] The suggested mechanism involves an α-cleavage step and is outlined in Scheme VI.

Irradiation of *N*-(*p*-toluenesulfonyl)diphenylcyclopropenimine (**202**) produced a mixture of diphenylacetylene, 1-cyano-2-*p*-toluenesulfonyl-*cis*-stilbene (**203**), 9-cyano-10-*p*-toluenesulfonylphenanthrene (**204**), and 9,10-dicyanophenanthrene (**205**).[270] These products can readily be attributed to α-cleavage of **202** followed by loss of *p*-toluenesulfonyl radical in the manner outlined in Scheme VII.

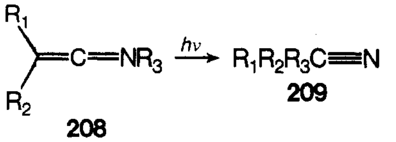
SCHEME VII



The photoisomerization of carbodiimides **206** into cyanamides **207** constitutes a rearrangement[271] reminiscent of the photochemical isomerizations of ketenimines into nitriles.[272] Both processes can be rationalized by an α-cleavage reaction. A similar type of cleavage has been observed to occur with hydrazones[274] and azines.[275]

$$R_1N{=}C{=}NR_2 \xrightarrow{h\nu} [R_1N{=}C{=}\dot{N}\quad \dot{R}_2] \longrightarrow R_1R_2NC{\equiv}N$$

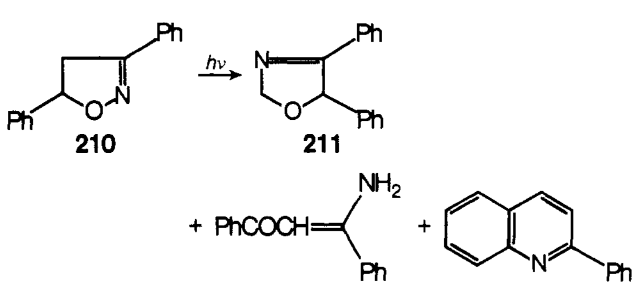
206 **207**

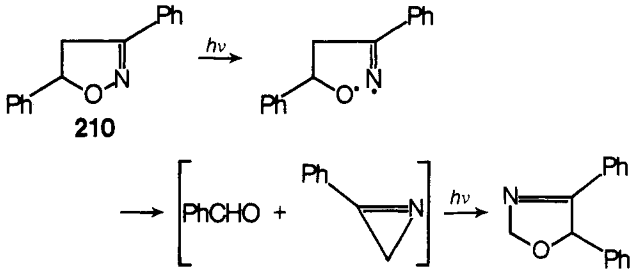


$$R_1R_2C{=}C{=}NR_3 \xrightarrow{h\nu} R_1R_2R_3C{\equiv}N$$

208 **209**

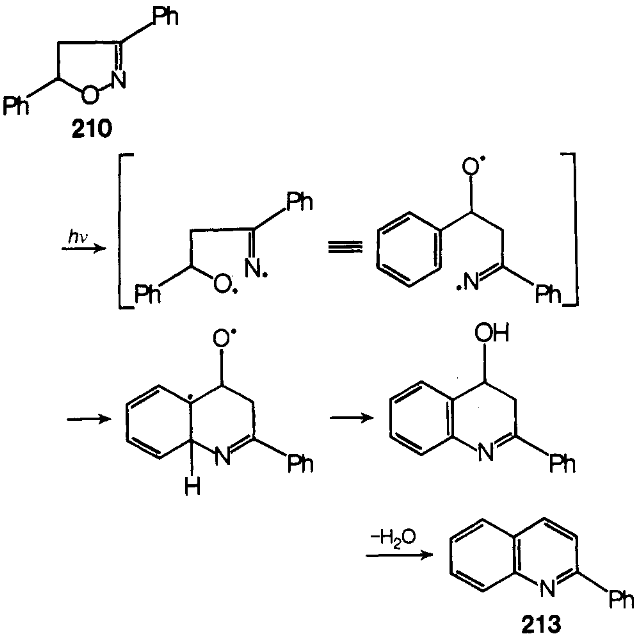
A number of nonaromatic five-membered nitrogen heterocycles are known to undergo fragmentation on irradiation. Thus, on irradiation in acetonitrile, 3,5-diphenyl-2-isoxazoline (**210**) is converted into a mixture of 4,5-diphenyl-3-oxazoline (**211**), β-aminochalcone (**212**), and 2-phenylquinoline (**213**).[275] The formation of oxazoline **211** was attributed to an initial N–O bond cleavage followed by scission to benzaldehyde and phenylazirine and subsequent recombination.





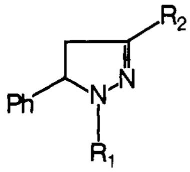
This sequence was strongly supported by the fact that irradiation of an equimolar mixture of 2-phenylazirine and benzaldehyde afforded oxazoline **211**.[276] The formation of 2-phenylquinoline from **210** was also attributed to a primary N–O bond cleavage followed by intramolecular attack on the benzene ring in the manner described in Scheme VIII. An analogous transformation was observed in the photolysis of 3,5-diphenyl-1,2,4-oxadiazole to 2-phenyl-4-quinazolone.[277]

SCHEME VIII

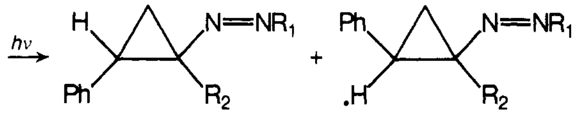


In contrast to the results observed with the isoxazoline system, ring contraction with the formation of nitrogen-containing side chains is observed in the photolysis of 5-phenylpyrazolines.[278] Irradiation of 1-methyl- and 1,3-dimethyl-5-phenyl-Δ^2-pyrazolines (**214** and **215**) yields the *cis*-**216** and *trans*-**217** isomers of the cyclopropane system.

Certain five-membered heterocyclic ring compounds are known to undergo transposition of ring carbon atoms on photolysis in a manner which is reminiscent of benzene photochemistry (see section XII). By contrast, 1,2,5-thiadiazoles and 1,2,5-oxadiazoles undergo photocleavage reactions.[279] Thus

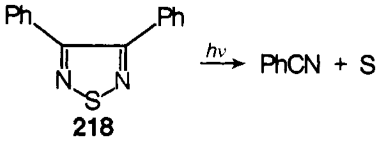


214, $R_1 = CH_3$; $R_2 = H$
215, $R_1 = R_2 = CH_3$



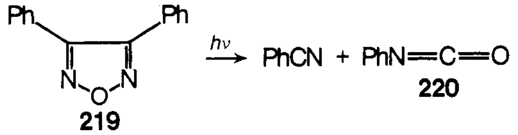
216 **217**

compound **218** yields elemental sulfur and benzonitrile on irradiation.



218

Diphenyl-1,2,5-oxadiazole (**219**) was initially reported to give benzonitrile and phenyl isocyanate on photolysis in ether,[279] while the dimethyl compound **221** forms acetonitrile and tarry products. In the latter case, the formation of the *N*-oxide of acetonitrile (**222**) was assumed to have been formed since adduct **223** was isolated from reactions carried out in the presence of cyclopentene.



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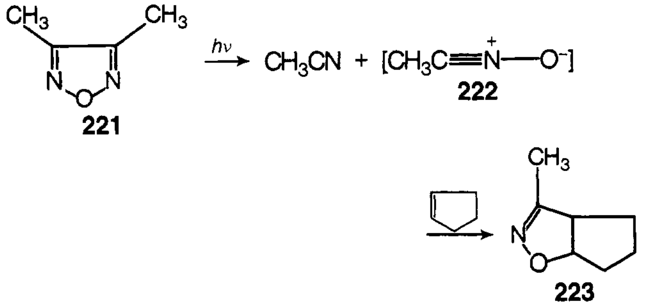
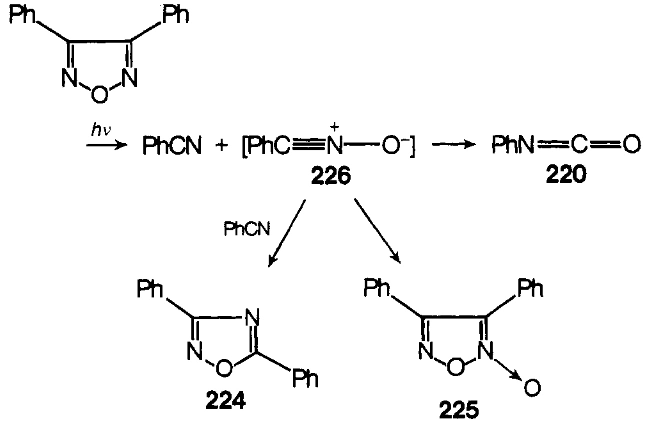
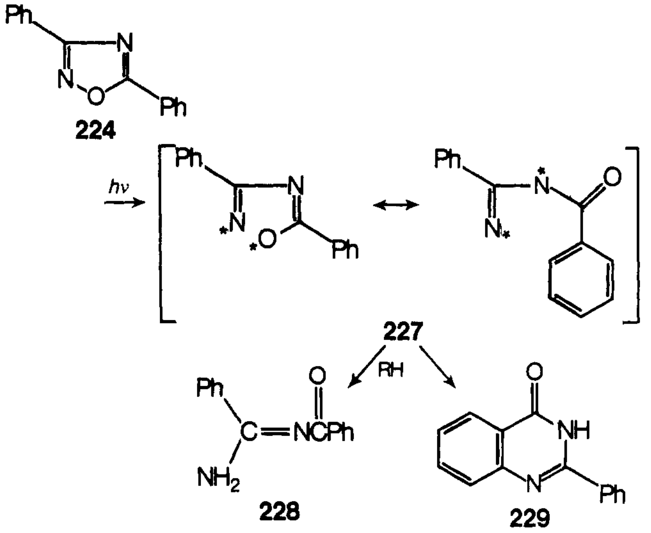


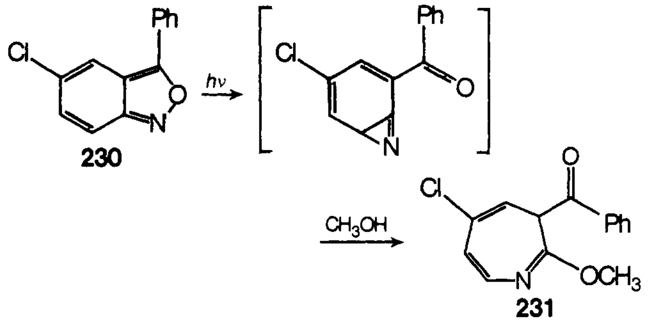
221

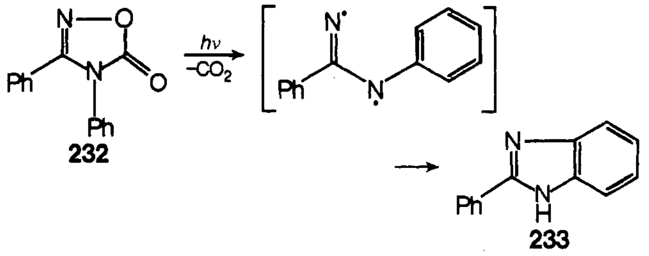
In a subsequent investigation, Mukai and co-workers[280] examined the photolysis of **219** in benzene and found that 3,5-diphenyl-1,2,4-oxadiazole (**224**) and diphenylfuroxan (**225**) were also formed. These products can be conveniently rationalized by assuming that oxadiazole **219** undergoes photofragmentation to benzonitrile and benzonitrile oxide (**226**). The initially produced 1,3-dipole subsequently reacts with benzonitrile to give **224** or dimerizes to give **225**. The 1,2,4-oxadiazole **224** was also shown to be photolabile and in aprotic media gave **228** and **229**.[281] The formation of **229** implicates a ring-opened species (i.e., **227**) which subsequently gives **229** by an intramolecular cyclization and hydrogen transfer route.



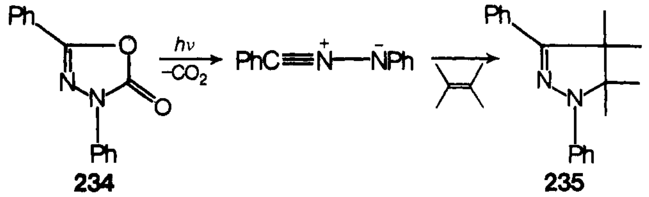


A number of interesting photoreactions of heterocyclic compounds possessing the –C=N—O– linkage have also been studied. Thus, N–O cleavage was observed with the following systems.[282,283]





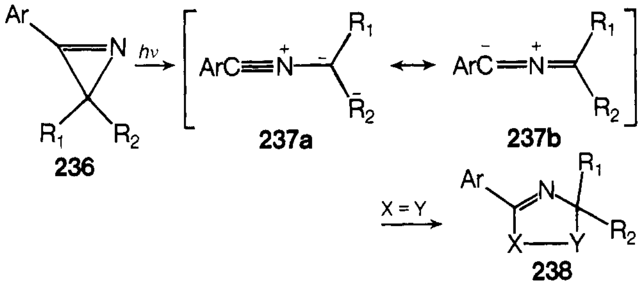
Irradiation of the isomeric oxadiazolinone system (**234**) in the presence of olefins was found to afford adducts derived from the expected nitrile imine intermediate.[283]



XI. Azirine Photochemistry

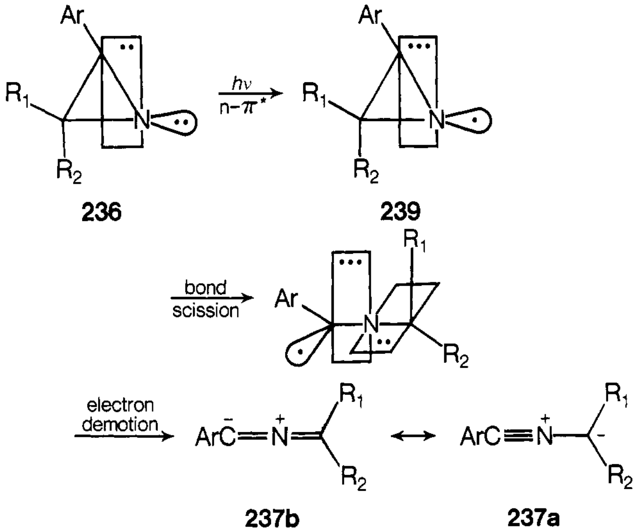
As was discussed in an earlier section, the low photoreactivity of the imine chromophore was attributed to facile deactivation of the excited state as a consequence of rotation about the C–N double bond. In rigid systems, this mode of energy dissipation

SCHEME IX



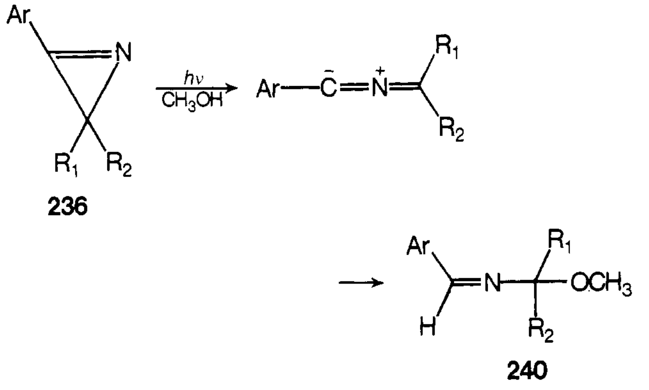
would not be available, and these molecules would have maximum opportunity to undergo reaction from an electronically excited state. Independent studies by Padwa and Schmid have shown that arylazirines undergo irreversible ring opening on electronic excitation to give nitrile ylides as reactive intermediates[284-305] (Scheme IX). These species can be intercepted with a wide variety of dipolarophiles to form five-membered heterocyclic rings. The cleavage of the C–C bond of the azirine ring proceeds from the n–π* singlet state[285] and was rationalized in terms of an electrocyclic transformation by analogy with the cyclopropyl → allyl cation rearrangement.[306] One may envisage the n–π* excitation process as leading to a species resembling structure **239**, where the nonbonding orbitals on nitrogen contain only one electron. The electron that was promoted to the antibonding π* orbital will partially reside on the carbon atom and consequently the nitrogen atom will become somewhat electrophilic and begin to resemble an aziridinyl cation. The remaining nonbonding electron on nitrogen, which is in the plane of the σ bonds of the ring, will overlap with the back lobe of the C–C bond of the saturated carbon and facilitate bond scission. Electron demotion would then result in the formation of nitrile ylide **237** (Scheme X).

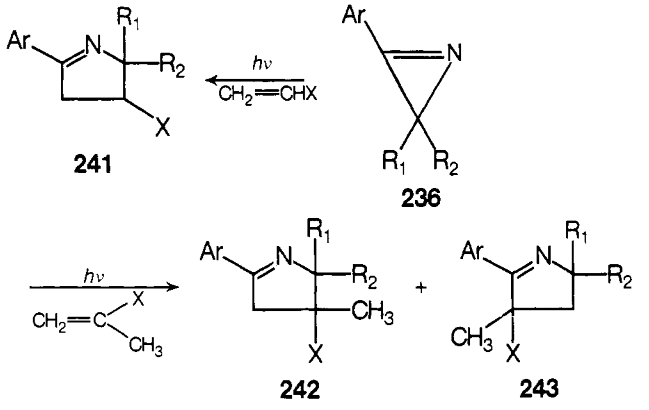
SCHEME X



Salem has carried out some ab initio computations on the ground-state and excited-state energy surfaces of the 2*H*-azirine molecule.[307] His calculations indicate that the ring-opened intermediate should be capable of dual reactivity when it is intercepted by an added dipolarophile. The behavior of the system was predicted to be dependent on the geometry of the transient intermediate generated from the photolysis of the azirine ring. If the ring is opened to give a species with bent geometry, a diradical state with partial dipolar character will be obtained. Opening of the azirine ring to an intermediate with linear geometry will result in the formation of a species having closed-shell zwitterion character. Salem's calculations indicate that the reactive dipolar intermediate with linear geometry is best reached by internal conversion from an n–π* singlet state at a C–N–C angle of 100°.

In order to predict regioselectivity in the photocycloaddition of arylazirirines, it is necessary to determine the relative magnitudes of the coefficients in the highest occupied orbital (HO) of the nitrile ylide. This problem was solved by carrying out the irradiation of several arylazirines in hydroxylic media.[308] The photoconversion of arylazirines (**236**) to alkoxyimines (**240**) indicates that in the highest occupied orbital of the nitrile ylide, the electron density at the disubstituted carbon is greater than at the trisubstituted carbon atom. With this conclusion, all of the regiochemical data found in the photoaddition of arylazirines with dipolarophiles can be explained. Thus, acrylonitrile and methyl acrylate react with various nitrile ylides to give only the 4-substituted regio isomers **241**. Photocycloaddition of arylazirines with α-methylacrylonitrile and methyl methacrylate, on the other hand, gives adducts of types **242** and **243** in a 3:2 ratio.[285] The formation of a mixture of cycloadducts in this case was attributed to the fact that whereas the cyano or ester group enhances the lowest unoccupied orbital (LU) coefficient at the unsubstituted carbon atom of the dipolarophile, the methyl group has the opposite effect.[309] The terminal coefficients in the LU of α-methylacrylonitrile and methyl methacrylate are more nearly the same than for the nonmethylated analogs, so that regioselectivity decreases for these dipolarophiles.

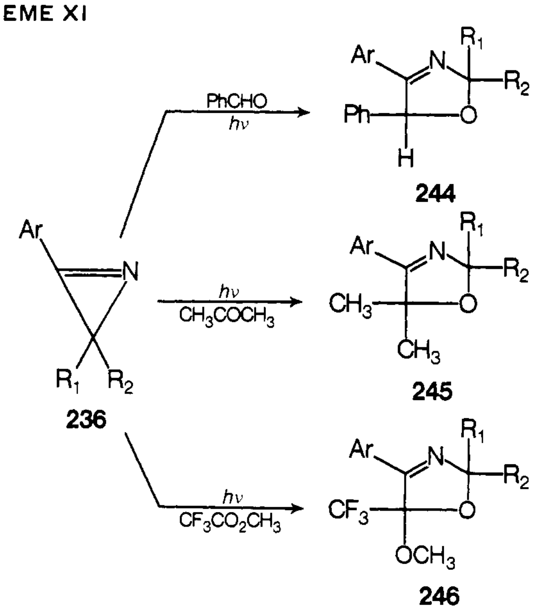




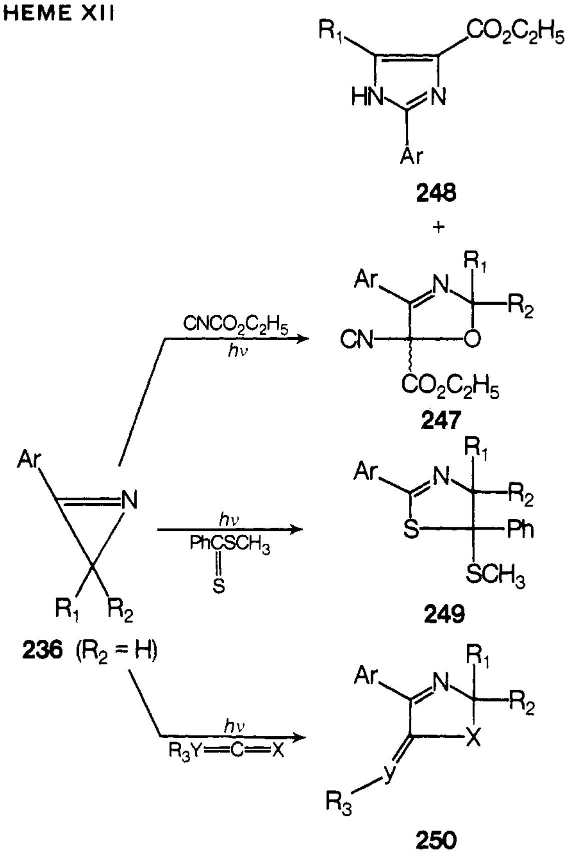
The photochemical additions of azirines to the carbonyls of aldehydes, ketones, and esters also show complete regiospecificity (Scheme XI). Besides the formation of the isomeric oxazolines from **236** and ethyl cyanoformate, there is also formed the imidazole **248** from addition to the C≡N bond in the expected regioselective manner. Thioesters lead to thiazolines (**249**) while isocyanates and ketenes produce heterocycles **250** (Scheme XII).

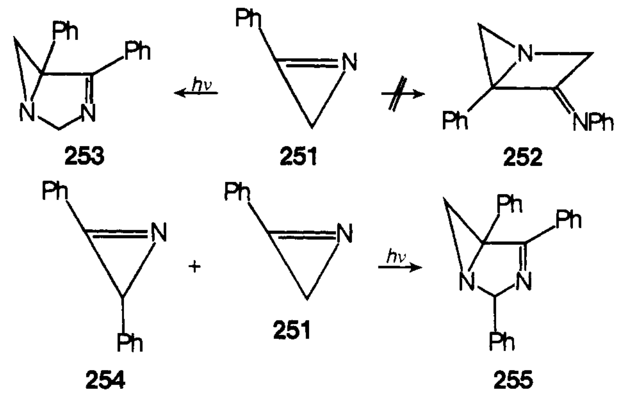
Irradiation of arylazirines with olefins of low dipolarophilic activity produced no photoadduct but instead gave dimers.[285] It was originally reported that photolysis of phenylazirine (**251**) gave azabicyclopentane (**252**).[310,311] However, in the light of the foregoing mechanistic rationale developed for the photolysis

SCHEME XI

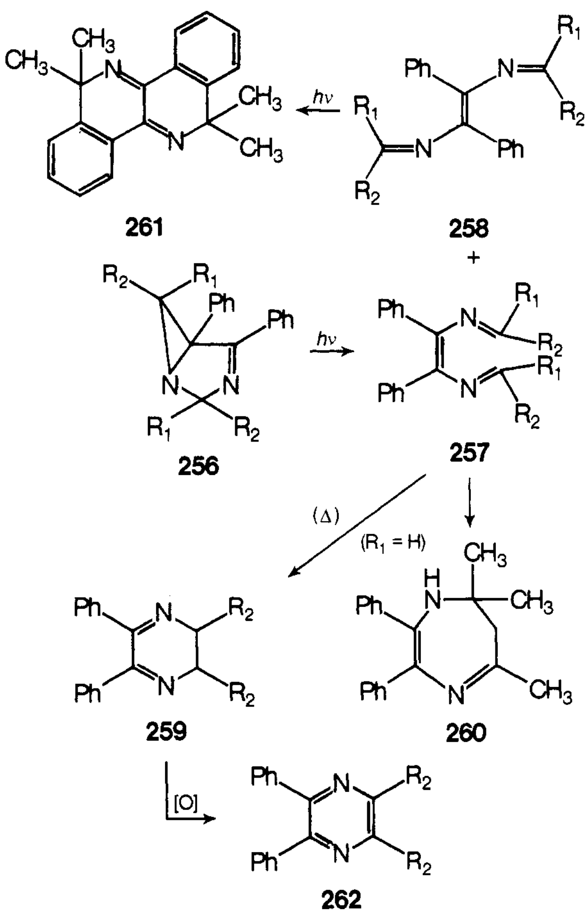


SCHEME XII

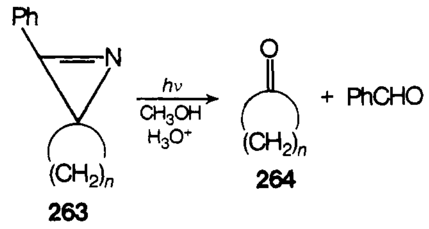




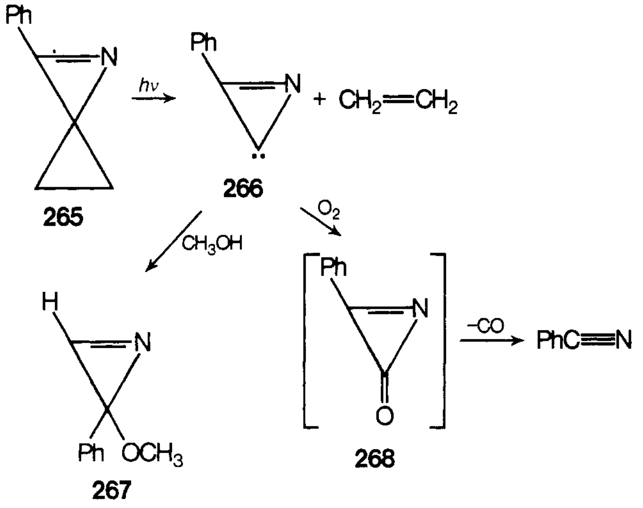
of azirines, Padwa and co-workers were able to show that the photodimer isolated is actually diazabicyclohexene **253.** Thus, in the absence of an external dipolarophile, the nitrile ylide generated photochemically simply adds to a ground-state azirine molecule.[285] A crossed dimerization of **254** to the ground state of **251** has also been realized.[312] Additional work showed that the photodimerization of arylazirines to 1,3-diazabicyclo-[3.1.0]hex-3-enes is a general reaction which is independent of the nature of the substituent groups attached to the C atom of the azirine ring.[286,293] Care is required in the choice of solvent, photolysis time, and substituents since the 1,3-diazabicyclohexenes are themselves photochemically labile. Indeed, extended photolysis leads to complete ring opening and the formation of diazahexatrienes **257.** These may be isolated when $R_1 = R_2 = CH_3$. Further photolysis of *trans*-**258** ($R_1 = R_2 = CH_3$) gives the diazachrysene **261.** The cis ($R_1 = R_2 = CH_3$) enediimine **257** very readily cyclizes to the dihydrodiazepine **260** on standing. On the other hand, if $R_1 = H$ in *cis*-**257**, then cyclization gives first the dihydropyrazine **259** and eventually the pyrazine **262.** The results indicate that the secondary photoproducts formed from the irradiation of the diazabicyclohexenes (**256**) depend on the substituent groups, the time of irradiation, and the particular solvent employed.[286,313,314]



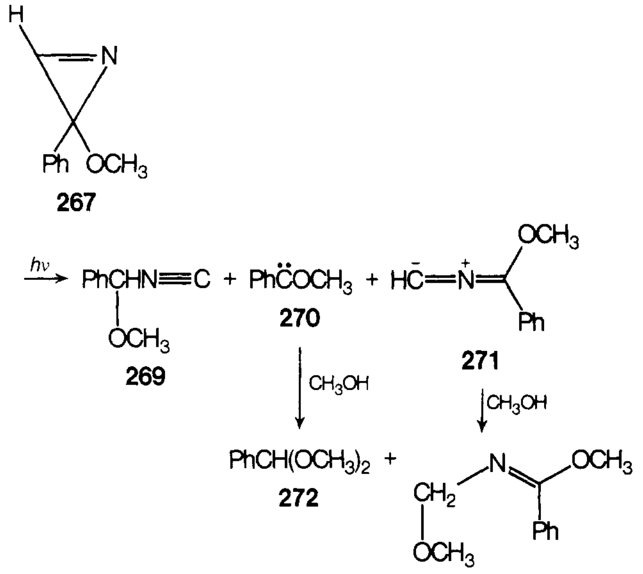
A new synthesis of cycloalkanones was recently devised and is based upon the photolysis of spiroazirines in alcohol followed by aqueous hydrolysis.[315]



In contrast to the above findings, irradiation of 2-phenyl-1-azaspiro[2.2.]pent-1-ene (**265**) in methanol resulted in a Griffin type fragmentation[316] and produced ethylene and 2-phenylazirinylidene (**266**). This novel carbene reacted with methanol to produce 2-methoxy-2-phenyl-2*H*-azirine (**267**). When the irradiation of **265** was carried out in the presence of oxygen, benzonitrile and carbon monoxide were formed. The formation of

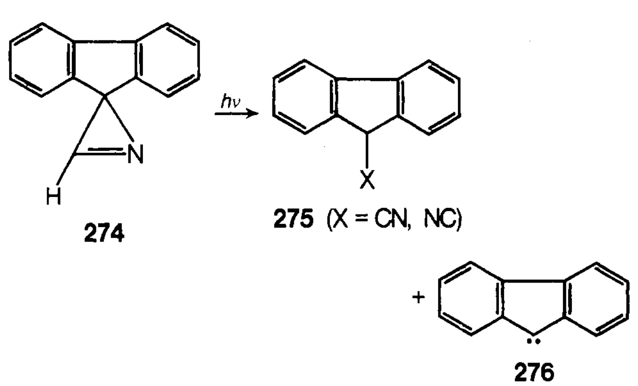


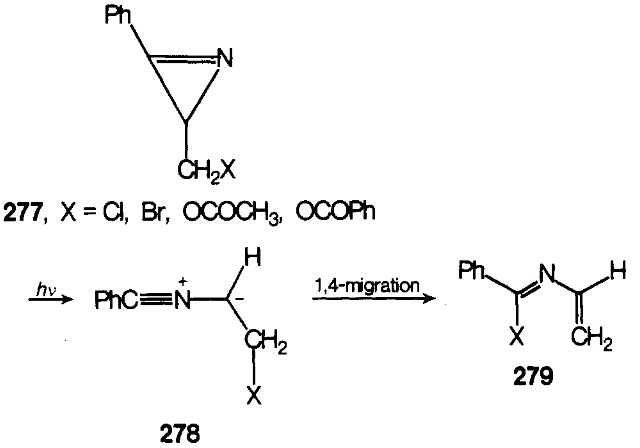
these products was rationalized in terms of 2-phenylazirinone as a transient intermediate. On further photolysis, azirine **267** is converted into isocyanide **269**, phenylmethoxycarbene (**270**), and nitrile ylide **271**. Both the carbene (**270**) and the 1,3-dipole (**271**) were trapped with methanol to give **272** and **273**, respectively.



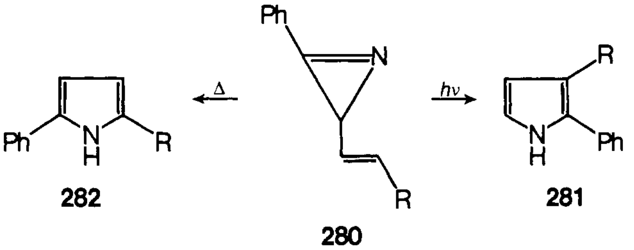
Hafner and Bauer had previously reported that the related spiro[2*H*-azirine-2,9′-fluorene] (**274**) leads to a mixture of 9-cyano- and 9-isocyanofluorene on photolysis.[317] These workers also reported that **274** undergoes loss of HCN and generates 9-fluorenylidene, thereby providing good precedent for the transformations observed with azirine **267**.

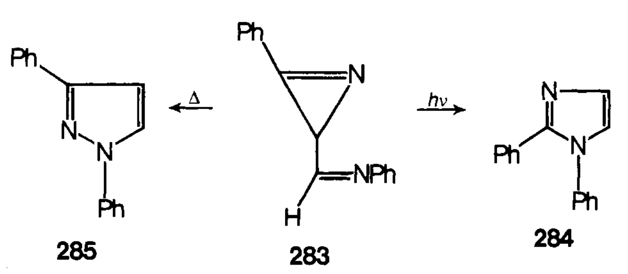
Irradiation of a series of 2-carbinyl-2*H*-azirines (**277**) which contain good leaving groups has been found to afford *N*-vinylimines via a novel 1,4-substituent shift.[318] The results indicated that the migrating substituent (X) must be a reasonably good leaving group in order for the rearrangement to occur. Involvement of a nitrile ylide intermediate (**278**) in the above rearrangement was demonstrated by trapping experiments.



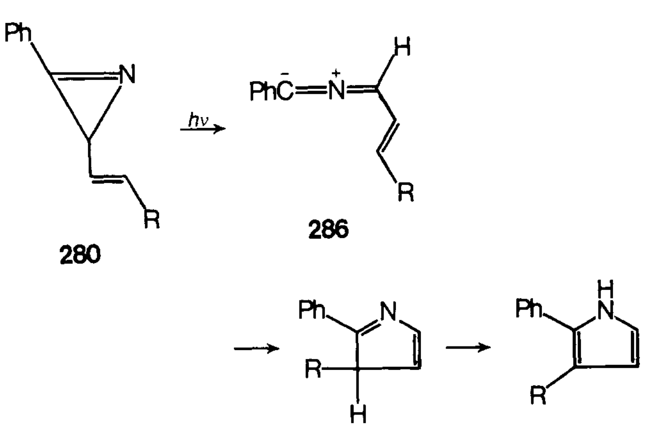


Whereas the cycloaddition of arylazirines with simple olefins produces Δ′-pyrrolines, a rearranged isomer can be formed when the alkene and azirine moieties are suitably arranged in the same molecule. This intramolecular photocycloaddition was first observed by Padwa and co-workers[318,320] using 2-vinyl-substituted azirines. Irradiation of azirine **280** in benzene afforded a 2,3-disubstituted pyrrole **281**, while thermolysis gave a 2,5-disubstituted pyrrole **282**. Photolysis of azirine **283** proceeded



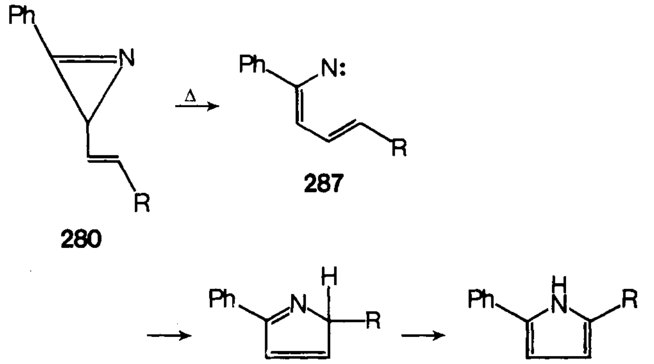


similarly and gave 1,2-diphenylimidazole **284** as the exclusive photoproduct. This stands in marked contrast to the thermal reaction of **283** which afforded 1,3-diphenylpyrazole (**285**) as the only product. The evidence obtained clearly indicates that the above photorearrangements proceed by a mechanism which involves a nitrile ylide intermediate. This conclusion was reached by carrying out the irradiation of **280** in the presence of a trapping agent and isolating an external cycloadduct. Intramolecular cycloaddition of the nitrile ylide **286** followed by a 1,3-sigmatropic hydrogen shift of the initially formed five-membered ring was proposed to account for the formation of the final product.



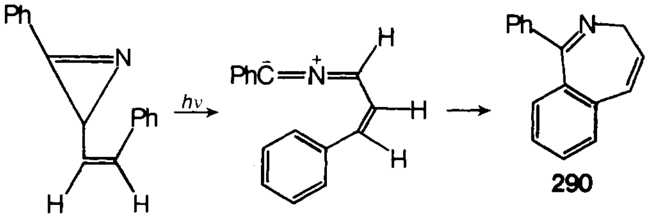
280 **286** **281**

The thermal transformations observed with these systems, on the other hand, have been rationalized in terms of an equilibration of the 2*H*-azirine with a transient vinyl nitrene (**287**) which subsequenty rearranges to the 2,5-disubstituted pyrrole.

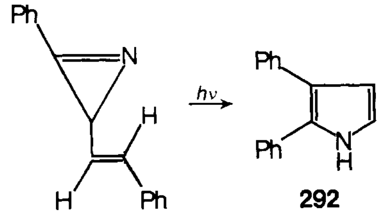


280 **287** **282**

In contrast to the photochemical results encountered with **280**, the presence of a *cis*-styryl side chain in the 2 position of the azirine ring (**288**) leads to ring expansion and gives benzazepine **290**. The 2-[2-(α- and β-naphthyl)vinyl]-3-phenyl-2*H*-azirine systems behaved similarly and proceeded with complete regiospecificity.[320] The photolysis of the isomeric *trans*-styrylazirine **291** took an entirely different course and produced 2,3-diphenylpyrrole (**292**) as the major product. The results indicate that opening of the azirine ring followed by intramolecular cyclization proceeds at a faster rate than isomerization about the C–C double bond.[319] The preference for cyclization of **289** to a seven-membered ring was attributed to stereoelectronic factors. Closure of the linear dipolar intermediate **289** obtained from **288** occurs more easily via a seven-membered transition state and leads to the preferential formation of benzazepine **290**.



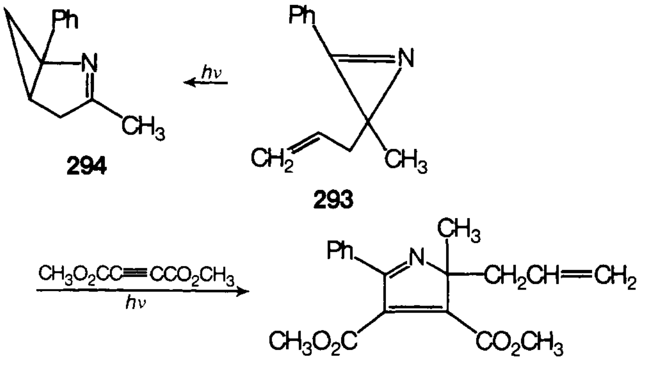
288 **289** **290**



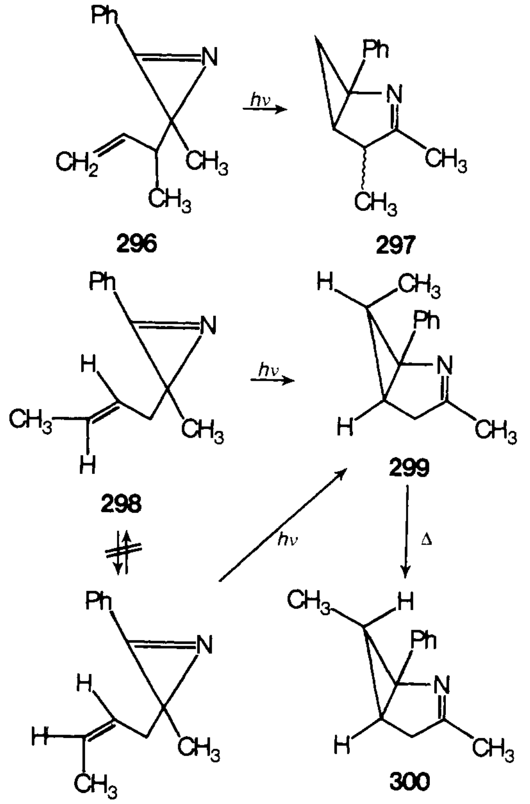
291 **292**

Cyclization of the nitrile ylide derived from the trans isomer (i.e., **291**) to a seven-membered ring is precluded on structural grounds, and formation of 2,3-diphenylpyrrole (**292**) occurred instead.

Irradiation of the homologous 3-phenyl-2-methyl-2-allyl-2*H*-azirine (**293**) system gave 1-phenyl-3-methyl-2-azabicyclo[3.1.0]hex-2-ene (**294**) as the exclusive photoproduct.[321] Photolysis of **293** in the presence of excess dimethyl acetylenedicarboxylate resulted in the trapping of the normal nitrile ylide and afforded cycloadduct **295** in high yield.[321] Under these conditions, the formation of **294**, which is produced in quantitative yield in the absence of a trapping reagent, was entirely suppressed. The photoreactions of the closely related methyl-substituted azirines **296** and **298** were also examined.[321] Irradiation of **296** produced cycloadduct **297** while photolysis of **298** gave bicyclohexene **299** as the primary photoproduct. Upon standing at room temperature in the dark, **299** epimerized to the thermodynamically more stable exo isomer **300**.

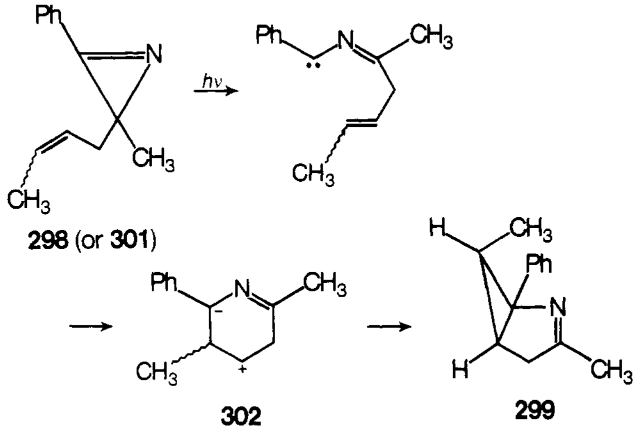


294 **293** **295**



296 **297** **298** **299** **301** **300**

More recent work[322] has shown that irradiation of the cis-substituted azirine **301** also produced azabicyclohexene **299**. This observation indicates that the internal photocycloaddition process is stereoselective but not stereospecific. A reasonable explanation to account for the observed stereoselectivity is that the cycloaddition process occurs by initial attack of the carbene carbon of the 1,3-dipole onto the terminal position of the double bond. Huisgen had previously pointed out that among the possible resonance forms of a nitrile ylide, a carbene structure can be envisioned which makes conceivable a 1,1-cycloaddition of this 1,3-dipole.[323] Attack by the carbene carbon of the 1,3-dipole will generate a six-membered ring dipole (**302**) which contains a secondary carbonium ion as well as an azaallyl anion portion. Collapse of this new 1,3-dipole to the thermodynamically favored exo product (**300**) will result in a severe torsional barrier on closure. On the other hand, collapse to the thermodynamically less favored endo isomer (**299**) moves the phenyl and methyl groups increasingly further apart and would account for the formation of the less stable product.

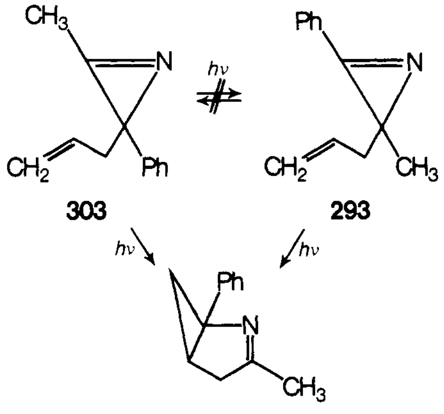


298 (or 301)

302

299

Supporting evidence for this scheme was obtained by irradiating the isomeric 3-methyl-2*H*-azirine system (**303**).[322] Photolysis of this azirine resulted in the quantitative formation of azabicyclohexene **294**. This is the same azabicyclohexene that was formed from the irradiation of azirine **293**. A control experiment showed that **293** and **303** were not interconverted under the photolytic conditions. The formation of **294** from **303** is perfectly consistent with the generation of a six-membered ring dipole (i.e., **306**). Thus, cyclization of the initially formed carbene (**304**) generates **306** which closes to azabicyclohexene **294**. The same six-membered ring dipole is also formed from azirine **293**. Thus the stereoselectivity observed with azirines **298** and **301** as well as the regiospecificity encountered with azirines **293** and **303** can be attributed to a two-step cyclization path which involves a six-membered ring dipole. The formation of *endo*-azabicyclohexene **299** from methylazirine **307** provides additional support for this interpretation.



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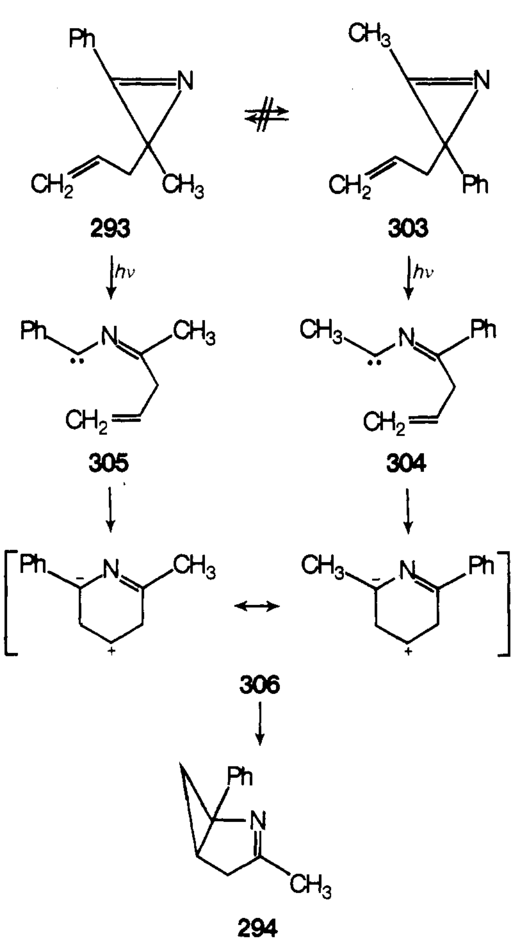

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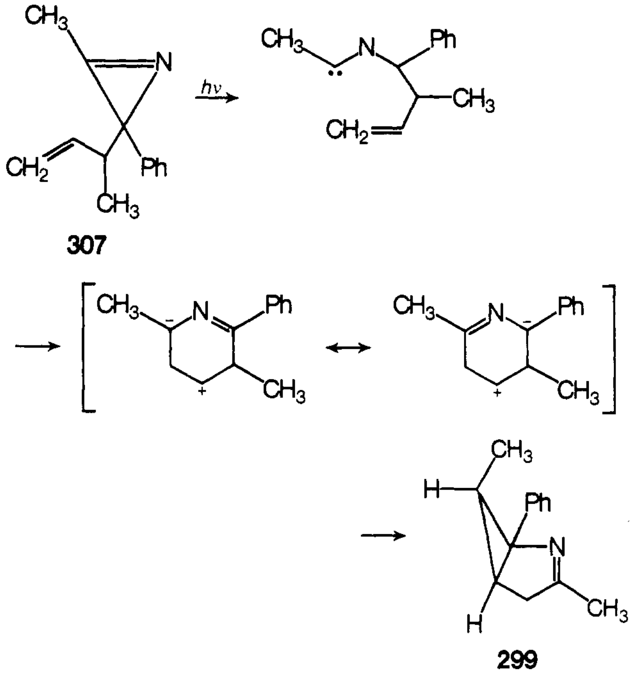

307

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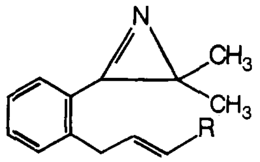
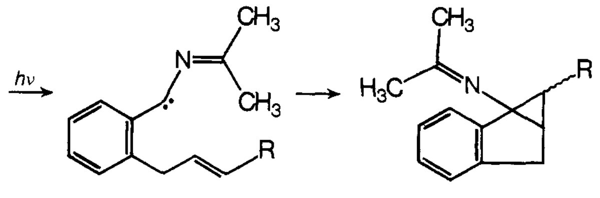
A related 1,1-cycloaddition reaction was also observed with 2-(*o*-allylphenyl)-3,3-dimethylazirine (**308**).[324] Irradiation of **308** gave benzobicyclo[3.1.0]hex-2-ene (**309**) as the only isolable cycloadduct. Photolysis of the closely related methyl substituted azirine system **310** (R = CH_3) gave a mixture of *endo*- and *exo*-benzobicyclohexenes **311** in quantitative yield. No detectable quantities of the isomeric 1,3-dipolar adduct was observed in the crude photolysate. In this case, the structure of the major product (i.e., *exo*-**311**) obtained from **310** corresponds to the thermodynamically more favored exo isomer.

When the chain between the azirine ring and the alkene end was extended to three carbon atoms, the normal mode of 1,3-intramolecular dipolar cycloaddition occurs. For example, irradiation of azirine **312** gave Δ'-pyrroline **313** in quantitative yield.[325] In this case, the methylene chain is sufficiently long to

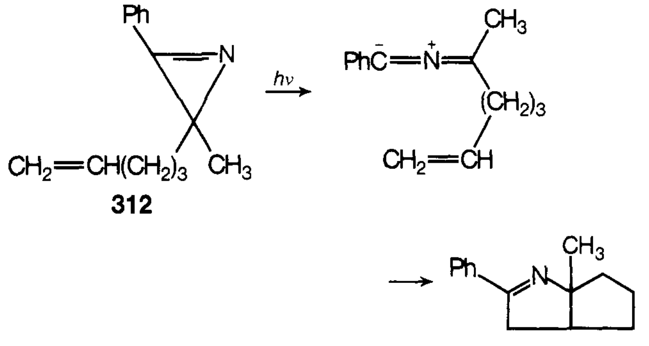


308, R = H
310, R = CH_3



309, R = H
311, R = CH_3

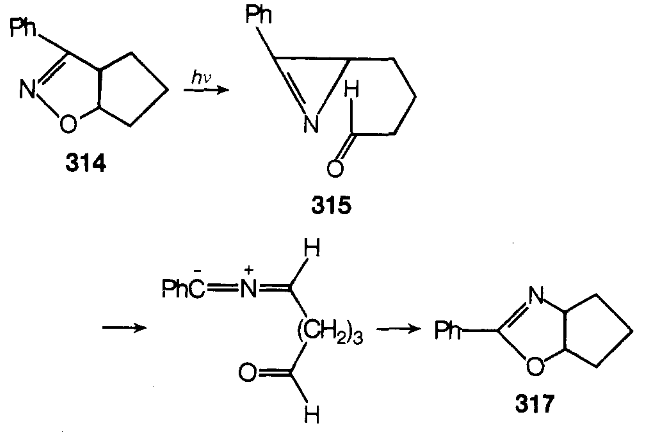
allow the dipole and olefinic portions to approach each other in parallel planes.



312

313

In a somewhat related case, Schmid and co-workers reported on the photoisomerization of dihydroisoxazole **314** to dihydrooxazole **317**.[288] The reaction was proposed to proceed via a transient azirine (**315**). This intermediate was not isolated but was suggested to undergo rapid ring opening to nitrile ylide **316** which cyclized to the observed photoproduct via an internal 1,3-dipolar cycloaddition reaction.



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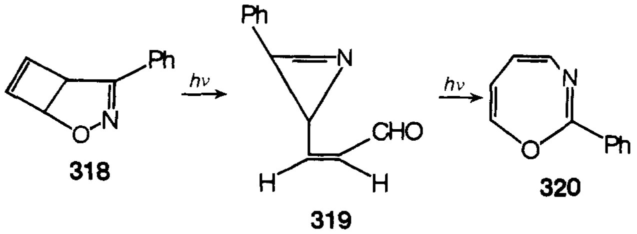
The related 4-phenyl-2,3-oxazabicyclo[3.2.0]hepta-3,6-diene (**318**) system undergoes a similar photochemical rearrangement to produce 2-phenyl-1,3-oxazepine (**320**).[326-328] This reaction has been proposed to involve an azirine intermediate (**319**) which subsequently cyclizes to the observed product.



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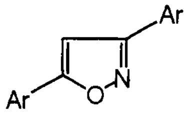
XII. Photorearrangement

Studies of the photochemical isomerizations of five-membered heterocyclic ring compounds which contain a C–N double bond have received considerable attention in recent years. Photoisomerization involving interchange of the positions of two ring atoms has been demonstrated for many of these systems. A ring contraction-ring expansion process in these reactions was first demonstrated by Ullman and Singh for the photorearrangement of 3,5-diarylisoxazoles (**321**) to 2,5-diaryloxazoles (**323**).[329] The photobehavior of azirine **322** was found to be dramatically controlled by the wavelength of the light used. With 3130-Å light, **322** rearranges almost quantitatively to oxazole **323**, whereas 3340-Å light causes rearrangement to isoxazole **321**. The formation of the isoxazole was suggested to occur via the $n-\pi^{*3}$ state of the carbonyl chromophore. Oxazole formation, on the other hand, was attributed to selective excitation of the $n-\pi^*$ state of the azirine ring.[329]



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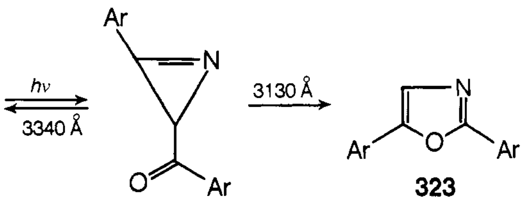

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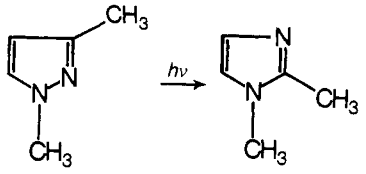
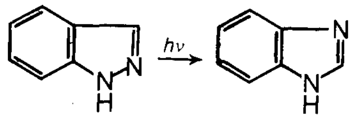
Analogous ring contraction–expansion sequences nicely accomodate the major products produced in the photoisomerization of other five-membered heterocyclic rings.[330-340] For example, the conversion of **324** to **325** and **326** to **327** can be rationalized in a similar fashion.[333]

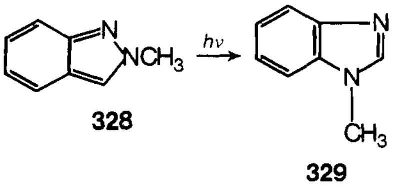


324 **325**



326 **327**

The existence of other photoisomerization pathways for diazole derivatives was suggested by the photorearrangement of 2-methylindazole (**328**) to 1-methylbenzimidazole (**329**)[333] and by the photorearrangement of 1,4,5-trimethylimidazole (**330**) to 1,2,5-trimethylimidazole (**331**).[336] The rearrangement of **330** to **331** was rationalized by internal cyclization and isomerization, although other possibilities were not excluded.



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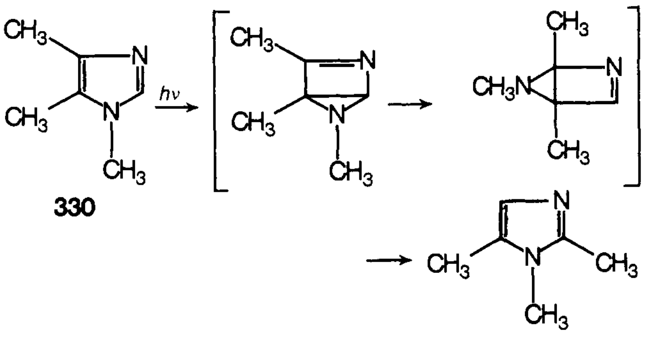
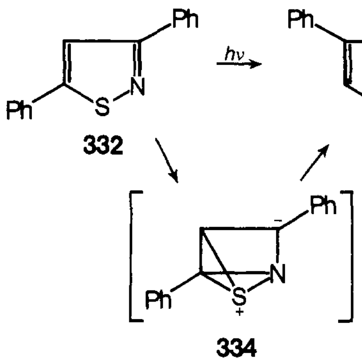
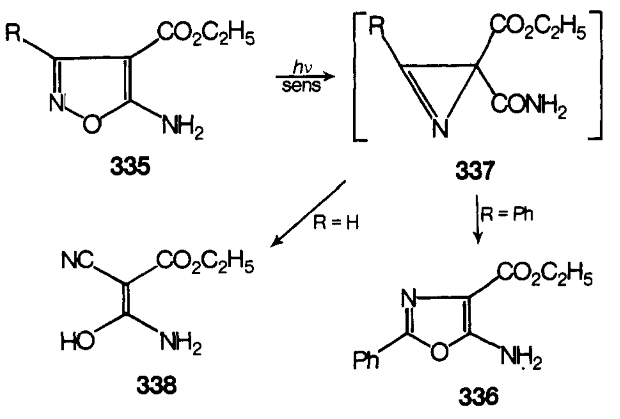
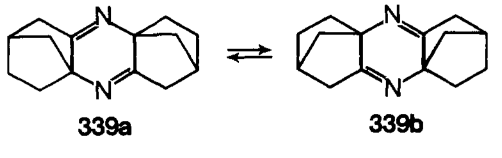


Photolysis of a series of phenylisothiazoles (**332**) gave products which cannot be rationalized in terms of the ring-contraction-ring-expansion mechanism,^{341,342} and, instead, an intermediate corresponding to **334** was proposed. A systematic study of various aryl-substituted thiazoles has also been reported.^{343,344} The reasons for the differences in behavior in these heteroaromatic systems are not always clear. The available evidence points to the existence of more than one pathway in these photorearrangements.^{345} The presence and nature of the substituents on the heterocyclic ring also seem to have a pronounced effect on the reaction. The phenylisoxazole **335** (R = Ph) is converted into phenyloxazole **336** on irradiation in the presence of a sensitizer,^{346} presumably via an azirine intermediate (**337**). In the absence of a phenyl group, however, the isoxazole (R = H) undergoes ring cleavage and gves nitrile **338**. In this case the alternative cleavage of the azirine involving a 1,2-hydrogen shift is preferred.

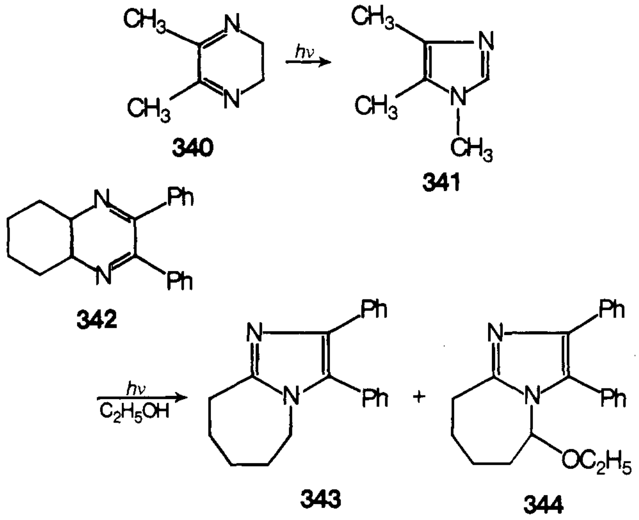


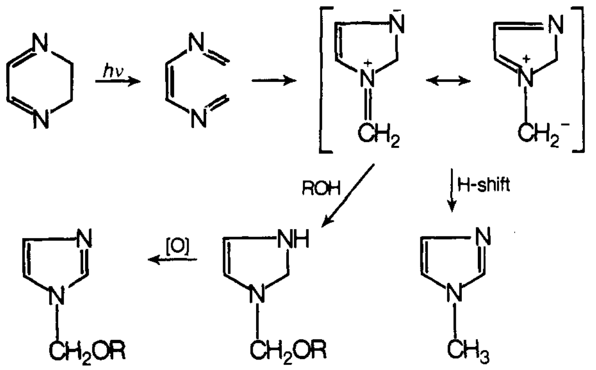


Rearrangement of systems containing a C–N double bond include the photochemistry of the optically active decahydropyrazine system **339**. Irradiation of **339** in methanol leads to racemization.^{347} This process would seem to occur via a pair of simultaneous Wagner–Meerwein-type shifts, and would be photochemically allowed if the configuration is retained at both migrating centers.



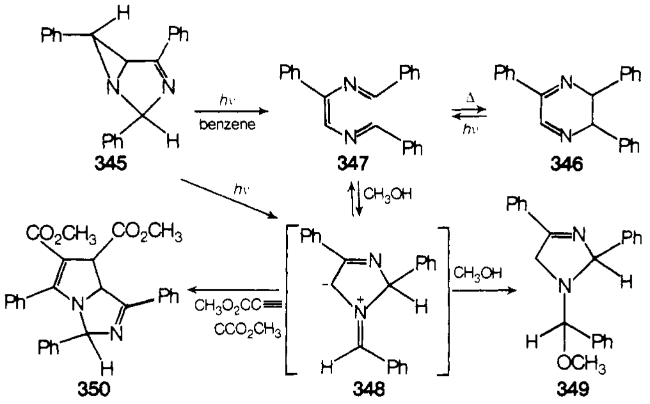
Despite the fact that photochemical isomerizations of cyclic dienes have been well documented, investigation of suitable heterocyclic analogs in light-induced reactions has been somewhat limited.^{348,349} One exception is the work of Beak and Miesel who reported the ready photoisomerization of 2,3-dialkyl-2,3-dihydropyrazines (**340**) to substituted imidazoles^{348} (**341**). In certain cases an alkoxy substituted imidazole (i.e., **344**) could also be isolated. The conversion of 2,3-dihydropyrazines to imidazoles was formulated as proceeding via an enediimine intermediate formed by photolytic ring opening. Subsequent ring closure would generate an intermediate which could lead to an *N*-alkylimidazole by proton transfer or to an *N*-alkoxyalkylimidazole by addition of alcohol followed by oxidation of the resulting imidazoline. These reactions were suggested to proceed through an n–π* singlet state since the rearrangements could not be sensitized nor quenched.





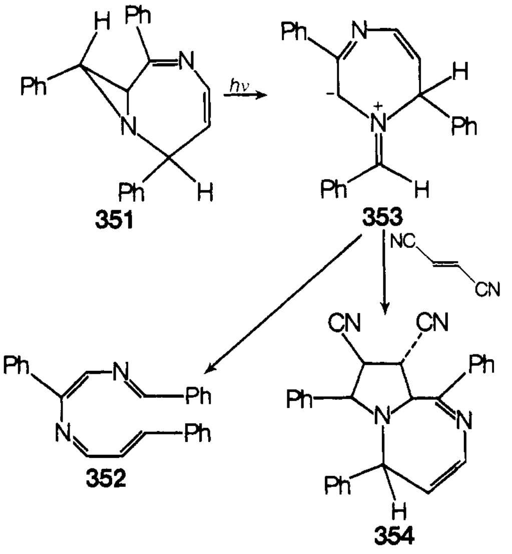
The photorearrangement of 1,3-diazabicyclo[3.1.0]hex-3-enes **345** to *cis*-dihydropyrazines **346** is closely related to the above system and has been studied by Padwa and co-workers.^{350,351} Irradiation results in ring opening to an enediimine intermediate (**347**) which undergoes subsequent thermal disrotatory closure to a *cis*-dihydropyrazine (**346**). The same enediimine intermediate was formed on irradiation of a *cis*- or *trans*-dihydropyrazine. An intriguing variation of the normal reaction pathway occurred when the irradiation was carried out in an alcoholic medium. In this case an alkoxyimidazoline (**349**) was isolated (Scheme XI). The formation of this compound was rationalized as proceeding via an azomethine ylide (**348**) produced by cleavage of the aziridine C–C bond of starting material or by cyclization of enediimine **347**. The azomethine ylide leads to imidazoline **349** by addition of methanol. Irradiation of related 1,3-diazabicyclohexenes in an ethanol glass at 77 K produced

SCHEME XI

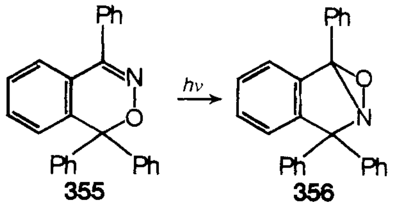


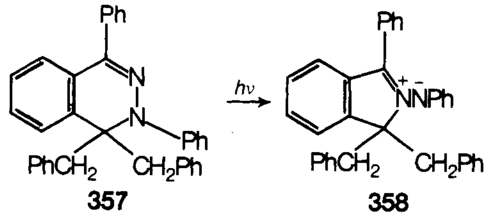
a bright red color which was attributed to the azomethine ylide.[352] The color of the azomethine ylide faded on warming, and its disappearance was also accelerated by the presence of dipolarophiles.[353] In the presence of dimethyl acetylenedicarboxylate, cycloadduct **350** was isolated in high yield.

An analogous reaction was reported for the vinylogous 1,5-diazabicyclo[5.1.0]octa-3,5-diene system.[354] Irradiation of **351** in benzene affords the diazatetraene **52** as the principal photoproduct. The formation of **352** was also shown to proceed via the formation of an azomethine ylide (**353**) which could be trapped with fumaronitrile to give cycloadduct **354**.

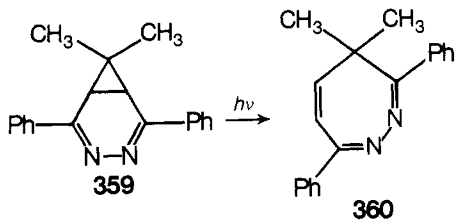


Conjugated cyclohexadienes and 1,3,5-hexatrienes are known to undergo light-induced rearrangements to bicyclo[3.1.0]-hexenes.[355] The photochemical formation of a bicyclo[3.1.0]-hexene derivative has also been observed in a heterocyclic compound containing a C–N double bond[355] and constitutes the first example of rearrangement of a 2,3-benzoxazine (**355**) to a fused oxaziridine (**356**). The photochemical generation of a stable azomethine imine (**358**) from a 1,2-dihydrophthalazine (**357**) has also been reported[356] and represents a closely related process. In this case, sensitization data suggest that the reaction **357** → **358** proceeds via the excited singlet state of **357**. These reactions can be rationalized by assuming an initial photochemical ring opening followed by an intramolecular photo Diels–Alder reaction.

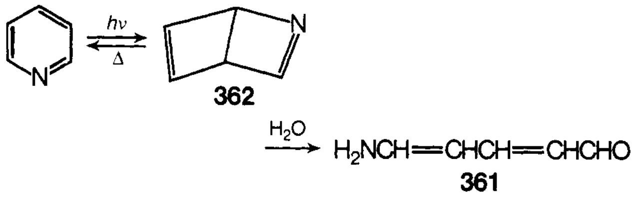




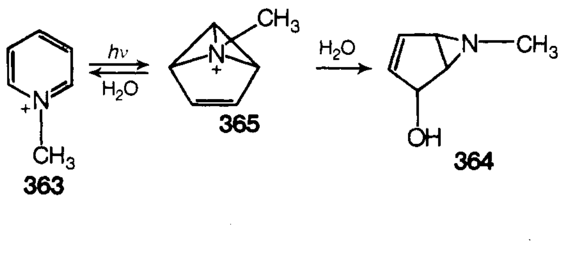
Zimmerman and Eberbach have reported on the existence of a photochemical heterocyclic walk process in which an isopropylidene moiety moves about the π system of 2,5-diphenylpyridazine.[357] In this reaction, 4,4-dimethyl-3,7-diphenyl-1,2-diazepine (**360**) is formed from 7,7-dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (**359**) on direct photolysis. Evidence was obtained which showed that the reaction originates from the first excited singlet, that this singlet is π–π*, and that the triplet state of **359** is unreactive. This reaction constitutes the first example of a photochemical heterocyclic walk process and is analogous to the transformations observed with trimethylcycloheptatrienes.[358]



In recent years there have been many accounts of the light-induced isomerization of simple benzenoid compounds into benzvalene, Dewar benzene, prismane, and fulvene derivatives.[359] The intermediacy of a Dewar benzene type has been suggested in order to account for the photohydration of pyridine to 5-aminopenta-2,4-dienal (**361**).[360] In fact, irradiation of neat pyridine at 254 nm in the absence of water gave Dewar pyridine (**362**) with a reported half-life of 2 min at 25 °C.[360]

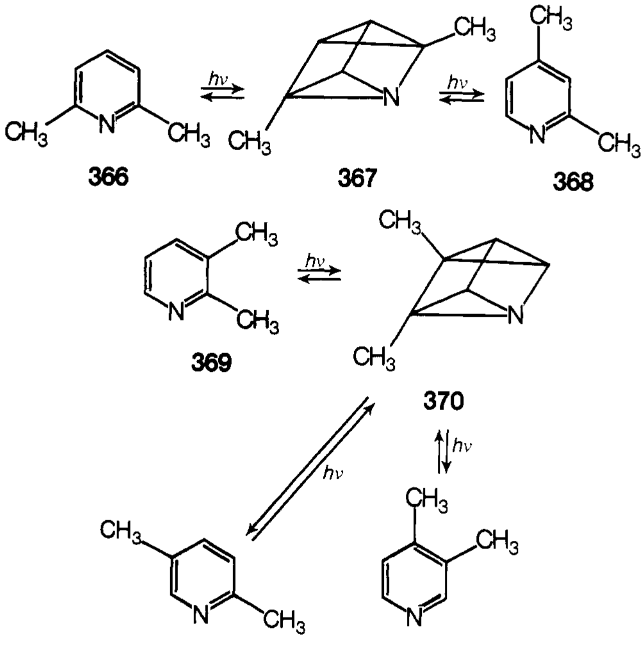


These results coupled with the study of the photochemistry of other nitrogen heteroaromatics indicate that the formation of transient nonaromatic isomers upon irradiation may be a general phenomenon among nitrogen heterocycles. Thus, when methylpyridinium chloride was irradiated at 254 nm in an aqueous solution, a good yield of 6-methylazabicyclo[3.1.0]-hex-3-en-2-*exo*-ol (**364**) was obtained.[361] The azabicyclohexenol



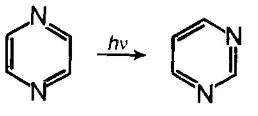
(**364**) was considered to be a result of hydration of 1-methylazoniabenzvalene (**365**).[361]

Vapor-phase irradiation in the π–π^* absorption region of 2-picoline yields the 3 and 4 isomers.[362] The author concluded that an azaprismane is the intermediate in this process. Similar studies have also been made by French workers, who have investigated the irradiation of 3-picoline and lutidines.[363] In this case, the involvement of an azabenzvalene intermediate is ruled out and azaprismanes are considered to participate in the isomerization process. Although such intermediates have been postulated in isomerization reactions, their isolation has never been achieved.[364]



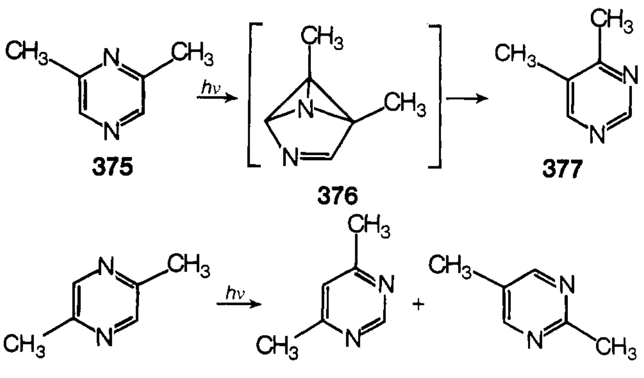
366 **367** **368** **369** **370** **371** **372**

Photoisomerization of pyrazine (**373**) to pyrimidine (**374**) occurs inefficiently in isooctane and somewhat more efficiently in the vapor phase.[365,366] Reaction occurs with light of wavelength 254 nm but not with light of wavelength 313 nm. The wavelength dependence was interpreted as indicating that reaction occurs via a π–π^* singlet and not through a n–π^* singlet.



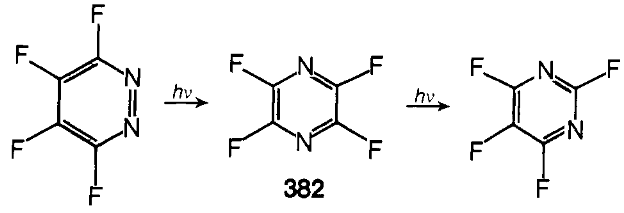
373 **374**

The course of this isomerization was further investigated by photorearrangement of the dihydropyrazines **375** and **378**, with the results as shown.[366] The same wavelength dependence was reported as for the unsubstituted case. The products observed are consistent with those expected for a benzvalene type of intermediate (**376**) and not with a Dewar or prismane type of valence bond isomer.



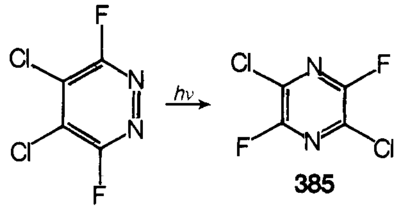
375 **376** **377** **378** **379** **380**

The solution-phase irradiation of tetrafluoropyridazine (**381**) has been shown to give tetrafluoropyrazine **382** which undergoes slow photoisomerization to tetrafluoropyrimidine (**383**).[367] The second step (i.e., **382** → **383**) has analogy to the parent pyrazine system,[366] but the conversion of **381** to **382** has no analogy in such systems and was originally suggested to involve a diazaprismane intermediate.[367]



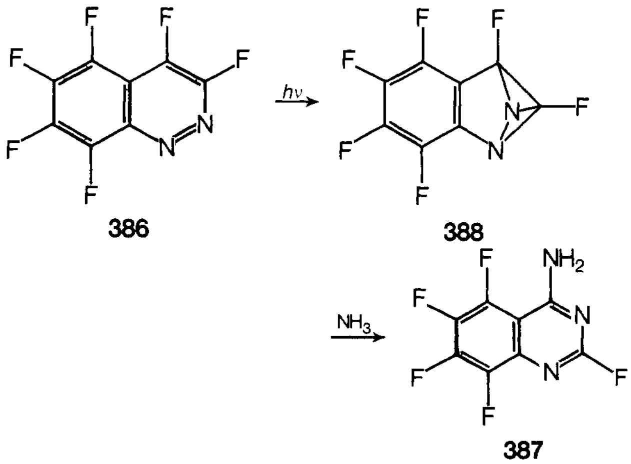
381 **382** **383**

Lemal and co-workers have reexamined the conversion of **381** → **382** with a more suitably double-labeled pyridazine than had been used previously in attempts to obtain evidence for the involvement of a diazaprismane.[368] Thus, photolysis of dichlorodifluoropyridazine (**384**) gave a single dichlorodifluoropyrazine (**385**), which is in agreement with the previous work,[367] but eliminates the involvement of a diazaprismane mechanism.[369] The bond-making and -breaking processes revealed by the above labeling experiments were considered not to be accomplished by "conventional" pathways for phototransposition of benzenoid rings. The photorearrangement proceeds without detectable amounts of intermediates even at 77 K, thus suggesting that no step requiring a significant activation is involved in the reaction mechanism. The quantum yield at various wavelengths indicates that the rearrangement is initiated by n–π^* excitation, and it seems that singlet states are involved. This finding contrasts sharply with the requirement for π–π^* excitation in the rearrangement of pyrazine and methyl-substituted pyrazines.[365]



384 **385**

A related rearrangement has also been observed with hex-



386 **388** **387**

afluorocinnoline[370] (**386**). Irradiation of **386** followed by workup with aqueous ammonia gave 4-aminopentafluoroquinazoline (**387**). Thus, in this case, a 1,2-shift and not a 1,3-shift is observed and, therefore, the intermediate benzodiazabenzvalene **388** was suggested.

XIII. Conclusion

The photochemistry of systems which possess a C-N double bond has been summarized, and the general outlines and potential analogies for these reactions have been noted. In summarizing this review on C-N double bond photochemistry, it is obvious that a great deal more quantitative work will be necessary before the nature of these reactions can be fully understood and generalized. The identification of the excited states involved, substituent effects, and quantum yields must be determined before a full understanding of this area can be accomplished. It is also apparent that the reactions in this field are so rich in variation that the photochemistry of this chromophore will remain intriguing and provide further challenge to the experimentalist as well as to the theoretical chemist for a long time to come.

XIV. Addendum

Irradiation of benzophenone *O*-acyloximes in benzene or toluene effects aromatic substitution on the solvent by diphenylmethaniminyl radicals to give *N*-diphenylmethyleneaniline or *N*-diphenylmethylenetoluidines. A mechanism involving participation of acyloxyl radicals was proposed to account for the substitution reaction.[371]

Diphenylmethyleneimino radicals, $Ph_2C{=}N\cdot$, generated from the photolysis of benzophenoxime benzoates, have been reported to undergo aromatic substitution on benzene as well as dimerization to the corresponding azine.[372] Photolysis of benzophenoxime benzoates in the presence of oxygen produces benzophenone. The formation of this ketone was attributed to the reaction of the imino radical with oxygen to give a peroxy radical which undergoes intramolecular addition followed by decomposition to give benzophenone and nitric oxide. Phenylmethylenimino radicals, $PhCH{=}N\cdot$, generated from the photolysis of benzaldoxime benzoate, are oxidized to benzonitrile in preference to dimerization.[372]

The triplet states of *O*-acyl aromatic ketoximes, $RCO_2N{=}CR_1R_2$, undergo homolytic cleavage into iminyl and acyloxyl radicals.[373] The triplet states of these ketoximes are close to those of their parent ketones and are abundant in π,π^* character. The excitation energies are dissipated through cleavage of the N-O bonds.

The mechanism of the photochemical conversion of isoxazoles to oxazoles and ketoketenimines has been investigated.[374] It was postulated that a vinyl nitrene is a likely precursor for these rearrangements.

The photochemical ring expansion of several unsaturated 2*H*-azirines has been examined.[375] The photoisomerization of 2-formyl-3-phenyl-2*H*-azirine-*N*-allylimine to 2-phenyl-*N*-allylimidazole is explicable on the basis of a photochemical ring opening to a nitrile ylide intermediate which subsequently undergoes intramolecular reorganization to the observed imidazole.

Electron-deficient nitriles, in contrast with nonactivated nitriles, have been found to undergo regiospecific photocycloaddition with 2*H*-azirines.[376] Whereas normal olefins of enol ethers do not react with the nitrile ylide derived from the photolysis of 2*H*-azirines, push-pull olefins do and give 3-alkoxy-2-phenyl-Δ'-pyrrolines in good yield.[376]

Houk and Caramella have recently carried out some LCAO-MO-SCF calculations of the geometry of the nitrile ylide derived from the photolysis of 2*H*-azirines.[377] Their calculations show that the bent nitrile ylide geometry is favored over the linear form by 11 kcal/mol. These calculations correctly account for the regioselectivity observed in the photocycloaddition of 2*H*-azirines with electron-deficient olefins.

The photochemical reactions of some pyrimidine-purine dinucleotides has been studied and found to undergo [2 + 2] cycloaddition.[378] This represents one of the few examples in which a C=N double bond undergoes intramolecular [2 + 2] cycloaddition with a C=C double bond.

Photolysis of 2-*o*-nitrophenyl-5-aryloxazoles results in the formation of 2-aroyl-1*H*-4-quinazolinones. The first step in this transformation involves isomerization of the oxazole to give a 2*H*-azirine.[379]

The interaction of photoexcited acridine with carboxylic acids was shown to yield radical pairs via simultaneous or consecutive proton and electron transfer from the carboxyl group to the acridine. The observed Hammett correlation for the quantum yields, the higher efficiency of the photoreaction in benzene than in acetonitrile, and the observation of CIDNP were compatible with the proposed scheme.[380]

Photolysis of *N*-ethoxycarbonyliminopyrazinium ylides in acetone affords pyrazoles in good yield.[381] The mechanism proposed to account for pyrazole formation involves initial ring expansion to a 1,2,5-triazepine via a diaziridine intermediate. The initially formed triazepine was suggested to isomerize to a bicyclic valence isomer followed by extrusion of HCN to produce pyrazole.[381]

2-Arylbenzazetes are produced by photolysis of 4-arylbenzotriazines and can be intercepted in cycloaddition reactions.[382] Appreciable loss of 2-phenylbenzazete occurs during the photochemical generation at low temperature. This appears to be the result of further photochemical transformations of the benzazete since the yield of dimer obtained by photolysis at −80 °C is markedly lower than that obtained by photolysis at room temperature.

Photooxidation of benzophenone oxime, benzophenone oxime *O*-methyl ether, or benzophenone oximate anion yielded benzophenone as the only observable product.[383] The formation of benzophenone was suggested to proceed via a dioxetane intermediate formed by the reaction of singlet oxygen across the C-N double bond of the oxime.

A new type of photorearrangement of triazanorcaradienes has recently been reported by Matsuura and co-workers.[384] Irradiation of 7-benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene in benzene produced *N*-benzyl-31*H*,7-1,2,4-triazepine by a mechanism in which the aziridine nitrogen undergoes migration along the surface of the heterocyclic π system. While the photochemical walk rearrangement in which a methylene group or a oxygen atom moves about the π system has been detected in several systems,[357] the present example is the first case in which the aziridine nitrogen undergoes migration. The photochemical rearrangement of the triazanorcaradiene to the triazepine involves the electronically excited singlet state since the triplet state was found to produce a pyridazine derivative.

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