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PHOTOCHEMISTRY OF 3-ARYL-2-ISOXAZOLINE[1]

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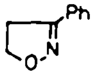
Abstract—3-Phenyl-2-isoxazoline (**1**) was irradiated to give 4-phenyl-2-oxazoline (**3**), β-aminoaldehyde (**14**) and benzonitrile from its π-π^* singlet excited state. Several related derivatives afforded similar photoproducts on irradiation. The quantum yields of the photoreactions were dependent on the magnitudes of the singlet energies of the 2-isoxazolines. *p*-Cyanophenyl-2-isoxazoline (**1c**) formed a one-to-one photoadduct (**22**) with benzene.

The photochemistry of the C=N double bond has attracted much attention in recent years. The excited state behavior of the azirine ring was independently developed by Schmid[2] and Padwa.[3] As was summarized in several monographs,[4-6] the photochemistry of compounds containing C=N double bonds has not developed as rapidly as carbonyl compounds. The main reason for this is probably related to the low reactivity of the excited imino group due to the rapid radiationless decay which results by twisting around the C=N bond. Another problem in this area arises from the difficulty in determining the nature of the excited state involved since little information can be gleaned from the emission spectra of typical imines.

On irradiation of the C=N–O chromophore, *syn-anti* isomerization was found to be a predominant process in oximes and oxime ethers. Padwa[7] and de Mayo[8] have suggested that these photoreactions originate from the π-π^* state. The photo-reactions of cyclic oxime ethers, namely 2-isoxazolines,[9] were studied by Schmid,[10,14] Matsuura[11] and Mukai[12,13] about ten years ago. The early results revealed that N–O bond fission mainly occurred upon irradiation but in some cases the C–O and C–C bond cleaved depending on the nature of the substituent located at the C_4- and C_5-position of 3-phenyl-2-isoxazoline ring. Since bond fission was never observed in the irradiation of oxime ethers, a sharp contrast in photochemical behavior between non-constrained and constrained Ph–C=N–O chromophores seems to exist. No emission from acetophenone oxime ether has been detected, whereas 3-phenyl-2-isoxazoline (**1**) was found to exhibit fluorescence but no detectable phosphorescence. In connection with this study, the UV and emission spectra of 2-phenylpyrroline (**2**), 4-phenyl-3-oxazoline (**3**) and 2-phenyl-2-oxazoline (**4**) has now been studied in order to gain additional insight into the excited state of these heterocycles containing a C=N double bond.

To our knowledge, a photochemical study of 3-phenyl-2-isoxazoline has not been carried out, although several derivatives possessing substituents at C_4- and/or C_5-position have been investigated. In this paper we wish to describe the photochemistry of 3-phenyl-2-isoxazoline (**1**) along with several derivatives possessing electron donating or withdrawing groups on the phenyl substituent as well as naphthyl and thienyl derivatives. Similar research dealing with substituent effects has already been reported by de Mayo *et al.* in the photochemistry of benzaldoxime derivatives where the electronic effect of the substituents plays an important role. For instance, these workers found that the irradiation of 4-cyanobenzaldoxime (**6c**) did not behave similarly to that encountered with other oximes.[8a,b] We have now found that 3-aryl-2-isoxazoline derivatives undergo N–O bond fission on irradiation. This reaction was found not to depend on the electronic character of the substituents but rather on the magnitude of the singlet energies of the substrates.



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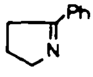

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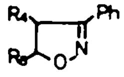

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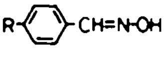

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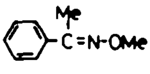

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During the course of our studies dealing with the photochemistry of 2-isoxazoline derivatives, a novel [2+2]-photocycloaddition reaction of the C=N double bond with some aromatics was discovered. 2-Isoxazolines having cyano and methoxycarbonyl groups on the 3-aryl moiety form one-to-one adducts with benzene or furan. Azetidine formation, which was induced on irradiation of the C=N–O chromophore, is a rather uncommon reaction of imines. This stands in contrast with the well-known Paterno-Büchi reaction of ketones. Only a few examples have been reported in the literature. For example,

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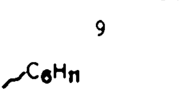

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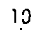

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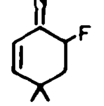

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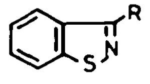

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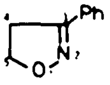
oxazolinone (**8**),[15] isoindolenone (**9**),[16] oxadiazole (**10**),[17] the imine of cyclohexenone (**11**),[18] and benzisothiazole (**12**)[19] are known to undergo azetidine formation on irradiation. In the [2 + 2]-photocycloaddition reactions of 2-isoxazoline derivatives, an electron withdrawing group on the 3-aryl substituent is essential in order to activate the C=N bond for the photocycloaddition. Thus, it would seem that exciplex formation is necessary for this novel type of cycloaddition.

RESULTS

Absorption spectra of 3-*phenyl*-2-*isoxazoline* (1)

It is still not absolutely clear which excited species, i.e. $n-\pi^*$ or $\pi-\pi^*$ singlet or triplet state, is responsible for the photoreactions of organic molecules containing C=N double bonds.[20,21] A survey of absorption and emission spectra of 5-membered heterocycles such as 1, 2, 3 and 4 might be expected to elucidate the multiplicity and consequently help determine the excited state responsible for the photoreactions. The UV spectra of 3-phenyl-2-isoxazoline (1)[22] and 2-phenylpyrroline (2)[23] are shown in Fig. 1. The strong absorption with the maximum at 264.3 nm (ϵ 13,480) for 1 and 241.0 nm (ϵ 12,720) for 2 can be assigned to $\pi-\pi^*$ absorption of the Ph–C=N– chromophore. In the case of 2-isoxazoline (1), the shift of the absorption maximum by about 23 nm to longer wavelength compared with that of pyrroline (2) can be accounted for in terms of a perturbation by the neighboring O-atom. The introduction of the Ph–C=N–O chromophore into the rigid 5-membered ring results in a red shift of 11–23 nm compared with the absorption maxima of the 6-, 7- and 8-membered ring analogs[24] as well as acetophenone oxime ethers.[8] The shape of the spectra of all of these compounds are similar. A characteristic shoulder at 291 nm is noticed in the UV spectrum (*line-b*) of 1. This shoulder disappeared in polar media like ethanol. Accordingly, it is possible to assign this to the $n-\pi^*$ band. However, the UV spectrum (*line-c*) measured at − 196° is devoid of this possibility and consequently it seems more reasonable to assign this band to one of the fine structures of $\pi-\pi^*$ excitation. The shoulder at 291 nm corresponds to the absorption maximum (ϵ 3,160) at 292.8 nm in methyltetrahydrofuran matrix at liquid nitrogen temperature. This absorption was also observed at 292.0 nm in pentane–methylcyclohexane, 292.1 nm in EPA and 291.8 nm in MeOH-EtOH matrix. These energy absorptions are assigned to the 0–0 bands of $\pi-\pi^*$ excitation of the Ph–C=N–O chromophore on the basis of their high intensities and the absence of a solvent effect. Careful analyses of the low temperature spectra give some information regarding the vibronic character of 2-isoxazoline in the excited state. The absorption maxima and molar extinction coefficients of 1 that were measured in several solvents at −196° are listed in Table 1. The intervals of about 1420 cm^{-1} can be attributed to the C=N stretching frequencies of the excited state of the 2-isoxazoline system. The intervals of about 840 cm^{-1} may be assigned to the N–O stretching mode. In the ground state of 1, the corresponding C=N stretching modes are observed at 1570 cm^{-1} in the IR spectrum and at 1562 cm^{-1} in the fluorescence spectrum. Also, the stretching frequency at 929 cm^{-1} in the IR[25] and the interval of 977 cm^{-1} in the fluorescence spectrum can be reasonably assigned to the N–O stretching mode in the ground state of 1. The fact that both C=N and N–O stretching modes have smaller energies in the excited state is ascribed to the flexible configurations of the C=N



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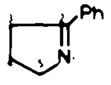

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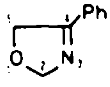

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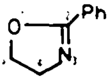

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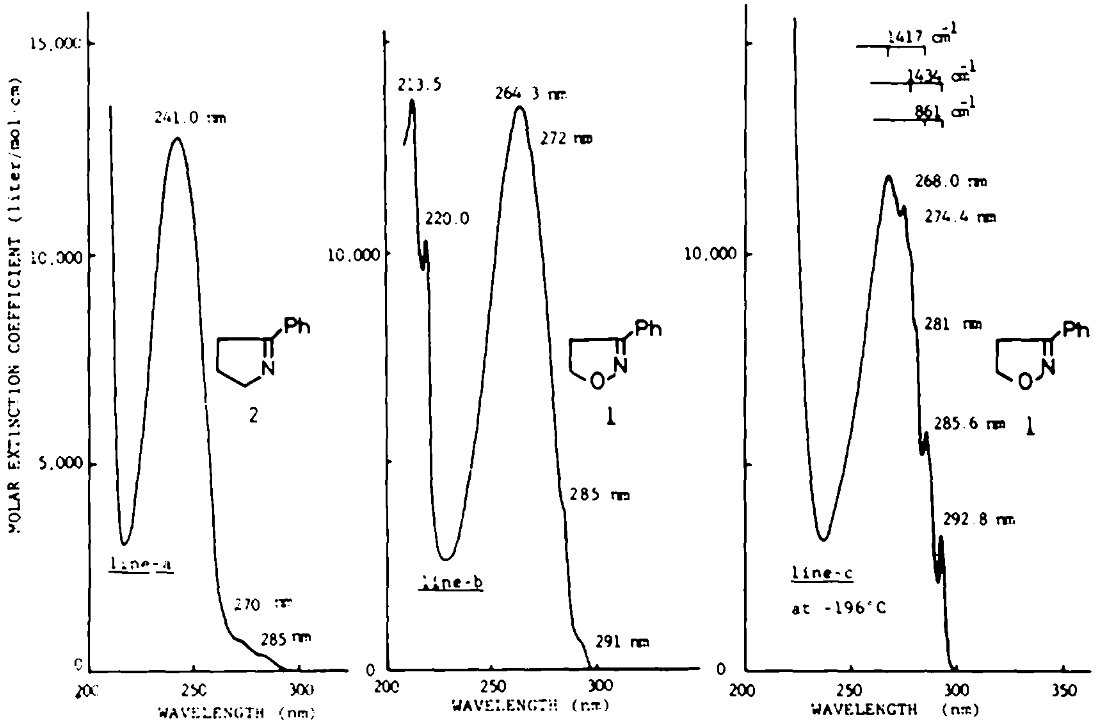


Fig. 1. Absorption spectra of 3-phenyl-2-isoxazoline (1) and 2-phenylpyrroline (2). *line-a*: The absorption spectrum of 2 in cyclohexane at 25°. *line-b*: The absorption spectrum of 1 in cyclohexane at 25°. *line-c*: The absorption spectrum of 1 in 2-methyltetrahydrofuran at −196°.

Table 1. Absorption maxima and molar extinction coefficients of 3-phenyl-2-isoxazoline (1) in the absorption spectra at −196°.

	λ_{max}		ε	λ_{max}		ε	λ_{max}		ε	λ_{max}		ε
	nm	cm^{-1}	l/mol cm	nm	cm^{-1}	l/mol cm	nm	cm^{-1}	l/mol cm	nm	cm^{-1}	l/mol cm
	216.0	(46,296)	17,030							214.3	(46,664)	17,900
	222.2	(45,005)	14,200				221.0	45,086	11,520	220.6	45,331	13,350
	265.0	(37,736)	12,500				266.0	37,594	12,550	265.2	37,707	13,400
Band-V				268.0	(37,313)	11,820	269.2	(37,286)	12,420	267.8	(37,341)	13,500
Band-IV	274.0	36,496	11,050	274.4	36,443	11,150	274.0	36,496	11,640			
Band-III	280.5*	35,651	7,600	281*	35,587	8,200	280.5*	35,651	8,200	280.2*	35,689	8,300
Band-II	285.1	35,075	5,800	285.6	35,014	5,620	285.1	35,075	5,900	284.9	35,100	6,180
Band-I	292.0	34,247	2,360	292.8	34,153	3,160	292.1	34,235	2,750	291.8	34,270	2,800
Solvent	n-pentane-methyl-cyclohexane (1:4)			2-methyl-tetrahydrofuran			EPA (ether-iso-pentane-ethanol, 8:3:5)			ethanol-methanol (1:1)		
Intervals between Band-I and Band-II, Band-I and Band-III, Band-II and Band-IV, respectively.												
	828 1,404 1,421 cm^{-1}			861 1,434 1,417 cm^{-1}			840 1,416 1,421 cm^{-1}			830 1,419 cm^{-1}		

*Shoulder.

and N–O bond in the excited 2-isoxazoline molecule. The photoreactions initiated by N–O scission and the photocycloadditions taking place with the C=N double bond will be described in a later section.

Emission spectra of 3-phenyl-2-isoxazoline (1) *and its related compounds*

Upon irradiation at room temperature, 3-phenyl-2-isoxazoline (1) immediately undergoes photoreaction without any detectable emission. At liquid nitrogen temperature, however, the singlet excited state of 1 is chemically unreactive and exhibits strong fluorescence even though phosphorescence could not be detected under degassed conditions. The excitation and emission spectra of 1 are shown in Fig. 2. The emission from the singlet state of 1 has several fine structures possessing intervals of 586, 977 and 1562 cm^{-1} in methylcyclohexane. The emission at 297.6 nm is assigned to the 0–0 band which has a Stokes shift of 5 nm from the 0–0 band of the absorption or excitation spectrum. The intervals correspond to the C–H out-of-plane bending mode, the stretching mode of the N–O bond and that of the C=N bond, respectively.

In contrast to the results encountered with 1, the fluorescence of 2-phenyl-1-pyrroline (2) could not be detected under similar conditions. Its phosphorescence is easily observed at −196°, however. The 0–0 band at 386.0 nm and C=N stretching mode of 1630 cm^{-1} are shown in Fig. 3. In order to gain insight into the perturbation of the oxygen atom in the pyrroline system, the emission spectra of 4-phenyl-3-oxazoline (3) and 2-phenyl-2-oxazoline (4) were measured under similar conditions and the results are summarized in Fig. 3. The observation of their phosphorescence stands in sharp contrast to the emission of 1. This difference can be attributed to the role played by the O-atom. In the case

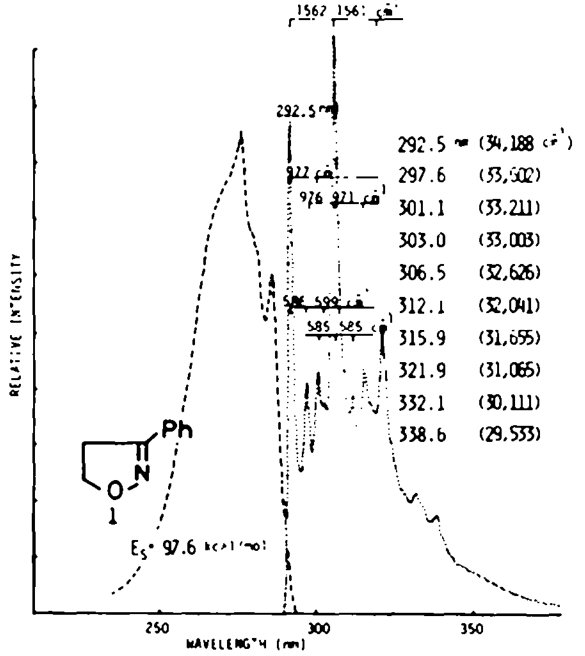


Fig. 2. Excitation and emission spectra (uncorrected) of 3-phenyl-2-isoxazoline (1) in methylcyclohexane at −196°.

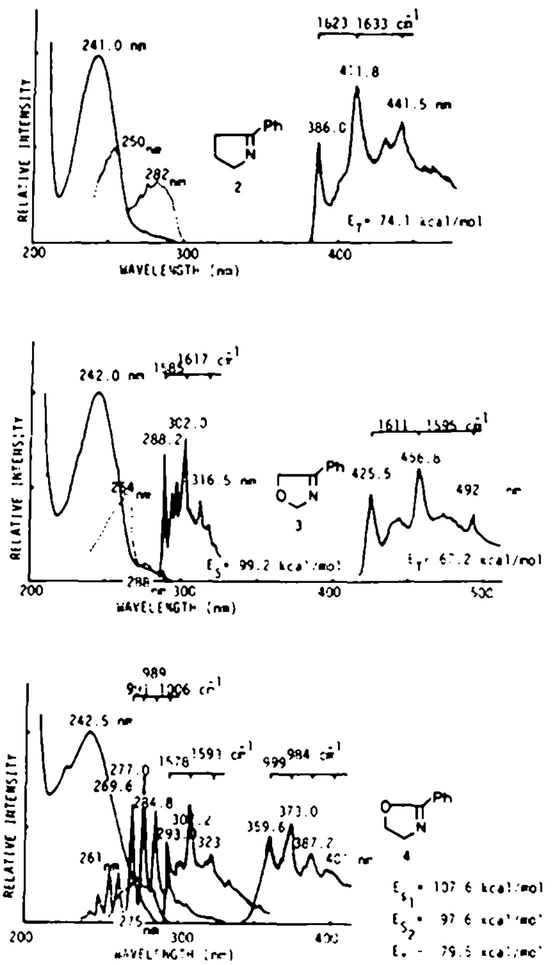


Fig. 3. Absorption, excitation and emission spectra of 2-phenylpyrroline (1), 4-phenyl-3-oxazoline (3) and 2-phenyl-2-oxazoline (4) in methylcyclohexane at −196°.

of 2-isoxazoline 1, the high electronegativity of the neighboring O-atom diminishes the availability of the non-bonding electrons on the N-atom. As a result, intersystem crossing of 1 through spin-orbit coupling decreases in probability. This, in turn, leads to a high reactivity of the singlet excited state at room temperature as well as a strong intensity of emission in the fluorescence at liquid N_2 temperature. The high efficiency ($\Phi = 0.61$) of the photoreaction of 1 at 25° suggests that the singlet excited state is predominantly responsible for the photoreactions.

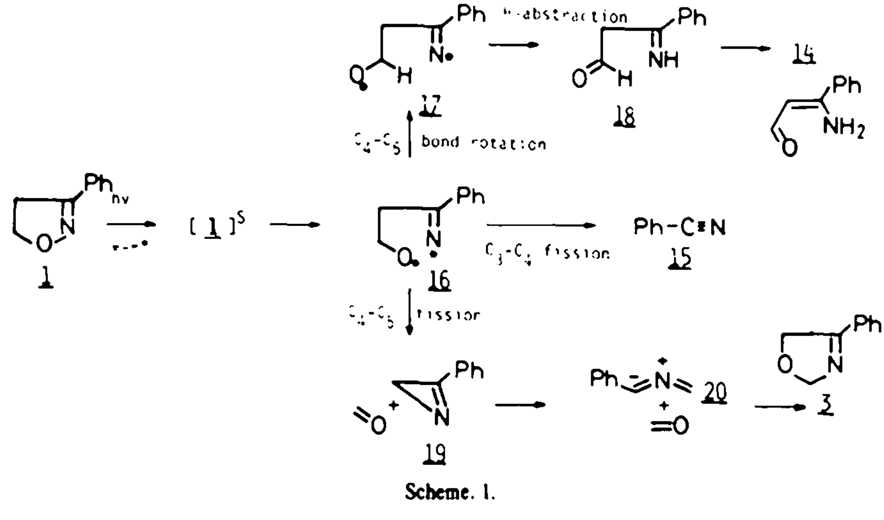
One of the peculiar phenomena encountered is the observation of upper singlet states in the excitation spectra of several of the isoxazolines except for the case of 1. The excitation to S_2 is most effective at 250, 264 and 261 nm, respectively, in the case of 2, 3 and 4. In addition, a remarkable finding is that two types of fluorescences are observed in the emission of 2-phenyl-2-oxazoline (4). In general, upper singlet states usually decay rapidly to the lowest excited state and no fluorescence is observed from that state except for some special cases.[26] Therefore, the finding of two type of fluorescence with 4 is a strange result.[27] Although the explanation is not clear at present, it is conceivable that certain geometric factors concerning the electron configuration in the rigid N=C–O system does not allow for rapid internal conversion from the S_2 state with π–π^* character to the S_1 state with n–π^* character.

Another important factor influencing the photochemistry of 1 is that the 2-isoxazoline ring has a N–O bond that is easily cleaved. The bond dissociation energy of 44 kcal/mol[28] for the N–O bond and the rigidity of the five-membered ring along with the loose and active character of the N–O stretching mode in the excited state easily accounts for the facile scission of N–O bond.

Photoreactions of 3-aryl-2-isoxazolines

Although it is known that 2-pyrroline (2) gives bipyrrolidine on irradiation in 2-propanol,[23c] the irradiation of 2 in cyclohexane solution afforded only polymeric materials. Also, the irradiation of 3 and 4 resulted in slow decomposition on the starting materials. 3-Phenyl-2-isoxazoline (1), on the other hand, is cleanly converted to three products, 3, 14 and 15, in high yield and with high efficiency. This stands in contrast with the results described for its derivatives.[10–14] Figure 4 shows the time-dependent changes in the UV spectrum observed during irradiation of 1 in cyclohexane with monochromic light of 280 nm.

When a benzene solution of 1 was irradiated with a Rayonet 3000 Å lamp on a preparative scale, 4-phenyl-3-oxazoline (3) and 3-amino-3-phenyl-2-propenal (14) were isolated in 5 and 62% yields accompanied by benzonitrile (24%) and a trace amount of 1. No interconversion



Scheme. 1.

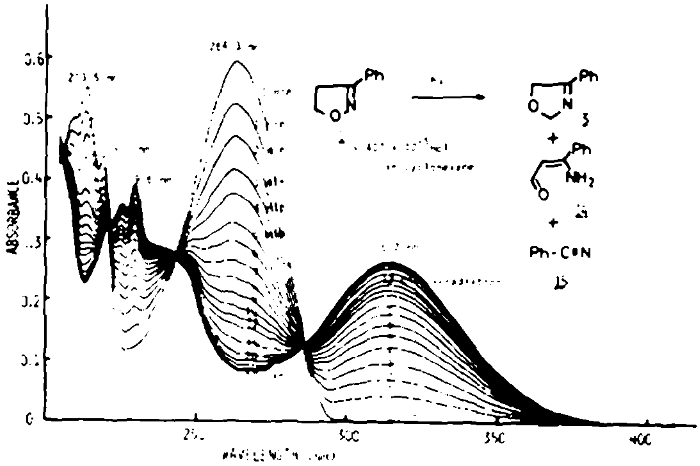


Fig. 4. Photoreaction of 3-phenyl-2-isoxazoline (1) in cyclohexane on irradiation of 280 nm monochromic light for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 20, 30, 40 and 50 min.

between the photoproducts occurred as was demonstrated from the isosbestic points at 221, 244 and 286 nm in Fig. 4, and also from product analyses in the initial and final stages of the photoreaction.

The mechanism for the photoreactions of 1 is summarized in Scheme 1. The main product (14) is formed by the isomerization of 3-phenyl-3-iminopropanal (18), which is derived from N–O bond fission followed by hydrogen abstraction of the imino-oxy diradical (17). The formation of 3 was previously described in the photoreactions of isoxazoline derivatives by Schmid[10] and Matsuura.[11] These workers reported that an initial photocleavage occurs to give formaldehyde and 2-phenylazirine (19) which undergoes a subsequent recombination via 1,3-dipolar cycloaddition.[2,3] The C_3–C_4 bond cleavage of the initially formed intermediate (16) gives benzonitrile, although the corresponding epoxide or aldehyde could not be detected in the irradiation. The photoreaction of 1 in cyclohexane solution does not exhibit a wave-length effect. Thus, irradiation with monochromic light ranging from 250 to 290 nm involves the same reactions and the quantum yields were found to be within experimental error of each other. A temperature dependency of 1 was not observed upon irradiation in cyclohexane between 5 and 70°. All of the photoproducts (3, 14 and 15) are considered to be formed from the singlet state since sensitization experiments using acetophenone failed to influence the photoreaction of 1.

Table 2. Absorption maxima, 0–0 bands of fluorescences and singlet energies of 3-aryl-2-isoxazolines with Hammett σ-values of their substituents

Compounds	Substituents	Absorption Maxima[a] (nm) and Molar Extinction Coefficients (l/mol cm)	0-0Bands[b] of Their Fluorescences (nm)	Singlet Energies (kcal/mol)	Hammet's σ-Values
1	Phenyl	213.5 (13, 730) 219.8 (10, 400) 264.3 (13, 480)	292.5	97.6	0.000
1	4-Methylphenyl	208.7 (13, 510) 213.8 (14, 160) 220.0 (10, 460) 264.0 (15, 710) 294 sh. (940)	298.1	95.9	-0.170
1b	4-Methoxyphenyl	270.0 (18, 290) 296 sh.(4, 200) 301 sh.(1, 970)	304.4	93.9	-0.268
1d	3-Cyanophenyl	228.3 (21, 770) 235.2 (21, 720) 271.0 (12, 410) 309.6 (850)	318.0	89.9	+0.56
1e	4-Chlorophenyl	212.5 (11, 800) 222.4 (11, 120) 269.2 (16, 340) 296.9 (1, 280)	301.2	95.0	+0.227
1	4-Nitrophenyl	233.1 (3, 900) 309.2 (12, 230)	—	73.3[c]	+0.778
1g	2-Thienyl	209.3 (4, 970) 287.1 (11, 460)	---	90.2[c]	—
1h	1-Naphthyl	230.0 (54, 200) 309.5 (15, 560) 322.0 (10, 710)	332.4	86.0	-

a) in cyclohaxane at 25°C, b) in methylcyclohexane at -196°C,

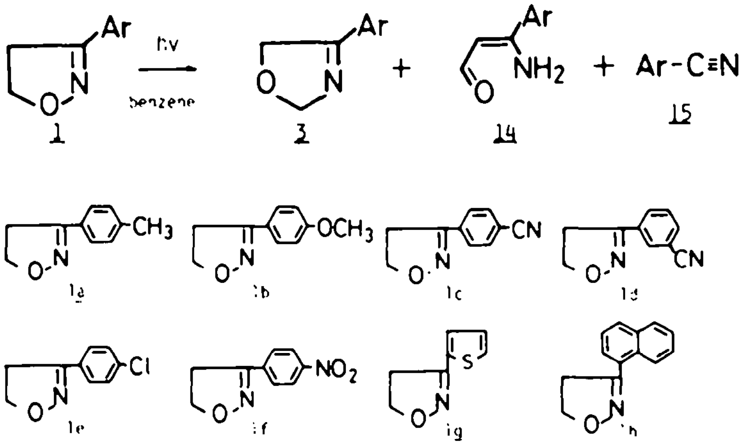
c) singlet energy was estimated from the absorption spectrum.

Intermediate **16**, which is derived by initial N–O bond fission, has been proposed as the common precursor of each product. The most remarkable feature of the photolysis of **1** is that the reaction was achieved with high efficiency and in high yield compared with the reported photoreactions of 3-phenyl-2-isoxazoline derivatives having substituents at the 4- and/or 5-position. These compounds always produced a complicated mixture of products depending on the type of substituent present.[10–14]

A study dealing with the substituent effect is of interest in order to gain additional insight into the nature of the common intermediate **16**. For this reason the electronic effect of substituents located on the benzene ring was investigated in detail. Several 3-aryl isoxazoline derivatives (**1a–1h**) were synthesized by 1,3-dipolar cycloaddition of suitable nitrile oxides with ethylene.[29] The 3-aryl isoxazolines synthesized include the methylphenyl, methoxyphenyl, cyanophenyl and chlorophenyl derivatives. These compounds exhibit analogous type of fluorescence and do not phosphorescence. Interestingly, 3-(2-thienyl)-2-isoxazoline (**1g**) does not fluorescence or phosphorescence. In the case of the 1-naphthyl derivative (**1h**), both emissions were observed, but photoreaction did not occur. The absorption maxima of the UV spectra as well as the singlet energies determined from the 0–0 bands of fluorescence spectra are listed in Table 2 along with Hammett σ-values for the substituents.

The results of the photoreactions of 3-aryl-2-isoxazoline derivatives in benzene solution are summarized in Table 3, where the quantum yields measured in cyclohexane are also listed.

Photoreactions of compounds **1a–1e** and **1g** were similar to that of **1** with only a slight variation in the product ratio. The quantum yields for the photoreactions, however, dramatically changed indicating the dependence on the substituents. The quantum efficiency of 3-cyanophenyl and 2-thienyl derivative, **1d** and **1g**, decreased to near zero. 4-Nitrophenyl and 1-naphthyl derivative, **1f** and **1h**, did not undergo photoreaction. No correlation was found to exist between the quantum efficiency of the photoreaction and the Hammett σ-constants of the substituents. As was mentioned previously, the photoreaction of **1** involves an initial N–O bond cleavage giving either diradical **16-I** or zwitterion **16-II** or **-III** (Scheme 3). The ease of N–O bond fission in the excited state was revealed in the fine structure of their UV spectra. The involvement of polar intermediates (**16-II** or **16-III**) for product formation can be eliminated by the fact that the quantum efficiency of the reaction decreased by changing the solvent from cyclohexane to acetonitrile. Under these conditions a



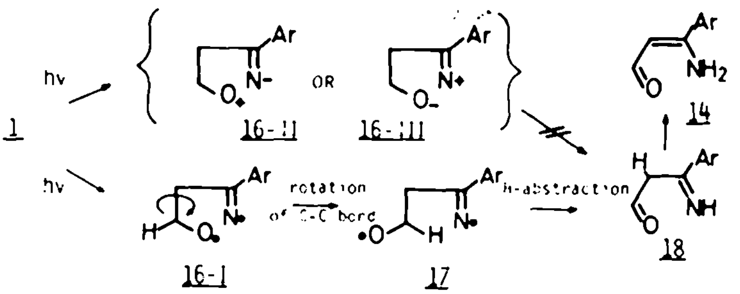
Scheme 2.

Table 3. Photoreactions of 3-aryl-2-isoxazolines (**1** and **1a–h**)

Reactants	Products on Irradiation in Benzene			Quantum Yields in Cyclohexane
2-Isoxazolines	3-Oxazolines	Aminoaldehydes	Nitriles	
3-Phenyl-, 1	5 %	62 %	24 %	0.61
3-(4-Tolyl)-, 1a	9 %	57 %	26 %	0.48
3-(4-Methoxyphenyl)- 1b	6 %	47 %	33 %	0.23
3-(4-Cyanophenyl)-**, 1c	2 %	61 %	10 %	0.24
3-(3-Cyanophenyl)-, 1d	---	24 %, (36 %)*	7 %, (12 %)*	0.039
3-(4-Chlorophenyl)-, 1e	5 %	53 %	23 %	0.34
3-(4-Nitrophenyl)-, 1f	---	---	---	---
3-(2-Thienyl)-, 1g	---	14 %, (33 %)*	2 %, (4 %)*	0.035
3-(1-Naphthyl)-, 1h	---	---	---	---

( )*: yield based on reacted starting material

**: a one-to-one adduct with benzene was also isolated.



Scheme 3.

significant alternation in the product ratio was not observed. In addition, the electronic effects of the 3-aryl substituents do not effect the electronic state of the photoreactions. The decrease in quantum yields between 1 and the 4-cyanophenyl derivative (1c) (0.38 vs 0.09) in acetonitrile solution can be attributed to an interaction between the polar media and the diradical intermediate (16-I) which accelerates the recombination to starting materials.

Isoxazolines possessing low singlet energies show lower quantum efficiencies on irradiation. The lack of reactivity of the 4-nitrophenyl derivative (1f) might be ascribed to a facile intersystem crossing giving rise to a triplet state or, instead, to its low singlet energy (E_S = 73 kcal/mol). The photoreaction of the 1-naphthyl derivative (1h) does not occur even after prolonged irradiation under various conditions. The only detectable photochemical process of 1h is fluorescence at room temperature and phosphorescence at liquid nitrogen temperature. We propose that the lack of reactivity of 1h is due to its low singlet energy (E_S = 86 kcal/mol). As shown in Fig. 5, there is a good linear relationship between the quantum yields of the photoreactions and the singlet energies of the 3-phenyl-2-isoxazoline derivatives.

A singlet energy more than 90 kcal/mol is neceseary in order for the reaction to occur. 2-Isoxazoline derivatives having even higher singlet energies are able to undergo the photoreaction with higher efficiencies. This finding suggests that some vibronic assistance inherent in the intermediate (16) helps control the photoreaction. For example, re-orientation from 16 to 17 and the conformational change needed for subsequent H-abstraction would be expected to be assisted by virbonic assistance. Thus, at liquid nitrogen temperature, the vibronic assistance is inhibited so that the diradical intermediate (16) promoptly recombines to regenerate the starting material. This is probably the reason for the lack of reactivity of the 1-naphthyl derivative (1h), which has too low a singlet energy to afford the photoproducts.

The photolysis of 5-methyl-3-phenyl-2-isoxazoline (1i) and 3-phenyl-4,5-tetramethano-2-isoxazoline (1j) also affords similar photoproducts (i.e. 3, 14 and 15). The photoreactivity of these systems can also be explained by the idea of vibronic assistance. Although their singlet energies (97.4 and 96.7 kcal/mol) are high enough to allow the reaction to proceed, their quantum yields are quite small (0.28 and 0.034 in cyclohexane) when compared with that of 1 (0.61). This difference may be ascribed to the disturbance of the vibronic assistance by the bulkiness of the Me substituent or perhaps to the rigidity of the fused cyclohexane ring.

Photocycloaddition of 2-isoxazoline derivatives

When 3-(4-cyanophenyl)-2-isoxazoline (1c) was irradiated in benzene with a set of Rayonet RUL-3000 Å lamps, a new photoproduct was isolated (4%), m.p. 113–114°, by means of silica gel thick layer chromatography

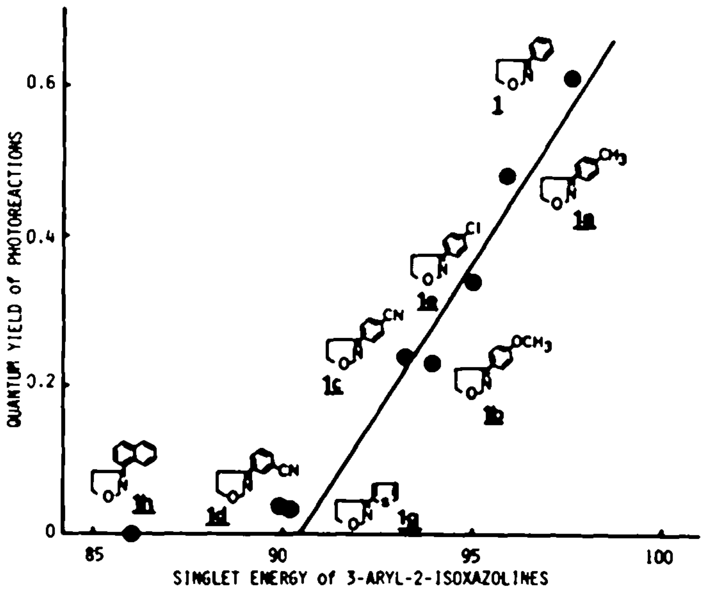
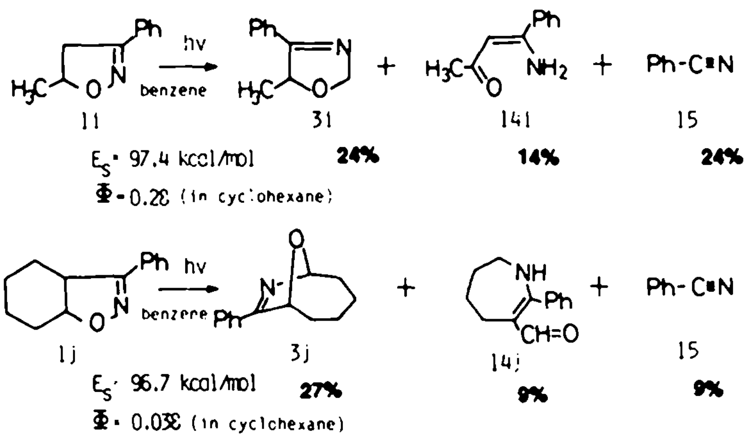
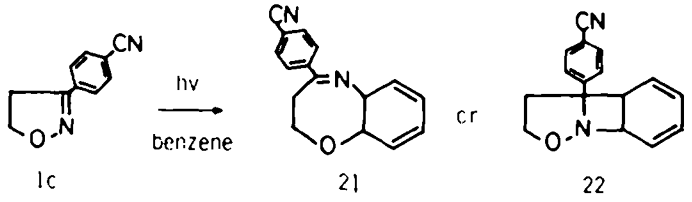


Fig. 5. Plot of quantum yields vs. singlet energies on the photoreaction of 3-aryl-2-isoxazolines.



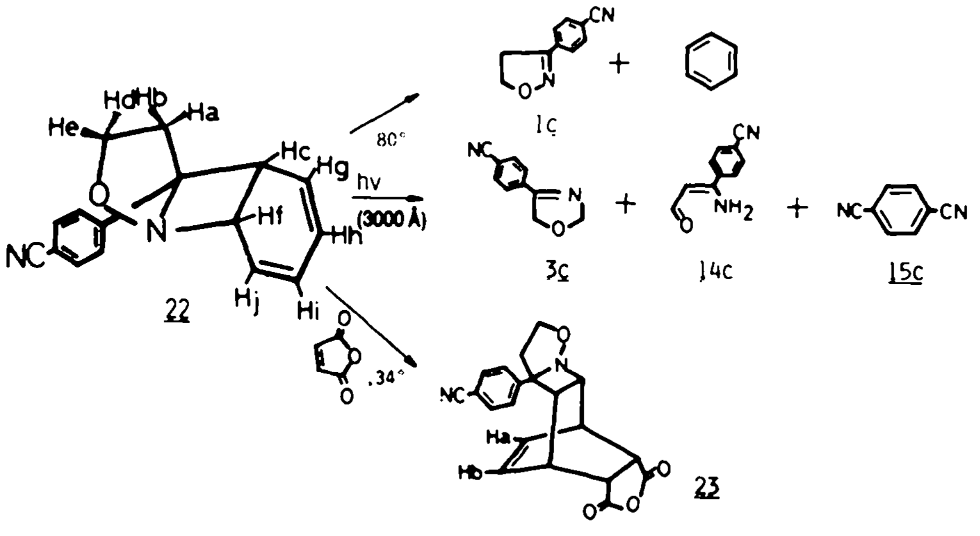
Scheme 4.

in addition to recovered starting material, 3-oxazoline (3c), aminoaldehyde (14c), and *p*-dicyanobenzene. The elemental analysis and mass spectrum of the product support a cycloadduct of 1c with benzene. The UV and NMR spectra do not differentiate between two possible structures 21 and 22. Structure 21 corresponds to a $[2\sigma + 2\pi]$-cycloadduct across the N–O bond of 1c with benzene while 22 is a $[2\pi + 2\pi]$-cycloadduct using the C=N double bond of 1c.



Scheme 5.

The fact that the photoadduct is quantitatively converted into benzene and 1c upon heating at 80° for 2 hr provides support for structure 22. Diels–Alder reaction of the photoadduct with maleic anhydride at 34° gave cycloadduct (23), m.p. 250–252°, in 80% yield. The NMR spectrum of 23 shows two signals for the olefinic hydrogens at δ 5.16 and 6.07 ppm. The high field shift (1.10 ppm) of one of the olefinic hydrogens in 23 when compared with that of the cyclohexadiene-maleic anhydride adduct (24)[30] can be explained by the anisotropic effect of the cyanophenyl group. This result suggests the anti-orientation of the cyclohexadienyl moiety and the isoxazolidine ring in structure 22. The yield of photoadduct (22) was rather low, but the formation of the photocycloadduct represents a major path in the initial stages of irradiation of 1c. The photoreaction was monitored in detail using high-pressure liquid chromatography. The results are shown in Table 4. The yield of 22 compared to unreacted starting material indicates that the cycloaddition of 1c with benzene is the main reaction occurring during the initial stages and that cycloreversion



Scheme 6.

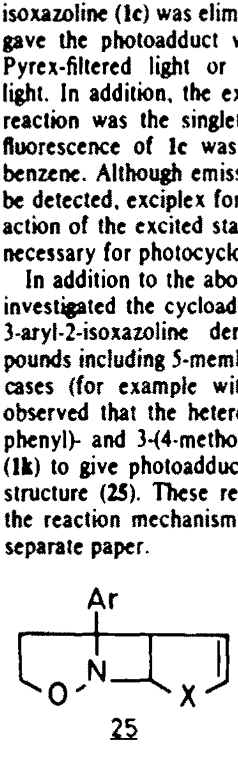
Table 4. Photoreaction of 3-(4-cyanophenyl)-2-isoxazoline (1c) in benzene

Irradiation Time		5 min	20 min	60 min	150 min	240 min
COMPOUNDS	1c	96.4 %	87.2 %	65.5 %	44.4 %	33.5 %
	3c	---	0.4 %	0.8 %	1.3 %	1.6 %
	14c	2.0 %	6.1 %	15 %	34.5 %	44.3 %
	22	1.5 % (42 %)*	3.1 % (24 %)*	4.7 % (15 %)*	5.9 % (11 %)*	5.6 % (8 %)*

( )* : yield based on reacted 1c

of 22 might occur after prolonged irradiation. In fact, it was found that photocycloadduct 22 afforded a trace of oxazoline (1c), aminoaldehyde (14c, 27%) and *p*-dicyanobenzene (4%) together with the starting material (65%) on irradiation in cyclohexane. The possibility that an excited benzene molecule forms the cycloadduct by reacting with the C=N bond of 3-(4-cyanophenyl)-2-isoxazoline (1c) was eliminated since it was found that 1c gave the photoadduct with benzene on irradiation by Pyrex-filtered light or by externally benzene-filtered light. In addition, the excited state responsible for this reaction was the singlet excited state of 1c since the fluorescence of 1c was quenched in the presence of benzene. Although emission from an exciplex could not be detected, exciplex formation or charge transfer interaction of the excited state of 1c with benzene would be necessary for photocycloadduct formation.

In addition to the above studies, we have extensively investigated the cycloaddition reactions of a number of 3-aryl-2-isoxazoline derivatives with aromatic compounds including 5-membered ring heterocycles. In some cases (for example with furan or thiophene) it was observed that the heterocycle reacted with 3-(4-cyanophenyl)- and 3-(4-methoxycarbonylphenyl)-2-isoxazoline (1k) to give photoadducts which can be formulated by structure (25). These results, including a discussion of the reaction mechanism, will be published shortly in a separate paper.



25

AR : (p–CN)C_6H_4
(p-MeOCO)C_6H_4

X : 0, S

EXPERIMENTAL

General. IR spectra were recorded on a Shimazu IR-27G spectrometer. The PMR spectra were carried out on a Varian HA-100 and EM-390 spectrometer, using deuterochloroform as the solvent and TMS as the internal standard, unless otherwise specified. The chemical shifts were recorded in ppm on the δ scale. The UV spectra were recorded on a Hitachi-340 spectrometer. The low temp UV spectra were measured in the quartz window dewar filled with liquid N_2 using 2 mm light path cell. The emission spectra were recorded at an angle of 90° from the excitation beam monochromated from an Ushio 150W xenon lamp on a Hitachi MPF-4 fluorescence spectrometer.

All column chromatographies were carried out using Wako Q-22 silica gel (through 200 mesh ASTM) and all preparative tlc were done on plates containing E. Merck Reagents silica gel 60 PF-254. High-pressure liquid chromatography was performed on a Hitachi-645 using a 25 cm × 4 mm column packed with LiChrosorb SI-100 (5 μm). Gas chromatography was performed a Hitachi-163 with a 20 m × 0.28 mm glass capillary column coated by FFAP and a flame ionization detector. Preparative gas chromatography was performed on a Varian Aerograph model 920.

Irradiations in a preparative scale were carried out in an internally water-cooled quartz reactor at 15–20° with Rayonet RUL-3000 Å lamps (43W). Monochromic light irradiations and the quantum yield measurements were done in a 10 mm quartz cell using a Hitachi MPF-4 fluorescence spectrometer at 25°.

General procedure for the preparations of 3-aryl-2-isoxazolines. The desired 2-isoxazolines were synthesized by a 1,3-dipolar cycloaddition of the corresponding nitrile oxides with ethylene. The nitrile oxides were synthesized following procedures A or B, depending on the substrates. The yields and physical data of synthesized isoxazolines are listed in Table 5.

Procedure A.[34] Arylhydroximic acid chlorides were synthesized from the oximes and Cl_2 gas in dry $CHCl_3$ soln and were used for the preparation of the nitrile oxides.

Procedure B.[35] Arylhydroximic acid chlorides were synthesized from the oxime and nitrosyl chloride in anhyd ether and were used for the preparation of the nitrile oxides.

Preparation of 2-phenylpyrroline (2). This was synthesized by the procedure of Craig.[23e] For purification, 2 was distilled (b.p. 107–109°/5 mm) and then its picrate, m.p. 197–199° was repeatedly recrystallized from ether.

Preparation of 2-phenyl-2-oxazoline (4). This was synthesized by the procedure of Witte.[36] After distillation (b.p. 68–70°/0.1 mm), 4 was purified by application of preparative GC on a PEG-20M column at 170°. For the purpose of emission spectroscopy, it was recrystallized as the picrate (m.p. 178.5–179.5°). The purified sample was regenerated from the picrate by alumina column.

Irradiation of 3-phenyl-2-isoxazoline (1). A soln containing 588 mg of 1 in 500 ml dry benzene was irradiated with a Rayonet RUL-3000 Å lamps (43W) in a quartz vessel for 12 hr. Removal of the solvent under reduced pressure left an oily solid which was subjected to column chromatography on silica gel using benzene–CH_2Cl_2 as the eluent. The first component isolated from the column contained 29 mg (5%) of 3 as a colorless oil; IR (neat) 3080, 2870, 1638, 1583, 1456 and 1347 cm^{-1}; NMR (CCl_4, 100 MHz) δ ppm 4.62 (2H, t, J = 4.9 Hz), 5.66 (2H, t, J = 4.9 Hz) and 7.3–7.8 (5H, m); UV (cyclohexane) λ_{max} 242.0 nm (ϵ 12,100); Mass. *m/e* 147 (M^+) and 117 (base); (Found: C, 73.55; H, 6.11, N, 9.48. Calc. for C_9H_9ON: C, 73.45; H, 6.16; N, 9.52%). The second component isolated from the column contained 364 mg (62%) of 14 as light yellow prisms, m.p. 73.0–74.5°; IR (KBr) 3320, 3170, 1613, 1598, 1534 and 1485 cm^{-1}; NMR (CCl_4, 100 MHz) δ ppm 5.37 (1H, m), 7.2–7.7 (5H, m) and 9.22 (1H, d, 2.5 Hz); UV (cyclohexane) λ_{max} 235.0 nm (ϵ 7,910) and 316.2 nm (ϵ 12, 670); Mass. *m/e* 147 (M^+) and 146 (base); (Found: C, 73.18; H, 6.22; N, 9.43. Calc. for C_9H_9ON: C, 73.45; H, 6.16; N, 9.52%). Benzonitrile was obtained from the third fraction and the yield (24%) was determined by GC.

Irradiation of 3-(p-tolyl)-2-isoxazoline (1a). A soln containing 322 mg of 1a in 300 ml dry benzene was irradiated for 20 hr. Removal of the solvent under reduced pressure left a light yellow oily solid which was subjected to column chromatography on silica gel using hexane–EtOAc as the eluent. The first component isolated from the column contained 27 mg (9%) of 3a as a colorless oil, IR (neat) 3055, 2870, 1645, 1586, 1460 and

Table 5. Physical data of synthesized 2-aryl-2-isoxazolines (**1** and **1a–j**)

Compd	Proc.	Yield	mp	IR (cm^{-1})	NMR (δ^{ppm})
1[22]	A	86 %	66-7°	3090,2980, 1570,1452, 1353,929	3.16(2H,t) 4.33(2H,t) 7.2-7.7(5H)
1a	A	80 %	58-9°	3000,2960, 2900,1609, 1439,1342, 935	2.38(3H,s) 3.29(2H,t) 4.47(2H,t) 7.1-7.7(4H)
1b[30]	B	76 %	81-2°	2980,2850, 1609,1595, 1515,1470, 1422,1244, 930	3.23(2H,t) 3.79(3H,s) 4.40(2H,t) 6.8-7.7(4H)
1c	A	92 %	102-3°	3060,2970, 2800,2230, 1608,1585, 1438,1342, 923	3.32(2H,t) 4.56(2H,t) 7.6-7.9(4H)
1d	A	63 %	74-5°	3080,2980, 2900,2230, 1594,1435, 1336,924	3.22(2H,t) 4.45(2H,t) 7.5-8.2(4H)
1e	A	98 %	116-7°	2970,2900, 1593,1490, 1340,1090, 923	3.28(2H,t) 4.47(2H,t) 7.3-7.7(4H)
1f[31]	B	80 %	164-5°	3120,2950, 2890,1599, 1573,1510, 1330,923	3.40(2H,t) 4.61(2H,t) 7.8-8.2(4H)
1g[32]	B	76 %	47-8°	3100,2960, 2900,1598, 1472,1436, 920	3.20(2H,t) 4.35(2H,t) 6.8-7.4(2H)
1h	B	48 %	bp 120-2° 0.005mm	3060,2980, 2900,1596, 1510,1435, 1312,928	3.30(2H,t) 4.32(2H,t) 7.1-7.9(6H) 9.0(1H)
1i	A	97 %	51-2°	3065,2980, 1593,1562, 1496,1447, 1378,1355, 923	1.36(3H,d) 2.77(1H,d.d) 3.33(1H,d.d) 4.75(1H,m) 7.2-7.8(5H)
1j	A	51 %	79-81°	3040,2940, 2865,1449, 1375,938, 927	1.0-2.5(8H) 3.1(1H,m) 4.4(1H,m) 7.2-7.6(5H)

1340 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ ppm 2.24 (3H, s), 4.83 (2H, t, J = 4.6 Hz), 5.65 (2H, t, J = 4.6 Hz) and 7.1–7.7 (4H, m); UV (cyclohexane)λ_{max} 243 nm; Mass. *m/e* 161 (M^+) and 131 (base). The second component isolated from the column contained 183 mg (57%) of 3-amino-3-(4-methylphenyl)-2-propenal as light yellow needles, m.p. 78.5–81°; IR (KBr) 3310, 3160, 1613, 1541, 1500, 1356, 1283 and 1140 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ ppm 2.43 (3H, s), 5.50 (1H, m), 7.3–7.8 (4H, m) and 9.45 (1H, m); Mass. *m/e* 161 (M^+, base); (Found: C, 75.54; H, 6.72; N, 8.71. Calc. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69%). The yield of *p*-tolunitrile was determined by GC.

Irradiation of 3-(4-methoxyphenyl)-2-isoxazoline (**1b**). A soln containing 707 mg of **1b** in 500 ml of dry benzene was irradiated for 24 hr. Removal of the solvent under reduced pressure left a yellow solid which was subjected to column chromatography on silica gel column using benzene–ether as the eluent. The first component isolated from the column contained 174 mg (33%) of *p*-methoxybenzonitrile as a colorless powder, m.p. 55–57° (lit. 57–59°).[37] The second component isolated from the column contained 41 mg (6%) of **3b** as colorless prisms, m.p. 60–62°; IR (KBr) 3020, 2960, 2845, 1632, 1610, 1400 and 1347 cm^{-1}; NMR (CCl_4, 100 MHz) δ ppm 3.78 (3H, s), 4.74 (2H, t, J = 5 Hz), 5.56 (2H, t, J = 5 Hz), 6.7–6.0 (2H, m) and 7.5–7.7 (2H, m); UV (cyclohexane) λ_{max} 248 nm; Mass. *m/e* 177 (M^+) and 147 (base). (Found: C, 67.96; H, 6.21; N, 7.49. Calc. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.9%). The third component isolated from the column contained 331 mg (47%) of **14b** yellow needles, m.p. 91–92°: IR (KBr) 3290, 3140, 1605, 1470 and 1364 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 3.83 (3H, s), 5.87 (1H, m), 6.8–7.0 (2H, m), 7.3–7.6 (2H, m) and 9.20 (1H, d, J = 2.0 Hz); UV (EtOH) λ_{max} 216 nm (ε 8, 890), 271 nm (ε 7, 540) and 333.5 nm (ε 19, 010); Mass. *m/e* 177 (M^+, base); (Found: 67.83; H, 6.39; N, 7.98. Calc. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.9%).

Irradiation of 3-(4-cyanophenyl)-2-isoxazoline (**1c**)-1. A soln containing 1.380 g of **1c** in 1.2 l dry benzene was irradiated for 48 hr. Removal of the solvent left a yellow solid which was subjected to column chromatography on silica gel using hexane-EtOAc as the eluent. The first component isolated from the column contained 102 mg (10%) of *p*-dicyanobenzene as a colorless powder, m.p. 223–225° (lit.[38] 223°). The second component isolated from the column contained 28 mg (2%) of **3c** as yellow needles, m.p. 131–133°; IR (KBr) 3060, 2940, 2880, 2330, 1632, 1610, 1400 and 1347 cm^{-1}: NMR ($CDCl_3$, 100 MHz) δ ppm 4.95 (2H, t, J = 5 Hz), 5.77 (2H, t, J = 5 Hz) and 7.6–8.0 (5H, m); UV (cyclohexane) λ_{max} 250.5 nm (ε 17, 870), 259 nm (sh, ε 16, 300), 269 nm (sh, ε 11, 010) and 295.0 nm (ε 1, 100); Mass. *m/e* 172 (M^+) and 142: (Found: C, 69.43; H, 4.69; N, 15.95. Calc. for $C_{10}H_8ON_2$: C, 69.75; H, 4.68; N, 16.27%). The third fraction contained 5 mg (1.4%) of **24**. The fourth one contained 840 mg (61%) of **14c** as yellow needles, m.p. 151–152°: IR (KBr) 3320, 3150, 2225, 1620, 1540 and 1498 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 5.38 (1H, m), 7.71 (4H, s) and 9.28 (1H, d, J = 2.2 Hz); UV (cyclohexane) λ_{max} 243 nm (ε 14, 600) and 328.2 nm (ε 11, 000); Mass. *m/e* 172 (M^+, base); (Found: C, 69.75; H, 4.68; N, 16.27 Calc. for $C_{10}H_8ON_2$: C, 69.46; H, 4.91; N, 16.09%).

Irradiation of 3-(4-cyanophenyl)-2-isoxazoline (**1c**)-2. A soln containing 1.030 g of **1c** in 1.2 l dry benzene was irradiated with a Rayonet RUL-3000 Å lamps (43 W) in a quartz vessel for 3 hr under a N_2. Removal of the solvent under reduced pressure at 20–30° left a yellow solid which was subjected to column chromatography on silica gel using hexane-EtOAc as the eluent. The initial and final fractions gave 41 mg (6%) *p*-dicyanobenzene and 376 mg (37%) of **14c** from the first and the final fractions, respectively. The middle fractions were composed of a mixture of the starting material **1c**, **3c** and **22**. Separations from thick layer chromatography on silica gel using benzene–ether (6:1) on repeated runs and following two times of recrystallizations from ether gave 55.3 mg (3.8%) of **22** as colorless needles, m.p. 113–114°: IR (KBr) 3050, 3000, 2950, 2870, 2240, 1609, 1588, 1501 and 1450 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 2.37 (Ha, d.d.d), 28.6 (Hb, d.d.d), 3.56 (Hc, d.d.d), 4.1–4.6 (Hd, He, Hf, m), 5.13 (Hg, d.d, t), 5.62 (Hh, m), 5.87 (Hi, Hj, m) and 7.55 (5H, s), $J_{Ha,Hb}$ = 12.4, $J_{Ha,He}$ = 10.2, $J_{Ha,Hf}$ = 7.4, $J_{Hb,He}$ = 2.8 Hz, $J_{Hb,Hf}$ = 6.0, $J_{Hc,Hd}$ = 12.4, $J_{Hc,Hg}$ = 4.6, $J_{Hc,Hh}$ = 1.0, $J_{He,Hf}$ = 10.0, $J_{Hg,Hi}$ = 1.4 and $J_{Hi,Hj}$ = 10 Hz; UV (cyclohexane) λ_{max} 232.5 nm (ε 16, 900), 238 nm (sh. ε 15, 300), 270 nm (ε 3, 460) and 280 nm (ε, 3, 250); Mass *m/e* 250 (M^+, 0.6%) and 172 (base); (Found: C, 76.76; H, 5.77, N, 11.22. Calc. for $C_{16}H_{14}ON_2$: C, 76.78; H, 5.64; N, 11.19%). After these procedures, 425 mg of the starting material was recovered.

Irradiation of 3-(4-cyanophenyl)-2-isoxazoline (**1c**)-3. Each 10 ml of benzene soln containing 15.7 mg of **1c** was irradiated separately under rotation with a merry-go-round apparatus for 5, 20, 60, 150 and 240 min in quartz test tubes with a Rayonet RUL-3000 Å lamp. Analysis of the products was performed on a Hitachi-635 high-pressure liquid chromatography in which 9% EtOAc/hexane was used as the eluent using UV monitor at 254 nm.

*Cycloaddition reaction of **22** with Maleic anhydride.* A mixture containing 66.5 mg of **22** and 30.6 mg of maleic anhydride in 30 ml of anhyd ether was refluxed for 14 hr under N_2. After cooling to 0°, the mixture was filtered to give 72.2 mg (80%) of adduct **23** as a colorless solid, m.p. 250–252°: IR (KBr) 2955, 2890, 2230, 1865, 1837, 1782, 1609 and 1220 cm^{-1}; NMR (DMSO-d_6, 100 MHz) δ ppm 1.82 (1H, d.d.d, J = 12.4, 10, 8Hz), 2.70 (1H, d.d, J = 12.4, 5 Hz), 3.1–3.3 (3H, m), 3.30 (2H, broad s), 4.00 (1H, d.d, J = 10, 4 Hz), 4.2 (1H, m), 4.3 (1H, m), 5.16 (1H, d.d, J = 8.2, 5.8 Hz), 6.07 (1H, d.d, J = 8.2, 5.8 Hz), 7.3–7.4 (2H, m) and 7.7–7.8 (2H, m); Mass. *m/e* 348 (M^+) and 172 (base); (Found: C, 68.36; N, 4.96; H, 7.96. Calc. for $C_{20}H_{16}O_4N$: C, 68.96; H, 4.63; N, 8.0%).

Irradiation of 3-(3-cyanophenyl)-2-isoxazoline (**1d**). A soln containing 500 mg of 1e in 500 ml dry benzene was irradiated for 120 hr. Removal of the solvent left a yellow solid which was subjected to column chromatography on silica gel using hexane–EtOAc as the eluent. The first component isolated from the column contained 9 mg (7%) of *m*-dicyanobenzene as a colorless solid, m.p. 158–160° (lit.[39] 158–160°). The second component from the column was 71 mg (41%) of 1d. The third component isolated from the column contained 36 mg (24%) of 14d as a yellow solid, m.p. 144–147°: IR (KBr) 3320, 3140, 2225, 1621, 1534, 1481, 1380, 1279 and 1130 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ ppm 5.48 (1H, m), 7.8–8.1 (4H, m) and 9.49 (1H, d, J = 2.0 Hz); UV (cyclohexane) λ_{max} 234 nm (ϵ 12, 500) and 315.3 nm (ϵ 13, 000); Mass *m/e* 172 (M^+, base): (Found: C, 69.55; H, 4.77; N, 15.81. Calc. for $C_{10}H_8ON_2$: C, 69.46; H, 4.91; N, 16.09%).

Irradiation of 3-(4-chlorophenyl)-2-isoxazoline (1e). A soln containing 500 mg of 1e in 500 ml dry benzene was irradiated for 33 hr. Removal of the solvent left a light yellow solid which was subjected to column chromatography on silica gel using hexane–EtOAc as the eluent. The first component from the column was 86 mg (23%) of *p*-chlorobenzonitrile, a colorless solid, m.p. 85.5–88.5° (lit.[40] 88–89°). The second component isolated from the column contained 23 mg (5%) of 3e as colorless needles, m.p. 96–98°: IR (KBr) 3090, 3060, 2910, 2860, 1632, 1491 and 1335 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ ppm 4.98 (2H, t, J = 5.4 Hz), 5.83 (2H, t, J = 5.4 Hz) and 7.4–7.9 (4H, m); UV (cyclohexane) λ_{max} 240.5 nm (ϵ 13, 500); Mass. *m/e* 181 (M^+) and 151 (base): (Found: C, 59.65; H, 4.36; N, 7.56. Calc. for C_9H_8ONCl: C, 59.52; H, 4.44; N, 7.71%). The third component isolated from the column contained 267 mg (53%) of 14e as light yellow plates, m.p. 137–137.5°: IR (KBr) 3280, 3140, 1614, 1596, 1534, 1484, 1360, 1278 and 1137 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ ppm 5.42 (1H, m), 7.4–7.7 (4H, m) and 9.40 (1H, d, J = 2.2 Hz); UV (cyclohexane) λ_{max} 330.5 nm (ϵ 11, 000); Mass. *m/e* 181 (M^+, base); (Found: C, 59.74; H, 4.28; N, 7.62. Calc. for C_9H_8ONCl: C, 59.52; H, 4.44; N, 7.71%).

Irradiation of 3-(2-thienyl)-2-isoxazoline (1g). A soln containing 612 mg of 1g in 500 ml dry benzene was irradiated for 73 hr. Removal of the solvent under reduced pressure left a brown oil which was subjected to column chromatography on silica gel using benzene–ether as the eluent. The first component isolated from the column contained 8 mg (2%) of 2-cyanothiophene as a colorless oil (lit.[41] b.p. 192°). The second component isolated from the column contained 352 mg (58%) of 1g. The third component isolated from the column contained 86.3 mg (14%) of 14g as yellow prisms, m.p. 98–99°: IR (KBr) 3350, 3170, 1600, 1544 and 1500 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 5.50 (1H, m), 7.07 (1H, d.d, J = 5.4, 3.5 Hz), 7.3–7.5 (2H, m) and 9.20 (1H, d, J = 2.6 Hz); UV (cyclohexane) λ_{max} 252 nm (ϵ 8, 050) and 333 nm (ϵ 11, 790); Mass. *m/e* 153 (M^+, base); (Found: C, 54.67; H, 4.54; N, 9.23. Calc. for C_7H_7ONS: C, 54.90; H, 4.61; N, 9.15%).

Irradiation of 5-methyl-3-phenyl-2-isoxazoline (1l). A soln containing 3.009 g 2l in 500 ml dry benzene was irradiated for 46 hr. Removal of the solvent under reduced pressure left a yellow solid which was subjected to column chromatography on silica gel using benzene–ether as the eluent. The first component isolated from the column contained 411 mg (14%) of 3l as a colorless oil, b.p. 60–62°/2 mm Hg; IR (neat) 3050, 2975, 2855, 1628, 1578, 1495, 1448 and 1342 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 1.36 (3H, d, J = 6.5 Hz), 5.56 (2H, d, J = 4.0 Hz) and 7.3–7.8 (5H, m); UV (cyclohexane) λ_{max} 243.5 nm (ϵ 11, 880) and 286 nm (sh, ϵ 400); Mass. *m/e* 161 (M^+) and 58 (base); (Found: C, 74.62; H, 7.02; N, 8.88. Calc. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69%). The second component contained 1.263 g (42%) of 1l. The third component isolated from the column contained 247 mg (8%) of 14l as yellow needles, m.p. 86–88°: IR (KBr) 3330, 3150, 1615, 1530 and 1487 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 1.98 (3H, s), 5.28 (1H, s) and 7.2–7.6 (5H, m); UV (EtOH) λ_{max} 238 nm (ϵ 8, 970) and 323 nm (ϵ 8, 970) and 323 nm (ϵ 14, 460); Mass. *m/e* 161 (M^+) and 146 (base); (Found: C, 74.48; H, 6.91; N, 8.77. Calc. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69%). The yield of benzonitrile was determined by GC.

Irradiation of 3-phenylhexahydrobenzisoxazole (1j). A soln containing 500 mg of 1j in 500 ml dry benzene was irradiated for 24 hr. Removal of the solvent under reduced pressure left a yellow solid which was subjected to column chromatography on silica gel using hexane–EtOAc as the eluent. The first component isolated from the column contained 26 mg (5%) of 3j as a colorless oil: IR (neat) 3050, 2940, 2850, 1627, 1578, 1496, 1449 and 1319 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 1.1–2.2 (8H, m), 5.32 (1H, b, J = 4.5 Hz), 6.08 (1H, d.d, J = 4.2, 3.6 Hz), 7.2–7.4 (3H, m) and 7.7–7.9 (2H, m); UV (cyclohexane) λ_{max} 242 nm (ϵ 11, 750): Mass. *m/e* 201 (M^+) and 158 (base); m.p. of the picrate 157°. (Found: C, 52.73; H, 4.10; N, 12.95. Calc. for $C_{19}H_{18}O_8N_4$: C, 53.02; H, 4.22; N, 13.02%). The second component contained 141 mg (29%) of 1j. The third component isolated from the column contained 49 mg (10%) of 14j as a yellow powder, m.p. 129–129.5°: IR (KBr) 3235, 3030, 2930, 2840, 1603, 1578, 1500 and 1352 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ ppm 1.6–2.0 (4H, m), 2.52 (2H, t, J = 5 Hz), 3.52 (2H, q, J = 5 Hz), 5.86 (1H, t, J = 5 Hz), 7.2–7.4 (5H, m) and 8.52 (1H, s); UV (EtOH) λ_{max} 235 nm (ϵ 9, 120) and 321 nm (ϵ 12, 020); Mass *m/e* 201 (M^+) and 158 (base). (Found: C, 76.69; H, 7.50; N, 6.61. Calc. for $C_{13}H_{15}ON$: C, 76.58; H, 7.51; N, 6.96%). The yield of benzonitrile was determined by GC.

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