Photorearrangements of Phenyloxazoles

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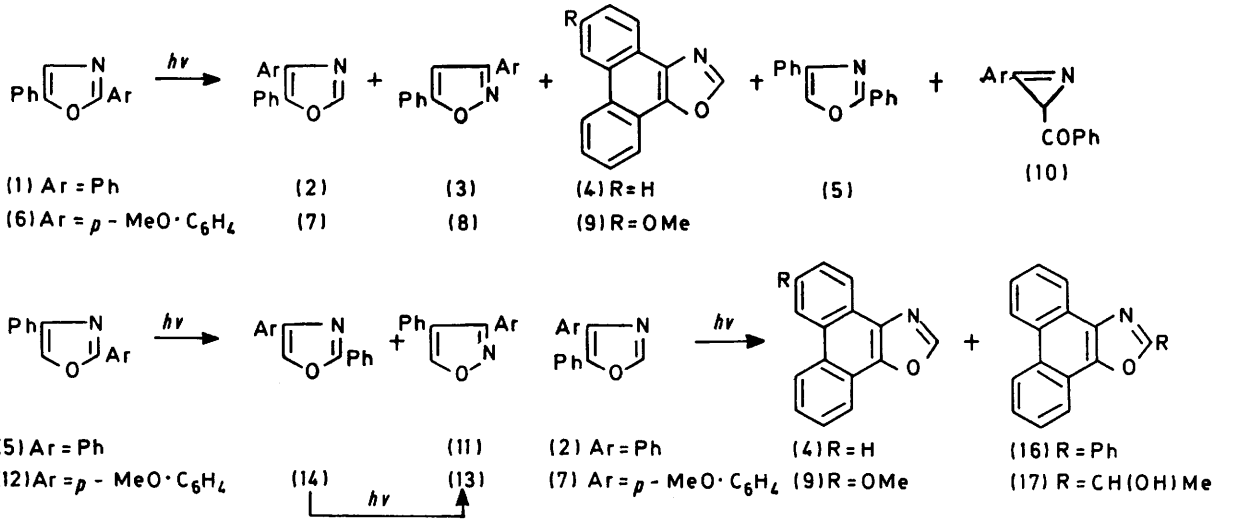
Various aryl oxazoles have been subjected to photolysis. The resulting photorearrangements have been classified as type A or B. Type A involves formal interchange of two adjacent ring atoms (exchange of positions 2 and 3, or 4 and 5). Type B involves formal exchange of positions 2 and 4, or 3 and 5. Irradiation of 2-phenyloxazole (18) in benzene or cyclohexane gives 3-phenyl-2*H*-azirine-2-carbaldehyde (19) [thermal rearrangement leads to 3-phenylisoxazole (21)] and 4-phenyloxazole (20). Similarly, irradiation of 5-methyl-2-phenyloxazole (23) results in 2-acetyl-3-phenyl-2*H*-azirine (24). The correlation between photolysis of the oxazole (18) and its electronic structure, as deduced from semiempirical SCF-MO and SCF-CI calculations, is discussed. The type A rearrangement can be rationalised in terms of a ring-contraction–ring-expansion sequence. A pathway involving a bicyclic intermediate is proposed for the type B rearrangement.

MANY studies on the photorearrangements of five-membered ring heteroaromatic compounds have been reported, and much attention has been directed towards understanding of the mechanisms of these processes.[1-10] This report describes in detail the photorearrangements of aryloxazoles,[11] from which certain mechanistic conclusions can be drawn.



SCHEME 1

Photochemistry of Diaryloxazoles.—Several diaryloxazoles were irradiated in benzene and/or ethanol. The conditions and results are summarized in Table 1, and the reactions studied can be represented as shown in Scheme 1.

Irradiation of 2,5-diphenyloxazole (1) in ethanol gave 4,5-diphenyloxazole (2), 3,5-diphenylisoxazole (3), and phenanthro[9,10-*d*]oxazole (4) as major products. When the irradiation was conducted in benzene, 2,4-diphenyloxazole (5) was produced, but neither compound (2) nor (4) was formed. Similar behaviour was observed in the case of 2-(*p*-methoxyphenyl)-5-phenyloxazole (6), and the azirine (10) which has been implicated as the intermediate in the conversion of (6) into (8) was isolated in low yield. However, nothing conclusive can be said about whether or not the azirine (10) was derived directly from the oxazole (6). Irradiation of 5-(*p*-methoxyphenyl)-2-phenyloxazole (15) in ethanol resulted in gradual disappearance of the starting material, but only decomposition products were obtained. 2,4-Diphenyloxazole (5) in benzene produced 3,4-diphenylisoxazole (11) in good yield. Although the oxazole (12) afforded products analogous to those from (6), similar

[1] H. Tiefenthaler, W. Dörsheln, H. Göth, and H. Schmit, *Helv. Chim. Acta*, 1967, **50**, 244, and work cited therein.
[2] B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, 1967, **89**, 6911; B. Singh, A. Zweig, and J. B. Gallivan, *ibid.*, 1972, **94**, 1199.
[3] (*a*) R. Srinivasan, *Pure Appl. Chem.*, 1968, **16**, 65; (*b*) E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, 1968, **90**, 3894; (*c*) H. Hiraoka and R. Srinivasan, *ibid.*, 1968, **90**, 2720 (*d*) E. E. van Tamelen and T. H. Whitesides, *ibid.*, 1971, **93**, 6129; (*e*) H. Hiraoka, *Tetrahedron*, 1973, **29**, 2955.
[4] D. W. Kurtz and H. Schechter, *Chem. Comm.*, 1966, 689.
[5] R. M. Kellogg, J. K. D. H. van Driel, and H. Wynberg, *J. Org. Chem.*, 1970, **35**, 2732; R. M. Kellogg, *Tetrahedron Letters*, 1972, 1429, and work cited therein.
[6] P. Beak and W. Messer, *Tetrahedron*, 1969, **25**, 3287.
[7] A. Couture and A. Lablanche-Combier, *Tetrahedron*, 1971, **27**, 1059; A. Couture and A. Lablanche-Combier, *Chem. Comm.*, 1971, 891.
[8] A. Lablanche-Combier and A. Pollet, *Tetrahedron*, 1972, **28**, 3141; M. Ohashi, A. Iio, and T. Yonezawa, *Chem. Comm.*, 1970, 1148; G. Vernin, C. Riou, H. J. M. Dou, J. Bouscasse, J. Metzger, and G. Loridan, *Bull. Soc. chim. France*, 1973, 1743; M. Maeda, A. Kawahara, M. Kai, and M. Kojima, *Heterocycles*, 1975, **3**, 389.
[9] N. T. Buu and J. T. Edward, *Canad. J. Chem.*, 1972, **50**, 3730.
[10] M. Kojima and M. Maeda, *Chem. Comm.*, 1970, 386; C. Riou, J. C. Poite, G. Vernin, and J. Metzger, *Tetrahedron*, 1974, **30**, 879; M. Maeda and M. Kojima, *Tetrahedron Letters*, 1973, 3523.
[11] Preliminary communications, (*a*) M. Kojima and M. Maeda, *Tetrahedron Letters*, 1969, 2379; (*b*) M. Maeda and M. Kojima, *J.C.S. Chem. Comm.*, 1973, 539.

irradiation of (14) led only to low consumption of the isoxazole (13). On the other hand, when a solution of the 4,5-diaryloxazole (2) or (7) was irradiated, ring closure to a phenanthrenoheterocyclic system occurred.[12]

Thus, apart from the exceptional conversion of (14) into (13), the photorearrangements of diaryloxazoles studied here can be classified into two types. One is a rearrangement involving formal interchange of two adjacent ring atoms (type A). The conversion of (1) to (3) is typical and the nature of the reaction pathway is of interest because of the reverse photorearrangement of (3) into (1) reported by Ullmann *et al.*[2] The other is a rearrangement involving formal exchange of positions 2 and 4 (type B), typified by the conversion of (1) into (2) (also see Table 1). The question arises as to whether the two types of product arise from the same excited state or from a single intermediate.* This problem is discussed later.

Photochemistry of Monophenyl- and Methyl-phenyl-oxazoles.—Photolyses of several monophenyl- and methyl-phenyl-oxazoles were examined. The conditions and results are summarized in Table 2.

Irradiation of 2-phenyloxazole (18) in benzene resulted in 3-phenyl-2*H*-azirine-2-carbaldehyde (19) and 4-phenyloxazole (20). Further, a trace of 3-phenyl-isoxazole (21) was detected by its n.m.r. spectrum. It was conceivable that the azirine (19) was derived directly from the isoxazole (21), because 2*H*-azirines are known to be formed photochemically or thermally from isoxazoles.[2,14] In fact, separate irradiation of the isoxazole (21) led to the azirine (19) and the oxazole (18). However, direct evidence for the formation of the azirine (19) from the oxazole (18) was obtained by irradiation with monochromatic light. This photo-

TABLE 1

Photolyses of diaryloxazoles [a]

	Irradiation conditions				Products (yield) [b]		
Compd.	Concn. ($\times 10^{-2}$M)	Solvent	Time (h)	Recovery(%)	Type A [c]	Type B	Others
(1)	2.3	EtOH	50	5	(3) (3%)	(2) (20%)	(4) (1.5%)
	2.3	PhH	72	17	(3) (7%)	(5) (4.5%)	$PhCO_2H$, $(PhCO)_2NH$
(2)	2.3	PhH	99	36.8			(4) (7.7%)
	2.5	EtOH	92.5	35.7			(4) (3.4%), (16), (17)
	0.16	EtOH [d]	9				(4) (42%)
(5)	1.5	EtOH	60				(decomp.)
	1.2	PhH	55		(11) (44.3%)		$(PhCO_2)NH$
(6)	1.9	EtOH	46	4	(8) (15.4%)	(7) (9.4%)	(9) (1.2%)
	1.7	PhH	46	18.9	(8) (16%)		
					(10) (0.7%)		
(7)	0.2	EtOH [d]	9				(9) (22%)
(12)	0.8	PhH	35		(13) (23%)	(14) (23.3%)	
(14)	1.6	PhH	45	41.1			(13) (5.7%)
(15)	1.9	EtOH	170	8.2			$PhCONH_2$, P-MeO·C_6H_4·CO_2H

[a] Reactions were carried out at 78—80 °C with a 100 W high-pressure mercury lamp (Pyrex filter) under constant nitrogen pressure. [b] Yields are based on the initial amount of starting material. [c] Type A also includes the azirine derivatives. [d] Open to air.

TABLE 2

Photolyses of monophenyl- and methyl-phenyl-oxazoles [a]

	Irradiation conditions				Products (yield) [b]		
Compd.	Conc. ($\times 10^{-2}$M)	Solvent	Time (h)	Recovery(%)	Type A [c]	Type B	Others
(18)	3.1	PhH	38	34.9	(19) (11.9%)	(20) (2.2%)	
					(21) (trace)		
(20)	3.4	PhH	30	87.3			
(23)	1.7	PhH	6	36.5	(24) (21.8%)		
					(25) (trace)		
(26)	1.9	PhH	30	2.3 [d]	(30) (14%)	(28) (5.9%) [d]	
					(31) (trace)		
(27)	2.3	PhH	35	16.5		(32) (4%)	(33) (1.2%)
	2.5	EtOH	20	2			(33) (18.9%)
(28)	3.0	EtOH	53	76			
(29)	1.1	EtOH	13		(20) (2.8%)		$PhCO_2H$

[a] Reactions were carried out at 78—80 °C with a 100 W high-pressure mercury lamp (quartz filter) under constant nitrogen pressure. [b] Yields are based on the initial amount of starting material. [c] Type A also includes the azirine derivatives. [d] Determined by n.m.r. analysis.

* The fluorescence emission quantum yield (ϕ_F) is 1.00 for 2,5-diphenyloxazole (1), and the fluorescence decay time (τ_F) is 1.4×10^{-9} s.[13] This suggests intuitively rearrangement through an excited singlet state.

[12] A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, 1966, **88**, 3759; H. Wynberg, H. van Driel, R. M. Kellogg, and J. Butter, *ibid.*, 1967, **89**, 3847; J. L. Cooper and H. H. Wasserman, *Chem. Comm.*, 1969, 200.

[13] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965; C. D. Amata and S. A. Rodemeyer, *J. Chem. Phys.*, 1968, **48**, 2374.

[14] T. Nishiwaki, A. Nakano, and H. Matsuoka, *J. Chem. Soc.* (*C*), 1970, 1825; T. Nishiwaki and F. Fujiyama, *J.C.S. Perkin I*, 1972, 1456.

reaction was carefully monitored by u.v. spectroscopy and g.l.c. of samples withdrawn during the irradiation.

Thus, a solution of 2-phenyloxazole (18) in benzene or cyclohexane at 24 °C was irradiated with 294 nm light. The absorption band (264 nm) of the starting material (18) decreased in intensity, and a new absorption band at 241 nm appeared (see Figure 1). This indicated the formation of the azirine (19); no absorption attributable to the isoxazole (21) [$\lambda_{max.}$ 239 nm (log ε 4.02)] was observed. Furthermore, the g.l.c. peak due to the oxazole (18) began to decrease on irradiation, and two peaks, corresponding to the azirine (19) and the oxazole (20), appeared with slightly higher retention times. Also irradiation of the oxazole (20) gave no isomeric product. Thus, we can conclude that the oxazole (18) is initially transformed into the azirine (19).

The photochemical behaviour of the azirine (19) in cyclohexane with light of various wavelengths was examined. At all wavelengths used (255, 282, 309, 327,

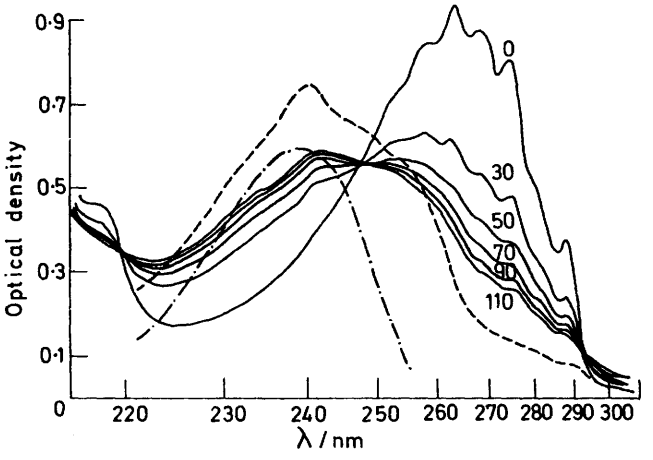
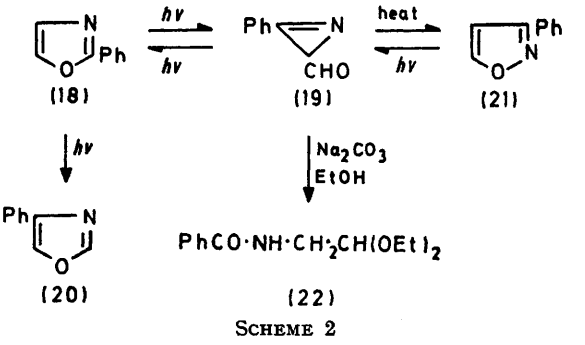


FIGURE 1 Spectral changes (——) of a 5.4 × 10^{-5}M-solution in cyclohexane of 2-phenyloxazole (18) on irradiation at 294 nm (numbers refer to time in seconds); the spectra of compounds (19) (– – – –) and (21) (— · — · —) in cyclohexane are displayed for comparison

and 335 nm) reversion to the starting oxazole (18) occurred, though the disappearance of the azirine (19) was very slow at longer wavelengths, and there was no observable conversion into the isoxazole (21). The resistance to the conversion of (19) into (21) under irradiation contrasts with the specific photorearrangements of 2-aroyl-3-aryl-2*H*-azirines into 3,5-diarylisoxazoles [2] but is analogous to the photorearrangement of 2-benzoyl-2,3-diphenyl-2*H*-azirine into 2,4,5-triphenyloxazole.[4]

In view of the lack of photoconversion of the azirine (19) into the isoxazole (21), and the information that several 3-aryl-2-benzoyl-2*H*-azirines undergo thermal isomerisation to give 3-aryl-5-phenylisoxazoles,[2,14] the thermal behaviour of the azirine (19) was investigated.[15] A slow conversion of (19) into the isoxazole (21) was found at 200 °C in benzene in a sealed tube (*ca.* 77% yield after 28 h). Although no chemical change was encountered when the azirine (19) in ethanol was refluxed for 4 h, heating the azirine (19) in refluxing



SCHEME 2

ethanol in the presence of a small amount of sodium carbonate for 2 h gave the acetal (22) in 16% yield. A similar phenomenon has been found in irradiation of 3,5-disubstituted isoxazoles in methanol.[16] Hence, we attempted irradiation of the azirine (19) in ethanol with light of wavelength 253.7 nm at 35—40 °C, but there was no appreciable formation of the expected product (22); only the oxazole (18) was obtained.

Further evidence for the formation of a 2*H*-azirine was obtained when 5-methyl-2-phenyloxazole (23) was irradiated. Irradiation in benzene led to 2-acetyl-3-phenyl-2*H*-azirine (24) † in 21.3% yield. Further, a trace of 5-methyl-3-phenylisoxazole (25) was readily apparent from its n.m.r. spectrum.

Figure 2 shows the successive changes in the u.v. absorption spectrum of the oxazole (23) in cyclohexane

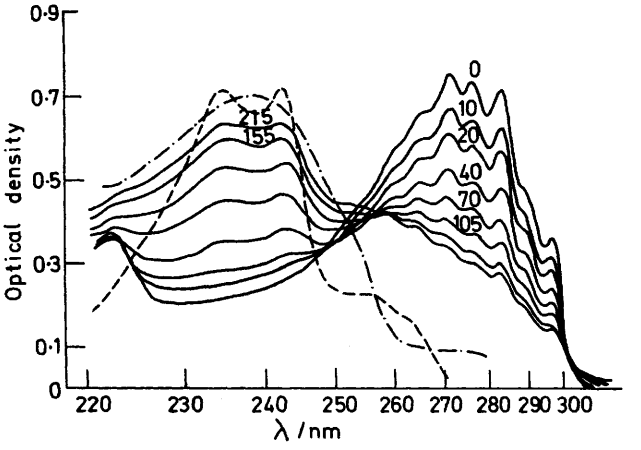


FIGURE 2 Spectral changes (——) of a 5.03 × 10^{-5}M-solution in cyclohexane of 5-methyl-2-phenyloxazole (23) on irradiation at 294 nm (numbers refer to time in seconds); the spectra of compounds (24) (– – – –) and (25) (— · — · —) in cyclohexane are displayed for comparison

with light of 294 nm at 24 °C, and illustrates the gradual disappearance of the oxazole (23) [$\lambda_{max.}$ 264—297 nm]

† Obtained as an analytically pure oil after repeated column chromatography on silica gel, though Singh *et al.*[2] did not isolate it in pure form.

[15] Recently the thermal and photochemical behaviour of the azirine (19) has also been reported; A. Padwa, J. Smolanoff, and A. Tremper, *J. Amer. Chem. Soc.*, 1975, **97**, 4682.

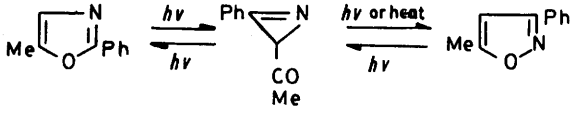
[16] T. Sato, K. Yamamoto, and K. Fukui, *Chem. Letters*, 1973, 111.

with simultaneous increase in absorbance at 234 and 242 nm, indicating photoconversion into the azirine (24) [$\lambda_{max.}$ 234 (log ε 4.14) and 242 nm (4.15)].

It has been reported that photochemical behaviour of the azirine (24) shows dramatic wavelength dependence: nearly quantitative rearrangement into the oxazole (23) occurs with <313 nm light and into the isoxazole (25) with >334 nm light.[2] This evidence was in agreement with our independent results. When the azirine (24) was heated in benzene for 26 h at 200 °C, it was transformed into the isoxazole (25) in 42% yield.

The interesting aspect of the photochemical behaviour of the azirine (19) is the difference from that of 2-aroyl-3-phenyl-2*H*-azirines.[2] The formation of the oxazole (18) from the azirine (19) regardless of the wavelength of light requires population of the ketimine chromophore in preference to the carbonyl (n,π^*) state, and intersystem crossing may merely be inefficient. The thermal transformation observed with the azirines (19) and (24) can be rationalised in terms of a vinylnitrene intermediate which subsequently isomerises to the isoxazoles (21) and (25).[14,17]

Irradiation of 4-methyl-2-phenyloxazole (26) in benzene gave 4-methyl-3-phenylisoxazole (30) and 2-methyl-4-phenyloxazole (28), which are rearrangement products analogous to those from the oxazole (12). In



(23) (24) (25)

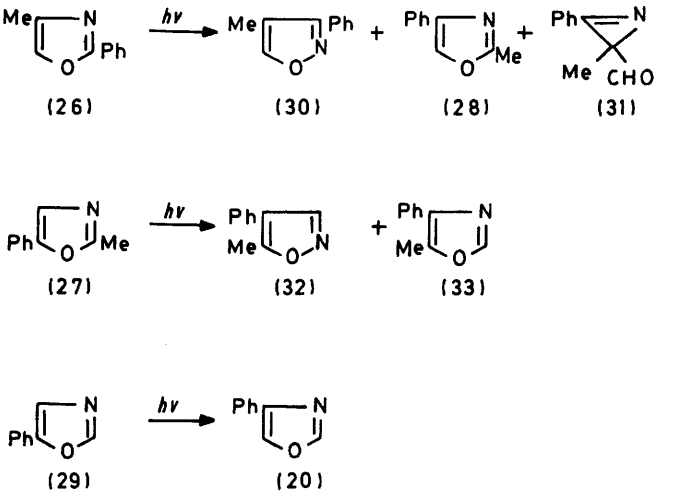
SCHEME 3

this case, the presence of the azirine (31) also was deduced from n.m.r. and i.r. spectra of the reaction mixture. The oxazole (28) was obtained in admixture with the starting material (26). Separate irradiation of the oxazole (28) in ethanol resulted in recovery of the starting material, and unidentified decomposition products were formed; an analogous observation was made on irradiation in benzene. On the other hand, irradiation of 2-methyl-5-phenyloxazole (27) in benzene gave 5-methyl-4-phenylisoxazole (32) and 5-methyl-4-phenyloxazole (33), and the same photolysis in ethanol resulted in the isolation of (33) only. Photolysis of 5-phenyloxazole (29) in ethanol gave 4-phenyloxazole (20) in low yield.

Mechanistic Considerations.—Our results demonstrate the formation of the azirines (19) and (24) directly from the oxazoles (18) and (23) and indicate that initial photoproduct, in the rearrangements of oxazoles proceeding with formal interchange of adjacent ring atoms carrying substituents (type A), is an azirine species which undergoes further photochemical and/or thermal rearrangement to the isoxazole. It is readily seen that the same mechanistic pathway is available for type A rearrangements of oxazoles shown in Tables 1 and 2.

[17] T. Nishiwaki, *J.C.S. Chem. Comm.*, 1972, 565; A. Padwa, J. Smolanoff, and T. Tremper, *Tetrahedron Letters*, 1974, 29.

The photochemical formation of the azirines (19) and (24) from the oxazoles (18) and (23) can be envisaged as



(26) (30) (28) (31)

(27) (32) (33)

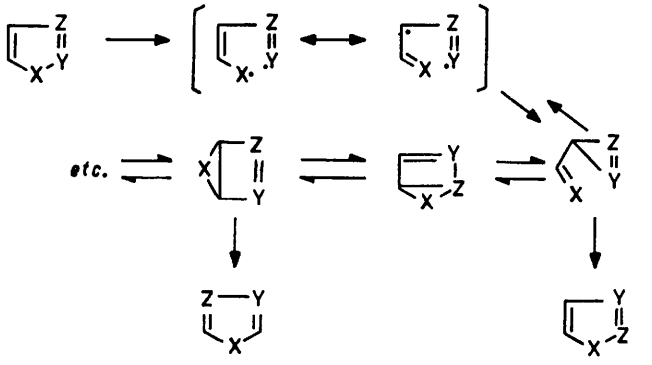
(29) (20)

SCHEME 4

proceeding through a reactive excited state which undergoes dissociative cleavage at the C(2)–O bond. However, the type A rearrangement was not observed in some cases. The efficiency of the process may depend primarily on the weakness of the C(2)–O bond in the excited state.

Although the majority of cases of formal interchange of two adjacent ring atoms have been observed with C(2) and O atoms, two examples of formal interchange between C(4) and C(5) have been found, *viz.* the conversions (1) ⟶ (5) and (29) ⟶ (20). These should be explicable in terms of formation of a 1*H*-azirine derivative [18] as a result of cleavage of the C(5)–O bond.

The type B rearrangements shown in Tables 1 and 2 cannot be rationalised by the above ring-contraction–ring-expansion mechanism. A general mechanistic proposal to account for the photorearrangements of all five-membered ring heteroaromatic compounds has been



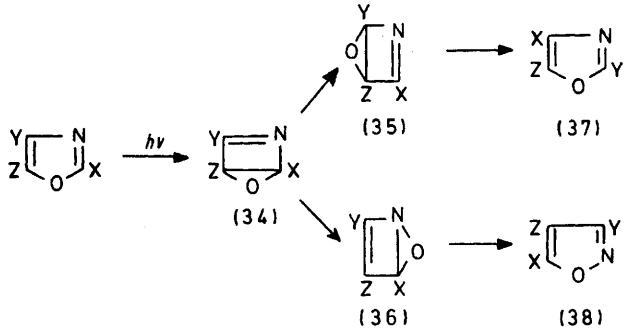
SCHEME 5

made by van Tamelen and Whitesides.[3d] This involves initial cleavage of the weakest single bond to form the

[18] For analogous mechanistic proposals for 1*H*-azirines, see M. Ogata, M. Matsumoto, and H. Kano, *Tetrahedron*, 1969, **25**, 5205; T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1973, 555.

cyclopropene or its heterocyclic analogue, in equilibrium with a bicyclic isomer as shown in Scheme 5, thus accounting for the formation of the alternative heterocyclic system. This mechanism, however, is not operative in the rearrangement of the oxazole system. The azirine (19) cannot be in equilibrium with the bicyclic isomer, because this azirine is characterised by its complete resistance to conversion into the alternative product (20).

The type B rearrangement must at least involve bonding between C(2) and C(5), and may proceed independently *via* an internal cyclisation and isomerisation mechanism.[6,19,20] In this mechanism, the initial bicyclic isomer (34) produced would react further as shown in Scheme 6. The process involves formal 1,3-oxygen migration.[21,22] Such a shift may terminate at either position 4 or 3 (N atom) to give a second bicyclic



SCHEME 6

isomer, either (35) or (36). Termination at both positions may be allowed in each case.* However, the aptitudes for migration indicated by the present work were as follows: the rearrangement product (37) was only produced when X was an aryl group, whereas the formation of (38) *via* the bicyclic isomer (36) only occurred in the case of the oxazole (27). The only apparent rationalisation for the observed selectivity involves preferred formation of the more stable bicyclic isomer.[23] Thus in the formation of a given bicyclic isomer [(35) or (36)], the 1,3-oxygen migration should take place in such a fashion as to place the aryl group on the double bond. As a result, in the photolysis of (26) or (27), the product (28) or (32), respectively, should predominate. Also, the selectivity noted in other oxazoles investigated here is similarly explained by the above consideration.

The failure of the oxazole (20) or (28) to undergo interchange of C(2) and C(4) or of C(5) and N (type B) is consistent with the above consideration: the initial bicyclic isomer resulting from internal cyclisation on irradiation would give back the starting material because its stability would be greater than that of the second bicyclic isomer resulting from 1,3-oxygen migration. The unusual conversions (14) ⟶ (13) and (27) ⟶ (33) belong to neither type A nor B. Although the origin of (13) and (33) is uncertain, they could be formed from rearrangements of the oxazoles (12) and (32) produced initially.

We have tried to correlate the electronic structure of excited 2-phenyloxazole (18),[24] as a model compound, and the course of its photoreaction on the basis of semi-empirical LCAO-SCF and SCF-CI calculations. † Calculations were performed by the Pariser–Parr–Pople method.[25] The molecular orbital parameters used for C, N, and O were those suggested by Hinze and Jaffé.[26] The two-centre repulsion integrals were calculated by use of the Mataga–Nishimoto formula.[27] The core resonance integrals (β_{rs}) were estimated from the equation $\beta_{rs} = -0.431\ 4\ S_{rs}(W_r + W_s)$, where S is the overlap integral[28] and W the valence-state ionisation potential. The molecular geometry for the planar 2-phenyloxazole molecule (18) was fed in as empirical data with currently accepted values for bond lengths and conventional hybridization angles.

From the coefficients of 2-phenyloxazole's LUMO and HOMO, we note that this one electron-excitation results in an increase in bonding between C(2) and C(5): negative π-overlap is possible between C(2) and C(5) AOs in the LUMO, whereas in the HOMO the corresponding partial bond order is negative (Table 3). Apparently the characteristics of the π*-orbital are in agreement with electrocyclic ring closure between C(2) and C(5). The excited oxazole (18) could thus be expected to pass by disrotatory motion to the bicyclic isomer (39). Furthermore, the C(5)–O bond would have a tendency to lengthen, but the lengthening of the C(2)–O bond is more pronounced. In Table 4, we have also listed the electron density and bond order of the first singlet excited state of the oxazole (18) obtained by the SCF-CI method. The result indicates that the weakest bond is the C(2)–O bond. Therefore the ring contraction may start with the cleavage of this bond, leading to the azirine (19), as observed. It could be said that the electronic structure in the lowest singlet state of the oxazole (18) is responsible for the formation of both the bicyclic isomer (39) and the azirine (19).

* The transformations are nominally [$_{\sigma}2 + _{\pi}2$] reactions with two allowed products being formed.

† Performed with a FACOM 230–60 computer at Kyushu University.

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[25] R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767; J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

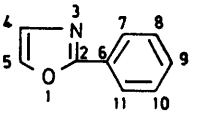
[26] J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1965, **84**, 540.

[27] N. Mataga and K. Nishimoto, *Z. phys. Chem.* (*Frankfurt*), 1957, **13**, 140.

[28] R. S. Mulliken, C. A. Reike, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

TABLE 3

Coefficients of the highest occupied orbital (HOMO) and lowest unoccupied orbital (LUMO) of 2-phenyloxazole according to LCAO-SCF-MO calculations



Atom numbering

Atom no.	Coefficients π-Orbital (HOMO)	Coefficients π*-Orbital (LUMO)	Variation in bond order Bond	Variation in bond order (ΔP_{rs}) [a]
1	0.072 9	0.198 6	1–2	−0.134 1
2	0.377 1	−0.537 5	2–3	−0.384 9
3	0.403 6	0.433 3	3–4	0.143 4
4	−0.387 9	0.030 3	4–5	−0.232 6
5	−0.579 8	−0.287 9	5–1	−0.014 9
6	−0.207 9	−0.265 0	1–3	0.056 6
7	−0.208 9	0.292 2	1–4	0.034 2
8	0.070 2	0.116 6	2–5	0.373 3
9	0.250 3	−0.359 2	2–4	0.130 0
10	0.084 4	0.091 8	3–5	0.109 3
11	−0.202 7	0.305 3		

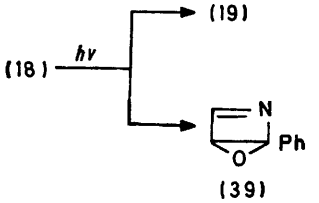
[a] Variation in bond order in a one-electron HOMO→LUMO.

TABLE 4

Electron density and bond order of the first singlet excited state of 2-phenyloxazole by the SCF-CI method

Atom	1	2	3	4	5
1	1.868 3				
2	0.241 7	0.958 0			
3	−0.116 7	0.402 2	1.316 3		
4	−0.137 0	0.021 8	0.628 7	0.855 6	
5	0.291 4	0.003 0	0.005 7	0.624 9	0.834 9

In conclusion, we propose that the photorearrangement of the oxazole systems presented here takes two different reaction courses: (i) ring-contraction–ring-expansion, and (ii) internal cyclisation and isomerisation. Moreover, structural changes in the oxazole molecules may render both paths or either inefficient.



SCHEME 7

EXPERIMENTAL

Unless otherwise noted, Mallinckrodt Silica ARCC-4 (100 mesh) was used for column chromatography [monitored by t.l.c. (Wakogel B-O silica gel)]. U.v. spectra were taken on a Hitachi 139 UV-VIS or a Shimazu SV-50A spectrometer. I.r. spectra were obtained on a JASCO DS-701G instrument and n.m.r. spectra on a JNM-60H spectrometer with Me_4Si as internal standard. Mass spectral determinations were performed with a JEOL JMS-OISG spectrometer. Analytical g.l.c. was carried out with a Hitachi 063 chromatograph equipped with a flame ionization detector.

Large-scale photolyses were performed with a Riko UVL-700P or UVL-100HP 100 W high-pressure mercury lamp, with a Pyrex or quartz filter. The high-pressure mercury lamp could be readily exchanged for a Riko 30 W low-pressure mercury lamp (253.7 nm). All photolyses were monitored by t.l.c. or periodic scanning of the u.v. spectra. The appropriate control tests run in the absence of light were satisfactory.

Monochromatic light (*ca.* ±7.5 nm band width) was obtained from a concave radiating monochromator (2 kW xenon discharge lamp, JASCO CRM-FA). In the monochromatic irradiations, solutions were purged initially with nitrogen for at least 30 min and the quartz sample cells (4 ml) were sealed during irradiation.

2-(p-*Methoxyphenyl*)-4-*phenyloxazole* (12).[29]—A mixture of *p*-methoxybenzamide (20 g) and 2-bromoacetophenone (26 g) was heated in an oil-bath until a liquid was obtained. The resulting mixture was extracted with benzene. The residue obtained on evaporation was chromatographed on silica gel, with benzene and then chloroform as eluant. The product was recrystallised from ethanol to give the *oxazole* (12) (1.2 g, 4%) as leaflets, m.p. 99—100°; $\lambda_{max.}$ (EtOH) 247 (log ε 4.23), 277 (4.38), and 295 nm (4.33); *m/e* 251 (M^+) (Found: C, 76.55; H, 4.95; N, 5.7. $C_{16}H_{13}NO_2$ requires C, 76.45; H, 5.2; N, 5.55%).

4-(p-*Methoxyphenyl*)-2-*phenyloxazole* (14).—The oxazole (14) was prepared similarly from benzamide and 2-bromo-4′-methoxyacetophenone. Chromatography and sublimation (100 °C and 5 mmHg) gave the *oxazole* (14) (10%), leaflets (from ethanol), m.p. 105—106°; $\lambda_{max.}$ (EtOH) 250 (log ε 4.34), 263 (4.32), and 279 nm (4.25); *m/e* 251 (M^+) (Found: C, 76.45; H, 5.0; N, 5.5. $C_{16}H_{13}NO_2$ requires C, 76.45; H, 5.2; N, 5.55%).

4-(p-*Methoxyphenyl*)-5-*phenyloxazole* (7).[30]—2-*Chloro*-4-*methoxy*-2-*phenylacetophenone*, prepared (40%) from 4-methoxybenzoin and thionyl chloride in pyridine and recrystallised from light petroleum, had m.p. 42—43° (Found: C, 68.95; H, 4.95. $C_{15}H_{13}ClO_2$ requires C, 69.1; H, 5.0%). This chloride (5.9 g), ammonium formate (8.9 g), and 99% formic acid (44 g) were refluxed for 6 h. After cooling, the mixture was made basic (2N-NaOH), diluted with water, and extracted with benzene. The benzene was removed and the residue was chromatographed on silica gel (chloroform) to give the *oxazole* (7) (623 mg, 12%), needles (from light petroleum), m.p. 68—69°; $\lambda_{max.}$ (EtOH) 234 (log ε 4.42) and 288 nm (4.26); δ ($CDCl_3$) 3.85 (3 H, s, OCH_3), 6.7—7.8 (9 H, A_2B_2m and five other aromatic), and 7.92 (1 H, s), ring proton); *m/e* 251 (M^+) (Found: C, 76.75; H, 5.45; N, 5.3. $C_{16}H_{13}NO_2$ requires C, 76.45; H, 5.2; N, 5.55%).

Photolysis of 2,5-*Diphenyloxazole* (1).—(*a*) A solution of the oxazole (1) (2.977 g) in refluxing ethanol (600 ml) was irradiated for 50 h. The mixture was evaporated and the residue was chromatographed on silica gel (with benzene as eluant) to give five fractions. The first fraction in order of elution, after rechromatography (benzene) and recrystallisation from ethanol, gave 3,5-diphenylisoxazole (3) (88 mg) as needles, m.p. 141°, identical with an authentic sample.[31] The second fraction, after rechromatography on silica gel (benzene) and recrystallisation from ethanol, gave unchanged (1) (132 mg). The third fraction, after rechromatography [benzene–light petroleum (1 : 2)] gave a light yellow semisolid which slowly crystallised. Recrystallisation from hexane gave 4,5-diphenyloxazole (2) (631 mg)

[29] F. Blümlein, *Ber.*, 1884, **17**, 2578.
[30] H. Bredereck and R. Gompper, *Chem. Ber.*, 1954, **87**, 700.
[31] T. Pösner, *Ber.*, 1901, **34**, 3985.

as a solid, m.p. 44°, identical with an authentic sample.[30] The fourth fraction, after recrystallisation from ether and sublimation (120 °C and 5 mmHg), gave phenanthro-[9,10-*d*]oxazole (4) (40 mg), m.p. 152—153°, identical with an authentic sample.[32] The last fraction gave benzoic acid (29 mg).

(*b*) The oxazole (1) (2.978 g) was similarly irradiated in benzene (600 ml) for 72 h. The benzene was removed and the residue was chromatographed on silica gel (benzene) to give five fractions. The first, after rechromatography [benzene–light petroleum (1 : 1)] gave two components: 2,4-diphenyloxazole (5) (119 mg), needles from ethanol, m.p. 103—104°, identical with an authentic sample,[29] and the isoxazole (3) (171 mg) (recrystallised from ethanol). The second fraction gave unchanged (1) (513 mg), the third gave benzoic acid (55 mg), and the last, dibenzamide (12 mg), m.p. 148°.

Photolysis of 2,4-*Diphenyloxazole* (5).—(*a*) A solution of the oxazole (5) (1.715 g) in refluxing benzene (600 ml) was irradiated for 55 h. The benzene was removed and the residue was chromatographed on silica gel [benzene–light petroleum (2 : 1)] to give two fractions. The first, after recrystallisation from ethanol, afforded needles, m.p. 85—88°. Sublimation (90 °C and 5 mmHg) gave pure 3,4-diphenylisoxazole (11) (761 mg), m.p. 88.5—90° (lit.,[33] 91°); δ ($CDCl_3$) 7.2—7.7 (10 H, m, aromatic) and 8.48 (1 H, s, ring proton); *m/e* 221 ($C_{15}H_{11}NO$, M^+), 193 ($C_{14}H_{11}N$), 192 ($C_{14}H_{10}N$), 104 (C_7H_6N), and 77 (C_6H_5) as reported [34] (Found: C, 81.45; H, 5.0; N, 6.15. Calc. for $C_{15}H_{11}NO$: C, 81.45; H, 5.01; N, 6.35%). The last fraction gave dibenzamide (102 mg), m.p. 147—148°.

(*b*) A solution of the oxazole (5) (2.005 g) in refluxing ethanol (600 ml) was irradiated for 60 h. Only decomposition and polymer formation occurred; attempts to isolate rearrangement products failed.

Photolysis of 2-(p-*Methoxyphenyl*)-5-*phenyloxazole* (6).—(*a*) A solution of the oxazole (6) (2.842 g) in refluxing ethanol (600 ml) was irradiated for 46 h. The solvent was removed and the residue was chromatographed on silica gel [benzene–light petroleum (4 : 1)] to give four fractions. The first, after rechromatography [benzene–light petroleum (9 : 1)], gave 3-(*p*-methoxyphenyl)-5-phenylisoxazole (8) (445 mg), needles from methanol, m.p. 119—120°, identical with an authentic sample.[35] The second fraction gave unchanged (6) (108 mg). The third fraction, after re-chromatography [benzene–light petroleum (2 : 1)], gave 6-*methoxyphenanthro*[9,10-d]*oxazole* (9) (34 mg), needles from ethanol, m.p. 135—137°; $\lambda_{max.}$ (EtOH) 242sh (log ε 4.70), 253 (4.82), 284 (4.04), and 306 nm (3.91); δ ($CDCl_3$) 4.06 (3 H, s, OCH_3), 8.25 (1 H, s, oxazole ring proton), and 7.4—8.7 (7 H, m, phenanthrene); *m/e* 249 (M^+) (Found: C, 76.9; H, 4.3; N, 5.85. $C_{16}H_{11}NO_2$ requires C, 77.1; H, 4.45; N, 5.6%). The fourth fraction, after recrystallisation from methanol, gave 4-(*p*-methoxy)-5-phenyloxazole (7) (267 mg), m.p. 67—69°, identical with material synthesised independently.

(*b*) The oxazole (6) (2.623 g) was similarly irradiated in benzene (700 ml) for 46 h. Work-up as above and chromatography [benzene–light petroleum (4 : 1)] led to the isoxazole (8) (420 mg), starting material (6) (498 mg), and 2-benzoyl-3-(*p*-methoxyphenyl)-2*H*-azirine (10) [2] (18 mg), m.p. 89.5°.

Photolysis of 2-(p-*Methoxyphenyl*)-4-*phenyloxazole* (12).—A solution of the oxazole (12) (1.251 g) in refluxing benzene (600 ml) was irradiated for 35 h. The solvent was removed and the residue was chromatographed on silica gel (chloroform) to give two fractions. The first, after recrystallisation from ethanol and sublimation (120 °C and 5 mmHg), afforded 4-(*p*-methoxyphenyl)-2-phenyloxazole (14) (291 mg), m.p. 105—106°, identical with material synthesised independently. The second fraction, after chromatography [benzene–light petroleum (1 : 1)], gave 3-(p-*methoxyphenyl*)-4-*phenylisoxazole* (13) (293 mg) as an oil; δ ($CDCl_3$) 3.80 (3 H, s, OCH_3), 6.6—7.5 (9 H, A_2B_2m and five other aromatic), and 8.46 (1 H, s, oxazole ring proton); *m/e* 251 ($C_{16}H_{13}NO_2$, M^+), 223 ($C_{15}H_{13}NO$), 222 ($C_{15}H_{12}NO$), 134 (C_8H_8NO), and 77 (C_6H_5) (Found: C, 76.55; H, 5.5; N, 5.4. $C_{16}H_{13}NO_2$ requires C, 76.45; H, 5.2; N, 5.55%).

Photolysis of 4-(p-*Methoxyphenyl*)-2-*phenyloxazole* (14).—A solution of the oxazole (14) (2.223 g) in refluxing benzene (700 ml) was irradiated for 45 h. Work-up as above and chromatography (benzene) led to unchanged (14) (915 mg) and the isoxazole (13) (131 mg). The isoxazole (13) was then purified by chromatography [benzene–light petroleum (1 : 1)].

Photolysis of 5-(p-*Methoxyphenyl*)-2-*phenyloxazole* (15).—A solution of the oxazole (15) (2.962 g) in refluxing ethanol (600 ml) was irradiated for 170 h and worked up as above. Chromatography of the residue gave unchanged (15) (243 mg), *p*-anisic acid (1.080 g), and benzamide (663 mg).

Photolysis of 4,5-*Diphenyloxazole* (2).—(*a*) A solution of the oxazole (2) (3.087 g) in refluxing benzene (600 ml) was irradiated for 99 h. The solvent was removed and the residue was chromatographed on silica gel [chloroform–light petroleum (4 : 1)] to give four fractions. The first gave biphenyl (10 mg). The second, after recrystallisation from petroleum, gave unchanged (2) (1.137 g). The third was recrystallised from ethanol to give (4) (238 mg), m.p. 153°, and the last gave benzoic acid (172 mg).

(*b*) A solution of the oxazole (2) (3.260 g) in refluxing ethanol (600 ml) was irradiated for 92.5 h. Work-up as above and chromatography on silica gel (benzene) led to 2-phenylphenanthro[9,10-*d*]oxazole (16) [36] (17 mg), m.p. 206—208°, the starting material (2) (1.163 g), compound (4) (112 mg), benzoic acid (41 mg), and a final fraction which, after sublimation (118 °C and 10^{-5} mmHg), gave 2-(1-*hydroxyethyl*)*phenanthro*[9,10-d]*oxazole* (17) (34 mg) as needles, m.p. 145—147°; $\lambda_{max.}$ (EtOH) 248 (log ε 4.79), 253 (4.82), 277 (4.14), 291 (4.05), and 303 nm (4.07); $\nu_{max.}$ (Nujol) 3 250 cm^{-1} (OH); δ ($CDCl_3$) 1.85 (3 H, d, *J* 7 Hz, CH_3), 3.55br (1 H, OH), 5.31 (1 H, q, *J* 7 Hz, CH), and 7.5—8.7 (8 H, m, phenanthrene ring protons); *m/e* 263 (M^+) (Found: C, 77.5; H, 4.95; N, 5.65. $C_{17}H_{13}NO_2$ requires C, 77.55; H, 5.0; N, 5.3%).

(*c*) A solution of the oxazole (2) (214 mg) in refluxing ethanol (600 ml), open to the air, was irradiated for 9 h. Work-up as above and chromatography (benzene) led to the phenanthro-oxazole (4) (90 mg), m.p. 149—150°.

Photolysis of 4-(p-*Methoxyphenyl*)-5-*phenyloxazole* (7).—A solution of the oxazole (7) (327 mg) in refluxing ethanol (600 ml), open to the air, was irradiated for 9 h. Work-up as above and chromatography on silica gel (chloroform) led

[32] A. Schönberg and W. I. Awad, *J. Chem. Soc.*, 1947, 651.
[33] E. P. Kohler and A. R. Davis, *J. Amer. Chem. Soc.*, 1930, **52**, 4520.
[34] B. K. Simons, R. K. M. R. Kallury, and J. H. Bowie, *Org. Mass Spectrometry*, 1969, **2**, 745.
[35] R. P. Barnes and A. Brandon, *J. Amer. Chem. Soc.*, 1943, **65**, 1017.
[36] F. R. Japp and E. Wilcock, *J. Chem. Soc.*, 1881, **39**, 225.

to *p*-methoxybenzonitrile (13 mg), benzoic acid (25 mg), and compound (9) (73 mg).

2-Phenyloxazole (18).—A mixture of benzamide (10 g) and dichloroethyl acetate (13 g) was heated in a sealed tube at 80 °C for 6 h. After cooling, the mixture was refluxed with 2N-hydrochloric acid for 5 min, made alkaline (6N-NaOH) at 0 °C, and extracted with ether. After drying (Na_2SO_4) and removal of the ether, chromatography on silica gel [benzene–light petroleum (2 : 1)] gave a dark oil. Distillation afforded the oxazole (18) (2.3 g, 20%) as an oil, b.p. 117—118° at 26 mmHg; $\lambda_{max.}$ (cyclohexane) 253sh (log ε 4.12), 259 (4.18), 263 (4.23), 269 (4.20), 275 (4.16), 281sh (3.96), and 288 nm (3.83); $\nu_{max.}$ (neat) 1 557, 1 485, 1 450, 1 260, 920, 780, 715, and 690 cm^{-1}; δ ($CDCl_3$) 7.23 (1 H, d, *J* 0.9 Hz), 7.67 (1 H, d, *J* 0.9 Hz), and 7.3—8.2 (5 H, m, aromatic); *m/e* 145 (M^+) (Found: C, 74.45; H, 4.8; N, 9.7. Calc. for C_9H_7NO: C, 74.45; H, 4.85; N, 9.65%), which showed the same spectral data as reported.[37,38]

Photolysis of 2-Phenyloxazole (18).—A solution of the oxazole (18) (2.738 g) in refluxing benzene (600 ml) was irradiated for 38 h. The benzene was removed and the residue was chromatographed on silica gel (chloroform) to give four fractions. The first consisted of a trace of 3-phenylisoxazole (21) with unidentified coloured material. The presence of the isoxazole (21) was deduced from n.m.r. absorptions at δ 6.65 (d) and 8.43 (d), identical with those of an authentic sample.[39] The second fraction, after chromatography [benzene–light petroleum (2 : 1)] gave 3-phenyl-2*H*-azirine-2-carbaldehyde (19) (326 mg) as needles, m.p. 44°; $\lambda_{max.}$ (cyclohexane) 241 (log ε 4.17) and 335 nm (110); $\nu_{max.}$ (KBr) 1 774 (C=N) and 1 712 cm^{-1} (CHO); δ ($CDCl_3$) 2.88 (1 H, d, *J* 7 Hz), 8.95 (1 H, d, *J* 7 Hz), and 7.5—8.0 (5 H, m, aromatic); *m/e* 145 (M^+) (Found: C, 74.15; H, 4.7; N, 9.55. C_9H_7NO requires C, 74.45; H, 4.85; N, 9.65%). The third fraction, after repeated chromatography (chloroform) gave 4-phenyloxazole (20) (62 mg), identical with an authentic sample.[30] The last fraction, after chromatography [benzene–light petroleum (2 : 1)], afforded unchanged (18) (958 mg) as a light yellow oil.

Consecutive Irradiations of 2-Phenyloxazole (18).—(*a*) The u.v. absorption spectrum of a solution of the oxazole (18) in cyclohexane (5.4×10^{-5}M) was recorded before irradiation and following successive exposures to 294 nm irradiation. The temperature was held at 24 °C. The characteristic 3-phenyl-2*H*-azirine-2-carbaldehyde (19) absorption increased on irradiation and there was no observed formation of 3-phenylisoxazole (21). The spectral changes are shown in Figure 1.

(*b*) A solution of the oxazole (18) (30 mg) in cyclohexane (10 ml) in a 4 ml quartz cell was irradiated in the manner described in (*a*) (297 nm). At appropriate intervals the cell was removed and the progress of the reaction was monitored by g.l.c. analysis. The azirine (19) could be separated from (18) and (20) with a 1 m × 3 mm column packed with 5% Carbowax 20M on 60—80 mesh Chromosorb WAW operated at 130 °C, and (19) could be separated from (21) with a 1 m × 3 mm in column packed with 1.5% Silicone SE-30 on 60—80 mesh Chromosorb WAW operated at 100 °C. Quantities injected (syringe) were always under 1 μl. G.l.c. analyses showed new peaks with retention times the same as those of (19) and (20), but no peak corresponding to (21) appeared.

[37] J. H. Bowie, P. F. Donaghue, H. J. Rodda, R. G. Cooks, and D. H. Williams, *Org. Mass Spectrometry*, 1968, **1**, 18.

Effect of Light of Various Wavelengths on 3-Phenyl-2H-azirine-2-carbaldehyde (19).—Dilute solutions (*ca.* 4×10^{-5}M) of the azirine (19) in cyclohexane were irradiated at 24—26 °C with light of wavelengths 255, 282, 309, 327, and 335 nm. The reactions were monitored by measuring the absorption spectra, which showed the appearance of 2-phenyloxazole (18) bands in the region 253—288 nm in all cases. There was no appreciable conversion into 3-phenylisoxazole (21). G.l.c. analysis gave the same results.

Thermolysis of 3-Phenyl-2H-azirine-2-carbaldehyde (19).—(*a*) The azirine (19) (31 mg) was heated in benzene (10 ml) in a sealed tube at 200 °C for 28 h. Removal of the benzene left an oil, which was chromatographed on silica gel. Elution with benzene–light petroleum (2 : 1) gave 3-phenylisoxazole (21) (21 mg, 77%) as an oil, identical with an authentic sample.[39] Elution with benzene–light petroleum ether (2 : 1) gave unchanged azirine (19) (4 mg, 16%).

(*b*) The azirine (19) (20 mg) was heated in refluxing ethanol (5 ml) for 4 h, but no reaction took place. The azirine (19) (19 mg) was refluxed in ethanol (5 ml) in the presence of a trace of Na_2CO_3 for 2 h. Then the solvent was removed and the residue was chromatographed on silica gel. Elution with chloroform gave unchanged azirine (19) (5 mg, 26%). Elution with chloroform gave 2-benzamidoacetaldehyde diethyl acetal (22) (6 mg, 16%), identical with an authentic sample.[40]

Photolysis of 4-Phenyloxazole (20).—A solution of the oxazole (20) (2.937 g) in refluxing benzene (600 ml) was irradiated. After 30 h, the solvent was removed and the residue was chromatographed on silica gel (benzene) to give unchanged (20) (2.563 g). No trace of any other isomer was observed. Analogous observations were made for a reaction in ethanol solution.

Photolysis of 3-Phenylisoxazole (21).—A solution of the isoxazole (21) (1.977 g) in cyclohexane (600 ml) was irradiated with a low-pressure mercury lamp at 30—33 °C After 56 h, the solvent was removed and the residue was chromatographed on silica gel (chloroform) to give unchanged (21) (1.463 g), the azirine (19) (55 mg), and the oxazole (18) (40 mg).

Photolysis of 5-Methyl-2-phenyloxazole (23).—A solution of the oxazole (23) (1.079 g) in refluxing benzene (400 ml) was irradiated for 6 h. The benzene was removed and the residue was chromatographed on silica gel [chloroform–cyclohexane (2 : 1)] to give three fractions. The first consisted of a trace of 5-methyl-3-phenylisoxazole (25) and unidentified decomposition products. The presence of (25) was apparent from the n.m.r. spectrum. The second fraction, after chromatography on silica gel [hexane–ether (5 : 1)], gave unchanged (23) (394 mg). The last fraction, after repeated chromatography [chloroform–cyclohexane (1 : 1)] afforded *2-acetyl-3-phenyl-2H-azirine* (24) (236 mg) as a light yellow oil; $\lambda_{max.}$ (cyclohexane) 234 (log ε 4.14) and 242 nm (4.15); $\nu_{max.}$ (neat) 1 695 (CO) and 1 769 cm^{-1} (=NCH); δ ($CDCl_3$) 2.01 (3 H, s, CH_3), 2.97 (1 H, s, =NCH), and 7.5—8.0 (5 H, m, aromatic); *m/e* 159 (M^+) (Found: C, 75.35; H, 5.95; N, 8.9. $C_{10}H_9NO$ requires C, 75.45; H, 5.7; N, 8.8%).

Consecutive Irradiations of 5-Methyl-2-phenyloxazole (23).—The u.v. spectra of solutions of the oxazole (23) (5.03×10^{-5}M) in cyclohexane held at 26 °C were recorded before

[38] D. J. Brown and P. B. Ghosh, *J. Chem. Soc.* (*B*), 1969, 270.
[39] K. V. Auwers and B. Otten, *Ber.*, 1925, **58**, 2079.
[40] E. Fisher, *Ber.*, 1893, **26**, 465.

irradiation and after successive exposures to light of wavelength 294 nm. The result (Figure 2) illustrates the gradual disappearance of starting material with simultaneous increase in absorbance at 234 and 242 nm, strongly indicative of the formation of 2-acetyl-3-phenyl-2*H*-azirine (24).

Thermolysis of 2-Acetyl-3-phenyl-2H-azirine (24).—The azirine (24) (64 mg) was heated in benzene (8.5 ml) in a sealed tube at 200 °C for 26 h. The solvent was removed and the residue was chromatographed on silica gel. Elution with chloroform gave 5-methyl-3-phenylisoxazole (25) (27 mg, 42%) as leaflets, m.p. 42° (lit.,[41] 42°). The u.v., mass, and n.m.r. spectral data agreed with those reported.[41-43] Elution with chloroform gave unchanged azirine (24) (20 mg).

Photolysis of 4-Methyl-2-phenyloxazole (26).—A solution of the oxazole (26) (1.538 g) in refluxing benzene (500 ml). was irradiated for 30 h. The solvent was removed; chromatography of the residue on silica gel [chloroform–cyclohexane (2 : 1)] gave three fractions. The first was rechromatographed [chloroform–cyclohexane (2 : 1)] to give a brown oil. Subsequent chromatography on alumina (300 mesh; Ishizu Pharm. Co., Ltd.) with benzene gave 4-methyl-3-phenylisoxazole (30) (216 mg) as an oil; $\lambda_{max.}$ (cyclohexane) 232 nm (log ε 4.16); $\nu_{max.}$ (neat) 1 615, 1 592, 765, and 697 cm^{-1}; δ ($CDCl_3$) 2.44 (3 H, s, CH_3), 7.14 (sharp) (5 H, aromatic), and 8.42 (1 H, s, isoxazole ring proton) (Found: C, 75.45; H, 5.85; N, 8.85. $C_{10}H_9NO$ requires C, 75.45; H, 5.7; N, 8.8%). The second fraction, after rechromatography [chloroform–cyclohexane (2 : 1)], gave a yellow oil (51 mg); $\nu_{max.}$ (neat) 2 820, 2 720, 1 720 (CHO), and 1 775 cm^{-1} (=NCH); δ ($CDCl_3$) 1.52 (s, CH_3), 1.0—2.5 (impurity), 7.5—8.0 (m), and 8.83 (s, CHO). Repeated chromatography did not remove the impurity (n.m.r.), which resisted further characterisation. The oil was considered, however, to be 2-methyl-3-phenyl-2*H*-azirine-2-carbaldehyde (31). The last fraction, after chromatography [chloroform–cyclohexane (2 : 1)], gave a light yellow oil (128 mg) shown by its i.r. and n.m.r. spectra to be a mixture of unchanged (26) and 2-methyl-4-phenyloxazole (28) [44] in the ratio 5 : 12.

Photolysis of 2-Methyl-5-phenyloxazole (27).—(*a*) A solution of the oxazole (27) (2.476 g) in benzene (690 ml) was irradiated for 35 h under conditions similar to those used for the other isomers. The brown oil left after removal of the solvent was chromatographed on silica gel (benzene) to give three fractions. The first, after rechromatography [benzene–light petroleum (2 : 1)], gave *5-methyl-4-phenylisoxazole* (32) (100 mg) as an oil; $\lambda_{max.}$ (EtOH) 238 nm (log ε 4.13); δ ($CDCl_3$) 2.15 (3 H, s, CH_3), 7.38 (sharp) (5 H, aromatic), and 8.33 (1 H, s, isoxazole ring proton); *m/e* 159 (M^+) (Found: C, 75.65; H, 5.55; N, 8.85. $C_{10}H_9NO$ requires C, 75.45; H, 5.7; N, 8.8%). The second fraction, after chromatography (chloroform), gave 5-methyl-4-phenyloxazole (33) (30 mg) as an oil, which showed mass, u.v., and n.m.r. spectral data as reported.[37,43,45] The last fraction gave unchanged (27) (409 mg).

(*b*) The oxazole (27) (2.764 g) in ethanol (700 ml) was irradiated for 20 h. The brown oil from removal of the solvent was chromatographed on silica gel (chloroform) to give the oxazole (33) (524 mg) and unchanged (27) (65 mg).

Photolysis of 2-Methyl-4-phenyloxazole (28).—A solution of the oxazole (28) (3.286 g) in ethanol (700 ml) was irradiated for 53 h. The residue obtained after removal of the solvent consisted of the unchanged (28) (2.500 g) and unidentified decomposition products. Analogous observations were made for a reaction in benzene solution.

Photolysis of 5-Phenyloxazole (29).—A solution of the oxazole (29) (665 mg) in ethanol (400 ml) was irradiated. After 13 h, evaporation left an oil which was chromatographed on silica gel (chloroform) to give two fractions. The first, after chromatography [benzene–light petroleum (2 : 1)], gave 4-phenyloxazole (20) (19 mg). The second gave benzoic acid (10 mg).

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