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PHOTOINDUCED REACTIONS—LXXX

PHOTOCHEMISTRY OF 2-ISOXAZOLINES[a]

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Abstract—Upon irradiation at 253·7 nm, 2-isoxazolines undergo three types of formal [2+2] cycloreversions, in addition to 1,2-bond cleavage followed by further transformation. To determine whether the localized excitation of a particular chromophore is responsible for each type of reaction, the effects of sensitizer, quencher and excitation wave-length were examined with selected 2-isoxazolines. It is suggested that for 2-isoxazolines having a phenyl ketoxime group and a 4-aryl and/or 5-aryl group an excited singlet state of the 4- or 5-aryl group is responsible for the formation of some products, while an excited singlet state of the phenyl ketoxime group is responsible for others.

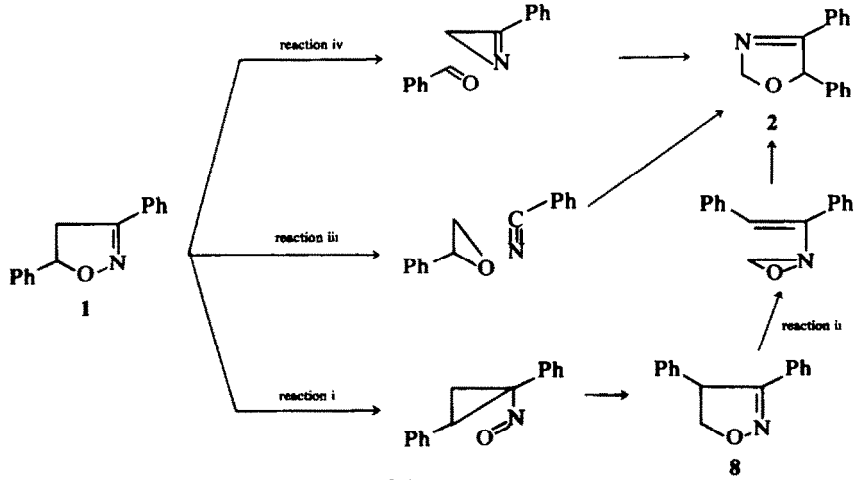
Photolysis products of substituted 2-isoxazolines. When solutions of 2-isoxazolines **1**, **5**, **6**, **8**, **11**, and **13** in acetonitrile were irradiated at 253·7 nm, they gave various products (Table 1). 3,5 - Diphenyl - 2 - isoxazoline **1** produced 4,5 - diphenyl - 3 - oxazoline **2** and β-aminochalcone as already reported,[3] in addition to 2-phenylquinoline **3**, benzonitrile, benzaldehyde, and styrene. Irradiation of the other substituted 2-isoxazolines gave products analogous to those from **1**. Among these products, acetonitrile oxide, which was trapped as 3 - methyl - 4,5 - trimethylene - 2 - isoxazoline[4] by irradiating **5** in the presence of cyclopentene in ether, is regarded as equivalent to 3-methyloxazirine, which is expected to form together with stilbene from **5** by reaction v.

The results indicate that the product distribution is largely depending upon substituents. Reaction i occurred to a small extent or not at all, and the corresponding product, an epoxide, could not be detected. Reaction iv occurred in most cases but reaction v predominated in the cases of 4,5-disubstituted 2-isoxazolines. Involvement of reaction iv in the rearrangement of **1**, **6**, and **8** into **2**, **7**, and **9**, respectively, will be discussed below.

Mechanistic consideration. For the rearrangement of **1** into **2**, the following three pathways were considered (Scheme 1). (1) Recombination of 2-phenylazirine and benzaldehyde formed by reaction iv.[3] (2) Recombination of benzonitrile and styrene oxide formed by reaction iii. (3) Type ii rearrangement of 3,4-diphenylisoxazoline **8**, formed through valence tautomerization involving reaction i.

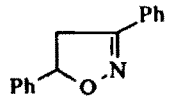
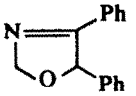
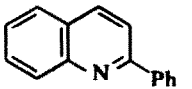
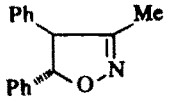
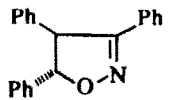
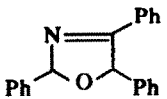
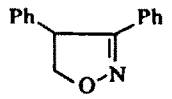
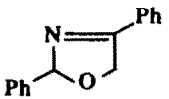
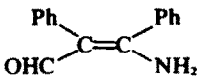
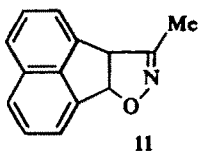
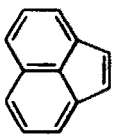
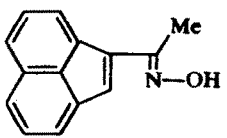
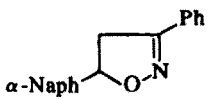
Path (2) was eliminated as no trace of **2** could be detected when a mixture of styrene oxide and benzonitrile was either irradiated under similar conditions or allowed to stand in the dark. Path (3) was eliminated because irradiation of **8** gave **9** and **10** but not **2** (Table 1). Path (1) had been supported by the fact that irradiation of an equimolar mixture of 2-phenylazirine and benzaldehyde afforded **2**,[3] which we confirmed. A similar photochemical formation of 3-oxazolines has also been reported.[5] Unfortunately it was impossible to detect the intermediate 2-phenylazirine by following the photochemical reaction of **1** by IR spectroscopy, as was expected since 2-phenylazirine and benzaldehyde reacted photochemically much faster than the conversion of **1** into **2**. However, irradiation of both **1** and **2** in the presence of a large excess of acrylonitrile gave 2 - phenyl - 4 - cyano - 1 - pyrroline **14**[6] in 29 and 42% yields, respectively, indicating that [2+2] cycloreversion into phenylazirine and benzaldehyde occurred with both **1** and **2**. On prolonged irradiation **2** gave a complex mixture of products including benzoic acid (17%) and phenanthro [9,10-d] -

[a]Part LXXIX, a preceding paper.[1] Part of this work was presented in a preliminary form.[2] For the introduction, see the preceding paper.[1]



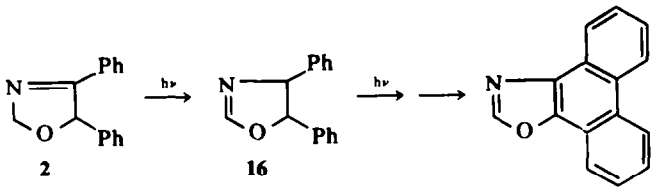
Scheme 1.

Table 1. Photolysis products from 2-isoxazolines

Compound	Concn ($\times 10^2$ M l^{-1})	Irrad time (hr)	Recovered (%)	Products (% yield)[a] Type iii	Type iv	Type v	Others
 **1**	4·0	24	24	PhCN (2·0)	 **2**(19)	$PhCH{=}CH_2$ (1·6)	 **3**(15)
 **5**	4·3	24	59	—	PhCHO (1·1) PhCHO (1·0)	$PhCH{=}CHPh$[b] (66) $MeC{\equiv}N{\rightarrow}O$[c] (29)	$PhCOCH{=}C(NH_2)Ph$ **4** (3) —
 **6**	3·3	25	31	PhCN (0·6)	 **7**[d](28)	$PhCH{=}CHPh$[e] (39)	—
 **8**	3·6	24	trace	—	PhCHO (0·7)  **9**(6)	—	 **10**(86)
 **11**	4·7	29	79	—	—	 (57)	 **12**(9)
 **13**	4·6	62	49	—	α-Naph—CHO (12)	α-Naph—$CH{=}CH_2$ (16)	—

[a]Yields were calculated on the basis of the reacted starting material. [b]Cis:trans = 1:1. [c]Trapped as a cyclopentene adduct (see Text). [d]Cis:trans[5] = 1·6:1. [e]Cis:trans = 2:1.

oxazole **15** (3%). Benzoic acid may originate from benzaldehyde, and **15** from **16** which can be formed by a 1,3-hydrogen shift of **2** as observed in the case of Δ^2-pyrazoline.[7]

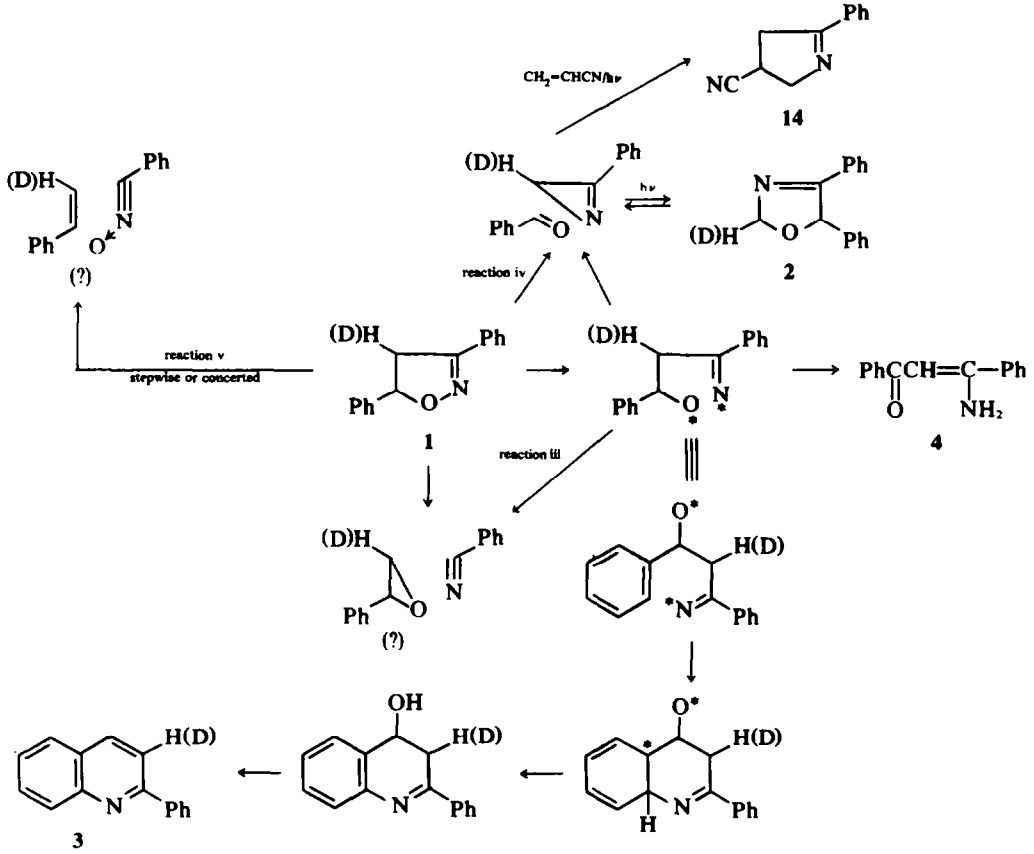


2 **16** **15**

All the products from reactions iii and iv as well as **4** and **10** may be attributed to the primary cleavage (homolytic or heterolytic) of the N–O bond of isoxazolines, as seen in the photoreaction of isoxazoles,[8] followed by the successive bond cleavage at the C3–C4 bond (reaction iii) and at the C4–C5 bond (reaction iv) or by intramolecular hydrogen shift in the cases of **4** and **10**. The one-step route leading to an azirine and an aldehyde or to a nitrile and an epoxide may be also possible. These pathways are shown in Scheme 2 for the photoreaction of **1**.

conditions gave **2**-d (1·2 D at C-2), **3**-d (1·0 D at C-3), and unlabeled benzaldehyde, the recovered **1**-d showed no deuterium scrambling. Unlabeled **3** was not detected by NMR spectroscopy, indicating that the C-4 proton of **1**-d had been released more readily than deuterium. This experiment was also consistent with path (1) of Scheme 1 for the formation of **2**.

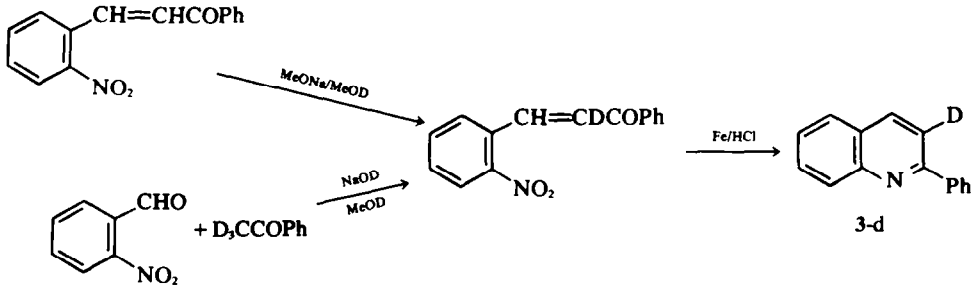
The position and content of deuterium in the above products were determined by NMR analysis. Three ring protons of **2** appeared as an AB_2 pattern at τ 4·24 (B_2 part) and 4·07 (A part) with J_{AB} = 5 Hz. Comparison of the J value with that of **9** (Experimental) showed that the two protons at C-2 of **2** correspond to the B_2 part and the one at C-5 to the A part. The NMR spectrum of **2**-d revealed one proton in the B_2 region, thus determining the position



Scheme 2.

The formation of **3** from **1** can also be attributed to primary N–O bond cleavage, followed by intramolecular cyclisation (Scheme 2). An analogous transformation has been observed in the photolysis of 3,5 - diphenyl - 1,2,4 - oxadiazole leading to 2 - phenyl - 4 - quinazolone.[9] This scheme was supported by a deuterium labeled experiment. Thus, irradiation of **1**-d (1·3 D at C-4) under similar conditions of the deuterium. This was supported by the mass spectrum of **2**-d showing a strong M^+–PhCHO peak at *m/e* 118, in contrast to that of **2** at *m/e* 117. The NMR spectrum of **3**-d showed almost complete disappearance of a doublet at τ 2·25 (J = 8·5 Hz) which was present in **3**. The position of deuterium was unequivocally established by a synthesis of **3**-d by reductive cyclization[10] of

2-nitrochalcone-α-d, which was prepared by applying two known methods, i.e. monodeuteration[11] of 2-nitrochalcone and condensation[12] of *o*-nitrobenzaldehyde with acetophenone - ω - d_3[13] as shown below.



The formation of the fragmentation products from the formal [2+2] reactions iii, iv, and v of 2-isoxazolines (Scheme 2), there are two possible routes, namely concerted or stepwise. A definite conclusion is difficult to draw from the available data. However, considering the fact that acetonitrile oxide could be trapped with cyclopentene in the photolysis of **5** but not in the case of **11**, it may be supposed that type v fragmentation of **5** leading to acetonitrile oxide and stilbene takes place concertedly but that of **11** leading to acenaphthylene stepwise. The much lower yield of amino ketone **4** from **1** than amino aldehyde **10** from **8** may imply that type iv fragmentation of **1** takes place more concertedly than that of **8**.

There are many reports[14] on the photochemistry of bichromophoric molecules in which the chromophores are not directly conjugated. In the present case, 2-isoxazoline **6**, which is trichromophoric (two phenyl and a Ph–C=N–O– groups), underwent mainly two types of reactions, iv and v, while bichromphoric **8** underwent a selective reaction to give **10** in high yield. In order to determine whether or not the localized excitation of a particular chromophore was responsible for each type of reaction, the effects of sensitizer, quencher, and excitation wave-length were examined for three selected compounds, **6**, **8**, and **13** (Table 2).

It can be seen from the data that irradiation through Pyrex (>ca 290 nm) selectively excited the phenyl ketoxime (PKO) group of **6** and **8**, because alkylbenzene does not absorb over 290 nm, and at this wavelength the naphthyl group of **13** is excited (cf. ϵ_{294} 7800 and ϵ_{316} 700 for 1-ethylnaphthalene[15]). Irradiation with a low-pressure mercury lamp with a Vycor housing (mainly 253·7 nm) caused excitation of both PKO and aryl groups at C-4 or C-5 in all these compounds. Compare λ_{max}^{EtOH} 245 nm (ϵ 10000) for acetophenone oxime,[16] 261 nm (ϵ 7000) for 1-ethylnaphthalene,[15] and 260 nm (ϵ 530) for ethylbenzene.[17]

With *trans* - 3,4,5 - triphenyl - 2 - isoxazoline **6**, the following observations were made. (a) On irradiation at 253·7 nm both type iv and type v products were obtained, irrespective of the initial concentration of **6** (Nos 1 and 2, Table 2). (b) Irradiation through Pyrex yielded the type v product but no type iv product, regardless of reaction temperature (Nos 3 and 4, Table 2), indicating that excitation of the PKO group is responsible, at least in part, for the formation of type v products, while excitation of a phenyl group at C-4 or C-5 is responsible for the formation of the type iv product. (c) The formation of type iv and type v products was neither quenched by piperylene (No 5, Table 2) nor sensitized by a triplet sensitizer such as benzophenone and xanthone (Nos 6 and 7, Table 2), which have a higher triplet energy, 69 and 74·2 kcal mol^{-1} respectively, than that expected for the PKO group (cf. $E_T < 60$ kcal mol^{-1} for benzaldoxime[18]). (d) Irradiation in benzene at 253·7 nm, under conditions such that 98·5% of the incident light was absorbed by benzene, caused efficient fragmentation into type v products (No 8, Table 2).

The experimental results, (a), (b), and (c), suggested that type v products may be formed from an excited singlet state of the PKO chromophor of **6**, and that reaction iv may not involve the excitation of the PKO group but possibly occurs through an excited singlet state of a phenyl group at C-4 or C-5. In experiment (d), benzene should act as a singlet sensitizer which may transfer the singlet energy to the PKO group but not to the 4- or 5-phenyl group. There has been ample evidence for singlet sensitization with benzene,[19] including the benzene-sensitized valence isomerization of indoxazene (1,2-benzisoxazole).[20] Photooxygenation of **6** gave tribenzamide and further decomposition products (No 9, Table 2) by the following reaction sequence.

With 3 - phenyl - 5 - (α - naphthyl) - 2 - isoxazoline **13**. (a) Irradiation at 253·7 nm gave both type iv and v products (No 10, Table 2). (b) Irradiation through Pyrex (more than 90% of the incident light excites 5-naphthyl group) gave almost exclusively type iv product (No 11, Table 2), eliminating the possible participation of the excited 5-aryl group in the type v reaction. (c) Xanthone-sensitization was ineffective and neither type iv nor type v product was formed (No 12, Table 2), while benzene-sensitization occurred efficiently to give both types of

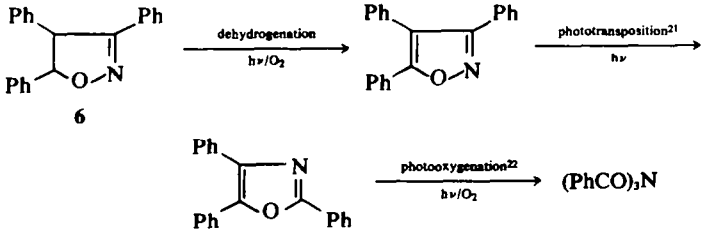


Table 2. Photolysis of 2-isoxazolines **6**, **8**, **13** under various conditions[a]

Expt. No.	Additive	Solvent (ml)	Concn ($X10^2$M l^{-1})	Irradn. conditions: Light source[b]	Irradn. conditions: Time (hr)	Products (% yield)[c]: Recovered	Type iii	Type iv		Type v		Others
trans-3,4,5-Triphenyl-2-isoxazoline **6**: ϵ_{254} 9500; ϵ_{300} 170; ϵ_{320} 0.							PhCN	PhCHO	**7**	PhCH=CHPh	Phenanthrene	$(PhCO)_3N$
1[d]	—	MeCN (220)	3·3	A	25	31	0·4	0·4	19[e]	20[f]	—	0
2	—	MeCN (1000)	0·10	A	25	0	nd	nd	8	Total 27		0
3	—	MeCN (200)	3·1	B	113	82	0	0	0	0	2	1
4	—	MeCN (100)	3·0	B	130 at 95°	93	0	0	0	0	4	0·9
5	Piperylene (0·107M l^{-1})	MeCN (14)	2·5	A[g]	27	22	nd	nd	33[h]	38[i]	0	nd
6	Benzophenone ($6·35 \times 10^{-2}$M l^{-1})	MeCN (90)	3·7	B[j]	62	~98	trace	0	0	0	2	0·3
7	Xanthone ($3·74 \times 10^{-2}$M l^{-1})	MeCN (15)	2·1	C[g,k]	46	~100	0	0	0	0	0	0
8	—	C_6H_6 (3450)	0·10	A	57	38	0	0	0	23[l]	6	0
9	Under air	MeCN (350)	0·98	C	280	0	trace	0	0	0	0	29 $(PhCO)_2NH$ 7 PhCOOH 12
3-Phenyl-5-(α-naphthyl)-2-isoxazoline **13**: ϵ_{254} 11700; ϵ_{300} 2900; ϵ_{320} 180.							PhCN	α-Naph–CHO		α-Naph–CH=CH_2		
10[d]	—	MeCN (240)	4·6	A	62	49	0	6		8		
11	—	MeCN (200)	2·1	B	46	68	0	3·5		trace		
12	Xanthone ($2·56 \times 10^{-2}$M l^{-1})	MeCN (180)	2·0	B[k]	43	81	0	0		0		
13	—	C_6H_6 (1600)	0·041	A	23	7	nd	12		22		
3,4-Diphenyl-2-isoxazoline **8**: ϵ_{254} 8300; ϵ_{300} 170; ϵ_{320} 0.							PhCN		**9**			**10**
14[d]	—	MeCN (100)	3·6	A	24	2	trace		6			86
15	—	MeCN (15)	1·1	C[g]	34	64	nd		0			16
16	Xanthone ($2·96 \times 10^{-2}$M l^{-1})	MeCN (15)	1·1	C[g,k]	50	92	nd		0			0

[a]The photolysis was done at room temperature, unless otherwise specified. Abbreviation nd denotes the compound was not determined. [b]A: 10-W low-pressure mercury lamp with Vycor housing. B: 100-W high-pressure mercury lamp (Pyrex filter). C: 450-W high-pressure mercury lamp (Pyrex filter). [c]Yields are based on the initial amount of the starting material. [d]Taken from Table 1. [e]Cis:trans = 8:5. [f]Cis:trans = 2:1. [g]Irradiated externally. [h]Cis:trans = 6:5. [i]Cis:trans = 4:5. [j]An aqueous solution of potassium biphthalate (5·0 g l^{-1}) was circulated through a cooling jacket. [k]A solution of naphthalene in isooctane (12·8 g l^{-1}) was used as a filter. [l]Cis:trans = 5:1.

products (No 13, Table 2), indicating again that benzene acts as a singlet sensitizer. Thus it appears, in accordance with the suggestion for **6**, that the excited states of the PKO and 5-naphthyl groups are responsible for the formation of type v and iv products, respectively, and that singlet states are possibly involved in the formation of both types of products.

With 3,4 - diphenyl - 2 - isoxazoline **8**. (a) In contrast to **6** and **13**, irradiation at 253·7 nm gave the type iv product in addition to **10** but no type v product (No 14, Table 2). (b) Irradiation through Pyrex yielded only **10** (No 15, Table 2). (c) The photoreaction was not sensitized with xanthone (No 16, Table 2). The results imply that an excited state of the 4-phenyl group, possibly a singlet state, is responsible for the formation of the type iv product, and that an excited singlet state of the PKO group is involved, at least in part, in the formation of **10**.

In conclusion, no general rule may be made for the photoreactions of 2-isoxazolines, since the problems of interaction between different chromophores in both the ground and excited states of these molecules are still unsolved. However, since the product distribution is dependent on the substituents, the following features are important for 2-isoxazolines having PKO and aryl groups.

1. Type iv reaction leading to products via the primary cleavage of C1–C2 and C4–C5 bonds possibly occurs through a singlet excited state of the 4- or 5-aryl group.

2. Type v reaction leading to products via the primary cleavage of C3–C4 and C1–C5 bonds occurs possibly through a singlet excited state of the phenyl ketoxime group.

3. The formation of **10** resulted from C1–C2 bond cleavage of **8** involved, at least in part, a singlet excited state of the phenyl ketoxime group.

EXPERIMENTAL†

Materials. All 2-isoxazolines were prepared according to the literature methods. 3,5-diphenyl- **1**,[23] m.p. 74–75° (lit.[23] 75°); 4,5 - diphenyl - 3 - methyl - **5**,[24] b.p. 144–146°/1 mmHg (lit.[24] 137°/0·11 mmHg); 3,4,5-triphenyl- **6**,[24] m.p. 145–146·5° (lit.[25] 140–141°); 3,4-diphenyl- **8**,[24] m.p. 121–122° (lit.[24] 121–121·5°); 3 - methyl - acenaphtho[1,2-d] - **11**,[26] m.p. 138·5–139·5° (lit.[26] 130°); 5 - (α - naphthyl) - 3 - phenyl - **13**,[27] b.p. 145° (bath temp)/10^{-4} mmHg, (lit.[27] m.p. 62°). These compounds gave satisfactory spectral and microanalytical data. 3,5 - Diphenyl - 2 - isoxazoline - 4 - d **1**-d was prepared by applying Henrich's method.[28] Thus, to a soln of chalcone (5 g) in 30 ml MeOD was added a soln of hydroxylamine hydrochloride (3 g) and KOH (5 g) in 20 ml MeOD. After refluxing for 1 hr, the mixture was filtered. The filtrate was evaporated to dryness to give a residue which was mixed with water (100 ml) and extracted with ether (3 × 100 ml). The ethereal layer was dried (Na_2SO_4) and evaporated to dryness. The residue (5 g) was recrystallised from EtOH (20 ml)-ligroin (10 ml), then from EtOH to give 1-d as colourless crystals (0·8 g), m.p. 73–74·5°. The deuterium content was estimated by NMR analysis to be 63% (1·3 D) at C-4 and 8% (0·08 D) at C-5.

All solvents and piperylene were distilled before use. Commercial benzophenone and xanthone were used without further purification.

Preparative photolysis of 2-isoxazolines. Irradiation was carried out with a 10 W low-pressure mercury lamp (Vycor housing, mainly 253·7 nm) under nitrogen and external water cooling. After removing the solvent under reduced pressure, the residue was separated by chromatography.

†For general descriptions, see ref 1 (except a JASCO IRA-1 spectrometer was used for IR and a Shimadzu UV-200 spectrometer for UV).

A soln of **1** (1·52 g) in acetonitrile (170 ml) was irradiated for 24 hr and the photo-products chromatographed on silica gel (50 g). Elution with 300 ml pet ether–benzene (2:1) afforded 125 mg of a yellow oil from which benzaldehyde (1·1%) and benzonitrile (2·0%) were isolated by VPC (20% PEG-6000 on 40–50 mesh Celite 545; 140°; 1 atm cm^{-2} gauge) and identified by IR. Further elution with 400 ml pet ether–benzene (1:1) followed by preparative TLC (30:1 pet ether–EtOAc) yielded **3** (150 mg, 15%), m.p. 78–80° (lit.[10] 85–86°) and recovered **1** (320 mg; 24%). Further elution with benzene (300 ml) and then with $CHCl_3$ (800 ml), followed by preparative TLC (15:1 pet ether–EtOAc) gave **2** (190 mg, 19%), m.p. 85·5–87° (lit.[3] 82·5–83·3°), and **4**[3] (45 mg, 3%) as an oil, which showed satisfactory spectral and microanalytical data. From this eluate and the subsequent one with acetone, an intractable brown material (440 mg) was obtained. Styrene, identified by IR, was isolated by VPC (Silicone DC 550 (20%) on 60–80 mesh Celite 545; 120°; 0·4 atm cm^{-2}) and the yield was estimated to be 1·6% by VPC analysis of the photolysis mixture obtained by the irradiation of **1** under the same conditions followed by removing most of the solvent carefully through a Vigreux column.

A soln of **5** (2·23 g) in acetonitrile (220 ml) was irradiated for 24 hr. The photolysis products were chromatographed on silica gel (70 g). Elution with 350 ml pet ether–benzene (2:1) followed by preparative TLC (pet ether) afforded *cis*-stilbene (230 mg, 33%) and *trans*-stilbene (230 mg, 33%), identified by IR. Elution with 200 ml pet ether–benzene (1:1) gave a yellow oil (90 mg) which was found to contain benzaldehyde (1·0% yield) by VPC. Further elution with the same solvent mixture (1 l) and then with benzene (200 ml) yielded **5** (1·305 g, 59%). Successive elution with $CHCl_3$ and acetone gave an intractable brown material.

Irradiation of 5 in the presence of cyclopentene. A soln of **5** (1·6 g) and cyclopentene (20 ml) in 200 ml ether was irradiated for 24 hr, followed by separation by CC and TLC ($CHCl_3$) to give 3 - methyl - 4,5 - trimethylene - 2 - isoxazoline[4] (110 mg, 29%), which was identical with an authentic sample[4] (IR), in addition to ca 1:1 mixture of *cis*- and *trans*-stilbenes (260 mg, 47%) and **5** (860 mg, 54%).

A soln of **6** (2·17 g) in acetonitrile (220 ml) was irradiated for 25 hr and the products separated by CC on silica gel (70 g). Elution with 600 ml pet ether–benzene (4:1) followed by preparative TLC (petroleum ether) gave *cis*-stilbene (220 mg, 26%) and *trans*-stilbene (110 mg, 13%). Further elution with benzene (250 ml) gave a yellow oil (65 mg) which was found by VPC to contain benzaldehyde (0·7%) and benzonitrile (0·6%). Further elution with benzene (800 ml) and then with $CHCl_3$ (200 ml) afforded **6** (620 mg, 31%). Further elution with $CHCl_3$ (1 l) followed by preparative TLC (benzene) yielded *trans*-**7** (150 mg, 11%), m.p. 99–109·5° (lit.[5] 107–108°) and *cis*-**7** as an oil (240 mg, 17%, lit.[5] m.p. 30–31°), the IR spectra of which were identical with those of authentic saples.[5] Further elution with $CHCl_3$ and acetone gave an intractable material (290 mg).

A soln of **8** (0·80 g) in acetonitrile (100 ml) was irradiated for 24 hr. The crude product mixture was crystallised from ca 1:1 benzene–pet ether to give **10** (580 mg), m.p. 131–133° (lit.[29] 127°), the spectral data agreed with those in the literature.[29] The residue from the mother liquor was chromatographed on silica gel (10 g). Elution with benzene (70 ml) afforded a trace of **8** (TLC). Further elution with benzene (100 ml) gave **9** (51 mg, 6%) as colourless crystals (benzene–pet ether), m.p. 100·5–101·5°. [m.p. 85·5–87° previously reported[2] was erroneus.] The structure of **9** was assigned from the spectral properties analogous to those of **2**.[2] (Found: C, 80·39; H, 5·79; N, 6·02. $C_{15}H_{13}NO$ requires: C, 80·69; H, 5·87; N, 6·27%). Further elution with 400 ml 1:1 benzene–$CHCl_3$ afforded **10** (110 mg, total yield 86%). No trace of **2** was detected in these fractions. On hydrolysis with hydrochloric acid **10** gave desoxybenzoin (94%), m.p. 56–57°, as described in the literature.[29]

A soln of **11** (2·17 g) in acetonitrile (220 ml) was irradiated for 29 hr. The photolysis mixture was chromatographed on silica gel (80 g). Elution with 500 ml pet ether–benzene (2:1) afforded acenaphthylene (190 mg, 57%), identified by IR. Further elution with benzene (400 ml) followed by preparative TLC (benzene) yielded a reddish yellow solid (50 mg, 2%), which was recrystal-

lised from benzene–pet ether (1:1) to give yellow crystals, m.p. 122–123·5°. Structure **12** was tentatively assigned from the spectral properties. IR (Nujol): 3200 (OH), 960 (N–O), 845 and 775 cm^{-1} (aromatic ring); NMR ($CDCl_3$) τ: 1·72 (1H, dd, J = 6 and 1 Hz), 2·08–2·68 (6H, m), ca 2·0 (1H, broads, disappeared with D_2O, OH), 7·65 (3H, s, CH_3); λ_{max}^{EtOH} 406 nm (ϵ 2040) and 332 nm (ϵ 13000); *m/e* 209 (M^+, RI. 32), 193 (61), 178 (100), 117 (76). (Found: C, 80·26; H, 5·37; N, 6·72. $C_{14}H_{11}NO$ requires: C, 80·36; H, 5·30; N, 6·69%.) Further elution with benzene (900 ml) and then with 800 ml 1:5 $CHCl_3$–benzene gave **11** (1·72 g, 79%). Further elution with $CHCl_3$ and acetone gave an intractable brown material (220 mg). The yield of **12** did not increase by prolonged irradiation and **12** was not transformed into acenaphthylene by photolysis at 253·7 nm.

Similar photolysis of **11** in the presence of cyclopentene in ether (200 ml) followed by the chromatographic separation, yielded acenaphthylene and **12**, but no 3 - methyl - 4,5 - trimethylene - 2 - isoxazoline could be detected.

A soln of **13** (3·01 g) in acetonitrile (240 ml) was irradiated for 62 hr and the photo-products separated on silica gel (120 g). Elution with 400 ml pet ether–benzene (1:1) gave 1-vinylnaphthalene (130 mg, 16%) identified by IR. Further elution with benzene (700 ml) followed by preparative TLC (3:1) pet ether–benzene or 15:1:0·2 pet ether–EtOAc–acetic acid) gave α-naphthaldehyde (105 mg, 12%) identified by IR, **13** (1·46 g, 49%) and an unknown substance (45 mg). This substance was not 2 - phenyl - 5,6 - benzoquinoline[30] (NMR and UV). Finally, successive elution with benzene and $CHCl_3$ yielded an intractable material (740 mg).

IR spectral monitoring of the photoreaction of **1**. Photolysis of **1** was carried out in the same manner as described above. Aliquots taken from the photolysate after 3, 6, 9 and 24 hr irradiation, were concentrated under reduced pressure and submitted for IR analysis (acetonitrile). None showed an absorption at 1745 cm^{-1} which is assignable to the C=N bond of 2-phenylazirine.[31]

Preparation of **2** *from 2-phenylazirine and benzaldehyde.* A quartz tube containing a solution of 2-phenylazirine[31] (138 mg) and benzaldehyde (115 mg) in acetonitrile (10 ml) was stoppered after flushing with nitrogen and irradiated externally with a 10 W low-pressure mercury lamp with Vycor housing for 24 hr. Evaporation of the solvent, followed by preparative TLC ($CHCl_3$) of the residue, yielded **2** (28 mg, 23% based on benzaldehyde) in addition to the recovered 2-phenylazirine (48 mg) and benzaldehyde (56 mg). Irradiation of a soln of **1** in acetonitrile under similar conditions yielded a trace of **2** (TLC and IR). Similar irradiation of a soln of equimolar amounts of styrene oxide and benzonitrile in acetonitrile did not give **2**.

Photolysis of **1** *in the presence of acrylonitrile.* A soln of **1** (2·00 g) and acrylonitrile (50 ml) in acetonitrile (180 ml) was irradiated with a 10 W low-pressure mercury lamp for 48 hr. Chromatographic separation of the product mixture on silica gel (80 g) afforded **1** (350 mg), benzaldehyde (45 mg), benzonitrile (55 mg), 2-phenylquinoline **3** (200 mg), and β-aminochalcone **4** (60 mg). Elution with $CHCl_3$ gave 2 - phenyl - 4 - cyano - Δ^1 - pyrroline (550 mg), purified by preparative TLC (3:1 benzene–EtOAc) followed by crystallisation from CCl_4–acetone, m.p. 100–102 (lit.[6] 95–96°). The NMR, IR and MS agrees with those reported.[6]

Photolysis of **2** *in the presence of acrylonitrile.* As a control experiment, a soln of **2** (410 mg) in acetonitrile (70 ml) was irradiated for 96 hr as above. After evaporation of the solvent, preparative TLC ($CHCl_3$) gave benzoic acid (35 mg), **2** (35 mg) and phenanthro - [9,10 - d]oxazole (15 mg), m.p. 147–153° (aq MeOH) (lit.[32] 152°), which was identical with an authentic sample[32] (IR). No trace of **1** could be detected.

A similar irradiation of **2** (280 mg) and acrylonitrile (20 ml) in acetonitrile (90 ml) for 46 hr followed by preparative TLC (5:1 benzene–EtOAc) gave **2** (185 mg) and 2 - phenyl - 4 - cyano - Δ^1 - pyrroline (30 mg).

Photolysis of **1**-*d.* A soln of 1-d (0·74 g) in acetonitrile (150 ml) was irradiated for 13·5 hr under the same conditions as described in the photolysis of **1**. After similar work up, **3**-d (79 mg, 11%), m.p. 85–87·5°, **2**-d (93 mg, 13%), m.p. 85·5–86·5°, unlabeled benzaldehyde (4 mg, 1·1%) and 1-d (59 mg, 8%) were obtained. The position and content of the deuterium in these compounds were determined by NMR and mass-spectroscopic analyses as follows. NMR (CCl_4): **2**-d: 62% (1·2 D) at C-2; 7% (0·07 D) C-5. **3**-d: signal intensity at τ 2·25 (1H, d, J = 8·5 Hz) of **3** decreased over 90%. Recovered **1**-d: 63% (1·3 D) at C-4; 7% (0·07 D) at C-5. Benzaldehyde: less than 16% (0·16 D) of the CHO proton. MS: **2**-d; 224 (M^+, RI 0·2), 121 (M–PhCN, 100), 118 (M–PhCHO, 40), 117 (12). [**2**; 223 (M^+, 0·3), 120 (M–PhCN, 100), 117 (M–PhCHO, 61).] The data showed that most of the D of **2**-d was present at C-2.

2 - *Nitrochalcone* - α - d. (i) According to the method[11] for the monodeuteration of chalcone, 2-nitrochalcone (425 mg)[10] in anhydrous ether (40 ml) was mixed with a soln of Na (11 mg) dissolved in MeOH (10 ml) under cooling with ice water and stirred for 48 hr. A small amount of solid precipitated was filtrated off and the filtrate evaporated under reduced pressure. The residue was taken up in $CHCl_3$ (40 ml) and the soln washed quickly with cold water (20 ml) and dried (Na_2SO_4). Evaporation under reduced pressure gave a brown solid, which was crystallised from EtOH to give 2 - nitrochalcone - α - d (245 mg, 58%), m.p. 124–125° (lit. m.p. of undeuterated 2-nitrochalcone, 122–123°[10]). The NMR showed complete disappearance of the doublet (τ 2·66, J = 15 Hz) of undeuterated 2-nitrochalcone and broadening of another (τ 1·80, J = 15 Hz).

(ii) According to the method[12] for the condensation of benzaldehyde with acetophenone - 2,2,2 - d_3. A soln of *o*-nitrobenzaldehyde (1·18 g) and acetophenone - 2,2,2 - d_3[13] (1·10 g) in MeOD (10 ml) was treated with 40% NaOD in D_2O (1·8 ml) and D_2O (5·2 ml) under cooling with ice water for 3 hr. The solid formed was filtered off and washed with EtOH (20 ml), the combined filtrates were evaporated under reduced pressure to give a brown solid (255 mg), which was submitted to preparative TLC (5:1 benzene–$CHCl_3$) followed by crystallisation from EtOH to give the titled compound (7 mg, 0·5%). The IR spectrum was identical with that of the sample obtained above.

2 - *Phenylquinoline* - 3 - d **3**-d. 2 - Nitrochalcone - α - d (52 mg) was converted to **3**-d by a known method,[10] omitting the procedure for the isolation of **3**-d hydrochloride. Thus, the reaction mixture was filtered and the filtrate evaporated to dryness. The residue was triturated with 2·5% aq ammonia (6 ml) and collected by filtration. The residue dissolved in EtOH (10 ml) was filtered again and evaporated to give a brown solid (44 mg), which was purified by preparative TLC (benzene) to afford **3**-d (18 mg) as a colourless solid. The IR and NMR spectra were identical with those of **3**-d obtained by the photolysis of **1**-d.

Photolysis of 2-isoxazolines **6**, **8**, *and* **13** *under various conditions.* (Table 2). External irradiation was carried out in a Pyrex tube (light source B and C) or a quartz tube (A), which was stoppered after passing nitrogen through a sample solution. Products were isolated by CC and/or preparative TLC and identified by spectroscopic and TLC techniques.

Experiment No 9 (Table 2) was performed as follows. A soln of **6** (1·02 g) in acetonitrile (350 ml) was irradiated under air with occasional shaking. The product was submitted to CC (silica gel, 40 g). Elution with 400 ml pet ether–benzene (1:1) gave an oil (12 mg) which was found by TLC and IR to contain a trace of benzonitrile. Successive elution with the same solvent mixture (300 ml), benzene (1 l) and $CHCl_3$ (200 ml), followed by preparative TLC (1:10 pet ether–benzene) yielded tribenzamide (325 mg, 29%), m.p. 216–218° (lit.[33] 208°) and benzoic acid (155 mg, 12%), identified by IR. Further elution with 200 ml $CHCl_3$–acetone (10:1) followed by preparative TLC (50:1 $CHCl_3$–acetone) afforded dibenzamide (55 mg, 7%), m.p. 149·5–151° (lit.[34] 147°). Further elution with the same solvent system and then with acetone gave an intractable material (300 mg) which was not further examined.

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