

Table II. Irradiations of 3-Methylindoxazene^a

Solvent	Time, min	Comments
H ₂ O	20	MB (83%) absorption
EtOH	10	MB (94%) absorption
C ₆ H ₁₂ ^b	30	MB (40%) absorption
pH 4.6	10	Only MB absorption

^a MB = 2-Methylbenzoxazole; solute concentrations were 10^{-4} M; solutions were irradiated with 254-nm lamps. Yields based on the uv absorption of 2-methylbenzoxazole at 270 nm.
^b Solution irradiated with 300-nm lamps.

phenol (reaction a) and an aqueous solution of 9×10^{-3} M cyanophenol and 2.7×10^{-4} M indoxazene (reaction b) were degassed and irradiated with a 300-nm source for 20 min. Tlc analysis (methylene chloride) of the ether extract of reaction a revealed the presence of only benzoxazole (R_f , DNP color, and uv spectrum). Tlc analysis of reaction b revealed the presence of a comparable

yield of benzoxazole along with salicylaldehyde and indoxazene. The indoxazene-sensitized formation of benzoxazole was not observed; the added indoxazene was absorbing 2–5% of the light. Furthermore, any indoxazene that was formed in reaction a should have been detected since a 3% yield could be detected when admixed with the 2-cyanophenol (reaction b).

Irradiations of 3-Methylindoxazene. (a) The photolysis of 3-methylindoxazene was carried out under a variety of conditions and the reactions were followed by uv spectra. The results are tabulated in Table II. (b) A 150-ml solution of 3-methylindoxazene (1.6×10^{-3} M) in ethanol was irradiated at 300 nm for 45 min. The solvent was distilled *in vacuo* and the 2-methylbenzoxazole was isolated by preparative tlc (methylene chloride–cyclohexane, 3:1) and identified by R_f values and uv spectrum.

Acknowledgment. We thank Dr. James Kuder for preparing some of the compounds used in this study. This work was supported by Grants GM 15915 CA 14511 and a Career Development Award GM 6380 (to J. P. F.) from the National Institutes of Health.

Mechanisms of the Photochemical Rearrangements of Ortho-Substituted Benzene Derivatives and Related Heterocycles¹

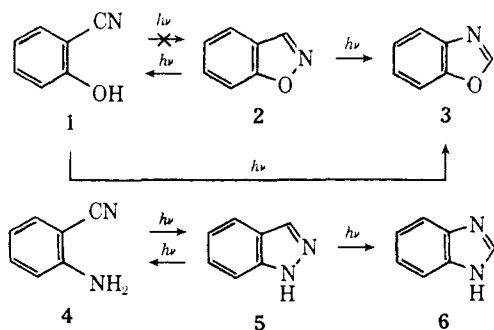
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Abstract: The mechanisms of the photochemical rearrangements of isoxazoles, 2-cyanophenol, pyrazoles, and anthranilonitriles have been investigated using low-temperature techniques. Isonitrile **14** was detected by ir (2130 cm^{-1}) and uv in the photoconversion of indoxazene (**2**) to benzoxazole (**3**). Compound **14** was further identified by independent synthesis and hydrolysis to the formanilide **15** in acid. 2-Cyanophenol (**1**) is also formed on photolysis of **2**; however, no intermediate could be detected in this conversion. Quenching and sensitization studies suggest that the formation of **3** proceeds from the singlet and **1** from the triplet excited states. The solvent dependence of the reaction suggests that **3** is formed from an initial π, π^* excitation and **1** is formed from an n, π^* excitation. The photoconversion of **1** to **3** may also proceed by **14** as shown by the uv spectrum of the reaction mixture after irradiation at -77° . No intermediates were identified in the photochemical conversion of indazoles to benzimidazoles and anthranilonitriles using the above techniques. Emission measurements of the singlet and triplet energies of all the compounds used in this study are reported.

In the accompanying paper we reported our observations on the scope of the photochemical rearrangement of ortho-substituted benzene derivatives.¹ Some of the findings are summarized in Scheme I. The

Scheme I



intermediates and excited states in the photocyclization of 2-cyanophenol (**1**) and anthranilonitrile (**4**) and the

(1) Chemical Evolution. XVII. For the previous paper in this series, see J. P. Ferris and F. R. Antonucci, *J. Amer. Chem. Soc.*, **96**, 2010 (1974).

photoisomerization of indoxazene (**2**) and indazole (**5**) are discussed in this report.^{2,3}

Azirines have been isolated as intermediates in the photochemical conversion of 3,5-diarylisoxazoles (**7**) to oxazoles (**9**).⁴ Sensitization studies suggest that **7** and **8** photoequilibrate by the triplet excited state while **9** is formed from **8** via the singlet state. It has been suggested that the high energy ground states **10** and **11** may be intermediates in these transformations.^{4,5} Azirines have been detected or postulated as intermediates in the photorearrangement of a number of other isoxazoles.⁶

No intermediates have been isolated in the photo-

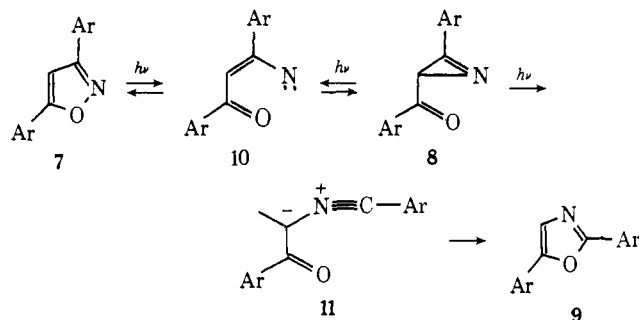
(2) A portion of this work has been reported in preliminary form: J. P. Ferris, F. R. Antonucci, and R. W. Trimmer, *J. Amer. Chem. Soc.*, **95**, 919 (1973).

(3) This research is described in greater detail in the Ph.D. dissertation of F. R. Antonucci, Rensselaer Polytechnic Institute, 1972.

(4) B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, **89**, 6911 (1967).

(5) B. Singh, A. Zweig, and J. B. Gallivan, *J. Amer. Chem. Soc.*, **94**, 1199 (1972).

(6) D. W. Kurtz and H. Schechter, *Chem. Commun.*, 689 (1966); H. Wamhoff, *Chem. Ber.*, **105**, 748 (1972); R. H. Good and G. Jones, *J. Chem. Soc. C*, 1196 (1971); H. Hiraoka and J. Picone, *Proc. Int. Congr. Pure Appl. Chem.*, 23rd, **93**, 222 (1971).



chemical rearrangement of pyrazoles and indazoles to imidazoles and benzimidazoles, respectively.^{7,8} Different photoproducts are obtained from N-substituted imidazoles depending on the position of the substituent. N(1)-alkylated indazoles yield only N-alkylamino-benzonitriles, while N(2)-alkylated indazoles yield N(1)-alkylated benzimidazoles.⁷ Indazole (5) yields both products on irradiation. These data suggest that the intermediate or excited state formed during the photo-rearrangement is dependent on the nitrogen substitution, and both pathways are available to indazole because of a facile tautomeric shift of the N-H hydrogen.

Results and Discussion

Photolyses at Low Temperatures. When a liquid film or Nujol mull of indoxazine (2) is irradiated at -77° in a low-temperature cell,⁹ characteristic infrared absorption bands are observed at 3350 ($-\text{OH}$), 2220 ($-\text{CN}$) and 2130 ($\text{N}\equiv\text{C}$) (*Figure 1*).¹⁰ When the cryostat is warmed to 0° , the absorption bands at 3350 and 2130 cm^{-1} assigned to isonitrile 14 disappear and a new band appears at 1065 cm^{-1} which is one of the major peaks in the infrared spectrum of benzoxazole (3). The peak at 2220 cm^{-1} , assigned to the nitrile grouping of 2-cyanophenol (1), did not change in intensity on warming the irradiation cell to 0° . No ir bands developed at 1740 – 1800 or 1650 – 1665 cm^{-1} characteristic of either 2-substituted^{4,11} or 2-unsubstituted azirine,¹² respectively. A small amount of 2-unsubstituted azirine might not be detected because of the strong absorption bands at 1650 cm^{-1} in 2 (*Figure 1*). The formation of 1 and 3 was confirmed by tlc analysis and uv spectral measurements on the product mixture obtained from the low-temperature photolysis.

When the photolysis was performed at -196° instead of -77° for the same length of time, there was an increase in the ratio of 1 to 14 as shown by a decrease in the intensity of the 2130 cm^{-1} ($-\text{N}\equiv\text{C}$) peak. This temperature effect suggests that another ground state intermediate is formed first which is thermally converted to isonitrile 14. The absence of a temperature

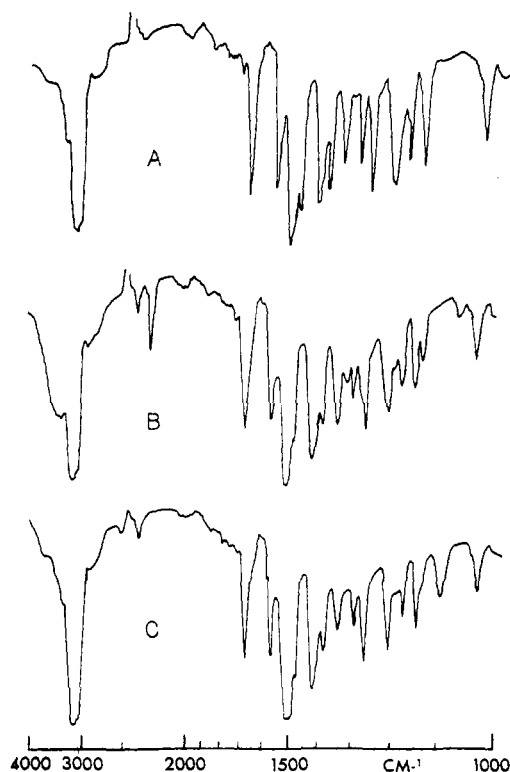
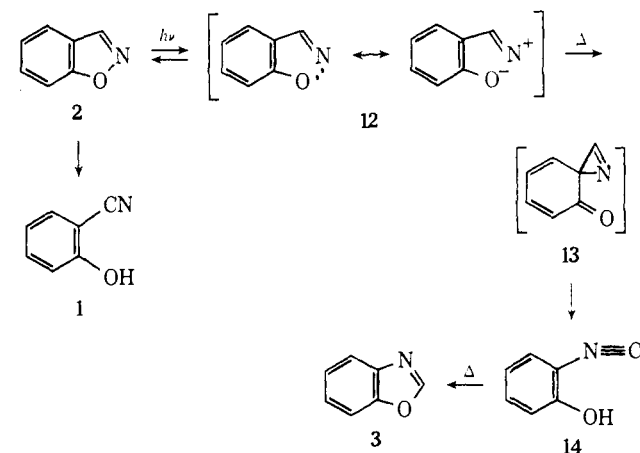


Figure 1. Low-temperature infrared study of the photoisomerization of indoxazine to 2-hydroxyphenyl isocyanide at -77° : curve A, before irradiation at -77° ; curve B, after a 3-hr irradiation at -77° ; curve C, after warming to room temperature.

effect for the formation of 2-cyanophenol suggests that it is formed directly from 2.

The observed isonitrile and hydroxyl bands in the infrared are consistent with structure 14, a compound which, as was observed, could be expected to cyclize readily to 3 on warming with loss of both hydroxyl and isonitrile absorption (Scheme II).^{4,13,14} The inter-

Scheme II



mediate that is formed prior to 14 may be either 12 or 13 by analogy to the reaction scheme of Singh and Ullman;⁴ however, there is no evidence for either structure.

Support for structure 14 was obtained by its independent synthesis by the dehydration of 2-hydroxy-

(7) H. Teifenthaler, W. Dörschelen, H. Göth, and H. Schmid, *Helv. Chim. Acta*, **50**, 2244 (1967).

(8) H. Labhart, W. Heinzlmann, and J. P. Dubois, *Pure Appl. Chem.*, **24**, 495 (1970); P. Bircher, E. R. Pantke, and H. Labhart, *Chem. Phys. Lett.*, **11**, 347 (1971).

(9) The cell used is that of H. H. Richtol and F. H. Klappmeier, *Appl. Spectrosc.*, **18**, 113 (1964); H. H. Richtol and F. H. Klappmeier, *J. Chem. Phys.*, **44**, 1519 (1966); O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).

(10) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 37.

(11) D. J. Cram and M. J. Hatch, *J. Amer. Chem. Soc.*, **75**, 33 (1953); G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

(12) K. Isomura, M. Okada, and H. Taniguchi, *Tetrahedron Lett.*, 4073 (1969); W. Bauer and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, **8**, 772 (1969).

(13) I. Hagedorn, U. Eholzer, and H. Eting, *Chem. Ber.*, **98**, 193 (1965).

(14) A. M. van Leusen, B. E. Hoogenboom, and H. Siderius, *Tetrahedron Lett.*, 2369 (1972), and references cited therein.

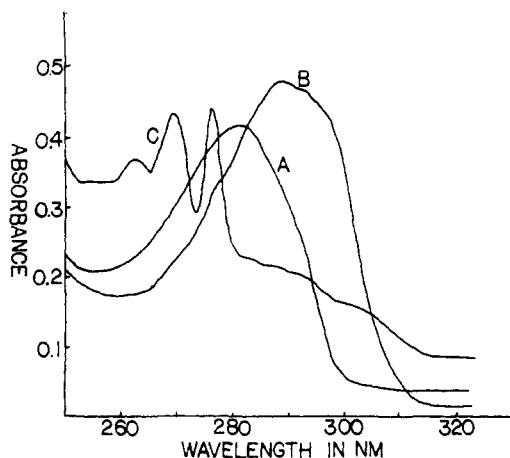


Figure 2. Low-temperature ultraviolet study of the photoisomerization of indoxazene to 2-hydroxyphenyl isocyanide at -77° : curve A, before irradiation at -77° ; curve B, after a 10-min irradiation at -77° ; curve C, after warming to room temperature.

formanilide (**15**) with phosgene at -77° .¹⁵ An isonitrile band was observed at 2130 cm^{-1} when the crude reaction mixture was maintained at -77° . The 2130-cm^{-1} band decreased in intensity when the product was warmed to room temperature. Benzoxazole was detected as a reaction product after warming suggesting that the isonitrile (**14**) that was formed cyclized to benzoxazole on warming.

The mechanistic conclusions drawn from the low-temperature ir studies were confirmed by uv analyses at -77° . Irradiation of indoxazene at -77° in ethanol resulted in the formation of a new maximum at 288 nm, which disappeared on warming to room temperature, and two peaks at 276 and 269 nm characteristic of benzoxazole (**3**) appeared in its place (Figure 2). The peak at 288 nm was assigned to **14** because benzoxazole was formed on warming the reaction solution and because, in results that will be discussed later, a similar maximum was observed when indoxazene is photolyzed at pH 3 and 4.

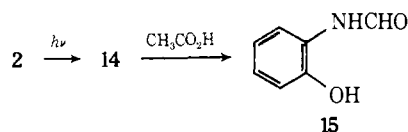
When the photolysis of **2** was performed at a lower temperature (-196°) in an ethanol-methanol (4:1) glass a peak was generated at 294 nm which remained on warming to room temperature. This maximum corresponds in wavelength to 2-cyanophenol. A smaller yield of benzoxazole was also noted from the intensity of the peaks at 276 and 269 nm when the glass was warmed to room temperature. These data are completely in accord with those obtained by ir measurements at -196° and are consistent with the steps outlined in Scheme I.

Many attempts were made to follow the photolysis of 2-cyanophenol by ir in a KBr pellet at low temperatures; however, no intermediates or products could be detected. It was possible to follow the low-temperature reaction by uv. Irradiation of 2-cyanophenol in methanol- H_2O (3:2) at -77° with a 300 nm source for 1 hr resulted in a decrease in absorption at 295 nm along with a shift from 295 to 293 nm. When this solution was warmed to room temperature benzoxazole (**3**) absorption at 276 and 269 nm was observed. These data are consistent with the photochemical formation

(15) F. Hoffmann, G. Gokel, D. Marquarding, and I. Ugi, "Isonitrile Chemistry," I. Ugi, Ed., Academic Press, New York, N. Y., 1971, pp 11-14.

of **14** (uv max 288 nm) from **1** followed by the thermal cyclization of **14** to **3**. The photochemical and thermal isomerization of isonitriles to nitriles has been reported;¹⁶ however, to our knowledge this is the first suggestion of the direction isomerization of a nitrile to an isonitrile. Other low-temperature photolysis studies were not as informative as those described above and are outlined in the Experimental Section.

Irradiation in Acidic Media. Irradiations in acidic media provided additional support for the conclusions reached by the low-temperature studies. Since isonitriles are known to react thermally with carboxylic acids to produce the corresponding formamide and acid anhydride,¹⁷ indoxazene **2** was photolyzed in glacial acetic acid for 10 min with the aim of trapping the isonitrile intermediate as the formanilide. A 14% yield of 2-hydroxyformanilide (**15**) was obtained.¹⁸



The formanilide **15** was not formed when **3** was allowed to stand in the dark in glacial acetic acid for 10 min.¹⁹

Brief irradiation of indoxazene (**2**) in dilute acid (pH 3 and 4) or in glacial acetic acid resulted in the formation of the characteristic benzoxazole absorption along with a maximum at 285 nm. The peak at 285 nm disappeared after a few minutes and at the same time the benzoxazole peaks at 276 and 269 nm increased in intensity. The maxima at 285 nm is assigned to the isonitrile **14** since the isonitrile would be expected to be more stable in acid than neutral media because the ionization of the phenol to phenoxide ion is repressed.

Although formanilide **15** was produced on irradiation of 2-cyanophenol (**1**) in aqueous acid medium it was not possible to conclude that **15** was formed from the isonitrile **14**. The photolysis of **1** to **3** is slow and comparable in rate to the acid hydrolysis of **3** to **15** in the dark.

It was not possible to detect products resulting from isonitrile intermediates upon irradiation of indazole (**5**) and 1- and 2-methylindazole in acetic acid or mildly acidic (pH 4) solution. Irradiation of these compounds in 1 N H_2SO_4 yielded products which appeared to be similar in structure to the photoproducts of substituted indazoles that were obtained in strong acid by Labhart, *et al.*, and Georganakis, *et al.*²⁰

Luminescence Measurements. The singlet and triplet energies of the compounds studied in this work were determined from fluorescence and phosphorescence spectra and are listed in Table I. The emission spectra of indazole (**5**) and benzimidazole (**6**) have been reported previously and our results are in agreement with these data.²¹ In the present study it was possible to

(16) D. H. Shaw and H. O. Pritchard, *J. Phys. Chem.*, **70**, 1230 (1966); B. K. Dunning, D. H. Shaw, and H. O. Pritchard, *ibid.*, **75**, 580 (1971); V. T. Ramakrishnan and J. H. Boyer, *Chem. Commun.*, 429 (1972).

(17) T. Saegusa and Y. Ito, "Isonitrile Chemistry," I. Ugi, Ed., Academic Press, New York, N. Y., 1971, p 73.

(18) The overall material balance is low because $\sim 75\%$ of the benzoxazole is lost in the work-up as shown by control experiments; see Experimental Section.

(19) E. Bamberger, *Ber.*, **36**, 2042 (1903).

(20) M. Georganakis, Th. Doppler, M. Märky, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **54**, 2916 (1971).

(21) T. Adler, *Anal. Chem.*, **34**, 685 (1962); J. W. Longworth, R. O. Rahn, and R. G. Schulman, *J. Chem. Phys.*, **45**, 2930 (1966).

Table I. Triplet and Singlet Energies of Compounds Studied^a

Compd	Glass	E_t , kcal/ mol	E_s , kcal/ mol
Indazole	MCIP	67.3	94
Indazole	EM	67.3	93.2
1-Methylindazole	MCIP	76.5 ^b	90.5
1-Methylindazole	MCIP	82 ^b	92
Benzimidazole	EPA	76	99.7
Benzimidazole	EM	nd ^d	101.7
Anthranilonitrile	EPA	nd ^d	81 ^b
Anthranilonitrile	EM	80 ^b	82 ^b
2-Cyanophenol	EPA	82 ^b	93 ^b
2-Cyanophenol	EM	nd ^c	93 ^b
Indoxazene	MCIP	82 ^b	94.4 ^b
Indoxazene	EPA	82 ^b	91 ^b
Indoxazene	EM	nd ^c	93.8
3-Methylindoxazene	EM	nd ^d	92
2-Methylbenzoxazole	EM	nd ^d	102.5
Benzoxazole	EPA	76	102.5
Benzoxazole	EM	75.7	103

^a MCIP = methylcyclohexane-isopentane (5:1 by volume); EPA = ether-isopentane-ethanol (5:5:2 by volume); EM = ethanol-methanol (4:1 by volume) at 77°K; nd = not determined; E_s and E_t at uv max of the 0-0 band unless otherwise indicated. ^b High energy end of emission band. ^c No phosphorescence. ^d Weak phosphorescence.

determine the singlet energy of indoxazene from luminescence data rather than from the absorption spectrum.²²

The ratio of phosphorescence to fluorescence decreased as solvent polarity increased for indoxazene (Table II,

Table II. ϕ_p/ϕ_f Ratio from Indoxazene Luminescence at 77°K^a

Glass	ϕ_p/ϕ_f
EM ^b	0
EPA	0.46
MCIP	0.63

^a EM = ethanol-methanol (4:1 by volume); EPA = ether-isopentane-ethanol (5:5:2 by volume); MCIP = methylcyclohexane-isopentane (5:1 by volume) at 77°K; quantum yield ratio was determined by measuring the area of the phosphorescence and fluorescence spectra.²³ ^b No phosphorescence noted, only fluorescence.

Figure 3).²³ These data suggest that the $^1(n,\pi)^*$ state is the lowest lying singlet excited state in nonpolar solvents while the $^1(\pi,\pi)^*$ is the lowest lying singlet in polar solvents.²⁴⁻²⁶ The solvent effect observed in the photolysis of indoxazene may be rationalized on the basis of these two different singlet excited states. The $^1(n,\pi)^*$, which predominates in nonpolar solvents, undergoes intersystem crossing to a triplet state which results in cyanophenol formation. The $^1(\pi,\pi)^*$ state predominates in hydroxylic solvents and yields benzoxazole (3) more rapidly than it undergoes intersystem crossing to the triplet state.

(22) S. Carson and H. Rosenberg, *J. Mol. Spectrosc.*, **32**, 242 (1969).

(23) The relative ratio in quantum yields was determined from the areas under the phosphorescence and fluorescence spectra: (a) C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **57**, 1894 (1961); (b) C. A. Parker and C. G. Hatchard, *Analyst (London)*, **87**, 664 (1962).

(24) (a) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley-Interscience, New York, N. Y., 1969, p 167; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 59; (c) M. Zander, "Phosphorimetry," Academic Press, New York, N. Y., 1968, p 91.

(25) E. C. Lim and J. M. H. Yu, *J. Chem. Phys.*, **45**, 4742 (1966).

(26) M. Kasha, *Radiat. Res., Suppl.*, **2**, 243 (1960).

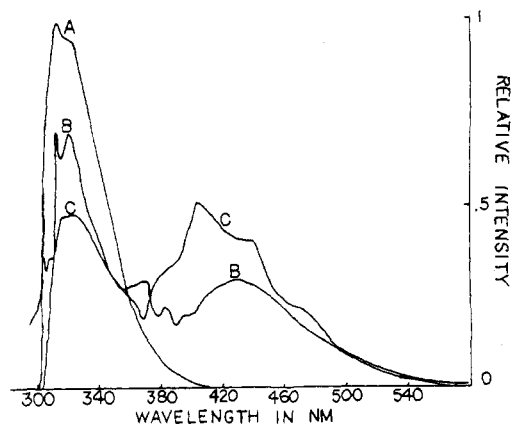


Figure 3. Luminescence spectra of indoxazene in EM, MCIP, and EPA at 77°K: curve A, luminescence spectrum in EM; curve B, luminescence spectrum in EPA; curve C, luminescence spectrum in MCIP.

Sensitization and Quenching Studies. The conversion of indoxazene (2) to cyanophenol in nonpolar solvents is inhibited by the triplet quenchers biacetyl ($E_t = 55$ kcal/mol),²⁷ piperylene ($E_t \sim 60$ kcal/mol),²⁸ and cyclohexene ($E_t \sim 70-75$ kcal/mol).^{29,30} The formation of benzoxazole (3) from indoxazene (2) in polar solvents is not inhibited by these same triplet quenchers (Table III). These data suggest that cyanophenol (1) is formed from the triplet excited state while benzoxazole (3) is formed from the singlet. Quenching by exciplex formation does not seem likely because a similar quenching efficiency is noted with three structurally different quenchers and because quenching was still observed at relatively low (0.01 M) piperylene concentrations.³¹

The rearrangement of indoxazene to benzoxazole in ethanol solution is sensitized by benzene but not acetone; however, the rearrangement of 3-methylindoxazene is sensitized by both benzene and acetone (Table IV). Since the singlet energy of acetone (≥ 92 kcal/mol)³² is less than that of indoxazene (94 kcal/mol) but is greater or equal to that of 3-methylindoxazene (92 kcal/mol), these data suggest that both acetone and benzene ($E_s = 109$ kcal/mol)⁵ are serving as singlet sensitizers.³²⁻³⁴ When the benzene sensitized reaction of indoxazene is done in a nonpolar solvent cyanophenol is the exclusive product. The solvent effect on products (benzoxazole formation in polar solvents, cyanophenol formation in nonpolar solvents) is identical with the sensitized and direct irradiation reactions of indoxazene, a result consistent with singlet sensitization.

(27) Reference 24b, p 132.

(28) Reference 24b, p 179.

(29) The E_t value of cyclohexene was assumed to be the same as that estimated for norbornene and cyclopentene: N. J. Turro in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Wiley-Interscience, New York, N. Y., 1969, p 138.

(30) There have been several reports of olefins being used as triplet quenchers: R. B. Cundall and P. A. Griffiths, *Chem. Commun.*, 194 (1966); G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **73**, 1815 (1969); I. H. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 5742 (1970).

(31) L. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966).

(32) M. A. Golub, *J. Amer. Chem. Soc.*, **91**, 4925 (1969).

(33) W. A. Henderson, Jr., R. Lopresti, and A. Zweig, *J. Amer. Chem. Soc.*, **91**, 6049 (1969); J. T. Dubois and F. Wilkinson, *J. Chem. Phys.*, **38**, 2541 (1963).

(34) P. S. Engel and B. M. Monroe *Advan. Photochem.*, **8**, 245 (1971).

Table III. Effect of Solvent and Quenchers on Photoproducts^a

Compd	Solvent	Quencher (M)	Time of irradiation, min	Heterocycles (%)	Cyano compd (%)
Indoxazene ^b	H ₂ O		15	B (70)	CP (13) ^f
Indoxazene	Cyclohexane		10	B (trace)	CP (80) (42) ^f
Indoxazene	Cyclohexane	Cyclohexene (0.1)	15	B (+)	CP (11) ^f
Indoxazene	Cyclohexane	Cyclohexene (1.0)	15	B (+)	CP (5) ^f
Indoxazene	Cyclohexane	Biacetyl (0.1)	15	B (+)	CP (10) ^f
Indoxazene ^c	Cyclohexane		50 ⁱ	B (36) ^e	CP (29) ^f
Indoxazene ^c	Cyclohexane	Cyclohexene (0.1)	50 ⁱ	B (43) ^e	CP (21) ^f
Indoxazene	Cyclohexane	Piperylene (0.1)	20 ⁱ	B (+)	CP (5) ^f
Indoxazene	Cyclohexane	Piperylene (0.01)	20 ⁱ	B (+)	CP (22) ^f
Indoxazene	EtOH	Piperylene (0.1)	4	B (+)	nd
Indoxazene	EtOH	Piperylene (0.01)	3	B (+)	nd
3-Methylindoxazene	Cyclohexane		30	MB (40)	
3-Methylindoxazene	H ₂ O		20	MB (83)	
3-Methylindoxazene	Cyclohexene (neat)		10	MB (+)	
3-Methylindoxazene	2-Methyl-1-butene (neat)		45	MB (+)	
3-Methylindoxazene ^d	Cyclohexane	Piperylene (0.1)	45	MB (+)	
2-Cyanophenol	H ₂ O		1020	B (62)	
2-Cyanophenol ^{d, g}	EtOH-H ₂ O (1:1)		60	B (+)	
2-Cyanophenol ^{d, g}	EtOH-H ₂ O (1:1)	Piperylene (0.01)	60	B (+)	
Indazole ^{d, g}	H ₂ O		170	BI (48)	A (trace)
Indazole ^{d, g}	Cyclohexane		10	BI (-)	A (56)
Indazole ^d	Cyclohexane	Cyclohexene (0.1)	10	BI (-)	A (+) ^h
Indazole ^d	Cyclohexane	Piperylene (0.1)	20	BI (-)	A (+) ^h
Indazole ^{d, g}	Cyclohexane	Biacetyl (0.1)	30	BI (-)	A (-)
1-Methylindazole ^{d, g}	Cyclohexane		30	MBI (-)	MA (62)
1-Methylindazole ^{d, g}	Cyclohexane	Cyclohexene (0.1)	10	MBI (-)	MA (+) ^h
Anthranilonitrile ^{d, g}	CH ₃ CN		195	BI (20), ^f I (trace)	
Anthranilonitrile ^d	CH ₃ CN	Piperylene (0.01)	180	BI (-), I (-)	

^a B = benzoxazole, CP = 2-cyanophenol, MB = 2-methylbenzoxazole, BI = benzimidazole, A = anthranilonitrile, MBI = 1-methylbenzimidazole, MA = *N*-methylantranilonitrile, I = indazole, (+) = reaction product observed but yield not determined, (-) = reaction product was not detected, nd = not determined if the reaction product was present. Solutions (10⁻⁴ M) were irradiated with a 300-nm source and the product yields were determined by the uv spectra of the reaction solution unless noted otherwise. ^b 6.2 × 10⁻⁴ M. ^c 10⁻³ M. ^d Degassed. ^e Yield determined by vpc on 10% SE 30 column. ^f Yield determined by uv spectra after separation by tlc on silica gel. ^g 254-nm light source. ^h Rate of product formation less than in absence of quencher. ⁱ Irradiation time incorrectly listed as 15 min in ref 2.

Table IV. Effect of Sensitizers on the Reaction Products^a

Compd	Solvent	Time of irradiation, min	Heterocycle (%)	Cyano compd (%)
Indoxazene	Benzene	30		CP (76)
Indoxazene	Benzene-EtOH (1:1)	15	B (13) ^d	CP (30) ^d
Indoxazene	Acetone	60	B (-)	CP (-)
3-Methylindoxazene	Benzene	30	MB (10) ^d	
3-Methylindoxazene ^b	Acetone	60	MB (25) ^d	
3-Methylindoxazene ^b	Ethanol + 10 ⁻³ M triphenylene	120	MB (-)	
2-Cyanophenol	Benzene	40	B (-)	
2-Cyanophenol	Benzene-EtOH (1:1)	30	B (-)	
2-Cyanophenol	Acetone	60	B (-)	
Indazole ^c	CH ₃ CN + 10 ⁻³ M benzophenone	3 days	BI (-)	A (-)
Indazole	Benzene	75	BI (-)	A (+)
Indazole ^b	Acetone	60	BI (-)	A (-)
1-Methylindazole	Benzene	60		MA (+)
1-Methylindazole ^b	Acetone	60		MA (-)
Anthranilonitrile ^b	Acetone	60	BI (-), I (-)	
Anthranilonitrile	Benzene	120	BI (-), I (-)	
Anthranilonitrile ^c	CH ₃ CN + 10 ⁻³ M benzophenone	3 days	BI (-), I (-)	

^a B = benzoxazole, CP = 2-cyanophenol, MB = 2-methylbenzoxazole, BI = benzimidazole, A = anthranilonitrile, MBI = 1-methylbenzimidazole, MA = *N*-methylantranilonitrile, I = indazole, (+) = reaction product observed but yield not determined, (-) = reaction product was not detected. Degassed 10⁻⁴ M solutions were irradiated with a 254 nm light source and the products were identified by uv spectra unless noted otherwise. ^b 300 nm light source. ^c 350 nm light source with Pyrex filter. ^d Yield determined by uv spectra after separation by tlc on silica gel.

The conversion of cyanophenol (1) to benzoxazole (3) is not quenched by piperylene. Presumably this reaction proceeds from the singlet excited state. The conversion of indazole (5) and 1-methylindazole to the corresponding anthranilonitriles is inhibited by piperylene, cyclohexene, and oxygen in nonpolar solvents

(Table III). However, unlike the quenching studies on indoxazene no increase in the yield of benzimidazole (6) was noted when indazole (5) was irradiated in the presence of these quenchers. Therefore, this quenching may be due to a chemical reaction between the excited state species and the quencher.

The photoisomerization of indazole (5) ($E_s = 94$ and $E_t = 67$ kcal/mol) to anthranilonitrile in a nonpolar solvent and benzimidazole in a polar solvent is sensitized by benzene (Table IV). Presumably benzene is serving as a singlet sensitizer since the products observed are the same as those formed by direct irradiation since neither acetone [$E_t = 79$ kcal/mol]³² nor benzophenone ($E_t = 68$ – 69 kcal/mol)³⁴ sensitize the photoisomerization of indazole.

Experimental Section^{3,35}

Luminescence Measurements. Luminescence measurements were made on 10^{-4} M solutions at 77°K using a spectrofluorimeter and cell constructed by Richtol and Klappmeier.⁹ All solvents used were of spectroquality grade and were checked for impurity emission before use. Anthranilonitrile, benzimidazole, and indazole were obtained from Aldrich Chemical Co. and used without further purification. Indoxazene, benzoxazole, and 2-methylbenzoxazole were distilled and 2-cyanophenol was recrystallized prior to use. The N-methylated indazoles and 3-methylindoxazene were prepared and purified as described previously.¹

Irradiation of 2-Cyanophenol in Glacial Acetic Acid. A 100-ml solution of 2-cyanophenol (8.4×10^{-3} M) in glacial acetic acid was irradiated at 300 nm for 4 days. The solvent was distilled *in vacuo* and the residue was fractionated by preparative tlc. No 2-hydroxyformanilide could be detected by tlc, DSA color test, or uv spectrum. A trace of benzoxazole and an unidentified compound, uv max (EtOH) 298, (base) 270 and 325 nm, were also isolated by tlc.

Irradiation of Indazole in Glacial Acetic Acid. A 250-ml solution of indazole (8.1×10^{-4} M) in glacial acetic acid was irradiated with a 254 nm light source for 30 min. The uv spectrum of the reaction solution revealed the presence of benzimidazole and indazole and these substances were isolated from the reaction mixture by preparative tlc.

Irradiation of Indazole in 1 N H₂SO₄. An aqueous solution of indazole (10^{-4} M) in 1 N H₂SO₄ was degassed and irradiated at 254 nm for 15 min. The photolysis was followed by uv spectra and formation of peaks at 305 and 252 nm was noted. Basification of the reaction solution resulted in formation of a peak at 410 nm; reacidification of the solution resulted in the formation of the 305- and 252-nm peaks again. This compound is assumed to be an aromatic aldehyde because of the similarity of its uv spectrum with that reported for hydroxyaldehydes of similar structure^{8,30} and because of a positive 2,4-dinitrophenylhydrazine test after separation by tlc (chloroform-ethanol, 7:1). Similar results were obtained when 1- and 2-methylindazole were irradiated in 1 N H₂SO₄.

Irradiation of Indoxazene in Acid Solution. A 100-ml solution of indoxazene (3.1×10^{-4} M) in glacial acetic acid was irradiated at 300 nm for 10 min. The solvent was distilled *in vacuo* and the reaction products separated by tlc (methylene chloride-ethyl acetate, 5:1). The compound, 2-hydroxyfermanilide (14%), was identified by comparison of R_f , DSA color test (orange), uv spectra (in acid and base), and ir spectrum with an authentic sample. Benzoxazole (10%) and 2-cyanophenol (10%) were identified by comparison of R_f and uv spectra. Yields were based on extinction coefficients from the material recovered from the tlc plate with >99% of indoxazene reacted. The benzoxazole yield is low due to loss of material during work-up; in a control run ~50% of benzoxazole is lost upon concentrating the glacial acetic acid and ~80–90% is lost after concentrating, tlc, and elution from the tlc plate.

Low-Temperature Irradiations Monitored by Infrared Spectra. The photolyses discussed in this section were conducted in a cryo-

stat⁹ and the course of the reactions was followed by ir. (a) A thin film of indoxazene (mull) was irradiated at 254 nm for 3.5 hr at -77° . Formation of the 2220- and 2130-cm⁻¹ peaks were noted as well as increase in the -OH region (3350 cm⁻¹), 1300 cm⁻¹ (increase), 1200 and 1100 cm⁻¹ (new). On warming to room temperature a new peak at 1065 cm⁻¹ formed which is one of the major peaks of benzoxazole. A preparative tlc (chloroform) was performed and benzoxazole and 2-cyanophenol were eluted from the plate. The compounds were identified by comparison of their R_f values and uv spectra with authentic samples. (b) A thin film of indoxazene (neat) was irradiated at 254 nm for 3 hr at -77° . A new peak was observed at 2130 cm⁻¹ (together with the nitrile peak at 2220 cm⁻¹) which on warming to room temperature disappeared. Tlc (methylene chloride) of the reaction product showed the presence of some indoxazene, benzoxazole, and a majority of 2-cyanophenol. (c) A thin film of indoxazene (neat) was irradiated at 2 nm for 2.5 hr at -196° . The infrared spectrum showed an increase in nitrile absorption at 2220 cm⁻¹, -OH region, and a peak at 1470 cm⁻¹. Only a slight increase in absorption was noted at 2130 cm⁻¹ which disappeared on warming to room temperature.

Irradiations of 3-Methylindoxazene. (a) A thin film of 3-methylindoxazene (mull) was irradiated at 254 nm for 3 hr at -77° . Peaks at 1695 and 1200 cm⁻¹ formed and disappeared on warming to room temperature; however, no peaks which could be assigned to 2-methylbenzoxazole were observed. (b) A thin film of 3-methylindoxazene (neat) was irradiated at 254 nm for 3 hr at -77° . Formation of the peak at 1695 cm⁻¹ was noted which disappeared on warming to room temperature.

Low-Temperature Photolyses Monitored by Ultraviolet Spectra. All of the photolyses discussed in this section were conducted in a low-temperature uv cell⁹ and the reactions were followed by uv spectra.

Irradiations of Indoxazene. An ethanol (95%) solution of indoxazene (10^{-4} M) was irradiated at 254 nm for 10 min at -77° . A peak at 288 nm formed which upon warming to room temperature is converted to benzoxazole (uv max 269 and 276 nm). (See Figure 2.) (b) An ethanol-methanol (4:1) glass of indoxazene (10^{-4} M) was prepared and irradiated at 254 nm for 15 min at -196° . A peak at 294 nm formed which remained on warming; some benzoxazole absorption was noted but not as much as in the experiment carried out at -77° . As in the low-temperature infrared studies, 2-cyanophenol formation is favored at -196° .

Irradiations of 2-Cyanophenol. A methanol-water (3:2) solution of 2-cyanophenol (10^{-4} M) was irradiated at 300 nm for 1 hr at -77° . A decrease in nitrile absorption was noted as well as a blue shift from 295 to 293 nm. Benzoxazole absorption at 276 and 269 nm was observed on warming the solution to room temperature.

Synthesis of 2-Hydroxyphenyl Isocyanide. A solution of 0.5 g of 2-hydroxyformanilide in 30 ml of methylene chloride and 20 ml of triethylamine was cooled to -77° and phosgene bubbled through the solution for 10 min. Salt formation was noted and the system flushed with nitrogen and then ammonia for 20 min. The reaction mixture was filtered with the filtrate being kept at -77° . The methylene chloride was distilled *in vacuo* at -77° , leaving a yellow semicrystalline oil; ir showed a 2130-cm⁻¹ peak which diminished on standing at room temperature for 5 min. Many other peaks were also noted over the entire spectrum, including a strong peak at 1750 cm⁻¹. To remove any traces of methylene chloride or triethylamine, the reaction mixture was concentrated at room temperature *in vacuo*. The infrared spectrum (neat) exhibited a weak absorption at 2130 cm⁻¹. Tlc (chloroform) analysis of this material showed the presence of benzoxazole which indicates that the 2130-cm⁻¹ peak remaining on warming is due to another isonitrile product.

Acid Hydrolysis of Benzoxazole. (a) An aqueous solution of benzoxazole (10^{-4} M) at pH 4 was allowed to stand at room temperature and the formation of 2-hydroxyformanilide was followed by uv spectra. Complete hydrolysis to the amide occurred within 24 hr. At pH 3 complete formation of the amide occurred within 3 hr. (b) A solution of benzoxazole (10^{-4} M) in glacial acetic acid was allowed to stand at room temperature for 4.5 hr and at 65° for 1 hr. No change was observed in the uv spectra of the solution.

Acknowledgment. We thank Professor H. Richtol for the use of his luminescence apparatus. This work was supported by Grants GM 15915 and CA 14511 and Career Development Award GM 6380 (to J. P. F.) from the National Institutes of Health.

(35) Most of the general experimental procedures are given in ref 1. Cyclohexane was distilled from lithium aluminum hydride and then passed through a silica gel column to remove traces of benzene.³⁶ Piperylene, biacetyl, and 2-methyl-1-butene were distilled immediately before use. Cyclohexene was treated with maleic anhydride, then lithium aluminum hydride, and was finally passed over alumina before use. Triphenylene was recrystallized from ethanol-ethyl acetate and sublimed. Benzophenone (Fisher) was used without further purification.

(36) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, N. Y., 1966, p 121.