# Photochemistry of Ortho-Substituted Benzene Derivatives and Related Heterocycles[1]

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Abstract: The scope of the photochemical cyclization of aromatic enaminonitriles and related systems has been investigated. The following photochemical transformations have been observed: β-aminocinnamonitrile to 4(5)-phenylimidazole (4c); 4-aminoimidazole-5-carbonitrile to 1,6-dihydroimidazo[4,5-d]imadazole (5); anthranilonitrile to indazole (7); N-methylanthranilonitrile to 1-methylindazole (10); N-phenylanthranilonitrile to carbazole (12); 2-cyanophenol to benzoxazole (15); 2-aminophenylacetylene to indole (17) and 2-aminoacetophenone (18); 2-hydroxyphenylacetylene to benzofuran (20) and 2-hydroxyacetophenone (21); salicylaldoxime to benzoxazole (15) and 2-cyanophenol (13); and 2-hydroxyacetophenone oxime to 2-methylbenzoxazole (27) and 3-methylindoxazene (28).

I midazoles may be prepared by the photochemical cyclization of enaminonitriles.[2] This photochemical transformation was first observed when the irradiation of diaminomaleonitrile (1) yielded 4-aminoimidazole-5-carbonitrile (2), a key step in a proposal for the chemical evolution of purines.[3] Aminoacrylonitrile (3a), β-aminocrotononitrile (3b), and β-aminocinnamonitrile (3c) are readily photolyzed to imidazole (4a),[2c] 4(5)-methylimidazole (4b),[2a] and 4(5)-phenyl-

a. R = H
b. R = CH₃
c. R = phenyl
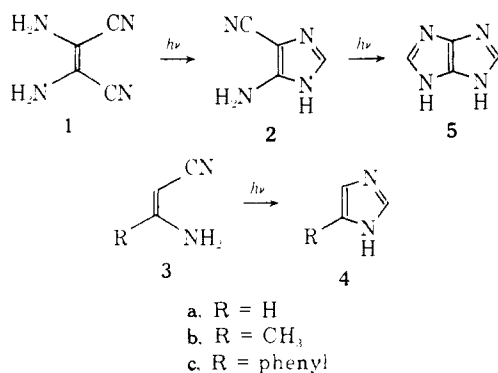
imidazole (4c), respectively. These data established that simple enaminonitriles such as 3 rearrange photochemically to imidazoles. We now report the results of an investigation of the photochemical rearrangement of enaminonitriles and related structures where the chromophore is part of an aromatic ring system.[4,5] Mechanistic studies are reported in an accompanying paper.[6]

Results and Discussion

Photolysis of 4-aminoimidazole-5-carbonitrile (2) at

254 nm gave a 20% yield of 1,6-dihydroimidazo[4,5-d]-imidazole (5), a result of particular interest in the area of chemical evolution in view of the central role of 2 in the proposed prebiotic synthesis of purines.[3,7] The structure of 5 was proved by the absence of a nitrile absorption band in the 2200-cm⁻¹ region of the infrared and the presence of only one signal at δ 7.72 in the nmr spectrum which did not exchange with D₂O. The resonance position of the structurally comparable proton at the 2 position of benzimidazole occurs at δ 8.30.[8] Furthermore, the mass spectrum of 5 is similar to the mass spectrum of 2 and is consistent with the stepwise loss of HCN from the molecular ion.

The irradiation of anthranilonitrile (6) resulted in the formation of indazole (7) and a 20% yield of benzimidazole (8). Analysis of the reaction mixture after
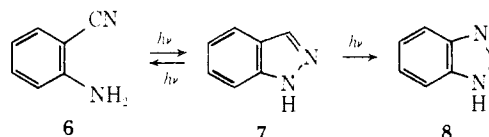
short irradiation times revealed that indazole is the initially formed product which is converted to benzimidazole on further irradiation.[9] This is the first example of pyrazole formation on irradiation of an enaminonitrile. Pyrazoles are not formed as intermediates in the photochemical rearrangement of aliphatic enaminonitriles.[2b]

Only 1-methylindazole (10) (17%) is obtained on irradiation of N-methylanthranilonitrile (9). No N-methylbenzimidazole could be detected, a result which is in agreement with the observation that photolysis of 10 yields only 9 and no N-methylbenzimidazole.[9]

A completely different reaction pathway was observed upon photolysis of N-phenylanthranilonitrile (11). Carbazole (12), formed by cyclization of the N-phenyl grouping, was obtained in 87% yield. This reaction is related to the oxidative photochemical con-

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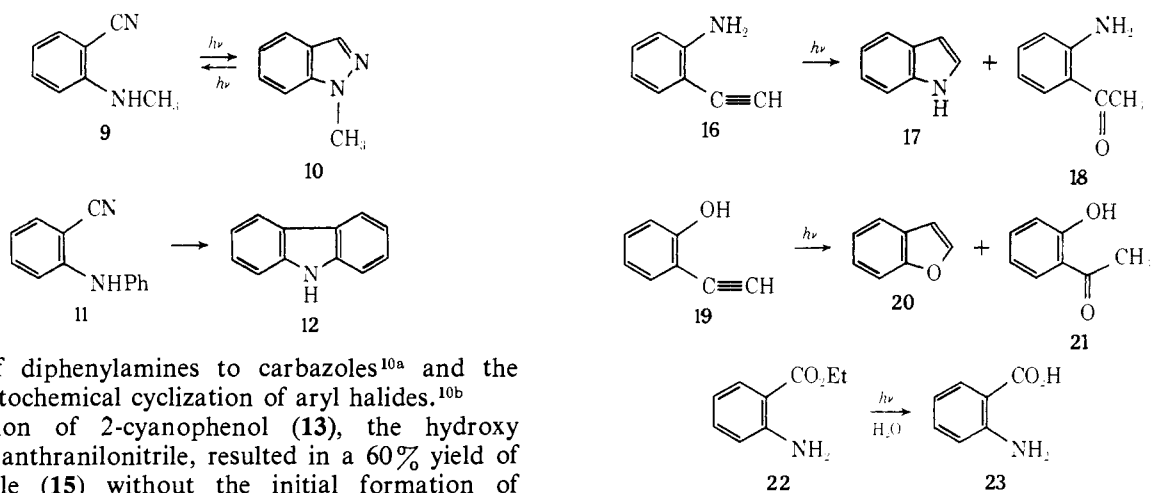
version of diphenylamines to carbazoles[10a] and the direct photochemical cyclization of aryl halides.[10b]

Irradiation of 2-cyanophenol (13), the hydroxy analog of anthranilonitrile, resulted in a 60% yield of benzoxazole (15) without the initial formation of
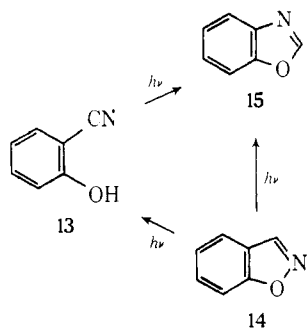
indoxazene (14).[11] When this photochemical transformation is carried out with low conversion under conditions where the 2-cyanophenol is absorbing over 95% of the light, 15 was the only detectable product. Furthermore, 13 does not sensitize the conversion of 14 to 15.

The photochemical cyclization was still observed when the cyano group of anthranilonitrile was replaced by an acetylene grouping (2-aminophenylacetylene (16)) or when both the cyano and amino groups are replaced with acetylene and hydroxyl groups (2-hydroxyphenylacetylene (19)). Indole (17) is obtained in 1–2% yield upon irradiation of 16 in cyclohexane solution. A 20% yield of 2-aminoacetophenone (18) was obtained when the photolysis was performed in aqueous solution. Benzofuran (20) (60%) and 2-hydroxyacetophenone (21) are obtained on irradiation of 19 in 10^{-2} M aqueous base. The photochemical hydration of the acetylene groupings in 16 and 19 may be due to participation of ortho amino[12] and hydroxyl[13] groupings. Anthranilic acid (23) is the main product formed in the photolysis of ethyl anthranilate (22) in aqueous solution.[5]

Photolysis of aromatic o-hydroxy oximes constituted a further investigation of the scope of the photocyclization. The photolysis of salicylaldoxime (24) has been reported to yield benzoxazole (15) in polar solvents and indoxazene (14) in hydrocarbon solvents.[14] We

did observe a very facile cyclization of 24 to 15 (75% yield) in aqueous solution. Benzoxazole was also the main product (72%) in aqueous base together with a 15% yield of 2-cyanophenol (13)[15] and a trace of salicylaldehyde (25).[16] No indoxazene (14) was ob-

served on irradiation of 24 in hexane solution; instead compounds 15, 13, and 25 were observed.

A trace of the corresponding indoxazene (28) was observed on irradiation of 2-hydroxyacetophenone oxime (26). However, the main product was 2-methylbenzoxazole (27). The ratio of compound 28 to com-

pound 27 was greater in the beginning of the reaction than at the end, suggesting that some of the initially formed 28 is photolyzed to 27. However, it was not possible to adjust the reaction conditions (initial concentration of 26 or the time of irradiation) where 27 was not observed as well. Therefore, we conclude that both 27 and 28 are formed directly on excitation of 26.

Attempted extension of the cyclization reaction to the preparation of 5-phenyloxazole (31) from benzoyl-

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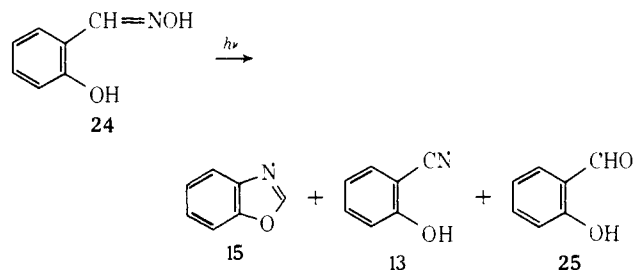
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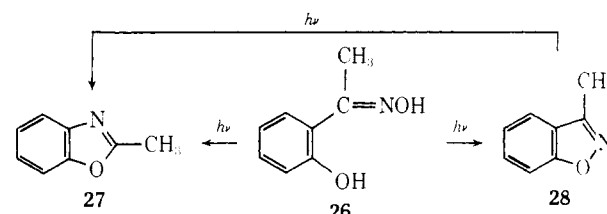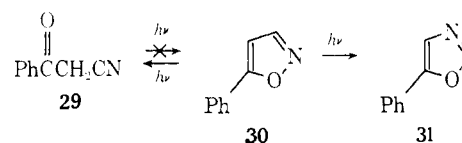(13) G. Fräter and H. Schmid, *Helv. Chim. Acta*, **50**, 255 (1967).

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acetonitrile (**29**) was unsuccessful. The reverse reaction, photolysis of **30** to **29** (32%) together with the formation of **31** (6%), was observed.

Experimental Section[5,17]

Materials. 1,1-Diamino-2,2-dicyanoethylene,[20] β-aminocinnamonitrile,[21] N-methylanthranilonitrile,[22] 2-hydroxyphenylacetylene,[23] 2-aminophenylacetylene,[24] salicylaldoxime,[25] 2-hydroxyacetophenone oxime,[25] 5-phenyl-1,3-oxazole,[26] 5-phenylisoxazole,[27] indoxazene,[28] 3-methylindoxazene,[29] 4-aminoimidazole-5-carbonitrile,[2a] 4(5)-phenylimidazole,[30] benzoylacetonitrile,[31] N-phenylanthranilonitrile,[9] and N-methylbenzimidazole[32] were prepared according to known procedures. The other compounds used in this investigation were obtained commercially and purified as necessary by recrystallization, distillation, or tlc.

1- and 2-Methylindazole. A procedure similar to that used to prepare N-methylbenzimidazole[32] was used to prepare 1- and 2-methylindazole. The reaction product was chromatographed over silica gel using chloroform-acetonitrile (5:1) as the eluent. The separation was followed by uv spectra and the fractions containing 1- and 2-methylindazole were combined separately and concentrated *in vacuo;* each crystallized on standing. 1-Methylindazole: mp 58–60° (lit.[33] 60–61°); uv max (EtOH) 255 (log ε 3.6), 263 (3.6), and 294 nm (3.7). 2-Methylindazole: mp 53–54° (lit.[33] 56°); uv max (EtOH) 273 (log ε 3.8) and 294 nm (3.8). The uv spectra of the two isomers were in accord with the spectra reported by Rousseau and Lindwall.[34]

1,6-Dihydroimidazo[4,5-d]imidazole. A 500-ml solution of 1.04 × 10⁻² M 1,1-diamino-2,2-dicyanoethylene in tetrahydrofuran was irradiated at 254 nm for 35 hr. The tetrahydrofuran was distilled *in vacuo* and the residue was chromatographed over silica gel using ether-methanol (5:1) as the eluent. The fractions giving the

(17) Irradiations were performed in a Rayonet photochemical reactor equipped with lamps with principal emission at 254, 300, or 350 nm. The following instruments were used for spectral measurements: Perkin-Elmer Infracord (ir), Unicam SP-800 or Beckman DK-2A (uv), Varian T-60 or A-60 (nmr), Hitachi RMU-6E (mass spectra). Solutions were degassed on a vacuum line using four freeze–pump–thaw cycles. Acetonitrile was purified by the procedure of O'Donnell, Ayres, and Mann.[18] Tetrahydrofuran was distilled from lithium aluminum hydride before use. Paper chromatography was carried out on Whatman 3MM paper and tlc was carried out on alumina G (Woelm) or silica gel (Mallinckrodt). Photoproducts were identified by direct chromatographic comparison with authentic samples. The product was further identified by the uv spectrum of the compound after elution from the chromatogram. Diazotized sulfanilic acid (DSA) was used to detect imidazoles,[19a] Folins reagent was used to detect amines,[19b] iodoplatinate was used to detect heterocycles,[19c] and 2,4-dinitrophenylhydrazine (2,4-DNP) was used to detect aldehydes and ketones.[19d]

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blue DSA test were combined and concentrated. The residue was chromatographed again over silica gel using chloroform-methanol (1:9) as the eluent. The fractions giving a blue DSA test were combined and concentrated giving 114 mg (20% yield) of 1,6-dihydroimidazo[4,5-d]imidazole as a tan solid. The sample was purified by recrystallization from ethanol: Folin test positive (purple-violet); mp 265° dec; uv max (MeOH) 210 (log ε 3.64) and 242 nm (3.79); ir (KBr) 3120, 2990, 2780, 1630, 1470, 1230, 952, and 800 cm⁻¹; nmr (DMSO-d₆) δ 3.70 (broad, 2, NH, exchanged with D₂O), 7.72 (s, 2, CH); mass spectrum (70 eV) m/e (rel intensity) 109 (6), 108 (100), 81 (16), 80 (3), 71 (4), 57 (2), 55 (4), 54 (16), 53 (5), 52 (2), 45 (3), 44 (4), 43 (5), 42 (2), 41 (4), 39 (4), 38 (4), 32 (5), 31 (12), 29 (6), 28 (13), 27 (5). It was not possible to obtain an analytically pure sample of 1,6-dihydroimidazo[4,5-d]imidazole as the free base. The ditosylate salt was prepared by dissolving 63 mg of the free base in 7 ml of warm acetonitrile-methanol (5:2) and removing the insolubles by filtration. To this solution was added a warm acetonitrile solution (3 ml) of p-toluenesulfonic acid (111 mg). The reaction mixture was warmed for 5 min and some solvent was removed by a stream of nitrogen until crystals appeared. The reaction mixture was refrigerated overnight and the crystals filtered and recrystallized from acetonitrile-methanol (10:1): mp 260° dec; ir (KBr) 3060, 2740, 1700, 1530, 1430, 1235, 1155, 1110, 1030, 1000, 900, 810, and 670 cm⁻¹; nmr (DMSO-d₆) δ 2.30 (s, 3, CH), 7.0–7.6 (quartet, 4, aromatic H), 8.40 (s, 1, CH). *Anal.* Calcd for C₁₈H₂₀N₄S₂O₇: C, 47.78; H, 4.46; N, 12.38. Found: C, 47.58; H, 4.40; N, 12.45.

The bicyclic imidazole **5** was also formed on direct photolysis of a 10⁻⁴ M solution of 4-aminoimidazole-5-carbonitrile (**2**) in acetonitrile for 10 min. Imidazole **5** was detected by its Rf value (BAW) and blue color when sprayed with DSA reagent.

Irradiation of β-Aminocinnamonitrile. (a) An acetonitrile solution of β-aminocinnamonitrile (1.17 × 10⁻⁴ M) was degassed and irradiated at 254 nm for a total of 2.5 hr. The formation of 4(5)-phenylimidazole was monitored by uv spectra and isosbestic points at 337, 275, 239, and 220 nm were observed. The product, 4(5)-phenylimidazole (60%), was isolated and identified by comparison of paper chromatography Rf (0.76 in BAW, DSA spray reagent (red)) and uv spectrum with an authentic sample. (b) When a degassed solution of β-aminocinnamonitrile (10⁻⁴ M) in ethanol was irradiated at 350 nm for 5.5 hr, the only change observed was a shift in the uv max from 288 to 283 nm; this blue shift is probably due to cis–trans isomerization.[2b] Only starting material was detected by paper chromatography (BAW) of the concentrated reaction solution.

Irradiation of N-Phenylanthranilonitrile. An ethanol-acetonitrile (1:4) solution of N-phenylanthranilonitrile (10⁻⁴ M) was degassed and irradiated at 254 nm for 10 min. The photolysis was followed by uv spectra and the uv absorption spectra of carbazole (uv max (EtOH) 294 (log ε 4.26) and 257 nm (4.32)) developed. The solution was concentrated and carbazole (87%) was identified by comparison of tlc (methylene chloride-hexane, 1:1) and uv and ir spectra with an authentic sample. Carbazole was also formed from the irradiation of 1-phenylindazole in which N-phenylanthranilonitrile[9] is the initial photoproduct.

Irradiations of Salicylaldoxime. (a) An aqueous solution of salicylaldoxime (3 × 10⁻³ M in 10⁻¹ M NaOH) was irradiated through Pyrex at 350 nm for 105 min. An aliquot of the reaction solution was diluted and the uv spectrum showed benzoxazole and 2-cyanophenol absorptions. Benzoxazole, 2-cyanophenol, salicylaldehyde, 2-hydroxyformanilide, and salicylaldoxime were separated from the reaction mixture by preparative tlc (chloroform) and were identified by tlc and uv spectra comparison with authentic samples. (b) A hexane solution of salicylaldoxime (3.1 × 10⁻⁴ M) was irradiated at 300 nm for 10 min. Benzoxazole, 2-cyanophenol, and salicylaldehyde were separated by preparative tlc and were identified by tlc and uv spectra comparison with authentic samples. (c) Irradiations of salicylaldoxime in both degassed and nondegassed water at 300 nm resulted in a 75% yield of benzoxazole as determined from its uv absorption. In aqueous base benzoxazole (75%) and 2-cyanophenol (15%) were detected as reaction products.

Irradiations of 2-Hydroxyphenylacetylene. (a) An aqueous solution of 2-hydroxyphenylacetylene (1.1 × 10⁻² M) in 10⁻² M NaOH was degassed and irradiated at 254 nm for 13 hr. The yellow solution was extracted with ether (100 ml) and the benzofuran (60%) was purified by preparative tlc (hexane). The purified sample was identified by tlc and uv spectra (uv max 242, 275, 282 nm and log ε 3.94, 3.25, and 3.25, respectively) comparison with an authentic sample. The basic solution (after ether extraction) was

acidified and extracted with ether (100 ml) and the 2-hydroxyaceto-phenone was purified by preparative tlc (hexane–methylene chloride, 1:2). The 2-hydroxyacetophenone (20%) was identified by tlc (positive test with 2,4-dinitrophenylhydrazine) and uv spectral (uv max (base) 360 and 255 nm and log ϵ 3.8 and 3.9, respectively; (acid) 253 and 324 nm and log ϵ 4.1 and 3.6, respectively) comparison with an authentic sample. (b) Irradiations of 2-hydroxyphenylacetylene (10^{-4} M) in degassed water at 254 nm resulted in a 60–68% yield of benzofuran. (c) Benzofuran was also detected when 2-hydroxyphenylacetylene was irradiated in degassed acetonitrile using either a 254 or 300 nm light source.

Thermal Stability of 2-Hydroxyphenylacetylene. (a) When an aqueous solution of 2-hydroxyphenylacetylene (10^{-4} M) in 10^{-2} M NaOH was refluxed for 2.5 hr some benzofuran absorption was noted by the uv absorption at 275 nm, but since the photochemical reaction occurs within minutes at 35° it is unlikely that the thermal formation of benzofuran is occurring during the course of the photolysis. (b) An aqueous acetonitrile solution of 2-hydroxyphenylacetylene (10^{-4} M) was refluxed for 2.5 hr with no change in its uv spectrum.

Irradiation of 2-Aminophenylacetylene. (a) A 100-ml solution of 2-aminophenylacetylene (7.2 × 10^{-4} M) in cyclohexane was irradiated at 300 nm for 15 min. Indole was separated from the reaction solution by preparative tlc and was identified by tlc (2,4-DNP, red-brown; DSA, yellow) and uv spectral (uv max (EtOH) 218 (log ϵ 4.44), 271 (3.79), and 287 nm (3.66)) comparison with an authentic sample. The total concentration of indole based on the 288-nm peak was 6 × 10^{-6} M which is equivalent to a 1–2% yield. (b) A 100-ml aqueous solution of 2-aminophenylacetylene (5 × 10^{-4} M) was irradiated at 300 nm for 15 min. The cloudy solution was extracted with ether and the combined ethereal solutions dried over MgSO$_4$ and concentrated and subjected to preparative tlc (methylene chloride). The product, 2-aminoacetophenone (20%), was extracted with ether, was separated by preparative tlc, and was identified by tlc (DNP, yellow-brown) and uv spectral (uv max (EtOH) 257 (log ϵ 3.84) and 367 nm (3.71)) comparison with an authentic sample. A trace amount of indole was present as shown by its R_f value and uv spectrum.

Irradiation of 5-Phenylisoxazole. (a) A 250-ml solution of 5-phenylisoxazole (1.03 × 10^{-2} M) in ether was irradiated at 254 nm for 40 min. The ether solution was washed with base and the ether was dried and concentrated to dryness and the residue was chromatographed on silica gel. Elution with CH$_2$Cl$_2$ resulted in (1) 40 mg of starting material, (2) 19 mg of an unknown compound, uv max (EtOH) 251 nm, (3) 21 mg (6%) of 5-phenyloxazole, respectively. The basic extract was acidified and extracted with ether to yield 106 mg (32%) of benzoylacetonitrile which was identified by ir, uv, and tlc comparison with an authentic sample. When the irradiation of 5-phenylisoxazole was performed at 254 nm in water, acetonitrile, or 1 N HCl, benzcylacetonitrile was the only product that could be identified.

Irradiation of Benzoylacetonitrile. A 100-ml solution of benzoyl-acetonitrile (2 × 10^{-2} M) in ether was irradiated with a 254-nm source until no more starting material could be detected in the uv (1.5 hr). No 5-phenylisoxazole was detected as a reaction product. The ether was concentrated and white crystals precipitated. This unknown material was recrystallized from ethyl acetate–cyclohexane: mp 212–214° taken slowly and 220–221° when taken fast; ir (KBr) 3450, 2275, 1335, 1055, 735, and 698 cm^{-1}; nmr (DMSO-d_6) δ 7.4 (s, aromatic H) 6.0, 2.2–3.8; mass spectrum (70 eV) m/e (rel intensity) 241 (5), 240 (32), 207 (6), 147 (21), 120 (6), 105 (29), 104 (55), 94 (79), 93 (16), 91 (57), 78 (27), 77 (62), 76 (11), 65 (19), 64 (21), 52 (11), 51 (100), 50 (20), 39 (24).

Anal. Found: C, 72.58; H, 5.44; N, 9.17.

Irradiation of 2-Hydroxyacetophenone Oxime. (a) A solution of 2-hydroxyacetophenone oxime (10^{-4} M) in 95% ethanol was irradiated at 300 nm for 5 min, and the photolysis was monitored by uv spectra. A peak at 395 nm developed as well as 2-methylbenzoxazole absorptions at 271 and 277 nm. (b) A 100-ml solution of 2-hydroxyacetophenone oxime (1.92 × 10^{-4} M) in 10^{-2} M NaOH was irradiated at 300 nm for 15 min. Preparative tlc (methylene chloride–cyclohexane, 3:1) resulted in the separation of 2-methylbenzoxazole (82%) and a trace amount of 3-methylindoxazene. Larger concentrations of 3-methylindoxazene were observed on shorter term irradiation. However, 2-methylbenzoxazole was always observed as well.

Irradiations of N-Methylanthranilonitrile. (a) A 100-ml solution of N-methylanthranilonitrile (2.42 × 10^{-3} M) in acetonitrile was degassed and irradiated at 254 nm for 4 days. The acetonitrile was distilled *in vacuo* and the product subjected to column chromatog-

raphy over silica gel using methylene chloride as the eluent. N-Methylanthranilonitrile (25%) and 1-methylindazole (17% based on recovered starting material) were separated and identified by comparison of R_f values and uv spectra with authentic samples. (b) The photolysis of N-methylanthranilonitrile was carried out in degassed solutions of water, ethanol, acetonitrile, and cyclohexane at 254 nm, and 1-methylindazole was detected as a product by uv spectral measurements.

Irradiations of 1-Methylindazole. Aqueous and cyclohexane solutions of 1-methylindazole (10^{-4} M) were degassed and irradiated at 254 nm. The photolyses were monitored by uv spectra and the yields (56% and 64% respectively) of N-methylanthranilonitrile were calculated from the maximum at ca. 254 nm.

Irradiations of 2-Methylindazole. Both aqueous and cyclohexane solutions of 2-methylindazole (10^{-4} M) were degassed and irradiated at 254 nm for 2–5 min. The formation of N-methylbenzimidazole was followed by uv spectra and essentially a quantitative yield was obtained.

Irradiations of Indazole. (a) The photolysis of indazole was carried out under a variety of conditions and the reactions were followed by uv spectra. The results are tabulated in Table I.

Table I. Irradiations of Indazole[a]

Solvent	Time, min	Comments[b]
Water*	170	BI (48%) absorption noted
CH$_3$CN*	170	BI (49%) and A (18%) absorption noted
C$_6$H$_{12}$	10	A (40%) absorption noted
C$_6$H$_{12}$*	20	A (56%) absorption noted

[a] * means degassed; BI = benzimidazole; A = anthranilo-nitrile; solute concentrations were 10^{-4} M; solutions were irradiated with 254-nm lamps. [b] Yields of benzimidazole and anthranilonitrile were based on the absorptions of the products when a maximum absorption was reached

(b) Acetonitrile solutions of indazole (10^{-4}, 10^{-3}, and 10^{-2} M) were degassed and irradiated at 254 nm for 70 min. Tlc analysis (ethyl acetate–benzene, 1:1) demonstrated the presence of both anthranilonitrile and benzimidazole in these reactions. It was calculated from the uv spectra that anthranilonitrile was absorbing 29, 10, and 2% of the light at the end of the photolysis.

Irradiations of Anthranilonitrile. (a) A 100-ml acetonitrile solution of anthranilonitrile (3.4 × 10^{-4} M) was degassed and irradiated at 254 nm for 5 hr. Benzimidazole and indazole were separated from the reaction mixture by preparative tlc (chloroform) and were identified by comparison of R_f's, color reaction with iodoplatinate reagent (blue), and uv spectra with authentic samples. A 20% yield of benzimidazole was estimated from the uv spectrum of the sample eluted from the preparative tlc plate. (b) Acetonitrile solutions of anthranilonitrile (10^{-4}, 10^{-3}, and 10^{-2} M) were degassed and irradiated at 254 nm for 7 hr. Tlc (ethyl acetate–benzene, 1:1) showed the presence of anthranilonitrile, benzimidazole, and indazole in the 10^{-4} M run. However, only anthranilonitrile and indazole could be detected in the 10^{-3} and 10^{-2} M photolyses; no benzimidazole was found even after a very careful and thorough tlc analysis.

Direct Irradiation of 2-Cyanophenol. (a) Irradiation of 2-cyanophenol in degassed acetonitrile, diglyme, and hexane solutions resulted only in the decrease in 2-cyanophenol absorbance. Decreasing yields of benzoxazole were observed when the irradiations were performed in water, ethanol–water, and ethanol solutions, respectively; a 62% yield was obtained from a 10^{-4} M aqueous solution using a 300 nm light source. (b) The possible direct formation of indoxazene which is subsequently converted to benzoxazole was investigated by irradiating 100 ml of a 5.3 × 10^{-4} M degassed, aqueous solution of 2-cyanophenol with 300-nm lamps for 12.5 hr. Weak benzoxazole absorption was noted on the side of the more intense 2-cyanophenol maximum in the uv. Preparative tlc (chloroform) of the ether extract revealed the presence of benzoxazole and the absence of indoxazene. Any indoxazene that was formed should have been photochemically stable since 2-cyanophenol was absorbing greater than 90% of the light at the end of the irradiation. From these data it is concluded that benzoxazole is formed directly on irradiation of 2-cyanophenol.

Attempted Indoxazene Sensitization of the Conversion of 2-Cyanophenol to Benzoxazole. An aqueous solution of 9 × 10^{-3} M cyano-

Table II. Irradiations of 3-Methylindoxazene[a]

Solvent	Time, min	Comments
H₂O	20	MB(83%) absorption
EtOH	10	MB(94%) absorption
C₆H₁₂[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.

Mechanisms of the Photochemical Rearrangements of Ortho-Substituted Benzene Derivatives and Related Heterocycles[1]
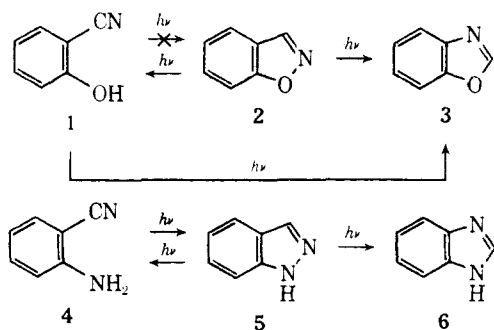
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Abstract: The mechanisms of the photochemical rearrangements of isoxazoles, 2-cyanophenol, pyrazoles, and anthranilonitriles have been investigated using low-temperature techniques. Isonitrile 14 was detected by ir (2130 cm⁻¹) and uv in the photoconversion 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

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-

(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).

(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).

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