was obtained 3.18 g of oily solid. Slurrying with benzene afforded 0.90 g (22.8%) of solid, mp 122–157°. Recrystallization from ethanol gave N-(*p*-chlorobenzenesulfonyl)-*p*-chlorobenzamide (XVI): constant mp 181–182°;[13] ir 3250 and 1690 cm^{-1}.

Evaporation of the solvent produced an oil.

Another reaction with the same ratio of II and $AlCl_3$ was carried out as above, except that the mixture was heated under reflux for 3.5 hr. A solid, 3.55 g, mp 75–129°, was obtained, which, after slurrying with benzene, gave 0.96 g (19.3%) of XVI: constant mp 179–181°; mmp 180–182° with XVI prepared at RT.

The filtrate was concentrated under reduced pressure and 1.36 g (31.4%) of solid was obtained. Recrystallization from ethanol gave a product with constant mp 147–149.5° which showed no NH or C=O absorption in the ir. The literature reported[14] *p,p'*-dichlorodiphenyl sulfone (XVII) to melt at 147.5°.

E. With Naphthalene.—A solution of 2.74 g (0.0126 mol) of XI in 20 ml of CS_2 was added dropwise at RT to 4.34 g (0.0316 mol) of $AlCl_3$ and 3.23 g (0.0253 mol) of naphthalene in 60 ml of CS_2 under N_2 during 20 min. After the mixture was stirred for an additional 3.5 hr at RT and hydrolyzed, 3.79 g of sticky solid was obtained. Recrystallization from benzene yielded 3.17 g (72.5%) of N-(*p*-chlorobenzenesulfonyl)-α-naphthamide (XVIII): mp 145–146.5°; ir 3300 and 1680 cm^{-1}.

Anal. Calcd for $C_{17}H_{12}ClNO_3S$: C, 59.13; H, 3.47; Cl, 10.14; N, 4.05; S, 9.26. Found: C, 59.27; H, 3.27; Cl, 10.35; N, 4.12; S, 9.06.

Registry No.—I, 4083-64-1; X, 22187-53-7; XI, 5769-15-3; XIV, 22187-55-9; XV, 22187-56-0; XVIII, 22187-57-1; benzene, 71-43-2; anisole, 100-66-3; toluene, 108-88-3; chlorobenzene, 108-90-7; naphthalene, 91-20-3; anthracene, 120-12-7.

(13) W. Hentrich and H. Engelbrecht, German Patent 765,524 (1952); *Chem. Abstr.*, **49**, 15967 (1955).

(14) J. Huismann, German Patent 701,954 (1941); *Chem. Abstr.*, **36**, 98 (1942).

Photochemical Cyclizations. I. Preparation of Benzo[*f*]quinolines by Photolysis of 2-Stilbazole Derivatives[1]

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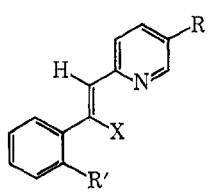
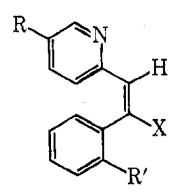
The photochemical behavior of a series of 2-stilbazole derivatives **1a–1f** has been investigated. In general, these compounds undergo oxidative photocyclization to benzo[*f*]quinolines **4**. The effect of various experimental parameters (wavelength of light, solvent, and additives) on the photocyclization reaction is reported and discussed. In two cases, additional photoproducts have been isolated and characterized.

The photochemical behavior of a series of 2-stilbazole derivatives **1a–1f** was investigated as part of a program



1



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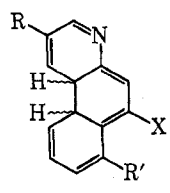

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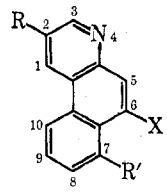


4

a, X = H; R, R′ = H
b, X = CN; R, R′ = H
c, X = CN; R = OCH_3; R′ = H
d, X = $COOCH_3$; R, R′ = H
e, X = H; R = H; R′ = $NHCOCH_3$
f, X = H; R = H; R′ = NO_2

directed toward the synthesis of various ergot and clavine alkaloids.

Irradiation of these compounds could be expected to cause rapid *trans–cis*[3] isomerization (**1** ⇄ **2**) and subsequent cyclization to the dihydrobenzo[*f*]quinolines **3**, which should be readily oxidized to the benzo[*f*]quinolines **4**. The photochemical cyclization of stilbene and its derivatives has received considerable attention,[5] but the photochemistry of stilbazoles has not been as thoroughly investigated.[6]

The mechanism of the photocyclization reaction has not been completely elucidated, but is generally believed to involve formation of dihydrophenanthrene derivatives analogous to **3**[7,8] and subsequent oxidation of these species. The multiplicity of the excited state responsible for photocyclization has not been clarified but is generally believed to be the singlet state.[8] Recent Hückel molecular orbital calculations for cyclization of monosubstituted stilbenes suggest, however, that cyclization proceeds from a vibrationally

(1) Abstracted in part from the dissertation submitted by P. L. Kumler to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the Ph.D. degree, May 1967.

(2) (a) National Institutes of Health Predoctoral Fellow, 1966–1967. To whom correspondence should be addressed: Department of Chemistry, University of Chicago, Chicago, Ill. 60637. (b) National Institutes of Health Predoctoral Fellow, 1968–present.

(3) We have chosen to describe the configuration about the double bond of these compounds as being derivatives of *cis*- and *trans*-2-stilbazole. If the configuration of these compounds is specified by use of the descriptors *E* and *Z*,[4] compounds **1a**, **1e**, and **1f** are of the *E* configuration and compounds **1b–1d** are of the *Z* configuration; compounds **2** are described by the opposite descriptors.

(4) J. E. Blackwood, C. L. Gladys, K. L. Loenig, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968); J. E. Blackwood, C. L. Gladys, A. E. Petrarca, W. H. Powell, and J. E. Rush, *J. Chem. Soc.*, **8**, 30 (1968).

(5) F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, pp 247–282.

(6) (a) C. E. Loader, M. V. Sargent, and C. J. Timmons, *Chem. Commun.*, 127 (1965); (b) C. E. Loader and C. J. Timmons, *J. Chem. Soc., C*, 1457 (1967); (c) C. E. Loader and C. J. Timmons, *ibid.*, 1078 (1966); (d) C. E. Loader and C. J. Timmons, *ibid.*, 1343 (1967); (e) C. E. Loader and C. J. Timmons, *ibid.*, 330 (1968); (f) P. Bortolus, G. Cauzzo, and G. Galiazzo, *Tetrahedron Lett.*, 239 (1966).

(7) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Amer. Chem. Soc.*, **85**, 829 (1963).

(8) K. A. Muszkat and Ernst Fischer, *J. Chem. Soc., B*, 662 (1967), and references cited therein.

excited *ground* state of *cis*-stilbene.[9] Laarhoven, Cuppen, and Nivard have suggested that the ability of stilbenelike systems to undergo photocyclization is dependent upon the summation of the free valence numbers (ΣF_r^*) of the bonding atoms in the first excited state.[10]

Even though the detailed mechanism of the photocyclization reaction has not been elucidated, the utility of this procedure as a synthetic tool for polycyclic systems difficult to obtain by conventional methods is well established.[5]

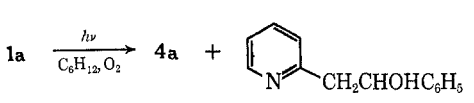
Results

The 2-stilbazole derivatives **1a–1d**, upon solution-phase photolysis in the presence of oxygen, were converted in good yield into the corresponding benzo[*f*]-quinolines **4a–4d**.

Prolonged irradiation of the acetamidostilbazole **1e** resulted in a complex mixture of photoproducts from which the expected benzo[*f*]quinoline **4e** could not be isolated by column chromatography. However, **4e** was shown to be present in the reaction mixture by tlc comparison with an authentic sample. If the photolysis was terminated after brief exposure to the irradiation source, the *cis*-stilbazole derivative **2e** could be isolated in 64% yield by column chromatography on alumina. Irradiation of the expected photocyclization product **4e**, under the same experimental conditions used above, resulted in complete decomposition of **4e** to a complex mixture which was not further characterized. Failure to isolate the benzo[*f*]quinoline **4e** from the photolysis of **1e** is thus probably due to the photodecomposition of **4e** under the reaction conditions.

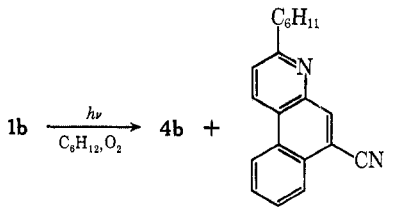
Irradiation of the nitrostilbazole **1f** under a wide variety of experimental conditions (variation of solvent, wavelength, and oxidizing agent) resulted in disappearance of starting material; however, the expected photocyclization product **4f** could not be detected in the photolysate by tlc comparison with an authentic sample. Control experiments established that **4f** was stable to the reaction conditions, and thus failure to isolate the photocyclization product is probably due to failure of this stilbazole to undergo the initial photocyclization reaction to the dihydrobenzo[*f*]quinoline **3f**. Previous workers have noted that stilbenes containing nitro substituents would not undergo the photocyclization reaction,[11] but large amounts of starting material were recovered after prolonged irradiation.

When the photolysis of *trans*-2-stilbazole (**1a**) was conducted in cyclohexane solution in the presence of oxygen, benzo[*f*]quinoline (**4a**) was isolated in 35% yield by column chromatography of the complex photolysate. A minor photoproduct, to which the structure **5** was assigned, was isolated in 10% yield. Control experiments established that **5** was a true photoproduct and not merely formed during work-up of the photolysate. This result complements the findings of earlier workers,[6c,f] who reported only the formation of benzo[*f*]quinoline in approximately the same yield.



5

From the photolysis of the cyanostilbazole **1b** in cyclohexane solution in the presence of oxygen, the expected benzo[*f*]quinoline-6-carbonitrile (**4b**) was isolated in 35% yield by column chromatography of the complex mixture. A minor photoproduct, 3-cyclohexylbenzo[*f*]quinoline-6-carbonitrile (**6**), was isolated in 8.4% yield. Control photolyses established that the



6

minor photoproduct could be formed by photolysis of the photocyclization product **4b** under the reaction conditions. The incorporation of a cyclohexyl moiety into a benzoquinoline nucleus during the photolysis of 4-stilbazole has been reported by Loader and Timmons,[6c] and several other photoalkylation reactions of heterocyclic aromatic amines are known.[12]

In an attempt to increase the yield of the photocyclization reaction and perhaps decrease the yields of undesirable by-products, a study of the effect of various experimental parameters (solvent, wavelength, additives) on the photocyclization of the nitrile **1b** was carried out. Removal of short-wavelength light from the irradiation source by use of Vycor or Corex filters had essentially no effect on the isolated yields of either **4b** or **6**, as shown in Table I. It should be noted,

TABLE I
EFFECT OF VARIOUS FILTERS ON THE PHOTOLYSIS[a] OF **1b**

Filter	Irradiation time, hr	Yield[b] of 4b, %	Yield[b] of 6, %
None	31	35	8.4
Vycor	24	36	7.4
Corex	34	38	8.9

[a] Hanovia 450-W lamp in a quartz immersion well; cyclohexane solution in the presence of oxygen. [b] Isolated yield by column chromatography on alumina.

however, that use of a Corex filter resulted in a much cleaner reaction mixture (less polymeric material). The effect of solvents and additives on this reaction was also investigated, and the results are summarized in Table II. It can readily be seen that polar solvents generally increase the rate of disappearance of starting material, but the amount of photocyclized material isolated is generally less than in nonpolar solvents. The major exception to this generalization is the use of *t*-butyl alcohol as solvent. In this solvent, reaction times for complete disappearance of starting material are dramatically less than in nonpolar solvents but the yield of isolated photocyclization product is comparable with that obtained when benzene is used as solvent. It therefore appears that *t*-butyl alcohol is the preferred

(9) H. Gusten and L. Klasinc, *Tetrahedron*, **24**, 5499 (1968).
(10) W. H. Laarhoven, T. J. H. M. Cuppen, and R. J. F. Nivard, *Rec. Trav. Chim. Pays-Bas*, **87**, 687 (1968).
(11) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).
(12) (a) F. R. Stermitz, R. Pua, and H. Vyas, *Chem. Commun.*, 326 (1967); (b) F. R. Stermitz, C. C. Wei, and W. H. Huang, *ibid.*, 482 (1968); (c) F. R. Stermitz, R. Pua Seiber, and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968).

TABLE II
EFFECT OF SOLVENTS AND ADDITIVES ON THE PHOTOLYSIS[a] OF 1b

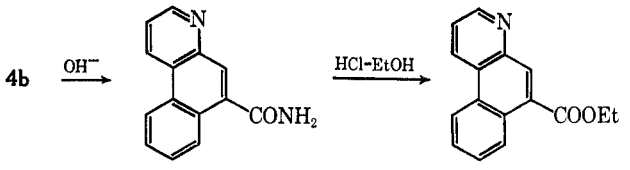
Solvent	Filter	Irradiation time,[b] hr	Yield[c] of 4b, %
C_6H_{12}	Corex	34.0	38[d]
C_6H_6	Corex	27.0	70
CH_3CN	Vycor	7.0	17
CH_3CN	Corex	5.0	30
DME[e]	Corex	4.5	0
C_2H_5OH	Corex	2.5	14
C_2H_5OH, $CuBr_2$[f]	Vycor	8.0	0
t-C_4H_9OH[g]	Corex	3.0	62

[a] Hanovia 450-W lamp in a quartz immersion well; all solutions were saturated with oxygen prior to and during the irradiation. [b] Time required for essentially complete disappearance of starting material as shown by tlc. [c] Isolated yields by column chromatography. [d] Also isolated was 6 (89%). [e] 1,2-Dimethoxyethane. [f] Ethanol solution containing **1b** and cupric bromide in equimolar amounts; see Discussion. [g] This solution also contained 7.5% (by volume) benzene to prevent freezing of the solution on the water-cooled immersion well during irradiation.

solvent for the photocyclization reaction (see Discussion) and the generality of this phenomenon was demonstrated in one other case. Thus, photolysis of the stilbazole **1c** in *t*-butyl alcohol containing small amounts of benzene (see footnote *g*, Table II) as solvent required 4 hr for complete disappearance of starting material (tlc) and benzo[*f*]quinoline **4c** was isolated in 64% yield. As comparison, photolysis of this substrate in benzene as solvent required 23 hr and the isolated yield of **4c** was 70%.

Structural Assignments.—The stilbazole derivatives **1a, 1b,** and **1f** have been reported and the structures of **1c–1e** were obvious from their spectral properties and method of synthesis (see Experimental Section). The configuration about the double bond in the stilbazole derivatives **1b–1f**, though not rigorously proven, was suggested primarily by ultraviolet spectroscopy. In simple substituted stilbenes it has been found possible to make stereochemical assignments on the basis of ultraviolet spectra[13–15] even when only one of the isomers is available.[16,17] Most stilbene derivatives exhibit two major absorption bands (>250 nm) in their ultraviolet spectra; the band at shorter wavelength is more intense for *cis*-stilbenes and that at longer wavelength is more intense for the *trans* isomers. This observation is valid in the stilbene series even when the double bond is substituted with a cyano, carboxy, or carboxamido group.[15] These observations have been extended to *cis*- and *trans*-3-stilbazole derivatives by Clarke and coworkers.[18] Therefore, it is felt that the assignment of *trans* stereochemistry to the 2-stilbazole derivatives **1b–1f** can be validly made without having authentic samples of both geometric isomers. The ultraviolet spectra of the derivatives **1b–1f** were all very similar to that of *trans*-2-stilbazole (**1a**); each spectrum exhibited two absorption bands above 250 nm and in all cases the longer wavelength band was the more intense (see Experimental Section for complete spectra). As further support for the stereochemical assignments, when the photolyses of the stilbazoles **1a–1f** were monitored by ultraviolet spectroscopy, changes occurred in the spectra which were consistent with initial *trans–cis* isomerization. In one case the *cis* isomer could be isolated from the photolysis after brief irradiation times (see photolysis of **1e** in the Experimental Section).

The benzo[*f*]quinolines **4b–4d** and **6** exhibited ultraviolet spectra very similar to that of the parent compound (see Experimental Section). Other spectral data (ir and nmr) and elemental analyses were in agreement with the structural assignments. In order to establish that no migration of substituents had occurred during the photocyclization,[19] the structure of compound **4b** was unambiguously established by base-catalyzed hydrolysis to the amide **7** and acid-catalyzed ethanolysis to the reported ester **8**.



7 8

The gross structure of the cyclohexylated benzo[*f*]-quinoline **6** was evident from the spectral data. The uv spectrum (see Experimental Section) was very similar to that of benzo[*f*]quinoline (**4a**). Both the nmr spectrum and the ir spectrum suggested the presence of a cyclohexyl group, which was confirmed by mass spectral data. Thus, the mass spectrum showed strong peaks at *m/e* 286 (molecular ion, M) and 203 (M − 83, loss of cyclohexyl). The exact location of the cyclohexyl substituent was suggested by mechanistic considerations (see Discussion) and was confirmed by nmr spectroscopy (see Experimental Section). It was immediately obvious that the signal due to H_3 was absent in the spectrum of **6**.[21]

The structure of 1-phenyl-2-(2-pyridyl)ethanol (**5**) was obvious from spectral data and elemental analysis and the physical constants agreed with those reported (see Experimental Section).

Discussion

It appears from the present work and that of earlier workers[6] that the oxidative photocyclization of stilbazoles to benzoquinolines is a rather general synthetic method. This is in direct contrast to an early report that 2- and 4-stilbazole did not photocyclize.[23] When considering the feasibility of any photocyclization reaction, it is perhaps important to bear in mind the admonition of Stermitz: "...the cyclization seems to

(13) L. Crombie, *Quart. Rev.* (London), **6**, 101 (1952).
(14) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," 2nd ed, Edward Arnold Ltd., London, 1957, p 269.
(15) J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**, 1027, 1035 (1952).
(16) D. F. DeTar and L. A. Carpino, *J. Amer. Chem. Soc.*, **78**, 475 (1956).
(17) K. Rorig, *ibid.*, **75**, 5381 (1953).
(18) F. H. Clarke, G. A. Felock, G. B. Silverman, and C. M. Watnick, *J. Org. Chem.*, **27**, 533 (1962).
(19) There are examples known of the loss of substituents during photocyclization (see ref 5, p 261) and there has been at least one report of methyl migration during photocyclization.[20] It was therefore imperative to determine that no migration of the cyano substituent had occurred.
(20) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Aust. J. Chem.*, **17**, 1036 (1964).
(21) Our analysis of the nmr spectra of the benzo[*f*]quinoline derivatives was facilitated by an excellent paper of R. H. Martin and coworkers[22] on the nmr spectra of polycyclic heteroaromatic compounds.
(22) E. Vander Donckt, R. H. Martin, and F. Geerts-Evrard, *Tetrahedron*, **20**, 1495 (1964).
(23) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

be so general that a proper outlook in regard to failures would perhaps be that the proper conditions for the particular cyclization have not yet been found."[24] In the present work, two of the compounds failed to give the cyclization product in synthetically useful yields. The failure of the cyclization reaction with the acetamidostilbazole **1e** is at least in part due to the demonstrated instability of the expected product under the reaction conditions. However, failure of the nitrostilbazole **1f** to undergo the desired cyclization *cannot* be due to the instability of the product (as shown by control experiments). The nitrostilbazole is, however, rapidly consumed during the photolysis, and thus this behavior is in contrast to that of nitrostilbenes.[11]

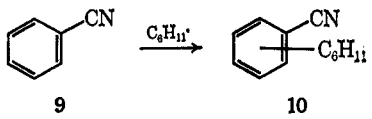
Even though removal of short-wavelength light (>260 nm) did not significantly affect the yield of the photocyclization reaction, it did result in much "cleaner" reaction mixtures.

The effect of various solvents and additives on the photocyclization reaction (see Table II) is rather confusing. It is obvious, however, that the rate of disappearance of starting material is much faster in polar solvents. This could be a result of the nature of the lowest excited state being dependent on the polarity of the solvent. Such solvent effects are well-known photochemical phenomena,[25] but it would be very premature to speculate in any more detail on the significance of this solvent effect until much more is known concerning the detailed mechanism of the photocyclization reaction.

In contrast to the work of Collins and Hobbs[26] on the photocyclization of stilbenes, the addition of cupric bromide to the photolysis mixture had a detrimental effect on the present system, as shown in Table II.

It is evident that the preferred solvent for photocyclizations of the type described here is *t*-butyl alcohol. Use of this solvent allows the photolyses to be completed in short irradiation times and the yields of photocyclized products are comparable with those obtained when benzene—the preferred nonpolar solvent—is used as solvent. The reason for the advantage of *t*-butyl alcohol over other polar solvents is probably related to suppression of undesirable side reactions which occur with other polar solvents (see below).

Isolation of the cyclohexylated benzo[*f*]quinoline **6** strongly suggested the intervention of radical species during the photolysis. An obvious route to the alkylated product is alkylation of **4b** by cyclohexyl radicals. The position of the cyclohexyl substituent in the benzo[*f*]quinoline nucleus is also consistent with a radical alkylation. For example, Shelton and Uzelmeier[27] found benzonitrile (**9**) to be very susceptible to alkylation by cyclohexyl radicals (yield of arylcyclohexanes **10** was 57%) and the cyano group had a considerable directing effect on the orientation of the product. Pyridine and quinoline derivatives are in general more susceptible to radical alkylation than their carbocyclic analogs, and substitution takes place predominantly α to the nitrogen atom.[28] Thus the alkylated product **6** probably arises from homolytic alkylation of the benzo[*f*]quinoline **4b** by cyclohexyl radicals. The cyclohexyl radicals could arise by at least three distinct pathways: (a) autoxidation of cyclohexane, (b) abstraction of a hydrogen atom from cyclohexane by some electronically excited state, and (c) abstraction of a hydrogen atom from cyclohexane by some radical species produced during the photolysis. The autoxidation of saturated hydrocarbons, including cyclohexane, is well known and the formation of cyclohexyl radicals during the photolysis of cyclohexane in the presence of oxygen has been observed.[29] The second pathway has been postulated by Stermitz and coworkers[12] to explain related photoalkylations. Finally, abstraction of hydrogen atoms from species containing aliphatic C–H bonds by various radical species is well documented.[30] Control experiments established that the cyclohexylated material could be produced by photolyzing benzo[*f*]quinoline **4b** in cyclohexane saturated with oxygen, which suggests either path a or path b for the production of cyclohexyl radicals, but the possibility of these radicals arising *via* path c cannot be eliminated.



9 **10**

ortho, 52%
meta, 4%
para, 44%

The formation of the by-product **5** during the photolysis of **1a** could also be explained by the intervention of radical species at some point during the reaction sequence. The fate of the hydrogen atoms originally on the aromatic rings at the point of cyclization has been determined for some cases of stilbene cyclizations using molecular oxygen as the oxidizing agent. In these cases the hydrogen atoms appear as hydrogen peroxide.[31] Presumably, therefore, hydrogen peroxide is also produced when the dihydrobenzo[*f*]quinolines **3** are oxidized to the benzo[*f*]quinolines **4** by oxygen. The photochemical decomposition of hydrogen peroxide to two hydroxyl radicals occurs in solution at wavelengths of 2537–3650 Å.[32] Therefore, one possible route for the production of **5** involves addition of the hydroxyl radical to the stilbazole double bond of **1a** (or **2a**), leading predominantly to the radical **11**, and conversion of the radical into **5** by hydrogen abstraction.[33] It is possible that the hydroxyl radical is, in part at least, the species responsible for production of the cyclohexyl radicals discussed above. The hydroxyl radical *cannot*, however, be the only species responsible for production of cyclohexyl radicals because the alkyl-

$$\mathbf{1a} \xrightarrow{\cdot OH} \underset{\mathbf{11}}{C_6H_5CHOH\dot{C}HC_5H_4N} \xrightarrow{RH} \mathbf{5}$$

(24) Reference 5, p 259.

(25) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 528 ff.

(26) D. J. Collins and J. J. Hobbs, *Aust. J. Chem.*, **20**, 1905 (1967).

(27) J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, **88**, 5222 (1966).

(28) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960, pp 45–79 and 94–109 and references cited therein.

(29) W. A. Cramer, *J. Phys. Chem.*, **71**, 1112 (1967).

(30) For discussions of this reaction, see C. J. M. Stirling, "Radicals in Organic Chemistry," Oldbourne Book Co. Ltd., London, 1965, pp 37, 46–49, 56, 74, 77, and 102–103.

(31) Reference 5, pp 263–270, and ref 8.

(32) See ref 25, p 202, for leading references.

(33) The direct photohydration of **1a** (or **2a**) by traces of water present during the photolysis cannot, however, be eliminated. For a discussion of such reactions, see G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, Chapter IV.

ated product **6** can be formed by photolysis of pure **4b** in cyclohexane saturated with oxygen.

Because radical species seem to be generated at some stage during the photolysis of the stilbazoles **1**, and based upon the assumption that the photocyclization reaction is *not* a radical reaction, the advantage of *t*-butyl alcohol as a solvent can be easily explained. All of the other polar solvents utilized (see Table II) would be susceptible to abstraction of hydrogen atoms by any radical source (especially by electrophilic hydroxyl radicals). For example, abstraction of an α-hydrogen atom from aliphatic alcohols,[34] nitriles,[34] and ethers[35] is well established, and hydroxyl radicals are especially noted for their ability to perform abstractions of this type.[34] Generation of any of these solvent-derived radicals would be expected to decrease the efficiency of the photocyclization reaction, because the stilbazoles should be susceptible to radical addition reactions at any (or all) of three sites—the benzene nucleus, the pyridine nucleus, or the stilbenelike double bond.[36] It is therefore postulated that the reason for the advantage of *t*-butyl alcohol as solvent for the photocyclization reaction is twofold. By virtue of being a polar solvent, it increases the rate of the desired reaction, and, because it lacks reactive C–H bonds, undesirable homolytic reactions are suppressed.

Experimental Section[37]

Photolyses.—The substrate was dissolved in the solvent (*ca.* 1.0 g in 950 ml) and oxygen was bubbled through the solution for 0.5 hr prior to and then during the irradiation. The light source was a 450-W Hanovia medium-pressure mercury arc placed in a water-cooled quartz immersion well containing the appropriate filter sleeve (when indicated). All photolyses were monitored by tlc and by periodic scanning of the ultraviolet spectrum. The irradiations were generally continued until most of the starting material was consumed as evidenced by tlc.

trans-**2-Stilbazole (1a).**—This compound was prepared by condensation of benzaldehyde with 2-picoline in the presence of acetic anhydride, potassium acetate, and iodine by the reported[38] method. The crude stilbazole was recrystallized once from ethanol to give colorless crystals (57%): mp 87–89° (lit.[38] mp 90–91°); ir (KBr) 1635 (C=C), 1330, and 983 cm^{-1} (*trans*-disubstituted olefin); uv max (C_6H_{12}) 310 (ϵ 19,000), 275 (sh, ϵ 10,400) 235 (sh, ϵ 6100), 227 (ϵ 8000), and 221 nm (ϵ 7600); nmr ($CDCl_3$) τ 1.40 (br d, 1 H, pyridyl α proton) and 2.0–3.7 (m, 10 H, vinyl and aromatic protons).

2-Phenyl-3-(2-pyridyl)acrylonitrile (1b).—A solution of 2-pyridinealdehyde (11.7 g, 0.10 mol) and phenylacetonitrile (10.7 g, 0.10 mol) in 80 ml of absolute ethanol was heated to 50°. Potassium *t*-butoxide (MSA Research Corp., 0.5 g) was added in one portion; the reaction mixture immediately became deep red. The solution was kept at 50° for 5–10 min, allowed to stand at room temperature for 1 hr, and finally cooled in a refrigerator. The pale yellow, crystalline mass was filtered and air dried to give **1b** as pale yellow needles (13.8 g, 67%), mp 63–65°. Recrystallization from ethanol after clarification with charcoal gave colorless needles: mp 65–66° (lit.[39] mp 65°); ir (KBr) 2200 (C≡N) and 1615 cm^{-1} (C=C); uv max (C_6H_{12}) 315 (ϵ 20,600), 280 (sh, ϵ 8045), and 223 nm (ϵ 8600); nmr ($CDCl_3$) τ 1.10 (br d, 1 H, pyridyl α proton) and 1.8–3.2 (m, 9 H, vinyl and aromatic protons).

5-Methoxy-2-pyridinecarboxaldehyde.—Ethyl 5-methoxypyridine-2-carboxylate[40] (13.6 g, 0.08 mol) was dissolved in 225 ml of toluene and the solution was cooled to −70°. To the magnetically stirred solution maintained at −70° was added a toluene solution of diisobutylaluminum hydride (70 ml, *ca.* 1.1 *M*). The yellow reaction mixture was stirred for 2 hr at −70° and the excess hydride was then destroyed by the slow addition of 50 ml of saturated aqueous ammonium chloride solution. The mixture was warmed to room temperature and the two layers were separated. The aqueous phase was extracted with toluene and the combined organic extracts were washed with water and dried over sodium sulfate. After removal of the toluene (reduced pressure) the residual pale yellow oil (9.8 g, 95%) was purified by distillation *in vacuo*. The major fraction was a colorless oil (8.7 g, 85%), bp 81–84° (0.10 mm), which solidified upon standing: mp 40–42°; ir (neat) 1695 cm^{-1} (C=O); nmr ($CDCl_3$) τ 6.04 (s, 3 H, OCH_3), 2.67 (d of d, 1 H, H_4), 2.02 (d, 1 H, H_3), and 1.53 (d, 1 H, H_6).

Anal. Calcd for $C_7H_7NO_2$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.52; H, 5.03; N, 10.01.

2-Phenyl-3-(5-methoxy-2-pyridyl)acrylonitrile (1c).—A solution of 5-methoxy-2-pyridinecarboxaldehyde (22.2 g, 0.16 mol) and phenylacetonitrile (19.0 g, 0.16 mol) in 110 ml of absolute ethanol was heated to 50–55°. Potassium *t*-butoxide (1.0 g) was added in one portion and the solution immediately turned orange. The reaction mixture was maintained at 55° for 20 min, during which time off-white crystals began to separate. The reaction mixture was placed in the refrigerator to complete crystallization. The off-white crystals of **1c** (37.3 g, 97.5%) were collected by filtration and air dried. Recrystallization from ethanol gave colorless crystals: mp 94.5–95°; ir (Nujol) 2200 cm^{-1} (C≡N); uv max (95% EtOH) 329 (ϵ 23,800), 300 (sh, ϵ 14,200), and 225 nm (ϵ 12,100); nmr ($CDCl_3$) τ 1.59 (d, 1 H, pyridyl α proton), 2.44 (s, 1 H, vinyl proton), 2.05–2.93 (m, 7 H, aromatic protons), and 6.20 (s, H, OCH_3).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.31; H, 4.83; N, 12.17.

2-Phenyl-3-(2-pyridyl)acrylic Acid.—A sample of **1b** (5.2 g, 0.025 mol) was added to a stirred solution of 85% (v/v) aqueous sulfuric acid and the reaction mixture was stirred at 100° for 2 hr. The deep purple solution, after being cooled to 0°, was carefully basified with 50% aqueous sodium hydroxide and extracted with methylene chloride. The aqueous phase was acidified with glacial acetic acid and extracted with chloroform. The combined chloroform extracts were washed with saturated salt solution and dried over sodium sulfate. Evaporation of the solvent and recrystallization of the tan residue from ethanol–dimethyl sulfoxide gave 2-phenyl-3-(2-pyridyl)acrylic acid as brown needles (3.7 g, 56%), mp 160–166° dec. Two additional recrystallizations from ethanol–dimethyl sulfoxide (with charcoal treatment) gave tan crystals: mp 170–172° dec; ir (KBr) 3300 (br, bonded OH) and 1715 cm^{-1} (C=O); uv max (95% ethanol) 305 (ϵ 25,700) and 224 nm (ϵ 10,900).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.61; H, 5.19; N, 6.20.

Methyl 2-Phenyl-3-(2-pyridyl)acrylate (1d).—An ether solution of diazomethane was prepared as follows. About 3 g of damp N-nitrosomethylurea (Columbia Organic Chemicals, dampened with 20% acetic acid) was added to a magnetically stirred mixture of 100 ml of ether and 50 ml of 30% aqueous potassium hydroxide in a 250-ml erlenmeyer flask maintained at 0°. After being stirred for 5 min, the two-phase mixture was cooled in a Dry Ice–acetone bath. When the aqueous phase had solidified, the anhydrous ethereal solution of diazomethane was decanted. The diazomethane solution was added to a suspension of 2-phenyl-3-(2-pyridyl)acrylic acid (2.0 g, 0.009 mol) in 60 ml of methylene chloride. The solid dissolved with the evolution of gas and after 30 min the excess diazomethane was destroyed by the careful addition of magnesium sulfate. The methylene chloride solution was washed once with 10% potas-

(34) Reference 30, pp 153–157.

(35) Reference 30, p 63.

(36) For a review of the radical-addition reactions of the type considered here, see ref 33. For a recent review on photoinduced *ionic* additions to unsaturated systems, see J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

(37) Melting points were obtained on a Fisher-Johns apparatus and are reported uncorrected. Infrared spectra were determined using a Perkin-Elmer Model 137 "Infracord" or a Perkin-Elmer Model 421 spectrophotometer; all spectra were calibrated with polystyrene. Ultraviolet spectra were measured with a Cary Model 11 or Model 14 recording spectrophotometer. Nuclear magnetic resonance spectra were taken on a Varian Associates A-60 spectrometer or on a Japan Electron Optics Model JNM-4H-100 spectrometer; spectra were recorded in deuteriochloroform solution and chemical shifts are reported in τ (parts per million) relative to tetramethylsilane as internal standard. Elemental analyses are by Micro-Tech Laboratories, Skokie, Ill., or by Crobaugh Laboratories, Cleveland, Ohio.

(38) J. Stanek and M. Horak, *Collect. Czech. Chem. Commun.*, **15**, 1037 (1950).

(39) R. N. Castle and W. S. Seese, *J. Org. Chem.*, **20**, 987 (1955).

(40) H. C. Beyerman, *Rec. Trav. Chim. Pays-Bas*, **77**, 249 (1958).

sium bicarbonate and once with water and dried over sodium sulfate. Evaporation of the solvent yielded the crude ester (2.1 g) as a red, viscous oil. The ester was purified by elution (methylene chloride) through a 50-g column of Woelm alumina (activity III) and subsequent formation of the picrate, mp 158–160°. Regeneration of the free base gave the ester as a colorless oil: ir (film) 1725 (C=O) and 1620 cm^{-1} (C=C); uv max (95% ethanol) 305 (ε 28,000), 275 (sh, ε 17,500), and 226 nm (14,200); nmr ($CDCl_3$, 100 Mcps) τ 1.45 (br d, 1 H, pyridyl α proton), 2.1–3.3 (m, 9 H, vinyl and aromatic protons), and 6.12 (s, 3 H, $COOCH_3$).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.60; H, 5.61; N, 5.77.

2′-Nitro-2-stilbazole (1f).—A mixture of 2-picoline (9.31 g, 0.10 mol), *o*-nitrobenzaldehyde (15.1 g, 0.10 mol), and acetic anhydride (15.3 g, 0.15 mol) was refluxed for 10 hr. After the excess *o*-nitrobenzaldehyde was removed by steam distillation, the reaction mixture was made basic with 10% sodium hydroxide and extracted with methylene chloride. The combined organic extracts were dried over sodium sulfate and the solvent was removed under reduced pressure to give a red-brown oil which was purified by vacuum distillation. The major fraction distilled at 172–180° (0.15 mm) as a yellow oil (15.0 g, 67%) which solidified upon standing. Recrystallization from methanol gave pale yellow needles: mp 98–99.5° (lit.[41] mp 101°); ir (KBr) 1515 and 1340 (NO_2) and 966 cm^{-1} (*trans*-disubstituted C=C); uv max (95% ethanol) 296 (ε 12,600) and 262 nm (ε 12,600).

2′-Amino-2-stilbazole.—Stannous chloride reagent was prepared by adding 107 g of stannous chloride dihydrate to 180 ml of glacial acetic acid, saturating the mixture with gaseous hydrogen chloride, and diluting the solution to 240 ml with glacial acetic acid. A sample of 2′-nitro-2-stilbazole (8.0 g, 0.036 mol) was dissolved in 112 ml of the stannous chloride reagent. The temperature of the reaction mixture rose rapidly and ice cooling was necessary. After the light yellow reaction mixture was allowed to stir at room temperature for 24 hr, it was basified with 8 *N* sodium hydroxide. The basic solution was extracted with methylene chloride and the combined organic extracts were dried over sodium sulfate. Evaporation of the solvent gave the crude aminostilbazole as bright yellow crystals (6.13 g, 87%). Recrystallization from hexane gave fluffy yellow needles: mp 83–84° (lit.[42] mp 85–86°); ir (Nujol) 3200 (NH_2) and 961 cm^{-1} (*trans*-disubstituted C=C); uv max (95% ethanol) 354 (ε 7800), 300 (ε 10,400), 242 (sh, ε 9620), 238 (ε 9950), and 209 nm (ε 15,000).

2′-Acetamido-2-stilbazole (1e).—To a solution of 2′-amino-2-stilbazole (8.5 g, 0.043 mol) in 15 ml of pyridine was added 6.6 ml of acetic anhydride. The reaction mixture was stirred for 3 hr, poured into ice–water, and extracted with methylene chloride. The combined organic extracts were washed with sodium bicarbonate solution and with water and then were dried over sodium sulfate. Evaporation of the solvent gave the crude acetamido stilbazole as an off-white crystalline solid (10.7 g). Recrystallization from benzene–hexane gave colorless needles (9.88 g, 96%): mp 114.5–115°; ir (Nujol) 1650 (C=O) and 985 cm^{-1} (*trans*-disubstituted C=C); uv max (95% ethanol) 310 (ε 20,800), 280 (sh, ε 12,800), 246 (ε 11,400), and 230 nm (sh, ε 10,000); nmr ($CDCl_3$) τ 1.47 (br, d, 1 H, pyridyl α proton), 1.85–3.12 (m, 10 H, vinyl, aromatic, and amide nitrogen protons), and 7.91 (s, 3 H, $COOCH_3$).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.69; H, 5.90; N, 11.64.

Photolysis of 2-Stilbazole (1a).—A sample of 2-stilbazole (1.00 g, 5.5 mmol) was dissolved in 950 ml of spectral grade cyclohexane and oxygen was passed through the solution for 0.5 hr prior to irradiation. After irradiation for 54 hr the solvent was removed under reduced pressure and the residual orange oil was chromatographed through a 40-g column of activity III Woelm alumina. Elution with petroleum ether–benzene (3:2) gave benzo[*f*] quinoline (**4a**, 355 mg, 35%) as a yellow oil which crystallized upon standing, mp 85–89°. Recrystallization from hexane gave colorless needles, mp 89–90° (lit.[43] mp 90–91°), which were identical (tlc, ir, mixture melting point) with an authentic sample: ir (CCl_4) 3030 (aromatic C–H stretch), 1605, 1580, and 1565 cm^{-1} (aromatic C–C stretch); uv max (95% ethanol) 346 (ε 2900), 330 (ε 2300), 315 (ε 1280), 290 (sh, ε 5650), 266 (ε 13,900), 233 (ε 27,500), and 215 nm (ε 24,600); nmr ($CDCl_3$) τ 1.15 (d of d, 1 H, H_3), 1.47 (d of d, 1 H, H_1), 2.03 (d, 1 H, H_5), 2.26 (d, 1 H, H_6), and 1.67–2.89 (m, 5 H, other aromatic protons). Elution of the column with benzene gave 1-phenyl-2-(2-pyridyl)ethanol (**5**, 144 mg, 13%) as a tan solid, mp 90–95°.[44] Two recrystallizations from hexane gave colorless needles: mp 107.5–108° (lit.[45] mp 107–108°); ir (CCl_4) 3300 (OH) and 1055 cm^{-1} (secondary alcohol); uv max (C_6H_{12}) 268 (ε 1900), 262 (ε 2700), 258 (ε 2700), and 208 nm (ε 11,400); nmr ($CDCl_3$) τ 1.52 (br d, 1 H, pyridyl α proton), 2.1–3.3 (m, 8 H, other aromatic protons), 4.58 (br s, 1 H, OH), 4.87 (t, 1 H, CHOH), and 6.88 (d, 2 H, CH_2).

Photolysis of 2-Phenyl-3-(2-pyridyl)acrylonitrile (1b). A. Cyclohexane.—The unsaturated nitrile **1b** (1.00 g) was irradiated in 950 ml of spectral grade cyclohexane in a quartz apparatus for 31 hr. After evaporation of the solvent, the residue was chromatographed on 40 g of activity III Woelm alumina. Elution with petroleum ether–benzene (4:1) gave 3-cyclohexylbenzo[*f*]quinoline-6-carbonitrile (**6**) as an orange oil (285 mg) which crystallized upon standing, mp 124–130°. Two recrystallizations from hexane gave colorless needles (121 mg, 8.4%): mp 132–133°; ir (KBr) 3050 (aromatic CH), 2220 (C≡N), 2920, and 2850 cm^{-1} (aliphatic CH); uv max (C_6H_{12}) 353 (ε 6430), 336 (ε 5270), 322 (ε 3020), 306 (ε 12,300), 293 (ε 11,800), 268 (ε 26,800), 259 (ε 25,400), 238 (ε 45,300), and 223 nm (ε 35,400); nmr ($CDCl_3$) τ 1.40 (d, J = 9 cps, 1 H, H_1), 2.57 (d, J = 9 cps, 1 H, H_2). 1.83 (s, 1 H, H_5), 1.59–2.65 (m, 4 H, other aromatic protons), 7.13 (br s, 1 H, cyclohexyl methine proton), and 8.00–8.75 (m, 10 H, cyclohexyl methylene protons); mass spectrum *m/e* 286 (M, molecular ion) and 203 (M − 83, loss of cyclohexyl moiety).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.91; H, 6.18; N, 9.79.

Elution with petroleum ether–benzene (1:4) gave benzo[*f*]-quinoline-6-carbonitrile (**4b**) as a pale yellow solid (347 mg, 35%), mp 155–159°. Two recrystallizations from hexane and subsequent sublimation at 130° (0.05 mm) gave colorless needles: mp 163–164°; ir (KBr) 3050 (aromatic CH) and 2220 cm^{-1} (C≡N); uv max (95% ethanol) 353 (ε 4000), 336 (ε 3650), 320 (ε 3200), 308 (ε 9900), 295 (ε 9600), 271 (ε 21,400), 262 (ε 21,600), 239 (ε 38,000), and 225 nm (ε 35,000); nmr ($CDCl_3$) τ 1.00 (d of d, 1 H, H_3), 1.20 (br d, 1 H, H_1), 1.73 (s, 1 H, H_5), and 1.42–2.69 (m, 5 H, other aromatic protons); mass spectrum *m/e* 204 (M, molecular ion).

Anal. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72. Found: C, 82.05; H, 3.88; N, 13.93.

B. *t*-Butyl Alcohol.—The unsaturated nitrile **1b** (1.60 g) was dissolved in 925 ml of *t*-butyl alcohol and 75 ml of spectral grade benzene. The solution was saturated with oxygen and photolyzed for 3 hr through a Corex filter sleeve. Chromatography of the crude photolysate on Woelm activity III alumina gave benzo[*f*]-quinoline-6-carbonitrile (**4b**, 966 mg, 62%), mp 159–162°. Recrystallization from hexane gave colorless needles, mp 162.5–163°.

C. Other Conditions.—The unsaturated nitrile **1b** was photolyzed under a wide variety of other conditions, and the results are summarized in Tables I and II.

Photolysis of Stilbazole Derivative 1c. Method A.—The unsaturated nitrile **1c** (1.80 g) was dissolved in 950 ml of spectral grade benzene and the solution was saturated with oxygen. Photolysis was conducted through a Corex sleeve for 22 hr. Column chromatography (Woelm activity III alumina) of the crude photolysate gave 2-methoxybenzo[*f*]quinoline-6-carbonitrile (**4c**) as yellow flakes (1.27 g, 70%). Two recrystallizations from benzene–hexane gave colorless needles (850 mg, 47%): mp 200–201°; ir (Nujol) 2210 (C≡N) and 1245 cm^{-1} (C—O stretch); uv max (C_6H_{12}) 355 (ε 11,500), 338 (ε 9900), 323 (ε 7060), 315 (ε 20,900), 311 (ε 18,500), 302 (ε 19,700), 282 (ε 28,400), 273 (ε 25,500), 255 (ε 38,300), 249 (ε 37,500), and 235 nm (ε 45,100); nmr ($CDCl_3$–trifluoroacetic acid) τ 0.87 (d, 1 H, H_3), 0.98 (d, 1 H, H_1), 1.36 (s, 1 H, H_5), 1.05–2.00 (m, 4 H, other aromatic protons), and 5.73 (s, 3 H, OCH_3).

Anal. Calcd for $C_{15}H_{10}N_2O$: C, 76.91; H, 4.30; N, 11.96. Found: C, 77.21; H, 4.22; N, 12.16.

Method B.—The unsaturated nitrile **1c** (1.60 g) was dissolved in 925 ml of *t*-butyl alcohol and 75 ml of benzene. The solu-

(41) B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 77 (1933).
(42) J. C. E. Simpson, *ibid.*, 673 (1946).
(43) D. H. Hey and J. M. Osbond, *ibid.*, 3164 (1949).
(44) This compound was observed in the photolysate (tlc) prior to evaporation and chromatography.
(45) K. Loffler and H. Grunert, *Chem. Ber.*, **40**, 1343 (1907).

tion was photolyzed, as above, for 4 hr. Work-up as in method A gave 996 mg (63%) of the crude cyclization product **4c**. Recrystallization from benzene–hexane gave colorless needles (786 mg, 49%).

Photolysis of Stilbazole Derivative 1d.—The unsaturated ester (1.005 g) was dissolved in 940 ml of reagent grade cyclohexane, saturated with oxygen, and irradiated through quartz for 29 hr. Work-up of the crude photolysate by column chromatography (Woelm activity III alumina) gave methyl benzo[*f*]-quinoline-6-carboxylate (**4d**) as an oil (256 mg, 25%) which crystallized upon standing, mp 63–70°. For further purification the ester was converted into its picrate (mp 260–262° after four recrystallizations from ethanol–dimethyl sulfoxide). Regeneration of the free base gave colorless needles: mp 91–92°; ir (KBr) 1710 (C=O), and 1250 cm^{-1} (C–O stretch); uv max (95% ethanol) 352 (ϵ 1560), 336 (ϵ 1650), 303 (ϵ 4260), 271 (ϵ 11,300), 236 (ϵ 19,800), and 218 nm (ϵ 17,500); nmr ($CDCl_3$, 100 Mcps) τ 0.7–2.7 (m, 8 H, aromatic protons) and 5.96 (s, 3 H, $COOCH_3$).

Anal. Calcd for $C_{15}H_{11}NO_2$ (ester): C, 75.93; H, 4.67; N, 5.90. Found: C, 75.52; H, 4.89; N, 5.75. Calcd for $C_{21}H_{14}N_4O_9$ (picrate): C, 54.08; H, 3.03; N, 12.01. Found: C, 54.29; H, 3.10; N, 11.76.

Photolysis of Stilbazole Derivative 1e. Method A.—The acetamido stilbazole **1e** (1.80 g) was dissolved in 950 ml of spectral grade benzene; the solution was saturated with oxygen and irradiated through a Corex filter for 40 min. Examination of the solution by tlc indicated that all starting material was gone and only one other product was present. Column chromatography of the photolysate (Woelm activity III alumina) gave the *cis* isomer of starting material (**2e**) as a colorless oil (1.16 g, 64%) which solidified upon standing, mp 72–76°. Two recrystallizations from benzene–hexane gave colorless needles: mp 101–102°; ir (Nujol) 3130 (NH) and 1680 cm^{-1} (C=O); uv max (95% ethanol) 288 (ϵ 8000), 242 (sh, ϵ 9400), 236 (ϵ 9800), and 210 nm (ϵ 16,800); nmr ($CDCl_3$) τ 1.50 (br d, 1 H, pyridyl α proton), 1.87–3.30 (m, 10 H, vinyl protons, NH proton and other aromatic protons), and 8.12 (s, 3 H, $COCH_3$).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.61; H, 5.85; N, 11.92.

Method B.—If the above irradiation was continued for 7 hr, a very complex mixture of products resulted from which no pure materials could be isolated by column chromatography. However, the expected photocyclization product, 7-acetamidobenzo-[*f*]quinoline,[46] was detected in the mixture by tlc comparison with an authentic sample.

Photolysis of Stilbazole Derivative 1f. Method A.—The nitro stilbazole **1f** (1.11 g) was dissolved in 950 ml of spectral grade cyclohexane and oxygen was bubbled through the solution for 0.5 hr prior to irradiation. After 26-hr irradiation the photolysate was filtered and evaporated to give 600 mg of a yellow-orange oil. Analysis by tlc indicated a complex mixture of products (minimum of 5 spots), none of which corresponded to authentic cyclized material.[46] The ultraviolet spectrum of the photolysate showed maxima at 210 and 257 nm (tailing to 390 nm).

Method B.—The nitrostilbazole **1f** (2.00 g) was dissolved in spectral grade acetonitrile. Oxygen was bubbled into the solution during the entire photolysis, which was discontinued after 3 hr. Filtration and evaporation of the solvent gave 883 mg of a red-orange oil which showed a minimum of four components by tlc analysis, none of which corresponded to authentic cyclized material.[46] The ultraviolet spectrum of the photolysate showed maxima at 210 and 261 nm (tailing to 390 nm).

Control Photolysis of 7-Acetamidobenzo[*f*]quinoline (4e).—The benzo[*f*]quinoline **4e** (336 mg) was dissolved in 900 ml of spectral grade benzene and oxygen was bubbled through the solution for 15 min. The solution was irradiated through Corex for 6 hr, at which time the ultraviolet spectrum showed maxima at 209 and 238 nm and a shoulder at 270 nm. At least four components, none of which was starting material, were shown to be present by tlc. The photolysate was filtered from the polymeric material and the solvent was removed under reduced pressure to give 36 mg of a red-brown oil which showed the same four spots on tlc analysis.

Control Photolysis of 7-Nitrobenzo[*f*]quinoline (4f).—The benzo[*f*]quinoline **4f** (1.00 g) was dissolved in 950 ml of spectral grade acetonitrile and oxygen was bubbled through the solution for 0.5 hr prior to irradiation. Photolysis (Corex) was discontinued after 9.5 hr, since both ultraviolet and tlc analysis indicated no photodecomposition of the starting material.

6-Carboxamidobenzo[*f*]quinoline (7).—To a suspension of benzo[*f*]quinoline-6-carbonitrile (**4b**, 125 mg, 0.61 mmol) in 35 ml of water was added 0.5 g of freshly activated Amberlite IRA-400.[47] The suspension was heated to reflux, and ethanol (*ca.* 5 ml) was added until all of the nitrile had dissolved. The reaction mixture was stirred and refluxed for 6 hr and then the ion-exchange resin was removed by filtration of the hot solution. The resin was washed with hot ethanol and the combined filtrates were evaporated to dryness. The residual white solid (125 mg, 93%), mp 248–250°, was homogeneous by tlc. Recrystallization from methanol gave pure 6-carboxamidobenzo[*f*]quinoline: mp 249–250°; ir (KBr) 3300 and 3100 (NH_2), 1675 (amide I band), and 1640 cm^{-1} (amide II band); nmr ($CDCl_3$–trifluoroacetic acid, 100 Mcps) τ −0.1–2.9 (m).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54. Found: C, 75.63; H, 4.49.

Ethyl Benzo[*f*]quinoline-6-carboxylate (8).—A solution of 6-carboxamidobenzo[*f*]quinoline (**7**, 25 mg, 0.11 mmol) in 20 ml of ethanol was heated to reflux and gaseous hydrogen chloride was bubbled into the solution for 1 hr. Refluxing was continued for 28 hr with more hydrogen chloride being added periodically during this period. After the ethanol was removed by distillation, the residue was dissolved in 40 ml of water. The aqueous solution was neutralized by the careful addition of solid sodium bicarbonate and then extracted with three 10-ml portions of chloroform. The combined organic extracts were dried over sodium sulfate. The chloroform was removed and the residual oily solid (14 mg, 52%), mp 89–95°, was homogeneous by tlc and its infrared spectrum showed strong carbonyl absorption at 1710 cm^{-1}. Four recrystallizations from methanol–water gave colorless needles, mp 102–103° (lit.[48] mp 104–105°). The sample prepared in this way was identical (tlc, ir) with a sample prepared by the reported[48] method, having mp 102–103°; a 1:1 mixture of the two samples exhibited mp 101–103°.

Registry No.—**1a**, 538-49-8; **1b**, 22188-06-3; **1c**, 22188-07-4; **1d**, 22188-08-5; **1d** picrate, 22188-09-6; **1e**, 22188-10-9; **2e**, 22188-11-0; **4a**, 85-02-9; **4b**, 22187-92-4; **4c**, 22187-93-5; **4d**, 22187-94-6; **4d** picrate, 22187-95-7; **6**, 22212-32-4; **7**, 22212-33-5; 5-methoxy-2-pyridinecarboxaldehyde, 22187-96-8; 2-phenyl-3-(2-pyridyl)acrylic acid, 22188-12-1.

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(48) W. A. Jacobs and R. G. Gould, *J. Biol. Chem.*, **120**, 141 (1937).