Photochemical Cyclizations. II. Effect of Structural Features on the Photocyclization of 2-Stilbazole Derivatives[1,2]

PHILIP L. KUMLER[3a]* AND RICHARD A. DYBAS[3b]

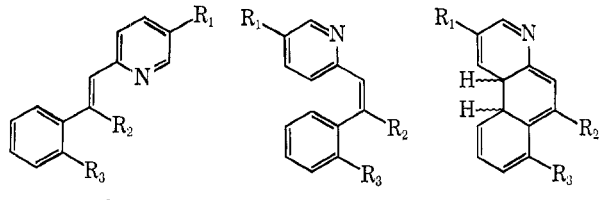
Department of Chemistry, University of Rochester, Rochester, New York 14627

Received February 24, 1970

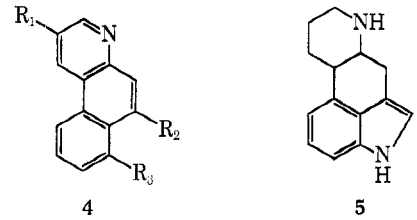
The photochemical behavior of a series of 2-stilbazole derivatives has been investigated as part of a synthetic scheme leading to the ergoline ring system of the ergot alkaloids. In general, these compounds undergo facile oxidative photocyclization to benzo[*f*]quinoline derivatives; it has been found, however, that certain structural features can prevent the desired photocyclization.

As part of a continuing program directed toward the synthesis of various ergot alkaloids[4] we are investigating the feasibility of utilizing photochemical cyclizations of suitably substituted stilbazoles **1** or **2**.

Irradiation of the trans[5] isomer **1** would be expected to cause initial trans–cis isomerization (**1** → **2**) and



1 **2** **3**



4 **5**

	R_1	R_2	R_3
a	H	H	H
b	H	CN	H
c	OCH_3	CN	H
d	H	$COOCH_3$	H
e	H	H	$NHCOCH_3$
f	H	H	NO_2
g	OCH_3	CN	Cl

subsequent cyclization to the dihydrobenzo[*f*]quinolines **3**,[7] which should be readily oxidized to the benzo[*f*]-quinolines **4**. The oxidative photocyclization of various stilbenes to phenanthrenes has received considerable attention[9,10] but the photocyclization of stilbazole derivatives has not been as thoroughly investigated.[11]

All of the alkaloids thus far isolated from the filamentous fungus *Claviceps purpurea* are collectively referred to as the ergot alkaloids.[12] The structures of all of these alkaloids are based upon the same tetracyclic ring system **5** that Jacobs and Gould[13] called ergoline. It was felt that successful preparation of suitably substituted benzo[*f*]quinolines **4** by photocyclization reactions would allow very facile entry into the tetracyclic ring system **5**.

Results and Discussion

In the previous paper in this series[4] we reported the successful photocyclization of the 2-stilbazole derivatives **1a–1d** to the benzo[*f*]quinolines **4a–4d**. At the same time we reported unsuccessful attempts at the photocyclization of **1e** and **1f** and discussed the reasons for lack of success in these cases. In addition we investigated the effect of various experimental parameters (wavelength of light, nature of the solvent, nature of the oxidizing agent) to determine the optimum conditions for the photocyclization of 2-stilbazoles. A notable result of this work was the very definite advantage of utilizing *tert*-butyl alcohol as solvent for the photocyclization of stilbazoles and various possible reasons for this effect were discussed.[14]

With a view toward utilizing substituents R_2 and R_3 to construct the five-membered ring present in the

* To whom correspondence should be addressed.

(1) Abstracted in part from the dissertations submitted by P. L. Kumler and R. A. Dybas to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the Ph.D. degree, May 1967 (P. L. K.) and Jan 1970 (R. A. D.).

(2) For paper I in this series, see ref 4.

(3) (a) National Institutes of Health Predoctoral Fellow, 1966–1967. To whom correspondence should be addressed: Department of Chemistry, Saginaw Valley College, University Center, Mich. 48710. (b) National Institutes of Health Predoctoral Fellow, 1968–1969.

(4) P. L. Kumler and R. A. Dybas, *J. Org. Chem.*, **35**, 125 (1970).

(5) The stereochemistry about the double bond of compounds of this type will be described as being derived from *trans*- and *cis*-2-stilbazole, **1a** and **2a**, respectively. Use of the descriptors *E* and *Z*[6] to define the configuration about the double bond in compounds of this type, although always leading to a completely unambiguous stereochemical assignment, sometimes leads to opposite descriptors for compounds having the same geometry of the two aromatic rings around the central stilbazole double bond. For example, stilbazole **1d** is of the *Z* configuration while **1e** is of the *E* configuration but both compounds contain a *trans*-2-stilbazole moiety.

(6) J E Blackwood, C. L. Gladys, K. L. Loening, 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. Doc.*, **8**, 30 (1968).

(7) There is apparently only one well documented example of isolation of a *stable* dihydro intermediate from a stilbene photocyclization[8] but this work appears to have been overlooked in recent reviews of this field.[9,10]

(8) D. Banes, *J. Ass. Offic. Agr. Chem.*, **44**, 323 (1961).

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

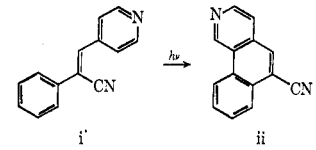
(10) E. V. Blackburn and C. J. Timmons, *Quart. Rev. (London)*, **23**, 482 (1969).

(11) See ref 4 and references contained therein.

(12) For a comprehensive review of the chemistry of the ergot alkaloids, see R. H. F. Manske and H. L. Holmes, "The Alkaloids," Academic Press, New York, N. Y.: Vol. II, 1952, pp 375–392, and Vol. VII, 1960, pp 9–36.

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

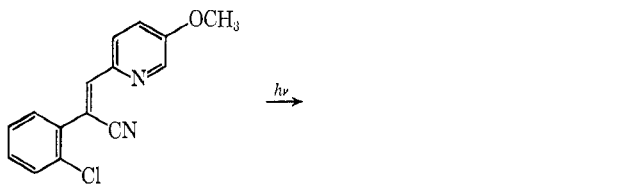
(14) As another example of the utility of this solvent for stilbazole photocyclizations, irradiation of the 4-stilbazole derivative i in oxygen-saturated *tert*-butyl alcohol through a Corex filter for 4 hr resulted in isolation of benz[*h*]isoquinoline-6-carbonitrile (ii) in 58% yield. Previous workers[15] have noted that 4-stilbazole derivatives (in contrast to 2-stilbazole derivatives) cyclize very sluggishly and in inferior yield.



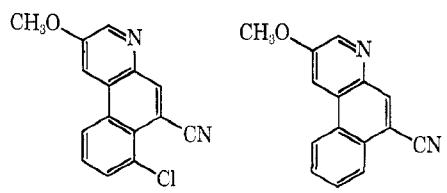
i ii

(15) C. E. Loader and C. J. Timmons, *J. Chem. Soc. C*, 1078 (1966).

ergoline skeleton **5** we investigated the photochemical behavior of the 2-stilbazole derivative **1g**. Photolysis of **1g**, using a variety of experimental conditions, proceeded at a slow rate with the formation of large amounts of polymeric material, to give two major products, **4g** and **4c**, in low yield (at least two other products were detected by tlc but not characterized). Of the experimental conditions investigated (*tert*-butyl alcohol, oxygen, Corex; benzene, oxygen, Corex; acetonitrile, oxygen, Pyrex) the *tert*-butyl alcohol solvent system gave the best results. Thus, photolysis of **1g** in this solvent through Corex for 5 hr, followed by column chromatography of the complex photolysate on alumina, led to isolation of both **4g** (11%) and **4c** (6%). The formation of **4c**, which formally corresponds to loss



1g

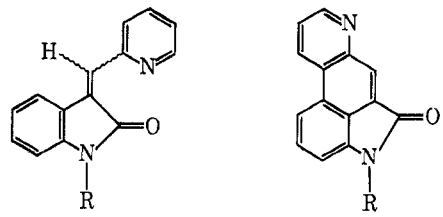


4g **4c**

of the elements of HCl, can be rationalized in a number of ways. Loss of substituents other than hydrogen during photocyclizations have been seen in a number of cases and the substituents "lost" include Cl, Br, CH_3, COOH, I, and OCH_3.[16,17] In almost all cases (loss of I appears to be an exception) the substituent which is "lost" is at a position on the ring where cyclization occurs. Whether the Cl substituent in the present cases is lost prior to the photocyclization (photoinduced homolytic cleavage of the C–Cl bond in **1g** or **2g**), by elimination of HCl from a dihydro intermediate of the type **3**, or by photoinduced homolytic cleavage of a C–Cl bond in the product **4g**, was not however investigated. It is possible that the presence (assumed) of HCl during photolysis could account for the inferior yields in the present case although this reaction was not investigated in any more detail.

The most desirable type of benzo[*f*]quinoline consistent with the rest of our anticipated scheme for the synthesis of the various ergot alkaloids would be one in which R_2 and R_3 form a five-membered lactam, that is compounds of the type **7**. Consistent with this idea we investigated the solution photochemistry of the stilbazole derivatives **6**.

Irradiation of the stilbazole derivative **6a**[18] under a wide variety of experimental conditions (see Experimental Section) failed to give any detectable evidence



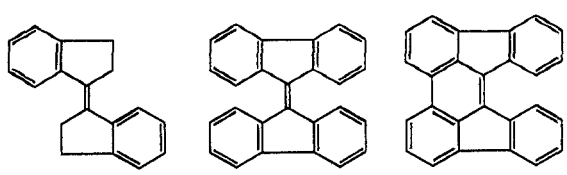
6 **7**

a, R = H
b, R = CH_2Ph

(ultraviolet spectra or tlc versus authentic **7a**) for the desired photocyclization. At wavelengths longer than 290 nm an unstable photoproduct (presumably the isomeric cis or trans olefin) could be detected by tlc but it was converted back to starting material upon attempted isolation. At wavelengths shorter than 290 nm extensive decomposition occurred but no photocyclization could be detected by tlc or ultraviolet spectroscopic analysis. However, control studies suggested that the expected photocyclization product **7a** might not survive the reaction conditions (see Experimental Section). It is of course possible that some structural feature present in **6a** was prohibiting the photocyclization from occurring at all (see below).

As in the case of **6a**, the irradiation of **6b** under a wide variety of experimental conditions led to extensive decomposition, but no detectable photocyclization, if light of wavelength shorter than 290 nm was utilized.

Examination of the literature revealed the successful photocyclization of various compounds containing *some* of the structural features present in **6a** (or **6b**). For example, various groups have reported the photocyclization of compounds incorporating five-membered rings;[19–21] photocyclization of systems in which the stilbene-like double bond is exocyclic to a fused ring system have also been reported.[22–24] However, none of these cases have the stilbene-like double bond exocyclic to a fused five-membered ring. During the preparation of this manuscript, three reports concerning the photochemistry of stilbene systems in which the stilbene double bond is exocyclic to a fused five-membered ring system have appeared. Goedicke and Stegemeyer[25] reported that the stilbene derivative **8** did



8 **9** **10**

not undergo either isomerization to the cis isomer or photocyclization to the dicyclopentanophenanthrene. At about this same time Gunst reported on the

(16) See ref 9, p 261, for pertinent references.

(17) M. P. Cava, M. J. Mitchell, S. C. Havlicek, A. Lindert, and R. J. Spangler, *J. Org. Chem.*, **35**, 175 (1970).

(18) The stereochemistry around the double bond in compounds **6a** and **6b** is uncertain but does not affect the present results since the initial step in the photocyclization sequence involves cis–trans isomerization.[9,10] Our work suggests, in fact, that the two isomers interconvert readily in solution (see Experimental Section).

(19) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

(20) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965).

(21) M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963).

(22) M. P. Cava, S. C. Havlicek, A. Lindert, and R. J. Spangler, *Tetrahedron Lett.*, 2937 (1966); also, see ref 17.

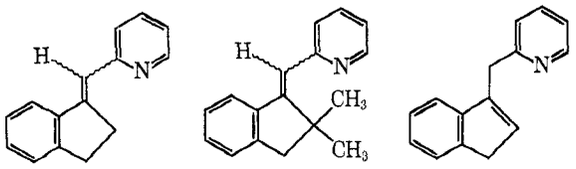
(23) N. C. Yang, G. R. Lenz, and A. Shani, *Tetrahedron Lett.*, 2941 (1966).

(24) For a review of the photocyclization of anthrone and bianthrone derivatives, see ref 9, pp 248–253.

(25) C. Goedicke and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **73**, 782 (1969).

photochemistry of 9,9′-bifluorenylidene (**9**)[26] and reported the isolation, in very low yield, of a compound tentatively identified as the phenanthrene derivative **10**. Other workers have not, however, detected this product during an independent study of the same stilbene derivative **9**.[27]

In light of the above considerations, it was decided to investigate whether the stilbazole derivative **11** would undergo the desired photocyclization. The failure or success of this photocyclization would allow a more



11 **12** **13**

a = *cis*

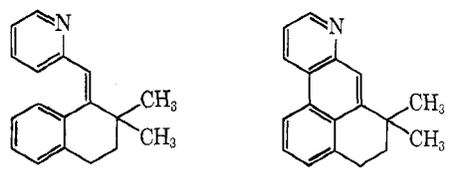
b = *trans*

realistic assessment of the effect of the fused five-membered ring. Under various conditions (see Experimental Section) the exocyclic olefin **11** was converted in moderate yield (20–35%) to the endocyclic olefin **13**. Although other products were formed none of these appeared to contain the benzo[*f*]quinoline skeleton (by uv spectroscopic examination of the photolysate and lack of the blue fluorescence on tlc plates which seems to be characteristic of the benzo[*f*]quinoline system). Although there are a number of examples of photoinduced isomerization of 1-alkylcycloalkenes to their analogous exocyclic isomers,[28] to our knowledge this represents one of the very few examples of the isomerization proceeding in the opposite direction under photochemical conditions.[29] The original purpose of this particular experiment (*i.e.*, is it the presence of the fused five-membered ring which prevents the desired photocyclization?) was not however fulfilled. It is possible that the availability of another reaction path (exo to endo isomerization), perhaps of lower energetic requirements, effectively masks the desired photocyclization. Therefore, a study of the photochemical behavior of the stilbazole derivative **12**, in which the exo to endo isomerization cannot occur, was undertaken.

Irradiation of **12a** in *tert*-butyl alcohol containing 7.5% benzene[30] through a Corex filter in the presence of oxygen led to very rapid trans–cis isomerization (photostationary state reached in 0.5 hr). Continued irradiation for a total of 6 hr led to no further changes as evidenced both by tlc and ultraviolet spectroscopy. Column chromatography of the photolysate resulted in isolation of **12b** (57%) and **12a** (38%).

At this stage of the investigation it was felt that one of the major factors contributing to the failure of photocyclizations in systems of the present type was the presence of the stilbazole double bond exocyclic to a fused *five-membered* ring. As a test of this empirical hypothesis we investigated the photochemical behavior of the stilbazole derivative **14**, in which the stilbazole double bond is exocyclic to a fused *six-membered* ring.

As expected, irradiation of the stilbazole derivative **14** in the presence of oxygen through a Corex filter led to isolation of the desired photocyclization product **15** in 53% yield.

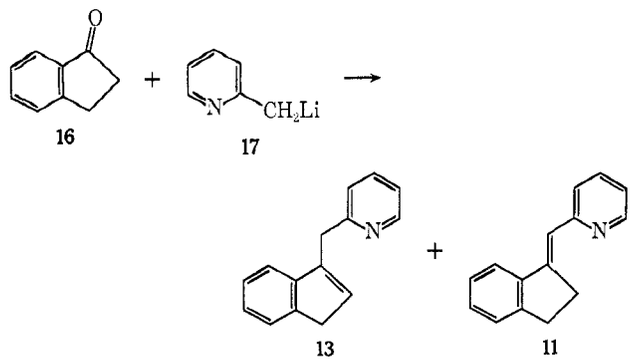


14 **15**

In summary, we have shown that in systems of the type considered in the present work one of the major reasons for failure to observe the desired photocyclization is the presence of the stilbazole double bond in a position exocyclic to a fused five-membered ring. This suggests that in order for photocyclization to occur, the stilbazole system (*i.e.*, the benzene and pyridine rings and the linking double bond) must be able to attain a geometry which approximates that of *cis*-2-stilbazole; the presence of any structural element (such as that described above) which precludes the attainment of such geometry will effectively inhibit the desired photocyclization.[31] To our knowledge the present study reports the first elucidated example of a structural feature which effectively prohibits the photocyclization reaction; the suggestion of Stermitz concerning the generality of the photocyclization reaction[32] should not be taken as an inviolable rule.

Syntheses and Structural Assignments.—Stilbazole **1g** was prepared by base-catalyzed condensation of 2-chlorophenylacetonitrile with 5-methoxy-2-pyridinecarboxyaldehyde. The oxindole derivative **6a** was prepared in an analogous fashion from oxindole and 2-pyridinecarboxaldehyde. The oxindole derivative **6b** was most conveniently prepared by condensation of 1-benzylisatin with 2-picoline in the presence of acetic anhydride.

Preparation of the stilbazole derivative **11** was attempted by the reported method.[33] Condensation of 1-indanone (**16**) with 2-picolyllithium (**17**) gave a



16 **17** **13** **11**

(26) G. P. de Gunst, *Recl. Trav. Chim. Pays-Bays*, **88**, 801 (1969).

(27) J. Nasielski, M. Jauquet, E. Vander Donckt, and A. Van Sinoy, *Tetrahedron Lett.*, 4859 (1969).

(28) (a) P. J. Kropp, *J. Amer. Chem. Soc.*, **88**, 4091 (1966); (b) P. J. Kropp, *ibid.*, **89**, 3650 (1967); (c) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967); (d) P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 3222 (1967); (e) P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969).

(29) A similar phenomenon has been briefly reported in ref 25.

(30) This solvent system seems to be the preferred one for photocyclizations in systems of this type. For a discussion of this solvent effect, see ref 4.

(31) The only apparent exception to this generality appears to be that concerning the isolation of **10** from the irradiation of the stilbene derivative **9**[26] which may be an anomalous case since this molecule contains two separate stilbene systems sharing the same central double bond.

(32) "... the cyclization seems to 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." Reference 9, p 259.

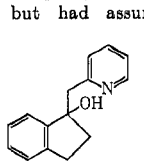
(33) J. Sam, J. Plampin, and D. Alwami, *J. Org. Chem.*, **27**, 4543 (1962).

mixture of the desired exo olefin **11** and the endo olefin **13** in the ratio 1:4 (exo:endo). The composition of the olefin mixture was determined by comparison of the spectral properties of the mixture with those of pure samples of each of the olefins (see below). Treatment of the olefin mixture with hydrogen bromide in ether resulted in the formation of a single hydrobromide in 77% yield. This hydrobromide salt was, in fact, the hydrobromide of the exo olefin **11**. Thus, from a mixture which was originally 80% endo olefin approximately 80% of the exo olefin hydrobromide was obtained. Pure exocyclic olefin **11** was obtained as a crystalline solid by treatment of the hydrobromide with dilute base.[34]

The exo olefin **11** gave satisfactory analytical data, the melting point of the hydrobromide salt was the same as that reported by previous workers,[33] and it gave a picrate which also exhibited the correct analytical data. The nmr, ir, and uv spectra were consistent with the assigned structure (see Experimental Section) with the following pertinent points. The ultraviolet spectrum was very similar to that of *trans*-2-stilbazole (see ref 4) and the ir spectrum showed characteristic absorption at 1635 cm^{-1} assigned to the exocyclic olefinic linkage. Both the picrate and the hydrobromide salts showed this same ir absorption.

The endo olefin **13** was a yellow liquid which gave unsatisfactory analytical data and was subject to decomposition at room temperature. Treatment of the endo olefin with hydrogen bromide in ether gave the hydrobromide of the exo olefin **11** as expected (see above). However, treatment of the endo olefin with picric acid in ethanol led to a picrate which was different from that of the exo olefin and satisfactory analytical data were obtained on the picrate. Spectral data consistent with the structural assignment were obtained on samples of olefin freshly regenerated from the picrate. The ir spectrum showed a band at 1615 cm^{-1} assigned to the endocyclic olefin and this band was also present in the ir spectrum of the picrate. The ultraviolet spectrum is very similar to that of indene[36] and the nmr spectrum is very similar to that reported for 1-benzylindene.[37]

(34) The previous workers[33] had not characterized the product of the original condensation between 2-picolyllithium and 1-indanone (only a boiling point is reported) but had assumed the product to be



iii

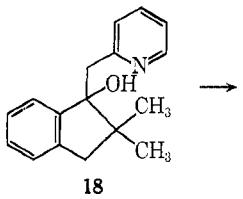
the carbinol iii which is certainly the immediate precursor of the olefin mixture. In order to dehydrate the "alcohol" iii they heated the condensation product in molten phosphorus pentoxide for 7 hr.[35] After distillation of the reaction mixture from the P_2O_5 treatment they obtained the desired exo olefin (probably the same mixture described in the present work) as a liquid. Again, only a boiling point is recorded and this olefin was analyzed in the form of the hydrobromide salt. Therefore, Sam and coworkers had probably carried out the same sequence observed in this study but did not realize it because of their failure to characterize both the initial product of the condensation and the product resulting from the molten phosphorus pentoxide treatment.

(35) Control experiments in the present work have shown that the composition of the olefin mixture is not changed by this rather drastic treatment and hence this mixture probably reflects the thermodynamic stability of the two isomers.

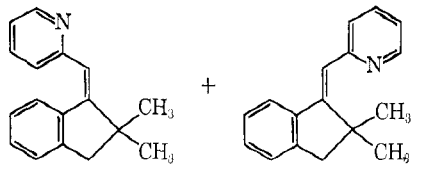
(36) Sadtler Standard Spectra, Sadtler Research Associates, Spectrum No. 308 UV.

(37) A. M. Weidler, *Acta Chem. Scand.*, **17**, 2724 (1963).

The stilbazole derivative **12** was prepared by dehydration of the carbinol **18**, formed by condensation of 2,2-dimethyl-1-indanone with 2-picolyllithium. If refluxing acetic anhydride is used for the dehydration a



18



12a 12b

54% yield of the olefin mixture is formed (considerable amounts of 2,2-dimethyl-1-indanone and 2-picoline are formed by reversal of the initial condensation) and the composition of this mixture is 77% **12a** and 23% **12b** as analyzed by nmr (see below). Dehydration with *p*-toluenesulfonyl chloride led to quantitative formation of the olefin mixture (72% **12a**, 28% **12b**). The two olefins could be separated by column chromatography and were each completely characterized. The stereochemical assignments were based upon ultraviolet spectra (similarity to *cis*- and *trans*-2-stilbazole; see Experimental Section and ref 4) and nmr spectra. The nmr resonance due to the vinyl proton of **12a** was at τ 3.47 while that due to the vinyl proton of **12b** was at τ 2.92. These values are quite consistent with those for a series of cis and trans stilbene derivatives.[38]

The stilbazole derivative **14** was prepared by condensation of 2,2-dimethyl-1-tetralone with 2-picolyllithium and dehydration of the resultant carbinol with *p*-toluenesulfonyl chloride in pyridine. The resultant olefin **14** gave consistent analytical and spectral data and was exclusively of the cis configuration as assigned by nmr analysis.[38]

Experimental Section[39]

2-(2-Chlorophenyl)-3-(5-methoxy-2-pyridyl)acrylonitrile (1g).—A mixture of 2-chlorophenylacetonitrile[40] (1.51 g, 0.01 mol) and 5-methoxy-2-pyridinecarboxaldehyde[4] (1.37 g, 0.01 mol) in 15 ml of absolute methanol was warmed to 50°. A sodium methoxide solution (3.66 *M* in methanol, 2.75 ml, 0.01 mol) was added and the reaction mixture was maintained at 55–60° for 1 hr and then cooled. The resultant crystals were removed by filtration. Recrystallization from pentane gave **1g** as colorless crystals (1.11 g, 41%): mp 82–83°; ir ($CHCl_3$) 2200 cm^{-1} (C≡N); uv max (95% ethanol) 318 nm (ϵ 26,900), 291 (sh, 16,250), and 210 (24,250); uv max (C_6H_{12}) 310 nm (21,400), and 208 (21,900); nmr ($CDCl_3$) τ 6.10 (s, 3 H, OCH_3), 1.55 (d, J = 2.9 cps, 1 H,

(38) H. Gusten and M. Salzwedel, *Tetrahedron*, **23**, 173, 187 (1967).

(39) 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 Model 11 or Model 14 Cary 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; chemical shifts are reported in ppm (τ) relative to tetramethylsilane as internal standard. Elemental analyses are by Micro-Tech Laboratories (Skokie, Ill.) or by Crobaugh Laboratories (Cleveland, Ohio).

(40) C. Viel, R. Dorme, and P. Rumpf, *Bull. Soc. Chim. Fr.*, **6**, 1956 (1966).

pyridyl H_3), 2.08 (d, J = 9 cps, 1 H, pyridyl H_6), and 2.38–2.87 (m, 6 H, vinyl and other aromatic protons).

Anal. Calcd for $C_{16}H_{11}N_2OCl$: C, 66.55; H, 4.09; N, 10.35. Found: C, 66.42; H, 4.11; N, 10.21.

Isatinylidene-3-(2-picoline) (**6a**).—To a solution of oxindole (40.0 g, 0.30 mol) and 2-pyridinecarboxaldehyde (32.1 g, 0.30 mol) in 95% ethanol was added 2 ml of piperidine. The solution was refluxed for 4 hr and then cooled to room temperature. The resultant red crystals (58.4 g, 87%, mp 199–201°) were removed by filtration, air dried, and then eluted through a short column of Woelm alumina (activity III) with methylene chloride to give bright orange needles which were recrystallized from 95% ethanol. This gave **6a** as orange needles: mp 202.5–203° (lit.[41] mp 205–207°); ir ($CHCl_3$) 1712 (C=O), and 3350 cm^{-1} (NH); uv max (95% ethanol) 347 nm (sh, ϵ 7840), 333 (11,470), 325 (sh, 9800), 257 (11,500), and 209 (20,900); nmr (CF_3COOH) τ 0.57–2.95 (m, 10 H, amide, vinyl, and aromatic protons).

1-Benzylisatinylidene-3-(2-picoline) (**6b**).—A mixture of 1-benzylisatin[42] (11.8 g, 0.05 mol) and 2-picoline (24 ml, 0.27 mol) was refluxed for 6 hr in the presence of acetic anhydride (30 ml). The warm reaction mixture was poured over ice and, after 5 hr, was basified with ammonium hydroxide. The orange-brown precipitate was filtered, washed with water, and air dried. The crude product was eluted through 125 g of activity I Woelm alumina to give, after removal of the eluting solvent, **6b** as bright orange needles (6.0 g, 40%), mp 134–136°. Recrystallization from 95% ethanol gave the analytical sample as yellow needles: mp 139–140°; ir (KBr) 1705 (C=O) and 1630 cm^{-1} (C=C); uv max (C_6H_{12}) 346 nm (sh, ϵ 13,900), 330 (16,500), 317 (13,000), 268 (14,400), and 210 (15,000); uv max (CH_3OH) 328 nm (ϵ 12,000), 256 (12,700), and 207 (27,000); nmr ($CDCl_3$) τ 0.8–1.3 (m, 2 H), 2.2–3.5 (m, 12 H) and 5.00 (s, 2 H, CH_2—N); the aromatic protons of the benzyl group gave a singlet at τ 3.30 easily discernible from the other resonances in this region.

Anal. Calcd for $C_{21}H_{16}N_2O$: C, 79.98; H, 5.37. Found: C, 80.15; H, 5.27.

1-Indanylidene-(2-picoline) (**11**).—Freshly cut lithium strips (3.45 g, 0.50 g-atom) were placed in 200 ml of anhydrous ether and then bromobenzene (39.2 g, 0.25 mol) was added at a rate sufficient to keep the ether at reflux. After all of the bromobenzene had been added the reaction mixture was stirred at reflux for 1 hr. To the resultant phenyllithium solution, 2-picoline (23.2 g, 0.25 mol) was added dropwise over a period of 5–10 min. The deep-red solution was stirred for 1 hr, cooled in an ice bath, and 1-indanone (30.0 g, 0.23 mol) dissolved in 75 ml of ether was added dropwise. The light-gray mixture was then immediately decomposed by the addition of 50 ml of concentrated hydrochloric acid and 50 ml of water, and the two phases were separated. The ether phase was extracted once with 10% HCl and the combined aqueous phases were added to a saturated solution of sodium carbonate. The oily layer which separated was extracted into ether and dried over Na_2SO_4. Evaporation of the ether gave a yellow oil (43.9 g) which was distilled under reduced pressure. After removal of a forerun (~8 g) of 1-indanone, the two major fractions [12.9 g, bp 123–129° (0.5 mm), and 14.9 g, bp 129–131° (0.5 mm)] were combined after their infrared spectra and tlc behavior were shown to be essentially identical. The dark brown distillation residue (6.8 g) was not characterized.

The tlc and spectral properties of the distillate were consistent with a mixture of endo (**13**) and exo (**11**) olefins in the ratio of 4:1 (endo:exo).

A 15.6-g sample of the olefin mixture was dissolved in 800 ml of anhydrous ether and the solution was saturated with gaseous hydrogen bromide. Removal of the ether gave a bright yellow amorphous residue, mp 248–256° dec, which was recrystallized from methanol (600 ml) to give the exo olefin hydrobromide (14.4 g) as very large (~1 × 1 × 10 mm) straw colored rods, mp 259–260° (lit.[33] mp 258–260°); an additional crop (2.3 g, mp 256–259°) was obtained by concentration and cooling of the mother liquor, making the total yield 16.7 g (77%).

The tlc behavior of the free base was determined by partitioning the salt between ether and 10% KOH and looking at the tlc of the ether layer. The free base was homogeneous and the R_f value was identical (2 solvent systems) with one component (that with the larger R_f value) of the original olefin mixture. The ir spectrum of the hydrobromide showed medium intensity absorption at 1640 cm^{-1} (exo C=C).

(41) M. Akkerman and H. Veldstra, *Recl. Trav. Chim. Pays-Bas*, **73**, 629 (1954).

(42) R. L. Autrey and F. C. Tahk, *Tetrahedron*, **23**, 901 (1967).

The above hydrobromide (14.4 g, 0.05 mol) was partitioned between 150 ml of 10% KOH–H_2O and 150 ml of ether. The ether phase was washed to neutrality with water, then with saturated salt solution, and dried over sodium sulfate. Evaporation of the ether gave 1-indanylidene-(2-picoline) as off-white crystals (9.9 g, 95%), mp 69–71°. Recrystallization from 100 ml of hexane gave colorless rosettes (8.7 g), mp 69–70°. Two additional recrystallizations gave the analytical sample as colorless needles: mp 72–73°; ir (KBr) 1635 cm^{-1} (exo C=C); uv max (C_6H_{12}) 343 nm (ϵ 17,300), 325 (22,100), 295 (sh, 10,000) 283 (11,700), 244 (6000), 236 (7350), and 228 (430); nmr ($CDCl_3$) τ 1.55 (br d, J = 6 cps, 1 H, pyridyl H_6), 2.2–3.2 (m, 8 H, vinyl proton and other aromatic protons), and 7.07 (m, 4 H, aliphatic protons).

Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.75; H, 6.30; N, 6.48.

The picrate of the exo olefin was prepared by addition of a solution of the exo olefin (207 mg, 1.0 mmol) in 10 ml of ethanol to a saturated solution of picric acid in ethanol (25 ml). Heating for 10 min on a steam bath and cooling gave the picrate as bright yellow needles (380 mg, 87%), mp 207–209° dec. For analysis the picrate was sublimed [185° (0.01 mm)] and the sublimate was recrystallized from a large volume of ethanol to give bright yellow crystals: mp 208–209°; ir (KBr) 1635 cm^{-1} (exo C=C).

Anal. Calcd for $C_{21}H_{16}N_4O_7$: C, 57.80; H, 3.70; N, 12.84. Found: C, 57.65; H, 3.72; N, 12.71.

1-(2-Pyridylmethyl)-2,2-dimethyl-1-indanol (**18**).—A solution of 2-picolyllithium was prepared as above from lithium (2.71 g, 0.39 g-atom), bromobenzene (30.6 g, 0.195 mol), and 2-picoline (18.1 g, 0.195 mol). To the ether solution of 2-picolyllithium at 0° was added 2,2-dimethyl-1-indanone[43] (25.0 g, 0.156 mol) in 30 ml of ether over a 25-min period. After 15 min, 40 ml of water and 40 ml of concentrated hydrochloric acid were added successively. The aqueous phase was separated and poured with stirring into 350 ml of saturated aqueous sodium carbonate. The resultant red oil was extracted into benzene and the benzene was washed with water and dried over sodium sulfate. Evaporation of the solvent gave the carbinol as an orange oil (40.0 g) which solidified on standing. The crude carbinol was eluted through a pad of Woelm activity V alumina with benzene; removal of the solvent gave a homogeneous (tlc) pale yellow solid (38.0 g, 96%), mp 70–77°. A further elution through activity III alumina and two recrystallizations from hexane gave colorless plates, mp 82–83°; ir ($CHCl_3$) 3150 (OH), and 1110 cm^{-1} (C—O stretch, 3° alcohol); nmr ($CDCl_3$) τ 9.01 (s, 3 H, CH_3), 8.82 (s, 3 H, CH_3), 7.21 (s, 2 H, Ar-CH_2), 6.93 (AB q, J = 14 cps, 2 H, Py-CH_2), 1.38 (m, 1 H, pyridyl α proton), and 2.25–3.52 (m, 8 H, hydroxyl and other aromatic protons).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.66; H, 7.52; N, 5.52.

2-(2,2-Dimethyl-1-indanylidenemethyl)pyridine (**12**). **Method A.**—A solution of **18** (25.3 g, 0.10 mol) and acetic anhydride (40.8 g, 0.40 mol) was stirred overnight at room temperature followed by refluxing for 1 hr. The acetic anhydride was removed by distillation and the residue was partitioned between water and benzene. The benzene solution was extracted with 10% HCl (200 ml), washed with water, and dried over sodium sulfate. Evaporation of the solvent gave a red oil (6.9 g, 43%) whose tlc, ir, and nmr were identical with that of 2,2-dimethyl-1-indanone.

The acid solution from above was basified with 10% NaOH and extracted with benzene. The combined benzene extracts were washed with water, dried over Na_2SO_4, and evaporated to give the olefin as an orange oil (12.6 g, 54%). Analysis by nmr indicated the oil to be a mixture of 77% cis isomer **12a** and 23% trans isomer **12b**. Vacuum distillation of the crude olefin gave a pale yellow oil (10.9 g), bp 130–135° (0.005 mm), which was dissolved in 30 ml of ethanol and added to a saturated solution of picric acid in ethanol to give the picrate of the cis isomer **12a** as bright yellow needles (10.6 g), mp 154.5–158.5°. Regeneration of the free base by partitioning the picrate between chloroform and 0.5 N lithium hydroxide solution gave the cis olefin **12a** as a colorless oil (4.5 g); ir (film) 1640 cm^{-1} (trisubstituted C=C); uv max (C_6H_{12}) 314 nm (ϵ 14,500), 282 (11,800), and 225 (15,400); uv max (95% ethanol) 310 nm (ϵ 10,800), 267 (sh, 7700), and 224 (14,000); nmr ($CDCl_3$) τ 8.70 (s, 6 H, gem CH_3), 7.14 (s, 2 H, CH_2), 3.47 (s, 1 H, vinyl proton), 1.28 (br d, 1 H, pyridyl α proton), and 2.13–3.08 (m, 7 H, other aromatic protons).

(43) M. Mousseron, R. Jacquier, and H. Christol, *Bull. Soc. Chim. Fr.*, **24**, 346 (1957).

Anal. Calcd for $C_{17}H_{17}N$ (olefin): C 86.76; H, 7.28; N, 5.95. Found: C, 86.39; H, 7.25; N, 5.92.

Anal. Calcd for $C_{23}H_{20}N_4O_7$ (picrate): C, 59.48; H, 4.34; N, 12.07. Found: C, 59.59; H, 4.35; N, 11.99.

The ethanolic mother liquors from cis picrate formation were partitioned between 0.5 *N* lithium hydroxide and chloroform as above, giving a pale yellow oil (5.5 g) which consisted of 56% cis isomer **12a** and 44% trans isomer **12b**. Column chromatography on grade III Woelm alumina and elution with hexane gave the trans isomer as a colorless oil (1.91 g) which was purified through its picrate (mp 181–182°); the purified trans olefin **12b** was a colorless oil: ir (film) 1665 cm^{-1} (C=C); uv max (C_6H_{12}) 346 nm (ϵ 13,400), 332 (23,100), 319 (21,700), 307 (sh, 15,400), 299 (sh, 13,000), 282 (13,000), 246 (7600), 238 (10,300), and 230 (10,000); uv max (95% ethanol) 340 nm (sh, ϵ 6950), 323 (sh, 13,400), 313 (14,800), 304 (14,500), 278 (br sh, 11,900), 245 (7750), 236 (sh, 8500), and 224 (sh, 10,300); nmr ($CDCl_3$) τ 8.48 (s, 6 H, gem CH_3), 7.10 (s, 2 H, CH_2), 2.92 (s, 1 H, vinyl proton), 1.33 (br d, 1 H, pyridyl α proton), and 2.23–3.17 (m, 7 H, other aromatic protons).

Anal. Calcd for $C_{17}H_{17}N$ (olefin): C, 86.76; H, 7.28; N, 5.95. Found: C, 86.48; H, 7.33; N, 5.91.

Anal. Calcd for $C_{23}H_{20}N_4O_7$ (picrate): C, 59.48; H, 4.34; N, 12.07. Found: C, 59.54; H, 4.34; N, 12.03.

Method B.—The carbinol **18** (1.27 g, 0.005 mol) was dissolved in 25 ml of dry pyridine, *p*-toluenesulfonyl chloride (1.90 g, 0.01 mol) was added, and the solution was heated at reflux for 8 hr. The pale yellow reaction mixture was poured over ice and basified with saturated sodium carbonate solution. The aqueous solution was extracted with benzene (two 75-ml portions); the benzene extracts were washed with water and then saturated salt solution, and then dried over sodium sulfate. Evaporation of the solvent gave a pale yellow oil (1.19 g, 100%) shown to contain only the isomeric (cis–trans) olefins by tlc analysis. Analysis by nmr indicated the mixture to be 72% cis (**12a**) and 28% trans (**12b**). The two olefins were separated by column chromatography on Woelm activity III alumina (**12b** eluted with hexane; **12a** eluted with hexane:benzene, 1:1). The isolated amounts were 300 mg **12b** (27%) and 812 mg **12a** (73%). All spectral properties of the two olefins were the same as those prepared by method A and they both gave picrates identical with those of method A.

2-(2,2-Dimethyl-1-tetralylidenemethyl)pyridine (14).—To a solution of 2-picolyllithium (prepared from 1.46 g of lithium, 16.5 g of bromobenzene, and 9.78 g of 2-picoline; theoretical yield of 2-picolyllithium, 0.105 mol) at 0° was added a solution 2,2-dimethyl-1-tetralone[42] (14.6 g, 0.084 mol) over a 20-min period. Then water (25 ml) and concentrated hydrochloric acid (25 ml) were successively added. After the excess lithium had reacted, the two phase mixture was separated. The ether phase was extracted once with 6 *N* hydrochloric acid and the combined aqueous extracts were poured with stirring into excess aqueous potassium carbonate. The basic solution was extracted several times with benzene; the benzene extracts were washed with saturated salt solution and dried over sodium sulfate. Evaporation of the solvent gave the crude carbinol as a red-brown oil (19.6 g, 87%); ir (film) 3180 (OH) and 1124 cm^{-1} (C—O stretch, tertiary alcohol).

The crude carbinol was dissolved in 175 ml of dry pyridine and *p*-toluenesulfonyl chloride (27.9 g, 0.146 mol) was added. The reaction mixture was refluxed for 72 hr, cooled, and poured into excess potassium carbonate. The basic solution was extracted several times with benzene and the combined benzene extracts were extracted with 10% hydrochloric acid. The acidic solution was basified with 15% sodium hydroxide and extracted with benzene. The benzene extract was washed with water and saturated salt solution and then dried over sodium sulfate. Evaporation of the solvent and subsequent vacuum distillation gave the olefin as a pale yellow oil (5.07 g, 28%), bp 134–139° (0.25 mm).

This olefin was purified by picrate formation (mp 152–153°) and regeneration of the free base. The olefin prepared in this way (only the cis isomer) was a colorless oil: ir (film) 1631 cm^{-1} (C=C); uv max (95% ethanol) 295 nm (ϵ 11,700), 220 (sh, 17,300), and 209 (21,700); uv max (C_6H_{12}) 293 nm (ϵ 13,600), 221 (sh, 19,800), and 210 (25,600); nmr ($CDCl_3$) τ 8.82 (s, 6 H, gem CH_3), 8.27 (t, 2 H, CH_2), 7.20 (t, J = 7 cps, 2 H, Ar-CH_2), 3.42 (s, 1 H, vinyl proton), 3.33–2.67 (m, 7 H, aromatic protons), and 1.53 (br d, 1 H, pyridyl α proton).

Anal. Calcd for $C_{18}H_{19}N$ (olefin): C, 86.70; H, 7.68; N, 5.62. Found: C, 86.64; H, 7.59; N, 5.57.

Anal. Calcd for $C_{24}H_{22}N_4O_7$ (picrate): C, 60.24; H, 4.64; N, 11.71. Found: C, 60.40; H, 4.56; N, 11.83.

Photolyses. General Considerations.—Unless stated otherwise, the substrate was dissolved in solvent 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 (where 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.

Photolysis of 1g. Method A.—The stilbazole derivative **1g** (2.000 g, 0.0074 mol) was dissolved in 50 ml of spectrograde benzene and 925 ml of *tert*-butyl alcohol and irradiated through Corex for 5 hr. After evaporation of the solvent the photolysate was dissolved in chloroform and the chloroform was washed with 10% NaOH. Evaporation of the solvent gave a brown solid residue which was purified by column chromatography on 90 g of activity III alumina. Elution with benzene:hexane (1:1) gave 2-methoxybenzo[*f*]quinoline-6-carbonitrile (**4c**) as an off-white solid (101 mg, 6%), mp 192–198°. Formation of the picrate (mp 223.5–227°) and regeneration of the free base gave **4c** as colorless needles, mp 200–201° (lit.[4] mp 200–201°); this sample was identical (ir, nmr, tlc, mixture melting point) with an authentic sample.[4]

Elution with benzene gave 2-methoxy-7-chlorobenzo[*f*]quinoline-6-carbonitrile (**4g**) as an off-white solid (225 mg, 11.3%): mp 214–216°; ir ($CHCl_3$) 2195 cm^{-1} (C≡N); uv max (C_6H_{12}) 362 nm (ϵ 9750), 345 (8800), 330 (8300), 324 (16,000), 318 (14,300), 310 (15,200), 298 (sh, 10,100), 285 (15,400), 262 (27,900), 256 (sh, 26,800), 241 (37,600), and 223 (sh, 22,500); nmr (CF_3COOH–$CDCl_3$) τ 5.67 (s, 3 H, OCH_3), and 0.78–2.08 (m, 6 H, aromatic protons).

Anal. Calcd for $C_{15}H_9N_2OCl$: C, 67.05; H, 3.38; N, 10.43. Found: C, 67.17; H, 3.43; N, 10.32.

Method B.—The stilbazole **1g** (2.000 g, 0.0074 mol) was dissolved in 950 ml of spectrograde benzene and photolyzed through a Corex filter for 37 hr. A considerable amount of polymeric material formed during the irradiation and the photolysate was filtered before evaporation to give a tan residue (473 mg). Chromatography as in method A gave 24 mg (1.4%) of a tan solid whose tlc and uv spectrum were identical with that of **4c** and 37 mg (1.9%) of a tan solid whose tlc and uv spectrum were identical with **4g**.

Method C.—The stilbazole **1g** (400 mg, 1.48 mmol) was dissolved in 200 ml of spectrograde acetonitrile and photolyzed for 1.25 hr through Pyrex. Evaporation of the solvent gave a dark red glassy solid (500 mg) which was chromatographed on 70 g of activity III alumina. Elution with benzene:hexane (1:1) gave **4c** (10 mg, 3%); elution with benzene gave **4g** (22 mg, 6%).

Photolysis of 6a.—The photolysis of the oxindole derivative **6a** was investigated under a wide variety of conditions. One irradiation will be described in detail, while the others will only be briefly summarized.

Method A.—The stilbazole **6a** (1.600 g, 0.0072 mol) was dissolved in 950 ml of iropropyl alcohol and irradiated through Pyrex for 24 hr. At this stage the uv spectrum showed only very minor changes and tlc indicated (in addition to starting material) trace amounts of a product (henceforth called photo-A) which was probably the isomeric (cis–trans) olefin. Removal of the solvent gave an orange solid, mp 194–198° (some melting and resolidification occurred at 181–182°). The uv and ir spectra of this material were essentially identical with that of the starting material.

Method B.—Same as method A but deoxygenation before and during irradiation was carried out by bubbling nitrogen through the irradiation vessel. Chromatography of the photolysate on activity III alumina gave a mixture in which photo-A was the main product, but removal of the solvent gave starting material.

Method C.—Same as method B, but through a Vycor filter for 35 hr. Extensive decomposition occurred, but photo-A was detected by tlc at intermediate stages of irradiation.

Method D.—Photolysis in benzene, in the presence of oxygen, through Pyrex for 17 hr (no change by tlc or uv) and then through Corex for an additional 17 hr resulted in no change (tlc or uv).

Method E.—Photolysis in acetonitrile, in the presence of oxygen, through Vycor for 42 hr resulted in extensive decomposition but no evidence (tlc or uv) for photocyclization.

Method F.—A saturated solution of the stilbazole in cyclohexane was placed in a quartz tube and irradiated at 2537 Å in a Rayonet reactor in the presence of oxygen. Extensive decomposition occurred but there was no evidence (uv) for photocyclization.

Method G.—Photolysis in 0.1 *N* hydrochloric acid, in the presence of oxygen, through quartz for 4 hr led to extensive decomposition but no evidence (tlc or uv) for photocyclization.

Method H.—Photolysis in 0.1 *N* hydrochloric acid, in the presence of oxygen, through Pyrex for 7 hr led to no apparent (tlc or uv) change. Continued irradiation for 90 hr led to disappearence of the orange color with loss of the uv maximum at 333 nm (no other obvious spectral changes from 200 to 300 nm). No further characterization was attempted.

Method I.—Photolysis in cyclohexane (with or without iodine present), in the presence of oxygen, through quartz for 4 hr led to extensive decomposition but no evidence (tlc or uv) for photocyclization.

Method J.—Photolysis in a KBr matrix (standard ir pellet) through quartz for 16 hr led to no change in the ir spectrum.

Control Photolyses of 7a. Method A.—A saturated solution of **7a**[44] in cyclohexane was irradiated in a quartz uv cell by placing the cell 2 in. from a 450 W Hanovia medium-pressure lamp contained in a quartz immersion well. The progress of the irradiation was followed by periodic scanning of the uv spectrum. After 4 hr of irradiation the solution exhibited an unstructured spectrum with a complete loss of the 282 nm band characteristic of the starting material; the spectrum was dominated by intense end absorption at ~210 nm. No further characterization was attempted.

Method B.—A 1-mg sample of authentic **7a**[44] was dissolved in 50 ml of 0.1 *N* hydrochloric acid and an aliquot (~3 ml) of this solution was photolyzed as in method A. Irradiation for 5 hr led to the same results described in method A.

Photolyses of 6b. Method A.—A 119-mg sample of the olefin was irradiated in 120 ml of methanol through quartz for 2 hr. Analysis by tlc showed the complete disappearance of starting material and formation of a complex mixture (minimum of 6 components by tlc). However, there was no evidence (tlc or uv) for photocyclization.

Method B.—Photolysis in benzene, in the presence of oxygen, through quartz for 122 hr led to formation of a complex mixture from which only recovered starting material (37%) could be isolated.

Method C.—Photolysis of the olefin in cyclohexane (with or without added iodine) through Vycor for 5 hr led to extensive decomposition but no evidence (tlc or uv) for photocyclization.

Photolyses of 11. Method A.—The exo olefin **11** (1.00 g) was dissolved in 950 ml of spectrograde cyclohexane and irradiated through Vycor for 70 hr (considerable amounts of polymeric material were present). Filtration of the photolysate and evaporation of the solvent gave a dark brown oil (834 mg) which showed a minimum of 7 components by tlc (none having the same R_f as starting material). Initial chromatography on activity III alumina gave a bright yellow oil (506 mg) which showed three components by tlc. Further attempts at chromatography led to no separation of this three-component mixture. The oil was dissolved in 30 ml of absolute ethanol and a saturated solution of picric acid in ethanol was added until no further precipitation took place. After heating on a steam bath for 5 min and then cooling, filtration gave a bright yellow solid which was washed with a small amount of ethanol, then with ether, and air dried to give the picrate of **13** as an amorphous yellow solid (364 mg), mp 170–173°. Recrystallization from methanol:dimethyl sulfoxide followed by sublimation [145° (0.05 mm)] gave the analytical sample as a bright yellow microcrystalline powder: mp 179–180°; ir (KBr) 1615 cm^{-1} (endo C=C). Regeneration of the free base from its picrate could be accomplished either by partitioning the picrate between methylene chloride and 1% aqueous lithium hydroxide or by chromatographing the picrate on activity III alumina (elution with methylene chloride containing 1% tetrahydrofuran). The endo olefin **13**, recovered from its picrate by either of the above methods, was distilled in a short-path still [~130° (0.1 mm)] to give a mobile yellow liquid, homogeneous by tlc, which slowly decomposed in air. (After 24 hr it was converted to a dark brown viscous gum.) Satisfactory analytical data could not be obtained on this olefin, but consistent spectral data were obtained on a sample freshly recovered from its picrate: ir (film) 1615 cm^{-1} (endo C=C); uv max (C_6H_{12}) 320 (ϵ 770), 278 (1420), and 253 (11,500); nmr ($CDCl_3$) τ 1.42 (br d, 1 H, pyridyl α proton), 2.1–3.3 (m, 7 H, other aromatic protons), 3.75 (br d,[45] 2 H, vinyl proton), 5.90 (d,[45] 2 H, "exo" CH_2), and 6.64 (d,[45] 2 H, ring CH_2).

Anal. Calcd for $C_{21}H_{16}N_4O_7$ (picrate): C, 57.80; H, 3.70; N, 12.84. Found: C, 57.90; H, 3.73; N, 12.83.

Method B.—Exo olefin **11** (1.000 g) was dissolved in 1000 ml of spectrograde cyclohexane in a quartz vessel and the solution was saturated with oxygen; irradiation was carried out in a Rayonet reactor at ~3000 Å (RUL-3000 lamps) for 12.5 hr. Filtration of the photolysate and evaporation of the solvent gave 888 mg of a dark brown oil which showed 5 components (in addition to starting material) by tlc. Preliminary chromatography on activity III alumina gave the same three component mixture described in method A. Formation of the picrate as in method A gave the picrate of **13** (590 mg, 33%), which was identical with that prepared in method A.

Photolysis of 12a.—The stilbazole cis isomer **12a** (1.800 g, 0.0076 mol) was dissolved in a mixture of 75 ml of spectrograde benzene and 925 ml of *tert*-butyl alcohol and irradiated through Corex for 6 hr. After the initial rapid cis–trans isomerization took place within 0.5 hr, no other tlc or ultraviolet spectral changes were detected throughout the photolysis. Removal of the solvent gave an orange oil which was dissolved in benzene and washed through a column of activity III alumina (100 g). Evaporation of the solvent gave a yellow-orange oil (1.73 g, 96%) which showed only two spots on tlc. Analysis by nmr indicated that the mixture consisted of trans isomer **12b** (60%) and cis isomer **12a** (40%). The olefin mixture was chromatographed on activity III alumina; elution with hexane gave **12b** (1.021 g, 60%) as a colorless oil whose nmr and tlc were identical with previously characterized material (see preparation of **12** above). Elution with hexane:benzene (1:1) gave **12a** as a colorless oil (0.686 g, 40%) whose nmr and tlc were identical with that of starting material.

Photolysis of 14.—The stilbazole **14** (1.75 g, 0.007 mol) was dissolved in a mixture of 75 ml of spectrograde benzene and 925 ml of *tert*-butyl alcohol and irradiated through Corex for 5.5 hr. Removal of the solvent gave a red-orange oil which was dissolved in benzene and washed through a column of activity III alumina. Removal of the solvent gave the crude benzo[*f*]quinoline derivative **15** as a pale yellow oil (913 mg, 53%) which slowly solidified on standing, mp 134–139°. Recrystallization from hexane gave colorless needles, mp 138.5–140°: uv max (C_6H_{12}) 353 nm (ϵ 5340), 337 (4590), 322 (2480), 300 (9660), 286 (sh, 12,600), 277 (sh, 18,300), 270 (22,100), 255 (24,800), 245 (sh, 27,500), 240 (32,700), 220 (29,100), and 213 (29,500); nmr ($CDCl_3$) τ 8.60 (s, 6 H, gem CH_3), 8.18 (t, J = 7 cps, 2 H, CH_2), 6.88 (t, J = 7 cps, 2 H, Ar—CH_2), 2.76–2.30 (m, 3 H, H_2, H_8 and H_9), 1.92 (s, 1 H, H_5), 1.57 (br d, 1 H, H_{10}), and 1.20 (br d, 1 H, H_3).

Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.34; H, 6.93; N, 5.52.

Registry No.—**1g**, 25791-26-8; **4g**, 25791-27-9; **6b**, 25791-28-0; **11**, 25791-29-1; **11** picrate, 25791-30-4; **12a**, 25791-31-5; **12a** picrate, 25791-32-6; **12b**, 25791-33-7; **12b** picrate, 25791-34-8; **13**, 25791-35-9; **13** picrate, 25791-36-0; **14**, 25791-39-3; **14** picrate, 25791-40-6; **15**, 25791-38-2; **18**, 25791-41-7.

Acknowledgments.—We acknowledge the financial support of the National Institutes of Health in the form of Predoctoral Fellowships to both authors and we would like to thank Dr. Marshall Gates for many helpful discussions throughout the duration of this work.

(44) We thank D. J. Werber of these laboratories for this sample.

(45) This spectrum shows significant amounts of second-order splitting and hence is not very susceptible to simple first order analysis, but the spectrum is very similar to that of 1-benzylindene.[37]