hexylamine. The control, prepared by bubbling oxygen into cyclohexylamine for 3 hr in the absence of uv light, turned the pink Co(II) color to greenish brown. The quantity of peroxides in the irradiated oxygen-saturated cyclohexylamine was determined by the method of Vogel.[23] After the irradiated solution was treated with triphenylphosphine, the peroxide content was gone.

Anhydrous copper sulfate turned blue in contact with the oxygen-saturated, irradiated cyclohexylamine solution. By comparison of glpc retention times and spiking procedures using a 8 ft × $^{1}/_{4}$ in. Porapak column, water was identified in the reaction mixture.

Ammonia was identified by its characteristic ir spectrum[24] and its glpc retention time using a Porapak column.

Irradiation of Oxygen-Saturated Cyclohexylamine Solution, Filter Studies.—A 1-cm quartz spectrophotometric cell was placed in a holder 2.5 cm from the outside surface of the Pyrex immersion well containing a 450-W lamp. Cyclohexylamine was flushed with oxygen and irradiated for 3 hr. The concentrations of *N*-cyclohexylidenecyclohexylamine and cyclohexanone oxime were 3.81×10^{-2} and 1.12×10^{-2} *M*, respectively, as determined by glpc. Upon repeating the procedure in a Rayonet reactor with the 350-nm phosphor, low-pressure lamps, the amounts of products were reduced to one-third that obtained with Pyrex. With a 100-W tungsten lamp, no products were obtained. Upon repeating the procedure with Pyrex using nitrogen rather than oxygen, no products were observed.

Thermal and Photochemical Reaction of Cyclohexanone Oxime in Cyclohexylamine.—Cyclohexanone oxime (4 g) was dissolved in 25 ml of cyclohexylamine, and 3 ml of this solution was transferred to a 1-cm quartz spectrophotometric cell. After irradiation with a 450-W lamp under nitrogen for 3 hr at a distance of 2.5 cm from the well, no *N*-cyclohexylidenecyclohexylamine was observed. The remaining solution was heated at 45° under nitrogen for 8 hr and a trace amount of *N*-cyclohexylamine was formed.

Oxidation of *N*-Cyclohexylhydroxylamine with Hydrogen Peroxide in Ethanol.—Hydrogen peroxide (30%, 50 ml) was gradually added to a stirred solution of 0.08 *M* *N*-cyclohexylhydroxylamine in ethanol. After being stirred under nitrogen at room temperature for 3 hr, the solution was then saturated with NaCl and extracted with chloroform. The mixture was dried over magnesium sulfate, filtered, concentrated, and poured into a small amount of water to form a white solid. The compound was recrystallized (petroleum ether) and identified as cyclohexanone oxime, mp 85–86° (lit.[25] mp 89–90°) and ir spectrum.

Photolysis of Hydrogen Peroxide–Cyclohexylamine Adduct in Cyclohexylamine.—Cyclohexylamine (3 ml) containing 0.162 mm of the hydrogen peroxide–cyclohexylamine adduct was irradiated in a 1-cm cell with the 450-W lamp in a Pyrex well. After 2.5 hr, 0.165 mm of *N*-cyclohexylidenecyclohexylamine was formed (glpc).

Thermal Decomposition of 1-Hydroperoxycyclohexylamine in Cyclohexylamine.—A 0.0394 *M* cyclohexylamine solution of 1-hydroperoxycyclohexylamine was stirred under nitrogen at 45° for 1 hr. *N*-Cyclohexylidenecyclohexylamine (0.0410 *M*) was produced (glpc).

Decomposition of *N*-Cyclohexyl-1-hydroperoxycyclohexylamine in Cyclohexylamine.—*N*-Cyclohexyl-1-hydroperoxycyclohexylamine (1.0 g) was added to 15 ml of cyclohexylamine, and the solution was stirred under nitrogen for 1 hr. *N*-Cyclohexylidenecyclohexylamine was found and isolated by gas chromatography. The product was identified by glpc retention times and comparing its ir spectrum with an authentic sample.

Registry No.—**1**, 10468-40-3; **4**, 24075-24-9; **6**, 2808-61-9; **8**, 37816-86-7; cyclohexylamine, 108-91-8; cyclohexanone oxime, 100-64-1; cyclohexylamine–oxygen adduct (1:1), 37817-06-4.

Acknowledgment.—We are grateful that this investigation was supported in part by a Public Health Service Research Career Development Award (1-K4-GM-9888; V. I. S.) and by a Sigma Xi research grant (to C. N.).

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(23) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 363.

(24) R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, **28**, 1218 (1956).

(25) R. C. Weast, S. M. Selby, and C. Hodgman, Ed., "Handbook of Chemistry and Physics," 45th ed, The Chemical Rubber Co., Cleveland, Ohio, 1964, p C-273.

The Effect of Biphenyl Geometry and Substituents on the Multiplicity and Efficiency of the Photocyclization Reactions of 2-Substituted Biphenyls

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The direct and sensitized photochemistry of the unsubstituted, 2′-, 3′-, 4′-, 4-, and 5-methoxy-2-biphenylyl isocyanates are reported. Direct excitation of these compounds yields carbazoles and 6(5*H*)-phenanthridinones. The carbazole arises from decomposition of the isocyanate in its singlet state to a nitrene which undergoes insertion into an aromatic C–H bond. The photocyclization of the isocyanates to 6(5*H*)-phenanthridinones occurs most efficiently *via* acetone sensitization in what is formally a nonoxidative cyclization to an aromatic ring. In contrast to the insensitivity of the singlet state decarbonylation to ring substituent, the photosensitized cyclization process is enhanced by a 4′-, 4-, or 5-methoxy group and dramatically retarded by a 2′- or 3′-methoxy substituent. The related acetone-sensitized photocyclizations of *N*-(2-propylidene)-2-aminobiphenyl and its 2′-, 3′-, and 4′-methoxy derivatives to the corresponding 6,6-dimethyl-5,6-dihydrophenanthridines were also studied. In this series the 3′-methoxy substituent markedly retarded the photocyclization reaction. In contrast to the photocyclization reactions of the isocyanate and imine groups, the imino ether linkage did not undergo the photocyclization reaction. The mechanism of these processes and the low intersystem crossing efficiency in these 2-substituted biphenyls is noted and discussed.

Our interest in the influence of ground- and excited-state geometry on photochemical reactivity[2] led us several years ago to initiate work on the photochemistry of biphenyl systems.[3] Aside from the consequences of markedly different equilibrium geometries of

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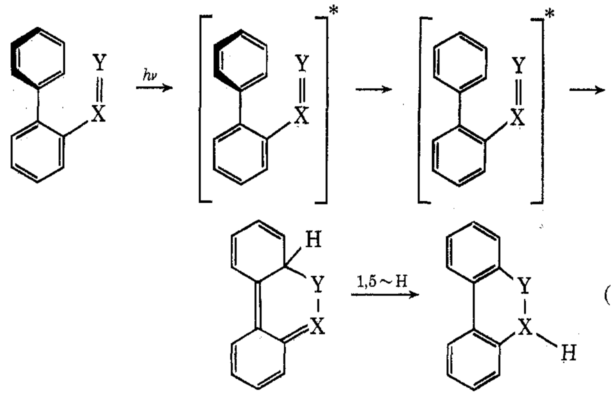
(1) (a) Alfred P. Sloan Foundation Fellow, 1971–1973; (b) Camille and Henry Dreyfus Teacher Scholar, 1972–1977.

(2) For a discussion of these factors in diene photochemistry, see J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *J. Amer. Chem. Soc.*, **93**, 4808 (1971); **92**, 1406 (1970).

(3) (a) J. S. Swenton, *Tetrahedron Lett.*, 2855 (1967); (b) *ibid.*, 3421 (1968); (c) J. S. Swenton, T. J. Ikeler, and B. H. Williams, *J. Amer. Chem. Soc.*, **92**, 3103 (1970); (d) J. S. Swenton, T. J. Ikeler, and B. H. Williams, "Excited State Chemistry," A Symposium, J. N. Pitts, Ed., Gordon and Breach, New York, N. Y., 1970, pp 93–106; (e) J. A. Hyatt and J. S. Swenton, *J. Heterocycl. Chem.*, **9**, 409 (1972); (f) J. A. Hyatt and J. S. Swenton, *J. Org. Chem.*, **37**, 3216 (1972).

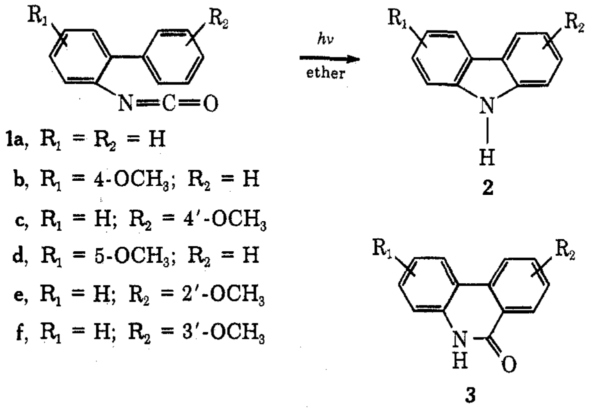
the ground and excited states in modifying the photochemical and photophysical processes in biphenyls,[4] there was the synthetic potential of nonoxidative cyclization[5] in suitable 2-substituted biphenyls. The latter possibility seemed especially attractive, since the approach to planarity in the biphenyl excited state would favor bond formation between the ortho position of the biphenyl and an unsaturated 2-substituent (eq 1). In view of the convenient synthetic routes to many 2-substituted biaryls, it was felt that these potential nonoxidative cyclizations would complement the well-studied photooxidative cyclizations[6] and were thus worthy of study in their own right. We wish to report here the nonoxidative photochemical cyclizations of 2-biphenylyl isocyanates and imines and the influence of substituents and biphenyl geometry on the efficiency and multiplicity of these processes.



(1)

Direct Irradiation of 2-Biphenylyl Isocyanates.—Our choice of the 2-substituted biphenyl system for study was based primarily on synthetic convenience and Yang's suggestion[7] that the ortho positions of excited biphenyl are electron rich. On this basis, it appeared that a weakly conjugating substituent, which would not markedly alter the nature of the biphenyl excited state yet had pronounced electrophilic character, would be an ideal test for the proposed photocyclization. Thus, the first system studied was a series of 2-biphenylyl isocyanates, **1a–f**.

The direct preparative irradiation of biphenyls **1a–f** produced in each case a mixture of carbazole(s) and phenanthridinone (Table I). The structures of the carbazoles were established by comparison of their melting points and ir spectra with those of the known carbazoles.[3c] Only the unsubstituted, **3a**, and 3-, **3b**, and 8-methoxy-6(5*H*)-phenanthridinones, **3c**, had been previously reported. The structures of the three remaining 6(5*H*)-phenanthridinones were established on the basis of spectroscopic data (see Experimental Section for details).



1a, $R_1 = R_2 = H$
b, $R_1 = 4\text{-}OCH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = 4'\text{-}OCH_3$
d, $R_1 = 5\text{-}OCH_3$; $R_2 = H$
e, $R_1 = H$; $R_2 = 2'\text{-}OCH_3$
f, $R_1 = H$; $R_2 = 3'\text{-}OCH_3$

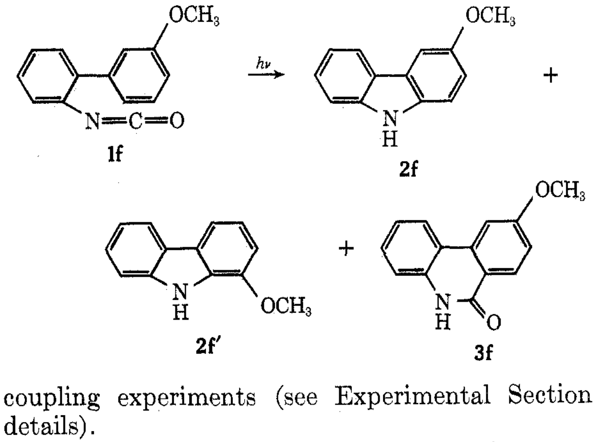
(2)

TABLE I
PREPARATIVE IRRADIATIONS FOR 2-BIPHENYLYL ISOCYANATES[a]

Compd	% Carbazole(s)[b]	% 6(5*H*)-Phenanthridinone[b]	% Recovered starting material[b,c]
1a	15	10	70
1b-4-OCH$_3$	15	55	34
1c-4′-OCH$_3$	20	29	46
1d-5-OCH$_3$	17	20	63
1e-2′-OCH$_3$	15	9	72
1f-3′-OCH$_3$	31	14	58

[a] Irradiations were performed for 3.5 hr using $\sim 10^{-2}$ *M* solutions under nitrogen with Vycor filtered light from a 450-W medium-pressure source. [b] The yields were calculated on the basis of crude weights eluted from the column and are uncorrected for the small amount of column residue. [c] Recovered as isocyanate and the corresponding urea.

In contrast to isocyanates **1a–e**, where only one carbazole and one 6(5*H*)-phenanthridinone were expected and observed, **1f** could produce two isomeric carbazoles and two isomeric phenanthridinones. While the two carbazoles **2f** and **2f′** were produced in identical amounts, only one 6(5*H*)-phenanthridinone could be isolated. This product was assigned as 9-methoxy-6(5*H*)-phenanthridinone (**3f**) on the basis of nmr decoupling experiments (see Experimental Section for details).



(3)

To evaluate the efficiencies of these reactive processes, quantum yield measurements were made (Table II). While the quantum yields for carbazole appearance and isocyanate disappearance could be measured by vpc, the production of the 6(5*H*)-phenanthridinones was less reliably determined. The determination for the latter was by uv analysis after correcting for carbazole absorption. The overlap of these two product absorp-

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(4) In the ground state of biphenyl the rings are twisted to the extent of 20–30°.[4a] By contrast, elementary theory would predict a planar excited state,[4b] and experimental work supports a planar geometry for the excited triplet.[4c] (a) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, pp 270–271; (b) A. Imamura and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5379 (1968); (c) P. J. Wagner, *ibid.*, **89**, 2820 (1967).

(5) For examples of nonoxidative cyclizations in heterocyclic systems, see (a) P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967); (b) O. L. Chapman and G. L. Eian, *J. Amer. Chem. Soc.*, **90**, 5329 (1968); (c) J. DeJong and J. H. Boyer, *Chem. Commun.*, 961 (1971); (d) R. A. Abramovitch and E. P. Kyba, *ibid.*, 265 (1969); (e) R. A. Abramovitch and E. P. Kyba, *J. Amer. Chem. Soc.*, **93**, 1537 (1971).

(6) For leading references see R. J. Hayward and C. C. Leznoff, *Tetrahedron*, **27**, 2085 (1971).

(7) N. C. Yang, A. Shani, and G. R. Lenz, *J. Amer. Chem. Soc.*, **88**, 5369 (1966).

tions varied with the substituent and thus only upper limits could be placed on some of the quantum yields for 6(5*H*)-phenanthridinone production. A complication in the direct irradiation is revealed by comparison of the quantum yields with the product ratios noted in preparative irradiations using Vycor-filtered light from a 450-W medium-pressure source. For each compound preparative irradiations showed a larger percentage of 6(5*H*)-phenanthridinone than would be expected from the quantum yield data at 253.7 nm. While control experiments established that secondary irradiation of 6(5*H*)-phenanthridinone to carbazole at 253.7 nm did not account for this discrepancy, studies at 300 nm[8] showed that the ratio of the 6(5*H*)-phenanthridinones to the carbazoles increased with length of irradiation. In view of the high triplet energy of carbazole (E_T = 70.1 kcal/mol),[9a] its moderate intersystem crossing efficiency ($\Phi_{ic} = 0.36$),[9b] and its strong absorption in the near-uv, it appears reasonable that carbazole is acting as a triplet sensitizer to produce the 6(5*H*)-phenanthridinone (*vide infra*). This postulate is further strengthened by an independent experiment wherein carbazole sensitization of **1a** to **3a** was demonstrated. Thus, at 253.7 nm the major process observed is decarbonylation of the isocyanate resulting in production of the respective carbazole(s).

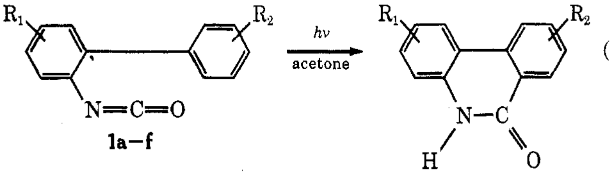
Sensitized Irradiations of 2-Biphenylyl Isocyanates.—To obtain evidence on the multiplicity of the excited state responsible for product formation, sensitization studies were undertaken. Owing to possible complications of inefficient energy transfer from low-energy sensitizers,[4c] the sensitization work was carried out using acetone as sensitizer and solvent.[10] In contrast to the direct irradiations, which yielded mixtures of carbazole(s) and 6(5*H*)-phenanthridinones, acetone-sensitized photolyses led primarily to phenanthridinones. To establish that these sensitizations were not due to singlet energy transfer from acetone,[11] sensitization experiments were performed on **1a** in the presence of piperylene as quencher. Should the singlet state of acetone be responsible for the sensitization, piperylene would have little effect on the reaction, since piperylene should not efficiently quench acetone singlets, while, if the triplet state of acetone were implicated in these sensitizations, piperylene would quench the triplet acetone with a diffusion-controlled rate and thus markedly lower the efficiency of the photocyclization of the isocyanate. Thus, the amount of phenanthridinone formed from low conversion irradiation of acetone solutions which were 0.10 *M* in isocyanate and 0.08 *M* in piperylene was compared with solutions containing no piperylene. In the presence of 0.08 *M* piperylene the yield of phenanthridinone was reduced by a factor of >5, while in 1.0 *M* piperylene runs the quenching of phenanthridinone formation was virtually complete (4% production relative to the unquenched irradiation could have been detected). These results support the proposal that singlet-state acetone is not responsible for the acetone sensitization results. While we believe that the most reasonable interpretation for the acetone sensitization work directly involves acetone triplet, attempts at employing sensitizers wherein singlet state energy transfer is not known to occur have met with only limited success. Thus, while acetophenone in benzene does sensitize the photocyclization of **1a** to **3a**, the quantum efficiency is only 5×10^{-4}, a factor of about 7.5 lower than the analogous acetone sensitization. Furthermore, acetophenone sensitizations of **1a** are of no preparative value.

TABLE II
QUANTUM YIELDS FOR DIRECT PHOTOLYSIS OF 2-BIPHENYLYL ISOCYANATES

2-Biphenylyl isocyanate	$\Phi \times 10^4$ [a,b] isocyanate, 253.7 nm	$\Phi \times 10^4$ [a,c] phenanthridinone, 253.7 nm	$\Phi \times 10^4$ [a,c] carbazole, 253.7 nm
Unsubstituted, **1a**	115	*d*	66
4-OCH$_3$, **1b**	49	<3	34
4′-OCH$_3$, **1c**	52	<7	45
5-OCH$_3$, **1d**	86	*d*	65
2′-OCH$_3$, **1e**	39	<1	41
3′-OCH$_3$, **1f**		<1	55

[a] The estimated error in these numbers is 20%. [b] The quantum yields for disappearance of isocyanates were measured at 1–10% conversion. [c] The quantum yields were determined at 0.5–2% conversion. [d] The strong overlap of the respective carbazole and 6(5*H*)-phenanthridinone uv spectra prevented determination of this value.

As noted below, the sensitized reactions of **1a–d** proceed in high preparative yield, while in marked contrast the 2′- and 3′-OCH$_3$ compounds photocyclize in poor yields. The low reactivity of these compounds toward acetone sensitization is further confirmed from the quantum yields for these sensitizations recorded in Table III. Here the inherent efficiency of the triplet state cyclizations for the methoxy compounds spans a factor of about 30. Of special note is the much higher quantum yields for cyclization in the sensitized irradiations as compared to the direct photolyses. Where comparisons can be made (*i.e.*, **1b**, **1c**) the sensitized cyclization is approximately 20 to 40 times more efficient than the analogous process from direct irradiation.



(4)

1a–f

3a, 70% **3d**, 91%
b, 95% **e**, 10%
c, 91% **f**, 15%

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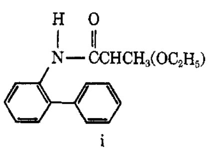
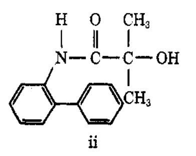
(8) Quantum yield measurements at 300 nm suggested that there was a slight wavelength effect on the production of carbazole as its quantum efficiency decreased relative to the values at 253.7 nm. However, the interpretation of these results is unclear owing to the time dependence of the product ratios at this wavelength and the 253.7 contamination in the RPR-3000 Å source utilized.

(9) (a) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 298; (b) p 309.

(10) Sensitizations of **1a** in acetone (1–3 *M*)-ether gave, in addition to **3a**, i and ii. The structures for the latter compounds were assigned on the



i



ii

basis of their ir and nmr spectra and their hydrolyses to 2-aminobiphenyl. While the mechanisms for formation of i and ii were not studied, they reasonably arise from radicals generated by hydrogen abstraction processes of acetone. Their formation suggests that, even with acetone, energy transfer to these biphenyls may not be diffusion controlled.

(11) M. A. Golub, *J. Amer. Chem. Soc.*, **92**, 2615 (1970).

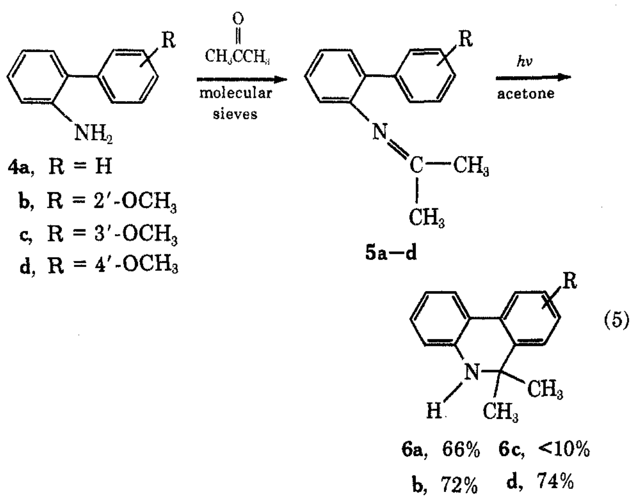
TABLE III

QUANTUM YIELDS FOR ACETONE-SENSITIZED IRRADIATION AT 3000 Å[a]

2-Biphenylyl isocyanate	$\Phi \times 10^4$ [b] isocyanate	$\Phi \times 10^4$ [c] Phenanthridinone	$\Phi \times 10^4$ [c] carbazole
Unsubstituted, **1a**	50	38	5
4-OCH_3, **1b**	157	136	2
4'-OCH_3, **1c**	120	118	*d*
5-OCH_3, **1d**	65	45	1
2'-OCH_3, **1e**	13	7	*d*
3'-OCH_3, **1f**	10	3	1

[a] See Table I, footnote *a*. [b] The isocyanate conversion was 10–15%. [c] The conversion to products was 1–15%. [d] No carbazole was detected for these compounds.

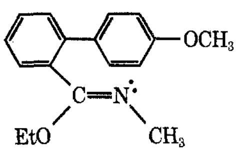
Irradiation Studies of *N*-(2-Propylidene)-2-aminobiphenyls.—The high yields of cyclized products in certain of the isocyanate cyclizations prompted us to briefly explore the chemistry of the simple imine linkage in these nonoxidative processes.[12] The ground-state polarity of the carbon–nitrogen double bond, while not so pronounced as that of the isocyanate, would certainly be in the proper direction for bonding interaction with the supposed electron-rich ortho positions of biphenyl. The imines **5a–d** were prepared in 50–70% yield by condensation of the appropriate aminobiphenyl with acetone in the presence of molecular sieves.[13] Isolation of the imines by distillation yielded material of >96% purity by vpc. Since the synthetic yields from these freshly distilled samples were comparable with those recorded from samples obtained by preparative vpc, the majority of the work was done on imines containing 1–3% of the corresponding amine as impurity.



(5)

In agreement with the isocyanate work, direct excitation of the imines in ether proceeded slowly and was of no preparative value. However, acetone-sensitized photolysis of the imines **5a**, **5b**, and **5c** produced cyclized products in moderate to good yield. The structures of the products were assigned as the respective 6,6-dimethyl-5,6-dihydrophenanthridines on the basis of analytical and spectroscopic data. It is noteworthy that, as in the case of the corresponding isocyanate, the 3'-methoxy substituent lowered reactivity such that no cyclization product could be isolated from **5c**. In contrast to the isocyanate system, the 2'-methoxy derivative **5b**, did afford the photocyclization product **6b** in good yield. In view of the difficulty of obtaining and maintaining 100% pure imine, no quantum yield studies on the imines were attempted. The length of preparative irradiations suggested quantum yields slightly less than those noted with the corresponding isocyanates.

Attempted Photocyclization of the Imino Ethers of 4'-Methoxybiphenyl.—While many of the nonoxidative cyclizations observed in the case of the isocyanates and imines were of good preparative yield, the quantum efficiencies were rather low. The recent demonstration of the importance of rotational freedom in reducing the reactivity of olefin systems suggested that the low quantum efficiency in these nonoxidative cyclizations might be related to a similar phenomenon.[2] For these nitrogen systems deactivation mechanisms could involve either rotation about the –N=C– linkage or an inversion mechanism involving the nitrogen lone pair. Unfortunately, neither the isocyanate nor the imine system allow a steric constraint to be placed on the rotational or inversion deactivation mechanism by incorporation of the linkage into a ring (if a neutral species is to be maintained). Thus, we briefly explored the photocyclization reactivity of the imino ethers **7** and **8**. If either of the deactivation processes noted above were important in these systems, **8** would be expected to be significantly more reactive than **7**. Unfortunately, the imino ethers **7** and **8** would have a markedly different polar character than the isocyanate or imine linkage. Apparently, the nature of the substituent has a pronounced effect on the photocyclization efficiency, since both **7** and **8**, as compared to the isocyanate or imine systems, were quite unreactive toward cyclization in either direct or acetone-sensitized photolysis.[14] Thus, the importance of rotational or inversion deactivation mechanisms in accounting for the low efficiency of the nonoxidative cyclizations remains unanswered.



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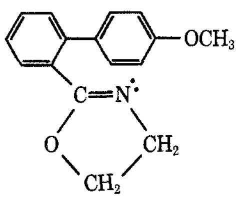

8

Discussion

Direct Excitation in Biphenyl Systems.—The direct photolyses of the 2-biphenylyl isocyanates produces carbazoles in low quantum efficiency ($\Phi \cong 0.005$). The most obvious mechanism for carbazole formation is loss of CO in excited **1** followed by insertion of the nitrene into the adjacent C–H bond, producing carbazole.[15] This proposal is strengthened by the identity

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[12] While this work was in progress, Abramovitch[5d] reported that **5a** generated from an azide precursor did photocyclize in low yield to 6,6-dimethyl-5,6-dihydrophenanthridine. By mutual consent we have explored the nature of the cyclization in more detail.

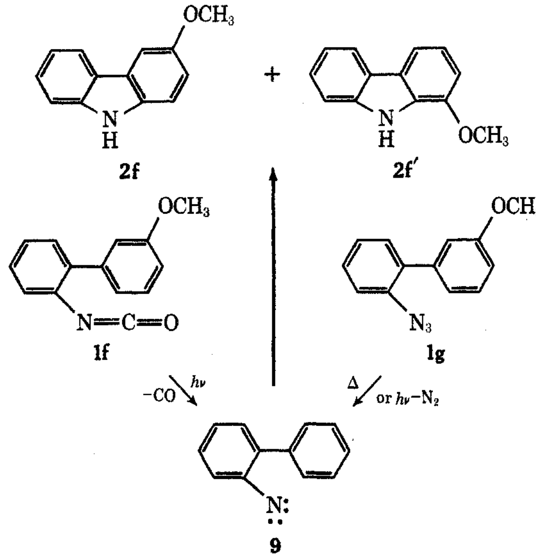
[13] Westheimer has independently noted the use of molecular sieves for imine formation: K. Taguchi and F. H. Westheimer, *J. Org. Chem.*, **36**, 1570 (1971).

[14] We wish to thank Mr. John Hyatt for this series of experiments.

[15] This process has analogy with the gas-phase photodecarbonylation of isocyanic acid.[15a,b] (a) W. D. Woolley and R. A. Back, *Can. J. Chem.*, **46**, 295 (1968); (b) J. N. Bradley, J. R. Gilbert, and P. Svejda, *Trans. Faraday Soc.*, **64**, 911 (1968).

of the ratio of carbazoles produced from photolysis of **1f** and photolysis or thermolysis of the corresponding azide, **1g**. The nitrene has been directly implicated in the latter series of reactions.[3c] The differences in quantum efficiency in the azide *vs.* the isocyanate system (Φ = 0.42 *vs.* 0.005) seemingly reflects the much larger photostability of the isocyanate *vs.* the azide group.

Recently, several investigators have reported that photolysis of 2-biphenyl derivatives produced isomerized biphenyls (eq 7).[16] In our studies such isomers were not noted as major processes, although small amounts of such isomerizations may have gone undetected. It appears reasonable that the absence of such processes in our system is due to the even lower efficiency of these isomerizations *via* benzvalene intermediates than the decarbonylation reactions. Support for this comes from a recent study of Zimmerman and Crumrine,[16d] who showed that photoisomerization of 2,2′-dimethyl-6,6′-diethylbiphenyl *via* a benzvalene intermediate has a quantum yield of about 2 × 10^{-4}, a factor of about 30 lower than the decarbonylation efficiency of the isocyanates.



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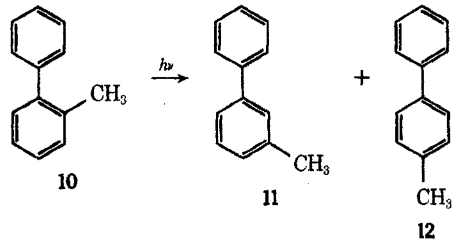
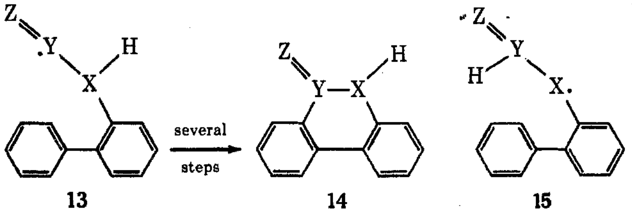


(7)

A final point worthy of mention concerns the efficiency of intersystem crossing in 2-substituted biaryl systems. As we noted several years ago[3d] for such varied compounds as the 2-azidobiphenyls and the isocyanate and imino systems reported here, the intersystem crossing efficiency based on quantum yields from direct and sensitized reactions is only 5–10%.[17] More recently Griffin and coworkers have concluded from their results on the photochemistry of 2-methylbiphenyls that intersystem crossing was low in these molecules also. The apparent low intersystem crossing noted in these systems could be a result of either exceptionally fast nonreactive decay processes of the singlet state or an especially slow rate of intersystem crossing. In view of the varied nature of 2-substituted derivatives which show this effect, it is tempting to conclude that the latter effect is operative. Since the equilibrium geometry of the biphenyl triplet should tend to be planar, and 2 substituents should exert steric hindrance toward planarity, an attractive postulate is that the low intersystem crossing in this system is related to a barrier to planarity in the excited state. Should this be the case, it provides another example of the importance of geometric factors in multiplicity-dependent photochemistry.

Sensitized Reactions of 2-Substituted Biphenyls.— Of the numerous mechanisms which can be envisioned for the formal nonoxidative photocyclization processes reported here, several deserve brief comment. One would involve the intermediate **13,** formed by hydrogen abstraction or hydrogen transfer processes.[18] While it seems reasonable that radical **15** would be formed in preference to **13,** the overall low quantum efficiency of the cyclization process would be explained if **15** were formed reversibly while the more reactive species **13,** even though formed less readily, was more reactive toward cyclization. A modification of this mechanism involving electron transfer from sensitizer to biphenyl followed by cyclization is also an *a priori* possibility. If such a mechanism were operative, additional products from radical recombinations would be expected (see footnote 10). Partial evidence against this mechanism is the failure to isolate such products either in the preparative direct excitation of the isocyanates in ether (Table I) or the high-yield acetone sensitizations. While solvent[19] and sensitizer[20] effects would be expected to markedly influence both of these mechanisms, experimentally meaningful studies in these particular systems are quite difficult.



13 **14** **15**

A fundamentally different mechanism would be photocyclization of **16** to **17** followed by 1,5-hydrogen shift to yield the aromatic species. While many electrocyclic processes bear formal analogy to the first step

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[16] (a) R. A. Finnegan and D. Knutson, *Tetrahedron Lett.*, 3429 (1968); (b) R. A. Abramovitch and T. Takaya, *Chem. Commun.*, 1369 (1969); (c) U. Mende, J. L. Laseter, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970); (d) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **94**, 498 (1972).

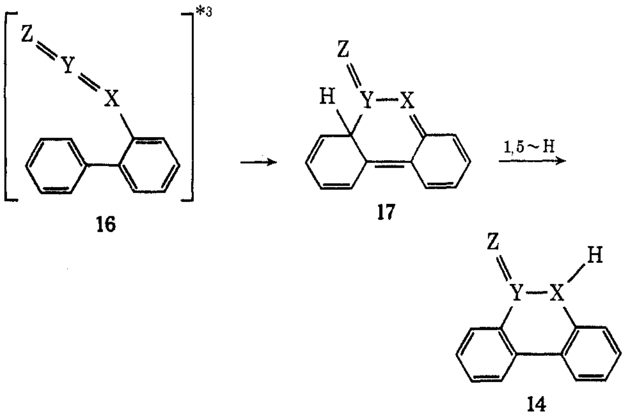
[17] A recent value for the intersystem crossing in benzene is 0.42,[17a] while most simple aromatic hydrocarbons have values greater than 0.2.[17b] (a) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968); (b) ref 8b.

[18] While hydrogen abstraction by excited isocyanate or imine group does not appear to have been reported, hydrogen transfer from radicals to imine groups is well recognized. For leading references see A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **90**, 4458 (1968); **91**, 2653 (1969).

[19] Solvent effect studies with the isocyanates are limited to nonnucleophilic media while a further complication is the low solubility of the products in many common solvents.

[20] In our experience acetone is the only good sensitizer for these cyclizations. While acetophenone in benzene does sensitize the reaction, the reaction is quite slow. The difficulty apparently rests with the high energy of the twisted biphenyl triplet.

(*i.e.*, **16** → **17**), these reactions are virtually exclusively singlet-state processes. In contrast, our evidence from acetone sensitization studies strongly suggests that the cyclization of the isocyanate and imine groups involves the triplet state. If the triplet state does produce **17**, it would be necessary for intersystem crossing to proceed or be concurrent with formation of **17**. While we consider it instructive to point out the more reasonable mechanistic possibilities of the cyclizations, the exact molecular details of these reactions remain to be established.



A final point is the effect of methoxy substituents and the nature of the ortho-unsaturated substituent on the yield of the photocyclization. While a detailed discussion of the effect of methoxy groups on the cyclization would be premature, since the mechanism has not been established, several relevant points can be made. In the case of 4-methoxy, **1b**, and 4′-methoxy, **1c**, substituents the reactivity as evidenced by the quantum yields is enhanced by a factor of 3–4 relative to the unsubstituted systems. Thus, experimentally, methoxy groups which are meta to either the position of cyclization or the position bearing the cyclizing substituent show enhancement of reactivity. This increased reactivity at positions meta to an electron-donating group is reminiscent of similar effects in photosolvolyses[21] and photodeuteration[22] studies of anisole derivatives and suggests the importance of substituents which enhance reactivity at these positions for good synthetic processes. The markedly lower reactivity of the 2′-methoxy (isocyanate series only), **1e**, and 3′-methoxy, **1f** and **5c**, is less readily rationalized, as it is probably due to a combination of steric and electronic effects. Interestingly, while a 3′-methoxy markedly retards reaction, a 5-methoxy substituent exerts very little effect on the efficiency of the process.

While photocyclizations involving only three unsaturated ortho substituents were noted here, it appears that the yield of the cyclization is markedly influenced by the nature of this group. Molecules undergoing successful cyclization have ground-state polarizations in which the cyclizing atom may be regarded as electron deficient. The one attempted cyclization of an electron-rich 2 substituent was unsuccessful and thus the character of the side chain as well as the ring substituents is important. Unfortunately, the importance of Yang's suggestion of the increased electron density at the ortho position of excited biphenyl is not readily assessed from either the methoxy substituent effects or the variation of cyclizing substituent.

Summary.—The direct irradiation of 2-substituted biphenyls results in poor intersystem crossing and inefficient nonoxidative cyclizations. The acetone-sensitized photolyses results in photocyclization reactions, whose efficiencies and yields vary with the position of ring substituent and the nature of the unsaturated 2 substituent. The high preparative yields noted in some of these systems suggest good synthetic utility for selected transformations.

Experimental Section

Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer. Uv spectra were determined with a Cary 14 recording spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer. Nmr spectra were measured at 60 MHz using TMS as internal standard. All elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All photolyses were carried out in an atmosphere of purified nitrogen.

2′-Methoxy-2-biphenylyl Isocyanate (1e).—A solution of 7.4 g (37 mmol) of 2′-methoxy-2-aminobiphenyl[23] in 30 ml of dry ethyl acetate was added over 15 min to a stirred solution of 9 g of phosgene in 30 ml of dry ethyl acetate. Phosgene was bubbled through the solution for an additional 1.5 hr, after which the solvent was removed *in vacuo*. The residue was chromatographed on a 64 × 1.9 cm silica gel column slurry packed in 2% ether in hexane. Fractions (60 ml) were eluted with 2% ether in hexane. Removal of the solvent from fractions 3–8 followed by vacuum distillation of the residue yielded 5.3 g (63%) of the isocyanate as a colorless liquid: bp 116–117° (0.24 mm); ir (neat) 4.43 (vs) and 13.2–13.3 μ (vs); uv max (hexane) 277 nm (ϵ 4100).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.52; H, 5.04; N, 6.14.

3′-Methoxy-2-biphenylyl Isocyanate (1f).—A mixture of 10.0 g (44 mmol) of 3′-methoxy-2-biphenylcarboxylic acid[24] and 20 ml (0.28 mol) of thionyl chloride was refluxed for 1 hr. The excess thionyl chloride was removed by vacuum distillation, and the remaining traces of thionyl chloride were removed by gently heating the oil under vacuum for 4 hr. There remained 11.0 g of 3′-methoxy-2-biphenylcarbonyl chloride as a red oil, ir (neat) 5.61 (vs), 11.2–12.0 (vs), 12.96 (s), 13.25 (s), 14.02 (m), and 14.30 μ (m).

A solution of 11.0 g of the acid chloride in 10 ml of acetone was added to a stirred solution of 5 g (77 mmol) of sodium azide in 25 ml of water at 0°. Stirring was continued for 1 hr after which the phases were separated. The organic phase was dried over sodium sulfate at 0° for 5 min and was added to refluxing benzene (30 ml). The aqueous phase was extracted with benzene, and the benzene was dried and also added to the refluxing benzene. The benzene solution was refluxed for 1 hr, after which the benzene was removed *in vacuo*. Vacuum distillation of the red residue yielded 7.1 g (72%) of the isocyanate as a colorless liquid: bp 114–115° (0.15 mm); ir (neat) 4.40 (vs), 11.40 (m), 11.56 (m), 11.70 (m), 12.7 (s), 13.2 (vs), and 14.27 μ (s); uv max (hexane) 281 nm (ϵ 3900) and 251 (7100).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.72; H, 4.95; N, 6.27.

4′-Methoxy-2-biphenylyl Isocyanate (1c).—Using a procedure analogous to that of the 3′-methoxy isomer, a mixture of 4.21 g (18.5 mmol) of 4′-methoxy-2-biphenylcarboxylic acid[25] and 16 ml (0.22 mol) of thionyl chloride was converted to 4′-methoxy-2-biphenylcarbonyl chloride in 95% yield, mp (hexane) 60.0–61.5°. Reaction of 4.2 g (17 mmol) of the acid chloride with 2.7 g (42 mmol) of sodium azide in the usual manner yielded 2.62 g (64%) of the isocyanate as a colorless liquid: bp 111–112° (0.09 mm); ir (neat) 4.36 (vs), 11.92 (s), 12.30 (m), and 13.0–13.2 μ (vs); uv max (diethyl ether) 228 nm (ϵ 21,000) and 258 (12,000).

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[21] H. E. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, **85**, 922 (1963); H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963).

[22] E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968).

[23] G. Smolinsky, *J. Amer. Chem. Soc.*, **83**, 2489 (1961).

[24] G. W. Kenner, M. H. Murray, and C. M. B. Tylor, *Tetrahedron*, **1**, 259 (1957).

[25] M. J. Malawski and T. Drapala, *Rocz. Chem.*, **34**, 1371 (1960).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.64; H, 4.89; N, 6.17.

4-Methoxy-2-biphenylyl Isocyanate (1b).—In a procedure analogous to that of the 2′-methoxy isomer, 10.3 g (52 mmol) of the amine[26] was treated with phosgene to yield 9.0 g (77%) of the isocyanate **1b** as a colorless liquid: bp 113–114° (0.12 mm); mp 25.0–25.5°; ir (neat) 4.38 (vs), 11.00 (m), 13.00 (s), and 14.23 μ (vs); uv max (diethyl ether) 228 nm (ε 18,000) and 257 (11,900).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.70; H, 5.04; N, 6.24.

5-Methoxy-2-biphenylyl Isocyanate (1d).—In an analogous fashion to that of the 2′-methoxy isomer, 8.8 g (44 mmol) of the amine[26] was treated with phosgene to produce 9.6 g (98%) of the isocyanate as a colorless liquid: bp 113–115° (0.13 mm); ir (neat) 4.40 (vs), 12.28 (br, m), 12.95 (s), and 14.24 μ (vs); uv max (diethyl ether) 226 nm (ε 26,000) and 295 (3200).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.25; H, 4.98; N, 6.47.

Preparative Direct Photolyses of Biphenylyl Isocyanates. General.—Direct photolyses of the isocyanates were performed in a stirred reactor under a nitrogen atmosphere with Vycor filtered light from a 450-W Hanovia medium-pressure source. After irradiation the solvent was removed *in vacuo* and the residue was chromatographed on a silica gel (2.3 × 75 cm) column slurry packed in 2% ether in hexane. Elution was carried out with increasing percentages of ether–hexane (E–H) to pure ether (E), 250-ml fractions being collected.

2′-Methoxy-2-biphenylyl Isocyanate (1e).—Photolysis of 0.96 g of the isocyanate in 300 ml of anhydrous ether for 3.5 hr followed by chromatography yielded these results: fraction 1–2, 2% E–H, nil; 3–4, 4% E–H, 0.30 g (33%) of recovered **1e**; 5–6, 8% E–H, nil; 7–8, 16% E–H, nil; 9–11, 16% E–H, 0.12 g (15%) of 4-methoxycarbazole; 12–18, E, 0.37 g (39%) of 2,2′-bis(2-methoxyphenyl)carbanilide; and 19–30, E, 0.08 g (9%) of 10-methoxy-6(5*H*)-phenanthridinone (**3e**): mp (acetone) 297.5–298.0°; ir (KBr) 2.90 (w), 6.03 (s), 6.22 (s), 11.1 (m), 12.23 (m), 12.92 (m), 13.47 (s), 13.59 (s), 14.15 (m), and 14.52 μ (s); uv max (diethyl ether) 233 nm (ε 51,000), 253 (12,000), 262 (11,000), 269 (9700), 278 (7400), 291 (4100), 302 (4900), 318 (7200), 331 (12,600), and 347 (11,700); nmr (100°, dimethyl sulfoxide-d_6) δ 11.30 (broad s, 1 H, –NH), 7.00–9.15 (m, 7 H, aromatic), and 4.06 (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.63; H, 4.91; N, 6.24.

3′-Methoxy-2-biphenylyl Isocyanate (1f).—Photolysis of 0.96 g of the isocyanate in 300 ml of anhydrous ether for 3.5 hr followed by chromatography gave these results: fraction 1, 20% E–H, 0.19 g (20%) of recovered **1f**; 2–3, 20% E–H, 0.13 g (15%) of 1-methoxycarbazole; 4, 20% E–H, 0.024 g (3%) of a mixture of 1- and 3-methoxycarbazoles; 5–8, 20% E–H, 0.11 g (13%) of 3-methoxycarbazole; 9–20, E, 0.38 g (38%) of 2,2′-bis(3-methoxyphenyl)carbanilide; and 21–36, E, 0.16 g (14%) of 9-methoxy-6(5*H*)-phenanthridinone: mp (acetone) 235–236°; ir (KBr) 2.90 (w), 6.03 (s), 6.23 (s), 11.84 (m), 13.35 (m), and 14.9 μ (m); uv max (diethyl ether) 242 nm (ε 47,000), 266 (16,000), 309 (4600) 320 (5900), and 334 (5700); nmr (100°, dimethyl sulfoxide-d_6) δ 11.0 (broad s, 1 H, –NH), 7.0–8.5 (m, 7 H, aromatic), and 3.98 (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.53; H, 4.86; N, 6.29.

4′-Methoxy-2-biphenylyl Isocyanate (1c).—Irradiation of 0.84 g of **1c** in 300 ml of anhydrous ether for 3.5 hr resulted in precipitation of a white solid. Concentration of the heterogeneous reaction mixture to 30 ml followed by filtration and washing of the collected white solid with ether afforded 0.19 g of 8-methoxy-6(5*H*)-phenanthridinone (**3c**), mp 271–273° (lit.[27] mp 271–272°). Chromatography of the combined mother liquors on silica gel yielded the following results: fraction 1–14, 8% E–H, nil; 15–17, 60% E–H, 0.144 g (20%) of 2-methoxycarbazole as a white solid; 18–24, 60% E–H, 0.40 g (46%) of 2,2′-bis(4-methoxyphenyl)carbanilide as a white solid; 25–27, E, nil; 28–33, E, 0.05 g of 8-methoxy-6(5*H*)-phenanthridinone as a white solid: mp (acetone) 271.5–273.0°; ir (KBr) 2.90 (w), 6.00 (s), 6.21 (s), 11.92 (m), 13.30 (s), 13.52 (w), 13.98 (w), and 14.35 μ (w); uv max (diethyl ether) 228 nm (ε 46,000), 233 (sh, 44,000), 242 (sh, 20,000), 264 (18,000), 272 (sh, 13,000), 280 (sh, 10,000), 312 (10,500), 328 (9600), and 343 (7600); nmr (100°, dimethyl sulfoxide-d_6) δ 11.10 (broad s, 1 H, –NH), 7.1–8.5 (m, 7 H, aromatic), and 3.97 (s, 3 H, $-OCH_3$).

4-Methoxy-2-biphenylyl Isocyanate (1b).—A stirred solution of 0.76 g of **1b** in 300 ml of dry diethyl ether was irradiated for 3.5 hr. After 1.75 and after 3.5 hr, the solution was filtered to remove the phenanthridinone which had formed (0.263 g). Chromatography yielded the following results: fractions 1–4, 4% E–H, nil; 5–8, 8% E–H, nil; 9–12, 16% E–H, 0.10 g (15%) of 2-methoxycarbazole; 13–18, E, 0.27 g (34%) of 5,5′-dimethoxy-2,2′-diphenylcarbanilide as a white solid; 19, E, nil; 20–31, E, 0.16 g (a total yield of 55%) of 3-methoxy-6(5*H*)-phenanthridinone (**3b**) as a white solid: mp (acetone) 255–256° (lit.[27] mp 251°); ir (KBr) 2.90 (w), 5.97 (vs), 6.22 (s), 13.00 (vs), and 13.86 μ (m); uv max (diethyl ether) 228 nm (ε 52,000), 237 (sh, 40,000), 246 (sh, 23,000) 263 (15,000), 278 (12,500), 312 (11,600), 325 (13,400), and 339 (9800); nmr (100°, dimethyl sulfoxide-d_6) δ 11.19 (broad s, 1 H, –NH), 6.75–8.40 (m, 7 H, aromatic), and 3.90 (s, 3 H, $-OCH_3$).

5-Methoxy-2-biphenylyl Isocyanate (1d).—Photolysis of 0.81 g of the isocyanate in 300 ml of anhydrous ether for 3.5 hr followed by chromatography on silica gel gave the following results: fractions 1–7, 4% E–H, nil; 8–12, 16% E–H, 0.12 g (17%) of 3-methoxycarbazole; 13–20, E, 0.53 g (63%) of 4,4′-dimethoxy-2,2′-diphenylcarbanilide; 21–23, E, nil; 24–40, E, 0.164 g (20%) of 2-methoxy-6(5*H*)-phenanthridinone as a white solid: mp (acetone) 231–232°; ir (KBr) 2.89 (w), 5.99 (s), 6.22 (s), 12.32 (m), 13.01 (s), and 14.73 μ (m); uv max (diethyl ether) 227 nm (ε 43,000), 233 (38,000), 242 (22,000), 264 (12,700), 273 (10,500), 343 (8500), and 357 (6930); nmr (100°, dimethyl sulfoxide-d_6) δ 11.11 (broad s, 1 H, –NH), 7.0–8.5 (m, 7 H, aromatic), and 3.93 (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.55; H, 4.86; N, 6.19.

Preparative Sensitized Irradiations of 2-Biphenylyl Isocyanates. General.—All sensitized irradiations were performed under an atmosphere of purified nitrogen in 300 ml of acetone using Corex filtered light from a 450-W medium-pressure source. Chromatographic separations were carried out as described for the direct irradiations unless otherwise noted.

2′-Methoxy-2-biphenylyl Isocyanate (1e).—A stirred solution of 0.92 g of the isocyanate was irradiated for 3.5 hr and the reaction mixture was chromatographed on silica gel. There was recovered 0.03 g (4%) of carbazole **2e**, 0.60 g (63%) of the carbanilide, and 0.09 g (10%) of the phenanthridinone **3e**. Prolonged irradiation did not lead to markedly different conversions.

3′-Methoxy-2-biphenylyl Isocyanate (1f).—Irradiation of 0.70 g of the isocyanate for 3.5 hr followed by chromatography of the reaction, gave 0.04 g (5%) of recovered isocyanate, 0.02 g (3%) of a mixture of carbazoles, 0.62 g (84%) of carbanilide, and 0.11 g (15%) of 9-methoxy-6(5*H*)-phenanthridinone (**3f**). Prolonged irradiation did not lead to substantially increased yields of cyclization product.

4′-Methoxy-2-biphenylyl Isocyanate (1c).—Irradiation of 0.80 g of the isocyanate led to rapid formation of phenanthridinone, which was filtered from the solution every 1.5 hr. After a total irradiation time of 6 hr, concentration of the acetone solution resulted in crystallization of additional phenanthridinone for a total yield of 0.73 g (91%) of **3c**, mp 271–273°.

4-Methoxy-2-biphenylyl Isocyanate (1b).—Irradiation of 0.72 g of the isocyanate for 3.5 hr followed by filtration of the precipitated phenanthridinone yielded 0.61 g of pure product. Chromatography yielded an additional 0.11 g for a total yield of 0.77 g (100%) of **3b**.

5-Methoxy-2-biphenylyl Isocyanate (1d).—Irradiation of 0.82 g of the isocyanate for 3.5 hr resulted in precipitation of 0.61 g of the phenanthridinone **3d**. Chromatography of the residue yielded 0.05 g of the carbanilide and 0.14 g of **3d**, a total yield of 0.75 g (91%).

Irradiation of 2-Biphenylyl Isocyanate in the Presence of Piperylene.—An acetone solution, 0.10 *M* in isocyanate and 0.08 *M* in piperylene, was prepared by dilution of 0.4885 g of isocyanate to 25 ml with a stock solution of freshly distilled piperylene in anhydrous acetone (0.551 g of piperylene in 100 ml of acetone). A 15-ml portion of this solution was transferred to a Pyrex test tube, degassed, sealed, and irradiated simultaneously with 15 ml of 0.1 *M* isocyanate in acetone containing no piperylene. The photolysis was performed for 1.5 hr in a merry-go-round apparatus with light from 16 RPR-3000 Å lamps. After irradiation the solvent was removed *in vacuo* and the residual oil

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[26] P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, **84**, 480 (1962).

[27] L. P. Walls, *J. Chem. Soc.*, 1405 (1935).

was dissolved in anhydrous ether and diluted to an appropriate volume. Ultraviolet analysis as for the quantum yield determinations showed the production of 0.7% of phenanthridinone in the tube containing piperylene and 4% production of phenanthridinone in neat acetone. In an analogous series of experiments, quenching irradiations were performed on acetone solutions 1.0 *M* in piperylene and 0.08 *M* in isocyanate. These solutions were irradiated as above for 30 min. Ultraviolet analysis showed the production of 0.09% phenanthridinone in the solution containing piperylene while 1.5% of phenanthridinone was formed in neat acetone. Both in the presence and absence of piperylene measurable amounts of carbazole (<0.001%) could not be detected.

Irradiation of 6(5*H*)-Phenanthridinone (3a) at 254 nm.—A solution of 0.101 g (0.51 mmol) of **3a** in dry diethyl ether (60 ml) in a quartz tube was degassed for 5 min with purified nitrogen and irradiated for 6 hr in a Rayonet apparatus equipped with RPR 2537 Å lamps. Tlc indicated an absence of carbazole (**2a**) where less than 0.5 mg easily would have been detected. Removal of the solvent left a white solid, mp (before crystallization) 295–296° (lit.[3a] mp 295–296° for **3a**).

Quantum Yield Determinations for Biphenylyl Isocyanates. Acetone Sensitized Photolyses.—The quantum yields for acetone sensitizations were determined on 10^{-1} to 10^{-2} *M* solutions of the isocyanate in acetone using 16 RPR-3000 Å lamps and potassium ferrioxalate as actinometer in a merry-go-round assembly. In a typical determination the acetone solutions under nitrogen in quartz test tubes (13.5 ml of solution) were simultaneously irradiated with the actinometer (quartz test tube). The quantum yields for products were essentially invariant from 1 to 15% conversion. Owing to the difficult analysis for disappearance of starting material at very low conversion, $\Phi_{\text{isocyanate}}$ was determined only in the 10–15% conversion runs. Later, when a high intensity grating monochromator became available, spot checks of the quantum yields determined on the Rayonet were made. These determinations were found to be within ±15% of those using the unfiltered light from the RPR-3000 Å source. The quantum yields for products reported in Table III represent the average of 3–7 measurements, while those for the isocyanate disappearance are the average of two determinations.

Direct Photolyses at 254 nm.—The quantum yields were determined with light from 16 RPR-2537 Å lamps in a Rayonet photochemical reactor essentially as described for the sensitization runs. The measurements were performed on 10^{-1} to 10^{-2} *M* solutions of isocyanate under nitrogen in quartz test tubes (13.5 ml of solution). The quantum yields reported in Table II were determined at 1–10% conversion and showed no dramatic time dependence. The reported values represent the average of at least four measurements at different per cent conversions.

Analytical Procedure for Quantum Yields.—The analysis for unreacted isocyanate and carbazole was by flame ionization vpc (5 ft × 0.125 in., 5% SE-30 on 100–120 mesh Varaport 30) at 150–200° (depending on the isocyanate) using added benzophenone, fluorenone, or dimethyl diphenate as internal standard. The instrument was calibrated immediately prior to analysis using known mixture of the isocyanate, carbazole, and internal standard closely approximating the photolysis mixture. The amount of phenanthridinone was determined by uv analysis correcting for the known amount of carbazole in the irradiated solution. The average value of phenanthridinone present, determined from analysis at a minimum of two wavelengths, was used for calculating the quantum yield of phenanthridinones.

***N*-(2-Propylidene)-2-aminobiphenyl (5a).**—The following is typical of that used for preparation of the imines used in this work. A solution of 10.0 g (60 mmol) of 2-aminobiphenyl in 50 ml of acetone was refluxed with stirring over molecular sieves for 1 hr. The progress of imine formation was followed by vpc (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh Varaport 30) at 190°. After filtration and solvent removal *in vacuo*, 50 ml of hexane and an equivalent of phenyl isocyanate, as determined assuming equal thermal combustibility of amine to imine, was added to remove unreacted 2-aminobiphenyl. The solution was warmed for 5 min, cooled to 0°, and then filtered to remove the urea. After solvent removal *in vacuo*, the residue was distilled to afford 6.3 g (50%) of a slightly yellow viscous oil, **5a**: bp 94–95° (0.07 mm); $\lambda_{\max}^{\text{EtOEt}}$ 245 nm (ϵ 14,000), 283 (4600); ir (neat) 3.28 (s, broad), 6.00 (s), 6.25 (s), 6.70 (m), 6.80 (s), 7.00 (s), 7.24 (s), 8.10 (s), 8.23 (s), 8.67 (m), 9.03 (m), 9.34 (m), 9.62 (m), 9.93 (m), 10.92 (m), 11.80 (m), 12.55 (s), 12.91 (s), 13.4 (s, broad), 13.92 (m), and 14.30 μ (s, broad); nmr (CCl_4) δ 1.38 (s, 3 H), 1.87 (s, 3 H), 6.61 (m, 1 H), and 6.9–7.4 (m, 8 H). Exact mass measurement: theoretical 209.1204; observed 209.1201.

***N*-(2-Propylidene)-4′-methoxy-2-aminobiphenyl (5d).**—A solution of 5.06 g (25 mmol) of 4′-methoxy-2-aminobiphenyl in 25 ml of acetone was refluxed over 5 g of molecular sieves for 1 hr. After filtration and solvent removal *in vacuo*, the residue was distilled to yield 4.2 g (70%) of a slightly yellow viscous oil, **5d**. The product contained a slight trace (<3%) of starting material as analyzed by vpc (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh Varaport 30) at 190°: bp 121–125° (0.03–0.04 mm); ir (neat) 3.19 (m), 3.31 (m), 6.04 (s), 6.23 (s), 6.31 (m), 6.40 (m), 6.48 (m), 6.68 (s), 6.86 (s), 7.05 (s), 7.26 (m), 7.47 (s), 7.87 (s), 8.07 (s), 8.30 (s, broad), 8.63 (s), 9.28 (m), 9.85 (s, broad), 10.06 (m), 10.21 (m), 12.10 (s, broad), 12.56 (m), 12.66 (s), 13.30 (s, broad), 13.46 (s), and 14.50 μ (w, broad); nmr (CCl_4) δ 1.43 (s, 3 H), 1.92 (s, 3 H), 3.67 (s, 3 H), and 6.5–7.5 (m, broad, 8 H). Exact mass measurement: theoretical 239.1310; observed 239.1305.

***N*-(2-Propylidene)-2′-methoxy-2-aminobiphenyl (5b).**—A mixture of 3.9 g (20 mmol) of 2′-methoxy-2-aminobiphenyl, 5 g of molecular sieves, and 25 ml of acetone was refluxed for 1 hr. After filtration and solvent removal *in vacuo*, the residue was distilled to yield 2.72 g (60%) of a slightly yellow, viscous oil, **5b**: bp 118–122° (0.08 mm); product contained a slight impurity (<5%) as analyzed by vpc (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh on Varaport 30) at 172°; ir (neat) 3.44 (m, broad), 6.00 (s), 6.24 (m), 6.70 (s), 6.84 (s), 7.02 (s), 7.36 (s), 8.05 (s, broad), 8.95 (m), 9.54 (m), 9.76 (s), 10.00 (m), 12.60 (m, broad), and 13.30 μ (s, broad); nmr (CCl_4) δ 1.50 (s, 3 H), 1.80 (s, 3 H), 3.60 (s, 3 H), and 6.5–7.5 (m, broad, 8 H). Exact mass measurement: theoretical 239.1310; observed 239.1305.

***N*-(2-Propylidene)-3′-methoxy-2-aminobiphenyl (5c).**—A solution of 8.71 g (40 mmol) of 3′-methoxy-2-aminobiphenyl was dissolved in 25 ml of acetone. To this was added 5 g of molecular sieves and the solution was refluxed for 0.5 hr. An additional 5 g of molecular sieves was added and the solution was refluxed for an additional 0.5 hr. The solution was filtered and the solvent was removed by distillation. The remaining viscous residue was distilled [bp 124–126° (0.10 mm)] to yield 8.87 g (85%) of a slightly yellow, viscous oil, **5c**: product contained <1% starting material by vpc analysis (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh Varaport 30) at 165°; ir (neat) 3.40 (m, broad), 6.02 (s), 6.25 (s), 6.82 (s), 7.04 (s), 7.35 (s), 7.71 (s), 7.92 (s), 8.06 (s), 8.25 (s), 8.54 (s), 9.55 (s), 9.81 (s), 11.50 (m, broad), 12.68 (s, broad), 13.30 (s, broad), and 14.32 μ (m, broad); nmr (CCl_4) δ 1.45 (s, 3 H), 1.90 (s, 3 H), 3.68 (s, 3 H), and 6.5–7.5 (m, 8 H). Exact mass measurement: theoretical 239.1310; observed 239.1312.

Sensitized Irradiation of *N*-(2-Propylidene)-2-aminobiphenyl (5a).—A solution of 1.10 g (5.2 mmol) of **5a** in 150 ml of acetone was irradiated for 11 hr under a nitrogen atmosphere. The reaction was monitored by vpc analysis (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh Varaport 30) at 190° until no more starting material was detected as reacting (<10% remained as unreacted). The solvent was removed *in vacuo* from a slightly yellow reaction mixture and the dark, oily residue was chromatographed on a silica gel (3 × 50 cm) column slurry packed in 2% ether–hexane (E–H). Elution proceeded as follows: 900 ml, 2% E–H, nil; 1250 ml, 5% E–H, 0.72 g of a yellow oil which solidified. The product was then sublimed (100°, 0.10 mm) to afford 0.72 g (66%) of a yellow, crystalline solid, mp 96–98°. A portion was then recrystallized from hexane to yield white, crystalline 6,6-dimethyl-5,6-dihydrophenanthridine (**6a**): mp 102–103° (lit.[5d] mp 104–105°); ir (KBr) 6.24 (m), 6.73 (m), 6.96 (s), 13.07 (s), 13.28 (s), 13.39 (s), and 13.78 μ (s); nmr (CCl_4) δ 1.38 (s, 6 H), 3.45 (s, broad, 1 H), 6.2–7.2 (m, 6 H), and 7.55 (m, 2 H).

Anal. Calcd for $C_{15}H_{15}N$: C, 86.12; H, 7.18; N, 6.70. Found: C, 86.18; H, 7.48; N, 6.66.

Sensitized Irradiation of *N*-(2-Propylidene)-4′-methoxy-2-aminobiphenyl (5d).—A solution of 1.01 g (4.2 mmol) of **5d** in 150 ml of acetone was irradiated for 1 hr under a nitrogen atmosphere. After solvent removal *in vacuo* the dark, oily residue was impregnated on 10 g of silica gel and chromatographed on a silica gel (3 × 50 cm) column slurry packed in 2% ether–hexane. Elution proceeded as follows: 1 l. 2% E–H, nil; 1 l., 5% E–H, 0.04 g of a yellow oil; 1.25 l., 10% E–H, 0.74 g (74%) of a yellow oil which solidified, mp 95–100°. The solid was then sublimed (100°, 0.05 mm) to yield 0.73 g (73%) of **6d**, mp 103–106°. Recrystallization of this material from hexane yielded 8-methoxy-6,6-dimethyl-5,6-dihydrophenanthridine (**6d**) as a

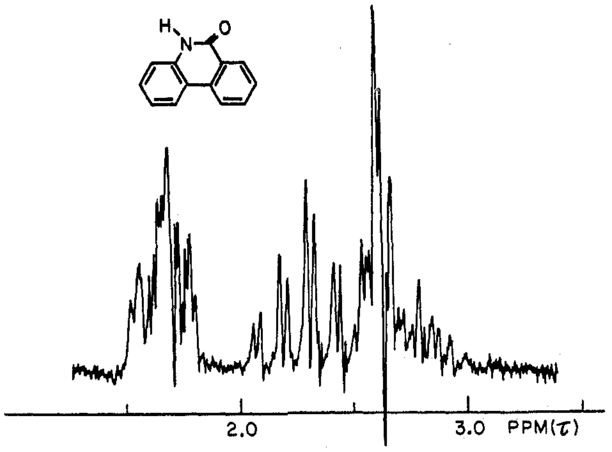

Figure 1.—Nmr spectrum of 6(5*H*)-phenanthridinone (**3a**) in the aromatic region.

white, crystalline solid: mp 108–109°; ir (KBr) 3.38 (m, broad), 6.21 (m), 7.06 (m), 7.68 (s), 7.78 (s), 8.20 (s), 8.48 (m), 9.56 (m), 9.63 (m), 11.42 (m), 12.13 (m), 13.08 (m), 13.43 (s), and 13.72 μ (m); nmr (CCl_4) δ 1.39 (s, 6 H), 3.61 (s, broad, 1 H), 3.74 (s, 3 H), 6.4–7.2 (m, broad, 5 H), and 7.45–7.7 (m, broad, 2 H).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 80.14; H, 7.13; N, 5.69.

Sensitized Irradiation of *N*-(2-Propylidene)-2′-methoxy-2-aminobiphenyl (5b).—A solution of 0.91 g (3.8 mmol) of **5b** in 150 ml of acetone was irradiated for 1.5 hr under a nitrogen atmosphere. The progress of the reaction was monitored by vpc analysis (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh Varaport 30) at 170°. After 1 hr the reaction had proceeded to greater than 90% conversion. After solvent removal *in vacuo*, a dark oil remained which was impregnated on 10 g of silica gel and chromatographed on a silica gel (3 × 48 cm) column slurry-packed in 10% ether–hexane. Elution proceeded as follows: 250 ml, 10% E–H, nil; 250 ml, 10% E–H, 0.08 g of a yellow oil which solidified, impure by vpc analysis; 1 l., 10% E–H, 0.65 g (72%) of a yellow oil which solidified pure as analyzed by vpc. The solid was then sublimed (100°, 0.02 mm) and recrystallized from hexane to yield 0.62 g (68%) of 10-methoxy-6,6-dimethyl-5,6-dihydrophenanthridine (**6b**): mp 108–109°; ir (KBr) 2.98 (m), 3.40 (m), 6.23 (m), 6.36 (m), 6.73 (m), 6.86 (s), 7.00 (s), 7.27 (m), 7.39 (m), 7.64 (m), 7.71 (m), 7.94 (s, broad), 8.36 (m), 8.45 (m), 8.58 (m), 8.74 (m), 9.50 (s), 8.60 (s), 10.01 (m), 10.67 (m), 12.55 (s), 13.20 (s, broad), and 13.83 μ (s); nmr (CCl_4) δ 1.38 (s, 6 H), 3.56 (s, broad, 1 H), 3.74 (s, 3 H), 6.5–7.4 (m, broad, 6 H), and 8.2–8.4 (m, 1 H).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 80.16; H, 7.15; N, 5.83.

Sensitized Irradiation of *N*-(2-Propylidene)-3′-methoxy-2-aminobiphenyl (5c).—A solution of 1.04 g (5.0 mmol) of **5c** in 150 ml of acetone was irradiated for 1 hr under a nitrogen atmosphere. The reaction was monitored by vpc (5 ft × 0.125 in., 5% SE-30 on 100/120 mesh Varaport 30) at 170° and was complete within 1 hr. From vpc analysis, two products were produced in the ratio of 2.86:1. The solvent was removed *in vacuo* from a slightly yellow reaction mixture and the dark, oily residue was chromatographed on silica gel. There were isolated two products in low yield. Owing to the low yield and the difficulty of purification, further work was not attempted.

1-(4′-Methoxy-2-biphenylcarbonyl)aziridine.[28]—To a rapidly stirred mixture of 20 ml of benzene, 0.65 g of sodium hydroxide, 25 g of crushed ice, and 1.70 g (39 mmol) of ethylene imine was added dropwise a solution of 0.95 g (3.9 mmol) of 2-(4-methoxyphenyl)benzoyl chloride in 10 ml of benzene. After the reaction mixture had warmed to room temperature, the phases were separated. The organic phase and ether washings of the aqueous phase were combined and dried over sodium sulfate. Removal of the solvent *in vacuo* yielded a light yellow solid which was recrystallized from ethanol to yield 0.8 g of the amide as white crystals: mp 126–128°; ir (KBr) 5.99 (s), 7.41 (s), 8.07 (s), 11.88 (s), and 13.02 μ (s); nmr ($CDCl_3$) δ 2.07 (s, 4 H), 3.85 (s, 3 H), and 6.8–8.0 (m, 8 H).

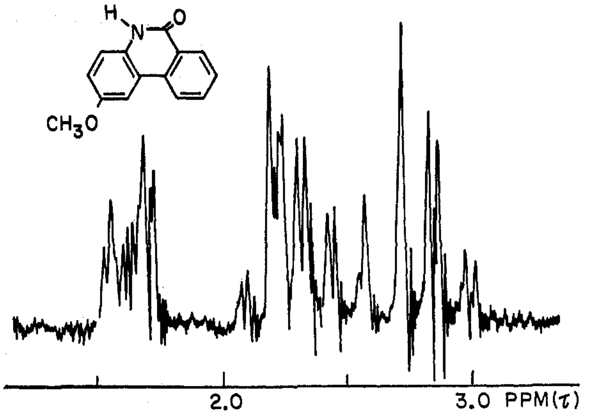

Figure 2.—Nmr spectrum of 2-methoxy-6(5*H*)-phenanthridinone (**3d**) in the aromatic region.

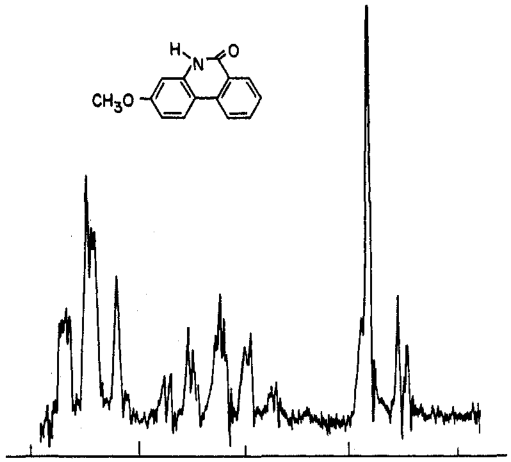

Figure 3.—Nmr spectrum of 3-methoxy-6(5*H*)-phenanthridinone (**3b**) in the aromatic region.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.67; H, 5.97; N, 5.53. Found: C, 75.41; H, 5.98; N, 5.50.

2-(4′-Methoxy-2-biphenyl)-2-oxazoline (8).—A solution of 2.30 g of sodium iodide and 1.06 g (4.2 mmol) of the aziridine in 100 ml of acetone was refluxed for 44 hr with protection from moisture. Work-up yielded a viscous yellow oil. Chromatography of this material on silica gel (ether–benzene elution) followed by molecular distillation yielded 1.5 g (65%) of a colorless, viscous oil, **8**: ir (neat) 6.05 (s), 8.08 (s), 8.52 (s), 9.67 (s), 10.67 (s), 12.02 (s), and 13.15 μ (s); nmr ($CDCl_3$) δ 3.86 (s, 3 H), 4.08 (center of A_2B_2, 4 H), and 6.8–8.0 (m, 8 H).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.67; H, 5.97; N, 5.53. Found: C, 75.24; H, 6.03; N, 5.55.

4′-Methoxy-*N*-methyl-2-biphenylcarboxamide.—The amide was prepared in the usual fashion by treating the acid chloride with methylamine. Recrystallization of the crude material from benzene gave white crystals: mp 133.0–134.5°; ir (KBr) 6.10 (s), 6.25 (s), 7.15 (s), 9.95 (s), 9.72 (s), and 13.09 μ (s); nmr ($CDCl_3$) δ 2.66 (d, $J = 5$ Hz, 3 H), 3.81 (s, 3 H), 5.5 (br s, 1 H), and 6.8–7.7 (m, 8 H).

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.20; H, 6.21; N, 5.75.

Ethyl 4′-Methoxy-*N*-methyl-2-biphenylcarboximidate (7).—To a stirred, cold (0°) solution of 1.90 g (10.0 mmol) of triethyloxonium tetrafluoroborate in 50 ml of dry methylene chloride was added a solution of 2.0 g (8.3 mmol) of amide **19** in 10 ml of methylene chloride dropwise. The reaction mixture was stirred for 12 hr at room temperature followed by addition of 3 ml of 50% aqueous potassium carbonate, filtration, and evaporation of the solvent. The resulting crude oil was passed through a Florisil column (ether–benzene elution) and the resulting colorless oil (1.1 g, 49%) was stored under nitrogen. Further purification by either short-path distillation or preparative vpc resulted in

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[28] H. Heine, M. Fetter, and E. Nicholson, *J. Amer. Chem. Soc.*, **81**, 2202 (1959).

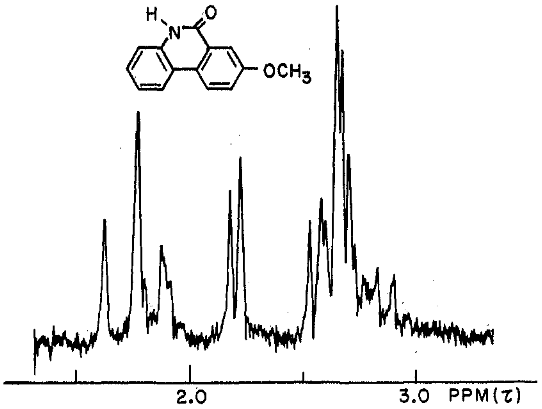


Figure 4.—Nmr spectrum of 8-methoxy-6(5*H*)-phenanthridinone (**3c**) in the aromatic region.

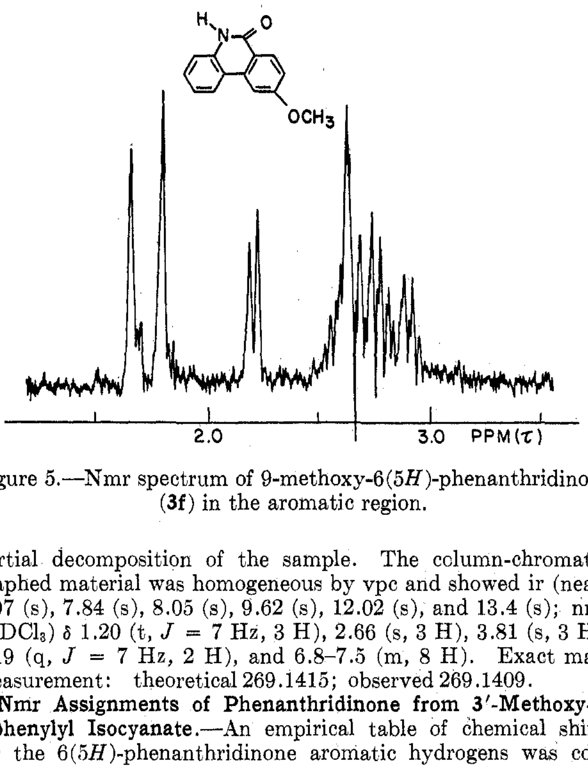


Figure 5.—Nmr spectrum of 9-methoxy-6(5*H*)-phenanthridinone (**3f**) in the aromatic region.

partial decomposition of the sample. The column-chromatographed material was homogeneous by vpc and showed ir (neat) 5.97 (s), 7.84 (s), 8.05 (s), 9.62 (s), 12.02 (s), and 13.4 (s); nmr (CDCl$_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.66 (s, 3 H), 3.81 (s, 3 H), 4.19 (q, J = 7 Hz, 2 H), and 6.8–7.5 (m, 8 H). Exact mass measurement: theoretical 269.1415; observed 269.1409.

Nmr Assignments of Phenanthridinone from 3′-Methoxy-2-biphenylyl Isocyanate.—An empirical table of chemical shifts for the 6(5*H*)-phenanthridinone aromatic hydrogens was constructed for the nmr spectra of the unsubstituted, 2-, 3-, 7-, 8-, 9-, and 10-methoxy compounds (Table IV). Good agreement with observed values (Figures 1–6) was obtained by assigning base values to the chemical shifts for the protons in **3a**: τ 1.7 region, H_1 and H_{10} (deshielding by the ring), H_7 (deshielding by the amide carbonyl); τ 2.3 region, H_8 and H_9; τ 2.6 region, H_2, H_3, and H_4. The observed chemical shift values of the remaining compounds, 2-, 3-, 8-, 9-, and 10-methoxy, were in good agreement with those calculated by assuming that the methoxy group would shield ortho protons by approximately τ 0.5 and meta protons by about τ 0.1.

The nmr spectrum of the product from irradiation of 3′-methoxy-2-biphenylyl isocyanate showed a two-proton doublet at τ 1.7 (J = 9 Hz), a one-proton doublet at 2.3 (J = 3 Hz), and a multiplet at 2.5–2.9. This nmr is most consistent with **3f**, since it shows two protons in the τ 1.7 region having ortho coupling and one proton in the τ 2.2 region showing meta coupling. Structure **3f′** would be expected to show only two protons below τ 2.3. In agreement with this assignment irradiation of the protons at τ 1.7 simplified the τ 2.8 region. Likewise, when irradiation was carried out in the τ 2.8 region, the doublets at 1.7 and 2.3 collapsed to singlets. It was concluded that this cyclization product was the 9-methoxy-6(5*H*)-phenanthridinone (**3f**).

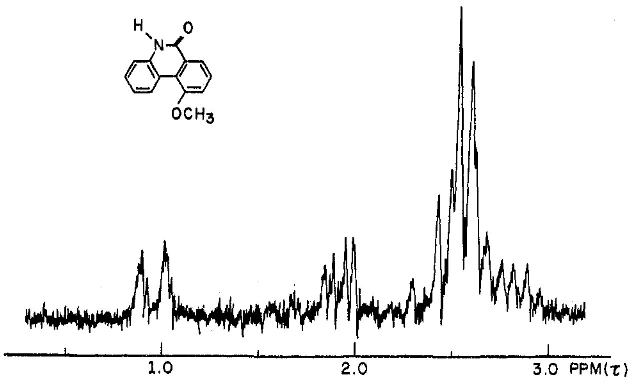
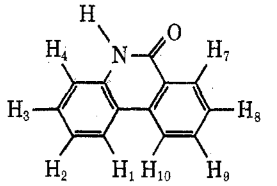


Figure 6.—Nmr spectrum of 10-methoxy-6(5*H*)-phenanthridinone (**3e**) in the aromatic region.

TABLE IV

EXPECTED τ VALUES FOR THE AROMATIC HYDROGENS IN SUBSTITUTED 6(5*H*)-PHENANTHRIDINONES



Compd	H_1	H_2	H_3	H_4	H_7	H_8	H_9	H_{10}
Unsubstituted (**3a**)	1.7	2.6	2.6	2.6	1.7	2.3	2.3	1.7
2-Methoxy (**3d**)	2.2		3.1	2.7	1.7	2.3	2.3	1.7
3-Methoxy (**3b**)	1.8	3.1		3.1	1.7	2.3	2.3	1.7
7-Methoxy (**3f′**)	1.7	2.6	2.6	2.6		2.8	2.4	1.7
8-Methoxy (**3c**)	1.7	2.6	2.6	2.6	2.2		2.8	1.8
9-Methoxy (**3f**)	1.7	2.6	2.6	2.6	1.8	2.8		2.2
10-Methoxy (**3e**)	1.7	2.6	2.6	2.6	1.7	2.4	2.8	

Registry No.—**1a**, 17337-13-2; **1b**, 38088-88-9; **1c**, 38088-89-0; **1d**, 38088-90-3; **1e**, 38088-91-4; **1f**, 38088-92-5; **3a**, 1015-89-0; **3b**, 38088-94-7; **3c**, 38088-95-8; **3d**, 38088-96-9; **3e**, 38088-97-0; **3f**, 38088-98-1; **3f′**, 38088-99-2; **4a**, 90-41-5; **4b**, 1206-76-4; **4c**, 38089-02-0; **4d**, 38089-03-1; **5a**, 29666-58-8; **5b**, 38089-05-3; **5c**, 38089-06-4; **5d**, 38087-93-3; **6b**, 38165-84-3; **6d**, 38087-94-4; **7**, 38087-95-5; **8**, 38087-92-2; acetone, 67-64-1; 3′-methoxy-2-biphenylcarboxylic acid, 38087-96-6; 3′-methoxy-2-biphenylcarbonyl chloride, 38087-97-7; 4′-methoxy-2-biphenylcarboxylic acid, 18110-71-9; 4′-methoxy-2-biphenylcarbonyl chloride, 38087-99-9; 4-methoxy-2-biphenylamine, 38088-00-5; 5-methoxy-2-biphenylamine, 38088-01-6; 1-(4′-methoxy-2-biphenylcarbonyl)aziridine, 38088-02-7; 4′-methoxy-*N*-methyl-2-biphenylcarboxamide, 35158-67-9.

Acknowledgment.—We wish to thank the Eli Lilly Co., Indianapolis, Ind., for partial support of this work.