and was corrected for back reaction. The data were plotted as in Figure 4.

Conclusion

The sensitized photoracemization of alkyl aryl sulfoxides has been shown to result from energy transfer from the singlet state of naphthalene. The possibility of exothermic electronic energy transfer has been ruled out spectroscopically. It is postulated that an exciplex is formed from an excited singlet state naphthalene molecule and a ground state molecule of the sulfoxide. This excited complex then undergoes radiationless decay converting electronic energy to vibrational energy partitioned between the two components of the exciplex. Enough vibrational energy appears in the aryl sulfinyl center to effect thermal pyramidal inversion with high efficiency. Steric and electronic effects on the rates of fluorescence quenching or photoracemization are small.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF49(638)-1479. R. S. Cooke also acknowledges support from a grant from the General Electric Foundation, a graduate research assistantship from the California Institute of Technology, and a graduate research fellowship from the National Institutes of Health, General Medical Sciences Division.

Photochemistry of Quinoline and Some Substituted Quinoline Derivatives[1]

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Abstract: Irradiation of quinoline and 8-methylquinoline in acidic ethanol yielded the 2- and 4-ethylquinolines. Irradiation in 95% ethanol yielded the 2-α-hydroxyethylquinolines together with the corresponding 1,2,3,4-tetrahydroquinolines. Irradiation of quinoline in *t*-butyl alcohol yielded 2-(2-hydroxy-2-methylpropyl)quinoline. Photoalkylation did not proceed in 2-propanol but instead a low yield of a reduced quinoline dimer occurred. If 2-substituted quinolines containing a γ-hydrogen were irradiated in inert solvents, an elimination corresponding to ketone type II cleavage would occur with quantum yields varying from 0.014 to 0.29 depending upon the structure of the starting quinoline. This reaction was shown (by quenching studies) to proceed through an excited singlet, probably of n–π^* configuration. The photoelimination had a McLafferty rearrangement counterpart in the electron-impact fragmentations of the 2-substituted quinolines.

Systematic studies on the photochemistry arising from the C=N portion of aza aromatic molecules are infrequent in the chemical literature in spite of the fact that ample evidence indicates that this should be a fruitful area of investigation. Indeed, electronic spectroscopy of aza aromatics, both in theory and in experiment, has developed side by side with that of the carbonyl group and the similarities obtaining between the two have been pointed out.[2] With few exceptions, however, the literature of organic photochemistry is lacking in studies which compare C=N photoreactivity in aza aromatics with knowledge of the excited states of these molecules.[3] One exception has been in the case of acridine, whose physical and organic photochemistry has been somewhat thoroughly investigated.[5] Surprisingly, this large body of work has not led to similar studies on other N-heteroaromatics. A second exception is the case of riboflavin, a very complex molecule whose photochemistry has engaged the attention of numerous groups of workers[6] over a considerable span of years. Our original interest[7] in this area arose from an accidental observation on the photolability in alcohol solution of the alkaloid papaverine. However, it was soon apparent that, beyond the discovery[7,8] of a somewhat novel variant of C=N photochemistry, the importance of future work lay in establishing the individual mechanistic details and generality[9] of aza aromatic photochemistry involving

(1) Photochemistry of N-Heterocycles. V. Previous Paper: F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, **91**, 3103 (1969). This work was supported in part by Grant GM-14525 from the National Institute of General Medical Sciences, U. S. Public Health Service.

(2) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969.

(3) The voluminous work on nucleic acid derivatives[4] up to the present time has almost invariably dealt with two basic reactions (exemplified by thymine dimerization and uracil hydration) which do not appear to involve the C=N of these molecules directly. However, purine and pyrimidine bases do undergo the type of reaction we are here discussing although such reactivity has not yet been demonstrated in the more complex biologically important derivatives.

(4) J. G. Burr, *Advan. Photochem.*, **6**, 193 (1968).

(5) (a) V. Zanker and P. Schmidt, *Z. Physik. Chem.*, **17**, 11 (1958); (b) H. Goth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965); (c) A. Kira, Y. Ikeda, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **39**, 1673 (1966); (d) V. Zanker, E. Erhardt, and J. Thies, *Ind. Chim. Belge*, **32** (III), 24 (1967); (e) E. Van der Donct and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967); (f) K. Nakamaru, S. Niizuma, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **42**, 255 (1969). These few (of many) studies can be used by the interested reader as an entrance into the acridine photochemistry literature.

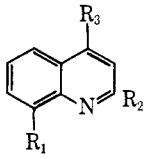
(6) (a) P. Karrer and H. F. Meerwein, *Helv. Chim. Acta*, **18**, 1126 (1935); (b) W. M. Moore, J. T. Spence, F. A. Raymond, and S. D. Colson, *J. Amer. Chem. Soc.*, **85**, 3367 (1963); (c) P.-S. Song, E. C. Smith, and D. E. Metzler, *ibid.*, **87**, 4181 (1965); (d) M. Green and G. Tollin, *Photochem. Photobiol.*, **7**, 129 (1968); (e) W. E. Kurtin and P.-S. Song, *ibid.*, **9**, 127 (1969). These few (of many) studies can be used by the interested reader as an entrance into the riboflavin photochemistry literature.

(7) F. R. Stermitz, R. Pua, and H. Vyas, *Chem. Commun.*, 326 (1967).

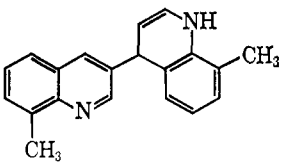
(8) F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968).

Table I. Photoalkylation of Quinolines

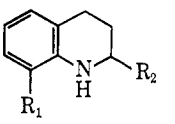
Compound	Solvent	Lamp	Major products
Quinoline	EtOH, HCl	Hanovia 450-W	I, II
8-Methylquinoline	EtOH, HCl	Hanovia 450-W	III, IV, X
Quinoline	EtOH	Hanovia 450-W	V, XI
8-Methylquinoline	EtOH	Hanovia 450-W	VI, XII
Quinoline	2-Propanol, HCl	Hanovia 450-W	No reaction
Quinoline	2-Propanol, HCl	Rayonet, 3000 Å	Dimers of XIII
Quinoline	2-Propanol	Rayonet, 3000 Å	No reaction
Quinoline	*t*-Butyl alcohol	Hanovia, 450-W	VII, VIII
2-*n*-Butylquinoline	EtOH, HCl	Hanovia, 450-W	IX



I, $R_1 = R_3 = H$; $R_2 = CH_2CH_3$
II, $R_1 = R_2 = H$; $R_3 = CH_2CH_3$
III, $R_1 = CH_3$; $R_2 = CH_2CH_3$; $R_3 = H$
IV, $R_1 = CH_3$; $R_2 = H$; $R_3 = CH_2CH_3$
V, $R_1 = R_3 = H$; $R_2 = CH(OH)CH_3$
VI, $R_1 = CH_3$; $R_2 = CH(OH)CH_3$; $R_3 = H$
VII, $R_1 = R_3 = H$; $R_2 = CH_3$
VIII, $R_1 = R_3 = H$; $R_2 = CH_2C(OH)(CH_3)_2$
IX, $R_1 = H$; $R_2 = CH_2CH_2CH_2CH_3$; $R_3 = CH_2CH_3$



X



XI, $R_1 = H$; $R_2 = CH(OH)CH_3$
XII, $R_1 = CH_3$; $R_2 = CH(OH)CH_3$
XIII, $R_1 = R_2 = H$

the C=N group. For this purpose, we have initiated studies on quinoline, isoquinoline, pyridine, and some other simple heterocycles. The present paper presents some of our results with quinoline. Portions of our initial chemical results have previously appeared.[1,11]

Results

We originally suggested[8] that at least a formal parallel between the reactions of the C=N and the C=O seemed to exist and our results with quinoline irradiations have shown new parallels. However, some striking differences have been noted. Thus, the photoalkylation reaction was successful with quinoline in acidified ethanol. Irradiations in ethanol without added acid produced hydroxyalkyl derivatives. Irradiation in *t*-butyl alcohol produced an hydroxyalkyl product which can formally be represented as arising from abstraction of a hydrogen from a methyl group of the *t*-butyl alcohol. In contrast to ketone photoreduction, irradiation of quinoline in 2-propanol produced product at only a very slow rate. The only product finally produced was a partially reduced quinoline dimer rather than a quinoline with incorporated 2-propanol. Our photoalkylation results are summarized in Table I.

In a search for other parallels between C=N and C=O photoreactivity, we examined the reactions of some 2-substituted quinolines where a hydrogen γ to the C=N is present on the side chain. Indeed, these derivatives underwent photoelimination in a similar manner to the Norrish type II cleavage of carbonyl compounds. Where no γ hydrogen was present, no reaction occurred. As is the case with carbonyl compounds, a correlation between the electron impact fragmentation of the 2-substituted quinolines and their photoreactivity was obtained. These results are summarized in Tables II and III.

With these product formation studies in hand we proceeded to investigate the detailed mechanisms involved. Quantum yields of product formation were determined for both photoalkylation and photoelimination and then the effects of various quenchers on quantum yields were examined. A study was also made on the effect of solvent on the quantum yields of photoelimination. These results are summarized in Table IV. An attempt to sensitize the photoelimination with benzophenone was unsuccessful (see Table VI of the Experimental Section).

Absorption spectra for quinoline and various substituted quinolines have been published and discussed elsewhere.[12] Our results agreed closely with published values[12] of 314 nm (ϵ 3000) and 300 (2600) for quinoline in 95% ethanol. Addition of acid changes the spectrum to a single peak in the long-wavelength region,

(9) The following reported aza aromatic photoalkylations and photohydroxyalkylations are apparently similar to those we have found: (a) pyrimidines and pyrazolo[3,4-*d*]pyrimidines: M. Ochiai and K. Morita, *Tetrahedron Lett.*, 2349 (1967), and M. Ochiai, E. Mizuta, Y. Asahi, and K. Morita, *Tetrahedron*, **24**, 5861 (1968); (b) purines: H. Linschitz and J. S. Connolly, *J. Amer. Chem. Soc.*, **90**, 2979 (1968), and J. S. Connolly and H. Linschitz, *Photochem. Photobiol.*, 7, 791 (1968); (c) benz[*h*]isoquinolines: C. E. Loader and C. J. Timmons, *J. Chem. Soc., C*, 1457 (1967); (d) cinnolines and quinoxalines: T. T. Chen, W. Doerscheln, H. Goth, M. Hesse, and H. Schmid, *Helv. Chim. Acta*, **51**, 632 (1968); (e) caffeine: D. Elad, I. Rosenthal, and H. Steinmaus, *Chem. Commun.*, 305 (1969). We earlier suggested[7,8] that a number of photoreactions of the C=N group in aliphatic imines (as here now opposed to aza aromatics) could also be incorporated mechanistically into the picture presented in the present paper. However, other workers have presented[10] evidence leading them to propose independent pathways in some such cases. For the present, we are therefore only considering the C=N in an aromatic system. Additional references to other nonaromatic C=N photochemical studies have been compiled.[8,10b]

(10) (a) P. J. Collin, J. S. Shannon, H. Silberman, S. Sternhell, and G. Sugowdz, *Tetrahedron*, **24**, 3069 (1968); (b) A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2653 (1969).

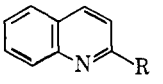
(11) F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968).

(12) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N.Y., 1962, p 368.

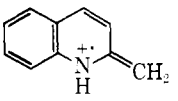
Table II. Photoelimination of 2-Substituted Quinolines[a]

Compd	Products	Rate,[b] sec^{-1}	Compd	Product	Rate[b]
XIV	XV, $CH_3CH=CH_2$	2.5×10^{-6}	XIX	XV, CH_2O	6.6×10^{-5}
XVI	XV, CH_2O	2.3×10^{-5}	XX	No reaction	
XVII	XVIII, CH_2O	1.8×10^{-5}	I	No reaction	

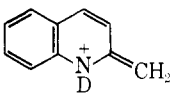
[a] Rayonet reactor, 3000-Å lamps, benzene solution. [b] Single runs.



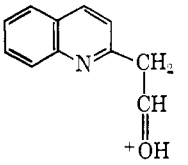
XIV, R = $CH_2CH_2CH_2CH_3$
XV, R = CH_3
XVI, R = CH_2CH_2OH
XVII, R = CH_2CH_2OD
XVIII, R = CH_2D
XIX, R = CH_2OCH_3
XX, R = $CH_2CH_2OCH_3$



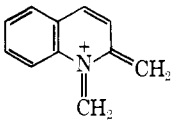
XXI



XXII



XXIII



XXIV

Table III. Base Peaks in the Mass Spectra of 2-Substituted Quinolines

Compd	Base peak and suggested structure
XIV	*m/e* 143, XXI
XVI	*m/e* 143, XXI
XVII	*m/e* 144, XXII
VIII	*m/e* 143, XXI
XX	*m/e* 172, XXIII
I	*m/e* 156, XXIV[a]

[a] S. D. Sample, D. A. Lightner, O. Burchardt, and C. Djerassi, *J. Org. Chem.*, **32**, 997 (1967).

Table IV. Quantum Yields of Photoalkylation and Photoelimination

Compound	Solvent	Quencher	Quantum yield of product formation
Quinoline	EtOH, HCl	None	0.020
Quinoline	EtOH, HCl	0.5 *M* piperylene	*a*
XIX	Benzene	None	0.27
XVI	Benzene	None	0.11
XVI	*t*-Butyl alcohol	None	0.029
XVI	Acetonitrile	None	0.019
XVI	Benzene	Air	0.094
XVI	Benzene	0.5 *M cis*-piperylene	0.11
XVI	Benzene	0.5 *M trans*-piperylene	0.10
XIV	Cyclohexane	None	0.014
XIV	Benzene	None	0.015
XIV	*t*-Butyl alcohol	None	0.021
XIV	Acetonitrile	None	0.025
XIV	Benzene	Air	0.0087
XIV	Benzene	0.5 *M cis*-piperylene	0.015

[a] Quinoline disappeared at about the same rate as in the absence of piperylene. However, no alkylation products were formed, but instead the piperylene apparently reacted with the quinoline.

315 nm (ε 7000). Generally, the absorption data for all the substituted quinolines were similar in shape and extinction coefficients. Extinction coefficients for the substituted quinolines in benzene at 3130 Å were all close to 2100. There has been much literature discussion regarding the emission spectra of quinoline under various conditions and this will be mentioned subsequently. Our emission spectra also showed the previously discussed trend of decreased phosphorescence and increased fluorescence in going from nonpolar solvents (3-methylpentane) to solvents containing alcohol (EPA). Since piperylene failed to quench the photoelimination reactions (see Table IV), we examined its effect on the emission spectrum of 0.1 *M* 2-*n*-butylquinoline, XIV, in EPA at 77°K. The phosphorescence was quenched completely by 0.15 *M* piperylene. Further studies on the emission spectra of the various substituted quinolines are proceeding and will be published elsewhere.[12a]

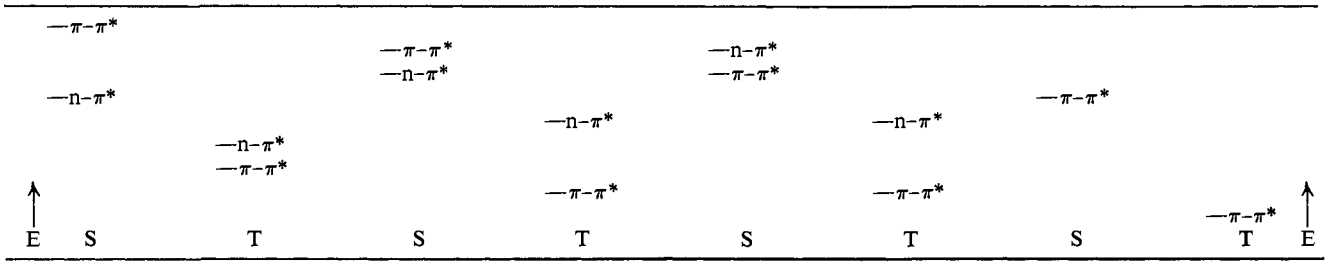
Discussion

It is convenient to discuss our results on the photoalkylation and photoelimination separately and since the data on the latter are more complete, the discussion will begin there.

Photoelimination. Our results, although not complete for each of the eliminations studied, nevertheless show a very clear pattern which can be summarized by the following statements: (1) all products isolated are exactly those one would expect if the reaction proceeded analogously to ketone type II cleavage; (2) only those compounds undergo photoelimination which have a hydrogen γ to the C=N; (3) only those compounds which undergo photoelimination also exhibit a McLafferty rearrangement ion as the base peak in the mass spectrum; (4) the γ hydrogen is transferred selectively in both the photoelimination and McLafferty rearrangement; (5) the rates of elimination (and quantum yields) follow the expected order of ease of abstraction of the γ hydrogen; and (6) since the photoelimination is not sensitized by benzophenone, is not quenched by piperylene (although phosphorescence of the quinoline *is* quenched by piperylene), and does not proceed in acidic solution, the photoreactive state can be uniquely defined as the n–π* first excited singlet for

(12a) Note Added in Proof. The methylpentane emission spectrum of XVI, 2-(2-hydroxyethyl)quinoline is virtually identical in shape, position, and lifetime with that of quinolinium ion. Hence, the elimination reaction in this case proceeds from the intermediate where a proton has been transferred from oxygen to nitrogen.

Table V. Energy Levels and Configurations of Quinoline Excited States



[a] Reference 13d. [b] Reference 13a–c.

2-*n*-butylquinoline. These statements will now be expanded upon somewhat in reverse order.

The ordering and configuration of the excited states of quinoline itself have been discussed several times[13] and Table V displays current thought on the subject. Although there is general agreement on the states in the gas phase (or hydrocarbon solvent) and in acid, there are two viewpoints regarding the situation when hydroxylic solvents are present. In the gas phase or in hydrocarbon solvents, quinoline shows little or no fluorescence and a strong phosphorescence. However, when as little as 1% of a hydroxylic solvent is added to the hydrocarbon, increased fluorescence and decreased phosphorescence are observed. It has been suggested[13a–c] that the addition of the hydroxylic solvent changes the lowest excited singlet from n–π^* to π–π^* and decreases spin–orbit coupling and hence the rate of intersystem crossing to the triplet manifold. On the other hand, Lim[13d] states that these effects do not necessarily mean that the order of the first excited singlet has been inverted, but merely that the two states have been brought so close together that vibronic interactions can take place and hence the observed solvent effects are due to a second-order spin–orbit coupling. Absorption spectra are little affected by hydroxylic solvents, although a slight enhancement of extinction coefficient is observed. Indeed, addition of small amounts of weak acids (*e.g.*, acetic acid) have about the same effect as hydroxylic solvents although a trace of trifluoracetic acid or mineral acids shift both the absorption and emission to that of the quinolinium ion. In the latter case, of course, π–π^* states must be lowest in both the singlet and triplet manifolds since the nonbonded pair is now protonated.

It seems clear then, from the quenching studies, that the photoelimination reaction of 2-*n*-butylquinoline in benzene must occur from the singlet state and, from Table V, that state should have the n–π^* configuration. At the other extreme it was noted that irradiation of 2-*n*-butylquinoline in acidic ethanol produced only photoalkylation with a complete lack of photoelimination. Low-fluorescence intensity is observed with the quinolinium ion and hence it must be concluded that the lowest excited singlet (in this case of π–π^* configuration) is not highly populated and photoelimination cannot proceed (or proceeds only very slowly) from that state. Since photoalkylation nevertheless does take place from a π–π^* state (no others are available) and since we are still postulating similar mechanisms for the two types of reactions (see below) some explanation for the lack of photoelimination in acidic ethanol is needed. Although several possibilities suggest themselves, we prefer to wait until we have time to study some of the other compounds in this medium.

The case of 2-(2-hydroxyethyl)quinoline is an interesting one since it contains within the molecule itself the requisite hydroxylic group for decreasing phosphorescence and increasing fluorescence. Indeed, we have found that in methylpentane solvent this quinoline shows a high intensity of phosphorescence.[12a] Quenching studies indicated that the photoelimination proceeded through a singlet state, but the configuration of that state cannot be defined exactly. (However, see ref 12a.) Experiments underway in other ring systems may have a bearing on these problems. Thus, isoquinoline, phenanthridine, and acridine are all considered[13d] (unlike quinoline) to have lowest excited singlets of π–π^* configuration and hence photoelimination reactions of suitable derivatives of these compounds will be interesting to study. It is already known that each of these undergoes photoalkylation readily and photoelimination studies on such compounds should provide information regarding any possible dichotomy of mechanism between the two reaction types.

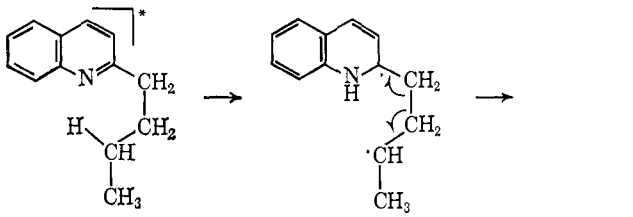
The effects of solvent on quantum yield (Table IV) are striking, with the most noteworthy result being the opposite trends for photoelimination from 2-*n*-butylquinoline and 2-(2-hydroxyethyl)quinoline. In view of the above discussion of the effects of solvent on the rate of intersystem crossing, the gradual increase of quantum yield for photoelimination of the 2-*n*-butyl compound with increasing solvent polarity could be readily explained as an effect on the excited states. The order would, however, mean that the decrease in intersystem crossing rate would be due to the *polarity* of solvent, and not an effect specifically due to a *hydroxylic* solvent as has been maintained.[13] This possibility is being checked. Although the abstraction of a hydrogen from an alkane molecule (or alkane portion of a molecule) has been noted in the literature a number of times, abstraction of a hydroxylic hydrogen is rare.[14] Therefore, the high quantum yield for photoelimination

(13) (a) M. Mataga and S. Tsuno, *Bull. Chem. Soc. Jap.*, 30, 368 (1957); (b) V. L. Ermolaev and I. P. Kotlyar, *Opt. Spektrosk.* (USSR), 9, 183 (1960); (c) M. A. El-Sayed and M. Kasha, *Spectrochim. Acta*, 15, 758 (1959); M. A. El-Sayed, *J. Chem. Phys.*, 38, 2834 (1963); (d) E. C. Lim and J. M. H. Yu, *ibid.*, 45, 4742 (1966); E. C. Lim and J. M. H. Yu, *ibid.*, 47, 2203 (1967).

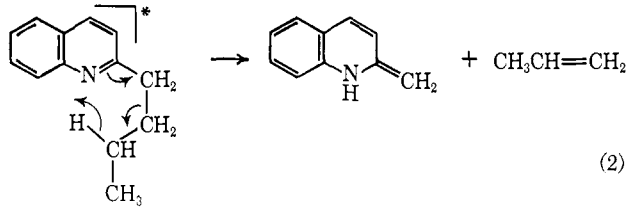
(14) Such an abstraction in a 9-substituted isoalloxazine has been observed by W. M. Moore and C. Baylor, *J. Amer. Chem. Soc.*, 88, 5677 (1966), and private communication (1969).

from 2-(2-hydroxyethyl)quinoline in benzene is unexpected, while the quantum yields in *t*-butyl alcohol and acetonitrile are perhaps "normal." One possible explanation for the high quantum yield in benzene may reside in the strong intramolecular hydrogen bond from the OH to the quinoline nitrogen in the solvent. This would be destroyed in the more polar solvents.[12a]

Solvent effects may, however, be important in another aspect of the mechanism. As in ketone type II cleavage we are faced with deciding, once the reactive excited state has been reached, whether or not subsequent reaction is stepwise (eq 1) or concerted (eq 2). In the



(1)



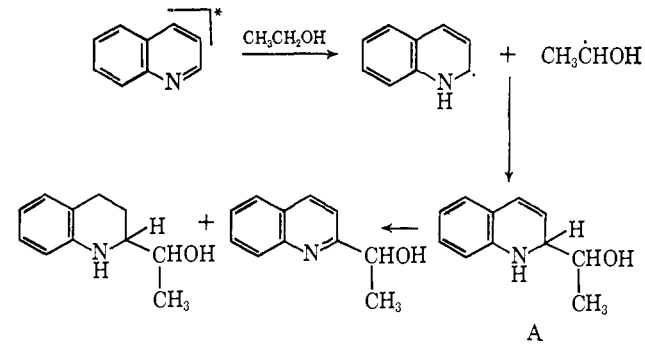
(2)

case of ketones, observation of an increase in quantum yield with increasing solvent polarity has been taken[15] as evidence for diradical species (as in eq 1) since the OH bond which was formed (NH in our case) could be stabilized by solvation in the more polar solvents. However, as noted above, in the case of the quinolines there is a marked solvent effect on the excited states which would enhance the quantum yield and hence this criterion is not easily applied in the present case. The decrease in quantum yields of photoelimination in the presence of oxygen may favor a diradical mechanism. Oxygen should have little effect on a short-lived singlet excited state, but could easily react with a diradical to lower the quantum yield. In general, the quantum yields for an intramolecular reaction which proceeds exclusively in one direction might be expected to be higher than we have observed. One possibility for the general low quantum yield of photoelimination may be that the diradical mechanism is the correct one and hence there may be considerable reversibility in the first step of eq 1. We are presently designing other experiments to help decide between these two possibilities.

Photoalkylations. Much of our mechanistic effort has been placed on the elimination reaction so less progress on the more complex photoalkylation is available to report. Alkylations in the relatively strong acid solutions we have employed must proceed through a $\pi-\pi^*$ excited state. Sensitization employing a ketone such as benzophenone would be meaningless since early conclusions[5] that acridine dimerization and alkylations proceeded partly through a triplet (because of benzophenone sensitization) were shown to be incorrect.[5e] Use of benzophenone gave acridine reactions through transfer of a hydrogen to acridine from the benzophenone ketyl radical, not through energy transfer. Ketones such as methoxyacetophenone (which have high triplet energies, but do not abstract hydrogens from alcohols) cannot be used since their weak absorption (extinction coefficients of about 60) around 310 nm would be completely outweighed by the 7000 extinction coefficient of the quinolines at the same region. Hence, selective absorption by the sensitizer would not be achieved even at high ketone concentration. The use of piperylene as a quencher was not entirely successful since, although piperylene quenched formation of alkylated products, it also reacted with the quinoline. In view of our results with the photoelimination and in view of the fact[5] that acridine photochemistry proceeds through a singlet state, it seems likely that the photoalkylation probably does also, although we have yet to perform the experiment necessary to conclusively demonstrate this.

Since our original experiments[7,8] and those of Ochiai[9a] dealt only with alkylations in acid, we repeated the work on quinolines without acid present. The isolation of the hydroxyalkylated derivatives has provided additional evidence for our mechanism,[8] which, in the case without acid, can be written as in Scheme I. In

Scheme I

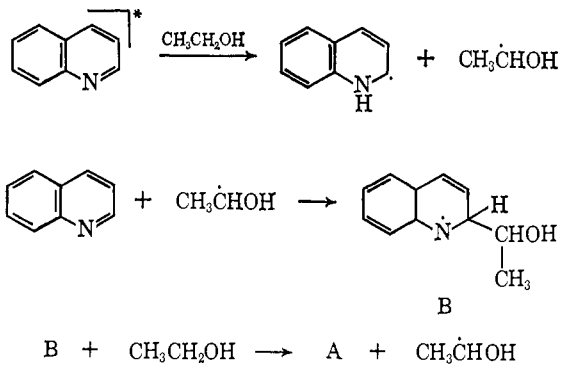


A

the case of 8-methylquinoline, intermediate A yields nearly equal amounts of the two disproportionation products, while in the case of quinoline itself only a trace of the tetrahydro compound was formed. In the latter case some other oxidizing agent, perhaps traces of oxygen, must have been involved. Although Scheme I is perhaps the simplest mechanism, some other variants have been suggested,[9] all of which cannot as yet be conclusively ruled out. Ochiai's suggestion[9a] that the excited heterocycle may split the alcohol into H· and $CH_3(OH)CH\cdot$ is energetically unfeasible. Chain-type variations where the alcohol radical formed attacks an unexcited quinoline, *e.g.*, Scheme II, are possible, but one might expect a higher quantum yield if such were the case. If the mechanisms in acid and without acid are the same, one might have expected 4-alkylation under both conditions and our failure to observe any 4-alkylation when acid was not present is as yet unexplained. The particular type of product we observed in the alkylation with *t*-butyl alcohol would be that expected from a hydrogen abstraction and coupling mechanism as in Scheme I. The isolation of 2-methyl-

(15) P. J. Wagner, *J. Amer. Chem. Soc.*, 89, 5897 (1967).

Scheme II



quinoline from this reaction is undoubtedly due to photoelimination from the product VIII.

Our results with 2-propanol are puzzling. The formation of a quinoline dimer is normal (*e.g.*, benzpinacol formation from benzophenone irradiation in 2-propanol), but the rate of reaction is anomalous. Workers studying polyaza aromatics[9b,e] have found 2-propanol incorporation and this has been the case with acridine.[5d] In the photoalkylation of purine, Linschitz has found[9b] that the quantum yield of purine disappearance was nearly the same for methanol, ethanol, and 2-propanol. However, his measured quantum yields were some ten times larger than the one we were able to measure for quinoline in acidic ethanol. We have not yet completed quantum yields for the alkylations without acid, but from a comparison of product yields in the preparative reactions (run under identical conditions) we do not expect the quantum yields for quinoline photoalkylation in ethanol to be greatly different from that in acidic ethanol. The low reactivity of 2-propanol does not carry over to the case of isoquinoline,[16] although the products in that case are again not alkylation products, but reduced dimers.[16]

Although a quinoline dimer (2,2′-biquinolyl) was observed[17] when quinoline was irradiated neat, we found no dimers when quinoline was irradiated in ethanol (either with or without acid). However, the dimer X was isolated from the 8-methylquinoline irradiation in acidic ethanol. Dimer X is unique in that the 3 position of the quinoline is substituted and Scheme I or II mechanisms cannot account for the genesis of such a structure. A possible mechanism for the formation of X would be a dimerization between the 3,4 positions of two quinoline molecules to form a cyclobutane intermediate, which then either thermally or photochemically cleaves to X.

Experimental Section[18]

Materials. Quinoline, 2-(2-hydroxyethyl)quinoline, 2-(methoxymethyl)quinoline, benzophenone, and benzhydrol were purchased from Aldrich Chemical Co. 2-(2-Hydroxyethyl)quinoline was recrystallized twice from $CHCl_3$–ether, and benzophenone and benzhydrol from ether to give constant melting points of 102–104, 46–47, and 65–67°, respectively. Quinoline and all solvents for the irradiation experiments were redistilled and only the middle fraction was used. The 2-(methoxymethyl)quinoline as purchased contained a considerable portion of 2-methylquinoline and hence was purified by several vacuum distillations until glpc showed only one peak.

Irradiation Procedures. An approximately 0.01 *M* solution of the quinoline was flushed with nitrogen for 0.5 hr prior to irradiation and continued throughout the irradiation. Either an immersion reactor with an Hanovia Type L 450-W lamp (13.2 W at 313 nm) or a Rayonet reactor with twelve 3000-Å lamps (21 W at 313 nm) was used. Control tests were run without light for all reactions and were negative unless otherwise noted.

Isolation Procedures. The irradiation solvent was removed *in vacuo* with a rotary evaporator and an nmr of the crude residue was obtained. The residue was then dissolved in ether or $CHCl_3$ and extracted with 0.1 *N* HCl. The acidic solution was made basic and then extracted three times with equal volumes of $CHCl_3$. The $CHCl_3$ solutions were combined, dried over Na_2SO_4, and evaporated. This procedure is referred to as the "standard isolation." Final separation and purification of the basic products was then accomplished on silica gel or alumina (Woelm neutral, activity grade 1) column chromatography or glpc using a column of 10% silicone rubber on Chromosorb W. Unless otherwise noted, comparison of the crude nmr with those of the products isolated was used to establish the fact that the products isolated represented the major products. Where these did not total 100%, the remainder was usually nonbasic polymer. Percentage yields of various products were either based on glpc peak areas or specific nmr absorptions. Where good accuracy in product percentage determinations was necessary, internal standards in both glpc and nmr were used.

Irradiation of Quinoline in Ethanol. A solution of 5.85 g of quinoline in 4.5 l. of 95% ethanol to which 36 ml of concentrated HCl had been added was irradiated (Pyrex, Hanovia lamp) for 80 hr. By the standard isolation, 5.0 g of crude basic product was obtained which was shown by glpc to consist of quinoline, 2-ethylquinoline (I) and 4-ethylquinoline (II) with the products represented in 7 and 10% overall yield, respectively. The nmr spectrum of I was consistent with the structure, it formed a picrate of mp 153° (lit.[19] mp 154°) and was identical with an authentic sample synthesized from ethyllithium and quinoline. The 4-ethylquinoline structure, II, could be unequivocally established by its nmr, uv, and mass spectra. It also formed a picrate of mp 194–195° (lit.[20] mp 192°).

A solution of 6.3 g of quinoline in 95% ethanol was irradiated (Pyrex, Hanovia lamp) for 80 hr and the basic products isolated as usual. A total of 53% starting material was recovered along with 20% **2-(1-hydroxyethyl)quinoline** (V): mp 67–70° (*Anal.* Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.55; H, 6.30; N, 8.03); nmr no peak at 8.80 ppm for proton at the 2 position, 7.3–8.3 (m, 6, aromatic), 5.12 (q, J = 7 cps, 1, $-CH-(OH)CH_3$), 1.58 (d, J = 6 cps, 3, CH_3); mass spectrum, *m/e* (relative intensity) 173 (20), 171 (30), 158 (95), 129 (100).

Only a trace (on glpc) of a compound having the proper retention time and uv spectrum for **2-(1-hydroxyethyl)-1,2,3,4-tetrahydroquinoline** (XI) was noted.

Irradiation of 8-Methylquinoline in Ethanol. A solution of 6.44 g of 8-methylquinoline in 4.5 l. of 95% ethanol and 36 ml of concentrated HCl was irradiated (Corex, Hanovia lamp) for 80 hr and yielded 5.9 g of crude product after the usual isolation. By alumina chromatography and glpc, 42% 8-methylquinoline was recovered along with 10% of an oil, **2-ethyl-8-methylquinoline** (III) (*Anal.* Calcd for $C_{12}H_{13}N$: C, 84.21; H, 7.68; N, 8.11. Found: C, 83.99; H, 7.70; N, 8.19); nmr no peak at 8.90 ppm for the proton at the 2 position, 7.18–8.20 (m, 5, aromatic), 3.10 (q, J = 7 cps, 2, $-CH_2CH_3$), 2.82 (s, 3, aromatic CH_3), 1.40 (t, J = 7 cps, 3, $-CH_2CH_3$). Compound III formed a picrate, mp 154–156°. In addition to the above, we isolated 30% of an oil, **4-ethyl-8-methylquinoline** (IV): nmr 8.80 (d, J = 5 cps, 1, aromatic proton next to N), 7.10–8.05 (m, 5, aromatic), 3.10 (q, J = 7 cps, 2, $-CH_2CH_3$), 2.85 (s, 3, aromatic CH_3), 1.48 (t, J = 7 cps, 3, $-CH_2CH_3$). Compound IV formed a hydrochloride: mp 187–189° (*Anal.* Calcd for $C_{12}H_{14}NCl$: C, 69.40; H, 6.75; N, 6.75. Found: C, 69.28; H, 6.72; N, 6.61); ir (KBr) 1585, 1530, 1400, 1308, 1250, 1200,

(16) F. R. Stermitz and W. H. Huang, unpublished results.
(17) K. Pfordte and F. Leuschner, *Ann.*, **646**, 30 (1961).
(18) Melting points are uncorrected and were recorded on a Thomas-Hoover Unimelt apparatus. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. Instruments for general spectra were AEI MS-12 at 70 eV (mass spectra), Varian A60-A (nmr) Perkin-Elmer 237 (ir), and Cary 14 and Bausch and Lomb Spectronic 505 (uv). Emission spectra were recorded on both a 0.75-m Spex spectrometer with appropriate filters and on an Hitachi-Perkin-Elmer spectrophotofluorimeter. Nmr chemical shifts are all reported in parts per million from internal TMS in $CDCl_3$. Ir data are all in $CHCl_3$ solvent.
(19) O. Cervinka, A. Fabryova, and L. Matouchova, *Collect. Czech. Chem. Commun.*, **28**, 535 (1963).
(20) L. Reher, *Chem. Ber.*, **19**, 3000 (1886).

1168, 850, 833, 767, 509. Also, we isolated 6% **8-methyl-4-(3-quinolinyl)-8-methyl-1,4-dihydroquinoline** (X): mp 219–220° (*Anal.* Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 82.60; H, 6.55; N, 9.41). Two other attempts at achieving an acceptable analysis were not successful and although all samples had the same melting point none had identical analyses. The following data are, however, sufficient to assure the structure: ir 3300 (NH), 3000, 1600, 1475, 1280, 1100, 1030, 750, 730, 650; uv (CH_3OH) 290, 303, 316 nm; nmr 8.95 (s, 1, proton on 2 position of an 8-methylquinoline nucleus), no doublet of doublets at 8.0 (proton at position 3 of the 8-methylquinoline nucleus), 6.5–7.6 (m, 7, aromatic), 4.50 and 5.0 (two doublets of one proton each, J = 4 cps, $-CH{=}CH-$), 3.90 (s, 1, N*H*, disappeared on addition of D_2O), 2.78 (s, 3, CH_3 at position 8 of the quinoline nucleus), 2.40 (m, 1, aliphatic), 1.98 (s, 3, CH_3 at position 8 of a quinoline nucleus which is not fully aromatic in the N-hetero ring; see nmr for XII); mass spectrum, *m/e* (relative intensity) 286 (60), 285 (100), 284 (60), 144 (40), 143 (50), 142 (30), all other peaks below 20% relative intensity. The nmr spectrum could also have held for a 1,2-dihydroquinoline, but addition of 1 drop of trifluoroacetic acid to the nmr solution moved one olefinic proton downfield without affecting the aliphatic proton. This ensured the 1,4 structure as the reverse would have occurred with the 1,2 structure.

A solution of 3.5 g of 8-methylquinoline in 4.5 l. of 95% ethanol was irradiated (Corex, Hanovia lamp) for 40 hr and the usual isolation yielded 46% recovered starting material. Also obtained was 15% of an oil, **2-(1-hydroxyethyl)-8-methylquinoline** (VI) (*Anal.* Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.73; H, 7.24; N, 7.54); nmr no peak at 8.90 ppm for the proton at the 2 position, 7.20–8.30 (m, 5, aromatic), 5.10 (q, J = 7 cps, 1, $-CH(OH)CH_3$), 2.80 (s, 3, aromatic CH_3), 1.55 (d, J = 7 cps), 3, $-CH(OH)CH_3$; mass spectrum, *m/e* (relative intensity) 187 (45), 186 (75), 172 (45), 169 (75), 156 (45), 143 (100), 115 (40). Compound VI formed a *p*-nitrobenzoate of mp 235–237°. In addition, we obtained 20% of another oil, **2-(1-hydroxyethyl)-8-methyl-1,2,3,4-tetrahydroquinoline** (XII) (*Anal.* Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.07; H, 8.70; N, 7.52); uv (CH_3OH) 248, 296 nm; nmr 6.6–7.9 (m, 3, aromatic), 3.05 (s, 1, N*H*), 3.0 (q, J = 7 cps, 1, $-CH(OH)CH_3$), 2.32 (s, 3, aromatic CH_3), 1.6–2.5 (m, 4, CH_2CH_2), 1.50 (d, J = 7 cps, 3, $-CH(OH)CH_3$); mass spectrum, *m/e* (relative intensity) 191 (20), 185 (38), 172 (38), 169 (36), 146 (100), 143 (90). Compound XII formed a *p*-nitrobenzoate derivative, mp 214–216°.

Irradiation of Quinoline in 2-Propanol. Quinoline was irradiated in 2-propanol at a similar concentration to the above experiments with the Hanovia lamp and Pyrex filter, but was unreactive with or without added acid. The same experiment was repeated using quinoline in 2-propanol in a Rayonet reactor with 3000 Å lamps, but again no reaction occurred. However, in the presence of acid reaction did occur. A solution of 1.42 g of quinoline in 650 ml of 2-propanol to which 10 ml of concentrated HCl had been added was irradiated for 40 hr (Rayonet, Pyrex, 3000 Å). After the solvent had been evaporated, the residue was recrystallized from ethanol to yield 0.13 g of an unknown compound, mp 271–273°. The filtrate was evaporated and the residue was chromatographed through silica gel to yield 0.10 g of a second unknown, mp 153–155°. The uv spectra (CH_3OH) of both were similar: 242, 298 nm and 244, 294 nm, respectively. The nmr spectra of both were complex and difficult to interpret uniquely. Both the uv and nmr were consistent with structures for the unknowns as dimers of tetrahydroquinoline. They were not further investigated.

Irradiation of Quinoline in *t*-Butyl Alcohol. A solution of 0.6 g of quinoline in 300 ml of *t*-butyl alcohol was irradiated (Pyrex, Hanovia lamp) for 50 hr. Chromatography through silica gel of the residue left after evaporation of the solvent yielded 14% starting material, about 30% of what appeared to be a polymeric material, 3% 2-methylquinoline (as compared to an authentic sample[8]), and 14% of an oil **2-(2-hydroxy-2-methylpropyl)quinoline** (VIII) (*Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.67; H, 7.48; N, 7.20); ir 3450, 3000, 1600, 1480, 810, 750; nmr no peak at 8.80 for the proton at the 2 position of a quinoline, 7.20–8.25 (m, 6, aromatic), 3.12 (s, 2, $-CH_2-$ next to aromatic ring), 1.30 (s, 6, CH_3); mass spectrum, *m/e* (relative intensity) 201 (5), 143 (100), 128 (20), 115 (50). Compound VIII formed a picrate, mp 219–220° dec, and a *p*-nitrobenzoate, mp 189–191°.

Synthesis of 2-Ethylquinoline and 2-*n*-Butylquinoline. The method of Evans[21] was followed closely. In a three-necked flask fitted with a dropping funnel, mechanical stirrer, and reflux condenser (the whole being swept with dry nitrogen) were placed 8.5 g of lithium (cut into small pieces) and 200 ml of dry ether. The stirrer was started and 10 ml of a mixture of 72 g of ethyl bromide in 100 ml of dry ether was added. A vigorous reaction took place. The reaction mixture was cooled to −10° and the remainder of the ethyl bromide solution was added at an even rate over 30 min. From the dropping funnel was next slowly introduced with stirring 65 g of dry quinoline in 100 ml of dry ether over a period of 1 hr. The mixture was heated at reflux for 2 hr and then poured onto 200 g of ice. The ether layer was separated and mixed with 25 ml of nitrobenzene. The ether was removed from the solution by distillation and the residue solution was heated at reflux for 1 hr. Fractional distillation under reduced pressure yielded 45 g of 2-ethylquinoline. In a similar manner, 2-*n*-butylquinoline was quantitatively prepared. It gave a picrate of mp 161–162° (lit.[22] mp 162–163°).

Synthesis of 2-(2-Methoxyethyl)quinoline (XX). To a solution of 1.7 g of 2-(2-hydroxyethyl)quinoline in 30 ml of dry tetrahydrofuran was added slowly with stirring 0.5 g of NaH. The solution was stirred for 2 hr at room temperature and then 1.5 g of methyl iodide was added. The resulting solution was stirred an additional 3 hr and then evaporated to yield 1.45 g of a residue which was composed (by nmr and glpc analysis) of 90% 2-vinylquinoline and 10% XX. Without further purification, a solution of 0.6 g of Na in 40 ml of CH_3OH was added and the solution was heated at reflux for 3 hr. The solvent was evaporated and the residue chromatographed on silica gel to yield 0.26 g of 2-vinylquinoline and 0.65 g of 2-(2-methoxyethyl)quinoline as an oil (*Anal.* Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.77; H, 7.08; N, 7.57); ir 2920, 1600, 1650, 1430, 1110, 832, 760; nmr 7.10–8.20 (m, 6, aromatic), 3.82 (distorted t, J = 7 cps, 2, $-CH_2CH_2O-$), 3.30 (s, 3, $-OCH_3$), 3.20 (distorted t, J = 7 cps, 2, $-CH_2CH_2O-$); mass spectrum, *m/e* (relative intensity) 187 (5), 172 (100), 156 (45), 143 (42). Compound XX formed a picrate, mp 155–156°.

Irradiation of 2-*n*-Butylquinoline in Ethanol. A solution of 0.9 g of 2-*n*-butylquinoline in 600 ml of 95% ethanol, to which 8 ml of concentrated HCl was added, was irradiated (Rayonet, Pyrex) for 24 hr. By the standard isolation a basic residue was obtained which, by glpc, was composed of 80% starting material and 20% **4-ethyl-2-*n*-butylquinoline** (IX) isolated (by preparative glpc) as an oil (*Anal.* Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.48; H, 9.16; N, 6.54); nmr 7.2–8.2 (m, 5, aromatic with 4 position absorption gone), 2.85–3.35 (m, 4, two CH_2 groups next to nitrogen, both split with multiplicity undetermined because of overlapping), 1.42 (t, J = 7 cps, $-CH_2CH_3$ for 4 position ethyl group), 1.0 (t, J = 7 cps, $-CH_2CH_3$ for end of the *n*-butyl group), 2.1–1.1 (m, 4, $-CH_2CH_2-$ of *n*-butyl group); mass spectrum *m/e* (relative intensity) 213 (2), 186 (25), 171 (100), 156 (30), 154 (30), 128 (40), 115 (30).

Irradiation of 2-(2-Hydroxyethyl)quinoline. A solution of 0.86 g of 2-(2-hydroxyethyl)quinoline in 650 ml of benzene was irradiated (Rayonet, Pyrex) for 18 hr. During the irradiation, dry N_2 was bubbled through the irradiation flask and into a trap containing a solution (concentrated H_2SO_4, H_2O, ethanol) of 2,4-dinitrophenylhydrazine. After the irradiation was completed, a 62% yield of formaldehyde as the 2,4-dinitrophenylhydrazone, mp 164–165° (lit.[23] mp 166°) was isolated from the trap. The mass spectrum of the phenylhydrazone was identical with that of an authentic sample. The benzene solution was evaporated to dryness and the crude nmr showed the residue to be a mixture of 27% starting material and 73% 2-methylquinoline, identical with an authentic sample. A separate kinetic study by nmr analysis of starting material disappearance and 2-methylquinoline formation showed the reaction to be first order ($k = 2.3 \times 10^{-5}$ sec^{-1}).

Irradiation of 2-(2-Deuterioxyethyl)quinoline. A sample of the 2-hydroxyethyl compound was warmed with D_2O and evaporated to dryness. This was repeated three times and the resulting compound was shown to be completely the 2-deuterioxy compound by nmr, ir, and mass spectrum. It was then irradiated in exactly the same manner as the 2-hydroxy compound. Thus, 0.85 g in 650 ml of benzene yielded (after 18 hr irradiation) 67% 2-monodeuteriomethylquinoline. By nmr integration and mass spectrum, no 2-methylquinoline was present. The formaldehyde was again trapped as the 2,4-dinitrophenylhydrazone and this was shown by mass spec-

(21) J. C. W. Evans and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1946, p 517.

(22) H. Gilman and S. M. Spatz, *J. Amer. Chem. Soc.*, **63**, 1553 (1941).

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1965, p 320.

trum to have incorporated no deuterium. The reaction was first order ($k = 1.8 \times 10^{-5}$ sec^{-1}).

Irradiation of 2-Ethylquinoline. A solution of 0.64 g of 2-ethylquinoline in 600 ml of benzene was irradiated (Rayonet, Pyrex) for 60 hr. Starting material was quantitatively recovered.

Irradiation of 2-*n*-Butylquinoline. A solution of 1.4 g of 2-*n*-butylquinoline in 650 ml of benzene was irradiated (Rayonet, Pyrex) for 58 hr. A trap for gases was again provided, this time containing a solution of bromine in CCl_4 which was protected from room light. The benzene solution was evaporated and found to contain 55% starting material and 45% 2-methylquinoline. The trap was found to contain 1,2-dibromopropane, which was identified by nmr and mass spectrum. Sufficient oily 1,2-dibromopropane was recovered for nmr and mass spectral analysis, but not for a quantitative determination of yield. A separate kinetic study by nmr analysis of starting material disappearance and 2-methylquinoline formation showed the reaction to be first order ($k = 2.5 \times 10^{-6}$ sec^{-1}).

Irradiation of 2-(2-Methoxyethyl)quinoline. A solution of 0.54 g of 2-(2-methoxyethyl)quinoline in 450 ml of benzene was irradiated (Rayonet, Pyrex) for 24 hr. Starting material was quantitatively recovered.

Irradiation of 2-(Methoxymethyl)quinoline. A solution of 0.9 g of 2-(methoxymethyl)quinoline was irradiated (Rayonet, Pyrex) for 15 hr. Work-up in the usual manner resulted in isolation of 78% 2-methylquinoline, while formaldehyde was again isolated from the trap as the 2,4-dinitrophenylhydrazone derivative. As usual, a dark reaction test was negative. However, if heat was used in the isolation or glpc a portion of the starting material could be thermally converted to 2-methylquinoline. The presence of 2-methylquinoline in the commercial sample of the methoxymethylquinoline could well be the result of this thermal reaction.

Quantum Yield Determinations. Stock solutions of benzophenone, benzhydrol, 2-(2-hydroxyethyl)quinoline, 2-methoxymethylquinoline, and 2-*n*-butylquinoline in benzene were prepared at concentrations of 0.10, 0.40, 0.20, 0.20, and 0.20 *M*, respectively, and those of quinoline and 8-methylquinoline 0.20 *M* in ethanol containing 0.4% HCl. Quantum yields were measured in a Southern New England Ultraviolet Co. "merry-go-round" with the Hanovia Type L lamp at the center in a quartz immersion well surrounded by a quartz jacket containing a filter solution of 0.25 g of potassium chromate per liter of 0.05 *N* sodium hydroxide solution. This solution isolates the mercury band at 3130 Å. The benzophenone–benzhydrol system[24] was used for actinometry in measuring the quantum yields for 2-*n*-butylquinoline and 2-(2-hydroxyethyl)-quinoline photoeliminations and the 2-*n*-butylquinoline reaction was then used for the quantum yield determination of quinoline photoalkylation. Samples in 15 × 60 mm Pyrex test tubes were degassed through three freeze–thaw cycles to 0.005 Torr and sealed *in vacuo*. Product analyses were performed by nmr for the photoeliminations and by glpc for the photoalkylation. The mole ratio to area ratio response of the gas chromatograph was calibrated with 2-ethylquinoline and *o*-dichlorobenzene. Conversions ranged from 5 to 25% for various determinations. Since the products also absorbed light at 3130 Å, a correction[25] was made for competitive absorption. Details of our procedures are available.[26]

Results on the effect of quenchers or changes in solvent on the quantum yields were determined in a similar manner except with added quencher or with a change of solvent.

Sensitization studies on the photoalkylation reaction were not carried out since use of the standard sensitizer, benzophenone, in alcohol solvents leads to "chemical" sensitization through ketyl radicals[5e] rather than energy transfer. In addition, the high extinction coefficient of the quinolines tails into the long-wavelength absorption of benzophenone and isolation of the latter is difficult. We found, however, that a qualitative sensitization experiment could be carried out on the photoelimination using benzophenone as a sensitizer and a 0.05 *M* naphthalene in benzene solution (2 cm thickness) as a filter. The results are given in Table VI. Entry three in the table shows that the 2-*n*-butylquinoline was still absorbing a small portion of light with the filter system and reacting. However, with benzophenone present (entry two) the benzophenone absorbed the majority of the light and no reaction occurred.

Table VI. Lack of Sensitization of 2-*n*-Butylquinoline Photoelimination

Compound (4 ml of soln in benzene)	Irradiation time, hr	Results
0.05 *M* benzophenone and 0.2 *M* benzhydrol	10	All pinacol. No benzophenone left
0.1 *M* 2-*n*-butylquinoline and 0.1 *M* benzophenone	20	No reaction
0.1 *M* 2-*n*-butylquinoline	20	1.5% yield of 2-methylquinoline

(24) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, 84, 1368 (1962).

(25) P. J. Wagner and G. S. Hammond, *ibid.*, 88, 1245 (1966).

(26) C. C. Wei, Ph.D. Thesis, Colorado State University, 1969.