

Photoelimination Reactions of *N*-Heteroaromatic Compounds (I)

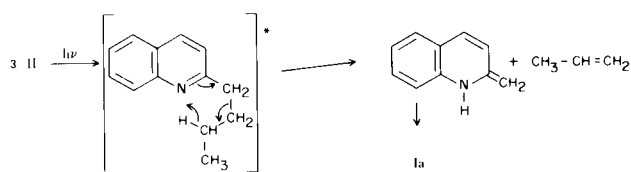
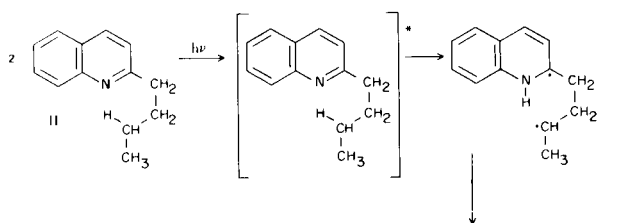
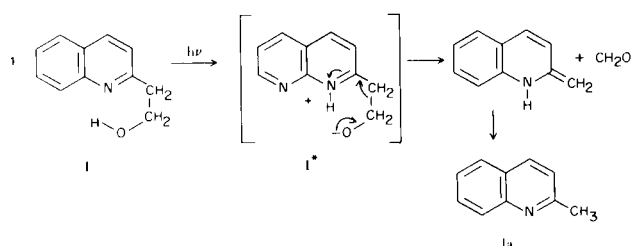
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N-Heteroaromatic compounds substituted with a side chain next to the nitrogen and bearing a hydrogen *gamma* to the ring, undergo a photoelimination reaction to yield the methyl-substituted heterocycle and an alkene (if the *gamma* hydrogen is on a side chain carbon) or an aldehyde (if the *gamma* hydrogen is on a side chain oxygen). The reaction has been shown to occur with substituted isoquinolines, phenanthridines, pyridines and pyrazines.

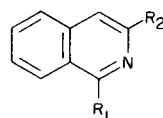
We have shown (2,3) that 2-substituted quinolines having a *gamma* hydrogen on the side chain undergo photoelimination according to Equations 1 and 2 or 3:



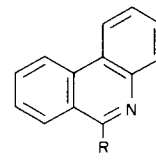
Although a mechanism similar to that of Equation 1 obtains for pyridylacetic acid photolytic decarboxylation (4), the discovery of alcohol proton transfer from I was unique. The alkene elimination of Equation 2 or 3 yielded information about the excited state reactivity of quinoline. It was, therefore, appropriate to determine whether or not these reactions were unique to quinoline or could be generalized for a variety of *N*-heteroaromatics. In the present work we report the generality of these

reactions as well as some preliminary studies related to the excited states involved. Future publications will report in detail results in each of the individual systems as these are studied in the depth necessary for the full elucidation of photochemical mechanisms.

For this study, compounds III-X were obtained and their photolyses to the corresponding methyl derivatives IIIa-IXa were studied in comparison (2,3) with the photolyses of I and II to Ia. Compounds XI-XIII were



III: R₁ = CH₂CH₂CH₂CH₃, R₂ = H
 IIIa: R₁ = CH₃, R₂ = H
 IV: R₁ = CH₂CH₂CH₂CH₃, R₂ = CH₃
 IVa: R₁ = CH₃, R₂ = CH₃



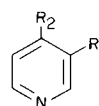
V: R = CH₂CH₂CH₂CH₃
 Va: R = CH₃



VI: R = CH₂CH₂CH₃
 VIa: R = CH₃
 VII: R = CH₂CH₂OH
 VIII: R = CH₂CH₂CH₂OH



IX: R = CH₂CH₂CH₂CH₃
 IXa: R = CH₃
 X: R = CH₂CH₂OH



XI: R₁ = H, R₂ = CH₂CH₂OH
 XII: R₁ = H, R₂ = CH₂CH₂CH₂OH
 XIII: R₁ = CH₂CH₂CH₂OH, R₂ = H

available and were also irradiated in order to determine whether only those alkyl groups which are adjacent to the ring nitrogen were susceptible to photolysis.

Results.

Irradiations of III-V and IX-X were conducted under various conditions using a Pyrex filter since these compounds all absorbed light in the 310-330 nm region. Irradiation of the pyridine derivatives was conducted in quartz since these did not have long wave length absorption. Absorption spectral data will not be reported here since they are covered well in the literature (5).

Compounds III-X did indeed photoeliminate, while XI-XIII were found to yield no photoelimination products. The reactions of III-V and IX-X were clean and gave no products other than the methyl derivatives IIIa-Va and IXa together with the side chain product alkene or formaldehyde, when conducted under degassed conditions. If the isoquinolines and phenanthridine were irradiated without degassing, a yellow polymer formed on the flask walls. This polymer absorbed light and decreased quantum yields. Freeze-thaw degassing or addition of piperylene to the non-degassed solutions eliminated the polymer formation and quantum yields of product formation were identical under these conditions. In the case of the pyridines, light absorbing intermediates occurred with any solvents containing water and, although photoelimination products were observed with VI-VIII, there was some concomitant loss of total pyridine ring containing products. The light absorbing intermediates had spectral data identical to those reported (6) for the ring-opened products of photohydration. Irradiations of the pyridines in non-polar solvents such as benzene or xylene were much cleaner and did yield photoelimination products, but in these cases the aromatic solvent of necessity was the absorber of the light and we were therefore dealing with sensitized reactions. It is also known (7) that pyridines are photoisomerized through Dewar benzene or prismane-type intermediates and these processes could clearly interfere with straight-forward photoelimination. Pyrazines also photoisomerize (8), but only with 254 nm light and hence our irradiations of IX and X encountered none of the problems associated with the pyridines.

General results of these irradiations are given in Table I. Data (2) for I and II are included for comparison. As can be seen from the Table, overall quantum yields of product formation varied considerably among the various heterocycle systems and some solvent effects were observed.

As a preliminary probe to discover what excited states might be involved in the photochemistry, some quenching studies were attempted. For the butylisoquinolines III and IV and the butylphenanthridine V, the quantum

yields of product formation were identical in freeze-thaw degassed benzene and in degassed benzene to which 0.5 M piperylene had been added and thus, no quenching was observed. As mentioned above, oxygen had an adverse effect on the photoelimination from these derivatives, but this was due to polymer formation in a photoreaction unrelated to photoelimination. This side reaction could be quenched with piperylene, but the elimination was not

TABLE I

Photoelimination Reactions of Substituted *N*-Heteroaromatics

Compound	Solvent	Product	Quantum Yield (a)
Quinolines, Isoquinolines, Phenanthridine:			
I	benzene	Ia	0.10
II	benzene	Ia	0.015
I	<i>t</i> -butyl alcohol	Ia	0.029
II	<i>t</i> -butyl alcohol	Ia	0.021
III	benzene	IIIa	0.004
IV	benzene	IVa	0.002
V	benzene	Va	0.008
Pyridines:			
VI	acetonitrile	VIa	0.002
VII	acetonitrile	VIa	0.003
VIII	acetonitrile	VIa	0.008
VII	<i>m</i> -xylene	VIa	0.016
VIII	<i>m</i> -xylene	VIa	0.004
VII	water	(b)	0.000 (b)
Pyrazines:			
IX	benzene	IXa	0.004
X	benzene	IXa	0.068
X	<i>t</i> -butyl alcohol	IXa	0.003
IX	cyclohexane	(c)	0.017 (d)
X	cyclohexane	(c)	0.17 (d)

(a) Quantum yields of the product Ia, IIIa, etc. (b) No VIa was formed. (c) No IXa was formed, but photoreduction and cyclohexylation occurred. (d) Quantum yield of disappearance of pyrazine IX or X.

quenchable. For the pyridines VI-VIII, the quenching studies had a different result. Addition of 0.02 M piperylene caused an approximate 15-30% decrease in product formation quantum yield depending upon structure of the pyridine derivative and conditions of irradiation. Further increases in piperylene concentration caused a continuing, but much more gradual decrease in the quantum yield. Pyridine photoeliminations were also

apparently quenched by oxygen. Stern-Volmer plots will be given in detail at a later date, but the present results indicate the possibility of the occurrence of two quenching processes. The effects of oxygen and piperylene on the pyrazine (IX and X) photoeliminations were also studied. Photoelimination from X in benzene was unaffected by oxygen or piperylene. Oxygen completely negated the photoreactivity of IX in benzene, while piperylene apparently reacted with IX photochemically and no photoelimination was observed.

The excited states of *N*-heteroaromatics are known (9) to be strongly affected by solvent character and hence, to complement the photochemical studies, emission spectra in two solvents (one polar, one non-polar) were also conducted. Although quantum yields for each of these emissions need to be determined before these results are meaningful in detail, some general trends and qualitative information can be elicited from the data given in Table II. The isoquinolines III and IV and the phenanthridine V behaved similarly to what was expected based upon previous work (9) on the unsubstituted parent systems.

TABLE II

Emission Spectra of Substituted *N*-Heteroaromatics

Compound	Solvent	Fluorescence	Phosphorescence
Quinolines, Isoquinolines, Phenanthridine:			
I	EPA (a)	strong	strong
I	eMP (b)	very weak (c)	very weak (c)
II	EPA	strong	weak
II	3MP	strong	strong
III	EPA	strong	none
III	3MP	strong	weak
IV	EPA	strong	none
IV	3MP	strong	weak
V	EPA	strong	weak
V	3MP	strong	strong
Pyrazines:			
IX	EPA	none	strong
IX	3MP	none	strong
IX	EPA + HCl	none	none
X	EPA	none	strong
X	3MP	none	very weak

(a) Ether, isopentane, ethanol (a polar solvent). (b) 3-Methylpentane (a non-polar solvent). (c) Between the very weak normal emissions was a strong, broad emission characterized (3) as coming from the zwitterion I*.

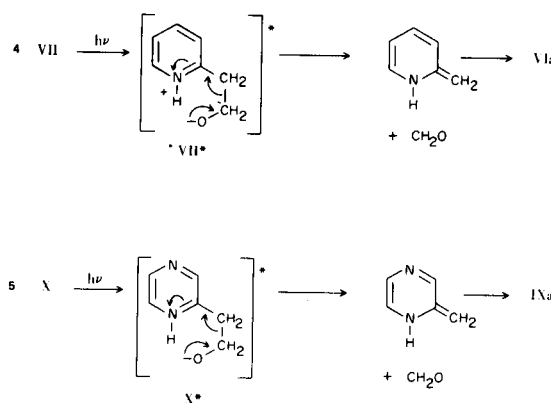
The EPA solvent presumably ties up the non-bonded electron pair on the heterocycle nitrogen with a resulting enhancement of fluorescence over phosphorescence. The physical reasons for this have been discussed (9). One strong anomaly is observed in the case of the pyrazines. Thus, pyrazine IX showed typical strong phosphorescence in both solvents with no detectable fluorescence in our system. Pyrazine X, on the other hand, although giving a normal intense pyrazine phosphorescence in the polar solvent, showed only extremely weak phosphorescence in the non-polar solvent. Because of our presumption (see below) that this behavior of X in a non-polar solvent was the result of an intramolecular proton transfer in the excited state, we also examined whether or not the pyrazinium ion was an emitter by dissolving IX in EPA and bubbling HCl through the solution prior to examination for emission. This treatment completely quenched all emission from IX.

Emission from pyridines has been observed only rarely and in the case of very special substituted derivatives (7,10). We did attempt to observe emission from VI-VIII, but were unsuccessful.

Discussion.

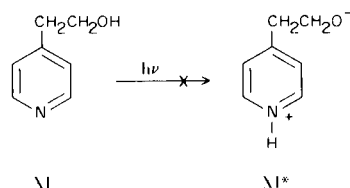
It is evident from the above results that the photoelimination of *N*-heteroaromatic side chains according to Equations 1 and 2 or 3 is a general reaction of these heterocycles and is not restricted to the quinoline series. Some of the details of reactivity will now be examined.

First, the data on VII and X indicate that the photoeliminations probably proceed as in Equations 4 and 5:

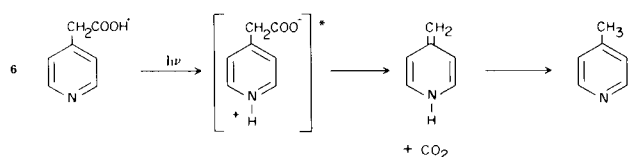


The data of Table I shows that the photoelimination of VII does not occur in water and that the photoelimination quantum yields are 0.002 and 0.016 in acetonitrile and *m*-xylene, respectively. This very large increase in quantum yield in the non-polar as compared to polar solvent is similar to that observed with the corresponding quinoline (2,3). This behavior, particularly taken together with the emission spectral data on I in a non-polar solvent (see I in

3-MP of Table II), was taken (3) as evidence for the excited state proton transfer mechanism of Equation 1. Hence, it is likely that Equation 4 obtains for the similar pyridine derivative. Unfortunately, since pyridine VII was not an emitter, the confirmatory evidence of a changed emission spectrum in the non-polar solvent was not available. It is also to be noted that we are dealing, in *m*-xylene solvent, with a sensitized reaction since the *m*-xylene absorbed nearly all the light. Attempts to conduct the photoelimination reaction of VII in non-polar, but non-absorbing solvents such as cyclohexane were not successful due to solubility problems. It may at first seem incongruous that a zwitterion excited intermediate, such as I* or VII*, is proposed to be involved in a non-polar solvent, but not in a polar one. It seems likely that in the polar solvent, intramolecular hydrogen bonding of the side chain alcoholic proton to the nitrogen is not possible, while in the non-polar solvent such an intramolecular hydrogen bond does occur and that this is necessary for the mechanism of Equation 1 or 4 to hold. This idea is strengthened by the inertness of pyridine XI to photoelimination. If there is no need for an intramolecular hydrogen bond, then XI should give XI*, which surely should eliminate as well as VII*. Since no elimination



product is observed, this means XI* was not formed. It is instructive to compare the present result with our work (4) on pyridylacetic acid photodecarboxylation. In that case, Equation 6 was found to hold. It is, therefore, suggested that if the proton to be transferred in the



excited state is sufficiently acidic (e.g. from a carboxyl group) the position of that proton relative to the ring nitrogen may be unimportant, while a less acidic proton (e.g. from an alcohol group) must perhaps be within hydrogen-bonding distance of the nitrogen. These suggestions are currently being explored in a series of compounds designed to more exactly establish the structural relationships necessary for excited state proton transfer.

The situation in regard to the pyrazine derivative X is a little more clearly defined and Equation 5 is more

firmly established. Thus, the photoelimination quantum yield for X in benzene is some 20 times greater than in the polar solvent *t*-butyl alcohol. In addition, the emission spectral data of Table II shows that the normally intense phosphorescence of X is nearly completely quenched if determined in a non-polar solvent. This emission behavior is unique to X as it is not observed with IX. This suggests that proton transfer may be occurring in the excited state to give X* and that this is a non-emitter. Seemingly contradictory to this was the report (11) that pyrazine hydrochloride did indeed emit in EPA solvent. We discovered, however, that if IX or X were dissolved in EPA and gaseous hydrogen chloride was bubbled through the solution prior to determination of the emission, then the emission was completely quenched. Pyrazine is a very weak base and it is possible that Goodman's result (11) occurred because pyrazine hydrochloride was partially deprotonated in EPA whereas our hydrogen chloride saturated solution was sufficient to assure that no free pyrazine base was present. At any rate, our result shows that the pyrazinium ion does not emit. The weak phosphorescence which does occur with X in the non-polar solvent is perhaps a measure of the amount of excited X which has not undergone proton transfer.

It should be mentioned that the intermediate case of proton transfer from a phenol hydrogen to the excited nitrogen of a heterocycle has been reported in a number of instances (12).

We can now turn to the cases of III-VI, VIII, and IX where the *gamma* hydrogen is on the carbon rather than oxygen. The photoelimination does occur, but with a lower quantum yield than in the just discussed cases. Details of the elimination process have not as yet been worked out and Equations 2 or 3 (or both) could still hold. The diradical mechanism of Equation 2 would provide a nice rationale for the lowered quantum yield because of return to starting material from the diradical intermediate. This idea is strengthened by the fact that IX and X both photoreduced in cyclohexane with a higher quantum yield than they underwent photoelimination (Table I). The photoelimination in the cases of the isoquinolines III and IV and the phenanthridine V was not quenchable with piperylene. This is usually taken for evidence of singlet state reactivity since non-quenchable triplets appear to be rare intermediates. Singlet reactivity would be in accordance with our view (2) of the quinoline case and that of others in cases such as acriding photo-reduction (13). It has been shown (13) that acridine photoreduction very likely proceeds from the n, π^* singlet rather than from the fluorescing π, π^* singlet. Since we have so far only measured overall quantum yields of product formation, we do not yet have the necessary data to discuss this question in detail as related to our com-

pounds. However, it is to be noted that isoquinoline and phenanthridine are considered to have π, π^* lowest singlet states in non-polar solvents as compared with quinoline's n, π^* lowest singlet. This should also hold for our derivatives III-V since they are strong fluorescent emitters. Intersystem crossing quantum yields for isoquinolines have been reported to be lower than for quinolines and, if one assumes that non-radiative processes and purely chemical factors on the elimination steps of Equations 2 or 3 are comparable for isoquinolines and quinolines, then a positive correlation between relative fluorescence ability and quantum yield of elimination might have been expected if the reacting singlet was also the fluorescing singlet. Such is clearly not the case and one can, therefore, hypothesize that the isoquinolines (and probably the phenanthridine) are photoeliminating from the non-fluorescent n, π^* S_2 state. This suggestion must remain a hypothesis until data on the reactivity of the excited states themselves (rather than mere overall quantum yields) are available.

In contrast to the case with pyrazine X, the results with pyrazine IX are not unequivocal. The low quantum yield photoelimination was quenched with oxygen and no IXa was formed. This was not a case of by-product reaction with oxygen as was apparently true with the isoquinolines and phenanthridine, but appeared to be a true physical quenching. Unfortunately, piperylene reacted photochemically with IX and hence, this did not provide a true measure of its normal triplet quenching ability. We had hoped for more clear-cut results since pyrazines have been well studied spectroscopically (11) and have a lowest excited singlet of n, π^* configuration (87 kcal) which is energetically well-removed from the π, π^* singlet (112 kcal/mole). Both the spectroscopy and photochemistry of quinolines are complicated (2) by the energetic nearness of the singlet n, π^* and π, π^* states. On the other hand, this result would indicate the foundering of the naive hope that photochemistry of various *N*-heterocycles would be simply related to the configuration of the lowest excited states and not a complex function of the entire array of photophysical processes.

In the case of the pyridines VI-VIII some quenching of the photoelimination by piperylene did occur and the first results indicate that the Stern-Volmer plot will have two slopes: a relatively steep one at low piperylene concentration and a relatively flat but perceptible one at high piperylene concentration. Such behavior tentatively suggests that we may be dealing with both singlet and triplet reactivity in the pyridines. However, more detailed work will be necessary here since, as mentioned in the Results section, the pyridine photoeliminations were accompanied by other photoreactions. Definitive statements regarding the pyridine excited states must await considerable further study.

EXPERIMENTAL

Materials.

Quinoline, isoquinoline, 3-methylisoquinoline, phenanthridine, piperylene, and 2-methylpyrazine were purchased from Aldrich Chemical Co. and purified by recrystallization or distillation. The 2-*n*-propylpyridine (VI), 2-(2-hydroxyethyl)pyridine (VII), 2-(3-hydroxypropyl)pyridine (VIII), 4-(2-hydroxyethyl)pyridine (XI), and 4-(3-hydroxypropyl)pyridine (XII) were purchased from K and K Laboratories, Inc., and redistilled before use. The 2-*n*-butylpyrazine (IX) was a gift from Eli Lilly and Co. The preparations of the other substituted *N*-heterocycles are described below. Solvents used for irradiations were reagent grade and redistilled.

1-*N*-Butylisoquinoline (III).

In a three-neck, round bottom flask fitted with a dropping funnel, mechanical stirrer, and reflux condenser was placed *n*-butyllithium (42 ml. of 90% solution in hydrocarbon solvent). This solution was cooled to -10° and a solution of isoquinoline (15 g.) in ethyl ether (40 ml.) was added dropwise with stirring. After addition was complete, the mixture was allowed to warm to room temperature, was left overnight, and finally poured onto ice. The ether layer was separated, dried over magnesium sulfate and evaporated. Nitrobenzene (10 ml.) was added and the solution was heated at reflux for three hours. When the solution was cool, benzene and an excess of 1 *N* hydrochloric acid were added. The acidic layer was separated and the benzene layer extracted with 1 *N* acid solution again. The acidic solutions were combined, washed three times with benzene, and made basic with aq. NaOH. The basic solution was extracted with benzene, the benzene was dried over magnesium sulfate and evaporated. Distillation of the residue yielded 12 g. (56%) of III (14), which was pure by nmr and gc and whose mass spectrum was identical to that reported (14).

1-*n*-Butyl-3-methylisoquinoline (IV) and 6-*n*-Butylphenanthridine (V).

Identical procedures to that listed for the butylisoquinoline yielded 1-*n*-butyl-3-methylisoquinoline (b.p. $80-83^\circ$ at 0.01 mm).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.45; H, 9.05; N, 7.50 and 6-*n*-butylphenanthridine (15). Nmr, uv, and mass spectral analyses assured the correctness of the structures, which are also the only ones expected from the preparation procedure.

2-(2-Hydroxyethyl)pyrazine (X).

The method of Kitchen and Hanson (16) was used. Thus, 75 g. of 2-methylpyrazine and 5 g. of paraformaldehyde were heated at 165° for 8.5 hours in a sealed tube. The resulting liquid was distilled to remove the methylpyrazine (b.p. $130-141^\circ$) and then with an air condenser to remove unreacted paraformaldehyde. The pot residue was then purified by kugelrohr distillation at 90° and 0.5 mm pressure to yield X (3% based on 2-methylpyrazine), lit. b.p. $128-129^\circ$ at 10 mm. Nmr: δ 3.08 (2H, t, $ArCH_2$); 4.05 (2H, t, $HOCH_2$); 4.51 (1H, s, OH); 8.5 (3H, m, ArH).

Isolation and Identification of Photolysis Products.

Each successful photolysis yielded a methyl-substituted heterocycle and a side chain fragment alkene or formaldehyde. The formaldehyde was trapped as the 2,4-DNP derivative and the alkenes as the dibromides according to procedures described (2,4) earlier. The same references (2,4) described isolation and identification of 2-methylpyridine and 2-methylquinoline. The other methylsubstituted heterocycles were isolated similarly and com-

pared with standard samples.

In the experiments involving irradiation of pyrazines in cyclohexane solutions, gc analysis showed the presence of several peaks at much higher retention volumes than 2-methylpyrazine. These fractions were collected together and the nmr showed extensive absorption in the 0.8-2.0 ppm from TMS region. This was indicative of cyclohexylated products and this result was confirmed by a mass spectrum analysis of the combined high retention volume fraction which showed peaks indicative of di- and monocyclohexylated products. No attempt was made to separate and characterize the individual products.

Irradiation Procedures and Quantum Yield Determinations.

Irradiations were conducted in a Rayonet reactor with a "merry-go-round" attachment using 15 ml. Vycor tubes and 2537 Å lamps for the pyridines and in the same reactor using Pyrex tubes and 3130 Å lamps for the other heterocycles. Analyses for 2-methylpyridine and quantum yield determinations for the pyridine photoeliminations were as described previously (4).

For the pyrazine work, all sample solutions were 0.020 M pyrazine in the specified solvents which were redistilled reagent grade. Five ml. samples were placed in Pyrex tubes and sealed directly or degassed through three freeze-thaw cycles to 0.005 mm Hg and sealed *in vacuo*. For each type of irradiation, one sample tube was wrapped in aluminum foil and subjected to identical irradiation conditions and analysis as described below. In all cases, this "dark" experiment showed no reaction. The progress of reaction was determined by direct gas chromatography [8% carbowax 1540 on Chromosorb P (AW-DMCS) 80/100 mesh at 110°] using *o*-dichlorobenzene as an internal standard (for photoeliminations) or by measuring the decrease in the pyrazine 320 mm band (photoreduction). The benzophenone-benzhydrol actinometer of Moore and Ketchum (17) was used for primary quantum yield determination. The photoelimination of X in benzene (quantum yield = 0.068) was then used as a secondary standard. Quantum yields reported in Table I were measured at from 5% to 9% conversion.

Irradiations of the isoquinolines and pheanthridine were at 0.02 M concentrations and the solvents used were redistilled reagent grade. For quantum yield determinations, 15 ml. Pyrex tubes were employed and these were sealed directly, flushed with nitrogen prior to sealing, or degassed by the freeze-thaw method prior to sealing. Analysis for quantum yield was by glc determination of 2-methylquinoline, 1-methylisoquinoline, or 6-methylphenanthridine using an 8 ft. x 1/8 in. column of 3% SE-52 on Chrom G at 140-150° and dimethylphthalate as a standard. Conversions were from 4-22%. "Dark" reactions were shown not to occur. The high conversion figure represented cases where III, IV and V were irradiated simultaneously for the same length of time and V reacted to 22% conversion. Separate experiments were also run with V and II together to a lower conversion. At the lowest conversions, quantum yields were similar for each derivative (II, III, IV, and V) no matter what the conditions of sample preparation: sealed in air, sealed after nitrogen flush, sealed after degassing, or sealed by any of these methods but in the presence of 0.5 M piperylene. Quantum yields determined at high conversions were lower for the sealed-in-air or nitrogen-flushed samples than for the freeze-thaw degassed samples; but even at high conversions, the presence of piperylene could counteract this effect. Thus, for example, a 24-hour irradiation yielded

49% 1-methylquinoline from nitrogen-flushed, piperylene containing III, 45% from degassed, non-piperylene III solution, and 34% from a nitrogen-flushed solution of III without piperylene. Examination of the walls of tubes from these extended conversions showed, in the case of each derivative, deposition of a yellow polymer-like film if the sample had not been degassed or did not contain piperylene in conjunction with the other methods of preparation.

Emission Spectra.

Emission spectra were routinely recorded on a Perkin-Elmer Model MPF-2A fluorescence spectrophotometer. For higher resolution and sensitivity, the light from a 200-W xenon lamp was passed through a 0.25-m Jarrel-Ash monochromator for excitation while passing the emission through a 0.75-m Spex 1700-11 monochromator. The detection system consisted of an EMI 6256 S photomultiplier tube, a Keithley Model 414 picoammeter and a Moseley 7100 B strip chart recorder. EPA (5:5:2 by volume ether, isopentane, and ethanol) was used as obtained from Hartman-Leddont Company. 3-Methylpentane (Phillips Petroleum pure grade) was passed through a 90-cm column of alumina saturated with silver nitrate and checked for purity by absorption spectroscopy.

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