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THE PHOTOCHEMICAL HYDROLYSIS OF N-SUBSTITUTED IMINES[1]

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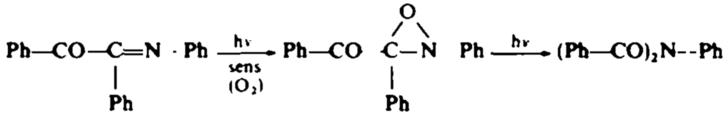
Abstract— The benzophenone-sensitized photolysis of benzaldehyde anil in anhydrous alcoholic solvents in an atmosphere of oxygen leads mainly to the formation of benzaldehyde and aniline. The incorporation of oxygen has been shown not to involve direct attack on the substrate but rather the formation of water and hydrogen peroxide. Each of these reagents can effect the photo-sensitized hydrolysis of the anil, but the contribution by water is minor compared to that by hydrogen peroxide. Other minor products formed in the reaction are 1,2,N,N'-tetraphenylethylenediamine and 2-phenylquinoline. Other imines are shown to undergo similar photochemical hydrolysis.

INTRODUCTION

THE photochemical behavior of compounds containing the C=N bond as the central structural feature has been the subject of a number of investigations.[3] In a previous paper[4] it was reported that the monoanil of benzil (I) undergoes a photochemical oxidation to an oxazirane, (II) which in turn rearranges to N, N-dibenzoylaniline (III). Subsequent photochemical processes gave the reaction such complexity that benzaldehyde anil (IV) was selected as a simpler model for the study of the photochemical oxidation. The sensitized photolysis of this anil in the presence of oxygen, however, led mainly to the formation of benzaldehyde and aniline as primary products, so that in effect a photochemical hydrolysis had taken place. We present here the results of our studies aimed at elucidating the nature of this hydrolytic process.



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RESULTS AND DISCUSSION

When a solution of benzaldehyde anil in ethanol or isopropanol is left to stand in the dark for 18 hr in an atmosphere of oxygen, no hydrolysis is observed, irrespective of the presence or absence of benzophenone as sensitizer. The subsequent irradiation of such a mixture leads to the disappearance of the substrate with the formation of benzaldehyde and aniline only when the sensitizer is present. The latter is recovered unchanged after termination of the reaction. The quantitative data of these experiments are listed in Table 1.*

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* In most of the reactions employing ethanol as solvent, quantities of 2-phenylquinoline were obtained in yields varying from 9–14%, depending on the reaction conditions.[5]

The yields of aniline obtained in this work are not comparable to those of benzaldehyde since aniline undergoes a second photochemical reaction,[6] leading largely to polymeric materials. This process is retarded when the irradiation is conducted at -70°, at which time the ratio aniline/benzaldehyde increases. The hydrolysis of an anil being a reversible process, the contribution to recovered substrate made by the recombination of the products must be ruled out. This was done without difficulty by the demonstration that a solution of benzaldehyde and aniline in concentrations comparable to those used in our work contained no detectable anil after sensitized irradiations. The results described above show conclusively that the hydrolysis of benzaldehyde anil is an irreversible photosensitzed process and that contributions of dark reactions are negligible.

To distinguish between extraneously supplied oxygen gas and the solvent as the source of oxygen in the product, the reaction was studied also under atmospheres of commercial nitrogen and argon. Commerical nitrogen is well known to contain appreciable amounts of oxygen,[*] and not unexpectedly benzaldehyde was again observed as a product, but whereas formerly the yield of aldehyde was equivalent to the amount of substrate converted, in nitrogen much more substrate disappeared than could be accounted for by the (photochemically stable) benzaldehyde (Table 1). From the latter reactions other products could be isolated, such as 1,2,N,N'-tetraphenylethylenediamine. Interestingly the rate of substrate conversion is greater in nitrogen than in oxygen, a fact that is in agreement with the triplet quenching power of oxygen, which reduces the efficiency of the photosensitized reaction. To circumvent the difficulties inherent in the removal of all traces of oxygen from nitrogen, we selected argon gas[*] to provide an atmosphere free of oxygen. Negligible amounts of benzaldehyde formed during irradiations in an atmosphere of this gas, even though substrate disappearance was considerable, as may be seen from Table 1. Besides large amounts of polymeric material, considerable amounts of 1,2,N,N'-tetraphenylethylenediamine could again be isolated. The need for oxygen gas in the photochemical hydrolysis is thus demonstrated.

TABLE 1. BENZOPHENONE-SENSITIZED IRRADIATIONS OF BENZALDEHYDE ANIL (1 g) IN ETHANOL (400 ml)

Light	Gas	Time (hr)	Benzophenone	% Anil reacted	% Benzaldehyde[a]
–	O_2	18	–	0	0
–	O_2	18	100 mg	0	0
+	O_2	12	–	0	0
+	O_2	12	100 mg	17	16
+	N_2	12	100 mg	63	14
+	Ar	12	100 mg	59	2

[a] The yields of benzaldehyde reported in all Tables are determined by GLC (±2%) and are based on the total amount of anil present at the start of the irradiation. All numbers are based on reproducible duplicate runs.

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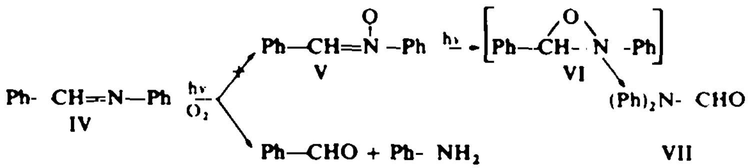
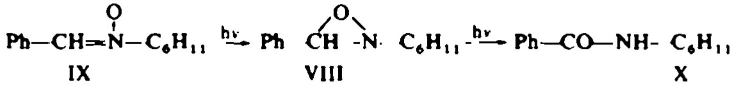
[*] High Purity grade nitrogen (Linde) contains no less than 0·01 % O_2 according to the manufacturer. Calculations have shown this amount to be more than sufficient to account for all oxidation products formed; Argon gas (99·996 %) contains less than 10 ppm O_2, which is approx 0·001 %.

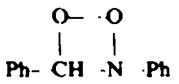
It was attractive to postulate the formation of a nitrone (V), or its corresponding oxazirane (VI), as an intermediate leading to hydrolysis products. Accordingly α,N-diphenylnitrone was irradiated in ethanol in the presence of benzophenone, but the only product obtained was N,N-diphenylformamide (VII), analogous to the type of rearrangement reported in our earlier work[4] and by Splitter and Calvin.[7]



Since the oxazirane of benzaldehyde anil is not available by synthesis, due to its instability, we studied the photochemical behavior of the analogous oxazirane (VIII) and nitrone (IX) of benzaldehyde N-cyclohexylimine. This imine undergoes photochemical hydrolysis to benzaldehyde and cyclohexylamine in a fashion identical with that of the anil. The nitrone of this imine, upon irradiation, was converted quantitatively to the oxazirane, while the latter, on prolonged irradiation, yielded only N-cyclohexylbenzamide (X). These results indicate that if hydrolysis were to occur via attack of oxygen on substrate or vice versa, no intermediate oxazirane or nitrone is involved.



A second alternative is the formation of the cyclic intermediate (XI) shown below.



XI

However, such an intermediate may be expected to undergo fission to benzaldehyde and nitrosobenzene. The latter material was never observed among the products, and when irradiated alone it was converted almost quantitatively to nitrobenzene, which was similarly absent from the products, notwithstanding its photochemical stability under the conditions employed in our work. It became thus evident that oxygen was likely to be involved in an indirect fashion, and the role of water and hydrogen peroxide in the reaction were subsequently investigated.

The effect of the presence of water on the reaction is shown in Table 2. The data clearly demonstrate that although a dark reaction occurs in 95% aqueous ethanol, the rate of hydrolysis is greatly accelerated upon irradiation, but only in the presence of a sensitizer (benzophenone). It thus appears that in addition to usual hydrolysis, taking place presumably via the well-known polar mechanism, a photochemical hydrolysis occurs, in which excited substrate attacks water:

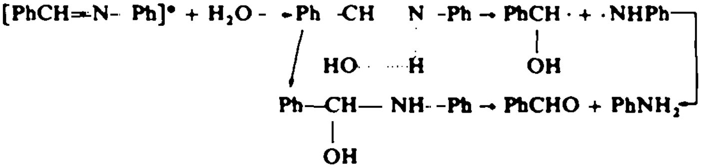


Table 2. Benzophenone-sensitized irradiations of benzaldehyde anil (1 g) in 95% aqueous ethanol (400 ml)

Light	Gas	Time (hr)	Benzophenone	% Anil reacted	% Benzaldehyde
–	O_2	12	–	15	14
–	O_2	12	100 mg	13	12
+	O_2	12	—	16	15
+	O_2	12	100 mg	80	74

There is no good evidence that favors one of the terminal steps over the other; pinacol formation can be expected to occur much slower than hydrogen loss, while 1,2-diphenylhydrazine is photochemically labile.

Since Karl Fisher titrations of ethanol employed in our work showed it to contain less than 0·01 % of water, the possibility that water is generated during the irradiation was investigated. Indeed, when substrate was added to a mixture of solvent and sensitizer that had been subjected to prior irradiation, the rate of subsequent photochemical hydrolysis was considerably greater than was the case when no prior irradiation had been performed. This effect was absent when pre-irradiations were conducted without sensitizer (Table 3, runs 1–3).[*] The amount of water generated during these pre-irradiations was determined again by Karl Fisher titrations. It became evident,

Table 3. The effect of pre-irradiation of and addition of water to solvent-sensitizer mixtures (400 ml) on the rate of subsequent photochemical hydrolysis of benzaldehyde anil (1 g)[a]

Run number	Sensitizer	Time (hr)	Solvent	Anil present	Light	% Anil reacted	% Benzaldehyde
1	+	11	ethanol	–	–		
	+	12	ethanol	+	+	19	18
2	–	12	ethanol	–	+		
	+	12	ethanol	+	+	17	16
3	+	11	ethanol	–	+		
	+	12	ethanol	+	+	76	46
4	+	11	i-propanol	–	–		
	+	12	i-propanol	+	+	8	8
5	+	11	i-propanol	–	+		
	+	12	i-propanol	+	+	37	34
6	+	7	i-propanol	–	+		
	+	1	i-propanol	+	+	36[b]	
7	+[c]	1	i-propanol	+	+	2	

[a] All irradiations in this series were carried out under oxygen; benzophenone is the sensitizer employed.

[b] Amount of water formed, by titration: 620 mg ± 12 mg.

[c] In addition, 650 mg of water was added to the solution.

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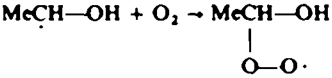
[*] Comparable results were obtained using acetophenone and fluorenone as sensitizers.

however, that water was not the *main* agent responsible for the photochemical hydrolysis, by the demonstration that reaction mixtures containing solvent, sensitizer, substrate, and an amount of water precisely equal to that formed during pre-irradiations, underwent hydrolysis at rates minimal compared to those in which actual pre-irradiation had taken place (Table 3, runs 6 and 7).

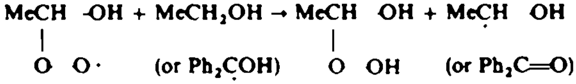
The possibility that photochemical oxidation of the solvent (ethanol) to acetic acid merely caused a rapid acid-catalyzed hydrolysis to occur was eliminated by showing the same enhancement in isopropanol (Table 3, runs 4 and 5) which is unlikely to form acidic oxidation products.

The formation of water can be accounted for by a mechanistic sequence such as shown below, featuring hydrogen abstraction from the solvent by excited sensitizer as the first step (Eq. 1) followed by attack of oxygen on the solvent radical (Eq. 2). The resulting hydroxyhydroperoxide radical may then accept hydrogen from either solvent or sensitizer, leading to regeneration of the latter (Eq. 3). The homolytic fission of hydroxyhydroperoxides, occurring either as a dark or a light reaction can be followed by a disproportionation yielding water (Eq. 4). Further examples of termination reactions are shown in Eq. 5, 6 and 7.

$$\mathrm{Ph_2C{=}O^{\bullet} + EtOH \rightarrow Ph_2\underset{\cdot}{C}{-}OH + Me\underset{\cdot}{C}HOH} \qquad (1)$$

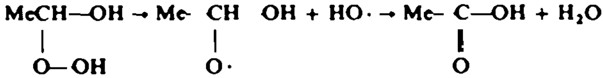


$$\mathrm{Me\underset{\cdot}{C}H{-}OH + O_2 \rightarrow Me\underset{\substack{|\\ O{-}O\cdot}}{C}H{-}OH} \qquad (2)$$

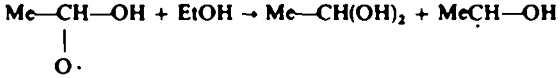


$$\mathrm{Me\underset{\substack{|\\ O{-}O\cdot}}{C}H{-}OH + MeCH_2OH \rightarrow Me\underset{\substack{|\\ O{-}OH}}{C}H{-}OH + Me\underset{\cdot}{C}H{-}OH} \qquad (3)$$

$$\mathrm{(or\ Ph_2\underset{\cdot}{C}OH) \qquad (or\ Ph_2C{=}O)}$$



$$\mathrm{Me\underset{\substack{|\\ O{-}OH}}{C}H{-}OH \rightarrow Me{-}\underset{\substack{|\\ O\cdot}}{C}H{-}OH + HO\cdot \rightarrow Me{-}\underset{\substack{\|\\ O}}{C}{-}OH + H_2O} \qquad (4)$$



$$\mathrm{Me{-}\underset{\substack{|\\ O\cdot}}{C}H{-}OH + EtOH \rightarrow Me{-}CH(OH)_2 + Me\underset{\cdot}{C}H{-}OH} \qquad (5)$$

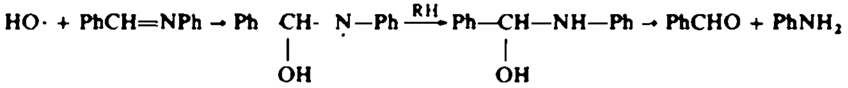
$$\mathrm{HO\cdot + Ph_2\underset{\cdot}{C}{-}OH \rightarrow H_2O + Ph_2C{=}O} \qquad (6)$$

$$\mathrm{2HO\cdot \rightarrow H_2O_2} \qquad (7)$$

Because the formation of water is irrevocably connected to that of hydroperoxides and hydrogen peroxide (Eq. 7) the effect of the latter was investigated next. Pitts *et al.*[8] have suggested that hydrogen peroxide is the major peroxide formed upon irradiation of benzophenone in isopropanol and consequently we have limited our studies to hydrogen peroxide itself.

Hydrogen peroxide is capable of effecting some dark reaction with benzaldehyde anil. The rate of this reaction is slightly enhanced upon irradiation in the absence of a sensitizer (Table 4), but noticeably so when a sensitizer is present. The slight enhancement without a sensitizer is likely to be due to an increase in the concentration of hydroxyl radicals:

$$H_2O_2 \xrightarrow{h\nu} 2HO\cdot$$



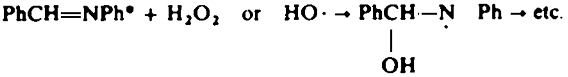
$$HO\cdot + PhCH{=}NPh \rightarrow Ph\,\underset{OH}{\underset{|}{CH}}{-}\underset{\cdot}{N}{-}Ph \xrightarrow{RH} Ph{-}\underset{OH}{\underset{|}{CH}}{-}NH{-}Ph \rightarrow PhCHO + PhNH_2$$

TABLE 4. HYDROLYSIS OF BENZALDEHYDE ANIL (1 g) IN THE PRESENCE OF 3·2 ml OF 30% H_2O_2 IN ETHANOL (400 ml)*

Time (hr)	Gas	Light	Sensitizer	% Anil reacted	% Benzaldehyde
1	O_2	–	–	3	3
1	O_2	+	–	7	7
1	O_2	+	benzophenone (100 mg)	18	17

* Similar figures are obtained when N_2 is used instead of O_2.

The observed rate-increasing effect of hydrogen peroxide upon *sensitized* photolysis can be accommodated by the fact that the excited (triplet) substrate has a greater diradical character than its ground state, increasing its reactivity towards hydroxyl radicals as well as undissociated hydrogen peroxide:



$$PhCH{=}NPh^{*} + H_2O_2 \text{ or } HO\cdot \rightarrow PhCH{-}\underset{\cdot}{N}\;Ph \rightarrow \text{etc.}$$
$$\text{(OH on CH)}$$

Titration of pre-irradiated solvent-sensitizer mixtures demonstrated the presence of 1·77 g of H_2O_2 after 1 hr; the amount of anil that hydrolyzes after 1 hr of irradiation in this mixture (36%) is almost the same as that obtained (40%) after 1 hr irradiation in a solution to which 1·77 g of H_2O_2 had been added. The substitution of an equal amount of water led only to 6% of hydrolysis in the same period of time.

CONCLUSION

From the data presented above it is evident that the photochemical hydrolysis of benzaldehyde anil occurs as a result of the photosensitized formation of water and hydrogen peroxide, each of which is capable of effecting a photosensitized hydrolysis. The slow disappearance of sensitizer during pre-irradiations, not observed during irradiations in the presence of substrate, is likely to be due to the formation of benzpinacol and mixed pinacols, a process too slow to be capable of competing with hydrogen abstraction by $Ph{-}\underset{OH}{\underset{|}{CH}}{-}\underset{\cdot}{N}{-}Ph$. An entirely analogous hydrolysis may be observed with benzophenone anil, benzaldehyde N-cyclohexylimine and benzil monoanil. It is obvious that further quantitization of the several processes involved necessitates quantum yield studies.

EXPERIMENTAL

General. Irradiations were carried out in a cylindrical Pyrex vessel of 400 ml capacity. An appropriate gas was introduced through a fritted disc in the bottom of the vessel in order to agitate the soln; the flow rate was 5-10 ml/min. The lamp used was a 450 watt Hanovia Hg arc which was surrounded by a Pyrex filter sleeve to eliminate light below 2800 Å. The lamp and filter were placed in a quartz water jacket which was immersed in the soln to be irradiated. The water jacket was cleaned frequently with HCl to remove deposits left by the cooling water.

The progress of the reaction was followed by GLC and/or UV spectroscopy.

M.ps and b.ps were uncorrected. The gas chromatograph used was an F & M Model 700 with Model 240 Temperature Programmer and flame ionization detector. The columns were stainless steel, 6 in × $\frac{1}{4}$ in, containing 10% liquid phase on 60–80 mesh Diatoport W. The two liquid phases used were Carbowax 20M and Silicone Gum Rubber GE SE-52.

In determining yields by use of external standards, a standard soln of each product was used.

Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Galbraith Laboratories, Inc., Knoxville, Tennessee.

Absolute EtOH and isopropanol were dried by refluxing 900 ml of the solvent for 2 hr over 4 g Mg turnings in the presence of a few drops CCl_4. The solvent was then distilled.

Karl Fischer titrations. The Karl Fischer reagent had a water equivalence of 5·0 mg/ml. An aliquot (usually 50 ml) of the soln to be determined was transferred by a flame-dried pipet to an Erlenmeyer flask which had been dried in an oven at 120° and cooled in a dessicator. The soln was titrated rapidly with Karl Fischer reagent to the appearance of a permanent red-brown color. The accuracy was 0·2 ml reagent, equiv to 1·5 mg water per 50 ml.

Peroxide determinations. An aliquot (5–10 ml) of the soln to be determined was added with agitation to a soln of 2 g NaI in 50 ml water containing 3 ml AcOH. The liberated I_2 was titrated with 0·100N $Na_2S_2O_3$.

Benzaldehyde anil. The procedure of Bigelow and Eatough[9] was followed except that abs EtOH was used rather than 95% EtOH.

α,N-Diphenylnitrone. A mixture of 10·9 g (0·1 mole) phenylhydroxylamine,[10] 10·6 g (0·1 mole) benzaldehyde, and 15 g anhyd $MgSO_4$ in 300 ml benzene was allowed to stand in the dark at room temp for 20 hr. After filtration of the $MgSO_4$ the soln was concentrated under reduced press. to a volume of 100 ml, and petrol was added to precipitate the product. The crude material was recrystallized from MeOH–water to yield 15 g (76%) of product, m.p. 114–115°. (Reported[11] m.p. 116°).

Benzaldehyde N-cyclohexylimine. A mixture of 53 g (0·5 mole) benzaldehyde and 49·5 g (0·5 mole) cyclohexylamine was dissolved in 200 ml ether. The soln was washed with three 20 ml portions 2% AcOH and three 20 ml portions 10% $NaHCO_3$ aq, dried over Na_2SO_4 and evaporated. Distillation of the residue under reduced press. yielded 60·7 g (65%) product, b.p. 166–169°/30 mm (Reported[12] b.p. 280°).

Peracetic acid. To 100 ml $CHCl_3$ were added 7·5 ml 30% H_2O_2 and two drops of conc H_2SO_4. Ac_2O (41 g) was added dropwise over a period of 30 min while the mixture was stirred and cooled in ice. Stirring was continued for an additional 30 min in the ice bath and 16 hr at room temp, after which the soln was added with shaking to 30 g P_2O_5 in 100 ml $CHCl_3$ at 0°. After 15 min the clear soln was filtered and the titer determined iodometrically; the anhyd peracid soln (2 ml) was added with agitation to a soln of 2 g NaI in 50 ml water containing 5 ml AcOH and 5 ml $CHCl_3$. The liberated I_2 was titrated with 0·100N $Na_2S_2O_3$. The volume required was 11·2 ml, equiv to 0·213 g/ml peracetic acid soln.

α-phenyl N-cyclohexylnitrone. 2-Cyclohexyl-3-phenyloxazirane (1 g) was heated slowly to 190°. After cooling, the mixture was triturated with two 15 ml portions of boiling hexane. The clear soln upon cooling yielded the crystalline product, m.p. 81–83°. (Reported[13] m.p. 82–83°).

N-Cyclohexylbenzamide. N-Cyclohexylbenzamide was prepared by the Schotten-Baumann reaction, as described by Cheronis and Entrikin.[14]

2-Phenylquinoline. One gram of 2-phenylquinoline-4-carboxylic acid (Aldrich Chemical Co.) was heated in an open tube at 250° for 1 hr. Upon cooling, the residue was extracted with 10 ml boiling hexane to yield 300 mg (34%) 2-phenylquinoline, m.p. 81-83°. (Reported[15] m.p. 81–82°). Picrate m.p. 189 191°). (Reported[16] m.p. 187–188°).

Benzil dianil. A mixture of 10·5 g (0·05 mole) benzil and 10 g (0·11 mole) aniline was heated with 2 drops conc HCl at 130–140° for 2 hr in an atmosphere of CO_2. After cooling the mixture to room temp, 25 ml 95% EtOH was added. The crude product was filtered and recrystallized from 95% EtOH to yield 20·8 g (58%) yellow benzil dianil, m.p. 139–140°. (Reported[17] m.p. 141–142°).

1,2,N,N'-Tetraphenylethylenediamine. A soln of 500 mg benzil dianil in 40 ml anhyd ether was added dropwise with magnetic stirring to a slurry of 2·5 g LAH in 25 ml ether. The mixture was refluxed for 3 hr and left to stand for 10 hr with continual stirring. The excess hydride was decomposed by the dropwise addition of water. The ether soln was separated, dried over Na_2SO_4, and evaporated under a stream of N_2. To the residue was added 10 ml of a 1:1 mixture of ether and EtOH. The product was filtered and recrystallized from a benzene–EtOH mixture to yield 185 mg (37%) of the diamine, m.p. 164–167°. (Found: C, 85·64; H, 6·61; N, 7·70. Calc. for $C_{26}H_{24}N_2$: C, 85·67; H, 6·64; N, 7·69%). IR: ν_{max} ($CHCl_3$) 3400 w, 3000 m, 2880 w, 1600 s, 1500 s. UV: λ_{max} (CH_3CN) 251 mμ (ϵ = 29,500) and 295 mμ (ϵ = 3900). NMR ($CDCl_3$): 2·6–3·6 τ (multiplet, 20H), 5·04 τ (doublet, J = 6 c/s, 2H), 5·5 τ (broad, 2H).

Irradiation of benzaldehyde anil. A soln of 1·00 g benzaldehyde anil and 100 mg benzophenone in 400 ml abs EtOH was irradiated in a stream of O_2 for 12 hr during which time 43% of the anil reacted, as determined by GLC. The product yields, determined by GLC using external standards, were 79% benzaldehyde, 8% aniline, and 2% 2-phenylquinoline.

A soln of 590 mg benzaldehyde in 200 ml abs EtOH was mixed with a soln of 506 mg aniline in the same solvent. GLC showed that the formation of anil was negligible. The benzophenone-sensitizer irradiation of this mixture led only to the disappearance of aniline, and no anil was formed.

Pre-irradiation of the sensitizer. A soln of 100 mg benzophenone in 400 ml abs EtOH was allowed to stand in the dark for 11 hr while passing O_2 through the soln. Benzaldehyde anil (1·00 g) was then added and the soln was irradiated for 12 hr. GLC showed that 19% of the anil had reacted, with formation of 18% benzaldehyde.

Another soln of 100 mg benzophenone in 400 ml abs EtOH was irradiated for 11 hr. UV spectroscopy showed that essentially all of the sensitizer had disappeared. To this soln was added 1·00 g benzaldehyde and 100 mg benzophenone and the soln was irradiated for 12 hr, during which time 76% of the anil reacted with formation of 46% benzaldehyde.

Similar series of reactions were carried out using equiv amounts of acetophenone and 9-fluorenone as sensitizers and isopropanol as solvent.

Irradiation in the presence of peroxide. H_2O_2 aq (3·2 ml) was added to 400 ml abs EtOH. The amount of the peroxide present, as determined by titration, was 0·98 g. To this soln was added 1·00 g benzaldehyde anil. After standing for 1 hr in the dark in a stream of O_2, GLC showed that 3% of the anil had hydrolyzed. A similar soln prepared in the same manner was irradiated for 1 hr, whereupon 7% hydrolysis occurred. A third soln containing 100 mg benzophenone in addition to the peroxide and anil was irradiated for 1 hr, during which time 18% of the anil reacted with formation of 17% benzaldehyde and 12% aniline.

An identical series of irradiations was carried out in a N_2 atmosphere.

Isolation of 2-phenylquinoline. A soln of 2·00 g benzaldehyde anil and 200 mg benzophenone in 400 ml abs EtOH was irradiated in a stream of O_2 for 95 hr. The solvent was distilled under reduced press and the residue was dissolved in ether and extracted with four 10 ml portions of 1N HCl. The aqueous extracts were made basic with 25% NaOH aq and extracted with ether. The organic extracts were combined, dried over Na_2SO_4, and evaporated in a stream of N_2. The residue was dissolved in a mixture of benzene and petrol and chromatographed on a column of 15 g alumina. Elution with 1:1 benzene–petrol yielded a solid which was recrystallized from petrol. The pure product melting at 81–83° was identical (m.p. and picate) with an authentic sample of 2-phenylquinoline prepared as described above.

Isolation of 1,2,N,N'-tetraphenylethylenediamine. A soln of 1·00 g benzaldehyde anil and 100 mg benzophenone in 400 ml abs EtOH was irradiated for 20 hr in an atmosphere of argon. GLC showed that no benzaldehyde, aniline, or 2-phenylquinoline had been formed. The solvent was distilled under N_2 at reduced press, dissolved in 1:9 benzene–petrol and chromatographed on 88 g alumina. Elution with 1:9 benzene–petrol yielded a solid which was recrystallized from a benzene–MeOH mixture. The pure product, m.p. 165–167° was identical (m.m.p. and spectra) to an authentic sample of 1,2,N,N'-tetraphenylethylenediamine.

Irradiation of benzaldehyde N-cyclohexylimine. A soln of 2·00 g benzaldenyde N-cyclohexylimine and 200 mg benzophenone in 400 ml abs EtOH was irradiated in a stream of O_2 for 6 hr. At the end of this period, the imine had disappeared completely yielding 34% benzaldehyde and 29% cyclohexylamine, determined by GLC.

Irradiation of α,N-diphenylnitrone. A soln of 500 mg α,N-diphenyl-nitrone and 50 mg benzophenone in 400 ml abs EtOH was irradiated for 45 min. GLC showed that 2-cyclohexyl-3-phenyloxazirane was formed in 93% yield.

Irradiation of α-phenyl-N-cyclohexylnitrone. A soln of 500 mg α-phenyl-N-cyclohexylnitrone in 400 ml abs EtOH was irradiated under O_2 for 1 hr. GLC showed that 2-cyclohexyl-3-phenyloxazirane was formed in 89% yield.

Irradiation of nitrosobenzene. A soln of 500 mg nitrosobenzene and 50 mg benzophenone in 400 ml abs EtOH was irradiated under O_2 for 4 hr. The only product detected by GLC was nitrobenzene in 95% yield.

Irradiation of aniline. A soln of 2·00 g aniline and 200 mg benzophenone in 400 ml abs EtOH was irradiated under O_2. After 66 hr, one half of the substrate had reacted, but no products could be detected by GLC.

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