J. Org. Chem. 1983, 48, 2281–2285

tensities for the unhydrated, monohydrated, and dihydrated forms at apparent equilibrium.

Peaks for the monohydrate reached half their final heights at approximately 30 min in D_2O and 5 min in H_2O. Peaks for the dihydrate reached half their final heights after approximately 110 min in D_2O and 80 min in H_2O. After 1100 minutes in D_2O, the observed equilibrium constant for formation of the monohydrate (K_{eq} = (monohydrate)/(free pteridine)) was 0.30 ± 0.03, and the observed equilibrium constant for formation of the dihydrate (K_{eq} = (pteridine dihydrate)/(free pteridine)) was 0.22 ± 0.02. After 800 min in H_2O, the observed equilibrium constant for formation of the monohydrate was 0.29 ± 0.03, and the observed equilibrium constant for formation of the dihydrate was 0.23 ± 0.02. Thus the solvent isotope effects (K_{H_2O}/K_{D_2O}) were 0.97 ± 0.14 for the monohydrate and 1.0 ± 0.13 for the dihydrate. This value for formation of the monohydrate is consistent with the data reported by Pocker et al.,[5] who used UV spectrophotometry to study the kinetics and equilibria of formation of pteridine monohydrate. These investigators reported infinity point drifts in their runs, for which appropriate correction was made.

These near-unit solvent isotope effects on formation of both the mono- and the dihydrate are of special interest in view of the reported isotopic fractionation factors for *gem*-diol protons. These values averaged 1.25 per proton.[4] If the two hemiaminal protons in pteridine monohydrate were to exhibit this fractionation factor, the expected solvent isotope effect (K_{H_2O}/K_{D_2O}) would be 0.64. The four hemiaminal protons in pteridine dihydrate would result in an expected solvent isotope effect (K_{H_2O}/K_{D_2O}) of 0.41. Evidently the force constants acting on the hemiaminal protons are substantially different from those acting on *gem*-diol protons.

Experimental Section

Pteridine was prepared as described by Albert et al.[7] and was twice sublimed before use. The material gave no detectable NMR signals other than those characteristic of unhydrated pteridine[6] when spectra where taken in $CDCl_3$ or in D_2O before hydrate signals appeared. All spectra were measured with a Varian EM390 NMR spectrometer with a probe temperature of 34.2 °C. A H_2O solution of sodium 3-(trimethylsilyl)propanesulfonate in H_2O was used as an external shift standard.

Buffer solutions in H_2O and D_2O of the nonnucleophilic buffer *N*-(2-hydroxyethyl)piperazine-*N′*-2-ethanesulfonic acid (Hepes) (Sigma Chemical Co.) were prepared from a single solid mixture of the acidic and basic (Na^+ salt) components of the buffer in order to preserve the same buffer ratio. Equilibrium constants were calculated from the integrated peak intensities by using the assignments indicated in Figure 1. The standard error observed in measurement of the integrals within a run was approximately 7% while interrun error was 10%. A Model 501 Orion pH meter was used to measure pH or pD values (pD = meter reading + 0.4).[8] The pH or pD varied by about 0.05 unit during the course of each run when Hepes buffer, 0.17 M, was used.

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Registry No. a, 91-18-9; b (L = D), 85649-64-5; c (L = D), 14130-91-7; deuterium oxide, 7789-20-0; deuterium, 7782-39-0.

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Photochemistry of Diaryl Ketones: A New Photocyclization Reaction

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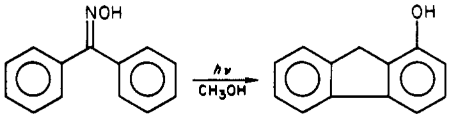
The photochemistry of oximes of aldehyde and ketones has been extensively studied. The reactions these systems undergo in the excited states are of many types,[1-6] e.g., syn–anti isomerization, photo-Beckmann rearrangement, regeneration of the parent ketone through an oxaziridine intermediate, and the formation of the iminyl radicals. However, our experience with benzophenone oxime[7] has been entirely different, and herein we report the results of an investigation on the photochemistry of diaryl keto oximes.

Results and Discussion

Benzophenone oxime in methanol (0.02 M) on photolysis (quartz filter) underwent a series of reactions involving regiospecific hydroxylation, cyclization of proximate phenyl groups, and Wolff–Kishner reduction, leading to 1-hydroxyfluorene in 34% yield. Its acetyl derivative showed mp 90 °C lit.[8] mp 90–91.5 °C). Structure 1 was further supported by NMR and mass spectra and elemental analysis. This is the first such reported reaction in the study of oximes. At this stage the following questions arose: (1) Is the photocyclization that of benzophenone oxime or is some other photoproduct undergoing a secondary reaction? (2) What is the effect of varying the solvent system on the reaction course? (3) What possible mechanisms for hydroxylation and what is the source of the hydrogens at C-9 of the fluorene nucleus? (4) What is the effect of oxygen and is the reaction caused by some impurities present in the solvents?



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When benzophenone oxime along with benzophenone (0.1 M) was photolyzed under exactly the same conditions (except Pyrex filter), the yield of 1-hydroxyfluorene increased to 64% (see Table I). When other oximes, 2-methyl-, 3-methyl-, and 4-methylbenzophenone oximes, were photolyzed separately with benzophenone under the same conditions, the major product (55–75%) obtained in all those cases was 1-hydroxyfluorene and not the methyl-substituted fluorene.

Photolysis of a solution containing both benzophenone oxime and 4-methylbenzophenone gave a mixture of methyl-substituted hydroxyfluorenes 2 and 3(15%) along with traces of 1-hydroxyfluorene. However, when a solu-

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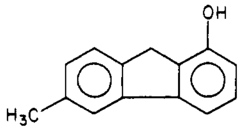

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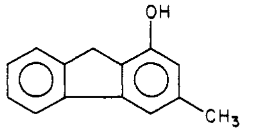

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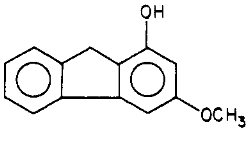
tion of 4-methylbenzophenone and its oxime were photolyzed together, only a mixture of methyl-substituted fluorenes 2 and 3 was obtained (32%) and there was no trace of 1-hydroxyfluorene. The structure determination and analysis of the mixture were carried out mass spectrometrically; details are given subsequently.

Benzophenone or substituted benzophenones when irradiated alone under the same conditions gave benzpinacols only and no cyclized product. Benzopenone on irradiation with hydroxylamine hydrochloride under the same conditions gave only 5% of 1-hydroxyfluorene, the major product being benzophenone oxime.

It is pertinent to point out here that hydroxyfluorenes are formed only if the oxime moiety is present and that benzophenone oxime alone is completely inert when irradiated by using a Pyrex filter but gives hydroxyfluorene when irradiated by using a quartz filter. This is understood as benzophenone oxime has absorption maxima at 254 nm only, and under quartz-filtered irradiation can give benzophenone through an oxaziridine intermediate,[9] thus providing the mixture of benzophenone and benzophenone oxime necessary for production of 1-hydroxyfluorene. So it would appear that it is excited benzophenone that reacts with ground-state benzophenone oxime to give the fluorene derivative. To verify this, acetone oxime was substituted for benzophenone oxime and photolyzed with benzophenone in methanol (0.1 M). Again a high yield of 1-hydroxylfluorene (60%) was obtained, showing thereby that any oxime could be used to photocyclize benzophenone systems. Similarly, when 4-methoxybenzophenone was photolyzed with acetone oxime under exactly the same conditions, a mixture of (16%) methoxy-substituted fluorenes, 4 and 5, was obtained.



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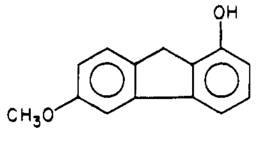

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The UV–vis spectrum of the ketone and oxime mixtures was studied and was found to be a simple sum of the spectra of the components (oximes are transpareent in this region). This eliminated the possibility that some complex or other product was being photolyzed.

Irradiation of fluorenone oxime under the same conditions did not give any 1-hydroxyfluorene, indicating thereby that the cyclization of the proximate phenyl rings is not the first step in the sequence of the reactions leading to 1-hydroxyfluorene.

Solvent Effects. The irradiation of benzophenone oxime in dry acetonitrile yields only benzophenone (90%) as the product; however, in acetonitrile (H_2O 0.1%) 2% of 1-hydroxyfluorene was obtained. In absolute methanol the yield of hydroxyfluorene was decreased to 20% from the 55–75% obtained in ordinary methanol. The only conclusion that can be derived from this is that hydroxylic solvents are required for this reaction. The presence of water may aid in stabilizing the excited species, and one reaction step may involve hydrogen abstraction. Similar results have also been noticed in 2-propanol 2-propanol–water systems. Padwa et al.[10,11] photolyzed Schiff bases with benzophenone in alcohol and did not report the isolation of any 1-hydroxyfluorene, an observation duplicated by us. This shows that the reaction is a reaction of the oxime system and not of the carbon–nitrogen double bond in general.

Table I. Irradiation[a] of Diaryl Keto Oximes

no.	diaryl ketone	oxime	solvent	cyclized product, % (amount, g)
1		BPO	methanol	34 (0.340)
2		BPO	methanol	42 (0.420)[b]
3		BPO	2-propanol	10 (0.100)
4		BPO	2-propanol–5% H_2O	40 (4.00)
5		BPO	acetonitrile	2 (0.020)
6		BPO	dry acetonitrile	0
7	BP	BPO	methanol	64 (0.640)
8	4-Me-BP	BPO	methanol	15 (0.120)[c]
9	BP	2-Me-BPO	methanol	55 (0.550)
10	BP	3-Me-BPO	methanol	52 (0.520)
11	BP	4-Me-BPO	methanol	75 (0.750)
12	4-Me-BP	4-Me-BPO	methanol	32 (0.300)[c]
13	BP	BPO	absolute methanol	20 (0.200)
14	BP	BPO	2-propanol	22 (0.220)
15	BP	BPO	2-propanol–5% H_2O	55 (0.550)
16	BP	AO	methanol	60 (1.7)
17	4-Me-BP	AO	methanol	32 (0.725)[c]
18	4-Meo-BP	AO	methanol	16 (0.335)[d]

[a] Irradiation in all experiments was carried for 12 h, and 0.02 M oxime solution was taken irrespective of the oxime; the % yield is based on the amount of starting oxime taken. BP, BPO, and AO stand for benzophenone, benzophenone oxime, and acetone oxime, respectively. No other photoproduct of any consequence was isolated. A quartz filter was used when oxime was irradiated alone, while a Pyrex filter was used when diaryl ketone and oxime were photolyzed together. [b] Nitrogen was bubbled throughout the irradiation. [c] Mixture of 3-methyl- and 6-methylhydroxyfluorene. [d] Mixture of 3-methoxy- and 6-methoxyhydroxyfluorene.

Some experiments were carried out also in spectrograde methanol, it was found that this reaction is definitely not due to the presence of any impurity in the solvent. When nitrogen was bubbled throughout the irradiation of benzophenone oxime solution under the same conditions, there was a slight increase in the yield of 1-hydroxyfluorene from 34% to 42%.

Isotopic and Mass Spectral Studies. Benzophenone-d_5 was prepared by Friedel–Crafts reaction of benzoyl chloride with benzene-d_6 by using aluminium chloride and with carbon disulfide as the solvent. The structure of benzophenone-d_5 was confirmed by NMR and mass spectral studies, where peaks at m/z 187, 110, 105, 82, and 77 were observed. The peaks at m/z 110, 105, 82, and 77 can be attributed to deuteration if only one of the rings of benzophenone is deuterated.

Benzophenone-d_5 oxime was photolyzed in methanol under the same conditions as ordinary benzophenone oxime, where 1-hydroxyfluorene was obtained in about 38% yield. Comparison of the mass spectra of ordinary 1-hydroxyfluorene and 1-hydroxyfluorene from the photolysis of benzophenone-d_5 oxime showed that the former had peaks at m/z 105 and 77 and the later peaks at m/z

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(9) T. Oine and T. Mukai, *Tetrahedron Lett.*, Eds., 157 (1959).

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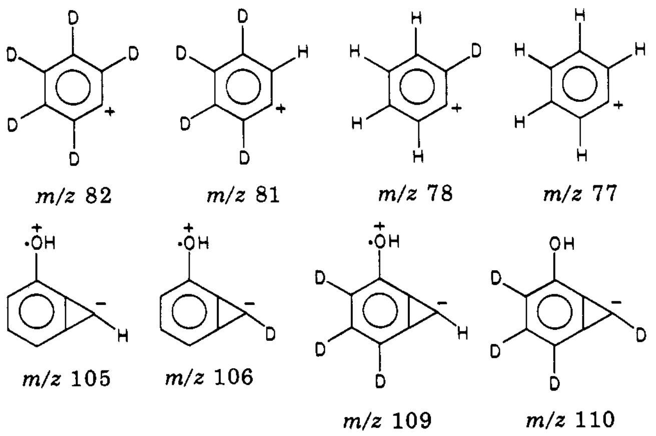
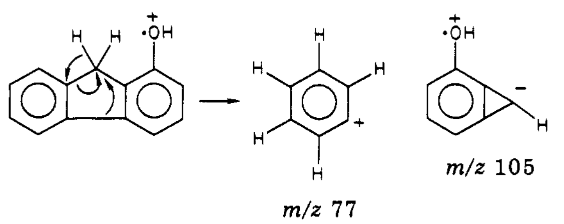
Chart I

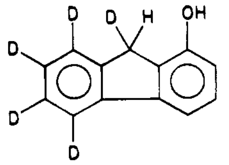


110, 109, 106, 105, 82, 81, 78, and 77 in addition to the M + 1 peaks at m/z 183 and 188 characteristic of a phenol.[12] This mass spectral fragmentation is explained as follows:



Similarly the peaks m/z 110, 109, 106, 105, 82, 81, 78, and 77 for the hydroxyfluorene obtained on photolysis of benzophenone-d_5 oxime can be explained by the ions in Chart I, in accordance with the fragmentation shown above.

The appearance of ions m/z 82, 81, 78, and 77 supports the hypothesis also supported by NMR spectrometry that there is one hydrogen and one deuterium and that the 1-hydroxyfluorene obtained from the photolysis of benzophenone-d_5 oxime is a mixture of at least two hydroxyfluorenes, **6** and **7**, and may also contain **8**, which cannot be distinguished mass spectroscopically. The peak at m/z 188 (100%) refers to structure **6**, and a peak m/z 18% abundance to structure **7**, as well as possibly to **8**.



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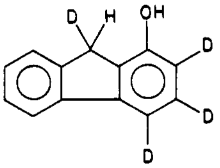

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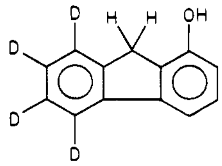

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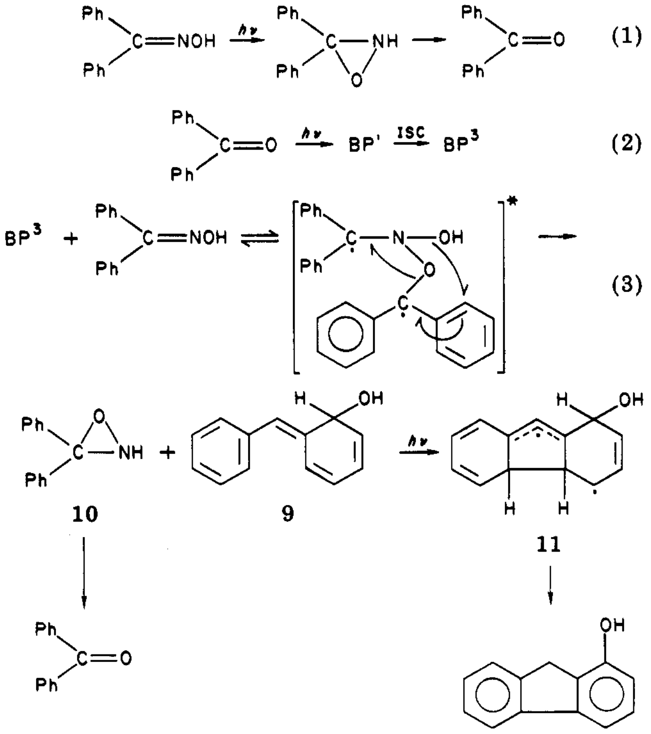
Similarly, the structures of methyl- and methoxy-substituted (**2**–**5**) 1-hydroxyfluorenes have also been confirmed on the basis of two possible ions that would be formed in mass spectral fragmentation. The positional assignments of the methyl and methoxyl groups is based on the assumption that there is no deep-seated rearrangement in the aromatic rings.

Mechanism. Saltial et al.,[13,14] Lewis and Hoyle,[15] and Yang et al.[16-18] have shown that in some of their systems exciplex formation is solvent dependent and that in these cases exciplex formation is reversible, maximum in case of alcohols and insignificant in case of acetonitrile.

Because diaryl ketoximes and acetone oxime are transparent, because benzophenone is the only absorbing species during irradiation (Pyrex filter), and because both the oxime moiety and ketone are necessary for the photocyclization, it is suggested that n–π* triplet benzophenone forms an exciplex with the ground state of the oxime. The amount of 1-hydroxyfluorene formed in different solvents (dry acetonitrile < acetonitrile < absolute methanol < methanol) is an indication of the extent of exciplex formation, which is in line with the work cited already. Such an exciplex can collapse to give intermediates **9** and **10** or **10** and **11** directly after hydrogen abstraction from the solvent in both pathways.



Decay of an exciplex to ground-state intermediate has also been suggested by Turro et al.[19] for the photoreaction of biacetyl with alkenes. The oxaziridines formed from oximes are known to decompose under photolysis to give the parent ketone and nitrene,[9] i.e., the path that intermediate **10** will follow to give parent benzophenone. The intermediate **9** can cyclize to give structure **11** followed by a 1,3 hydrogen shift to C-9 from the ring systems and aromatization to give 1-hydroxyfluorene. Such a 1,3 shift is supported by the mass spectral studies, which showed that 1-hydroxyfluorene obtained from the photolysis of benzophenone-d_5 oxime has one deuterium at C-9, the other being hydrogen abstracted from the solvent.

Another pathway through which intermediate **11** (along with **10**) could be directly formed from the exciplex would

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(12) M. Budzikiewics, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compound"; Holdon–Day, San Francisco, 1964.

(13) J. Saltiel and D. E. Townsend, *J. Am. Chem. Soc.*, **95**, 6140 (1973).

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(15) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **97**, 5950 (1975).

(16) N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, **94**, 1405 (1972).

(17) N. C. Yang, J. Libman, L. Barett, M. H. Hui, and R. L. Loeschen, *J. Am. Chem. Soc.*, **94**, 1406 (1972).

(18) N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, **94**, 9226 (1972).

(19) N. J. Turro, K. Shima, C. A. Chung, C. Tanielian, and S. Kanfer, *Tetrahedron Lett.*, 2775 (1980).

involve cleavage of the ·>C–O bond to give a transient carbene, followed by synchronous hydroxylation and cyclization during the collapse. Cyclization of a carbene to a fluorene would be in line with the work of Turro et al.[20] who have recently shown that diphenyl diazomethane when photolyzed gives fluorene and tetraphenylethylene via diphenylcarbene. In our case intermediate **9** would be more prone to undergo cyclization (as one of the rings is olefinic after hydroxylation) to give **11**, leading to 1-hydroxyfluorene.

When irradiation of benzophenone oxime was carried in CH_3OD, no incorporation of deuterium was noted mass spectroscopically in the 1-hydroxyfluorene isolated.

The great decrease in the yield of hydroxyfluorene in the case of the methyl- and methoxy-substituted system arises from the decrease in electrophilicity of the carbonyl oxygen in the triplet state of benzophenone ($n-\pi^*$ transition) caused by the effect of methyl or methoxy groups. This is in line with the quantum yield of photoreduction of benzophenone, which is 2, and that of 4-methylbenzophenone, which is 0.5, in alcohol, where transition involved is also the $n-\pi^*$ triplet.[21,22]

Experimental Section

Melting points are uncorrected and were taken in an open sulfuric acid bath. Silica gel G grade was used for making thin-layer chromatographic plates (of thickness 0.5 nm) that were used for following the course of the reaction and also for comparative study with authentic samples. Photolysis mixtures were usually separated by column chromatography for which neutral alumina was used. The NMR spectra were recorded on a Varian A-60 and EM 390 spectrometers in deuteriochloroform. Mass spectra were done on a Hewlett-Packard 5985 BMS unit using a 70-eV direct insertion probe. The photocell used was of immersion type provied with water a circulation arrangement for cooling.

Benzophenone oxime was prepared by the known procedure of Arthur Lachman:[23] mp 141–142 °C (lit.[8] mp 144 °C, 140 °C.

Irradiation of Benzophenone Oxime. Benzophenone oxime (0.02 M) in 220 mL of methanol was irradiated for 12 h with a 125-W Philips medium-pressure lamp using a quartz filter. The solvent was removed by distillation at low pressure, leaving a viscous mass that was chromatographed on an alumina column. The column was eluted with petroleum ether, benzene–petroleum ether (1:1), benzene and solvent ether. The petroleum ether fraction gave benzophenone (13–15%). The benzene–petroleum ether fraction gave the starting oxime (40%); solvent ether eluent after workup and recrystalization from benzene–petroleum ether (40:60) gave a cottony white solid (34%): mp 120 °C, (lit.[8] mp 119.5–120 °C) identified as 1-hydroxyfluorene (**1**); NMR δ 3.3 (s, 1 H), 4.22 (d, 2 H, J = 6 Hz), 7.5 (m, 7 H), addition of D_2O, the doublet at 4.22 collapses to a singlet and the singlet at 3.3 disappears; mass spectrum, m/z 183, 105, 77.

1-Acetoxyfluorene was prepared by heating with acetic anhydride and then pouring onto crushed ice. The white solid obtained was crystallized from petroleum ether: mp 91 °C (lit.[8] mp 90–91.5 °C).

However, benzophenone oxime in 300 mL of methanol on irradiation for 12 h using Pyrex-filtered light gave, on evaporation of methanol, the starting material quantitatively.

On irradiation of benzophenone oxime in methanol while nitrogen was being bubbled through the irradiation, the yield of 1-hydroxyfluorene obtained was 42% instead of 34%.

Benzophenone oxime under exactly the same conditions of irradiation in 2-propanol, 2-propanol–5% H_2O, acetonitrile, and dry acetonitrile using the same workup gave 10%, 40%, 2%, and 0% 1-hydroxyluorene, respectively.

Irradiation of Benzophenone Oxime with Benzophenone. Benzophenone oxime (0.02 M) and benzophenone (0.01 M) in 300 mL of methanol was irradiated for 12 h using a Pyrex filter under the same conditions as in the previous experiment. After partial removal of the methanol, benzpinacol (mp 185–186 °C (lit.[8] mp 185–186 °C) separated and was filtered off. Column chromatography of the filtrate yielded benzophenone (30%) from the petroleum ether fraction. Benzene–petroleum ether and benzene fractions gave the starting oxime (30%) and ether fractions gave 64% of 1-hydroxyfluorene: mp 120 °C.

Irradiation of benzophenone oxime and benzophenone under the same conditions, using absolute methanol, 2-propanol and 2-propanol–5% H_2O as solvents and using the same workup gave 20%, 22% and 55% of 1-hydroxyfluorene, respectively.

Irradiation of 2-Methylbenzophenone Oxime and Benzophenone in Methanol. 2-Methylbenzophenone oxime (0.02 M) and benzophenone (0.1 M) in 300 mL of methanol was irradiated for 12 h by using a Pyrex filter (conditions same as in previous experiment). It was worked up exactly in the same manner as in the case of Pyrex-filtered irradiation of benzophenone oxime and benzophenone. 1-Hydroxyfluorene (55% mp 120 °C) was isolated, in addition to some starting oxime and benzpinacol, as explained in the general procedure.

Irradiation of 3-Methylbenzophenone Oxime and Benzophenone in Methanol. A solution of 3-methylbenzophenone oxime (0.02 M) and benzophenone (0.1 M) in 300 mL of methanol was irradiated for 12 h and worked up exactly as in the previous case, and 1-hydroxyfluorene 52% was obtained.

Irradiation of 4-Methylbenzophenone Oxime and Benzophenone in Methanol. Solution of 4-methylbenzophenone oxime (0.02 M) and benzophenone (0.01 M) in 300 mL of methanol was irradiated for 12 h and worked up in the same manner as previously, the 1-hydroxyfluorene obtained being 75%. The oxime obtained (mp 153 °C) from the benzene–petroleum ether (1:1) fraction was found to be an isomer of the starting oxime.

Irradiation of Benzophenone in Methanol. Benzophenone (0.1 M) in 300 mL of methanol on irradiation for 12 h using Pyrex-filtered light, on evaporation of the solvent gave benzpinacol (70%) and starting benzophenone only.

Preparation of Benzophenone-d_5 and Benzophenone-d_5 Oxime. Benzophenone-d_5 was prepared by Friedel–Crafts reaction in which freshly distilled benzoyl chloride (6.5 mL) and carbon disulfide (10 mL) was added to a mixture of benzene-d_6 (5 mL). Anhydrous aluminium chloride (7.5 g) was slowly added over a period of 40–45 min. The mixture was refluxed till hydrogen chloride evolution ceased. Carbon disulfide was completely removed by evaporation on a water bath, and the contents of the flask were poured over crushed ice containing hydrochloric acid. Solid mass was alcohol gave 7.5 g of benzophenone-d_5: mp 46–47 °C; mass spectrum, m/z 187, 110, 105, 82, 77.

Benzophenone-d_5 oxime was prepared by the same method as benzophenone oxime: mp 140 °C; NMR δ 7.37 (5 H), 9.79 (1 H) (exchangeable with D_2O).

Irradiaton of Benzophenone-d_5 Oxime in Methanol. Benzophenone-d_5 oxime (0.02 M) in 220 mL of methanol was irradiated for 12 h by using quartz-filtered light. After usual workup, benzophenone (27%) from petroleum ether fraction, 30% of the isomer of the parent oxime (mp 139 °C, mmp with parent oxime 115–138 °C from the benzene–petroleum ether (1:1) fraction); NMR δ 7.4 (5 H), 9.1 (1 H)) with HCl gave benzophenone-d_5. Solvent ether eluent upon workup gave 38% deuterated 1-hydroxyfluorene: mp 119 °C; NMR δ 7.3 (4 H), 4.15 (1 H), 3.25 (1 H); mass spectrum, m/z 110, 109, 106, 105, 82, 81, 78, 77.

Irradiation of Benzophenone Oxime and 4-Methylbenzophenone in Methanol. Benzophenone oxime (0.02 M) and 4-methylbenzophenone (0.1 M) in 300 mL of methanol were irradiated for 12 by using Pyrex-filtered light. After the usual workup, the petroleum ether fraction gave 4-methylbenzophenone and benzophenone (mp 52–53 °C and 46 °C, respectively); benzene–petroleum ether (1:1) gave 22% benzophenone oxime (mp 142 °C); solvent ether and 10% $CHCl_3$ in MeOH eluents gave 15% of a mixture of 6-methyl-1-hydroxyfluorene and 3-methyl-1-hydroxyfluorene (as noted from mass spectrum containing traces of the later). Mixture on crystallization gave 10%

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6-methyl-1-hydroxyfluorene: mp 81–82 °C; NMR δ 7.3 (6 H), 4.15 (2 H), 3.32 (5.1 H), 2.3 (3 H); mass spectrum (mixture), m/z 197, 119, 105, 91, 77; TLC showed the prescence of 1-hydroxyfluorene also.

Irradiation of 4-methylbenzophenone (0.1 M) and 4-methylbenzophenone oxime (0.02 M) in 300 mL of methanol by the general method gave 32% of a mixture of 6-methyl- and 3-methyl-1-hydroxyfluorene, as noted from mass spectrum.

Irradiation of Acetone Oxime with Benzophenone. To a 300-mL methanolic solution of benzophenone (0.05 M diaryl ketone) was added 1 1 g of acetone oxime, and the solution was photolyzed for 12 h by using a Pyrex filter. The reaction solution was evaporated to about a 30-mL volume, when then pinacol formed separates out. Pinacol was filtered off, and the filtrate dried and was chromatographed over neutral alumina. Petroleum ether and 20% and 50% benzene–petroleum ether fractions removed the unreacted benzophenone and any traces of pinacol left in the filtrate. The column was then eluted with solvent ether and a 10% chloroform–methanol mixture, which gave 1.7 of 1-hydroxyfluorene (1): mp 120 °C (lit.[8] mp 120–121 °C).

1-Hydroxy-6-methylfluorene (2). On irradiation of acetone oxime and 4-methylbenzophenone by the procedure indicated, 0.725 g of **2**: mp 82 °C. Its mass spectrum indicated that it contained traces of 1-hydroxy-3-methylfluorene: NMR ($CDCl_3$) δ 2.3 (5.3 H), 4.15 (d, 2 H, J = 6 Hz), 3.32 (s, 1 H), 7.3 (m, 6 H) (on addition of D_2O, the doublet at δ 4.15 collapses to a singlet and the singlet at δ 3.32 disappears), mass spectrum, m/z 197 (P + 1), 105, 91.

1-Hydroxy-6-methoxyfluorene (5). According to the general procedure, irradiation of acetone oxime and 4-methoxybenzophenone gave 0.335 g of **5**: mp 100–101 °C; NMR ($CDCl_3$) δ 3.32 (s, 1 H) (exchangeable D_2O), 3.8 (s, 3 H), 4.2 (2 H, J = 6 Hz), 7.32 (m, 6 H); mass spectrum, m/z 213 (P + 1), 135, 107, 105, 77 (shows traces of 1-hydroxy-3-methoxyfluorene m/z 135, 77).

Irradiation of Benzophenone and Hydroxylamine Hydrochloride. Benzophenone (0.1 M) in 300 mL of methanol and 1 g of hydroxylamine hydrochloride were irradiated for 12 h. After the usual workup, 5% 1-hydroxyfluorene and 70% benzophenone oxime were isolated.

Irradiation of Fluorenone Oxime. Fluorenone oxime, 1 g in 300 mL of methanol, was photolyzed under the same conditions (quartz filter); only the starting material along with some fluorenone (10%) was isolated.

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Registry No. 2, 85257-18-7; 3, 85649-67-8; 4, 85649-68-9; 5, 85257-19-8; 2-MeBPO, 85515-91-9; 3-MeBPO, 27428-63-3; BPO, 574-66-3; 4-MeBPO, 38032-15-4; AO, 127-06-0; BP, 119-61-9; 4-MeBP, 134-84-9; 4-MeO-BP, 611-94-9; 1-hydroxyfluorene, 6344-61-2; benzophenone-d_5, 2694-78-2; benzophenone-d_5 oxime, 85649-65-6; deuterated 4-hydroxyfluorene, 85649-66-7.

Evidence for a Radical Decomposition Mechanism for Diphenyl-*N*-benzylketene Imine[1]

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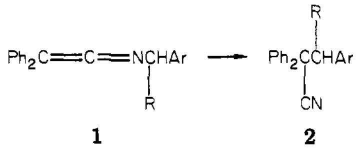
Thermolyses of diphenyl-*N*-(arylmethyl)ketene imines (**1**) in solution lead to essentially quantitative rearrangements to the substituted propanenitriles (**2**).[2] On the basis of the evidence presented below, it was concluded that these rearrangements **1** → **2** proceed via an intermediate geminate radical pair (Scheme I). (1) The rates of these reactions are not significantly affected by solvent polarity; (2) when Ar is p-X-C_6H_4 the reaction rate shows no correlation with σ_p or $\sigma_p{}^+$; (3) a chiral compound **1** (R = CH_3; Ar = phenyl) rearranges with about 50% net retention; (4) the same compound decomposes to give ca. 25% scavengeable radicals in carbon tetrachloride and ca. 37% scavengeable radicals in acetonitrile; and (5) for a series of Ar groups the decomposition rates of **1** correlate with the partial rate factors for radical phenylation of the parent aromatic hydrocarbons.



Scheme I

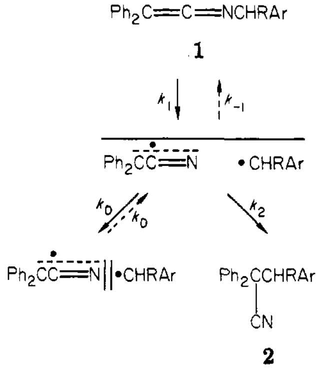


Table I. Pressure Dependence of the Decomposition Rate Constants for Diphenyl-*N*-benzylketene Imine in Chlorobenzene (60.1 °*C*)

P, atm	$k \times 10^{-5}$, s^{-1}
1	7.32 ± 0.43
1500	4.13 ± 0.20
2000	3.54 ± 0.13
2500	3.13 ± 0.22
3000	2.38 ± 0.17

[a] Singer[2] obtained values of 8.0×10^{-5} s^{-1} (CCl_4, 60 °C) and 20×10^{-5} s^{-1} (CD_3CN, 60 °C).

Since racemization of unreacted chiral **1** was not observed, there was no evidence for the likely recombination step k_{-1}. Additionally, the high yields (>95%) of **2** require that return of separatively diffused (scavengeable) radicals to a geminate encounter must occur and that the mixed coupling reaction to yield **2** is significantly more favorable than symmetric coupling of two nitrile or two benzyl radicals. The absence of these asymmetric coupling products and also any disproportionation products from **1** (Ar = phenyl; R = CH_3) is surprising. In addition, while the data generally support the radical pathway, they do not absolutely exclude the existence of a competing concerted reaction.

In the hope of providing a definitive choice among the mechanistic possibilities, we have studied the effect of pressure on the decomposition rate of diphenyl-*N*-benzyl ketene imine (**1**; R = H; Ar = phenyl) in the solvent chlorobenzene. The results confirm the radical mechanism.

Results and Discussion

Samples of 0.36 M diphenyl-*N*-benzylketene imine in chlorobenzene were decomposed at 60.1 °C, and the rearrangement reaction to 2,2,3-triphenylpropanenitrile was

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