Homolytic Aromatic Substitution by Iminyl Radicals. Photolysis of Aromatic Ketone *O*-Acyloximes in Aromatic Solvents

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(Received March 5, 1976)

Irradiation of benzophenone *O*-acetyloxime, *O*-phenylacetyloxime, *O*-benzoyloxime, and *O*-(*p*-chlorobenzoyl)-oxime in benzene, toluene, chlorobenzene, or *o*-xylene effected aromatic substitution on the solvent molecules by diphenylmethaniminyl radicals to give *N*-diphenylmethylenearylamines only when benzoxyl or *p*-chlorobenzoxyl radicals were generated concurrently. A mechanism involving a participation of the sufficiently long-lived acyloxyl radicals is proposed for the iminylation reaction on the basis of the reactivity patterns in this substitution reaction. *o*-Phenylbenzophenone *O*-benzoyloxime was also photolyzed in benzene to give 9-phenylphenanthridine, the intramolecular cyclization product of 2-biphenylylphenylmethaniminyl radicals.

Iminyl radicals are generated by various ways, among which thermal decomposition of oxime thionocarbamates[1] and hydrogen abstraction from imines[2] may be the most useful means. However, because of a lack of reactivity of iminyl radicals their chemistry has not received a great deal of attention and thus, recent interest has mainly been focused on their ESR spectra and electronic structure.[1a,b,2,3] Meanwhile, on irradiation of *O*-acyloximes formation of azines was reported and the results were rationalized by the intermediacy of iminyl radicals.[4-7] Recently it was found in our laboratory[5] that photolysis of benzophenone *O*-aroyloximes in benzene affords *N*-diphenylmethyleneaniline, the product formally derived from aromatic substitution of diphenylmethaniminyl radicals on the solvent molecule, together with benzophenone azine. Since there was no precedent for the aromatic substitution by iminyl radicals, we have undertaken to study the mechanism of this substitution reaction, and showed in a previous communication[6] that the above aromatic substitution occurs with an assistance of long-lived acyloxyl radicals. In the present paper we describe the details of our results.

Results

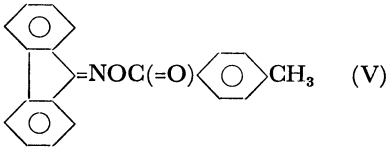
Products from Photolyses of O-*Acyloximes in Benzene.* The photolyses of benzophenone *O*-acetyloxime (Ia), *O*-phenylacetyloxime (Ib), and *O*-(*p*-chlorobenzoyl)-oxime (Ic) were carried out in benzene (0.1 M) so that a comparison could be made between the products from these *O*-acyloximes. The acyloxime Ic was the most feeble to light among them and decomposed completely within 20 h on irradiation with a 400 W high pressure mercury lamp. On the other hand the photolyses of Ia and Ib proceeded rather slowly. The products listed in Table 1 are readily interpretable in terms of the initial N–O bond homolysis followed by free-radical reactions of diphenylmethaniminyl radicals and acyloxyl radicals. Primarily, the results of the photolyses (Table 1) serve to point up the differences between the products resulting from the *O*-acetyloximes (Ia and Ib) and *O*-(*p*-chlorobenzoyl)oxime (Ic). The acetyloximes, Ia and Ib, yielded *N*-diphenylmethylenemethylamine (IIa) and *N*-diphenylmethylenebenzylamine (IIb), respectively, which would result from the coupling of diphenylmethaniminyl radicals (IV) with alkyl radicals derived from decarboxylation of the corresponding acyloxyl radicals, whereas the yield of such a coupling product, *N*-diphenylmethylene-*p*-chloroaniline (IIc), was negligible in the photolysis of Ic. The decomposition of Ib was highly accelerated with benzophenone, the addition of which did not

Table 1. Products from irradiation of benzophenone *O*-acyloxime (I), $Ph_2C{=}NOC(=O)R$, in benzene (0.1 M) with a 400 W high pressure mercury lamp

I	Ia	Ib	Ib[a]	Ic
R in I	CH_3	$PhCH_2$	$PhCH_2$	*p*-ClC_6H_4
React. time (h)	40	40	3	20
I decomposed (%)	73	100	100	100
Products (%)[b]				
$Ph_2C{=}O$	14	8		39
$Ph_2C{=}NH$		41	12	7
$Ph_2C{=}N{-}N{=}CPh_2$	15	14	8	19
$Ph_2C{=}NR$ (II)	23	30	51	1
$Ph_2C{=}NPh$ (III)	0	0	0	11
PhR	22	0		
R–R		13	15	
RCO_2Ph				4

a) Sensitized with benzophenone (0.1 M). b) Yield based on decomposed I.

Table 2. Products from irradiation of fluorenone *O*-(*p*-methylbenzoyl)oxime (V) in benzene (0.1 M) with a 1 kW high pressure mercury lamp[a]



(V)

Products	Yield,[b] %
Fluorenone	35
Fluorenone azine	18
N-Fluorenylideneaniline	4
N-Fluorenylidene-*p*-toluidine	1
4-Methylbiphenyl	35

a) 44% of V was decomposed on 20 h irradiation. b) Yield based on decomposed V.

Table 3. Total yields and isomer proportions of *N*-diphenylmethylenearylamines, $Ph_2C{=}NC_6H_4X$, formed in the iminylation of toluene and chlorobenzene[a)]

Substrate (PhX)	Acyloxime	Total Yield of $Ph_2C{=}NC_6H_4X$ (%)	Proportion of $Ph_2C{=}NC_6H_4X$		
			o-$CH_3C_6H_4Y$[b)]	*m*-$CH_3C_6H_4Y$	*p*-$CH_3C_6H_4Y$
$PhCH_3$	Id	9	28	66	5
	Ic	12	28	71	trace
			o-ClC_6H_4Y	*m*-ClC_6H_4Y	*p*-ClC_6H_4Y
PhCl	Id[c)]	14	15	83	2

a) A 0.1 M solution of I in aromatic solvent was irradiated with a high pressure mercury lamp.
b) Y stands for $Ph_2C{=}N$. c) Sensitized with benzophenone (0.1 M).

Table 4. Relative rates and partial rate factors for aromatic substitution of benzene derivatives by various radicals

Substrate (PhX)	Relative rate and partial rate factor[a)]	Attacking radical (Source of radical)			
		$Ph_2C{=}N\cdot$		$Ph_3C\cdot$ (BPO+$Ph_3C\cdot$)[b)]	$PhCO_2\cdot$ (BPO)[b)]
		($Ph_2C{=}NOCOPh$)	($Ph_2C{=}NOCOC_6H_4Cl$-*p*)		
$PhCH_3$	k_{PhCH_3}/k_{PhH}	2.30	4.36	2.82	2.47
	F_o	2.1	4.1	0.90	4.1
	F_m	4.3	8.8	6.85	1.5
	F_p	1.1	0.5	1.32	3.7
PhCl	k_{PhCl}/k_{PhH}	0.77		0.60	0.51
	F_o	0.30		0.22	0.79
	F_m	1.91		1.10	0.24
	F_p	0.18		0.97	0.98

a) F_o is the reactivity at one *ortho* site in PhX relative to reactivity of one site in benzene; similarly for F_m and F_p. b) BPO stands for dibenzoyl peroxide.

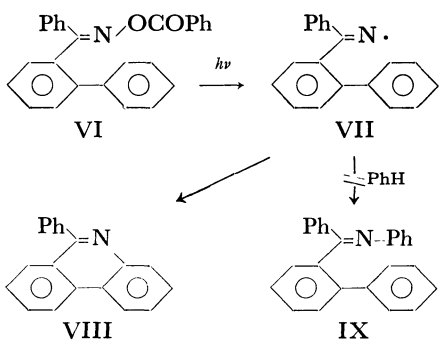
change seriously the product distribution. *N*-Diphenylmethyleneaniline (III), which would be expected to be produced by the homolytic substitution with diphenylmethaniminyl radicals (IV) on the solvent benzene, was found in an appreciable amount only in the photolysis of Ic, but none was obtained in the photolysis of Ia and Ib.

Fluorenone *O*-(*p*-methylbenzoyl)oxime (V) was also irradiated in benzene (0.1 M) to afford *N*-fluorenylidene-*p*-toluidine, the coupling product, in a similar manner to Ic (Table 2).

Reactivity Patterns in Free-Radical Aromatic Substitution by the Iminyl Radicals (IV). Photolyses of benzophenone *O*-benzoyloxime (Id) and *O*-(*p*-chlorobenzoyl)-oxime (Ic) were carried out in toluene and chlorobenzene. The total yields and the isomer proportions of *N*-diphenylmethylenearylamines formed in the iminylation of toluene and chlorobenzene are given in Table 3. In toluene *N*-diphenylmethylenebenzylamine was also obtained, which is supposed to be formed by the coupling of the iminyl radicals with benzyl radicals derived from the solvent. Irradiation of Id in *o*-xylene gave also the substitution products, *N*-diphenylmethylene-2,3-dimethylaniline and -3,4-dimethylaniline, in 4.2 and 0.5% yield, respectively

Conventional competition experiments were carried out in which mixtures of benzene with toluene and with chlorobenzene were allowed to compete for the iminyl radicals (IV), and their relative reactivities were deduced from the composition of *N*-diphenylmethylenearylamines. The relative rates (k_{PhX}/k_{PhH}: the ratio of the total rate of substitution in PhX to that in benzene) and the partial rate factors for iminylation are summarized in Table 4 with similar data for the triphenylmethylation[8)] and the benzoxylation.[9)]

Photolysis of o-*Phenylbenzophenone* O-*Benzoyloxime (VI).* In addition to the quantitative study of the reactivity patterns of the iminyl radical IV, the reaction was employed to effect intramolecular cyclization onto an aromatic ring. Irradiation of *o*-phenylbenzophenone *O*-benzoyloxime (VI) in benzene in the presence of an equimolar amount of benzophenone resulted in the formation of 9-phenylphenanthridine (VIII, 74% in VPC yield) along with small amounts of *o*-phenylbenzophenone (3%) and 2-biphenylylphenylmethanimine (11%), but afforded none of substitution products, *N*-(2-biphenylylphenylmethylene)aniline (IX), on the solvent benzene by a corresponding iminyl radical (VII)



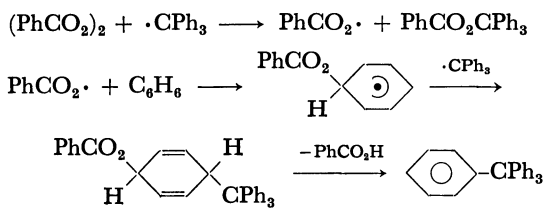
Scheme 1.

(Scheme 1). Isolated yield of the cyclization product (VIII) was 25% after purification.

Discussion

The principal reactions of iminyl radicals are dimerization to azines and β-scission to nitriles and alkyl radicals,[2,10] and only other reactions hitherto known are a hydrogen abstraction[11] and an intramolecular addition to an aromatic nucleus.[12] Thus, *N*-chloroketimines, on thermolysis in the presence of *n*-Bu_3SnH, gave ketimines, and the reduction was explained by a radical chain sequence involving hydrogen abstraction of iminyl radicals from *n*-Bu_3SnH.[11] When this reduction was carried out in the presence of 1-octene, no products derived from addition of iminyl radicals to 1-octene were observed.[11] Meanwhile, Forrester *et al.* reported that oxidation of *N*-substituted-methyleneaminooxy-acetic (XIV) or -propionic acids with peroxysulfate gave a phenanthridine (VIII), the product derived from intramolecular cyclization of iminyl radicals (VII) to an adjacent phenyl group[12] (Scheme 5).

In view of such an unreactive nature of iminyl radicals, it is highly notable that *N*-diphenylmethylenearylamines, the products of homolytic substitution by the iminyl radicals on the aromatic solvent, are formed only in the photolyses of benzophenone *O*-benzoyloxime (Id) and *O*-(*p*-chlorobenzoyl)oxime (Ic), whereas none was obtained in the photolyses of benzophenone *O*-acetyloxime (Ia) and *O*-phenylacetyloxime (Ib). These facts suggest that the aromatic substitution by the diphenylmethaniminyl radicals (IV) takes place only when the partner acyloxyl radicals are sufficiently alive like benzoxyl and *p*-chlorobenzoxyl radicals until they decarboxylate; the substitution does not occur when the iminyl radicals IV are generated together with short-lived acyloxyl radicals such as acetoxyl and phenylacetoxyl radicals. It is therefore likely that the aromatic substitution is not effected by IV alone, but is induced with an assistance of aroyloxyl radicals. These observations remind us of the role of benzoxyl radicals in the Wieland triphenylmethylation reaction,[13] in which tetraphenylmethane is a major product of the dibenzoyl peroxide-induced reaction of triphenylmethyl radicals with benzene. This reaction is now elucidated by the following reaction sequence (Scheme 2), in which induced decomposition of the peroxide is followed by attack of benzoxyl radicals on the solvent. The cyclohexadienyl radical formed is scavenged by a triphenylmethyl radical in a coupling reaction. Non-radical elimination of benzoic acid then gives tetraphenylmethane.

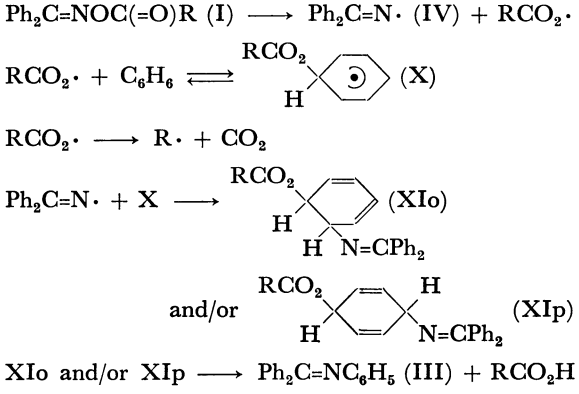


Scheme 2.

When toluene is used as a solvent, a major product is *m*-methyltetraphenylmethane, consistent with preferred *ortho* and *para* attack on toluene by a benzoxyl radical.

Consideration of the figures shown in Table 3 indicates that the proportions of substitutions at the *meta*-positions are unusually high irrespective of the polar character of the substituents. The results differ greatly from those obtained for usual homolytic substitution by free radicals such as alkyl and aryl radicals, which generally attack *ortho*- and *para*-positions of toluene or chlorobenzene in preference to *meta*-positions.[9] The unusual order of apparent reactivity among the nuclear positions ($m>o\gg p$) is again analogous to that of substitution by triphenylmethyl radicals or nitrogen dioxide in the presence of dibenzoyl peroxide. Anomaly in the same sense is also observed in the relative rates and the partial rate factors summarized in Table 4. It is worth noting that the relative rates and the partial rate factors for the iminylation of toluene and chlorobenzene with Id generally parallel those for the triphenylmethylation. With Ic the partial rate factor to toluene is considerably increased, although there is an overall similarity between Ic and Id. It is also observed in Table 4 that the relative rates of toluene and chlorobenzene for the benzoxylation are close to those for the iminylation with Id, but the benzoxylations occur preferentially at the *ortho*- and the *para*-positions. These findings suggest that the attack of the aroyloxyl radicals on the aromatic solvent is a key step in the aromatic substitution.

On the basis of the close correspondence with reactivity patterns in the iminylation and triphenylmethylation reactions as well as the above findings, it is concluded that the aromatic substitution by the iminyl radicals IV takes place through the following sequence of reactions (Scheme 3).



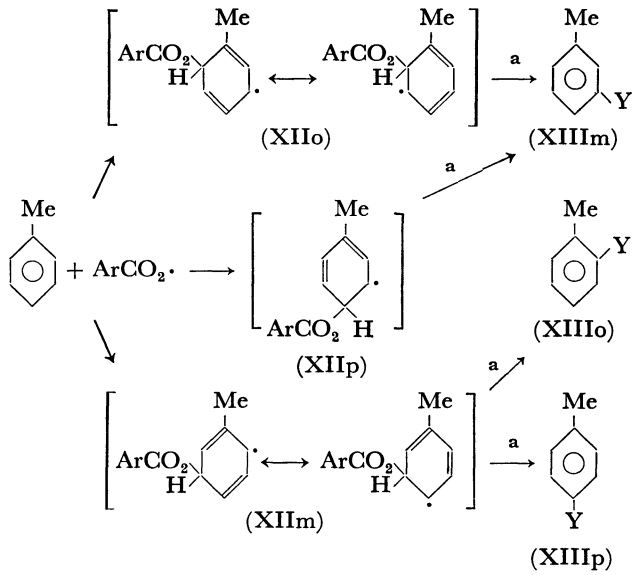
Scheme 3.

The acyloxyl radicals generated by photochemical cleavage of I either add reversibly to benzene to give cyclohexadienyl radicals (X) or decarboxylate. The resulting radicals, X, would combine with IV to give cyclohexadienes, XIo and/or XIp, which would subsequently decompose into III and carboxylic acid. In the irradiation of Ia or Ib, the intermediate acetoxyl or phenylacetoxyl radicals decarboxylate facilely before they add effectively to benzene. The formation of

N-fluorenylideneaniline in the photolysis of fluorenone *O*-(*p*-methylbenzoyl)oxime (V) in benzene is possibly explained in a similar manner.

Benzoxyl radicals are known[9] to add to the *ortho*- and *para*-positions of toluene to give cyclohexadienyl radicals, XIIo and XIIp, in preference to *meta*-positions to give XIIm (Scheme 4). The cyclohexadienyl radicals, XIIo and XIIp, would combine with IV exclusively at the position *meta* to methyl group to give *N*-diphenylmethylene-*m*-toluidine, XIIIm, and the cyclohexadienyl radical, XIIm, on the other hand, would combine necessarily at the positions *ortho* and *para* to methyl group to give *o*- and *p*-toluidine derivatives, XIIIo and XIIIp, respectively, the ratio of which would be regulated mainly by the steric factors of methyl and benzoxy groups on the cyclohexadienyl radical XIIm. This reaction scheme successfully explains the predominant production of XIIIm over XIIIo and XIIIp.

Taking account of the *ortho*- and *para*-orientation of benzoxyl radicals to chlorobenzene,[9] similar considerations can be applied to the preferential formation of *N*-diphenylmethylene-*m*-chloroaniline to *o*- and *p*-chloroaniline derivatives in the photolysis of Id in chlorobenzene.

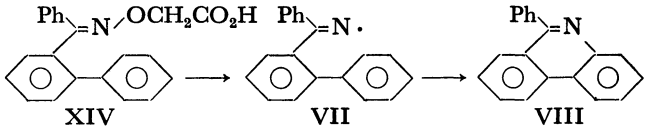


Y: $Ph_2C{=}N$; a: combination with Y· followed by elimination of $ArCO_2H$.

Scheme 4.

Instead of giving *N*-diphenylmethyleneaniline (III) irradiation of Ia and Ib in benzene afforded *N*-diphenylmethylenemethylamine (IIa) and *N*-diphenylmethylenebenzylamine (IIb), respectively, which would result from the combination of IV with the alkyl radicals derived from the decarboxylation of acyloxyl radicals (Scheme 3). We have reported previously[7] that the homolytic cleavage of *O*-acyloximes into iminyl and acyloxyl radicals takes place from the triplet states, in both direct and sensitized irradiation, with excitation energies comparable to those of their parent ketones. In view that the triplet pair of free radicals, in general, does not efficiently lead to a geminate product,[15] the formation of *N*-diphenylmethylenebenzylamine (IIb) from direct irradiation as well as from sensitization is not attributable to the geminate reaction between IV and benzyl radicals in a solvent cage, but to the combination between these radicals diffused out of the initial solvent cage. *A priori* it is reasonable to suppose that the production of *N*-diphenylmethylenemethylamine (IIa) from Ia is attributable to out-of-cage encounter of methyl and iminyl radicals.

Closely related to free-radical aromatic substitutions are intramolecular free-radical aromatic substitutions. The iminyl radicals (VII) produced by the photolysis of *o*-phenylbenzophenone *O*-benzoyloxime (VI) cyclize onto an adjacent phenyl group to give 9-phenylphenanthridine (VIII) (Scheme 1). Forrester *et al.* reported[12] that VII derived from the oxidation of the corresponding aminooxy-acetic acid (XIV) or -propionic acid gives 9-phenylphenanthridine (VIII) and hence the assistance of benzoxyl radicals is not necessarily required in the intramolecular cyclization. These results indicate that the iminyl radicals are sufficiently reactive in the addition to the benzene ring, provided the benzene nucleus is located adjacently to the radical center.



Scheme 5.

Experimental

All melting points are uncorrected. IR and UV spectra were recorded on a Hitachi EPI-G2 grating infrared spectrophotometer and a Hitachi EPS-3 recording spectrophotometer, respectively. NMR spectra were recorded with a Hitachi R-20B NMR spectrometer. Micro-analyses were performed by Organic Analytical Laboratory of our Department under supervision of Mr. S. Masuda. VPC analyses were performed on Hitachi 063 and K53 gas chromatographs equipped with flame ionization detectors. All quantitative results compared to internal standards were based on measured molar response factors determined from known mixtures of authentic materials. Irradiations were conducted with a Riko 400 W and a 1 kW high pressure mercury lamp in a water-cooled immersion well.

Materials. Special grade benzene, toluene, chlorobenzene, and *o*-xylene were distilled prior to use. Benzophenone (reagent grade) was crystallized from ethanol. Benzophenone *O*-acetyloxime,[16] *O*-benzoyloxime,[17] *O*-(*p*-chlorobenzoyl)oxime,[18] were prepared according to the methods described in literatures. Diphenylmethanimine,[19] *N*-diphenylmethylenemethylamine,[20] -benzylamine,[21] -aniline,[22] -*o*-toluidine,[23] -*m*-toluidine,[24] -*p*-toluidine,[22] -*p*-chloroaniline,[25] and -3,4-xylidine,[24] *N*-fluorenylidene-aniline,[22] and -*p*-toluidine,[26] 2-biphenylylphenylmethanimine,[27] and *N*-(2-biphenylylphenylmethylene)aniline[28] were prepared according to the methods described in literatures. Benzophenone azine[29] and fluorenone azine[30] were prepared according to the reported methods.

Benzophenone O-Phenylacetyloxime. Phenylacetic anhydride (14 g) was refluxed for 4 h with benzophenone oxime (6 g) in diethyl ether (100 ml). After cooling, the insoluble product was collected by filtration, and the ethereal filtrate was shaken with 10% sodium carbonate solution and then

water. A white crystalline solid precipitated was collected, combined with the above product, washed with ether, and dissolved in chloroform. To this solution was added hexane and the solution was cooled in an ice bath to afford white crystals (3 g), which were further purified on recrystallization from benzene–hexane; mp 112.5—113 °C (Found: C, 79.92; H, 5.30; N, 4.29%. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44%); IR (KBr) 1763 cm^{-1}; NMR ($CDCl_3$) δ 3.61 (s, 2H).

Fluorenone O-(p-*Methylbenzoyl*)*oxime.* Fluorenone oxime was acylated with *p*-methylbenzoyl chloride in the presence of pyridine according to the method of Renfrow *et al.*[18]; mp 143.5—144.5 °C (ethanol) (Found: C, 80.37; H, 4.90; N, 4.67%. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47%); IR (KBr) 1738 cm^{-1}; NMR ($CDCl_3$) δ 2.43 (s, 3H).

o-*Phenylbenzophenone* O-*Benzoyloxime.* *o*-Phenylbenzophenone oxime, prepared from *o*-phenylbenzophenone[31] by the method of Smith,[27] was acylated with benzoyl chloride in a way similar to fluorenone *O*-(*p*-methylbenzoyl)oxime; mp 115.5—116.5 °C (benzene–petroleum ether) (Found: C, 83.04; H, 4.96; N, 3.80%. Calcd for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71%); IR (KBr) 1742 cm^{-1}.

N-*Diphenylmethylene*-o-*chloroaniline.* A mixture of 3 g of benzophenone, 3.5 ml of *o*-chloroaniline, and 1 drop of 48% hydrobromic acid was heated for 0.5 h at 250 °C under nitrogen. After cooling, 15 ml of ethanol was added to give light yellow crystals, which were recrystallized three times from ethanol to give pure specimen (1.8 g); mp 101—103 °C (Found: C, 78.04; H, 4.98; N, 4.78; Cl, 12.20%. Calcd for $C_{19}H_{14}ClN$: C, 78.21; H, 4.84; N, 4.80; Cl, 12.15%).

N-*Diphenylmethylene*-m-*chloroaniline.* A mixture of 3 g of benzophenone, 3.5 ml of *m*-chloroaniline, and 2 drops of 48% hydrobromic acid was heated for 1 h at 210 °C under nitrogen. After cooling, 15 ml of ethanol added to give light yellow crystals. Twice recrystallizations from ethanol gave pure specimen (2.4 g); mp 75.5—76.5 °C (Found: C, 77.95; H, 4.74; N, 4.72; Cl, 12.27%. Calcd for $C_{19}H_{14}ClN$: C 78.21; H, 4.84; N, 4.80; Cl, 12.15%).

N-*Diphenylmethylene*-*2,3*-*xylidine.* A solution of equivalent amounts of benzophenone and 2,3-xylidine in xylene was refluxed for 4 h in the presence of a few drops of 48% hydrobromic acid. The water formed during the reaction was removed as xylene azeotrope. After evaporation of the solvent, the residue was recrystallized from ethanol; mp 60—61 °C (Found: C, 88.50; H, 6.61; N, 4.75%. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91%).

Photolyses of O-*Acyloximes.* A 0.1 M solution of benzophenone *O*-acyloxime in benzene was irradiated under nitrogen or argon in the absence or in the presence of benzophenone in a Pyrex immersion well with a 400 W mercury lamp. When toluene, chlorobenzene, or xylene was used as a solvent, irradiation was conducted in a Pyrex tube with a 1 kW mercury lamp using a Riko RH400—10 W rotary photochemical reactor.

Benzene solutions (0.1 M) of fluorenone *O*-(*p*-methylbenzoyl)oxime and *o*-phenylbenzophenone *O*-benzoyloxime were irradiated similarly by the 1 kW mercury lamp.

Volatile products other than starting acyloximes and ketazines were analyzed quantitatively by VPC using columns of Apiezon Grease L and Carbowax 20 M. Ketazines were separated by dry column chromatography on silica gel eluting with benzene, and analyzed quantitatively by UV spectrometry. In the photolyses of benzophenone *O*-acetyloxime the unreacted acetyloxime and the products, *N*-diphenylmethylenemethylamine and toluene, were analyzed also by NMR using an internal standard.

A solution of *o*-phenylbenzophenone *O*-benzoyloxime (0.377 g) in benzene (10 ml) in the presence of benzophenone (0.182 g) was irradiated by the 1 kW mercury lamp for 13.5 h. The reaction mixture was analyzed quantitatively by VPC using a column of Apiezon Grease L. 9-Phenylphenanthridine was separated by dry column chromatography on silica gel eluting with benzene as white crystals (0.064 g, 25%); mp 104—105 °C (lit,[32] 106 °C).

Competitive Experiments. A 0.1 M solution of benzophenone *O*-benzoyloxime or *O*-(*p*-chlorobenzoyl)oxime in a mixed solvent, benzene–toluene (22 : 8 in a volume ratio) or in benzene–chlorobenzene (8 : 17), was irradiated by the 1 kW mercury lamp. The distributions of substituted products, *N*-diphenylmethylene-aniline, -toluidines, and -chloroanilines, were determined by VPC analysis using a column of Apiezon Grease L.

The authors wish to thank Professor T. Suehiro in Gakushuin University for his helpful discussions. Partial financial assistance through the Ministry of Education for K. T. is gratefully acknowledged.

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