

PHOTOCHEMICAL OXIDATION OF IMINES

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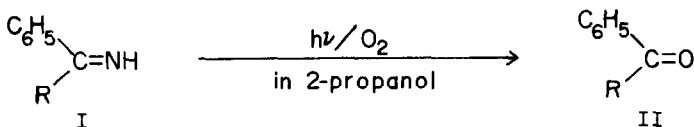
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Interest in the photochemical reaction, especially photoreduction, of C-N double bonds has considerably grown in recent years.(1-5) We now wish to report the photo-oxidation of imino compounds yielding ketones and amides.

A solution of 1,1-diphenylmethyleneimine Ia (1.0 g) in 2-propanol (50 ml) was irradiated in a stream of oxygen (5-20 ml/min) with a 100W high pressure mercury lamp without filters. Monitoring by glpc indicated the disappearance of the starting material in 20 hr. Evaporation of the solvent gave benzophenone IIa almost quantitatively.(6)



Ia; R=C₆H₅
Ib; R=C₆H₄-CH₃-p
Ic; R=C₁₀H₇-o

IIa; R=C₆H₅
IIb; R=C₆H₄-CH₃-p

This reaction did not take place on refluxing in the same conditions without the irradiation of light. Imine Ia was easily reduced photochemically to yield 1,1-diphenylmethylaniline III as previously reported.(1) However, III cannot be a precursor in the formation of IIa, since III did not give IIa under the same conditions.

Table I. Solvent Effect on Photoreaction of 1,1-Diphenylmethyleneimine Ia.

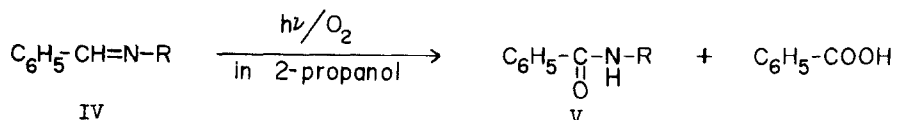
Solvent	Photo-oxidation Yield (%) ^a	Photoreduction Yield (%) ^b
2-Propanol	100	95
Methanol	82	53
Cyclohexane	47	2
n-Hexane	27	-

^a Irradiated for 20 hr.

^b Yield means the total conversion after 25 hr irradiation.(1)

The photo-oxidation proceeded more easily in 2-propanol than in methanol (see Table I). It can be concluded that a solvent with a more hydrogen-donating power is more effective on the photo-oxidation. The same tendency was found on the solvent effect on the photoreduction of Ia in the previous paper.(1)

The similar photo-oxidation was observed on irradiation of *p*-tolylphenyl-methyleneimine Ib. The α -naphthyl derivative Ic, however, was not oxidized photochemically. The difference between their reactivities was also found in the photoreduction in 2-propanol. These consistencies of the substitution and solvent effects on the photo-oxidation with those on the photoreduction suggest that the photo-oxidation of Ia involves the same reaction intermediate as that of the photoreduction.(1) In other words, this oxidation may proceed through the reaction of oxygen in the ground state with aminobenzhydryl radical, which has formed photochemically on the hydrogen-atom abstraction by Ia from the solvent. Indeed, acetone was obtained in this reaction in 2-propanol.



In order to search the fate of the nitrogen in the starting material, the photo-oxidation of N-benzylideneaniline IVa was investigated under the same conditions. Benzanilide Va was unexpectedly obtained in this reaction besides benzoic acid (15% yield) which was expected from the formation of ketones in the photo-oxidation of imines I.(7) Other aromatic and aliphatic N-substituted imines

Table II. Photo-oxidation of N-Substituted Imines IV in 2-Propanol.

Imine	Irradiation Time (hr)	Recovery* (%)	Yield of Benzamide V*
			(%)
IVa; R=C ₆ H ₅	20	63	10
IVb; R=C ₆ H ₄ CH ₃ -p	20	64	5
IVc; R=C ₆ H ₄ OCH ₃ -p	40	50	9
IVd; R=CH ₂ -C ₆ H ₅	5	-	8

* Determined by weight after a silica-gel-column chromatography based on the amount of the starting imine.

IVb-IVd also gave the corresponding benzamides (see Table II). It is noteworthy that no changes in the skeleton of Ph-C-N-R occurred.(6) These reactions did not take place without light. Recently, Furey and Kan reported the photochemical hydrolysis of IVa yielding benzaldehyde and aniline.(5) However, we did not obtain Va on irradiation of the mixed 2-propanol solution of aniline and benzoic acid, which may be formed by an oxidation of benzaldehyde with oxygen. Hence the present case must be a different type of photo-oxidation from the literature.(8)

The yield of Va increased on addition of acetophenone, whereas it did not on that of methylene blue, which was known to activate oxygen to a singlet state.(9, 10) This fact suggests that a singlet oxygen was not involved in these reactions. The acetophenone probably played a role in a chemical sensitization.(2,4,11)

The solvent effect on the photo-oxidation of IVa also shows the same tendency

Table III. Solvent Effect on Photo-oxidation of N-Benzylideneaniline IVa.*

Solvent	Recovery (%)	Yields of Products(%)	
		Benzanilide	Benzoic Acid
2-Propanol	10	11	15
Methanol	26	5	16
Acetonitrile	51	trace	1
Cyclohexane	81	-	-

* Irradiation was carried out for 40 hr. Yields were determined by weight after a silica-gel-column chromatography and were based on the amount of the starting imines.

