

MECHANISM FOR NOVEL HOMOLYTIC AROMATIC SUBSTITUTION BY DIPHENYLMETHANIMINYL
RADICAL IN PHOTOLYSIS OF BENZOPHENONE O-ACYLOXIMES IN AROMATIC SOLVENTS

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Irradiation of benzophenone O-acyloximes (I) in benzene or toluene effects aromatic substitution on the solvents by diphenylmethaniminyl radicals (IV) to give N-diphenylmethyleneaniline (II) or N-diphenylmethylenetoluidines (VIII) unless concurrently formed acyloxyl radicals facilely decarboxylate. A mechanism involving a participation of sufficiently lived acyloxyl radicals is proposed for the above substitution reactions.

Much attention has recently been paid to photochemistry of the carbon-nitrogen double bond,²⁾ and O-acyloximes have been shown to generate iminyl radicals on irradiation.^{3,4)} Previously it was found in our laboratory that in the irradiation of benzophenone O-aryloximes in benzene the intermediate diphenylmethaniminyl radicals, $\text{Ph}_2\text{C}=\text{N}\cdot$, effect an aromatic substitution to give N-diphenylmethyleneaniline.^{4,5)} We now wish to report that this new type of homolytic aromatic substitution occurs with an assistance of acyloxyl radicals.

Benzophenone O-acetyloxime (Ia), O-phenylacetyloxime (Ib), and O-(p-chlorobenzoyl)oxime (Ic) were irradiated in benzene with a high pressure mercury lamp. All of the products listed in Table 1 can be accounted for by initial photochemical

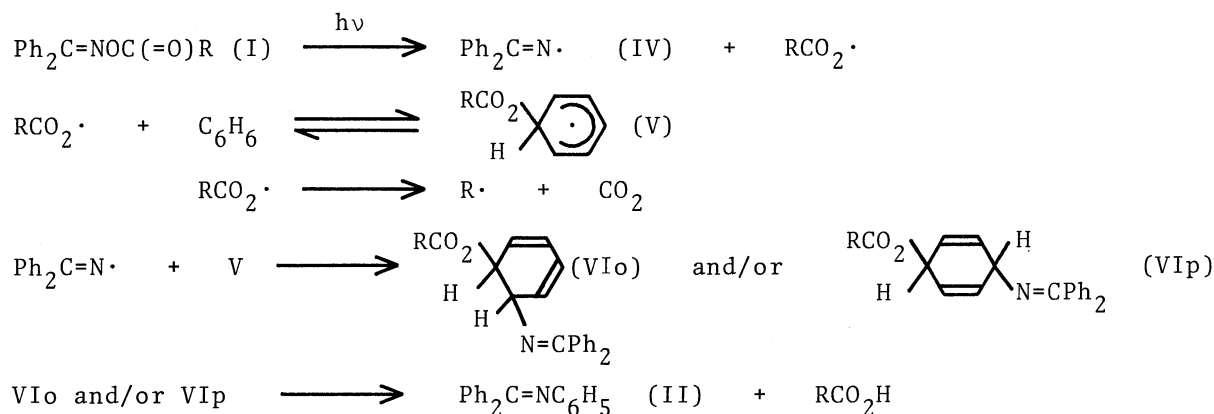
Table 1. Products from Irradiation of Benzophenone O-Acyloxime (I), $\text{Ph}_2\text{C}=\text{NOC}(=\text{O})\text{R}$, in Benzene with a High Pressure Mercury Lamp

I	Ia	Ib	Ib*	Ic
R in I	CH_3	PhCH_2	PhCH_2	p-ClC ₆ H ₄
Products (%)				
$\text{Ph}_2\text{C}=\text{O}$	14	8		39
$\text{Ph}_2\text{C}=\text{NH}$		41	12	7
$(\text{Ph}_2\text{C}=\text{N})_2$	15	14	8	19
$\text{Ph}_2\text{C}=\text{NPh}$ (II)	0	0	0	11
$\text{Ph}_2\text{C}=\text{NR}$ (III)	23	30	51	1
PhR	22	0		
R-R		13	15	
RCO_2Ph				4

*Benzophenone was used as a sensitizer.

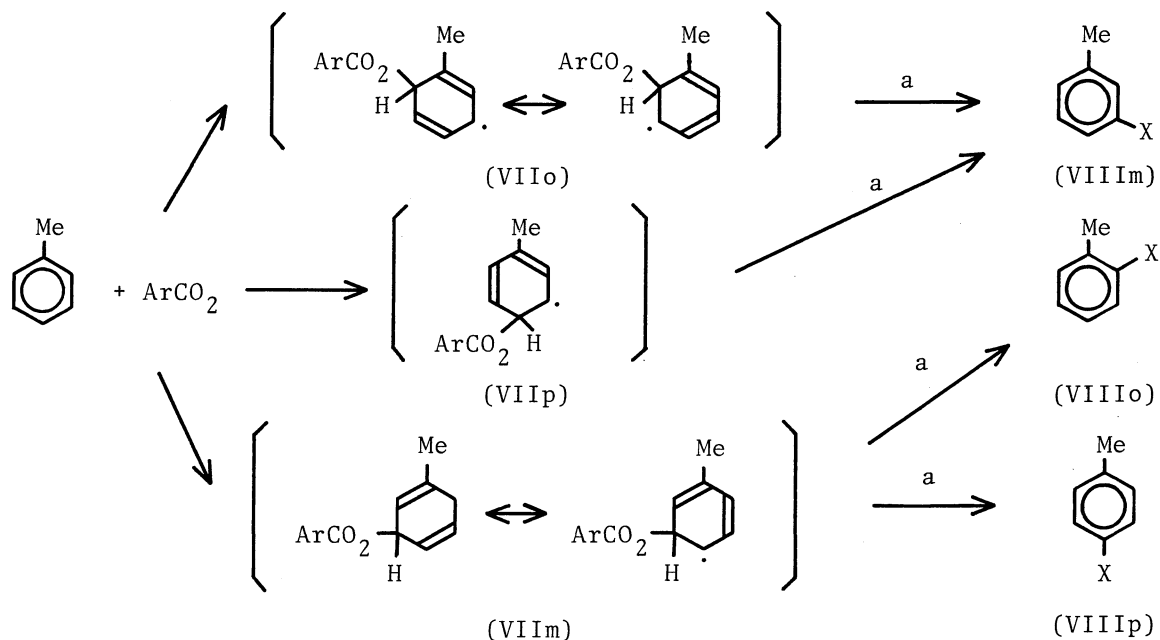
cleavage of the N-O bond of I followed by free radical reactions of diphenylmethaniminyl (IV) and acyloxyl radicals. The most remarkable feature among the products is that N-diphenylmethylenedianiline (II), the product of homolytic substitution by IV on the solvent benzene, is formed only in the photolysis of Ic, whereas none such was obtained in the photolysis of Ia and Ib. This fact suggests that the aromatic substitution by IV takes place only when the partner acyloxyl radicals are sufficiently alive like p-chlorobenzoyl radicals until they decarboxylate; the substitution does not occur when 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 effected with an assistance of acyloxyl radicals.

This view is further supported by the following experiments. When benzophenone O-benzoyloxime (Id) was irradiated in toluene, the aromatic substitution by IV took place on toluene to give N-diphenylmethylenetoluidines (VIII) in 9.2% yield. The proportions of VIII were 28, 66, and 5% for ortho- (VIIIo), meta- (VIIIm), and para- (VIIIp) isomers, respectively. Irradiation of Ic gave also the substitution products, VIII, in 12% yield with similar isomer distribution ratios (VIIIo, 28%; VIIIm, 71%; VIIIp, nil). These observations provide a striking contrast with the usual substitution by free radicals such as alkyl and aryl radicals, which generally attack ortho- and para-positions of toluene in preference to meta-positions.⁶⁾ The unusual order of apparent reactivity among the nuclear positions ($m > o \gg p$) is analogous only to that of substitution by triphenylmethyl radicals or nitrogen dioxide in the presence of dibenzoyl peroxide, which is proved to proceed with the assistance of the intermediate benzoyl radicals.⁷⁾ It is therefore reasonable to suppose that the aromatic substitution by the iminyl radicals (IV) takes place through the following sequences of reactions.



The acyloxyl radicals generated by photochemical cleavage of I either add reversibly to benzene to give cyclohexadienyl radicals (V) or decarboxylate.⁸⁾ The resulting radicals, V, would combine with IV to give cyclohexadienes, VIo and/or VIp, which would subsequently decompose into II and carboxylic acid. In the irradiation of Ia or Ib, the intermediate acetoxyl or phenylacetoxyl radicals decarboxylate readily before they add effectively to benzene.⁹⁾

Benzoyl radicals are known to add to the ortho- and para-positions of toluene to give cyclohexadienyl radicals, VIIo and VIIp, in preference to meta-positions to give VIIm.^{9,10} The cyclohexadienyl radicals, VIIo and VIIp, would combine with IV exclusively at the position meta to methyl group to give N-diphenylmethylene-m-toluidine, VIIIm, and VIIm, on the other hand, would combine necessarily at the positions ortho and para to methyl group to give o- and p-toluidine derivatives, VIIIo and VIIIp, respectively. These processes successfully account for the predominant production of VIIIm over VIIIo and VIIIp.



X: $\text{Ph}_2\text{C}=\text{N}$; a: combination with $\text{X}\cdot$ followed by elimination of ArCO_2H

Instead of giving II irradiation of Ia and Ib in benzene afforded N-diphenylmethylenemethylamine (IIIa) and N-diphenylmethylenebenzylamine (IIIb), respectively, which would result from the combination of IV with the alkyl radicals derived from the decarboxylation of acyloxyl radicals, whereas the yield of such a coupling product, N-diphenylmethylene-p-chloroaniline (IIIc), was negligible in the photolysis of Ic. The use of benzophenone as a sensitizer in the photolysis of Ib with 366 nm light accelerated its decomposition to give IIIb. On the other hand, the presence of 1,3-pentadiene in the direct irradiation of Ib retarded its decomposition. These results indicate that homolytic cleavage of Ib into free radicals takes place from its excited triplet state in both direct and sensitized irradiations. In view that the triplet pairs of free radicals, in general, do not efficiently lead to a geminate product,¹¹ the formation of IIIb 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.

The authors' thanks are due to Professor T. Suehiro in Gakushuin University for his helpful discussions and to the Ministry of Education for the partial support of this work through the research grant to K. Tokumaru.

References and Notes

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(Received June 9, 1975)