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THE HEAVY ATOM EFFECT ON THE PHOTOCHEMICAL REDUCTION AND ADDITION OF N-ACETYLDIPHENYLKETIMINE WITH TOLUENE: EVIDENCE FOR THE MECHANISM THROUGH THE EXCITED IMINE OTHER THAN THE CHEMICAL SENSITIZATION MECHANISM

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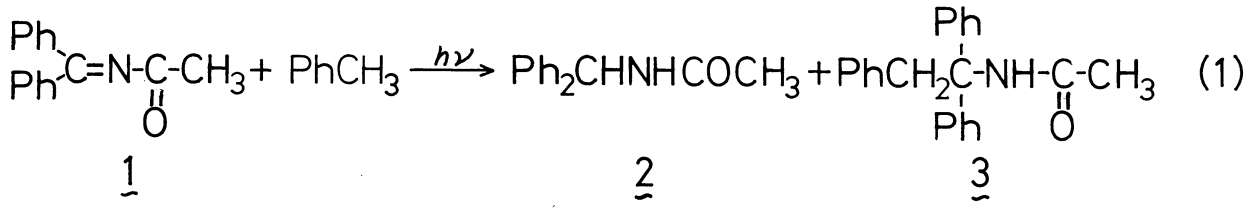
The photoreaction of N-acetyldiphenylketimine (1) with toluene was promoted by various kinds of halogenated solvents. This phenomenon was confirmed as an external heavy atom effect. The presence of this effect shows evidence that the excited state of the imine 1 has an ability to abstract a hydrogen atom.

Photoreaction of N-acetyldiphenylketimine (1) with toluene in the presence of a halo-hydrocarbon solvent has revealed a substantial external heavy atom effect. To our best knowledge, this is the first example that the photoproducts of the nitrogen-containing compounds increased in yields due to the heavy atom effect. This finding shows evidence that the photoreaction of N-acetylketimine 1 proceeds *via* the excited state of the imine other than *via* the chemical sensitization mechanism.[1)]

We have already found that irradiation of 1 in toluene gave N-acetyldiphenylmethylamine (a hydrogenation product, 2) and N-(1,1,2-triphenylethyl)acetamide (an adduct, 3).[2)]



(1)

In the course of investigation on the photoreaction of 1 witn p-halo-substituted toluene, the yields[3)] of the both products have been found to increase extremely in p-bromotoluene. This finding suggested the presence of the heavy atom effect on the photoreaction of equation (1). When a small amount of bromobenzene was added to the solution of 1 and toluene in benzene, the both products increased in yields on irradiation at room temperature for 30 hr. The dependence of the yields[3)] on the concentration of bromobenzene is shown in Fig. 1. This is the typical curve for the external heavy atom effect by a bromo-compound.[4)]

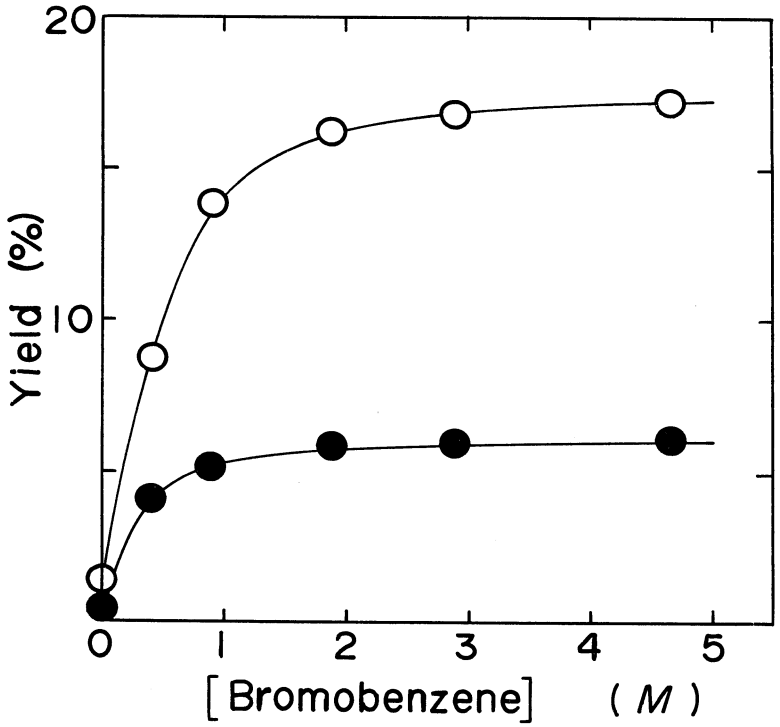


Fig. 1. Dependence of the yields of a hydrogenation product (2, ●) and an adduct (3, ○) in the photoreaction of N-acetyldiphenylketimine (1) with toluene upon the concentration of bromobenzene: Irradiation was carried out with 0.23 M of 1 for 30 hr in a Pyrex tube with the merry-go-round type apparatus using 5 ml of toluene and 5 ml of the mixed solvent of bromobenzene and benzene in various proportions.

Table 1. Solvent effect on the yields of the photoreaction of N-acetyldiphenylketimine (1) with toluene.[a)]

Solvent	Volume of solvent added					
	1 ml[b)]			5 ml[c)]		
	Hydrogenation product, 2 (%)	Adduct, 3 (%)	Total (%)	Hydrogenation product, 2 (%)	Adduct, 3 (%)	Total (%)
Benzene	0.8	3.4	4.2	0.4	1.3	1.7
1-Chloropropane	0.7	3.1	3.8	1.4	2.0	3.4
Chlorobenzene	0.7	3.1	3.8	1.9	3.7	5.6
Chloroform	2.0	5.0	7.0	2.2	6.0	8.2
1-Bromopropane	3.6	6.8	10.4	5.8	17.6	23.4
Bromobenzene	5.2	8.3	13.5	6.1	15.5	21.6
Dibromomethane	4.3	13.5	17.8	5.5	14.3	19.8

a) Irradiation was carried out with 0.23 M of 1 in a Pyrex tube with the merry-go-round type apparatus for 30 hr.

b) One milliliter of the solvent listed and 9 ml of toluene were used.

c) Five milliliters of the solvent listed and 5 ml of toluene were used.

Irradiation in the varieties of the halo-hydrocarbon solvents provided a marked change in the product yields. Namely, the reaction rate was accelerated with the increasing number of halogen atoms in a solvent molecule. The solvent containing the heavier halogen atom increased the product yields much more than the solvent with the lighter halogen atom. The results shown in Table 1 are in correlation with the $\Sigma(\zeta^2)$ value of the heavy atom solvent.[5] This linear correlation shown in Fig. 2 confirmed the existence of the heavy atom effect on the photoreaction of 1 with toluene.[6]

Photochemical hydrogen abstraction by the compound having a C=N bond has been investigated in some detail.[1,2,7] It has been proposed that the excited state of a simple acyclic imine is readily deactivated to the ground state accompanied by rotation about a C=N bond and that the photoreaction of an imine proceeds via a chemical sensitization mechanism because only the excited state of the carbonyl compound contained in the starting imine can abstract a hydrogen atom.[1] However, the heavy atom effect is generally known not to be observed in the processes involving the (n,π^*) triplet state.[8] In fact, no heavy atom effect has been detected on

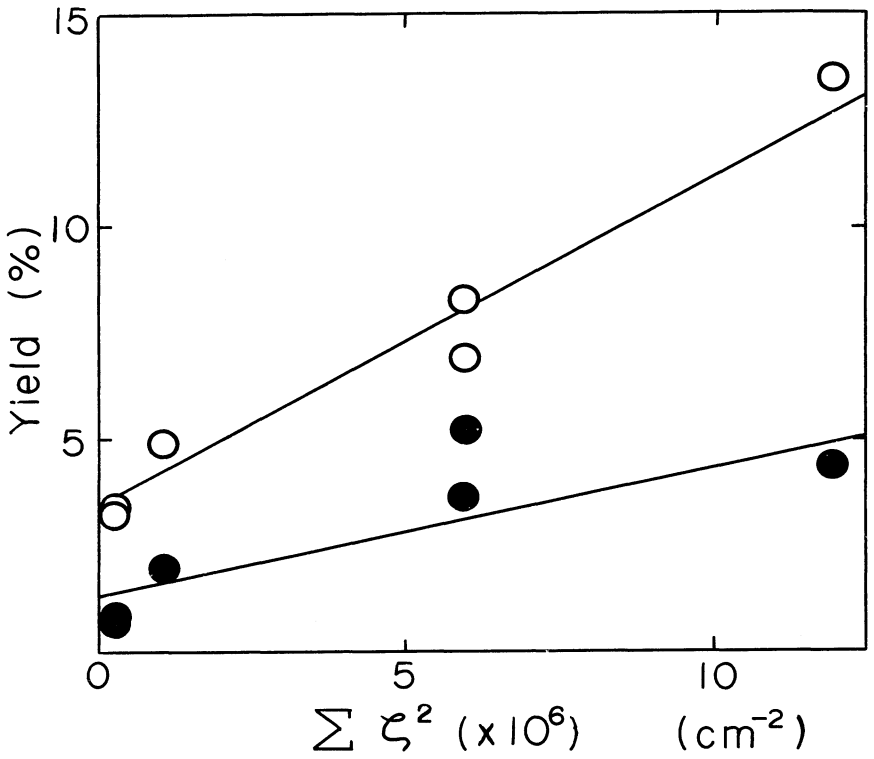


Fig. 2. Dependence of the yields of a hydrogenation product (2, ●) and an adduct (3, O) in the photoreaction of N-acetyldiphenylketimine (1) with toluene upon the $\Sigma(\zeta^2)$ value of the heavy atom solvent used: Irradiation was carried out for 30 hr in a Pyrex tube with the merry-go-round type apparatus using 1 ml of the heavy atom solvent and 9 ml of toluene.

the photoreaction of benzophenone,[9] which can act as a chemical sensitizer in the photoreaction of 1.[1]

Therefore, the present finding of the external heavy atom effect on the photoreaction of 1 demonstrates that the imine 1 can react with toluene not only via the intermolecular or intramolecular chemical sensitization mechanism[1] but also via the excited state, probably (π,π^*) triplet state,[10] of the imine 1.[11] The detail of the present work will be presented soon in a full paper.[9]

References and Footnotes

1) M.Fischer, Tetrahedron Lett., 5273(1966); Chem.Ber., 100, 3599(1967). T.Okada, M.Kawanisi, H.Nozaki, N.Toshima, and H.Hirai, Tetrahedron Lett., 927 (1969). T.Okada, K.Saeki, M.Kawanisi, and H.Nozaki, Tetrahedron, 26, 3661 (1970). A.Padwa, W.Bergmark, and D.Pashayan, J.Amer.Chem.Soc., 90, 4458(1968); 91, 2653(1969). A.Padwa and M.Dharan, Tetrahedron Lett., 1053(1972).

2) S.Asao, N.Toshima, and H.Hirai, Bull.Chem.Soc.Japan, 48, in press(1975).

3) The yields were obtained with a VPC or HLC on the basis of the amount of the starting imine 1 in the presented conditions. A hydrogenation product 2 and an adduct 3 were produced selectively and no byproduct from 1 was obtained. Therefore, the yields of both products can increase with the length of the irradiation time and can present the relative quantum yields in this paper.

4) For example, D.O.Cowan and R.L.Drisko, J.Amer.Chem.Soc.,92, 6286(1970). An unusual case with a maximum was reported recently; C.O.Cowan and J.C.Koziar, J.Amer.Chem.Soc., 96, 1229(1974).

5) S.K.Lower and M.A.El-Sayed, Chem.Rev., 66, 199(1966).

6) A referee pointed out the possibility that the halo-solvent decomposed on irradiation to produce the radicals which enhanced the reaction of the imine 1. However, the authors do not believe so because the reaction is very clear and no byproduct containing the halogen atom was detected in the present reaction.

7) M.Saeki, N.Toshima, and H.Hirai, Bull.Chem.Soc.Japan, 48, 476(1975) and references cited therein.

8) P.J.Wagner, J.Chem.Phys., 45, 2335(1966). D.R.Kearns and W.A.Case, J.Amer. Chem.Soc., 88, 5087(1966).

9) S.Asao, N.Toshima, and H.Hirai, to be published.

10) The lowest excited triplet state of an imine was shown to be a (π,π^*) state; H.Ohta and K.Tokumaru, Tetrahedron Lett., 2965(1974).

11) The photoreaction from the excited state of a simple acyclic imine was also reported recently; H.Ohta and K.Tokumaru, Chem.Lett., 1403(1974).

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