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An External Heavy Atom Effect upon the Photoreaction of *N*-Acetyldiphenylmethyleneamine in Toluene

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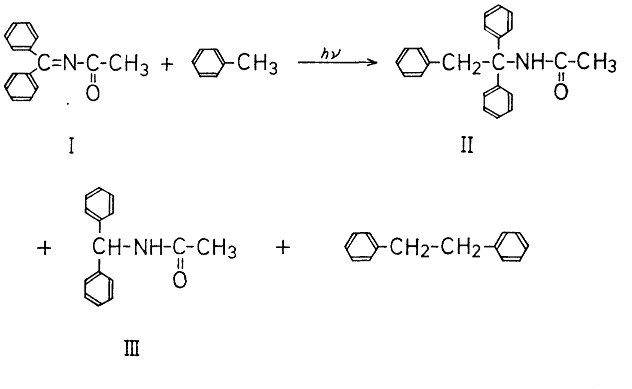
The photochemical conversion of *N*-acetyldiphenylmethyleneamine (I) in toluene to produce an addition product *N*-(1,1,2-triphenylethyl)acetamide and a hydrogenation product *N*-(diphenylmethyl)acetamide has been found to increase remarkably by displacement of *para*-hydrogen of toluene with a halogen (chlorine or bromine). A number of halogenated solvents, especially brominated solvents such as dibromomethane and bromobenzene, also promoted the photoreaction of the imine I with toluene. The extent of the promotion depends on the kind of a halogen atom of the solvent molecule. The reaction rate was accelerated with the number of halogen atoms of the solvent molecule. The conversion rate increased very remarkably when the concentration of bromobenzene increased from 0 to 1 mol/l. The reaction *via* chemical sensitization by benzophenone, a contaminant in imine I, was shown to be insensitive to the heavy atom solvent. The heavy atom effect can be attributed to an increase in the rate of intersystem crossing from the excited singlet state to the triplet state of the imine I. Imine I in the excited state was confirmed to have a hydrogen abstracting character.

The heavy atom effect in the field of molecular photochemistry is known to be a unique phenomenon for spectroscopists.[1–8] It is thought to arise from the increased spin-orbit coupling due to the interaction of the electronic spin with the nucleus of the heavy atom.[9] This effect cannot be observed in the photochemistry of the carbonyl compound. The asymmetry inherent in a carbonyl group was pointed out to produce a sufficient spin-orbit coupling greatly enhancing the rates of *T–S* transitions involving the n,π^* excited state. Such transitions were predicted to be hardly susceptible to heavy atom effects.[7,9]

Although there are many spectroscopic investigations on the heavy atom effect, little is known of the actual increase of the photoreaction yield due to it.[10–14]

Irradiation of a toluene solution of *N*-acetyldiphenylmethyleneamine (*N*-acetyldiphenylketimine, I), an *N*-analogue of α,β-unsaturated ketone, gave *N*-(1,1,2-triphenylethyl)acetamide (II) and *N*-(diphenylmethyl)acetamide (III) in 11 and 4.4% yields, respectively.[15]

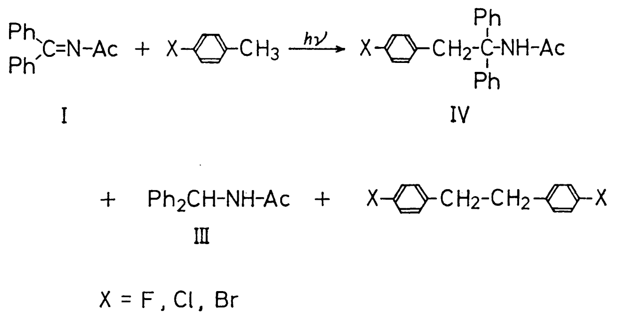


This photoreaction was proposed to proceed not only by the "chemical sensitization" mechanism, but also by the mechanism through the excited state of imine I. In the "chemical sensitization" mechanism, the reaction proceeds *via* an α-acetylamino radical formed by hydrogen atom transfer to imine I from a ketyl radical.[16] The benzophenone ketyl radical is photochemically derived from benzophenone present in the starting imine I as an impurity. Almost all the photoreduction of the imino compounds were proposed to be brought about *via* "chemical sensitization",[17] since the imino compound was easily hydrolyzed to the carbonyl compound which has a hydrogen abstracting character in the excited state.[16] However, we showed that[15] imine I in the excited state has a hydrogen abstracting character, from the fact that the relative reactivity of the substituted toluenes to imine I differs from that to benzophenone,[18] and that the products can be given in the absence of benzophenone based on the investigation of the dependence of the reaction yields on the concentration of benzophenone.

We wish to report the noticeable promotion of the photoreaction rate of imine I with toluene by the heavy atom solvent and the results of research on the heavy atom solvent effects.[19]

Results

Photoreaction of N-*Acetylketimine I with* p-*Halotoluene.* On irradiation of the *p*-halotoluene solution of *N*-acetylketimine I in a Pyrex vessel with a high pressure mercury lamp, the adduct, *N*-[1,1-diphenyl-2-(*p*-halophenyl)ethyl]acetamide (IV) and the hydrogenation product, *N*-(diphenylmethyl)acetamide (III) were obtained. *p*-Fluorotoluene, *p*-chlorotoluene, and *p*-bromotoluene were used as *p*-halotoluenes. The results are shown in Table 1 together with those of toluene as a standard.



The structures of the products were determined from spectroscopic data and elemental analyses (see Experimental).

TABLE 1. PHOTOREACTION OF *N*-ACETYLKETIMINE I WITH *p*-HALOTOLUENE[a]

Solvent	Yield (%)[b]			Relative reactivity	
	Adduct (IV)	Hydrogenation product (III)	Total	I	^{3}Ph$_2$CO[c]
Toluene	4.6	1.2	5.8	1.00[d]	1.00[d]
p-Fluorotoluene	4.2	1.2	5.4	0.93	1.2
p-Chlorotoluene	11.0	4.0	15.0	2.6	0.97
p-Bromotoluene	20.3	24.5	44.8	7.7	—

a) Irradiation was carried out in benzene (5 ml) solution, of 0.23 mol/l of I with *p*-halotoluene (5 ml) in a Pyrex tube for 50 hr with a high pressure Hg lamp. b) Total yield indicates the conversion of the imine I, in this paper, since the remainder is the starting imine only. See Ref. 20. c) Relative reactivity of alkylbenzenes to the triplet state of benzophenone. See Ref. 18. d) Standard.

The results show that the excited state of I has a quite different photoreactivity from that of benzophenone, *viz.*, in the photoreaction of imine I the total yield increased in the order, *p*-fluoro-<*p*-chloro-<*p*-bromotoluene, *p*-bromotoluene vigorously reacting with I. The extremely high reactivity of *p*-bromotoluene to I suggests the contribution of the so-called heavy atom effect on the photoreaction of I.

Heavy Atom Solvent Effects on the Photoreaction of N-*Acetylketimine I with Toluene.* The effect of the heavy atom solvent was investigated as regards the results of the photoreaction of I with *p*-halotoluene. The results are given in Table 2, with the use of 1 or 5 ml of propyl chloride, chlorobenzene, chloroform, propyl bromide, bromobenzene, or dibromomethane as a halogen-containing solvent in 10 ml of the solution of I (0.23 mol/l). The yields[20] increased in the presence of halogenated solvents, especially in brominated ones. Propyl chloride and chlorobenzene showed no significant heavy atom effect in a low (1 ml) concentration, but chloroform showed clearly since it contains a larger number of chlorine in the molecule. Increasing the amount of the chlorinated solvent from 1 ml to 5 ml enhanced the effect. The brominated solvents, on the other hand, were remarkably effective. The reaction yields[20] increased with the bromine content of the solvent molecules in a low (1 ml) concentration, although increasing the amount of the solvent to 5 ml altered the tendency. On irradiation of I in toluene in the presence of ethyl iodide, a deep coloration appeared indicating the depression of the reaction. The yields in the presence of 5 ml of the heavy atom solvent sometimes happened to be lower than those in the presence of 1 ml of the same solvent depending on concentration of toluene (Table 2).

Dependence of the Yield of Photoreaction of N-*Acetylketimine I with Toluene on the Concentration of the Heavy Atom Solvent.* The external heavy atom effect was clarified by the investigation of the relationship between the yield and the concentration of the heavy atom solvent. The photoreaction of I with toluene was carried out using the various concentrations of bromobenzene. The results are shown in Fig. 1. The product yield increased noticeably as the concentration of bromobenzene was increased from 0 to 1.5 mol/l. Further increase in the concentration of the heavy atom solvent, however, resulted in saturation of the increasing yield.

Dependence of the Yield of Photoreaction of N-*Acetylketimine I with Toluene on the Concentration of Benzophenone in the Presence of the Heavy Atom Solvent.* The dependence of the reaction yield upon the concentration of benzophenone was investigated in the presence of bromobenzene. The results are given in Fig. 2 together with those in the absence of bromobenzene.

The amount of benzophenone is the sum of that in the

TABLE 2. SOLVENT EFFECT ON THE YIELDS OF THE PHOTOREACTION OF *N*-ACETYLKETIMINE I WITH TOLUENE[a]

Solvent	Volume of solvent added					
	1 ml[b]			5 ml[c]		
	Adduct, II (%)	Hydrogenation product, III(%)	Total (%)	Adduct, II (%)	Hydrogenation product, III(%)	Total (%)
Benzene	3.4	0.8	4.2	1.3	0.4	1.7
Acetonitrile	—	—	—	1.4	0.2	1.6
Propyl chloride	3.1	0.7	3.8	2.0	1.4	3.4
Chlorobenzene	3.1	0.7	3.8	3.7	1.9	5.6
Chloroform	5.0	2.0	7.0	6.0	2.2	8.2
Propyl bromide	6.8	3.6	10.4	17.6	5.8	23.4
Bromobenzene	8.3	5.2	13.5	15.5	6.1	21.6
Dibromomethane	13.5	4.3	17.8	14.3	5.5	19.8

a) Irradiation was carried out with 0.23 mol/l of I 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 milliliter of the solvent listed and 5 ml of toluene were used.

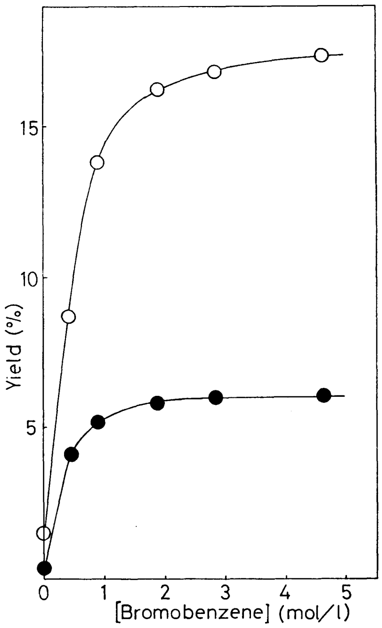


Fig. 1. Dependence of the yields of the photoreaction of *N*-acetylketimine I upon the concentration of bromobenzene in toluene: Adduct (○), hydrogenation product (●); [*N*-Acetylketimine] 0.23 mol/l, [Toluene] 5 ml: Irradiation was carried out above 300 nm for 30 hr at 25 °C.

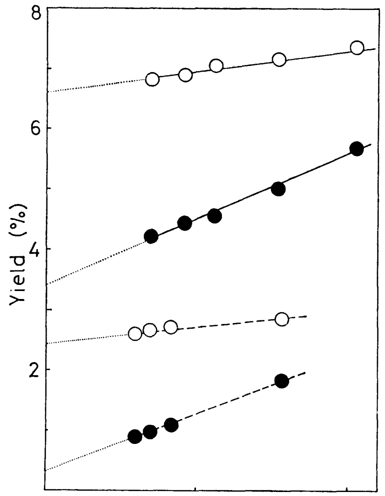


Fig. 2. Dependence of the yields of the photoreaction of *N*-acetylketimine I (0.23 mol/l) with toluene upon the concentration of benzophenone in the presence (—) (Toluene, 9 ml; Bromobenzene, 1 ml), and the absence (---) (Toluene, 10 ml) of bromobenzene: Adduct (○), hydrogenation product (●); irradiation was carried out above 300 nm for 30 hr at 25 °C.

starting imine I as an impurity determined by glpc and that added separately. The yields of both products increased linearly with the concentration of benzophenone, each slope in the presence of bromobenzene being nearly the same as that in its absence, respectively. The full and dashed lines indicate the experimental data and the dotted lines show the extrapolation of the results.

Discussion

The heteroaromatic compound containing a nitrogen atom has been thoroughly investigated both in spectroscopy and in photochemical reactions.[21] The simple acyclic compound containing a C=N bond shows very low photoreactivity,[17,22] and no photoemission.[17] Since the excited state of *N*-acetylketimine I cannot be clarified in spectroscopy, it is difficult to determine its photoreaction mechanism. The sensitization experiment, a procedure for determining the excited triplet state energy indirectly, are not useful for estimating the energy level of the triplet state, since the sensitizers with the hydrogen abstracting character in their excited states can act as the so-called "chemical sensitizer."[17] Sensitization technique is inadequate for determining the triplet state of I, since the sensitizer of a low triplet energy with a hydrogen abstracting character can promote the reaction of I.

Reaction Processes and Heavy Atom Effects. From the results of previous investigation, we proposed a reaction scheme as follows:[15]

Scheme 1.

$$\mathrm{D} \xrightarrow{h\nu} {}^3\mathrm{D} \tag{1}$$

$${}^3\mathrm{D} + \mathrm{RH} \xrightarrow{k_a} \cdot\mathrm{DH} + \cdot\mathrm{R} \tag{2}$$

$$\cdot\mathrm{DH} + \cdot\mathrm{R} \xrightarrow{k_{cc}} \mathrm{DHR} \tag{3}$$

$$2\dot{\mathrm{D}}\mathrm{H} \xrightarrow{k_D} \mathrm{DH_2} + \mathrm{D} \tag{4}$$

$$2\dot{\mathrm{R}} \xrightarrow{k_c} \mathrm{R_2} \tag{5}$$

$$\mathrm{B} \xrightarrow{h\nu} {}^3\mathrm{B} \tag{6}$$

$${}^3\mathrm{B} + \mathrm{RH} \xrightarrow{k_a'} \cdot\mathrm{BH} + \cdot\mathrm{R} \tag{7}$$

$$\cdot\mathrm{BH} + \mathrm{D} \xrightarrow{k_h} \cdot\mathrm{DH} + \mathrm{B} \tag{8}$$

where D is *N*-acetylketimine I, RH is toluene, B is benzophenone, ·DH is the α-amino radical derived from D by the hydrogen atom abstraction, ·BH is a benzophenone ketyl radical, and DHR and DH_2 are the adduct and the hydrogenation product, respectively.

For a detailed discussion of the external heavy atom effect, the primary processes (Eqs. 1 and 6) should be separated more precisely as shown in Scheme 2.

Scheme 2.

$$\mathrm{D} \xrightarrow{h\nu} {}^1\mathrm{D} \tag{1a}$$

$${}^1\mathrm{D} \xrightarrow{k_{1c}} \mathrm{D} \tag{1b}$$

$${}^1\mathrm{D} \xrightarrow{k_{1s}} {}^3\mathrm{D} \tag{1c}$$

$${}^3\mathrm{D} \xrightarrow{k_d} \mathrm{D} \tag{1d}$$

$$\mathrm{D} \xrightarrow{h\nu'} {}^3\mathrm{D} \tag{1e}$$

$$\mathrm{B} \xrightarrow{h\nu''} {}^1\mathrm{B} \tag{6a}$$

$$^1\mathrm{B} \xrightarrow{k_{\mathrm{ic}}'} \mathrm{B} \tag{6b}$$

$$^1\mathrm{B} \xrightarrow{k_{\mathrm{is}}'} {}^3\mathrm{B} \tag{6c}$$

$$^3\mathrm{B} \xrightarrow{k_{\mathrm{d}}'} \mathrm{B} \tag{6d}$$

$$\mathrm{B} \xrightarrow{h\nu'''} {}^3\mathrm{B} \tag{6e}$$

All possible processes influenced by the heavy atom effect should be considered. They are: (a) an intersystem crossing from the lowest singlet state to the triplet state of the imine I or benzophenone (Eqs. 1c and 6c), (b) a radiative or radiationless decay from the lowest triplet state to the ground state (Eqs. 1d and 6d), (c) light absorption to the triplet state directly from the ground state (Eqs. 1e and 6e), and (d) coupling of two radicals (Eqs. 3 and 5).

A heavy atom promotes the S–$T_{\pi,\pi}$ transition, but not S–$T_{n,\pi}$ transition.[7,23] In fact, no external heavy atom effect on the yield of the photoreaction of I with toluene was observed on irradiation with light over 390 nm in the presence of benzil. Since light in this region can be absorbed by benzil[24] but not by I or benzophenone, the lowest n,π^* triplet state of benzil not being influenced by the heavy atom effect, the reaction yields were insensitive to the heavy atom solvent. Consequently the processes of Eqs. 6c and 6d (the rate constants of which are k'_{is} and k'_{d}, respectively) and the transition from the ground singlet state to the excited triplet state of benzophenone (Eq. 6e) should not be susceptible to the heavy atom effect.

The heavy atom effect was negligible for the direct excitation from a ground state to a triplet state of imine I (Eq. 1e), since the toluene solution of imine I under the usual reaction conditions exhibited no S_0–T absorption in the presence of the heavy atom solvent.

A possible process influenced by a heavy atom solvent other than those described above is the hydrogen abstraction step of imine I (Eq. 2). In this process the halo-solvent would act as a polar solvent rather than as a heavy atom solvent. But this is not true since acetonitrile, a polar solvent, exerts no solvent effect (see Table 2). Another possibility is that the halo-solvent decomposes on irradiation to produce radicals which accelerate the photoreaction of I with toluene. In order to exclude this possibility, the heavy atom effect of 1-bromopropane and 2-bromopropane were compared. If the breaking of the C–Br bond occurred on irradiation of bromopropane under the present conditions, the effect of 2-bromopropane would be much larger than that of 1-bromopropane. The experiments indicated a tendency rather contrary to the hypothesis. (Total yield in 1-bromopropane is 5.2% and in 2-bromopropane 3.9% under the same conditions with the use of a merry-go-round type apparatus.)

Consequently, the processes of Eqs. 1c and 1d (k_{is} and k_{d}, respectively) are noticeably susceptible to the heavy atom solvent.

Comparison of the Two Main Processes Effected by the Heavy Atom Solvent. A heavy atom solvent influences the rate of the processes of Eqs. 1c and 1d. The next problem is whether the rate of the process of Eq. 1c or that of Eq. 1d is much more influenced by a heavy atom solvent. The heavy atom effect on the rate constant k_{is} causes an increase in the product yield, and the effect on the rate constant k_{d} a decrease in it.

The increasing reactivity of imine I in the heavy atom solvent demonstrates the influence of the heavy atom effect on the increase in the rate of process of Eq. 1c (k_{is}) in the present case. The results of the photoreaction of imine I with toluene in the presence of various amounts of bromobenzene are shown in Fig. 1, which shows a typical saturation curve.[10]

There are two possible mechanisms to explain the saturation in yields when a large amount of bromobenzene is added: One is the balance between the two successive processes, *i.e.*, the intersystem crossing process from the excited singlet state to the triplet state and the deactivation process from the excited triplet state to the ground state. The quantum yield of the intersystem crossing is known to increase greatly in the presence of a small amount of the heavy atom solvent, being effected to a greater extent by the heavy atom solvent than that of the radiative and radiationless decay.[4] However, when a greater amount of a heavy atom solvent is added, the increment of the intersystem crossing quantum yield becomes small, and the rate of the radiative and radiationless deactivation processes begins to increase gradually, the total yield of the photoreaction of imine I with toluene reaching saturation. If an extremely heavy atom solvent is used, the balance would break resulting in a decrease in the product yield.[25] However, this has not yet been reported to occur in the brominated solvent.

As regards the other explanation for the saturation, the total yield of the photoreaction depends only on the quantum yields of the intersystem crossing, which reach the upper limit at a high concentration of a heavy atom solvent, since only a limited number of heavy atoms can exist in the definite surroundings of an imine molecule under these conditions according to the special interaction between imine I and a heavy atom solvent molecule. In this case, it is assumed that the rate of deactivation of the excited triplet to the ground state is not so susceptible to the heavy atom solvent, or the rate of the intersystem crossing is great enough to neglect that of the deactivation process. The assumption is valid since the deactivation process of an imino compound from its excited triplet to the ground state has been proposed to be very rapid.[17] It is impossible in the present stage to determine which of the two views is adequate because of the absence of the means to see the excited state of *N*-acetylketimine I precisely.

Dependence of the Heavy Atom Effect upon the Kind of Halogenated Solvents. A strong evidence for the external heavy atom effect on the present photoreaction is that the photoreaction yield is dependent on the kind of solvent (Table 2). On irradiation of imine I in toluene with 1 ml of a chlorinated solvent, the reaction rate was promoted only by chloroform which contains three chlorine atoms in a molecule, while no promotion of the reaction rate was observed with 1 ml of propyl chloride or chlorobenzene having one chlorine atom in a molecule. However, the presence of 5 ml of each kind of chlorinated solvent in the solution slightly increased the reaction yield. On the other hand, 1 ml of each kind of brominated solvent in the reaction system drastically promoted the reaction of imine I to the same extent as did 5 ml of the bromo-solvent. The dependence of the yield on the kind of 1 ml of brominated solvent is contrary in the order to that of 5 ml of the solvent. The curious result suggests that the concentration of the bromo-solvent where the saturation of the heavy atom effect occurs is depending on the kind of brominated solvent. Namely, the reaction yield in the presence of 1 ml of dibromomethane could already start to saturated by the same way as shown in Fig. 2 or to decrease from the upper limit by the same way as proposed by Cowan and Koziar.[25]

The effect of a heavy atom solvent on the probability of the transitions in the present photoreaction can be attributed to the indirect mixing mechanism.[8,9,26,27] The singlet state of the solute is mixed electrostatically with the singlet state of the solvent, while the triplet state of the solute is mixed with the triplet state of the solvent. Since the solvent contains a heavy atom, the singlet and triplet states of the solvent are strongly mixed by a spin-orbit interaction. The allowedness of the solvent S–T transition relaxes the spin forbiddenness of the solute S–T transition under consideration.

The probability (P) of the transition has been proposed to be proportional to the square of the spin-orbit coupling parameter (ζ) of the solvent:

$$P \propto \zeta^2$$

Some experimental results were discussed in terms of ζ.[1,4,10] A certain correlation between the photoreaction of *N*-acetylketimine I and the ζ values of the heavy atom solvent is expected. The total product yields in the presence of 1 ml of the halo-solvent of Table 2 are plotted in Fig. 3 against the square of the ζ value of the various kinds of solvents. The yield and the square of the ζ value roughly show a linear relationship. This clarifies the fact that the solvent in this reaction shows an external heavy atom effect and that the mechanism we proposed is in good agreement with the experimental results.

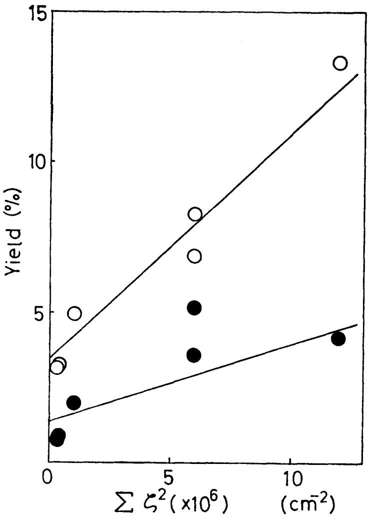


Fig. 3. Dependence of the yields of the photoreaction of *N*-acetylketimine I with toluene on $\sum$ (ζ^2) values of the heavy atom solvents: Adduct (○), hydrogenation product (●).

The other explanation proposed for the external heavy atom effect is the charge transfer complexation between the solute and the solvent.[4] The contribution of the charge transfer interaction might be small in our case, since the toluene solution of imine I in dibromomethane showed no absorption in an electronic spectrum. However, the yield in the presence of 1 ml of bromobenzene was larger than in propyl bromide, which result might be due to the acceptor character of the solvents, since no difference is expected in their ζ values. The charge transfer mechanism would be concluded to contribute a little to the photoreaction of imine I.

Relationship between Heavy Atom Effects and Chemical Sensitization. The spectroscopic data from the excited benzophenone was insensitive to the heavy atom solvent.[7] This is in line with the present finding that the effect of benzophenone exhibits no difference in the presence and the absence of a heavy atom solvent in the photoreaction of imine I with toluene. The product yields increase linearly with increasing amount of benzophenone both in benzene and bromobenzene, and the slopes of the line for the adduct and the hydrogenation product yields in the presence of the heavy atom solvent are nearly the same as those without any heavy atom solvent, as shown in Fig. 2. The photoreaction influenced by benzophenone is indifferent to the heavy atom effect. This result is in line with the conclusion that benzophenone can act only as a chemical sensitizer.[15]

The polar effect by the halogenated solvents was not observed in the reaction (Fig. 2), just as the photoreaction of I with toluene in acetonitrile showed no difference from that in benzene (Table 2). This result shows that the reaction *via* chemical sensitization by benzophenone is not influenced by the polar effect. It can be concluded that most parts of the products were produced *via* the excited state of imine I not *via* chemical sensitization in the presence of the heavy atom solvent.

Reaction State of N-*Acetylketimine I.* A point of further interest in connection with the photoreaction of imine I was its reactive state. In the present photoreaction, a high pressure mercury lamp with a Pyrex filter was used for irradiation. Imine I has a π-π^* absorption maximum at 250 nm and tailing with shoulders above 300 nm.[15] It is difficult to say whether the lowest excited singlet state is a π,π^* state or a n,π^*. On the basis of our previous work and the present results of the heavy atom effect,[15] it was confirmed that the reactive state was the excited triplet state of imine I. The observed heavy atom effects on its photochemical behavior support the view that the lowest excited triplet state has a π,π^* character. However, a hydrogen abstracting character may usually belong to the $T_{\mathrm{n},\pi}$ state.[28] Consequently, it could be concluded that $T_{\pi,\pi}$ and $T_{\mathrm{n},\pi}$ states lie closely and are mixed with each other in the case of imine I.

The photoreaction of *N*-acetylketimine I with toluene was noticeably susceptible to the heavy atom solvent and the yields of the adduct and the hydrogenation product remarkably increases in the presence of the heavy atom solvent. Though the imino compound has been explained to be not the active hydrogen-abstracting species on irradiation and the photoreduction of the imino compound has been interpreted by a chemical sensitization mechanism, the hydrogen abstracting character of the excited state of imine I is strongly supported by the external heavy atom effect.

Experimental

Materials. Toluene and benzene (Yoneyama Chemical Industry) were dried over sodium by refluxing and distilled. *p*-Fluorotoluene, *p*-chlorotoluene, *p*-bromotoluene, propyl chloride, propyl bromide, and dibromomethane (Tokyo Chemical Industry), and chlorobenzene and bromobenzene (Yoneyama Chemical Inductry) were dried over anhydrous magnesium sulfate and distilled. Benzophenone (Yoneyama Chemical Industry) and benzil (Tokyo Chemical Imdustry) were recrystallized from ethanol. *N*-Acetyldiphenylmethyleneamine (I), bp 168—170 °C/1 mmHg (lit,[29] bp 168—170 °C/1 mmHg), was prepared by the reaction of diphenylmethyleneamine[29] with acetic anhydride and distilled repeatedly.[30]

Instrumentation. Most comparative runs were carried out on a "merry-go-round" type reactor (Riko Kagaku Ltd.) with a turntable device holding ten rotating Pyrex tubes. This turntable also rotates around the irradiation lamp in a water cooled quartz immersion well. The turntable and tubes are held in a constant temperature water bath maintained at 25 °C. Irradiation was carried out with a 500 W high pressure mercury lamp (Eikōsha Ltd.). Glpc analysis was accomplished on an Ohkura Rikagaku gas chromatograph employing a 2 m × 3 mmϕ stainless steel column packed with 10% Apiezon Grease L on 60—80 mesh Chromosorb W (HP). High speed liquid chromatography was taken on a Waters ALC-202 high speed liquid chromatograph with a 600 type high pressure pump, a U6K universal injector, and a 660 type solvent programmer. A stainless steel column with Microporasil and chloroform as an eluting solvent were used. Infrared spectra were obtained on a JASCO IR-E spectrometer. NMR spectra were recorded on a JEOL PS-100 or a Hitachi Perkin-Elmer R-20B spectrometer. Mass Spectra were taken on a Hitachi RMS-4 spectrometer. Melting point was determined on a Yanagimoto micro melting point apparatus, and was not corrected.

Photoreaction of N*-Acetylketimine I with* p*-Fluorotoluene.* A *p*-fluorotoluene (30 ml) solution of *N*-acetylketimine I (0.14 mol/l) in a Pyrex tube was degassed in three successive freeze-thaw cycles, and was irradiated under nitrogen with a 500 W high pressure mercury lamp for 100 hr. After irradiation, *p*-fluorotoluene was distilled off at a reduced pressure and the residue were separated by a column chromatography on 100 mesh Marincrodt silica gel. The fraction eluted with benzene contained I. The adduct and the hydrogenation product were eluted separately with chloroform in 4.2 and 1.2% yields, respectively. Yields mean per cent conversion of the starting imine I.[20] The remainder of the imine was recovered in each case. These products were purified by repeated recrystallization from the mixed solvent of cyclohexane and ethanol. The hydrogenation product was identified by comparing the spectral data and by the fact that no melting point depression took place with an authentic sample.[22] The structure of the adduct (mp 197.0—197.7 °C) was inferred from its composition (Found: C, 79.52; H, 6.18; N, 4.49; F, 5.60%; mol wt, 333 by mass spectra. Calcd for $C_{22}H_{20}NOF$: C, 79.23; H, 6.06; N, 4.20; F, 5.70%; mol wt, 333.2.) and the spectral data: The infrared spectra had an amide absorption (ν_{NH}, 3400; ν_{CO}, 1600; δ_{NH} 1530 cm^{-1}) and NMR spectra in $CDCl_3$ showed ten phenyl protons at δ 7.32—6.84, an NH proton at δ 6.15, two methylene protons at δ3.92, and three acetyl protons at δ1.95. The A_2B_2 pattern of four phenyl protons of *p*-fluorobenzyl group splitts into two quartets (δ 6.82, 6.74, 6.60, 6.52; J=8 Hz: δ 6.74, 6.66, 6.54, 6.46; J=8 Hz).

Photoreaction of N*-Acetylketimine I with* p*-Chlorotoluene.* A *p*-chlorotoluene (30 ml) solution of *N*-acetylketimine I (0.14 mol/l) was irradiated under the same conditions as in the photoreaction of imine I with *p*-fluorotoluene, the adduct and the hydrogenation product being obtained in 11.0 and 4.0% yields, respectively. The structure of the adduct was identified as *N*-[1,1-diphenyl-2-(*p*-chlorophenyl)ethyl]acetamide mp 224.0—224.8 °C. Found: C, 75.80; H, 5.57; N, 4.30; Cl, 10.37%; mol wt, 349 by mass spectra. Calcd for $C_{22}H_{20}NOCl$; C, 75.51; H, 5.78; N, 4.00; Cl, 10.14%; mol wt, 349.6. Infrared spectra had an amide absorption (ν_{NH}, 3325; ν_{CO}, 1657; δ_{NH}, 1525 cm^{-1}). NMR spectra showed ten phenyl protons at δ 7.60—6.85, four phenyl protons of A_2B_2 pattern specific for *p*-disubstituted benzene at δ 7.02, 6.96, 6.53, and 6.47 with J=6 Hz, an NH proton at δ 6.10, two methylene protons at δ 3.93, and three methyl protons at δ 1.94.

Photoreaction of N*-Acetylketimine I with* p*-Bromotoluene.* A solution of *N*-acetylketimine I (0.14 mol/l) with *p*-bromotoluene (30 ml) was irradiated under similar conditions to those described before, the adduct and the hydrogenation product being obtained in 20.3 and 24.5% yields, respectively. The adduct was determined as *N*-[1,1-diphenyl-2-(*p*-bromophenyl)ethyl]acetamide: mp 223.0—223.6 °C. Found: C, 67.04; H, 5.12; N, 3.60; Br, 20.24%; mol wt, 394 by mass spectra. Calcd for $C_{22}H_{20}NOBr$: C, 66.99; H, 5.13; N, 3.55; Br, 20.25%; mol wt, 394.1. NMR analysis (in $CDCl_3$) showed ten phenyl protons (δ 7.46—6.78), four phenyl protons of A_2B_2 pattern specific for *p*-disubstituted benzene (δ 7.17, 7.09, 6.52, 6.44; J=8 Hz), an NH proton (δ 6.15), two methylene protons (δ 3.92), and three acetyl protons (δ 1.96), and IR spectra had an amide absorption (ν_{NH}, 3325; ν_{CO}, 1657; δ_{NH}, 1530 cm^{-1}).

Effect of the Solvents and Benzophenone Added. The benzene solution of *N*-acetylketimine I (2.3 mmol) and toluene (5 ml) with or without benzophenone in the presence of a certain amount of heavy atom solvents in a Pyrex tube was degassed in three successive freeze-thaw cycles and irradiated under nitrogen with a 500 W high pressure mercury lamp at 25±1 °C for 30 hr using a merry-go-round type reactor. After irradiation, toluene was distilled off at reduced pressure and the residue was analyzed by a gas chromatography equipped with a 2 m × 3 mmϕ column on 10% Apiezon Grease L 60—80 mesh Chromosorb W(HP) or a high speed liquid chromatography on Microporasil using chloroform as an elution solvent. Yields were shown in terms of per cent conversion of the starting imine I. The remainder of the imine was recovered in each case.[20]

Dependence of the Yields of the Photoreaction of N*-Acetylketimine I upon the Concentration of Bromobenzene.* Ten milliliters of benzene solutions containing 0.23 mol/l of *N*-acetylketimine *I*, 5 ml of toluene, and various amounts of bromobenzene (0—4.3 mol/l) were placed in Pyrex tubes, which were then degassed in three freeze-pump-thaw cycles, substituted by nitrogen, and irradiated with 500 W high pressure mercury lamp at 25±1 °C for 30 hr using a merry-go-round type reactor. The reaction mixtures were analyzed by a high speed liquid chromatography employing a stainless steel column with Microporasil using chloroform as an eluting solvent. Results are shown in Fig. 1. Yields are given in terms of per cent conversion of the starting imine I.[20]

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