Photoreduction and Photoaddition of *N*-Acetyldiphenylmethyleneamine in Alkylbenzenes

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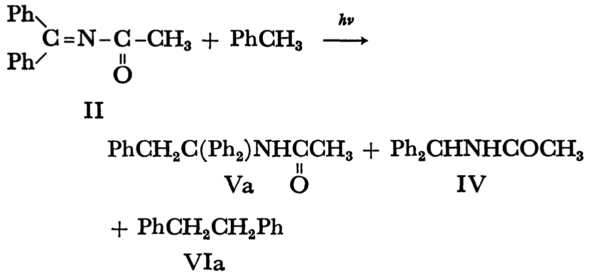
Irradiation of *N*-acetyldiphenylmethyleneamine (II) in toluene solution gave *N*-(1,1,2-triphenylethyl)acetamide and *N*-(1,1-diphenylmethyl)acetamide in 11% and 4.4% yields, respectively. The former is an addition product of toluene to the C=N bond of imine II, and the latter a hydrogenation product of II. The same kind of addition and hydrogenation products as those in toluene were obtained on irradiation of imine II in ethylbenzene, cumene, *o*-, *m*-, and *p*-xylene, mesitylene, *p*-methoxytoluene, and *p*-cyanotoluene, respectively. Two kinds of competitive reaction processes are proposed from the results of the substituent effects for the phenyl ring of toluene, the effect of the additives such as sensitizers and quenchers, and the dependence of the photoreaction yields on the concentration of the additive. The photoreaction proceeds not only by the "chemical sensitization" mechanism derived from the ketyl radical of benzophenone, a hydrolyzed product of II, but also by the mechanism through the excited state of II itself.

The photochemical behavior of acyclic imines is not very clear,[1-12] although it is well-known that heteroaromatic compounds containing nitrogen actively undergo photochemical reactions.[13] The photoreduction of benzophenone imine derivatives in particular has been investigated in detail.[1,3,4] On irradiation of diphenylmethyleneamine (I) in 2-propanol, benzhydrylamine and *N*-benzhydrylidenebenzhydrylamine were produced instead of a dihydro dimer of I corresponding to benzpinacol given by the photoreduction of benzophenone.[3] *N*-Alkyldiphenylmethyleneamine was also reduced photochemically on its C=N bond, the reaction mechanism being proposed by Fischer and Padwa as a "chemical sensitization" process.[1,4,14-18] "Chemical sensitization" means that the ketyl radical, derived photochemically from the carbonyl compound present in the starting materials as an impurity, transfers a hydrogen atom to the imine without any energy transfer. On the other hand, high photochemical reactivity of α,β-unsaturated ketones suggests that the imino ketone, the N-analogue of an enone, would undergo the photochemical reaction expected to be brought about *via* the excited state of itself.

In a previous paper,[19] the photoreduction of *N*-acetyldiphenylmethyleneamine (II) (*N*-acetyldiphenylketimine) in 2-propanol was reported to give *N*-diphenylmethylacetamide (IV). We now wish to report that the addition product and the hydrogenation product on the C=N bond were obtained on irradiation of imine II in several alkylbenzenes, indicating that the excited state of imine II has the character of hydrogen abstraction though it was generally proposed that the C=N group should scarcely abstract a hydrogen.[20]

Results

Photoreaction of N-*Acetyldiphenylketimine (II) with Toluene.* The toluene solution of *N*-acetyldiphenylketimine (II) in a quartz tube was irradiated under nitrogen atmosphere with a 500 W high pressure mercury lamp for 100 hr. After irradiation toluene was distilled off and three products were separated by column chromatography on silica gel: *N*-diphenylmethylacetamide (IV), *N*-(1,1,2-triphenylethyl)acetamide (Va), and dibenzyl (VIa) in 4.4%, 11%, and 3.4% yields, respectively.



$$\mathrm{Ph_2C{=}N{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3} \;(\text{II}) + \mathrm{PhCH_3} \xrightarrow{h\nu} \mathrm{PhCH_2C(Ph_2)NH\underset{\underset{\displaystyle O}{\|}}{C}CH_3}\;(\text{Va}) + \mathrm{Ph_2CHNHCOCH_3}\;(\text{IV}) + \mathrm{PhCH_2CH_2Ph}\;(\text{VIa})$$

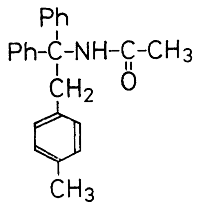
The remainder was the starting material. Compound IV was the same as that given on irradiation of II in 2-propanol: *i.e.*, it was identified by spectral data which included infrared absorption (3245, 1646, 1544 cm^{-1}) for the amide group, and the NMR spectrum at δ 7.07—7.46 (10H, m) for aromatic protons, δ 6.00—6.51 (m) for an amide proton, δ 1.97 (3H, s) for acetyl protons, and δ 1.77 (m) for a methine proton. Structure IV was further confirmed by comparing the spectral data with those of the authentic sample. Compound VIa was the coupling product of benzyl radicals brought about on hydrogen abstraction. Amide Va was the adduct of toluene to II. This kind of adduct was obtained on the photoreaction of II in cyclohexene[8] but not in 2-propanol. Structure Va was inferred from its composition ($C_{22}H_{21}NO$) and spectral data which included the infrared absorption bands for an amide group (3326, 1657, 1546 cm^{-1}), and confirmed by the NMR spectrum showing acetyl protons (3H, δ 1.94, s), aromatic protons (15H, δ 6.40—7.42), an amide proton (δ 6.17, m), and methylene protons (2H, δ 3.92) originating from toluene.

Photoreaction of N-*Acetylketimine II with Alkylbenzenes and Relative Reactivities of Alkylbenzenes.* On irradiation of II in substituted toluenes, the reactions proceeded *via* hydrogen atom abstraction from alkylbenzenes, the adducts, hydrogenation products and dimeric hydrocarbons being obtained. Irradiation of II in *p*-methyltoluene (*p*-xylene) gave Vb (37%) and IV (14%). Structure Vb was determined as *N*-[1,1-diphenyl-2-(*p*-tolyl)ethyl]acetamide by its NMR spectrum data. It showed signals for methyl protons (δ 2.22) derived from *p*-xylene, and fourteen aromatic protons, four

TABLE 1. PHOTOREACTION OF *N*-ACETYLKETIMINE II WITH ALKYLBENZENES(III)[a)]

Subscript	Alkylbenzene (III)	Product yield (%)[b)] Hydrogenation product (IV)	Adduct (V)	Relative reactivity toward $^3Ph_2CO$[c)]
a	Toluene	4.4	11	1.0
b	*p*-Xylene	14	37	4.3
c	Mesitylene	18	38	5.6
d	Ethylbenzene	11	25	3.3
e	Cumene	16	40	2.3

a) Irradiation was carried out in a quartz tube with an Eikōsha 500 W high pressure mercury lamp for 100 hr. Concentration of II was 0.14 mol/l and volume of III was 30 ml. b) Yields refer to the conversion in this paper, *i.e.*, the remainder is the starting imine. c) See Ref. 21.



Vb

of which showed the typical A_2B_2 signal pattern of *p*-disubstituted benzene. Only one methyl group of *p*-xylene was concerned with the addition reaction. In ethylbenzene *N*-(1,1,2-triphenyl-*n*-propyl)acetamide (Vc, yield 25%), *d,l*- and *meso*-2,3-diphenylbutane, and IV (yield 11%) were obtained. The reaction occurred *via* hydrogen atom abstraction in a benzylic position, not in a methyl group. These results and the yields of the reaction in other alkylbenzenes are summarized in Table I. Product yields were determined by glpc (Apiezon greese L on Chromosorb W(HP)). As the adduct of ethylbenzene was not detectable by glpc, the yield of Vd was given by the remainder after subtracting the yield of IV in glpc from that of the mixtures of Vd and IV obtained by column chromatography on silica gel. The same method was applied to the yield of the adduct of cumene.

TABLE 2. DEPENDENCE OF THE PHOTOREACTION YIELD OF *N*-ACETYLKETIMINE II WITH TOLUENE IN THE PRESENCE OF SEVERAL ADDITIVES[a)]

Additive	E_T[b)] (kJ/mol)	Yield (%) Adduct	Hydrogenation product
None		2.5	0.94
Xanthone	310	10	28
Triphenylamine	295	1.2	1.1
Benzophenone	290	12	12
Triphenylene	280	1.1	1.2
Diacetyl	235	6.6	1.4
Benzil[c)]	220	5.2	1.7
Fluorenone	220	0.40	0.27
1-Methylnaphthalene	250	0.36	0.20

a) Irradiation was carried out in toluene (10 ml) solution with 0.23 mol/l of II and 4.3×10^{-2} mol/l of additives in a pyrex tube for 30 hr unless otherwise stated. b) See Ref. 22. c) Irradiation with light of wave lengths greater than 390 nm for 60 hr.

Effect of Additives on the Photoreaction of N-*Acetylketimine II with Toluene upon Additives.* The photoreaction of II with toluene was carried out in the presence of several additives (Table 2). The toluene (10 ml) solution of II (0.23 mol/l) with benzophenone (0.043 mol/l) in a pyrex tube under nitrogen was irradiated with a 500 W high pressure mercury lamp at 25 °C. After 30 hr irradiation IV (yield 12%) and Va (yield 12%) were obtained.

When 1-methylnaphthalene was used in this photoreaction instead of toluene, no photoreaction of II was observed. This can be explained by quenching of the photoreaction of II with 1-methylnaphthalene. On the basis of this result, quenching studies were carried out with naphthalene. The results indicate a Stern-Volmer relationship for product appearance (Fig. 1). The slope for Va is 2.46×10^2 l/mol and that for IV is 1.00×10^2 l/mol.

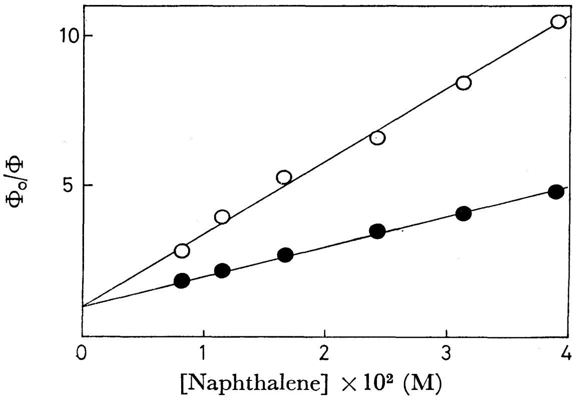


Fig. 1. Quenching of the photoreaction of *N*-acetylketimine II with toluene by naphthalene: Adduct (○), Hydrogenation product (●); [*N*-Acetylketimine] 0.23 mol/l, [Toluene] 10 ml; Irradiation was carried out with above 300 nm for 30 hr at 25 °C.

Dependence of the Photoreaction of N-*Acetylketimine II with Toluene upon the Concentration of Benzil.* The reaction yield increased in the presence of benzil (Table 2). The influence of benzil in the photoreaction was investigated on irradiation of II (0.23 mol/l) in toluene (10 ml) at wavelengths greater than 390 nm with various concentration of benzil. Benzil exhibits its absorption at 370 nm (ε_{max} 78) due to an n-π^* transition, the shoulder of the absorption appearing in the region of wavelengths greater than 390 nm. On the other hand,

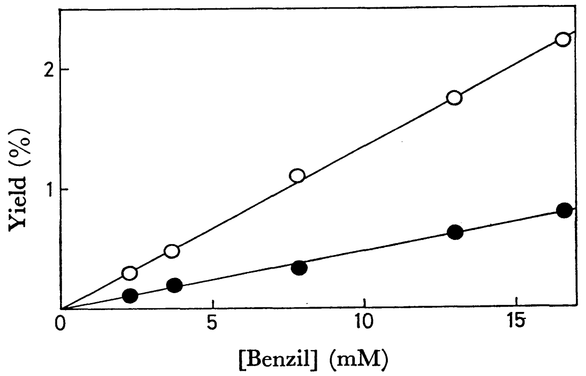


Fig. 2. Dependence of the yields of the photoreaction of *N*-acetylketimine II with toluene on the concentration of benzil: Adduct (○), Hydrogenation product (●); [*N*-Acetylketimine] 0.23 mol/l, [Toluene] 10 ml; Irradiation was carried out above 390 nm for 60 hr at 25 °C.

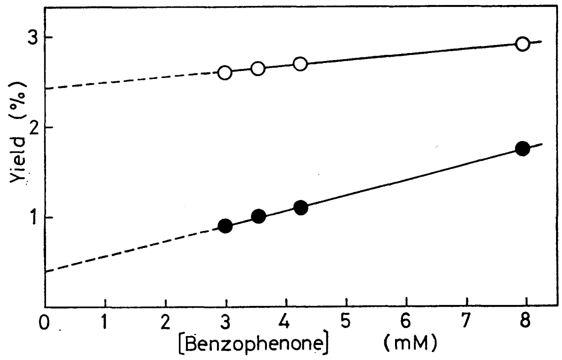


Fig. 3. Dependence of the yields of the photoreaction of *N*-acetylketimine II with toluene on the concentration of benzophenone: Adduct (○), Hydrogenation product (●); [*N*-Acetylketimine] 0.23 mol/l, [Toluene] 10 ml; Irradiation was carried out above 300 nm for 30 hr at 25 °C.

II shows no absorption in the region above 390 nm (Fig. 4, Experimental). No products were obtained at a light above 390 nm without sensitizers, the same results being obtained even with benzophenone under these conditions.[23)] Figure 2 shows the results of the sensitization experiments with II using benzil, the reaction yields increasing linearly with added benzil. The same kind of dependence was observed on the reaction of II with diacetyl. Thus benzil and diacetyl were found to be effective to the reaction as additives.

Dependence of the Photoreaction of N*-Acetylketimine II with Toluene on the Concentration of Benzophenone.* The starting sample II contains a small amount of benzophenone, hydrolysis product of II which is easily hydrolyzed. Benzophenone was added as a chemical sensitizer and was recovered without any change after irradiation. Figure 3 shows the relations of the photoreaction yields *vs.* the total amount of benzophenone which should be the sum of an added amount and a hydrolyzed amount determined by glpc. The full lines indicate the experimental data and the dotted lines the extrapolation of the results. Both products increase in yields linearly with the concentration of benzophenone.

Photoreaction of N*-Acetylketimine II with Substituted Toluenes.* The results of the photoreaction of II with various substituted toluenes are summarized in Table 3. The total yields of the adducts and the hydrogenation products are shown in relative values using the value in toluene as a standard. For the sake of comparison, the relative reactivity of substituted toluenes toward benzophenone triplet is cited.[21)] It is apparent that the reactivity of II differs a great deal from that of benzophenone, in the case of *p*-methoxytoluene. On the reaction of II with three isomers of methyltoluenes (xylenes), the yields decreased in the order *p*-CH_3>*m*-CH_3>*o*-CH_3.

Discussion

Effect of Additives. The mechanism of the photoreaction of II with alkylbenzenes appears to be complicated, since the energy of the excited triplet state of sensitizers is not concerned directly with the sensitization of the reaction of II (Table 2). As an example, benzophenone (E_T=290 kJ/mol) was effective in the reaction as a sensitizer, but not triphenylene (E_T=280 kJ/mol) with nearly the same triplet energy as that of benzophenone. Padwa and co-workers[1)] suggested that benzophenone works as a so-called "chemical sensitizer" in the photoreduction of *N*-benzoyldiphenylketimine (VIII) in 2-propanol. Benzophenone was regarded as not transferring its triplet energy to VIII because of the fact that phosphorescence of benzophenone was not appreciably quenched by VIII. If the photoreduction and photoaddition reaction of II with toluene occurs by "chemical sensitization," the species with a hydrogen abstracting character can play the role of a chemical

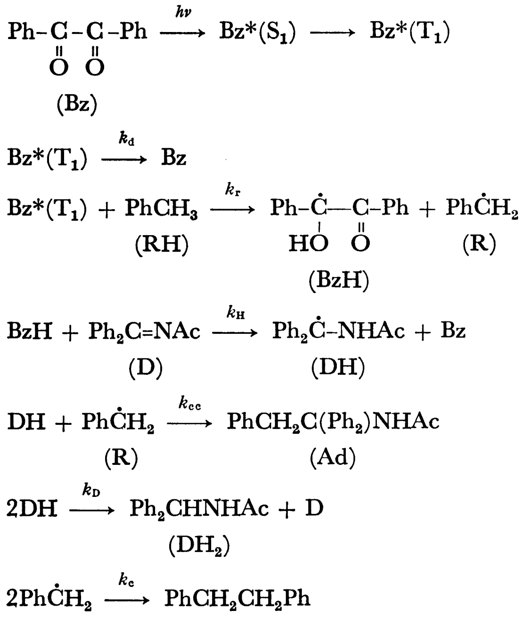
Table 3. Photoreaction of *N*-acetylketimine II with substituted toluene (III)[a)]

Substituted toluene (III)	Yields (%)			Relative reactivity	
	Hydrogenation product (IV)	Adduct (V)	Total (IV+V)	Imine II	$^3Ph_2CO$[b)]
Toluene	1.2	4.2	5.4	1.00[c)]	1.00[c)]
p-Xylene	10	14	24	4.4	4.3
m-Xylene	3.4	8.8	12.2	2.3	2.9
o-Xylene	4.1	6.8	10.9	2.0	—
p-Methoxytoluene	2.0	3.7	5.7	1.1	10.6
p-Cyanotoluene	2.9	2.5	5.4	1.0	—

a) Photoreactions were carried out in a solution of substituted toluene (5 ml), benzene (5 ml), and II (0.23 mol/l) in a pyrex tube with light above 300 nm for 30 hr. b) See Ref. 21. c) Standard.

sensitizer to increase the product yields, regardless of the excitation energy. In fact, triphenylamine with triplet energy higher than that of benzophenone did not sensitize the reaction, but xanthone with a hydrogen atom abstracting character was effective. On irradiation of II above 390 nm, no reaction occurred with or without benzophenone.[23,24] Irradiation of II above 390 nm in toluene in the presence of benzil or diacetyl gave IV and Va. Benzil (E_T=220 kJ/mol) and diacetyl (E_T=235 kJ/mol) with a hydrogen abstracting character exhibit maxima at 370 nm ($\varepsilon_{\max}$ 78) with tailing and at 422 nm ($\varepsilon_{\max}$ 22), respectively,[24,25] indicating n-π^* absorption. Benzil or diacetyl is considered to abstract a hydrogen atom of the triplet state after excitation with light above 390 nm and to transfer it to II. In contrast, fluorenone, whose lowest triplet state is (π, π^*) with E_T=220 kJ/mol, retarded the reaction above 300 nm. Fluorenone is not able to abstract a hydrogen atom from toluene on irradiation,[26] and probably acts as a quencher on irradiation of II in toluene.

Chemical Sensitization of the Reaction of II by Benzil. Benzil is effective as a sensitizer (Table 2) and the photochemical reaction yields of both the adduct and the hydrogenation product increased linearly with benzil added at the wavelengths above 390 nm (Fig. 2). The reaction scheme is proposed as follows (Scheme 1).



$$\underset{\text{(Bz)}}{\text{Ph-}\underset{\text{O}}{\overset{}{\text{C}}}\text{-}\underset{\text{O}}{\text{C}}\text{-Ph}} \xrightarrow{h\nu} \text{Bz}^*(\text{S}_1) \longrightarrow \text{Bz}^*(\text{T}_1)$$

$$\text{Bz}^*(\text{T}_1) \xrightarrow{k_d} \text{Bz}$$

$$\underset{\text{(RH)}}{\text{Bz}^*(\text{T}_1) + \text{PhCH}_3} \xrightarrow{k_r} \underset{\text{(BzH)}}{\text{Ph-}\underset{\text{HO}}{\dot{\text{C}}}\text{—}\underset{\text{O}}{\text{C}}\text{-Ph}} + \underset{\text{(R)}}{\text{Ph}\dot{\text{C}}\text{H}_2}$$

$$\text{BzH} + \underset{\text{(D)}}{\text{Ph}_2\text{C=NAc}} \xrightarrow{k_H} \underset{\text{(DH)}}{\text{Ph}_2\dot{\text{C}}\text{-NHAc}} + \text{Bz}$$

$$\text{DH} + \underset{\text{(R)}}{\text{Ph}\dot{\text{C}}\text{H}_2} \xrightarrow{k_{cc}} \underset{\text{(Ad)}}{\text{PhCH}_2\text{C(Ph}_2\text{)NHAc}}$$

$$2\text{DH} \xrightarrow{k_D} \underset{\text{(DH}_2\text{)}}{\text{Ph}_2\text{CHNHAc}} + \text{D}$$

$$2\text{Ph}\dot{\text{C}}\text{H}_2 \xrightarrow{k_c} \text{PhCH}_2\text{CH}_2\text{Ph}$$

Scheme 1.

Only benzil (Bz) can absorb light above 390 nm to cause excitation, since imine II (D) and benzophenone cannot absorb light in that region. The excited triplet state of benzil [Bz* (T$_1$)] abstracts a hydrogen atom from toluene (RH) and α-amino radical (DH) is formed by hydrogen atom transfer from BzH to II. An adduct (Ad) is obtained by cross-coupling between DH and R. A hydrogenation product (DH$_2$) is produced by disproportionation.

The usual steady-state treatment of Scheme 1 gives the following two equations for the adduct (Ad) and the hydrogenation product (DH$_2$).

$$\frac{\mathrm{d}[\mathrm{DH}_2]}{\mathrm{d}t} = k_D[\mathrm{DH}]^2 = \frac{k_r[\mathrm{Bz}^*(\mathrm{T}_1)][\mathrm{RH}]}{1+k_{cc}(k_Dk_c)^{-1/2}}$$

$$\frac{\mathrm{d}[\mathrm{Ad}]}{\mathrm{d}t} = k_{cc}[\mathrm{DH}][\mathrm{R}] = \frac{k_r[\mathrm{Bz}^*(\mathrm{T}_1)][\mathrm{RH}]}{1+(k_Dk_c)^{1/2}(k_{cc})^{-1}}$$

These equations show that yields of the adduct and the hydrogenation product should be proportional to the concentration of benzil, since [Bz* (T$_1$)] is proportional to [Bz]. The results in Fig. 2 indicate that Scheme 1 is valid. Consequently, the reaction *via* "chemical sensitization" is promoted linearly with the quantity of chemical sensitizer.

Quenching of the Photoreaction of N-*Acetylketimine II in Toluene.* Padwa and co-workers reported on the photoreduction of *N*-(diphenylmethylene)methylamine (IX) in 2-propanol[1] and suggested that the photoreduction of IX occurs *via* "chemical sensitization" due to the fact that a quantum yield of the photoreduction of IX was very low ($\Phi<10^{-3}$) and that only such the sensitizers with a hydrogen abstracting power as benzophenone (Φ=0.66) are effective.

If the photoreaction of II with toluene proceeds only *via* "chemical sensitization," the reaction does not involve the excited state of II as an intermediate and II serves as a hydrogen atom capture. The reaction path on the basis of "chemical sensitization" mechanism in the presence of a quencher can be considered to be that outlined in Scheme 2.

$$\text{Ph}_2\text{CO} \xrightarrow{h\nu} \text{Ph}_2\text{CO}^*(\text{S}_1) \longrightarrow \text{Ph}_2\text{CO}^*(\text{T}_1)$$

$$\text{Ph}_2\text{CO}^*(\text{T}_1) \xrightarrow{k_d} \text{Ph}_2\text{CO}$$

$$\text{Ph}_2\text{CO}^*(\text{T}_1) + \text{PhCH}_3 \xrightarrow{k_r} \text{Ph}_2\dot{\text{C}}\text{OH} + \text{Ph}\dot{\text{C}}\text{H}_2$$

$$\text{Ph}_2\dot{\text{C}}\text{OH} + \text{Ph}_2\text{C=NAc} \xrightarrow{k_H} \text{Ph}_2\dot{\text{C}}\text{NHAc} + \text{Ph}_2\text{CO}$$

$$\text{Ph}_2\dot{\text{C}}\text{NHAc} + \text{Ph}\dot{\text{C}}\text{H}_2 \xrightarrow{k_{cc}} \text{PhCH}_2\text{C(Ph}_2\text{)NHAc}$$

$$2\text{Ph}_2\dot{\text{C}}\text{NHAc} \xrightarrow{k_D} \text{Ph}_2\text{CHNHAc} + \text{Ph}_2\text{C=NAc}$$

$$2\text{Ph}\dot{\text{C}}\text{H}_2 \xrightarrow{k_c} \text{PhCH}_2\text{CH}_2\text{Ph}$$

$$\text{Ph}_2\text{CO}^*(\text{T}_1) + \text{Q} \xrightarrow{k_q} \text{Ph}_2\text{CO} + \text{Q}^*$$

Scheme 2.

The usual steady-state treatment of Scheme 2 gives the Stern–Volmer equation:

$$\frac{\Phi_A{}^0}{\Phi_A} = \frac{\Phi_R{}^0}{\Phi_R} = 1 + \frac{k_q[\mathrm{Q}]}{k_r[\mathrm{RH}]+k_d}$$

where Φ is the quantum yield of the reaction in the presence of a quencher, Φ^0 is that without a quencher, and subscripts A and R denote the adduct and the reduction product, respectively.

This equation being exactly the same as that for benzophenone, the Stern-Volmer plot should coincide with that of benzophenone. In the plot for Φ_A^0/Φ_A *vs.* [Q], the slope for the adduct was 2.46×10^2 l/mol. But the slope of the Stern-Volmer plots on the photoreaction of benzophenone in toluene was reported to be *ca.* 10^3 l/mol[27–32] differing from that for the reaction of II. This difference cannot be explained by the difference of viscosity of the solution between benzophenone and II. In fact, the viscosity of the solution of II in the experiment is 0.573 cp and does not influence the assumption of diffusion control. On the other hand, the slope of the plot for the adduct differs from that of the hydrogenation product. These results suggest that the photoreaction of II with toluene is not explicable by "chemical sensitization" of benzophenon , and that the excited state of II should influence the reaction.

Mechanistic Consideration on the Sensitization Effect of Benzophenone. The photoreaction yields increase linearly with the amount of a chemical sensitizer, and additives such as benzil and benzophenone act as chemical sensitizers.

The photoreaction of II with toluene in the presence of various amounts of benzophenone equal to the sum of an impurity in II and the added compound was investigated to see if the excited state of II could abstract a hydrogen atom from toluene. The linear dependence of the reaction yields on the total concentration of benzophenone (Fig. 3) agrees with the result of the reaction in the presence of benzil (Fig. 2). From the linearity, the plot of the experimental data can be extrapolated to the zero concentration of benzophenone. If the excited state of II cannot abstract a hydrogen atom, the reaction yields should converge on 0% at the point of no benzophenone. Actually, however, Fig. 3 indicates clearly the formation of the adduct and the hydrogenation product in about 2.5% and 0.4% yields, respectively, without benzophenone. These figures indicate exactly the yields of the reactions through the excited state of II.

Consequently, the present photoreaction is explained by the competition reactions between *via* "chemical sensitization" and *via* the excited state of II (Scheme 3).

$$\begin{aligned}
&Ph_2C{=}NAc \xrightarrow{h\nu} Ph_2C{=}NAc^*(S_1) \longrightarrow Ph_2C{=}NAc^*(T_1)\\
&Ph_2C{=}NAc^*(T_1) + PhCH_3 \longrightarrow Ph_2\dot{C}\text{-}NHAc + Ph\dot{C}H_2\\
&Ph_2\dot{C}\text{-}NHAc + Ph\dot{C}H_2 \longrightarrow PhCH_2C(Ph_2)NHAc\\
&2Ph_2\dot{C}\text{-}NHAc \longrightarrow Ph_2CHNHAc + Ph_2C{=}NAc\\
&2Ph\dot{C}H_2 \longrightarrow PhCH_2CH_2Ph\\
&Ph_2CO \xrightarrow{h\nu} Ph_2CO^*(S_1) \longrightarrow Ph_2CO^*(T_1)\\
&Ph_2CO^*(T_1) + PhCH_3 \longrightarrow Ph_2\dot{C}OH + Ph\dot{C}H_2\\
&Ph_2\dot{C}OH + Ph_2C{=}NAc \longrightarrow Ph_2\dot{C}\text{-}NHAc + Ph_2CO
\end{aligned}$$

Scheme 3.

Comparison of the Photoreactivity between N-*Acetylketimine II and Benzophenone.* The ability of hydrogen abstraction by the excited state of II is further emphasized by comparison of the photoreactivity of II with that of benzophenone. Walling and Gibian reported on the photoreduction of benzophenone in substituted toluenes.[21] The rate-determining step of the photoreduction was the process of a hydrogen abstraction,[27–32] the rate constant of formation of benzpinacol by radical reaction of benzophenone ketyl radicals being $3.6 \times 10^9\ M^{-1}\ s^{-1}$.[32] In the case of the reaction of II (0.15 mol/l) with large excess of alkylbenzenes in the presence of 0.25 molar equivalent of benzophenone, benzpinacol was not obtained, at least below 50% conversion, and added benzophenone was recovered without any change. If the reaction proceeds *via* "chemical sensitization" by benzophenone in II as an impurity, the rate for hydrogen atom transfer from a ketyl radical to II should be greater than that of disproportionation of the ketyl radicals. That is, if the situation were contrary, benzpinacol should have been formed on irradiation. In order to explain the photoreaction of II with toluene by "chemical sensitization," the rate-determining step should be the process of hydrogen atom abstraction by benzophenone. The photoreactivity of II with substituted toluenes should then coincide with that of benzophenone. However, the relative reactivity of II with *p*-methoxytoluene differs greatly from that of benzophenone. Furthermore, on irradiation of II with *p*-halotoluenes the adduct and the hydrogenation product increased in yields in the order *p*-F<*p*-Cl<*p*-Br.[33] The order is reverse to that in the photoreduction of benzophenone in *p*-halotoluenes. These findings support existence of the reactive excited state of II.

Hammond and co-workers reported on the photoreaction of benzophenone with alkylbenzenes which gives rise to the formation of benzpinacol, a reduction product, and a cross coupling product of benzophenone ketyl radical with benzyl radical.[34] Their results are shown in Table 4 with the present data of II.

TABLE 4. COMPARISON OF THE PHOTOREACTIVITY OF *N*-ACETYLKETIMINE II AND BENZOPHENONE

Ketone or imine	Alkylbenzene	Yield (%)[a]		
		Benz-pinacol	Hydrogenation product	Adduct
Ph_2CO[b]	$PhCH_3$	51	—	43
Ph_2CO[b]	$PhCH(CH_3)_2$	24	—	48—60
II	$PhCH_3$	—	29	71
II	$PhCH(CH_3)_2$	—	29	71

a) Yield based on the consumed benzophenone or II.
b) See Ref. 34.

The proportion of a cross coupling product in the photoproducts of *N*-acetylketimine II with alkylbenzenes is higher than that of benzophenone. This can be interpreted by the difference between the reaction mechanism of II and that of benzophenone. Although there is no band indicating an intermolecular interaction in the electronic spectra of II with toluene, the differences mentioned above suggest that II interacts with alkylbenzenes weakly in some way.

Experimental

Materials. Alkylbenzene such as toluene, ethylbenzene, *p*-xylene, cumene, and mesitylene (Yoneyama Chemical Industry), and *o*-, *m*-xylene, and, *p*-methylanisole (Tokyo Chemical Industry) were dried over sodium by refluxing and then distilled. Benzophenone (Yoneyama Chemical Industry), xanthone, fluorenone, and benzil (Tokyo Chemical Industry) were recrystallized from ethanol. Triphenylene and triphenylamine (Tokyo Chemical Industry) were used without further purification. Eluting solvents for column chromatography such as cyclohexane, benzene, methylene chloride, chloroform, and ethanol were used in the state they were received.

Instrumentations. Irradiation was performed with a 500

W Halos high pressure mercury lamp (Eikōsha Ltd.). Most comparative runs were carried out on a merry-go-round type reactor (Rikōkagaku Ltd.) with a turntable device holding the rotating pyrex tubes. This turntable also rotated around the lamp in a water cooled quartz immersion well. The turntable and tubes were held in a constant temperature water bath maintained at 25 °C. Glpc analysis was performed with a Ohkura Rikagaku gaschromatograph with a flame ionization detector, equipped with a 2 m × 3 mm ϕ stainless steel column packed with 10% Apiezon Grease L on 60—80 mesh Diasolid A or on 60—80 mesh Chromosorb W(HP). Infrared spectra were obtained using a JASCO IR-E spectrometer. Ultraviolet measurements were carried out on a Shimadzu MPS-50L spectrophotometer. The NMR spectra were recorded on a JEOL PS-100 or a Hitachi Perkin-Elmer R-20B spectrometer. A Hitachi RMS-4 mass spectrometer was used for mass spectrometry. Melting points were determined with a Yanagimoto micro melting point apparatus. Vapor pressure osmometer analyses were carried out on a Mechrolab Inc. Model 301A osmometer.

Preparation of N-*Acetyldiphenylmethyleneamine(II) (*N-*Acetyldiphenylketimine)*.[6,35,36] An ethereal solution of the Grignard reagent from bromobenzene was treated with a stoichiometric amount of benzonitrile. Completion of the decomposition of the Grignard-nitrile complex by addition of methanol gave a pale yellow slurry. The slurry was filtered, and the filtrate was distilled a few times. The fraction of bp 125 °C (1.0 mmHg) was diphenylketimine [lit,[36] bp 127 °C (3.5 mmHg)]. *N*-acetyldiphenylketimine (II) was prepared by refluxing diphenylketimine in twice the number of moles of acetic anhydride for six hr. bp 168—170 °C (1.0 mmHg)] [lit,[35] bp 168—171 °C (1 mmHg)]. UV spectrum of II is shown in Fig. 4.

Preparative Irradiation Procedure. The solution of *N*-acetylketimine II (0.14 mol/l) in toluene (30 ml) in a quartz tube was degassed in three succesive freeze-thaw cycles and irradiated under nitrogen with a 500 W high pressure mercury lamp for 100 hr. The photoreaction mixtures were worked up by evaporation of the solvent at a reduced pressure and separated by column chromatography on silica gel. The reaction mixtures were eluted in succession with 500 ml of cyclohexane, benzene, methylene chloride, chloroform, and ethanol. The coupling products of benzyl radicals were eluted with cyclohexane, and *N*-acetylketimine II and benzophenone, almost the entire amount of which is a hydrolysis product in the silica gel column, were eluted with benzene. The fractions eluted by chloroform contained both the adduct and the reduction product separately. Both products were purified by repeated recrystallization from the mixed solvent of cyclohexane and ethanol, or that of *n*-hexane and ethanol. The structure of the adducts and the coupling products were determined from their spectral data and elemental analyses. The analytical and spectral data are show in Tables 5 and 6. The hydrogenation product [*N*-(1,1-diphenylmethyl)acetamide, IV] was identi-

Table 5. Adducts of *N*-acetylketimine II with alkylbenzenes

Alkylbenzene	mp (°C)	Formula	MW	Elemental Analysis Found C	H	N	Calcd C	H	N
Toluene	167.3—168.0	$C_{22}H_{21}NO$	315	83.74	6.73	4.47	83.77	6.71	4.44
p-Xylene	198.6—199.0	$C_{23}H_{23}NO$	329	83.96	7.09	4.21	83.85	7.04	4.25
m-Xylene	187.5—188.0	$C_{23}H_{23}NO$	329	84.07	7.14	4.47	83.85	7.04	4.25
o-Xylene	186.6—187.3	$C_{23}H_{23}NO$	329	83.69	7.02	4.55	83.85	7.04	4.25
Mesitylene	192.3—193.0	$C_{24}H_{25}NO$	343	83.62	7.46	3.96	83.92	7.34	4.08
Ethylbenzene	189.5—190.2	$C_{23}H_{23}NO$	329[a)]	83.46	6.85	4.36	83.85	7.04	4.25
Cumene	171.2—171.7	$C_{24}H_{25}NO$	343	83.73	7.32	3.88	83.92	7.34	4.08
p-Methylanisole	181.5—181.8	$C_{23}H_{23}NO_2$	345	79.97	6.72	4.40	79.97	6.72	4.06
p-Cyanotoluene	253.3—254.0	$C_{23}H_{23}N_2O$	340	81.41	5.93	8.08	81.15	5.92	8.23

a) Analyzed by a vapour pressure osmometer in ethyl acetate at 37 °C.

Table 6. Spectral data of the adducts of alkylbenzenes to *N*-acetylketimine II

Alkylbenzene	IR (cm^{-1}) ν_{NH}	ν_{CO}	NMR δ in $CDCl_3$ Phenyl protones	NH	CH_2	Acetyl	Other protons
Toluene	3326	1657	7.48—6.60(15H)	6.16	3.91	1.94	
p-Xylene	3358	1656	7.34—6.66(10H) 6.39, 6.81, 6.56, 6.43 (4H, J=7.5 Hz)	6.13	3.83	1.89	*p*-CH_3 2.22
m-Xylene	3300	1656	7.54—6.62(14H)	6.30	3.89	1.91	*m*-CH_3 1.31
o-Xylene	3320	1660	7.39—6.75(14H)	6.30	3.89	1.91	*o*-CH_3 1.32
Mesitylene	3305	1662	7.47—6.87(10H) 6.80(1H), 6.25(2H)	6.30	3.80	1.87	CH_3 2.11(6H)
Ethylbenzene	3300	1657	7.70—7.54(15H)	6.19	—	1.81	CH 4.72, CH_3 1.25 $J_{CH—CH_3}$=7.2 Hz
Cumene	3340	1655	7.52—6.70(15H)	6.52	—	2.00	CH_3 1.38(6H)
p-Methylanisole	3380	1659	7.39—6.75(14H)	6.30	3.98	1.91	CH_3 1.32
p-Cyanotoluene	3360	1656	7.55—6.83(10H) 7.25, 7.17, 6.89, 6.81(4H, J=8 Hz)	6.23	4.05	1.98	

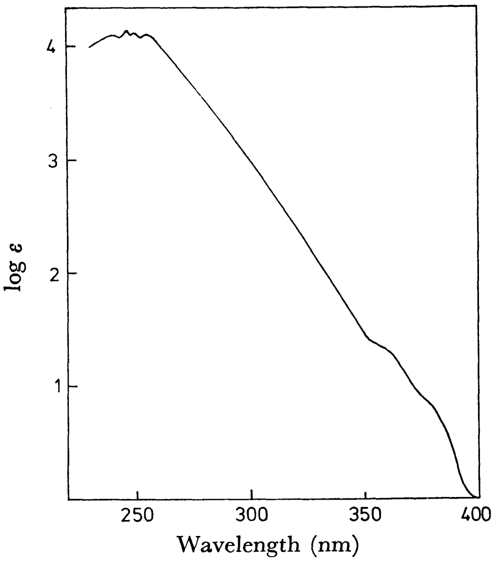


Fig. 4. UV spectrum of *N*-acetyldiphenylmethyleneamine (II) in *n*-hexane.

fied by comparing its spectral data with those of an authentic sample prepared otherwise, and by its inability to depress the melting point.

Irradiation for Mechanistic Study. A degassed solution of *N*-acetylketimine II (0.23 mol/l), substituted toluene (5 ml), and benzene (5 ml) in a pyrex tube under nitrogen was irradiated with a 500 W high pressure mercury lamp at 25±1 °C for 30 hr using a merry-go-round type reactor. The reaction mixtures were worked up by evaporation of the solvent at reduced pressure, and analysed by glpc. Column was a 2 m×3 mm ϕ in 10% Apiezon Grease L on 60—80 mesh Diasolid A or on 60—80 mesh Chromosorb W (HP). The results are summarized in Tables 1 and 3 in the case of alkylbenzenes and *p*-substituted toluenes, respectively. Yields are given in percentage of the starting imine II. No other products of the imine II except those in Table 3 could be obtained, and the remaining imine was recovered after the reaction.

Mechanistic Study in the Presence of Additives. A degassed solution of II (0.23 mol/l) in toluene (10 ml) in the presence of additives in a pyrex tube under nitrogen was irradiated with a 500 W high pressure mercury lamp at 25±1 °C for 30 hr with a merry-go-round type reactor described above. After irradiation, toluene was distilled off in a reduced pressure, and yields of both products, the adduct (Va) and the hydrogenation product (IV), were determined by glpc equipped with a 2 m× 3 mm ϕ column packed with 10% Apiezon Grease L on 60—80 mesh Chromosorb W (HP) at 222 °C at a nitrogen flow rate of 55 ml/min. The results are summarized in Table 2. Yields are shown in percentage with respect to the starting imine II. The remainder of imine was recovered in each case.

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