Photoaddition Reaction of *N*-Acetyldiphenylmethyleneamine with Cyclic and Acyclic Olefins. An Example of Heavy Atom Effect in Photoreaction

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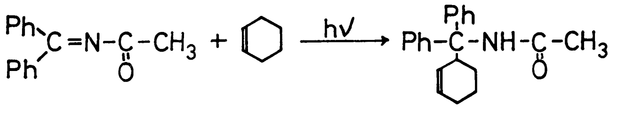
Irradiation of *N*-(diphenylmethylene)acetamide (*N*-acetyldiphenylmethyleneamine, **1**) in cyclopentene gave *N*-[1,1-diphenyl-1-(cyclopenta-2′-enyl)methyl]acetamide, the addition product of cyclopentene to the C=N bond of imine **1**, in 31% yield. The photoreaction of **1** was observed in other cyclic and acyclic olefins. The reactivity of the olefins decreases in the order; cyclopentene>cyclohexene>cyclooctene>2-pentene≃2-hexene. The photoreaction is promoted by the presence of the heavy atom solvent or the sensitizer. The mechanism of photoreaction is discussed in terms of the excited triplet state of the imine.

Increasing attention is being paid to the photochemistry of carbon-nitrogen double bonds.[1] Hydrogen abstraction is the most popular reaction occurring on irradiation of the imine. In 1969 Padwa and co-workers explained the photoreduction of *N*-alkylketimine in terms of chemical sensitization, where the carbonyl compound present in the reactant system as an impurity abstracts a hydrogen atom on irradiation and the ketyl radical produced transfers the hydrogen to the ketimine.[2] They applied a similar mechanism to the photoreduction of *N*-benzoylketimine in 2-propanol.[3] All photochemical hydrogen abstraction reactions of the imine seem to be explained by this chemical sensitization mechanism, the excited state of the imine not taking part. Padwa and co-workers suggested that only the cyclic imine has reactivity, the excited acyclic imine having none, since the acyclic imine easily undergoes syn-anti isomerization by which the excited energy should be consumed.[2]

There are some observations on the photochemistry of the acyclic imines that cannot be explained without taking participation of the excited state of the imine into account. Examples of the photoreaction of the acyclic imine through the excited states contain the deuterium exchange in *ortho*-alkyl derivatives of *N*-(*o*-tolylphenylmethylene)acetamide[4] and the cleavage of the bond between benzylic carbon and imino nitrogen on irradiation of *N*-benzylidenebenzylamine.[5]

Furthermore, even a simple cyclic imine was found to have low reactivity in the photochemical hydrogen abstraction, showing that the low photoreactivity of the imine is not due to the syn-anti isomerization.[6] In fact, the lowest excited states of the imine have been suggested to have the (π,π^*) character rather than the (n,π^*) character.[6,7] The hydrogen abstraction property is characteristic of the $^3(n,\pi^*)$ state rather than of the $^3(\pi,\pi^*)$ state.[8] *N*-(α-Alkylbenzylidene)benzamide has been reported to be reduced photochemically in 2-propanol through the excited triplet state, rather than *via* the chemical sensitization,[9] the mechanism of photochemical hydrogen abstraction thus differing entirely with the reaction system.

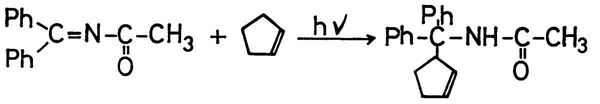
In a preliminary communication, a report was given on the photoreaction of *N*-(diphenylmethylene)acetamide (**1**) in cyclohexene.[10] The addition product was the only product isolated, although four kinds of products were reported to be obtained in the photoreaction of benzophenone in cyclohexene.[11] This suggests the photoreaction through the excited state of the acyclic imine. Further studies on this system have been carried out including the external heavy atom effect, which has been found to be convenient for demonstrating the participation of the excited state in the light-induced reaction.[12]



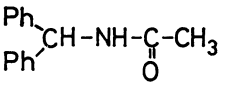
(1) (2b)

Results

Photoreaction of N-*(Diphenylmethylene)acetamide (*N-*Acetyldiphenylmethyleneamine, 1) with Cyclopentene.* Irradiation of cyclopentene solution of *N*-(diphenylmethylene)acetamide (*N*-acetyldiphenylmethyleneamine, **1**) was carried out in a quartz tube under nitrogen atmosphere with a 500 W high pressure mercury lamp for 100 h. After irradiation, cyclopentene was distilled off and the residues were chromatographed over silica gel. The addition product (**2a**) of the imine **1** to cyclopentene detected by HLC was obtained almost selectively except for a trace amount of the hydrogenation product, *N*-(diphenylmethyl)acetamide (**3**). The structure of **2a** was inferred from its composition ($C_{20}H_{21}NO$), olefin tests such as the Bayer test and bromine test, and spectral data. The spectral data included mass spectra

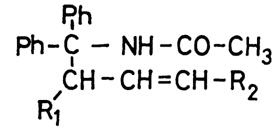


(1) (2a)



(3)

(M^+/e=291) and the infrared absorption bands for an amide group (ν_{NH} 3280, ν_{CO} 1658, δ_{NH} 1548 cm^{-1}). The structure of **2a** was confirmed by the NMR spectrum showing acetyl protons (3H, δ 1.90 ppm), methylene protons (4H, δ 2.08—2.20), a methine proton (1H, δ 4.29—4.66), olefin protons (2H, δ 5.71), an NH proton (1H, δ 6.02—6.42), and phenyl protons (10H, δ 6.93—7.51).



$Ph_2C(NH\text{-}CO\text{-}CH_3)\text{-}CH(R_1)\text{-}CH{=}CH\text{-}R_2$

2a R_1,R_2=$-(CH_2)_2-$
2b R_1,R_2=$-(CH_2)_3-$
2c R_1,R_2=$-(CH_2)_5-$
2d R_1=R_2=$-CH_3$
2e R_1=$-C_2H_5$, R_2=$-CH_3$
2e' R_1=$-CH_3$, R_2=$-C_2H_5$

Comparison of Photoreactivity of N-*Acetyldiphenylmethyleneamine (1) toward Several Kinds of Olefins.* On irradiation of imine **1** in other cyclic olefins such as cyclohexene and cyclooctene, and in the acylic olefins such as 2-pentene and 2-hexene, the same kind of product (**2**) as the amide **2a** was obtained. Amide **2** is the C-C bond formation product between the iminoyl carbon of imine **1** and the allylic carbon of the olefin. The results of the photoreaction are summarized in Table 1. Product yields determined by the silica gel column chromatography indicate the conversion of the starting imine under the given conditions, since amide **2** is the only product in this reaction, the yield increasing with irradiation time.

TABLE 1. PHOTOREACTION OF *N*-(DIPHENYLMETHYLENE)-ACETAMIDE (**1**) WITH OLEFINS[a]

1	Amount of **1** (mmol)	Olefin	Amount of olefin (mmol)	Yield[b] (%)
a	4.8	Cyclopentene	72	31
b	5.7	Cyclohexene	54	15
c	5.6	Cyclooctene	48	2
d	16	2-Pentene	37	0.9
e	16	2-Hexene	30	1.1

a) Olefinic solutions (*ca.* 5 ml) of **1** (1—3 g) were irradiated in quartz tubes under nitrogen atmosphere with a 500 W high pressure mercury lamp for 100 h. b) Conversion of the starting imine **1**. See Experimental.

Effect of Additives on Photoreaction of Imine 1 with Cyclohexene. The photoreaction of imine **1** with cyclohexene was carried out in the presence of several kinds of additives (Table 2). A cyclohexene (55 mmol) solution of imine **1** (4.6 mmol) with benzophenone (4.6 mmol) in a quartz tube under nitrogen atmosphere was irradiated for 100 h giving the adduct **2b** in 38% yield. Benzophenone (E_T=68.5 kcal/mol[13]) and acetophenone (E_T=73.6 kcal/mol[13]) acted as good sensitizers, benzil (E_T=53.7 kcal/mol[13]) sensitizing the reaction only slightly. Piperylene quenched the reaction completely. The results are nearly compatible with those of the photoreaction of imine **1** in toluene.[14]

TABLE 2. DEPENDENCE OF THE PHOTOREACTION YIELD OF *N*-ACETYLDIPHENYLMETHYLENEAMINE (**1**) WITH CYCLOHEXENE IN THE PRESENCE OF SEVERAL KINDS OF ADDITIVES[a]

Additive	Amount of additive (mmol)	E_T[b] (kcal/mol)	Product yield[c] (%)
None[d]	—	—	9
Benzophenone	4.6	68.5	38
Acetophenone	6.7	73.6	25
Benzil	4.1	53.7	12
Piperylene[e]	23	*trans* 59.3 *cis* 56.9	0

a) A solution of 4.6 mmol of **1** and 55 mmol of cyclohexene in the presence of the additive in a quartz tube was irradiated with a 500 W high pressure mercury lamp for 100 h. b) Excited triplet energy. See Ref. 13. c) Conversion of the starting imine **1**. See text. d) The starting imine **1** contained a small amount of benzophenone as an impurity (<3%). e) Mixtures of *cis*- and *trans*-piperylene.

Dependence of the Yield of Photoreaction of Imine 1 with Cyclohexene upon the Concentration of Benzophenone. Since benzophenone acts as a sensitizer on the photoreaction of *N*-acetyldiphenylmethyleneamine (**1**) with cyclohexene, the dependence of the reaction yield of **2b** upon the concentration of benzophenone was investigated. The data are plotted in Fig. 1. The starting sample **1** contains a small amount of benzophenone, the hydrolysis product of imine **1** which is easily hydrolyzed. The amount of benzophenone is the sum of that determined by GLPC in the starting imine as an impurity and that added separately. The full line in Fig. 1 indicates the experimental data and the dashed line the extrapolation of the results. The yield of product **2b** increases linearly with the concentration of benzophenone.

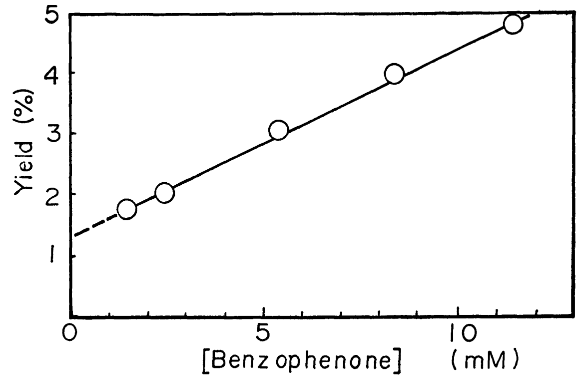


Fig. 1. Dependence of the yields of the photoaddition reaction of *N*-acetyldiphenylmethyleneamine (**1**) with cyclohexene on the concentration of benzophenone: [*N*-Acetyldiphenylmethyleneamine] 0.23 mol/l, [cyclohexene] 10 ml. Irradiation was carried out above 300 nm for 70 h at 25 °C.

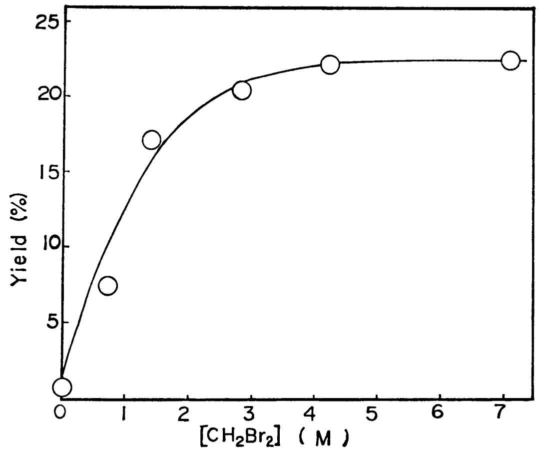


Fig. 2. Dependence of product yield on the concentration of dibromomethane in the photoreaction of *N*-acetyldiphenylmethyleneamine (**1**) in cyclohexene. A solution of **1** (1.22 mmol) and cyclohexene (5 ml) in benzene was irradiated.

*Dependence of the Yield of Photoreaction of Imine **1** with Cyclohexene upon the Concentration of the Heavy Atom Solvent.* The photoaddition product of imine **1** with alkylbenzene increases in yield in the presence of the heavy atom solvent.[14] In the case of the photoreaction of imine **1** with cyclohexene, the yield of **2b** also increases remarkably in the presence of the heavy atom solvent. The photoreaction of imine **1** with cyclohexene was carried out using various concentrations of dibromomethane. The results are shown in Fig. 2. The product yield increases noticeably as the concentration of dibromomethane increases from 0 to 2 M. Further increase in the concentration of heavy atom solvent over 3 M, however, resulted in constant yields.

Discussion

Effect of Additives. The effect of additives on the photoreaction of imine **1** in cyclohexene (Table 2) is in fair agreement with that of the imine in toluene.[14] Benzophenone (E_T=68.5 kcal/mol) and acetophenone (E_T=73.6 kcal/mol) act as sensitizers, and piperylene (*trans*-piperylene, E_T=59.3 kcal/mol; *cis*-piperylene E_T=56.9 kcal/mol) as a quencher. The results suggest that the reaction proceeds *via* a triplet state. However, benzil, whose triplet energy (E_T=53.7 kcal/mol) is lower than that of piperylene, can also sensitize the reaction a little. The curious result indicates that the sensitization concerns the hydrogen transfer *via* "chemical sensitization."[2] The hydrogen abstracting property is a character common to the compounds which sensitize the reaction. As shown in Scheme 1, benzophenone as well as benzil can act as a chemical sensitizer.[2,15]

Dependence of the Yield on the Concentration of Benzophonone. The photoproduct yields increase linearly with the amount of benzophenone (Fig. 1). The usual steady state treatment of Scheme 1 gives the following equation for the product (A_d):[16]

$$\frac{d[A_d]}{dt} = k_r[\text{Olefin}][\text{Ph}_2\text{CO}^*(\text{T}_1)] + k_r'[\text{Olefin}][\text{Ph}_2\text{CNAc}^*(\text{T}_1)]. \quad (1)$$

This shows that the yield should be proportional to the concentration of benzophenone ([Ph_2CO]) since [$Ph_2CO^*(T_1)$] is proportional to [Ph_2CO],[17] and [Olefin] and [$Ph_2CNAc^*(T_1)$] are almost constant.[18] The linear relation between the yield and the concentration of benzophenone (Fig. 1) agrees with the equation.

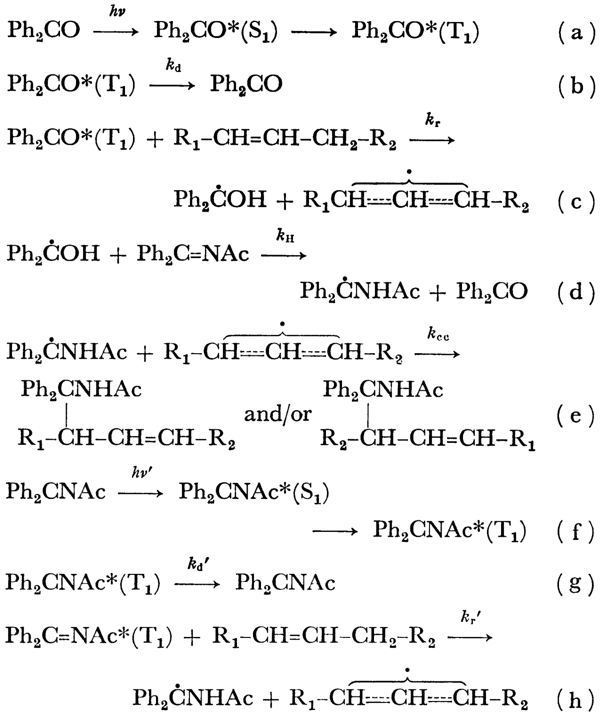
If imine **1** in excited state cannot abstract a hydrogen atom and the reaction proceeds only by chemical sensitization mechanism (only processes a—e taking place in Scheme 1), the reaction yields should converge to 0% at the point of no benzophenone according to the following equation:

$$\frac{d[A_d]}{dt} = k_r[\text{Olefin}][\text{Ph}_2\text{CO}^*(\text{T}_1)]. \quad (2)$$

Actually, however, Fig. 1 clearly shows the formation of 1.3% of the product without benzophenone. This is exactly the yield derived from the excited state of imine **1** itself, based on the second term of Eq. 1.

Relative Reactivity of Olefins towards N-*Acetyldiphenylmethyleneamine (**1**).* The yields in Table 1 show the relative reactivity of olefins toward imine **1**. The yields decrease in the following order depending on the kind of olefin: Cyclopentene>Cyclohexene>Cyclooctene>2-Hexene≃2-Pentene. The results indicate that the reactivity of an olefin is correlated with the stability of the allyl radical derived by hydrogen abstraction from the olefin, and that the lower reactivity of an acyclic olefin than that of a cyclic olefin is due to smaller conjugation of the allyl radical because of the flexibility of the molecule.

Heavy Atom Effect in Photoreaction. The heavy atom effect for increasing the yields in photoreactions



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

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

$$\text{Ph}_2\text{CO}^*(\text{T}_1) + \text{R}_1\text{-CH=CH-CH}_2\text{-R}_2 \xrightarrow{k_r} \text{Ph}_2\dot{\text{C}}\text{OH} + \overbrace{\text{R}_1\text{CH}\text{==}\text{CH}\text{==}\text{CH}}^{\bullet}\text{-R}_2 \quad (c)$$

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

$$\text{Ph}_2\dot{\text{C}}\text{NHAc} + \text{R}_1\text{-}\overbrace{\text{CH}\text{==}\text{CH}\text{==}\text{CH}}^{\bullet}\text{-R}_2 \xrightarrow{k_{cc}} \begin{array}{c}\text{Ph}_2\text{CNHAc}\\ |\\ \text{R}_1\text{-CH-CH=CH-R}_2\end{array} \text{ and/or } \begin{array}{c}\text{Ph}_2\text{CNHAc}\\ |\\ \text{R}_2\text{-CH-CH=CH-R}_1\end{array} \quad (e)$$

$$\text{Ph}_2\text{CNAc} \xrightarrow{h\nu'} \text{Ph}_2\text{CNAc}^*(\text{S}_1) \longrightarrow \text{Ph}_2\text{CNAc}^*(\text{T}_1) \quad (f)$$

$$\text{Ph}_2\text{CNAc}^*(\text{T}_1) \xrightarrow{k_d'} \text{Ph}_2\text{CNAc} \quad (g)$$

$$\text{Ph}_2\text{C=NAc}^*(\text{T}_1) + \text{R}_1\text{-CH=CH-CH}_2\text{-R}_2 \xrightarrow{k_r'} \text{Ph}_2\dot{\text{C}}\text{NHAc} + \text{R}_1\text{-}\overbrace{\text{CH}\text{==}\text{CH}\text{==}\text{CH}}^{\bullet}\text{-R}_2 \quad (h)$$

Scheme 1.

could be of importance for effective utilization of photoenergy. However, only a few examples are known.[12,19] The heavy atom effect in the present photoreaction was investigated in order to clarify the initial step of the photoreaction. The photoreaction of imine **1** with olefins is greatly susceptible to the heavy atom solvent, as observed in the photoreaction of imine **1** with alkylbenzenes.[12] Carbonyl compounds such as benzophenone are known not to be influenced by the heavy atom effect.[20] Thus chemical sensitization by the action of benzophenone would not be influenced by the heavy atom effect, though the excited state of imine **1** might be susceptible. The heavy atom effect is known to increase the probability of the transition between the singlet state and triplet state of a π,π^* character,[21,22] and the reactive state of the imine **1** would be the triplet state with some π,π^* character.[23] The reaction was confirmed to proceed *via* the excited triplet state of imine **1** by the fact that the photoreaction of **1** with cyclohexene was completely quenched by piperylene (Table 2).

The variation of the reaction yield depending on the concentration of dibromomethane shown in Fig. 2 seems to arise from the influence of the heavy atom effect toward the initial step of the excited state of imine **1** as shown in Scheme 2, where D is *N*-acetyldiphenylmethyleneamine (**1**) and the superscript is the multiplicity of the excited state of **1**.

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

$${}^1\mathrm{D} \xrightarrow{k_{ic}} \mathrm{D} \tag{j}$$

$${}^1\mathrm{D} \xrightarrow{k_{is}} {}^3\mathrm{D} \tag{k}$$

$${}^3\mathrm{D} \xrightarrow{k_d} \mathrm{D} \tag{l}$$

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

Scheme 2.

The main processes influenced by the heavy atom effect are (a) an intersystemcrossing from the lowest singlet state to the triplet state of **1** (Eq. k), and (b) a radiative or radiationless decay from the triplet state to the ground state (Eq. 1). Increase of the yield with concentration of heavy atom solvent demonstrates the importance of Step k in the heavy atom effect. This indicates that the excited triplet state of **1** is mainly produced by the singlet excited state of **1** and not by the energy transfer of benzophenone. The behavior of the excited imine **1** in the reaction with olefins is just the same as that in the reaction with alkylbenzenes.[12]

Experimental

Materials. Cyclopentene, cyclooctene, 2-pentene, 2-hexene, piperylene (Tokyo Chemical Industry), and cyclohexene (Yoneyama Chemical Industry) were dried over sodium by refluxing and distilled. Acetophenone (Yoneyama Chemical Industry) and dibromomethane were dried over magnesium sulfate and distilled. Benzophenone (Yoneyama Chemical Industry) and benzil (Tokyo Chemical Industry) were recrystalized from ethanol. Commercial cyclohexane, benzene, dichloromethane, chloroform, and ethanol were used as eluting solvents for column chromatograpy. The reagent for the bromine test was 2% carbon tetrachloride solution of bromine and that for the Bayer test 0.5% aq solution of potasium permanganate. *N*-Acetyldiphenylmethyleneamine (**1**), bp 168—170 °C/1 mmHg (lit,[24] bp 168—170 °C/1 mmHg), was prepared by the reaction of diphenylketimine[25] with acetic anhydride and distilled repeatedly.

Instrumentations. Irradiation was performed with a 500 W Halos high pressure mercury lamp (Eikosha Ltd.). Most comparative runs were carried out on a merry-go-round type reactor (Rikokagaku Ltd.) with a turntable device holding the rotating pyrex tubes. The turntable also rotates 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 carried out on an Ohkura Rikagaku gas chromatograph with a flame ionization detector employing a $2\ \mathrm{m} \times 3\ \mathrm{mm}\phi$ stainless steel column packed with 10% Apiezon Grease L on 60—80 mesh Diasolid A. High speed liquid chromatography (HLC) was performed with 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 equipped with a stainless steel colum packed with Microporasil. Chloroform was used as an eluting solvent. Infrared spectra were taken on a JASCO IR-E spectrometer. NMR spectra were obtained on a JEOL C-60, 4H-100, PS-100 or a Hitachi Perkin-Elmer R-20B spectrometer. Mass spectra were recorded on a Hitachi RMS-4 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus, and were uncorrected.

Photoreaction of N-*Acetyldiphenylmethyleneamine (1) and Cyclopentene.* A cyclopentene (72 mmol) solution of *N*-acetyldiphenylmethyleneamine (4.8 mmol) in a quartz tube was degassed in three successive freeze-thaw cycles, and then irradiated under nitrogen with a 500 W high pressure mercury lamp for 100 h. After irradiation cyclopentene was distilled off and the residue was chromatographed over silica gel. The fraction eluted with benzene contained imine **1** and benzophenone, most of which was produced by the hydrolysis of **1** in a column. The product **2a** was eluted with chloroform in 31% yield. The yield represents the conversion percentage of starting imine **1** since **2a** is the only product in the reaction. The product was purified by recrystalization several times from the mixed solvent of cyclohexane and ethanol. The structure of **2a** (mp 147.0—147.8 °C) was inferred from its composition (Found: C, 82.41; H, 7.11; N, 4.76%; mol wt, 291 by mass spectra. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81%; mol wt, 291.38), the results of olefin tests, and its spectral data. The bromine test and the Bayer test indicated the presence of a C=C bond in the molecule. Infrared spectra showed an amide absorption (ν_{NH}, 3280; ν_{CO}, 1658; δ_{NH}, 1548 cm^{-1}); NMR spectra (in $CDCl_3$) showed ten phenyl protons (δ 7.51—6.93), an NH proton (δ 6.42—6.02), two olefinic protons (δ 5.71), a methine proton (δ 4.66—4.29), four methylene protons (δ 2.20—2.08), and three acetyl protons (δ 1.90).

Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with Cyclohexene.* A cyclohexene (54 mmol) solution of imine **1** (5.7 mmol) in a qaurtz tube was irradiated in the same way as given above, the photoproduct **2b** being obtained in 15% yield. Its structure was identified as *N*-(1,1-diphenyl-1-cyclohexa-2′-enylmethyl)acetamide: mp 181 °C. Found: C, 82.37; H, 7.32; N, 4.61%; mol wt 305 by mass spectra. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59%; mol wt, 305.42. Infrared spectra showed an amide band (ν_{NH}, 3290, ν_{CO}, 1660; δ_{NH}, 1548 cm^{-1}). NMR spectra (in $CDCl_3$) showed ten phenyl protons at δ 7.70—6.99, an NH proton at δ 6.42—6.20, two olefin protons at δ 5.65, a methine proton at δ 4.00—3.65, six methylene protons at δ 2.08—0.85, and three acetyl protons at δ 1.89. An NH proton was assigned by disappearance in the present of deuteruim oxide. UV spectra gave four peaks of 253.6 nm (ε_{max} 5.12×10^2), 259.4 (5.58×10^2), 265.0 (4.69×10^2), and 270.5 (2.92×10^2).

Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with Cyclooctene.* A cyclooctene (48 mmol) solution of *N*-acetyldiphenylmethyleneamine (5.6 mmol) was irradiated in the same way as above, the product **2c** being obtained in 2% yield. Its structure (mp 233 °C) was determined by mass spectra (mol wt 333) and other spectral analysis: Infrared spectra have an amide group (ν_{NH}, 3310; ν_{CO}, 1667; δ_{NH}, 1525 cm^{-1}), and NMR spectra showed ten phenyl protons (δ 7.58—6.02), an NH proton (δ 6.24), two olefin protons (δ 5.83—5.39, 5.32—4.91), a methine proton (δ 4.40—4.00), three acetyl protons (δ 1.82), and ten methylene protons (δ 2.60—0.52).

Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with 2-Pentene.* A solution of imine **1** (16 mmol) and 2-pentene (37 mmol) was irradiated in the same way as given above, the product **2d** being given in 0.9% yield. Its structure was dentified to be *N*-(1,1-diphenyl-2-methyl-3-pentenyl)acetamide, from its spectral data and the results of the olefin tests. Infrared spectra showed an amide band (ν_{NH}, 3300; ν_{CO}, 1670; δ_{NH}, 1530 cm^{-1}) and molecular weight was observed to be 293 by mass spectra. NMR spectra showed ten phenyl protons (δ 7.50—6.70), an NH proton (δ 6.56—6.24), two olefinic protons (δ 5.62—4.99), a methine proton (δ 4.64—4.16), three acetyl protons (δ 1.79), three methyl protons adjacent to the olefinic carbon (δ 1.51), and three methyl protons adjacent to the methine carbon (δ 0.73).

Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with 2-Hexene.* A solution of imine **1** (16 mmol) and 2-hexene (30 mmol) was irradiated in the same way as described above. The products were eluted with 5% benzene solution of ether in 1.1% yield. They were identified to be two kinds of isomers (**2e** and **2e′**) by the spectral data. Mass spectra showed the molecular weight ($M^+/e=307$); the infrared spectra showed an amide group (ν_{NH}, 3300; ν_{CO}, 1670; δ_{NH}, 1530 cm^{-1}); NMR spectra showed the phenyl protons (δ 8.10—6.72), the NH proton (δ 6.63), the olefinic protons (δ 5.80—4.90), the methine proton (δ 4.59—4.24), the allylic methylene protons (δ 1.94), the allylic methyl protons (δ 1.45), the acetyl protons (δ 1.83), and the methyl protons adjacent to the tertiary carbon (δ 0.95).

Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with Cyclohexene in the Presence of the Additives.* A cyclohexene (55 mmol) solution of imine **1** (4.6 mmol) and the additive was irradiated in a quartz tube under nitrogen atmosphere after being degassed in three freeze-thaw cycles at 15 °C for 100 h. Separation was carried out in the same way as described in the photoreaction of the imine **1** with cyclopentene. No products derived from the additive were detected.

Dependence of Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with Cyclohexene upon the Concentration of Benzophenone.* A cyclohexene (10 ml) solution of imine **1** (0.23 M) in the presence of a fixed amount of the 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 70 h. After irradiation cyclohexene was distilled off and the reaction mixtures were analyzed with a gas chromatograph equipped with a 80 cm×3 mmϕ stainless steel column with 10% Apiezon Greese L on 60—80 mesh Diasolid A. Yields are given in terms of the conversion percentage of the starting imine.

Dependence of Photoreaction of N-*Acetyldiphenylmethyleneamine (1) with Cyclohexene upon the Concentration of Dibromomethane.* A cyclohexene (5 ml) solution of imine **1** (1.2 mmol) in the presence of benzene solutions (5 ml) of varying amounts of dibromomethane in a Pyrex tube was degassed and irradiated under nitrogen with a 500 W high pressure mercury lamp at 25±1 °C for 10 h. After irradiation solvents were distilled off, and the residue was analyzed by high speed liquid chromatography of Microporasil using chloroform as an eluting solvent. Yields are given in terms of the conversion percentage of the starting imine **1**.

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17) The concentration of excited triplet benzophenone is not proportional to the benzophenone concentration, but follows the equation

$$[\mathrm{Ph_2CO^*(T_1)}] = \mathrm{Ia}/(k_r[\mathrm{Olefin}]+k_d)$$

where, Ia is the rate of light absorption of benzophenone to form triplet state of benzophenone, k_r and k_d are constants. The concentration of olefin ([Olefin]) is very high and considered to be constant during the course of reaction.

18) [$Ph_2CNAc^*(T_1)$] is proportional to the concentration of imine **1** ([Ph_2CNAc]), which changes with reaction time. In this experiment, however, the change is less than 5% and the concentration of the imine is kept almost constant, since the conversion of the reactant imine is less than 5%.

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