ESR Study on the Photoreduction of *N*-Acetyldiphenylmethyleneamine in 2-Propanol

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Photoreduction of *N*-Acetyldiphenylmethyleneamine (**1**) in 2-propanol was studied both by the ESR spectroscopy of irradiated imine **1** in a matrix solvent at −196 °C and by the deuteration analysis of acetone formed from 2-propanol-*d* in the photoreduction process. The ESR spectrum consists of a broad singlet and a quartet. The latter is assigned to the $CH_3CH(OH)\dot{C}H_2$ radical, which can be produced by β-hydrogen abstraction by the excited imine **1** from 2-propanol, but not by the excited benzophenone. Formation of acetone-*d* on irradiation of **1** in 2-propanol-*d* suggests that the imine **1** in the excited state has a hydrogen abstracting character.

When acyclic imino compounds are irradiated in 2-propanol, a C=N bond is reduced to a –CH–NH– group. This photoreduction has been studied on various derivatives as one of the fundamental photoreactions of a C=N chromophore.[1-5] Two reaction mechanisms are proposed for this photoreduction. One is the "chemical sensitization" mechanism.[3] According to this mechanism, the reaction proceeds *via* an aminoalkyl radical formed by thermal hydrogen transfer from a ketyl radical to the imine. The ketyl radical is derived from the excited triplet state of the corresponding ketone present in the starting imine as an impurity. The other is the mechanism where imine itself has a hydrogen abstracting character in the excited state.[4,5]

We have reported that the irradiation of *N*-acetyldiphenylmethyleneamine (**1**) in 2-propanol gives the amide derivative and that only the C=N bond is selectively reduced.[4]

$$Ph_2C{=}NCOCH_3 + (CH_3)_2CHOH \quad (\mathbf{1})$$
$$\xrightarrow{h\nu} Ph_2CHNHCOCH_3 + (CH_3)_2C{=}O$$

In order to decide which mechanism is reasonable in this reaction, it seems important to compare the photoreaction of the imine **1** with that of benzophenone. The reaction proceeds in a radical fashion, whichever mechanism is adopted. So we have investigated this reaction by an ESR technique to detect the intermediate radical of the reaction.

Experimental

Materials. 2-Propanol was refluxed on anhydrous barium oxide and distilled. Acetonitrile was used after distillation. 2-Propanol-*d* was obtained from E. Merck Japan Ltd. Benzophenone was recrystallized from ethanol. *N*-Acetyldiphenylmethyleneamine (**1**), bp 170—172 °C/3 Torr (lit,[6] bp 168—170 °C/1 Torr) and *N*-propionyldiphenylmethyleneamine (**2**), mp 79.3—79.9 °C (lit,[6] mp 78—79.5 °C), were prepared by the reaction of diphenylmethyleneamine with acetic anhydride and propionic anhydride, respectively, and purified before use.

ESR Measurement. A solution of imine (*ca.* 250 mg) in a solvent (1 ml) was poured into an ESR tube and was degassed in four successive freeze-thaw cycles. The sealed sample tube in a transparent qaurtz Dewar bottle filled with liquid nitrogen was set in a cavity. UV light was irradiated from outside and ESR spectra were measured by using a JEOL 3BS-X type spectrometer. All irradiations were carried out with an Ushio type 500D ultrahigh pressure mercury lamp through a glass filter transparent to wavelengths longer than 320 nm. The field modulation was 100 kHz, and modulation width was 5.3 gauss during ESR measurements. *g*-Factors and hyperfine coupling constants were corrected by using a Mn^{2+} marker.

*Photoreaction of the Imine in 2-Propanol-*d. One gram of imine **1** was dissolved in 5 ml of 2-propanol-*d* in a quartz tube. Irradiation was carried out at room temperature or at −196 °C for 20 h in a similar manner as described in ESR measurements. A 2-propanol-*d* (5 ml) solution of benzophenone (260 mg) was also irradiated for 5 h at room temperature. After irradiation, the solvent was separated by vacuum distillation and mass spectra of acetone produced were measured by a Hitachi M-52 type GC-MS analyzer. The deuteration degree of the acetone was calculated from the base peak of the mass spectrum.

Results

ESR Measurements. On irradiation of imine **1** in 2-propanol at −196 °C, stable five lines were observed in an ESR spectrum as shown in Fig. 1A. When the system was warmed up to −154 °C, a broad single line remained and other four lines disappeared (Fig. 1B). The absorption and the second derivative type spectra of Fig. 1A are shown in Fig. 2A and 2B, respectively. The former indicates the intensity ratio of four lines to be *ca.* 1 : 3 : 3 : 1, and the latter indicates that four lines have the same splitting constant of 23.2 G

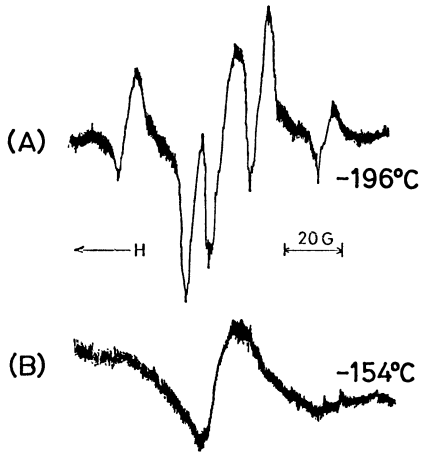


Fig. 1. ESR spectra (First Derivatives) of UV-irradiated *N*-acetyldiphenylmethyleneamine (**1**) in 2-propanol at (A) −196 °C and (B) −154 °C. Irradiations were carried out at —196 °C for 20 min.

Table 1. Parameters of observed ESR spectrum

Run	Imine	Solvent	Quartet		Singlet	
			a_H (G)	Intensity ratio	g	ΔH_{msl}[a] (G)
A	**1**	2-PrOH	23.2±0.4	*ca.* 1 : 3 : 3 : 1	2.002	10
B	**1**	2-PrOH/CH_3CN[b]	23.0±0.4	*ca.* 1 : 3 : 3 : 1	2.002	8
C	**2**	2-PrOH/CH_3CN[b]	22.5±0.4	*ca.* 1 : 3 : 3 : 1	2.003	9

a) The maximum slope distance. b) 1 : 1 by volume ratio.

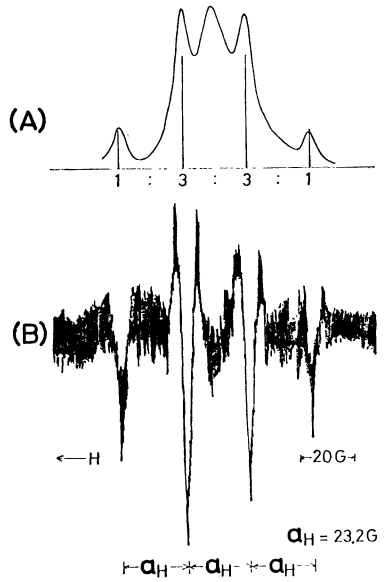


Fig. 2. Absorption (A) and 2nd derivative (B) of ESR spectra of UV-irradiated *N*-acetyldiphenylmethyleneamine (**1**) in 2-propanol at −196 °C.

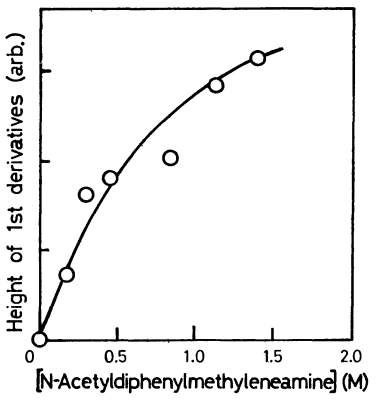


Fig. 3. Dependence of quartet intensity on the *N*-acetyldiphenylmethyleneamine (**1**) concentration. Samples of 2-propanol solution were UV-irradiated for 30 min at −196 °C with constant concentration of benzophenone (0.48 mol/l).

When *N*-propionyldiphenylmethyleneamine (**2**) was used instead of **1**, the ESR spectra of the solution gave the same signal.[7] A central singlet was broad in all cases and have no special relation to the quartet in intensity. The parameters of these ESR spectra are given in Table 1. The dependence of the intensities of a quartet upon the concentration of the imine **1** was investigated. The experiment was carried out with the constant concentration of benzophenone at each point. The heights of the outer lines of the quartet noticeably increased with the concentration of **1** as shown in Fig. 3.

*Photoreaction of Imine **1** in 2-Propanol-*d. In order to detect the position of hydrogens abstracted in 2-propanol, the deuteration degree of acetone was investigated. Acetone is formed from 2-propanol during the photoreaction of **1**. The results are shown in Table 2. The deuteration degree was small when benzophenone was used as a substrate, but relatively high when imine **1** was used .

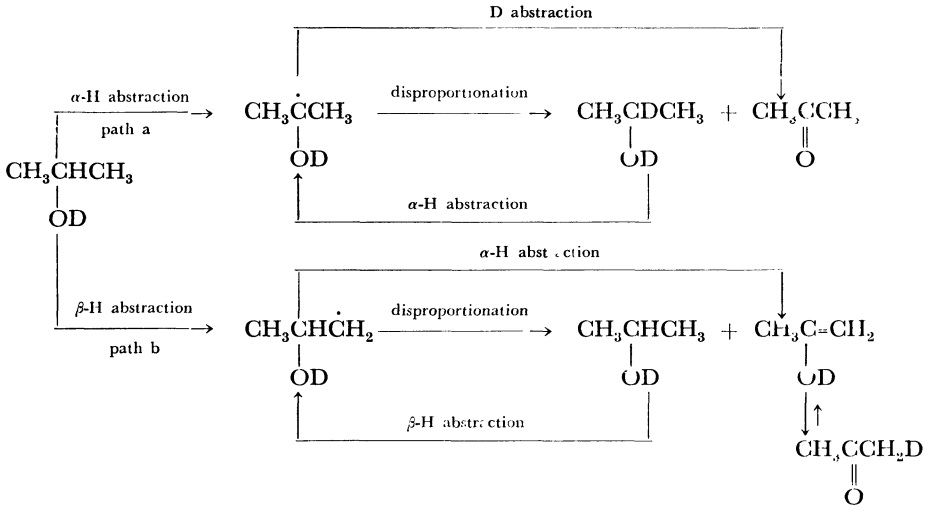
Table 2. Deuteration degrees of acetone formed by the photoreductions in 2-propanol-*d*

Substrate	Temperature	Deuteration degree of acetone (%)
Benzophenone	Room temperature	≈ 5
Imine **1**	Room temperature	≈ 15
Imine **1**	−196 °C	≈ 21

Discussion

Assignment of ESR Signals. From the temperature dependence of signals as shown in Fig. 1, it is concluded that the five lines observed on irradiation at −196 °C consist of a broad singlet and a quartet. A quartet is not due to the radical from imine because both ESR spectra from imine **1** and imine **2** show the same patterns (*cf.* Table 1, Runs A and C). As an acetonitrile solution of imines gives no quartet, the quartet is not due to a radical from acetonitrile either. Furthermore, quite different signals were observed when other alcohols than 2-propanol were used as a solvent. From these experimental facts, the quartet is attributed to a radical from 2-propanol used as a solvent. As regards 2-propanol radicals, the ESR spectra of two radicals have been reported.[8] One is an α-hydroxy radical $(CH_3)_2\dot{C}OH$ which is formed by α-hydrogen abstraction from 2-propanol with Fenton's reagent, and shows a septet signal with intensity ratio of 1 : 6 : 15 : 20 : 15 : 6 : 1 and a_H of 19.5 G. The other is a β-hydroxy radical $CH_3CH(OH)\dot{C}H_2$ by β-hydrogen abstraction and this radical shows a quartet signal with intensity ratio 1 : 3 : 3 : 1 and a_H of 22.5 G. Comparison of the experimental values (Table 1) with these reported values clearly indicates that the quartet observed in the present experiment is due to the radical $CH_3CH(OH)\dot{C}H_2$.

As regards a broad singlet, it may be attributed to



Scheme 1.

a mixed signal composed of $Ph_2\dot{C}NHCOCH_3$ from imine **1** and benzophenone ketyl radical from benzophenone as an impurity of **1**. Thus it is reported that the ESR spectra of both the ketyl radical[9] from benzophenone and the aminoalkyl radical $Ph_2\dot{C}NH_2$,[2] analogous to the radical $Ph_2\dot{C}NHCOCH_3$, were observed not to split by the coupling with the adjacent nitrogen atom and showed a broad singlet with the similar *g*-values on irradiation in a matrix solvent at a low temperature (ΔH_{msl} values of both radicals are 14 and 18 G, respectively). As the acetyl group of $Ph_2\dot{C}NHCOCH_3$ can be supposed not to effect also to the hyperfine structure of the radical in a rigid matrix, it is reasonable that $Ph_2\dot{C}NHCOCH_3$ shows a signal not so different from that of $Ph_2\dot{C}NH_2$. Therefore it is conceivable that the observed singlet is due to the mixed signal of radicals $Ph_2\dot{C}OH$ and $Ph_2\dot{C}NHCOCH_3$.

Reaction Processes. The ESR studies show the formation of the β-hydroxy radical $CH_3CH(OH)\dot{C}H_2$ on irradiation of imine **1** in 2-propanol in a rigid matrix at −196 °C. In the photoreduction of imine **1** in 2-propanol at low temperature, however, only acetone was produced from 2-propanol quantitatively, and no 2,5-hexanediol, a coupling product of the β-hydroxy radical, was detected. In order to satisfy the both facts, acetone must be formed from 2-propanol through the path b of Scheme 1. Contribution of both paths a and b to the reaction can be determined by product analysis when 2-propanol-*d* is used in the present photoreduction instead of 2-propanol.

The results show that the deuteration degree of acetone produced is low (5%) in the case of benzophenone which is recognized generally to abstract α-hydrogen of 2-propanol. In the case of the imine **1**, however, the deuteration degree is 15% when irradiation was carried out at room temperature, and 21% at −196 °C. As these values are apparently higher than that in the case of benzophenone, β-hydrogen abstraction from 2-propanol occurs more frequently in the photoreduction of the imine **1** in 2-propanol than that of benzophenone in 2-propanol.

As shown in Fig. 3, the quartet intensity of the β-hydroxy radical increased with the concentration of the imine **1**, and became zero when the concentration of the imine **1** was zero though benzophenone was exist in the solution. Since the concentration of benzophenone was equal at each point, it can be concluded that the $CH_3CH(OH)\dot{C}H_2$ radical is formed through the hydrogen abstraction from 2-propanol by the imine **1**. This conclusion is supported by the following experimental result. Thus, when the ESR spectrum of a 2-propanol solution of benzophenone was measured under irradiation in a matrix at −196 °C, the quartet due to $CH_3CH(OH)\dot{C}H_2$ was not observed, but weak outer bands of septet due to $(CH_3)_2\dot{C}OH$ and a strong broad singlet due to benzophenone ketyl radical were obtained. It is not clear why the imine **1** abstracts β-hydrogen from 2-propanol, but one of the reasons might be the specific interaction between the imine **1** and 2-propanol as a Fenton's reagent generally abstracts ω-hydrogen of alcohols.[8] It can be concluded that not the excited benzophenone, but the excited imine **1** abstracts β-hydrogen from 2-propanol especially in the photoreduction of imine **1** in 2-propanol. Namely the imine **1** in the excited state has a great deal to do with the photoreduction in contrast with the chemical sensitization mechanism.[3]

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References

1) E. S. Huyser, R. H. S. Wang, and W. T. Short, *J. Org. Chem.*, **33**, 4323 (1968); B. Fraser-Reid, A. Mclean, and E. W. Usherwood, *Can. J. Chem.*, **47**, 4511 (1969); G. Balogh and F. C. De Schryver, *Tetrahedron Lett.*, **1969**, 1371; P. Beak and C. R. Payet, *J. Org. Chem.*, **35**, 3281 (1970); N. Toshima, S. Asao, K. Takada, and H. Hirai, *Tetrahedron Lett.*, **1970**, 5123; N. Toshima, M. Saeki, and H. Hirai, *Chem. Commun.*, **1971**, 1424; Y. Ogata and K. Takagi, *Tetrahedron*, **27**, 2785 (1971); N. Baumann, *Helv. Chim. Acta*, **56**, 2227 (1973); A.

Castellano, J. P. Catteau, A. Lablache-Combier, and B. Planckaert, *Tetrahedron Lett.*, **1973**, 4185; K. N. Mehrotra and T. Singh, *Indian J. Chem.*, **11**, 499 (1973).

2) N. Toshima, H. Hirai, and S. Makishima, *Kogyo Kagaku Zasshi*, **72**, 184 (1969).

3) M. Fischer, *Chem. Ber.*, **100**, 3599 (1967); A. Padwa, W. Bergmark, and D. Pashayan, *J. Am. Chem. Soc.*, **91**, 2653 (1969); A. Padwa and M. Dharan, *Tetrahedron Lett.*, **1972**, 1053.

4) T. Okada, M. Kawanisi, H. Nozaki, N. Toshima, and H. Hirai, *Tetrahedron Lett.*, **1969**, 927; T. Okada, K. Saeki, M. Kawanisi, and H. Nozaki, *Tetrahedron*, **26**, 3661 (1970).

5) N. Toshima, S. Asao, and H. Hirai, *Chem. Lett.*, **1975**, 451; M. Saeki, N. Toshima, and H. Hirai, *Bull. Chem. Soc. Jpn.*, **48**, 476 (1975); S. Asao, N. Toshima, and H. Hirai, *Bull. Chem. Soc. Jpn.*, **48**, 2068 (1975); **49**, 224 (1976).

6) J. E. Banfield, G. M. Brown, F. H. Davey, W. Davies, and T. H. Ramsay, *Aust. J. Sci. Res.*, **A1**, 330 (1948).

7) The solubility of imine **2** in 2-propancl was so low that the mixed solvent of 2-propanol and acetonitrile (1 : 1 v/v) was used in this experiment. In this mixed solvent imine **1** showed the same ESR signal as that in 2-propanol.

8) T. Shiga, *J. Phys. Chem.*, **69**, 3805 (1965).

9) Y. Iwakura, K. Takeda, T. Nakazawa, and O. Watarai, *J. Polymer Sci. Part B*, **6**, 115 (1968).