

# Photochemical Deuteration of *ortho*-Substituted *N*-(Diphenylmethylene)acetamides<sup>1)</sup>

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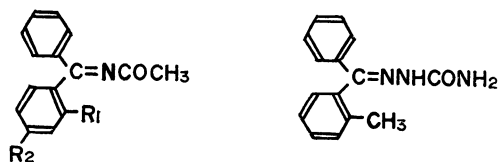
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The alkyl hydrogens of *N*-(2-alkyldiphenylmethylene)acetamides were found to be readily replaced with deuterium on irradiation in deuteriomethanol (CH<sub>3</sub>OD). It is proposed that the deuteration proceeds *via* an enamide isomer produced by intramolecular hydrogen transfer from the *o*-alkyl group to the excited C=N double bond. An intermolecular hydrogen atom abstraction pathway was excluded because neither *N*-(4-methyldiphenylmethylene)acetamide in deuteriomethanol (CH<sub>3</sub>OD) nor diphenylmethane in deuteriomethanol (CH<sub>3</sub>OD) in the presence of *N*-(diphenylmethylene)acetamide was deuterated. Intramolecular hydrogen abstraction is essential for the deuteration, because no deuteration occurs on irradiation of 2-methylbenzophenone semicarbazone which undergoes no photoreduction. The difference in reactivities of the *ortho*-substituted imines between in solution and in a rigid matrix is discussed from the viewpoint of *syn-anti* isomerization.

In previous papers we have reported that the imine **1** which has a C=N double bond conjugated with a carbonyl group undergoes photochemical reduction in hydrogen-donating solvents such as alcohol or ether,<sup>2)</sup> and reduction and reductive addition in alkyl benzenes or aliphatic olefins.<sup>3)</sup> In spite of the recent accumulation of reports of the photoreduction of simple imines,<sup>2-5)</sup> its reduction pathway has not yet been unambiguously characterized. Fischer<sup>4)</sup> and Padwa and others<sup>6,7)</sup> have proposed that the reactive intermediates in these reactions are exclusively the excited states of the carbonyl compounds contained as impurities in the reaction mixtures. The lack of reactivity of the excited states of imines was explained by a feasible deactivation *via syn-anti* isomerization.<sup>7)</sup> Nevertheless, it is still open to question whether this interpretation is applicable to different kinds of imine, *e.g.*, **1**.



- 1**; R<sub>1</sub>=H, R<sub>2</sub>=H  
**2a**; R<sub>1</sub>=CH<sub>3</sub>, R<sub>2</sub>=H  
**2b**; R<sub>1</sub>=CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R<sub>2</sub>=H  
**3**; R<sub>1</sub>=H, R<sub>2</sub>=CH<sub>3</sub>

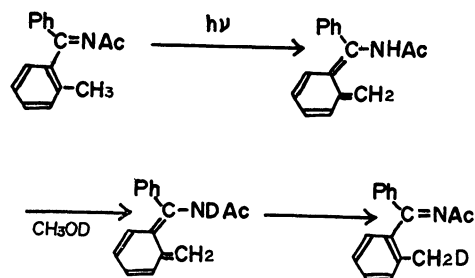
We expected that participation of an impurity in the hydrogen abstraction reaction could be prevented by setting the hydrogen-accepting imino group and the hydrogen-donating alkyl group in one molecule. *N*-(2-Methyldiphenylmethylene)acetamide (**2a**), *N*-(2-benzoyldiphenylmethylene)acetamide (**2b**), and *N*-(4-methyldiphenylmethylene)acetamide (**3**) were prepared and the photogenerated intermediates were detected by the exchange of hydrogen in the alkyl group with deuterium in deuteriomethanol (CH<sub>3</sub>OD). Changes in the absorption spectra during irradiation and the photochemical behavior of 2-alkylbenzophenone semicarbazone (**4**) were investigated as well.

## Results and Discussion

**Deuteration.** The 2- (**2a**) and 4-methyl (**3**) substituted *N*-(diphenylmethylene)acetamides were pre-

pared and photochemically deuterated at the 2- and 4-methyl positions. A solution of each compound in a deuteriomethanol (CH<sub>3</sub>OD)-benzene mixed solvent was irradiated with light of wavelength longer than 320 nm at room temperature for 8 hr. After irradiation, the solvent was removed and the NMR spectrum of the recovered imine was measured. The spectrum of the recovered **2a** revealed that 0.30±0.09 atoms of deuterium per molecule were incorporated in the 2-methyl group of **2a**, while no deuteration was observed in **3**. This striking contrast is apparently due to the difference between the geometrical positions of the hydrogen-donating methyl groups. In other words, this is an example of the *ortho*-effect. It is also noteworthy that the acetyl hydrogens in **2a** or **3** remained undeuterated throughout the above irradiations.

**Mechanism of Deuteration.** The lack of deuteration of **3** indicates that some intramolecular interaction between the *N*-acetylmino group and the 2-methyl group of **2a**, possibly intramolecular hydrogen atom abstraction *via* a six-membered cyclic transition state formation, is involved in the photodeuteration of **2a**.



The following experiment showed that the deuteration of **2a** does not proceed *via* an intermolecular hydrogen atom abstraction. Thus diphenylmethane and imine **1** were used as a hydrogen donor and an acceptor, respectively, for a typical intermolecular reaction. When a solution of diphenylmethane and **1** in deuteriomethanol (CH<sub>3</sub>OD)-benzene was irradiated at room temperature, even after irradiation for 86 hr NMR and mass spectra showed no evidence of deuteration. This shows that the deuteration of **2a** must proceed *via* an intramolecular hydrogen abstraction pathway.



77 K in a rigid matrix, the excitation energy is dissipated by radiative or radiationless processes without hydrogen abstraction.<sup>14)</sup> In fact, no deuteration could be detected on irradiation of **2a** at 77 K, which is consistent with the absence of coloration of the pure imine.<sup>15)</sup> On the contrary, irradiation of **2** at room temperature in solution results in the formation of the *anti*(*E*)-isomer by rotation about the C=N double bond.<sup>16)</sup> The excited state of the *anti*(*E*)-isomer is supposed to be the active species in the hydrogen abstraction and the photochemical deuteration. In fact, Ogata<sup>17)</sup> and Stermitz<sup>18)</sup> reported that azomethine **6** undergoes photochemical intramolecular hydrogen abstraction.

### Experimental

**General.** Ultraviolet spectra were recorded on a Shimadzu MPS-50L spectrophotometer. Infrared spectra were taken as liquid film or in Nujol mulls on a Jasco IR-E spectrophotometer. Nuclear magnetic resonance spectra were taken on a Japan Electron Optics Laboratory Model PS-100 spectrometer using tetramethylsilane as the internal standard. The mass spectra were recorded on a Hitachi RMS-4 mass spectrometer, in which the ionization energy was 80 eV. The samples were injected directly at 120 °C or injected through a Hitachi 063 gas chromatograph (SE30, 3 mm $\phi$   $\times$  2 m, 225 °C). Melting points were determined with a Yanagimoto micro melting point apparatus. All irradiations were carried out in a quartz reactor equipped with a Ushio type 501C 500W ultrahigh pressure mercury lamp through a glass filter transparent to wavelengths longer than 320 nm.

**Materials.** Monodeuteriomethanol(CH<sub>3</sub>OD) was obtained from Merck. Benzene, toluene, and cyclohexane were

dried over metallic sodium, methanol over magnesium, and 2-propanol over barium oxide, and distilled. Diphenylmethane was recrystallized from petroleum ether.

*N*-(Diphenylmethylene)acetamide (**1**) was prepared in the usual way.<sup>19)</sup> *N*-Acetylation was carried out with acetic anhydride.

*N*-(2- or 4-Methyldiphenylmethylene)acetamide (**2a** or **3**) was prepared by the coupling of benzonitrile with the Grignard reagent of the corresponding bromotoluene,<sup>19)</sup> followed by *N*-acetylation with acetic anhydride. **2a**: bp, 152 °C (1 mmHg); IR (liquid film): 1690(C=O), 1640(C=N) cm<sup>-1</sup>; NMR(CCl<sub>4</sub>):  $\delta$  1.9(acetyl CH<sub>3</sub>), 2.2(CH<sub>3</sub>), 7.1–7.8 (9H, aromatic ring protons). **3**: IR(liquid film): 1690(C=O), 1640(C=N) cm<sup>-1</sup>; NMR(CCl<sub>4</sub>):  $\delta$  1.9 (acetyl CH<sub>3</sub>), 2.3(CH<sub>3</sub>), 7.0–7.6(9H, aromatic).

*N*-(2-Benzoyldiphenylmethylene)acetamide (**2b**). The Grignard coupling of bromobenzene and 2-chlorobenzyl chloride gave 2-chlorodiphenylmethane.<sup>20)</sup> 2-Chlorodiphenylmethane was refluxed in pyridine in the presence of cuprous cyanide to give 2-benzylbenzonitrile.<sup>21)</sup> A solution of 20 g of 2-benzylbenzonitrile in 50 ml of dry diethyl ether was added to the Grignard reagent prepared from 15.7 g of bromobenzene and 2.5 g of magnesium in 100 ml of diethyl ether. The reaction mixture was refluxed for 6 hr, cooled, decomposed with 100 ml of methanol, and filtered. The solvent was evaporated and the residue was distilled under reduced pressure to give 2-benzoyldiphenylmethanimine; 22% yield; bp, 200 °C(1 mmHg); IR(liquid film): 3240(NH), 1605(C=N) cm<sup>-1</sup>; NMR(CCl<sub>4</sub>):  $\delta$  3.8(CH<sub>2</sub>), 6.9–7.7(14H, aromatic), 8.6(NH); Anal.: Found: C, 86.65; H, 6.00; N, 4.94%. Calcd for C<sub>20</sub>H<sub>17</sub>N: C, 88.52; H, 6.32; N, 5.16%.<sup>22)</sup> This imine was easily acetylated with acetic anhydride to give *N*-(2-benzoyldiphenylmethylene)acetamide. Careful recrystallization from cyclohexane was repeated several times until impurity-free white crystals were obtained: bp, 205 °C (1 mmHg); mp, 100–101 °C; Mass: *m/e*=313; IR(Nujol mull): 1690(C=O), 1640(C=N) cm<sup>-1</sup>;  $\lambda_{\text{max}}^{\text{MeOH}}$  (log  $\epsilon_{\text{max}}$ ):

TABLE 1. RESULTS OF THE PHOTODEUTERATION IN DEUTERIOMETHANOL(CH<sub>3</sub>OD)

| Compound                                         | Irr. time (hr) | Method | Analysis                                                   |                       |
|--------------------------------------------------|----------------|--------|------------------------------------------------------------|-----------------------|
|                                                  |                |        | Observed value (Calcd value)                               | Deuterium content (%) |
| <b>1</b> 200 mg + <b>Dm</b> 200 mg <sup>b)</sup> | 20             | NMR    | $\frac{\text{methylene}}{\text{phenyl}} = 0.20 \pm 0.01$   | 0                     |
| <b>1</b> 350 mg + <b>Dm</b> 200 mg <sup>b)</sup> | 86             | mass   | $\frac{M+1}{M} = 0.14 \pm 0.02$ (0.15) <sup>c)</sup>       | 0                     |
| <b>2a</b> 230 mg                                 | 8              | NMR    | $\frac{2\text{-methyl}}{\text{acetyl}} = 0.90 \pm 0.03$    | 10 $\pm$ 3            |
| <b>2a</b> 230 mg (at 77 K) <sup>d)</sup>         | 8              | mass   | $\frac{M+1}{M} = 0.19 \pm 0.02$ (0.19) <sup>c)</sup>       | 0                     |
| <b>2b</b> 150 mg <sup>e)</sup>                   | 20             | NMR    | $\frac{2\text{-methylene}}{\text{acetyl}} = 0.59 \pm 0.03$ | 12 $\pm$ 4            |
|                                                  |                | mass   | $\frac{M+1}{M} = 0.51 \pm 0.02$ (0.25) <sup>c)</sup>       | 15 $\pm$ 2            |
|                                                  |                | mass   | $\frac{M+2}{M} = 0.13 \pm 0.02$ (0.03) <sup>c)</sup>       | 14 $\pm$ 2            |
| <b>3</b> 500 mg                                  | 8              | NMR    | $\frac{4\text{-methyl}}{\text{acetyl}} = 1.00 \pm 0.03$    | 0                     |
| <b>4</b> 100 mg                                  | 20             | mass   | $\frac{M+1}{M} = 0.20 \pm 0.02$ (0.18) <sup>c)</sup>       | 0                     |

- a) The NMR spectra were taken in CCl<sub>4</sub> at room temperature. b) Recovered diphenylmethane (**Dm**) was analyzed in this run. c) The figure in the parentheses is the ratio calculated from the natural isotope abundance. d) Toluene was used in this run instead of benzene as a solvent. e) The corresponding ketone was completely eliminated from the starting material and dry toluene was used instead of benzene in this case.

215(4.54), 234(4.40), 253(4.40), 372(sh)(0.97), 382(0.66), 392(0.66)nm; NMR(CCl<sub>4</sub>):  $\delta$  1.8(acetyl CH<sub>3</sub>), 3.8(CH<sub>2</sub>), 6.9–7.6(14H, aromatic). Anal.: Found: C, 84.48; H, 6.09; N, 4.44%. Calcd for C<sub>22</sub>H<sub>19</sub>NO: C, 84.31; H, 6.11; N, 4.47%.

**2-Methylbenzophenone Semicarbazone(4)** To a solution of 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate in 10 ml of water was added 10 ml of ethanol containing 1 g of 2-methylbenzophenone. Ethanol was added until the mixture became transparent. The solution was heated for half an hour and allowed to stand at room temperature over a period of several days. A new crystalline compound **4** was separated from the reaction mixture and recrystallized from ethanol: mp, 156–157 °C; Mass:  $m/e$  = 253; IR(Nujol mull): 3300(NH), 1680(C=O)cm<sup>-1</sup>; NMR(CCl<sub>4</sub>):  $\delta$  2.2(CH<sub>3</sub>), 6.0(NH, NH<sub>2</sub>), 7.5(9H, aromatic). Anal.: Found: C, 71.19; H, 5.92%. Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O: C, 71.11; H, 5.98%.

**Deuterium Exchange.** Usually 2 ml of a deuterio-methanol (CH<sub>3</sub>OD)-benzene solvent containing 100–500 mg of an imine was degassed and pure nitrogen was introduced until the system reached atmospheric pressure for experimental convenience. After being irradiated at room temperature in a quartz tube, the starting material was recovered and analyzed by NMR and mass spectroscopy. The results are summarized in Table 1.

**Irradiation at Low Temperature.** Unless otherwise mentioned, an oxygen-free 10<sup>-1</sup> mol/l solution of the substrate in 4 ml of a methanol-2-propanol (1 : 1) solvent was irradiated at 77 K in a quartz cell with light of wavelengths longer than 320 nm. Changes in the absorption spectra were measured at 77 K in a quartz Dewar filled with liquid nitrogen.

## References and Notes

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