

Photochemical Reactions of Some Carbonyl Compounds with *N,N*-Dimethylaniline: Formation of β - and γ -Hydroxyamines[†]

Sung Sik Kim*, Ji Ae Chang and Yoon Jung Mah

Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea

Direct irradiation of carbonyl compounds such as some aldehydes, ketones and anthraquinone in *N,N*-dimethylaniline (DMA), without using other solvents, gave β -hydroxyamines as the major products. Irradiation of anthrone and DMA in methanol afforded γ -hydroxyamine. The structure of the photoproduct was confirmed by treatment with an acid to give a bicyclic compound.

key words: anthrone, *N,N*-dimethylaniline, γ -hydroxyamine, β -hydroxyamine

INTRODUCTION

The photochemistry of carbonyl compounds with amines is of particular interest since it is an efficient process for the synthesis of diols or other types of reductive products [1, 2]. Aromatic ketones undergo photoreduction in hydrogen donor solvents. Photoreduction of benzophenone by amines involves abstraction of hydrogen and leads to benzopinacol. In the case of the photochemical reactions of benzaldehyde with amines in methanol, β -hydroxyamine is produced in poor yield. In fact, the synthetic investigation and applications of hydroxyamines have been investigated in many areas [3-8]. Herein, we report that β - or γ -hydroxyamines can be made from the photoreactions of some carbonyl compounds with amines.

MATERIALS AND METHODS

Materials

Anthrone and *N,N*-dimethylaniline were purchased from Aldrich Chemical Co. and used without further purification. Methanol, *n*-hexane and ethyl acetate were purchased from Oriental Chemical Ind. and used after distillation. Silica gel (230-400 mesh, Merck Co.) was used for liquid column chromatography. Photoreactions were analyzed by TLC plates purchased from Merck Co. (silica gel 60 F254, 0.25 mm).

Methods

¹H and ¹³C NMR spectra were recorded on Bruker AM-400, AN-300, and AM-200 MHz spectrometers. Proton chemical shifts (δ) were reported in ppm downfield from tetramethylsilane (TMS), and ¹³C resonances were recorded using the 77.0 ppm CDCl₃.

[†]Dedicated to Professor Sang Chul Shim on the occasion of his 65th birthday.

*To whom correspondence should be addressed.

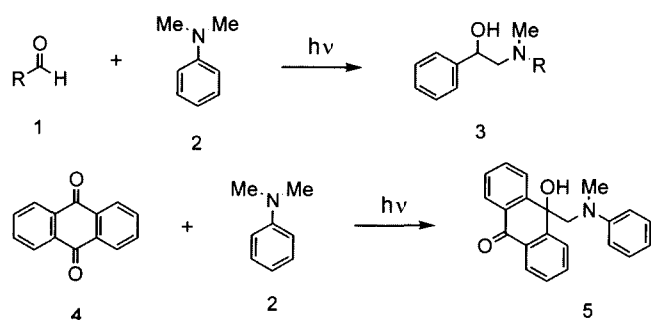
E-mail : hvssk@moak.chonbuk.ac.kr

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resonance of the solvent as an internal reference and reported in ppm downfield from TMS. Infrared (FTIR) spectra were recorded on a Nicolet 5-DX1 Fourier Transform spectrophotometer in KBr pellets or NaCl cell, reporting peaks in reciprocal centimeters (cm⁻¹). Relevant absorption maxima are designated in cm⁻¹ relative to the polystyrene 1644 cm⁻¹ band. Ultraviolet (UV) spectra were recorded on a Hitachi-556 spectrophotometer. Mass spectra were determined at 40-70 eV with a Hewlett-Packard 5985A GC/MS spectrometer by the electron impact (EI) method. Irradiation was carried out in a Rayonet photochemical reactor (The Southern New England Ultraviolet Company, Model RPR-208) equipped with 300 nm UV lamps, water-cooled reaction vessel and cooling fan.

RESULTS AND DISCUSSION

It is well known that irradiation of carbonyl compounds in the presence of amines may lead to a variety of products, depending upon the reaction conditions, *i.e.*, concentration or molar ratio of the starting materials, solvent polarity, irradiation sources, *etc.* We found that direct irradiation of some carbonyl compounds, *e.g.*, **1** and **4**, in *N,N*-dimethylaniline (DMA, **2**), without using other solvents, overcome a serious problem in these reactions, *i.e.*, low chemical yields of photoproducts and the formation of many kinds of products, as shown in Scheme 1 [9]. We selected some aldehydes such as benzaldehyde (R=C₆H₅), naphthaldehyde (C₁₀H₇), vanillin (C₆H₃(OH)(OCH₃)), 2-furaldehyde (C₄H₃O) and *t*-cinnamaldehyde (C₆H₅CH=CH) to investigate the photochemical reactions with DMA, in the atmosphere of dry nitrogen, by using 300 nm UV light. The photoproducts **3** were obtained in 36-79% yields with two conformeric mixtures, except for the case of naphthaldehyde. ¹H-NMR spectrum taken in DMSO-d₆ showed that the ratio of the conformers **3** depends upon the temperature in the range of 20-140°C. Acyclic and cyclic ketones such as acetone, cyclohexanone, *etc.* were also irradiated under the similar conditions to give β -hydroxyamines. Irradiation of anthraquinone



Scheme 1.

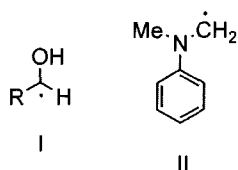


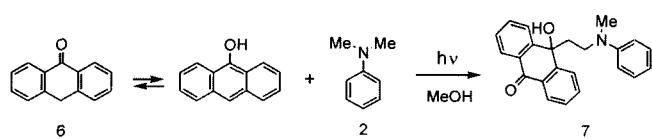
Figure 1.

4 in DMA with 300 nm UV light gave the same type of β -hydroxyamine **5**. In the case of tetrahalo-1,4-benzoquinones, it was found that the photoproducts were found to be 4-(dimethylamino)benzaldehyde and β -hydroxyamines. In contrast to these results, we found that irradiation of anthrone **6** and DMA **2** in methanol yielded γ -hydroxyamine, instead of β -hydroxyamines.

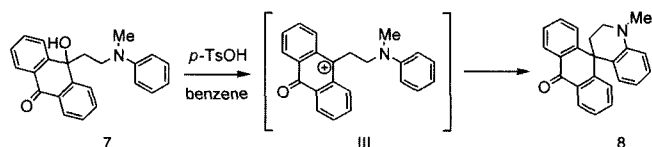
Irradiation of anthraquinone **4** (1 mmol) in DMA (10 mL) with 300 nm UV light also gave the same kind of product **5** in 11% yield. Three peaks were observed at δ 3.58 (NCH_2), 2.99 (NCH_3) and 6.60 (OH) in $^1\text{H-NMR}$ spectrum (CDCl_3). The formation of β -hydroxyamines, e.g., **3**, can be easily interpreted by the intermolecular H-abstraction which leads to radical intermediates **I** and **II**, as shown in Figure 1. Based on these results, it may be possible to make a variety of natural β -hydroxyamines by direct irradiation of the relevant carbonyl compounds in DMA in higher yields.

In the meantime, irradiation of a methanol solution of anthrone **6** and DMA **2** with 300 nm UV light afforded γ -hydroxyamine **7**, instead of β -hydroxyamine [10]. Dissolving anthrone **6** in methanol yields strongly fluorescent anthranol, i.e., enolic tautomer of **6**. Anthrone **6** (1 mmol) and an excess of DMA **2** (3 mL) were dissolved in methanol (30 mL), and purged with dry nitrogen for 30 min and followed by irradiation for 24 h. The major product was found to be γ -hydroxyamine **7** (37%) which was isolated as yellow solid by column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate as the eluent (20:1 to 2:1, v/v), as shown in Scheme 2.

Whereas the mechanism for the formation of compound **7** still remains unsolved, the structure of this new compound could be confirmed by refluxing a benzene solution of **7** in the



Scheme 2.



Scheme 3.

presence of *p*-toluenesulfonic acid (*p*-TsOH) for 3 h to yield bicyclic compound **8** in 45% yield, as shown in Scheme 3. The formation of this new heterocompound can be interpreted by acid-catalyzed dehydroxylation followed by intramolecular substitution reaction. Dehydroxylation of **7** by acid may result in carbocation intermediate **III**, in which the stable tertiary cation as electrophile took part in aromatic substitution reaction to give the final product **8** as a six-membered ring [11]. $^1\text{H-NMR}$ spectrum (CDCl_3) of **8** shows two methylene peaks of six-membered ring at δ 3.20 and 2.14 ppm. Mass spectrum (EI) was also obtained, in which the molecular ion peak of **8** was found at m/e 325. The bicyclic compound **8** was found to be less polar than **7**, when compared these two molecules by using thin layer chromatography.

In summary, we found that irradiation of carbonyl compounds including some aldehydes, ketones, anthraquinone, etc. in DMA afforded β -hydroxyamines as the major products. Meanwhile, γ -hydroxyamine **7** can be produced when irradiated anthrone **6** and DMA **2** in methanol. Irradiation of anthrone in DMA, without using other solvents, gave rise to different kinds of photoproducts. Characterization of this product and mechanistic investigation of these photoreactions are in progress.

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10. Spectral data of **7**: UV(MeOH), λ_{\max} 255 nm; IR(KBr) 3442, 3066, 2932, 1649, 1602, 1501, 1273, 749, 695 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 8.20 (2H, d), 7.90 (2H, d), 7.67 (2H, t), 7.48 (2H, t), 7.07 (2H, t), 6.65 (1H, t), 6.30 (2H, d), 3.38 (1H, s), 2.81 (2H, t), 2.62 (3H, s), 2.14 ppm (2H, t); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 183.5, 148.8, 146.9, 133-6-125.9, 117.2, 113.2, 71.8, 48.1, 43.6, 38.9 ppm; Mass(EI), *m/e* 343 (M).
11. Spectral data of **8**: $^1\text{H-NMR}(\text{CDCl}_3)$ δ 8.32 (2H, d), 7.47 (2H, t), 7.41 (2H, t), 7.21 (1H, t), 7.13 (2H, d), 6.86 (1H, d), 6.59 (2H, m), 3.20 (2H, t), 3.06 (3H, s), 2.14 (2H, t) ppm; $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 184.3, 151.9, 148.4, 132.9-125.7, 117.2, 111.7, 47.2, 46.3, 44.3 ppm; Mass(EI), *m/e* 325 (M).