

TiO₂-Mediated Photoreactions of Cinnamic Acid and Related Compounds in Methanol

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Photochemical reactions of some organic molecules on titanium dioxide were investigated in methanol. A methanolic solution of *trans*-cinnamic acid and titanium dioxide was irradiated with 300 nm UV lamps for 24 h to afford methyl cinnamate. In the case of *trans*-cinnamamide, the major product was found to be 3-phenylpropionamide, i.e., a saturation product of ethylenic double bond. However, irradiation of urocanic acid, caffeic acid, ethyl cinnamate, *trans*-chalcone, *trans*-cinnamitrile, *trans*-stilbene or *trans,trans*-1,4-diphenyl-1,3-butadiene on titanium dioxide under the same conditions did not give any noticeable products. Meanwhile, when irradiated some aromatic aldehydes, such as *trans*-cinnamaldehyde, 1-naphthaldehyde, and 2-naphthaldehyde in methanol, vicinal diols and alcohols derived from the diols were produced. On the other hand, irradiation of 9-anthraldehyde and titanium dioxide in methanol afforded only alcohols, in which diol was not observed.

key words: titanium dioxide, *trans*-cinnamic acid, *trans*-cinnamamide, *trans*-cinnamaldehyde, 1-naphthaldehyde, 2-naphthaldehyde, 9-anthraldehyde

INTRODUCTION

Titanium dioxide (TiO₂) is one of the most investigated semiconductors due to its ultraviolet-visible absorption band and chemical stability [1-3]. Irradiation of titanium dioxide promotes one electron from the valence band to the conduction band. The electron in the conduction band is readily available for transfer while the electron hole in the valence band is open for donation. A reactant that receives the electron from TiO₂ would be reduced, while a reactant that donates an electron to TiO₂ would be oxidized. Based on this redox system, a variety of organic reactions can be catalyzed by semiconductors. Extensive works have been carried out on the oxidation and oxidative cleavage sensitized by TiO₂ [4-6]. An interesting example of an oxidative photocleavage sensitized by semiconductor is the photo-oxidation of toluene to benzaldehyde and then to benzoic acid, sensitized by TiO₂ in acetonitrile. Reduction, isomerization and polymerization sensitized by TiO₂ have also been of great interest [7-9]. Reduction of aldehydes using metallic catalysts has been of great interest in many areas. The performance of the catalysts in these reactions can be enhanced through the use of reducible oxide supports including TiO₂. Herein we report the photoproducts identified by the irradiation of methanolic solutions of *trans*-cinnamic acid, *trans*-cinnamamide, *trans*-cinnamitrile, *trans*-cinnamaldehyde and some aromatic aldehydes on TiO₂ with 300 nm UV light.

MATERIALS AND METHODS

Materials

Titanium dioxide used in this work was Degusa P-25 powder, which was purchased from SHI. *trans*-Cinnamic acid, *trans*-cinnamamide, *trans*-cinnamitrile, *trans*-cinnamaldehyde, *trans*-chalcone, *trans*-stilbene, *trans,trans*-1,4-diphenyl-1,3-butadiene, *trans*-urocanic acid and caffeic acid were purchased from Aldrich Chemical Co. Some aldehydes such as 1-naphthaldehyde, 2-naphthaldehyde, and 9-anthraldehyde were also purchased from Aldrich Chemical Co. and used without further purification. Silica gel (Kieselgel 60 F254, Merck Co.) was used for thin layer chromatography. Kieselgel G (230-400 mesh) purchased from Merck Co. was used for liquid column chromatography. *n*-Hexane and ethyl acetate were obtained from Ducksan Chemical Co. to use as the eluent in TLC and column chromatography.

Methods

¹H and ¹³C NMR spectra were recorded on a Jeol JMN EX-400 spectrometer. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS), and ¹³C resonances were recorded using the CDCl₃ resonance (77.0 ppm) of the solvent as an internal standard and reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Nicolet 5-DXB Fourier transform spectrophotometer in KBr pellets or NaCl cell, peaks are reported in reciprocal centimeters (cm⁻¹). Ultraviolet (UV) spectra were recorded on a Beckman DU 7500 spectrophotometer. Mass spectra were determined at 40-70 eV with a Hewlett-Packard 5985A GC/MS spectrometer by electron impact (EI) method. All reactions were carried out under dry

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nitrogen atmosphere in oven-dried glassware. Evaporation of solvents was carried out with a rotary evaporator using vacuum pump.

Photoreactor

Irradiation was carried out with a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Model RPR-208) equipped with 300 nm UV lamps, water-cooled reaction vessels and a cooling fan.

Irradiation and Characterization

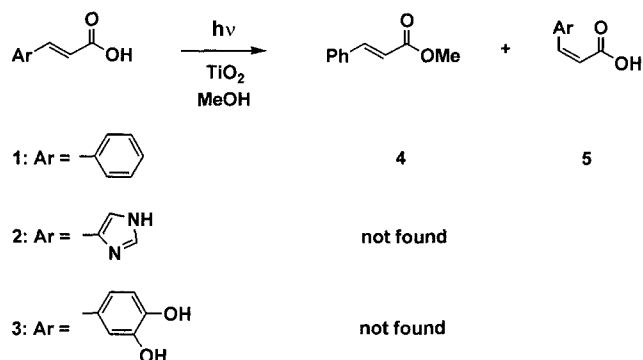
Reactants (1 mmol) were dissolved in methanol (30 mL) and added titanium dioxide (10 mmol). Reaction mixtures were purged with dry nitrogen gas to remove molecular oxygen gas for 30 min before irradiation with 300 nm UV lamps for 24 h. Progress of the photoreactions was analyzed by TLC and NMR spectra. A rotary evaporator was used to remove solvents followed by liquid column chromatography using *n*-hexane and ethyl acetate as the eluents. The photoproducts were characterized by spectral data such as UV, IR, NMR and Mass spectra.

Spectral Data

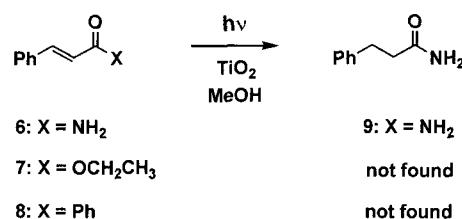
4: UV (MeOH), λ_{\max} 275 nm; IR (KBr), 3030, 2931, 1720, 1642, 1453, 1320, 1265, 769, 690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 7.70 (1H, =CH-Ph, d, $J=15.6$ Hz), 7.52 (2H, Ph), 7.38 (3H, Ph), 6.42 (1H, -CH=CHPh, d, $J=15.6$ Hz), 3.39 (3H, s, OCH₃); $^{13}\text{C-NMR}$ (CDCl_3), δ 167, 145, 134, 130, 129, 128, 118, 52. **9:** UV (MeOH), λ_{\max} 268, 210 nm; IR (KBr), 3308, 2931, 1673, 1547, 1453, 761, 683 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 7.26 (5H, Ph), 5.42 (2H, NH₂, s), 2.98 (2H, -CH₂-CH₂Ph, t, $J=15.2$ Hz), 2.54 (2H, -CH₂Ph, t, $J=15.2$ Hz); $^{13}\text{C-NMR}$ (CDCl_3), δ 174, 141, 128, 127, 126, 37.6, 31.5; Mass (EI), m/e 149 (M). **11:** UV (MeOH), λ_{\max} 274 nm; $^1\text{H-NMR}$ (CDCl_3), δ 7.33 (10H, Ph), 6.74 (2H, =CHPh), 6.28 (2H, -CH=CHPh), 4.44 (2H, -CHOH), 2.24 (2H, OH); Mass (EI), m/e 133 (M/2). **12:** IR (KBr), 3410, 3033, 2939, 1665, 1603, 1493, 1453, 1068, 966, 754, 699 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 7.25 (5H, Ph), 6.55 (1H, -CHPh), 6.30 (1H, -CH=CHPh), 4.26 (2H, CH₂OH), 2.80 (1H, OH); Mass (EI), m/e 134 (M). **19:** $^1\text{H-NMR}$ (CDCl_3), δ 7.95-7.41 (14H, aromatic), 5.97 (2H, CHOH); Mass (EI) m/e 314 (M). **20:** $^1\text{H-NMR}$ (CDCl_3), δ 8.21-7.44 (7H, aromatic), 5.14 (2H, CH₂OH); $^{13}\text{C-NMR}$ (CDCl_3), δ 136, 134, 131, 129, 127, 126, 125, 124, 64; Mass (EI), m/e 158 (M). **21:** $^1\text{H-NMR}$ (CDCl_3), δ 7.94-7.49 (14H, aromatic), 5.56 (2H, CHOH); Mass (EI), m/e 314 (M). **22:** $^1\text{H-NMR}$ (CDCl_3), δ 7.80-7.46 (7H, aromatic), 4.80 ppm (2H, CH₂OH); $^{13}\text{C-NMR}$ (CDCl_3), δ 135, 133, 132, 128, 127, 126, 125, 69; Mass (EI), m/e 158 (M). **23:** $^1\text{H-NMR}$ (CDCl_3), δ 8.47 (1H, aromatic), 8.42 (2H, aromatic), 8.03 (2H, aromatic), 7.57 (2H, aromatic), 7.49 (2H, aromatic), 5.68 (2H, CH₂OH); Mass (EI) m/e 208 (M).

RESULTS AND DISCUSSION

Titanium dioxide is one of the most interesting photocatalysts in many aspects. For this study on TiO₂-



Scheme 1.



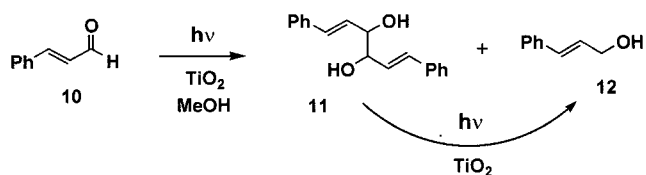
Scheme 2.

mediated photoreactions, we selected some cinnamyl and related compounds. Irradiation of a methanolic solution (30 mL) of *trans*-cinnamic acid **1** (1 mmol) and TiO₂ (10 equiv) with 300 nm UV light for 24 h afforded methyl *trans*-cinnamate **4** in 36% yield, along with trace amount of *cis*-isomer **5**, as shown in Scheme 1. However, other derivatives such as urocanic acid **2** and caffeic acid **3** did not yield any noticeable products, except for the corresponding *cis*-isomers, when irradiated them under the same conditions.

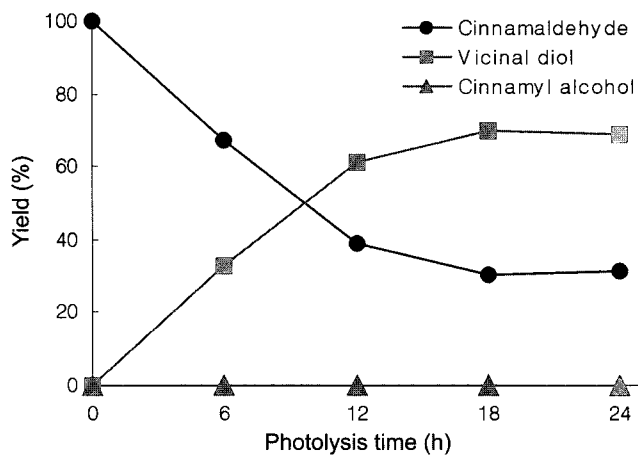
When a suspension of titanium dioxide containing *trans*-cinnamamide **6** was irradiated in methanol, the ethylenic unsaturation of the α,β -ethylenic compound **6** was found to be predominant, as shown in Scheme 2. Irradiation of a methanolic solution (30 mL) of **6** (1 mmol) and TiO₂ (10 equiv) with 300 nm UV light for 24 h afforded 3-phenylpropionamide **9** in 45% yield. In contrast, when irradiated ethyl *trans*-cinnamate **7** and *trans*-chalcone **8** under the same conditions, any noticeable products were not observed, except for the corresponding *cis*-isomers.

Photocatalytic reduction of *trans*-cinnamaldehyde **10** was also investigated to give unsaturated alcohols which are very useful intermediates in fine chemicals production [10]. Irradiation of a methanolic solution (30 mL) of **10** (1 mmol) and TiO₂ (10 equiv) with 300 nm UV light for 24 h afforded vicinal diol **11** in 45% yield and *trans*-cinnamyl alcohol **12** in 36% yield, as shown in Scheme 3. In this case, saturation product of ethylenic double bond was not found as judged by $^1\text{H-NMR}$ of the reaction mixture. It was found that irradiation of **11** and TiO₂ in methanol gives **12**, which was not produced when irradiated only **11**, in the absence of TiO₂, in methanol.

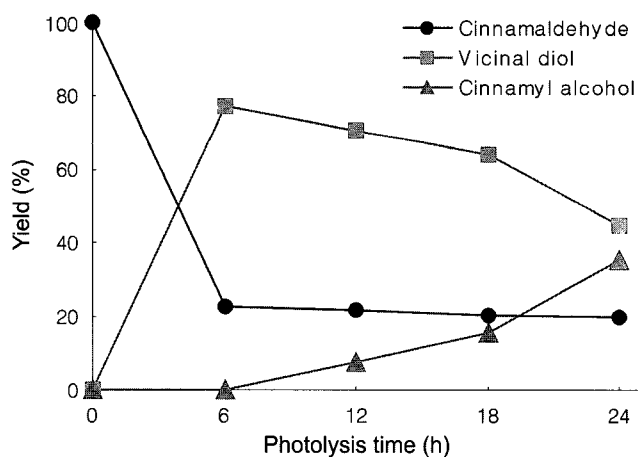
The photoreaction mixtures of **10**, in the absence and in presence of TiO₂, were compared in methanol. As shown in



Scheme 3.

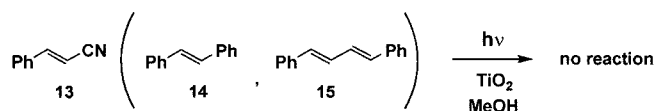


(a)



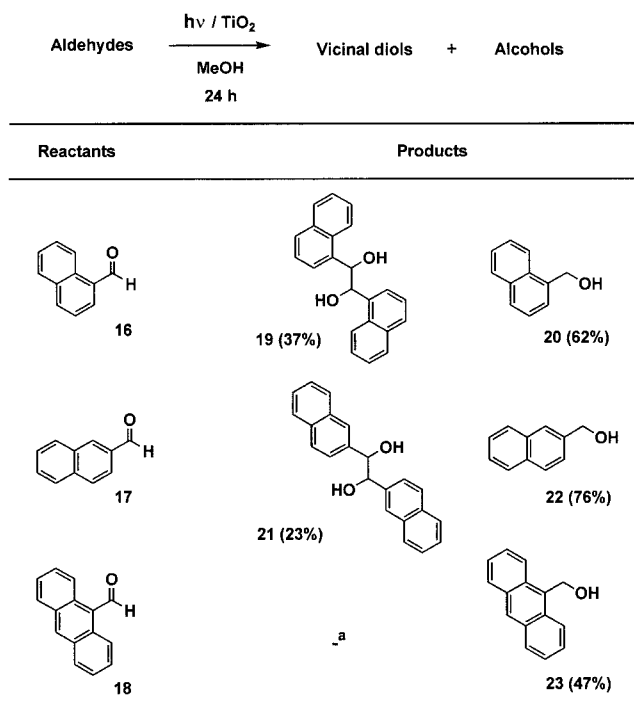
(b)

Figure 1. Irradiation of methanolic solutions of *trans*-cinnamaldehyde **10** in the absence (a) and in the presence (b) of TiO₂ with 300 nm UV lamps.



Scheme 4.

Figure 1, on irradiation of **10** in the absence of TiO₂, the amount of vicinal diol **10** increased with increase of irradiation time, in which cinnamyl alcohol **12** was not observed as determined by ¹H-NMR and HPLC. In contrast, when irradiated **10** in the presence of TiO₂, the amount of cinnamyl alcohol **12** increases with increase of irradiation time. It was found that **12** has formed as the final product,



^a: not found

Scheme 5.

when irradiated **11** and TiO₂ in methanol.

We also carried out the photoreactions of other compounds, such as *trans*-cinnamitrile **13**, *trans*-stilbene **14**, and *trans,trans*-1,4-diphenyl-1,3-butadiene **15**, on TiO₂, under the same conditions. However, any noticeable compounds were not produced as determined by ¹H-NMR (Scheme 4).

In the mean time, TiO₂-mediated photoreaction of benzaldehyde has been reported, in which the major products were found to be vicinal diol and benzyl alcohol [11]. We selected some aldehydes, such as 1-naphthaldehyde **16**, 2-naphthaldehyde **17** and 9-anthraldehyde **18**, to compare the photochemical reactivity, as shown in Scheme 5.

As shown in Scheme 5, irradiation of a methanolic solution (30 mL) of 1-naphthaldehyde **16** (1 mmol) on TiO₂ (10 equiv) with 300 nm UV lamps for 24 h afforded both vicinal diol **19** (37% yield) and 1-hydroxymethylnaphthalene **20** (62% yield) derived from **19**. Similarly, irradiation of 2-naphthaldehyde **17** under the same condition afforded the same type of products **21** (24% yield) and **22** (76% yield). However, in the case of 9-anthraldehyde **18**, the major product isolated was only 9-hydroxymethylantracene **23**, in which a vicinal diol was not observed as judged by ¹H-NMR.

In summary, we found some photochemical transformations of cinnamyl and related compounds, including aromatic aldehydes, when irradiated on TiO₂ in methanol. Methyl ester was the sole product of TiO₂-mediated photoreaction of *trans*-cinnamic acid in methanol. When irradiated aldehydes on TiO₂ in methanol, the major products were found to be vicinal diols and alcohols derived from the diols. In the case of *trans*-

cinnamamide, the saturation product of ethylenic double bond was predominant, in which 3-phenylpropionamide was produced.

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