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Photochemical Ring-Opening of Acid Anhydrides by TiO_2 Photocatalyst in Methanol

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Photoreactions of some carbonyl compounds with TiO_2 were investigated in methanol. Although 1,3-cyclohexanedione and phthalimide afforded 3-methoxy-2-cyclohexen-1-one and 3-methoxy-1-isoindolinone, respectively, acid anhydrides such as succinic, phthalic, and maleic anhydrides gave the monoesters of dicarboxylic acids in good to excellent yields, when they were irradiated on TiO_2 in methanol with 300 nm UV light.

key words: TiO_2, succinic anhydride, phthalic anhydride, maleic anhydride, photoreacton

INTRODUCTION

Titanium dioxide (TiO_2) is one of the most investigated photocatalysts due to its ultraviolet-visible absorption band and chemical stability.[1-3] Chemical substances that receive an electron from TiO_2 would be reduced, while substances that donate an electron to TiO_2 would be oxidized. Based on this redox system, a variety of organic reactions can be catalyzed by photocatalysts. Reduction, isomerization and polymerization mediated by TiO_2 have also been of great interest.[4-7] Oxidation and oxidative cleavage reactions sensitized by TiO_2 in water have been carried out in many groups.[8-10] Recently, we investigated the photochemical reactions of some 1,3-dicarbonyl systems on TiO_2 photocatalyst in methanol, instead of water. To compare the reactivities on TiO_2, we selected some 1,3-dicarbonyl compounds such as 1,3-diketone, imide, and acid anhydride to irradiate on TiO_2 with UV light in methanol. Our results showed that, in the case of 1,3-cyclohexanedione **1a** and phthalimide **1b**, the major products isolated in the photoreactions were an enol ether **2a** and an isoindolinone **2b**, respectively, as shown in Scheme 1. However, irradiation of acid anhydrides (**3**, X=O) on TiO_2 in methanol afforded different types of compounds, *i.e.*, ring-opened products **4**, as shown in Scheme 1. Herein we report that, when solutions of anhydrides on TiO_2 in methanol were irradiated with 300 nm UV light, *mono*-methyl esters of the corresponding dicarboxylic acids were produced in good to excellent yields.

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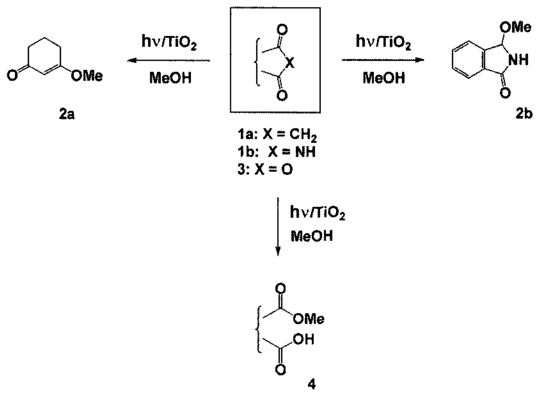


Scheme 1.

MATERIALS AND METHODS

Materials

Titanium dioxide (TiO_2) was Degussa P-25, which was purchased from Degussa. Phthalic anhydride, maleic anhydride, succinic anhydride, 1,3-cyclohexanedione, and phthalimide were purchased from Aldrich Chemical Company. *n*-Hexane, ethyl acetate, and methanol were obtained from Oriental Chemical Industries.

Methods

Evaporation of solvent was carried out with a rotary evaporator using vacuum pump. Merck pre-coated silica gel plates (Art. 5554) with fluorescent indicator were used as analytical TLC. Flash column chromatography was carried out on silica gel (230-400 mesh, Merck Co.). 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 vessels and a cooling fan. ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-EX400 spectrometer. Proton chemical shifts (δ) are reported in ppm downfield from tetramethyl-silane (TMS), and ^{13}C resonances were recorded using the 77.0 ppm $CDCl_3$ resonance of the solvent as the reference. Infrared (IR) 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 were 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. All the reactions were run under dry nitrogen atmosphere in oven-dried glassware.

*Photochemical formation of 3-methoxycyclohex-2-en-1-one **2a** by TiO_2*

A solution of 1,3-cyclohexanedione **1a** (224 mg, 1 mmole) and TiO_2 (799.0 mg, 10 mmole) in methanol (30 ml) was deoxygenated by passing dry nitrogen gas through the reaction vessel for 30 min, and then irradiated with 300 nm UV light for 24 h. The photoreaction mixture was analyzed by TLC using *n*-hexane and ethyl acetate (4:1, v/v) as the eluant. After irradiation of the reaction mixture, TiO_2 was removed by filtration over a silica gel pad. And then, the reaction mixture was concentrated in vacuo and followed by flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate as the eluant to give 3-methoxycyclohex-2-en-1-one **2a** in quantitative yield. Spectral data of **2a**; ^{1}H-NMR ($CDCl_3$) δ 1.9 (2H, m), 2.3 (6H, t and t, overlapped), 3.6 (3H, s), 5.3 (1H, s); ^{13}C-NMR ($CDCl_3$) δ 21.1, 28.7, 36.7, 55.6, 102.2, 178.7, 199.6; IR(KBr) 2945, 1666, 1608, 1003 cm^{-1}; Mass(EI) m/e 126 (M), 98.

*Photochemical formation of 3-methoxy-1-isoindolinone **2b** by TiO_2*

A solution of phthalimide **1b** (147 mg, 1 mmole) and TiO_2 (80 mg, 1 mmole) in methanol (40 ml) was deoxygenated by passing dry nitrogen gas through the reaction vessel for 30 min, and then irradiated with 300 nm UV light for 24 h. The photoreaction mixture was analyzed by TLC using *n*-hexane and ethyl acetate (4:1, v/v) as the eluant. After irradiation of the reaction mixture, TiO_2 was removed by filtration over a silica gel pad. And then, the reaction mixture was concentrated in vacuo and followed by flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate as the eluant to give 3-methoxy-1-isoindolinone **2b** in 21% yield as well as 1-hydroxy-isoindolinone (32%) which is produced when **1b** is irradiated in the absence of TiO_2 in methanol. In addition, an unidentified product was also isolated in 31% in this photoreaction. Spectral data of **2b**; ^{1}H-NMR ($CDCl_3$) δ 3.18 (3H, s, OCH_3), 6.00 (1H, s, CH), 6.78 (1H, s, NH), 7.53-7.86 (4H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 51.47, 84.31, 123.69, 123.78, 129.98, 132.06, 132.60, 142.66, 170.23; IR (KBr) 3306, 1678, 1650 cm^{-1}; LC/MS m/e 163 (M).

*Photoreactions of acid anhydrides **3** with TiO_2*

*Succinic anhydride **3a***: A solution of succinic anhydride **3a** (200 mg, 2 mmole) and TiO_2 (799.0 mg, 10 mmole) in methanol (30 ml) was deoxygenated by passing dry nitrogen gas through the reaction vessel for 30 min, and then irradiated with 300 nm UV light for 24 h. The photoreaction mixture was analyzed by TLC using *n*-hexane and ethyl acetate (4:1, v/v) as the eluant. After irradiation of the reaction mixture, TiO_2 was removed by filtration over a silica gel pad. And then, the reaction mixture was concentrated in vacuo and followed by flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate as the eluant to give *mono*-methyl succinate **4a** (263 mg) in quantitative yield. Spectral data of **4a**; ^{1}H-NMR ($CDCl_3$) δ 2.38 (2H, t), 2.42 (2H, t), 3.5 (3H, s), 9.3 (1H, br s); ^{13}C-NMR ($CDCl_3$) δ 28.8, 29.3, 51.0, 172, 174.

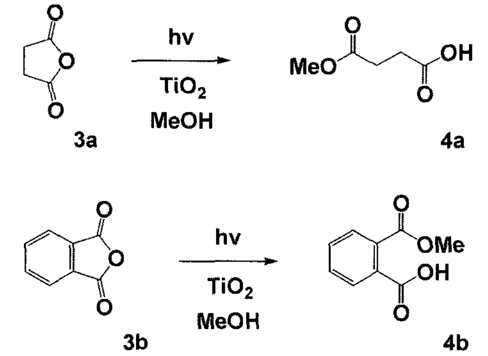
*Phthalic anhydride **3b***: Same procedure as above gave *mono*-methyl phthalate **4b** in quantitative yield. Spectral data of **4b**; ^{1}H-NMR ($CDCl_3$) δ 3.86 (3H, s), 7.5-7.8 (4H, m), 12.0 (1H, s).

*Maleic anhydride **3c***: Same procedure as above gave *mono*-methyl maleate **5** (36%), *mono*-methyl fumarate **6** (18%), and *mono*-methyl succinate **4c** (46%). Spectral data of **5**; ^{1}H-NMR ($CDCl_3$) δ 3.8 (3H, s), 6.6 (1H, d), 6.8 (1H, d), 10.4 (1H, s). Spectral data of **6**; ^{1}H-NMR ($CDCl_3$) δ 3.7 (3H, s), 5.8 (1H, d), 6.4 (1H, d), 10.4 (1H, s).

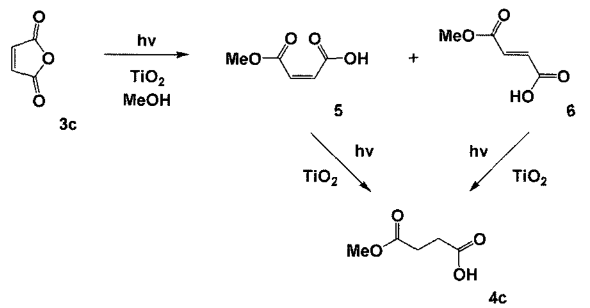
RESULTS AND DISCUSSION

In connection with the chemical transformation of organic molecules by TiO_2 photocatalyst, we have been interested in the photochemistry of some carbonyl compounds, such as 1,3-diketones, imides, and acid anhydrides. TiO_2 suspended in methanol was used to investigate their photochemical reactivity. Irradiation of solutions of 1,3-cyclohexanedione **1a** and phthalimide **1b** on TiO_2 in methanol afforded 3-methoxy-2-cyclohexen-1-one **2a** and 3-methoxy-1-isoindolinone **2b**, respectively, as shown in Scheme 1. On the other hand, it was found that acid anhydrides **3a-c** were cleaved into the monoesters of dicarboxylic acids, when they were irradiated on TiO_2 in methanol. No noticeable products were found from the photoreactions of **3a-c** in methanol. Irradiation of a solution of succinic anhydride **3a** and TiO_2 in methanol for 24 h afforded a ring-opened product, *i.e.*, *mono*-methyl succinate **4a** in quantitative yield, as shown in Scheme 2. Similarly, irradiation of a solution of phthalic anhydride **3b** and TiO_2 in methanol in the atmosphere of nitrogen gas also gave the same type of ring opening product, *i.e.*, *mono*-methyl phthalate **4b**, in quantitative yield, as shown in Scheme 2. It was reported that **3b** is produced by oxidation of *o*-xylene on TiO_2-V_2O_5 catalyst.[13-15] Interestingly, **3b** can be mineralized in aqueous solution over TiO_2 particles to give CO_2 and others.[16] It is noteworthy to note that phthalic anhydride **3b** produced from *o*-xylene on TiO_2 catalyst under different reaction conditions undergoes cleavage reaction by TiO_2 in methanol to yield *mono*-methyl phthalate **4b** in quantitative yield.

Meanwhile, it was reported that TiO_2 acts as a catalyst for the oxidation of 1-butene and furan to maleic anhydride **3c**.[11] As for the selective hydrogenation of **3c**, TiO_2 catalyst



Scheme 2.



Scheme 3.

was also used to get butyric acid for the gas phase.[12] In contrast, we found that irradiation of a solution of **3c** and TiO_2 (10 equiv.) in methanol for 24 h afforded not only two ring-opened products, *i.e., mono*-methyl maleate **5** (35%) and *mono*-methyl fumarate **6** (18%), but also their reduction product, *i.e., mono*-methyl succinate **4c** (46%), in which the starting material **3c** was completely consumed (Scheme 3). Irradiation of the primary photoproducts **5** and **6** on TiO_2 in methanol also gave the same product **4c**.

In summary, irradiation of acid anhydrides **3a**, **3b**, and **3c** on TiO_2 in methanol gave ring-opened products **4a**, **4b**, and **4c** as monoesters of the corresponding dicarboxylic acids. However ring-opened products were not observed, when irradiated imides under the same conditions, in which isoindolinone and an unknown compounds were isolated. The investigation on the mechanistic study of these TiO_2-photocatalyzed reactions of imides and anhydrides in alcohols are in progress.

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