

Photochemical Reductions of Benzil and Benzoin in the Presence of Triethylamine and TiO₂ Photocatalyst[†]

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Received May 1, 2002

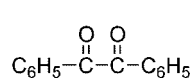
This paper reports the photochemical reduction of benzil **1** to benzoin **2** and the reduction of **2** to hydrobenzoin **4** in deoxygenated solvents in the presence of triethylamine (TEA) and/or TiO₂. Without TEA or TiO₂, the photolysis of **1** resulted in very low yield of **2**. The presence of TEA or TiO₂ increased the rate of disappearance of **1** and the yield of **2**, which were further increased considerably by the presence of water. The photoreduction of **1** to **2** proceeds through an electron transfer to **1** from TEA or hole-scavenged excited TiO₂ followed by protonation. In the reaction medium of 88 : 7 : 2 : 3 CH₃CN/CH₃OH/H₂O/TEA with 2.5 mg/mL of TiO₂, the yield of **2** was as high as 85 % at 50 % conversion of **1**. The photolysis of **2** in homogeneous media resulted in photo-cleavage to benzoyl and hydroxybenzyl radicals, which are mostly converted to benzaldehyde. The reduction product **4** is formed in low yield through the dimerization of hydroxybenzyl radicals. The addition of TEA increased the conversion rate of **2** and the yield of **4** significantly. This was attributed to the scavenging effect of TEA for benzoyl radical to produce N,N-diethylbenzamide and the photoreduction of benzaldehyde in the presence of TEA. The ratio of (±) and meso isomers of **4** obtained from the photochemical reaction is about 1.1. This ratio is the same as that from the photochemical reduction of benzaldehyde in the presence of TEA. In the TiO₂-sensitized photochemical reduction of **2**, meso-**4** was obtained in moderate yield. The reduction of **2** to **4** proceeds through two consecutive electron/proton transfer processes on the surface of the photocatalyst without involvement of α-cleavage. The radical **11** initially formed from **2** by one electron/proton process can also combine with hydroxy methyl radical, which is generated after hole trapping of excited TiO₂ by methanol, to produce 1,2-diphenylpropenone after dehydration reaction.

Key Words : Photochemistry, Reduction, Benzyl, Benzoin, TiO₂

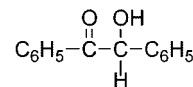
Introduction

Photochemistry of benzil **1**, one of the typical α-dicarbonyl compounds, has been an intriguing subject to many photochemists. The compound **1** is relatively photostable in non-hydrogen-donating solvents, while it undergoes photoreduction in hydrogen-donating solvents such as alcohols to give benzoin **2** and benzilpinacol **3**, together with a variety of decomposition products.¹⁻³ The reported yield of **2** by direct photochemical reaction of **1** is below 20%. It was also reported that **1** can undergo photochemical transformation in the presence of triethylamine (TEA) through electron-transfer pathway.²⁻⁸

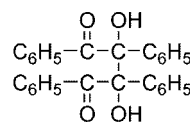
Benzoin **2** and its derivatives also undergo photochemical α-cleavage.⁹⁻¹² In the photolysis of **2** in benzene, benzaldehyde and benzoin benzoate were found as major and minor products, respectively.¹¹ The photolysis of benzoin ethers and benzoin esters gives pinacol ethers and pinacol esters, respectively, in ca. 30% yields by α-cleavage followed by free radical recombination reactions of the substituted



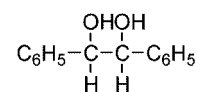
1: benzil



2: benzoin



3: benzilpinacol



4: hydrobenzoin

benzyl radicals.¹² However, photochemical conversion of **2** or its derivatives to hydrobenzoin **4** or its derivatives without involvement of α-cleavage and recombination of the photofragments has not been reported.

Photochemical reactions mediated by semiconductors have drawn a great amount of interest in transformation of organic functional groups,¹³⁻¹⁹ solar energy conversion and storage,²⁰ and photochemical clean-up of organic pollutants.²¹ Titanium dioxide (TiO₂) is one of the most studied semiconductor due to its uv-vis absorption and chemical stability. Compared to degradation and oxidation reactions, the reports on the TiO₂-mediated photoreduction of organic compounds has been rather limited: the reductions of pyruvate to lactate,¹⁴ organic

[†]This paper is dedicated to the deceased Prof. Sang Chul Shim of KAIST, Korea, for his great contribution to research and education in chemistry.

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nitro-¹⁵ and nitroso-compounds¹⁶ to amines, bis(2-dipyridyl)-disulfide to 2-mercaptopyridine,¹⁷ and aldehydes to alcohols¹⁸ have been studied. Recently, we reported TiO₂-sensitized photochemical reduction of 1,2-diketones, camphorquinone and 1-phenyl-1,2-propanedione, to the corresponding α -hydroxyketones in moderate to good yields.¹⁹ Here, we report efficient photoreduction of **1** to **2**, and **2** to **4** in the presence of TEA and/or TiO₂ photocatalyst.

Results and Discussion

Photochemical Reaction of Benzil 1. Photochemical reactions of **1** in the presence and the absence of TiO₂ were carried out in various deoxygenated solvents. In all cases, the rate of disappearance of **1** followed the first order kinetics (plots not shown) and the relative reaction rates are shown in Table 1. The yields of **2**, which were determined by hplc at ca. 50% conversion, are also included in Table 1: since **2** is also photolabile, the yield of **2** depends highly on the extent of conversion of **1**.

We first describe and discuss the results of direct photochemical reactions of **1** in the absence of TiO₂ photocatalyst. As can be seen in Table 1, the disappearance rate of **1** is much slower in CH₃CN than in CH₃OH (entries 1 and 5). This agrees well with the reports that the quantum yield for disappearance of **1** depends strongly on the hydrogen donating ability of the solvent.¹ The reaction could be rationalized with the pathways in Chart 1.

The photo-excited **1** is cleaved into benzoyl radicals or transformed to the radical **5** by hydrogen atom abstraction from solvent molecule.¹⁻⁴ In the non-hydrogen-donating solvent, the former pathway is dominating, and the benzoyl radicals readily recombine and go back to **1**. In hydrogen-donating solvent, the latter pathway leading to **5** becomes important. The radical **5** can be transformed to benzoin **2** by further hydrogen-atom abstraction, or dimerize to benzil pinacol **3**, or decompose to benzoyl radical and benzaldehyde.¹⁻³ In the reaction products in CH₃OH, we detected only trace amounts of **2**.

The rate of disappearance of **1** and the yield of **2** in CH₃CN were greatly increased by the presence of triethylamine (TEA) (entry 2). Such effects of TEA were also

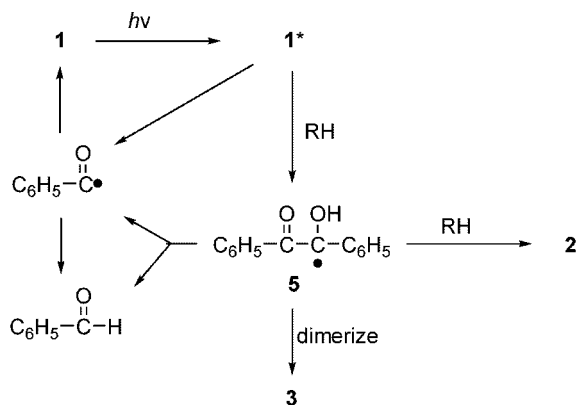


Chart 1. The Scheme of Direct Photochemical Reaction of Benzil 1.

Table 1. The Photochemical Reaction of Benzil **1**: Relative Disappearance Rate and the Yield of Benzoin **2**^a

entry	Medium	TiO ₂	Rel. Rate	Yield (%) of 2 ^b
1	CH ₃ CN	No	0.06	–
2	CH ₃ CN/TEA (95/5)	No	0.46	46
3	CH ₃ CN/TEA (95/5)	Yes	0.18	56
4	CH ₃ CN/CH ₃ OH(90/10)	Yes	0.26	47
5	CH ₃ OH	No	1.00	trace
6	CH ₃ OH	Yes	0.42	48
7	CH ₃ OH/ H ₂ O (80/20)	Yes	1.10	63
8	CH ₃ CN/CH ₃ OH/H ₂ O (88/10/2)	No	0.14	trace
9	CH ₃ CN/CH ₃ OH/H ₂ O (88/10/2)	Yes	0.47	50
10	CH ₃ CN/CH ₃ OH/H ₂ O/TEA (88/7/2/3)	Yes	1.8	85

^aTypical condition is 10 mM **1** (2 mg/mL) with 0 or 2.5 mg/mL of TiO₂ in nitrogen-purged solutions at 25 °C. ^bThe yield is based on the consumed **1** at about 50% conversion.

observed in 2-propanol² and in CH₃OH. Benzil **1** forms complexes with TEA in its excited triplet^{4,6,7} as well as in the ground state.^{2,6,7} It was suggested that the one-electron transfer from TEA to the excited triplet state of **1** gives benzil radical anion **6**.^{2,4} Okutsu *et al.* showed that the radical anion **6** in the contact-ion pair with TEA⁺ is protonated to **5** with rate constant of 1.5×10^6 s⁻¹ in benzene.⁷ They showed that the radical **5** is also formed from the ground-state complex of **1** with TEA with quantum yield of about unity by the intracomplex excited-state hydrogen-atom transfer. Such facile formation of **5** can explain the observed fast disappearance of **1** in the presence of TEA. However, one puzzling observation in the photochemical reaction of **1** in the presence of TEA was the low yield of benzil pinacol **3**, which could be formed by the dimerization reaction of **5**. Bunbury and Chan explained this in terms of complexation of **5** with TEA yielding **2** by hydrogen-atom transfer reaction while preventing the formation of **3**.² The reaction scheme involving TEA could be presented as Chart 2.

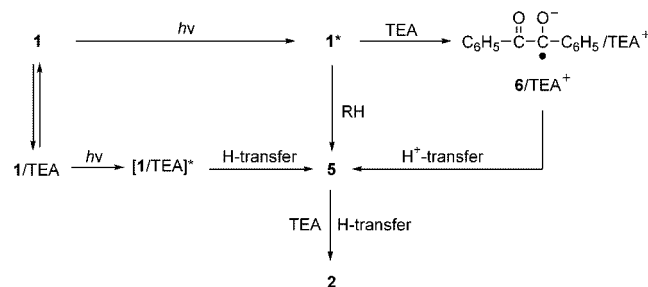
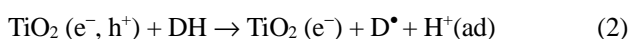


Chart 2. The Scheme of Photochemical Reaction of Benzil **1** in the Presence of TEA.

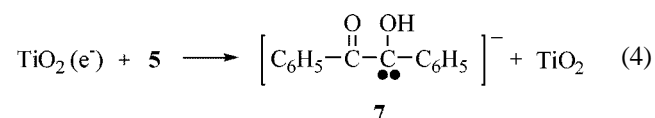
The disappearance rate of **1** was greatly affected by the presence of TiO₂. In CH₃OH and CH₃CN/TEA media, the rate was about 40% of that in the absence of TiO₂ in the corresponding media (compare entry 2 with 3, and entry 5 with 6 in Table 1). The rate retarding effect of TiO₂ for the

reaction of **1** is much less than that observed in the photochemical reaction of benzophenone (BP): the disappearance rate of BP was reduced to about one-tenth by the presence of TiO₂. The large retardation for the reaction of BP can be ascribed to the scattering and absorption of the irradiated light by TiO₂ which does not behave as photocatalyst for BP (see below).

In the presence of TiO₂, most of the irradiated light is absorbed by TiO₂ and conduction electron (e⁻) and hole (h⁺) pair are generated. Alcohols, amines, and water (abbreviated as DH) are good electron donors and trap holes giving conduction band electron, TiO₂(e⁻), and thus prevent the electron-hole recombination.¹³ DH dissociates into surface-bound D[•] radical and adsorbed proton in the process. The oxidation potential (E_b^0) of TiO₂(e⁻) in CH₃CN is about -0.8 V vs SCE;²² the value becomes more negative as pH of medium is higher.²³ The reduction potential of BP in CH₃CN was estimated as -1.88 V vs SCE,²⁴ whereas the first reduction potential of **1** in DMF was found to be *ca.* -1.0 V vs SCE.²⁵ Exact estimation of the thermodynamic driving force for the electron transfer from conduction band of TiO₂ to BP or **1** is not possible at this moment due to complicated nature of solvent reorganization energy and the effect of surface charge to E_b^0 . However, it appears that the electron transfer reaction from TiO₂(e⁻) to BP is not thermodynamically favorable, but the electron transfer to **1** occurs efficiently. The single electron transfer from TiO₂(e⁻) to **1** yields the radical anion **6**, which gives **5** after protonation. The electron transfer from TiO₂(e⁻) to **1** is analogous to the electron transfer from TEA to the excited **1**.



Reduction potential of the radical **5** was estimated to be about -1.4 V.²⁵ Thus, the further electron transfer from conduction electron of TiO₂ to the radical **5** producing anion **7** may also be thermodynamically feasible. The anion **7** might be finally transformed to **2** by proton transfer. This can



explain the high yield of **2** in the presence of TiO₂.

The addition of water to CH₃OH speeded up the TiO₂-mediated photochemical conversion rate of **1** and increased the yield of **2** significantly (compare entry 4 with 9, and entry 6 with 7 in Table 1). This suggests that water might be a better hole-scavenger than CH₃OH due to high affinity to the TiO₂ surface. Water could also act as a protonating agent for the anion **6** which is formed by initial electron transfer reaction.

The presence of TEA also speeded up the TiO₂-mediated photochemical conversion rate of **1** and increased the yield of **2**. Similar to this, Shen and coworkers reported the efficient photosensitized reduction **1** to **2** by TEA in the presence of anthracene dyes as photosensitizers.⁸ Since TiO₂ absorbs most of irradiated light, the photochemical reaction pathways depicted in Chart 2 would contribute little to the reaction of **1** in a medium containing TiO₂. Two roles of TEA in TiO₂-mediated photoreaction of **1** to **2** can be suggested. One is scavenging the hole to make the conduction band electron available for the reduction of **1** to **6**. The other is complexation with the radical **5**, which is formed from **6** by protonation, and conversion to **2** by intracomplex hydrogen-atom transfer (see Chart 2). With the synergetic effects of TiO₂, water, and TEA, we were able to obtain **2** in 85% yield with high quantum yield, *i.e.*, with high reaction rate (entry 10 in Table 1).

Photochemical Reaction of Benzoin 2. Benzoin **2**, which is a photoreduction product of **1**, also undergoes photochemical conversion.^{9,11} Table 2 summarizes the relative disappearance rates and the distribution of photoproducts of **2** under various conditions: hydrobenzoin **4** shows no appreciable photoreactivity under investigated conditions. The rate of disappearance of **2** in CH₃OH by direct photochemical reaction was about 1.1 times of that of **1**. Benz-

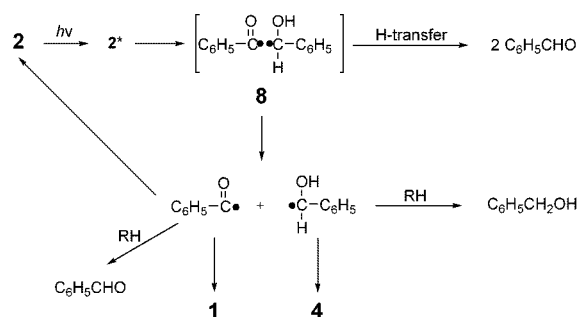


Chart 3. The Scheme for Photochemical Reaction of Benzoin 2.

Table 2. The Photochemical Reaction of Benzoin 2: Relative Disappearance Rate and the Yield of Major Products^a

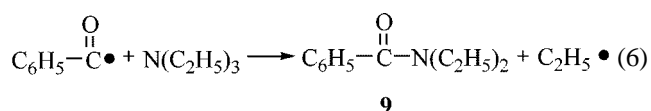
entry	Medium	TiO ₂	Rel. Rate	Yield (%) ^{b,c}			
				4		9	10
				±	meso		
1	CH ₃ CN/CH ₃ OH/H ₂ O (88/10/2)	No	1.00	9	8	—	<1
2	CH ₃ CN/CH ₃ OH/H ₂ O/TEA (88/7/2/3)	No	1.28	11	9	20	<1
3	CH ₃ CN/CH ₃ OH/H ₂ O/TEA (88/7/2/3)	Yes	0.73	trace	45	3	13

^aTypical condition is 20 mM benzil (4 mg/mL) with 0 or 2.5 mg/mL of TiO₂ in nitrogen-purged solutions at 25 °C. ^bThe yield is based on the consumed **2**. ^c**4**: hydrobenzoin; **9**: N,N-diethylbenzamide; **10**: 1,2-diphenylpropanone.

aldehyde was found as a major photoproduct and hydrobenzoin **4** was formed in about 10% yield. It is known that **2** undergoes photochemical α -cleavage to form a benzoyl and hydroxybenzyl radical pair.^{9,11} Further reactions of these radicals give various photoproducts (Chart 3).

The rate of disappearance of **2** in a medium of 88:10:2 CH₃CN/CH₃OH/H₂O was about half of that in CH₃OH. Such rate change is much smaller than that observed in the photolysis of **1**, one-seventh, by the same solvent variation (compare entries 5 and 8 in Table 1). This reflects the similar photochemical α -cleavage rates of **2** in CH₃OH and CH₃CN.⁹ The hydrogen-atom transfer reaction in the radical pair **8** yields benzaldehyde:¹¹ such reaction pathway is not possible in the reaction of **1**. The radical pair **8** can also recombine back to **2** or become separated into each radicals, which then react with hydrogen donating solvent to produce benzaldehyde and benzyl alcohol. The dimerization of hydroxybenzyl radicals gives hydrobenzoin **4** (see below). The yield of **4** by direct photochemical reaction in the same media was about 17% with the ratio of racemate to meso-form in *ca.* 1.1.

Replacement of a portion of CH₃OH in the above solvent mixture by TEA increased both the rate of photochemical reaction of **2** and the yield of **4** (compare entries 1 and 2 of Table 2). The isomeric composition of **4** was almost the same as that obtained in the absence of TEA. We also observed the formation of N,N-diethylbenzamide **9**, which might be produced by the reaction of benzoyl radical with TEA (Eq. 6). The scavenging of benzoyl radical by TEA would prevent the recombination of the radical with hydroxybenzyl radical to regenerate **2** and facilitate the dimerization of hydroxybenzyl radicals to **4**. Hydrobenzoin **4** is also formed from the photochemical reaction of benzaldehyde in the presence of TEA (*vide infra*). These can explain the observed effects of TEA on the direct photochemical reactions of **2**.



In the presence of 2.5 mg/mL TiO₂ in 88:7:2:3 CH₃CN/CH₃OH/H₂O/TEA medium, the rate of photochemical disappearance of **2** was about 60% of that observed in the absence of TiO₂. Again, the rate retarding effect of TiO₂ for the reaction of **2** is much less than that for benzophenone, suggesting that TiO₂ sensitizes the photochemical transformation of **2**. Analysis of the photoproducts gave **4** as mostly meso-form in 45% yield, **9** in 3% yield, benzyl alcohol in 20%, and 1,2-diphenylpropenone **10** in *ca.* 13% yield.

One of the interesting observations is the stereochemical difference between hydrobenzoin **4** formed in the presence and in the absence of TiO₂. Joyce-Pruden *et al.* reported photochemical reduction of benzaldehyde to benzyl alcohol and **4** in the presence of TiO₂ in ethanol:¹⁸ the reduction is

believed to occur *via* hydroxybenzyl radical formed by electron transfer followed by protonation reaction; the radical is further reduced to benzyl alcohol by another electron-proton transfer reaction or dimerizes to **4**. To examine the structures of **4** obtained from the reaction of benzaldehyde, we carried out the photochemical reaction of benzaldehyde in 88:7:2:3 CH₃CN/CH₃OH/H₂O/TEA medium in the presence and in the absence of TiO₂. In the absence of TiO₂, the reaction produced **4** in *ca.* 20% yield and the ratio of (\pm)-**4** to meso-**4** was about 1.1. However, in the presence of TiO₂, benzaldehyde was reduced mostly to benzyl alcohol and only trace amount of **4** (unresolved) was found.

The similarity of the composition of **4** obtained from the reaction of **2** in the absence of TiO₂ to that from the reaction of benzaldehyde strongly supports that **4** is produced from the α -cleaved product of **2**, *i.e.*, dimerization of hydroxybenzyl radicals. Hydroxybenzyl radicals could be also produced from the other α -cleaved product, benzoyl radical, by transformation to benzaldehyde and then reduction. The striking difference in the structure of **4** between TiO₂-sensitized reduction product and the product from direct photochemical reaction of **2** or benzaldehyde indicates that the TiO₂-sensitized reduction of **2** to **4** occurs without involvement of α -cleavage of **2**. The reaction might proceed by two consecutive electron transfer/protonation reactions as suggested in the reduction of **1** to **2** (Chart 4): in the presence of TiO₂, most of the α -cleaved products are believed to be transformed to benzyl alcohol, not to **4**. Clarification of the origin of the stereoselectivity in the formation of **4** from the TiO₂-sensitized reduction of **2** is beyond the scope of this work. However, it can be assumed that the stereoselectivity reflects that the reduction reaction occurs on the surface of the photocatalyst, not in solution.

Formation of 1,2-diphenylpropenone **10** in the TiO₂-sensitized reaction of **2** supports the presence of the radical **11**. Combination of the radical **11** with the hydroxymethyl radical formed from methanol after donating an electron to the hole of TiO₂ would yield 1,2,3-trihydroxy-1,2-diphenylpropane **12**, which is converted to **10** *via* dehydration reaction. (see Chart 4).

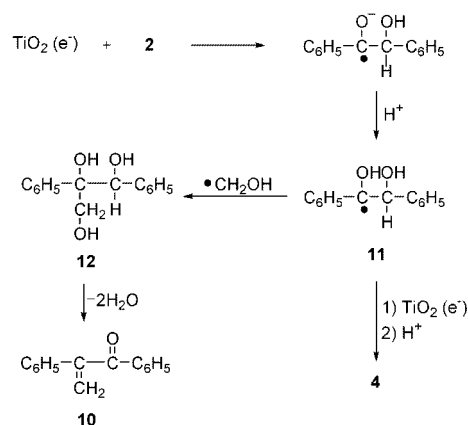


Chart 4. Scheme of TiO₂-sensitized Photochemical Reduction of Benzoin **2**.

Conclusions

The photoirradiation of benzil **1** in deoxygenated solvents with triethylamine (TEA) or TiO₂ gives benzoin **2** in moderate yield. The disappearance rate of **1** and the yield of **2** are increased considerably in the presence of water. The photo-reduction of **1** to **2** proceeds through an electron transfer to **1** from TEA or hole-scavenged excited TiO₂ followed by proton transfer. The photolysis of **2** in deoxygenated CH₃CN/CH₃OH/H₂O (88:10:2) medium results in α -cleavage to benzoyl and hydroxybenzyl radicals, which are mostly converted to benzaldehyde by hydrogen atom transfer in the contact-radical-pair. Hydrobenzoin **4** is produced with *ca.* 20% yield *via* separation of the radical pair followed by dimerization of the hydroxybenzyl radical. Replacement of a portion of CH₃OH with TEA increases the conversion rate of **2** and the yield of **4**, significantly. This is due to the scavenging effect of TEA for benzoyl radical to produce N,N-diethylbenzamide and the photoreduction of benzaldehyde to **4**. The ratio of (\pm)-**4** and meso-**4** from these photochemical reactions is about 1.1, which is the same as that obtained from the photoreduction of benzaldehyde in the presence of TEA. TiO₂ sensitizes the photochemical reduction of **2** to **4** and, in this case, the reduction product is mostly meso-form. The TiO₂-sensitized reduction of **2** to **4** occurs through two consecutive electron/proton transfer processes on the surface of the photocatalyst without involvement of α -cleavage of **2**. The radical **11** formed by the first one electron/proton transfer process can also combine hydroxymethyl radical, which is generated after hole trapping of excited TiO₂ by methanol, and then produce 1,2-diphenylpropenone **10** *via* dehydration reaction.

Experimental Section

General. Benzil, benzoin, and (\pm)- and meso-hydrobenzoin were obtained from Aldrich. TiO₂ (P-25 anatase) was obtained from Degussa Corp. All solvents were HPLC grade from Merck. All chemicals were used without further purification, except triethylamine which was distilled before use. ¹H NMR spectra were taken with a Bruker DPX-250 spectrophotometer. GC analysis was carried out on a HP 6890 II series GC with a FID detector. GC-MS measurements were carried out on a HP 6890 series II GC with a Model 5971A mass spectrometer. Elemental analysis was carried out at the Central Research Facilities of Chungnam National University. Mass spectra were taken at Korea Basic Science Institute.

Photochemical Reaction of Benzil 1. The photochemical reactions were carried out in a Rayonet Model RPR-100 chamber reactor equipped with 350 nm lamps. A solution of benzil (0.105 g) without or with TiO₂ (125 mg) in 50 mL of appropriate solvent was added into a water-jacketed 25 × 500 mm pyrex vessel. The solution was purged with solvent-saturated N₂ gas from at least 30 min prior to irradiation until the end of irradiation. During the irradiation, 25 °C water was circulated through the jacket. About 1 mL of the

reaction mixture was withdrawn at appropriate time intervals with a syringe and diluted 50 times with 37% H₂O/63% methanol: for the reaction mixture with TiO₂, it was filtered through a 0.2 μ m syringe filter. The diluted solution was analyzed with a Orom Vintage 2000 HPLC equipped with Rexchrom C18 column with eluent programming from 37% H₂O/63% methanol to 100% methanol. The composition of the reaction mixture was calculated from chromatograms by comparing a mixture of authentic samples. After irradiation, TiO₂ was removed by centrifugation and solvent was evaporated. The residue was dissolved in CHCl₃ and subjected to silica-gel column chromatography (eluent: 5 : 1 CHCl₃/EtOAc) to isolate benzoin, which was confirmed by NMR and mp.

Photochemical Reaction of Benzoin 2. The reaction was carried out and followed by the same manner employed for the reaction of **1**, using 0.200 g of **2**. N,N-Diethylbenzamide **9**, 1,2-diphenylpropenone **10**, unreacted benzoin **2**, and mixture of (\pm) and meso-hydrobenzoin **4** were isolated by silica-gel column chromatography of the residues by eluting with CHCl₃, CHCl₃/EtOAc (20 : 1), CHCl₃/EtOAc (10 : 1), and then CHCl₃/EtOAc (5 : 1). The compound **9** was identified by comparing with authentic sample obtained from the reaction between benzoyl chloride and diethylamine.²⁶ 1,2-Diphenylpropenone **10** was characterized by ¹H NMR, MS, and elemental analysis: ¹H NMR (CDCl₃) δ 5.65 (s, 1H, -C=CHH), 6.07 (s, 1H, -C=CHH), 7.26-7.56 (m, 8H, aromatic), 7.93 (d, 2H, *J* = 7 Hz, *o*-H of Ph-CO); MS(EI) *m/z* 208 (M⁺); Anal. Calcd for C₁₅H₁₂O: C, 86.51; H, 5.81. Found: C, 86.64; H, 5.89.

Analysis of Hydrobenzoin Isomers. It was carried out on a capillary column GC with temperature programming from 100 °C to 250 °C. The isomers were identified and quantized by the comparison with authentic samples, and confirmed by GC/MS data.

Photochemical Reduction of Benzaldehyde. 0.4 mL of benzaldehyde was added to 73 mL of N₂-purged 88 : 7 : 2 : 3 CH₃CN/CH₃OH/water/TEA medium with or without 180 mg of TiO₂ in the photochemical reaction vessel and irradiated. During the irradiation, N₂-purging was minimized to avoid the loss of benzaldehyde. After 200-300 min irradiation, the products were analyzed with GC and HPLC.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (97-05010-04-0103) and CRM/KOSEF, Korea University.

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