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Use of Isopropyl Alcohol as a Reductant for Catalytic Dehydoxylative Dimerization of Benzylic Alcohols Utilizing Ti–O Bond Photohomolysis

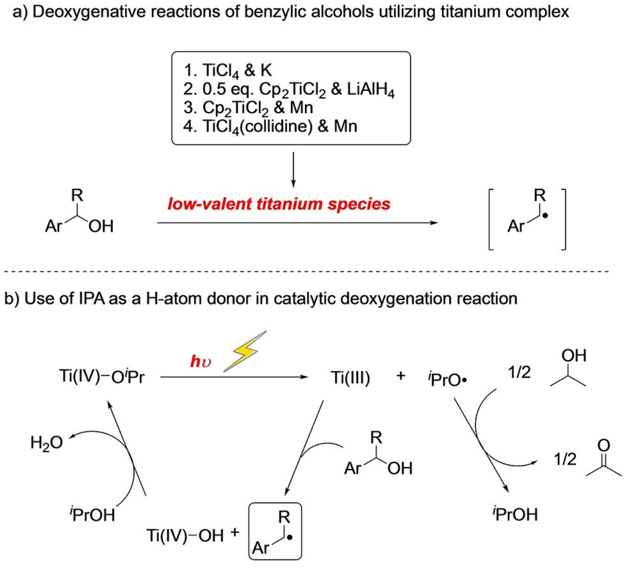
Keiichi Sumiyama,[a] Naoyuki Toriumi,[a] and Nobuharu Iwasawa*[a]

Photohomolysis of Ti–O bonds is utilized in photocatalytic generation of titanium(III) species for dehydroxylative dimerization of benzylic alcohols under UV-light irradiation by using isopropyl alcohol (IPA) as a stoichiometric reductant. In this reaction, IPA works not as a single-electron donor as in the photo-redox catalyzed reactions but as an H-atom-donor. The reaction also proceeds under visible-light irradiation in the presence of thioglycolic acid as a ligand.

Generation of carbon-centered radicals using trivalent titanium species (Ti(III)) is an attractive approach to transform various oxygen-containing substrates such as epoxides, aldehydes, ketones, and alcohols owing to the high oxophilicity of Ti species.[1] The use of a catalytic amount of Ti species has also been studied by the combined use of a strong metallic reductant such as Zn and Mn[2] or a unique dihydropyrazine type organic reductant.[3] The recent rapid development of photoredox reactions has enabled Ti(III) catalysis in combination with organo- or Ir-photoredox catalysts with amines or Hantzsch ester as an electron donor.[4] More recently, Gansäuer *et al*. found that Cp_2TiCl_2 itself could work as a photoredox catalyst, and in the presence of ${}^iPr_2NEt$, $Cp_2Ti(III)Cl$ is formed to promote the reductive generation of radicals from epoxides.[4f] However, utilization of easily available and less toxic, non-metallic reductants like alcohols still remains to be realized due to their low reducing ability.

It has long been known that photohomolysis of M^n–X bonds (X = halide, alkyl, hydroxide) affords reduced metallic species $M^{(n-1)}$ together with radical $X^\bullet$, which typically undergo dimerization of $X^\bullet$, H-atom abstraction, photoisomerization of metal complexes, etc.[5] More recently, photohomolysis of M–X bonds has attracted much attention as a new method of utilizing photo energy for synthetic catalytic reactions, and several metallic compounds including nickel, copper, cerium, iron, cobalt, etc. have been utilized for this purpose.[6] Concerning photohomolysis of Ti complexes,[7,8] cleavage of a Ti–OH bond in a well-designed ligand[7b–d] or a Cp–Ti bond for initiation of radical polymerization[8] has been reported to date. However, photohomolytic generation of Ti(III) species has not yet been applied to catalytic C–C bond formation reactions. We expected photohomolysis of Ti(IV)–OR bonds would be a promising strategy to develop a new type of Ti(III)-catalyzed reductive functionalizations using alcohols as a stoichiometric reductant (H-atom donor). To this end, we have focused on dehydroxylative reactions of benzylic alcohols. While there have been several reports on low-valent Ti-mediated or -catalyzed dehydroxylative transformations, they required a stoichiometric amount of metallic reductants (Scheme 1a).[9]

Herein, we report a catalytic dehydroxylation dimerization of benzylic alcohols by utilizing the photohomolysis of the Ti–OR bond for the generation of Ti(III) species from $Ti(O^iPr)_4$ using isopropyl alcohol (IPA) as an H-atom donor. The expected catalytic cycle is shown in Scheme 1b. Photohomolysis of the Ti–O^iPr bond of $Ti(O^iPr)_4$ under UV light irradiation would generate an active Ti(III) species along with isopropoxy radical $^\bullet O^iPr$. The generated Ti(III) species would reduce a benzylic alcohol to give a benzylic radical, which would undergo dimerization and Ti(IV) hydroxide. The generated Ti(IV) hydroxide would undergo a ligand exchange with HO^iPr to regenerate $Ti(O^iPr)_4$. The isopropoxy radical $^\bullet O^iPr$ would be reduced by HO^iPr via H-atom abstraction to afford HO^iPr and acetone. Here, HO^iPr would act not as an electron donor but as an H-atom donor, which is the key to accomplish Ti(III) catalysis via photohomolysis using alcohol as a reductant and is different



Scheme 1. a) Deoxygenative reaction of benzylic alcohols. b) Our design.

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[a] K. Sumiyama, Dr. N. Toriumi, Prof. Dr. N. Iwasawa
Department of Chemistry, Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152-8551, Japan
E-mail: niwasawa@chem.titech.ac.jp

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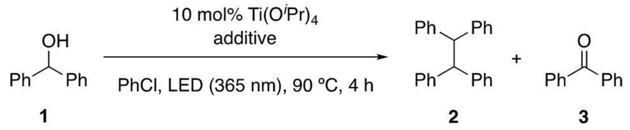
from the photoredox-mediated reduction using an amine as an electron donor.

Based on the above consideration, we first examined the dimerization reaction of benzhydrol **1** (Table 1). When benzhydrol **1** was irradiated with 365 nm LED light in the presence of 10 mol% amount of $Ti(O^iPr)_4$ in chlorobenzene at 90 °C for 4 h, the desired dimerized product **2** was obtained in 12 % yield along with ketone **3** in 6 % yield (entry 1). The generation of ketone **3** suggested that benzhydrol **1** acted as an H-atom donor. To suppress the formation of ketone **3**, the reaction was carried out in the presence of 5 equivalents of IPA as an H-atom donor. Although **2** was not obtained under similar conditions (entry 2), further examination of various additives revealed that the addition of 20 mol% amount of acetic acid improved the yield of **2** to 55 % along with 3 % of **3** (entry 3). When the reaction time was extended to 8 h, **2** was obtained in 74 % yield (entry 4). Several control experiments confirmed that this reaction necessitated both $Ti(O^iPr)_4$ and UV light (entries 5–7).[10]

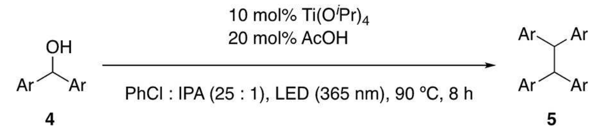
Table 1. Screening of reaction conditions with UV-light irradiation.



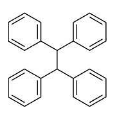
Entry	Additive & conditions	Yield[a] 2[b]	3
1	none	12 %	6 %
2	5 equiv. IPA	0 %	0 %
3	5 equiv. IPA & 20 mol% AcOH	55 %	3 %
4	5 equiv. IPA & 20 mol% AcOH for 8 h	74 %	0 %
5[c]	w/o light	0 %	0 %
6	LED(425) 5 equiv. IPA & 20 mol% AcOH	0 %	0 %
7[c]	w/o [Ti] & w 20 mol% AcOH	0 %	0 %

[a] ^{1}H NMR yields based on **1**. [b] Based on monomer. [c] 120 °C, 6 h.

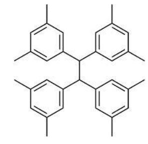
Table 2. Generality of the reaction.



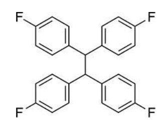
Product[a]



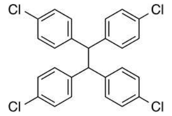
5 a 71 %



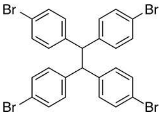
5 b 61 %



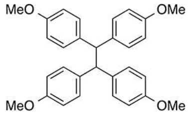
5 c 58 %[b]



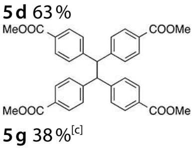
5 d 63 %



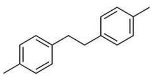
5 e 34 %



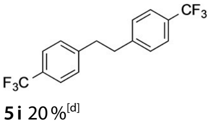
5 f 71 %[b]



5 g 38 %[c]



5 h 24 %[d]



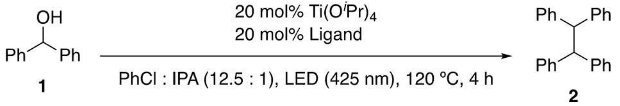
5 i 20 %[d]

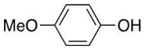
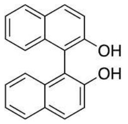
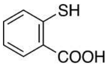
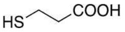
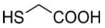
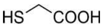
[a] Isolated yields based on monomer. [b] Chlorobenzene/IPA (12.5 : 1) [c] 10 equivalents of MeOH and 20 mol% amount of PhCOOH were used instead of IPA and AcOH, respectively. [d] 5 equivalents of AcOH were used without IPA at 120 °C for 6 h.

The generality of this reaction was investigated using 10 mol% amount of $Ti(O^iPr)_4$ and 20 mol% amount of acetic acid in chlorobenzene/IPA (25 : 1) at 90 °C under irradiation of 365 nm LED light (Table 2). This reaction showed reasonable generality, and the desired dimerized products were isolated in up to 71 % yield when benzhydrol derivatives containing alkyl, halo, ether, and ester groups were employed as substrates. Substrate **4 e** containing bromo groups partially decomposed under the present reaction conditions, but afforded the dimerized product **5 e** in moderate yield. Primary alcohols **4 h** and **4 i** showed low reactivity and the desired dimerized products **5 h** and **5 i** were isolated in about 20 % yield when the reactions were carried out using 10 mol% amount of $Ti(O^iPr)_4$ and 5 equivalents of acetic acid in chlorobenzene at 120 °C under the irradiation of 365 nm LED light.

We expected that this reaction could be promoted by visible-light irradiation with the addition of a suitable ligand. To this end, several ligands were investigated for reductive dimerization of **1** at 120 °C under irradiation of 425 nm blue LED light (Table 3).[11] When these ligands were mixed with $Ti(O^iPr)_4$, the color of the solution changed from colorless to yellow or orange, indicating visible-light active titanium complexes were generated in situ.[12] However, the reaction did not proceed well using phenol-type ligands such as 4-methoxyphenol and BINOL (entries 1,2). Then, several thiocarboxylic acids, which would form weak Ti–S bonds but could strongly coordinate to the titanium center with chelating carboxylate moieties, were examined (entries 3–5). Gratifyingly, it was found

Table 3. Screening of reaction conditions with visible-light irradiation.



Entry	Ligand	Conversion[a]	Yield[a,b]
1		13 %	0 %
2		81 %	4 %
3		26 %	7 %
4		2 %	3 %
5		48 %	43 %
6[c]		100 %	81 %

[a] Determined by ^{1}H NMR. [b] Based on monomer. [c] 12 h.

that the desired dimerized product **2** was obtained in moderate yield when thioglycolic acid was employed as an additive (entry 5). Further optimization of reaction conditions using thioglycolic acid as a ligand resulted in the formation of the desired dimerized product **2** in up to 81 % yield when the reaction mixture was irradiated with 425 nm LED light in the presence of 20 mol% amount of $Ti(O^iPr)_4$ with 20 mol% amount of thioglycolic acid in chlorobenzene/IPA (12.5 : 1) at 120 °C for 12 h (entry 6). Under these conditions, the yields of the products were improved in most cases (**5 b**: 71 %; **5 d**: 78 %; **5 e**: 51 %; **5 g**: 80 %) (Table S2). Thus, titanium(III) species was successfully generated catalytically by visible-light irradiation.

To obtain information on the mechanism of this reaction, several experiments were carried out (Figure 1). First, the reactivity of acetate **6** was examined to confirm whether the reaction proceeded from acetate **6** generated *in situ* in the presence of acetic acid. When the reaction was carried out using acetate **6** as a substrate, the desired dimer product was not obtained at all, and **6** was recovered completely (Figure 1a). This result suggests that this reaction proceeded from alcohol **1** directly. Next, UV-spectra of $Ti(O^iPr)_4$ with acetic acid were measured to confirm the effect of acetic acid as an additive (Figure 1b). Although $Ti(O^iPr)_4$ or $Ti(O^iPr)_4$ with 2 equivalents of benzhydrol showed a weak absorption at 365 nm, $Ti(O^iPr)_4$ with 2 equivalents of acetic acid showed much stronger absorption at 365 nm. Although the exact active species was not obvious, the generation of titanium acetates is thought to be important for promoting the reaction efficiently due to the stronger absorption of 365 nm light. We have also measured UV-vis spectra of the mixture of $Ti(O^iPr)_4$ and AcOH in chlorobenzene/IPA after irradiation with 365 nm LEDs at room temperature (Figure 1c). A broad absorption band appeared at 659 nm after photoirradiation, which corresponds to a color change from colorless to blue. This low-energy absorption band is similar to that of $Ti(acac)_3$,[13] indicating that the Ti(III) species was generated under the reaction conditions. In addition, to confirm the role of IPA as an H-atom donor NMR study was conducted in C_6D_6, and nearly the same amount of the dimerized product and acetone was detected in ^1H NMR (Figure 1d).[14] This result suggests that IPA acted as a sacrificial reducing reagent as shown in Scheme 2.

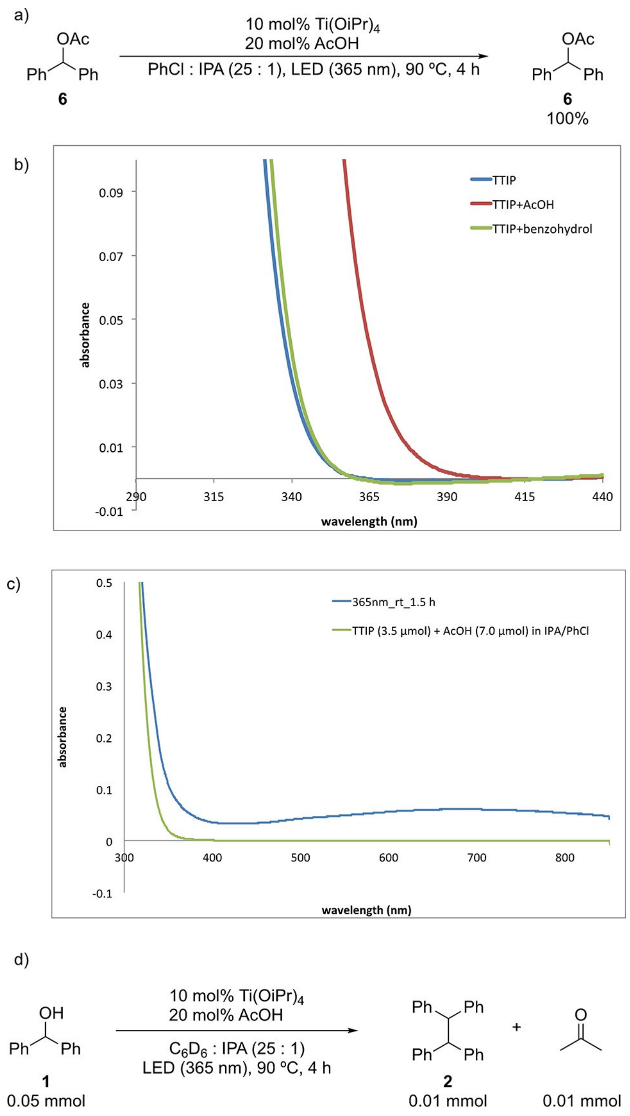
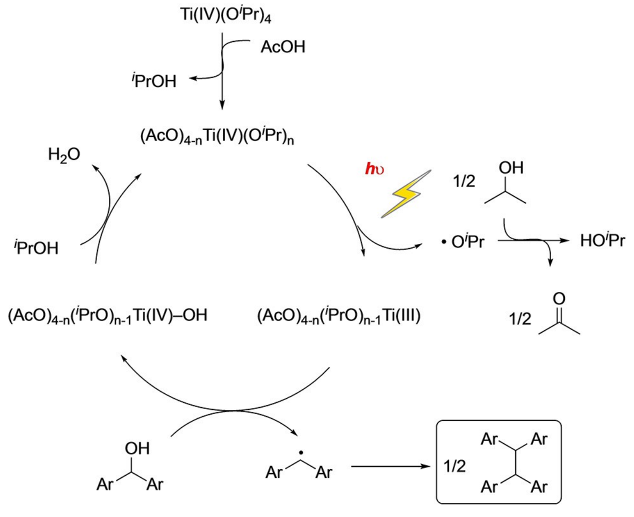
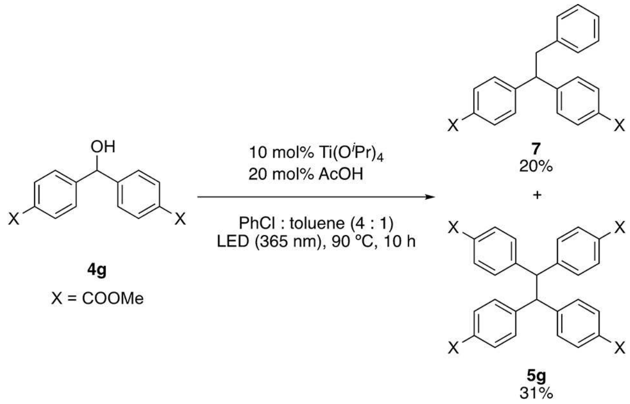


Figure 1. Mechanistic studies. a) Reaction of acetate **6**. b) UV-spectra of $Ti(O^iPr)_4$ (35 μmol) (blue), $Ti(O^iPr)_4$ (35 μmol) with benzhydrol (70 μmol) (green), and $Ti(O^iPr)_4$ (35 μmol) with acetic acid (70 μmol) (red) in chlorobenzene (3.5 mL). c) UV-spectra of $Ti(O^iPr)_4$ (3.5 μmol) with acetic acid (7.0 μmol) in IPA (28 μl) and chlorobenzene (0.35 mL) before (green) and after (blue) irradiation of LEDs (365 nm) at room temperature for 1.5 h. d) NMR experiment for confirmation of acetone formation.

From these results, the reaction mechanism is proposed as shown in Scheme 2. The ligand exchange of $Ti(O^iPr)_4$ with acetic acid occurs to generate $(AcO)_nTi(O^iPr)_{4-n}$ in situ. This ligand exchange is thought to be in equilibrium under the reaction conditions. The titanium(III) species along with the alkoxo radical is generated from $(AcO)_nTi(O^iPr)_{4-n}$ by irradiating 365 nm light.[15] The generated titanium(III) species reduces benzhydrols to give diarylmethyl radicals with $(AcO)_n(^iPrO)_{3-n}TiOH$ and the radical dimerizes to give products. The alkoxo radical abstracts hydrogen atoms from IPA to give acetone. $(AcO)_n(^iPrO)_{3-n}TiOH$



Scheme 2. Proposed mechanism.



4g

7
20%

5g
31%

Scheme 3. Use of toluene as an H-atom donor instead of IPA. The yields were determined by ^{1}H NMR based on monomer.

regenerates $(AcO)_nTi(O^iPr)_{4-n}$ by a ligand exchange reaction with IPA.

Finally, to utilize the alkoxo radicals generated from photohomolysis of Ti–(O^{i}Pr) bond, the reaction was conducted in the presence of a suitable H-atom donor instead of IPA to promote a hetero-coupling reaction. When the reaction of benzhydrol derivative **4g** with Ti(O^{i}Pr)$_4$ was conducted in chlorobenzene/toluene (4:1) without IPA, a dehydroxylative coupling product **7** with toluene was obtained in 20% yield along with 31% yield of homo-coupling product **5g** (Scheme 3). This result suggests that toluene acted as an H-atom donor of alkoxo radical to generate benzyl radical under the reaction conditions. Although primitive, this reaction would afford a new possibility for the cross-coupling between benzylic alcohols and hydrocarbons containing reactive C(sp^3)–H bonds.

In summary, we developed a catalytic dehydoxylative dimerization of benzylic alcohols using a catalytic amount of Ti(O^{i}Pr)$_4$ with 365 nm LED light irradiation using IPA as an H-atom donor based on the photohomolysis of the Ti–O bond. This is a rare example that titanium-catalyzed reduction is achieved without using metallic reductants. By adding thioglycolic acid as a ligand, this reaction could be carried out by visible light irradiation. The application of this reaction to other radical reactions is now in progress.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–O cleavage · Photocatalysis · Radical reactions · Synthetic methods · Titanium

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