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Carbon–carbon bond formation via benzoyl umpolung attained by photoinduced electron-transfer with benzimidazolines

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ABSTRACT

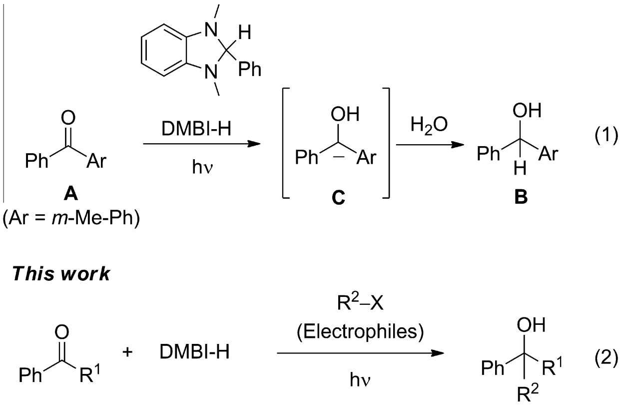
A photoreaction between benzoyl compounds, such as benzoylformate derivatives, and 2-(*p*-anisyl)-1,3-dimethylbenzimidazoline in the presence of allyl bromide was found to give various allylated alcohols. In the reaction of benzoylformates, α-hydroxy ester enolates, for which the negative charge occurs on the carbonyl carbon of benzoyl (umpolung reactivity), are proposed to be generated as intermediates by electron-transfer from benzimidazolines to the photoexcited benzoylformates; these species react with allyl bromide to produce α-allyl-α-hydroxy esters.

Organic hydride donors, such as 1-benzyl-1,4-dihydronicotinamide,[1,2] Hantzsch ester,[3] 9,10-dihydroacridine,[2,4] and 1-acetyl-2,3-dimethylimidazoline,[5] are attractive research targets for chemists and biochemists. 2-Aryl-1,3-dimethylbenzimidazolines (DMBI-H), which also belong to this group of reagents, are known to reduce olefins,[6] ketones,[7] organic halides,[6–8] sulfones,[7,8] cyclopropanes,[8] and epoxy compounds.[7,9] DMBI-H also acts as a hydrogen-storing material, releasing hydrogen gas upon contact with Brønsted acids.[10]

Previously, we reported that DMBI-H acts as an effective reagent to promote a photoinduced reduction of ketone **A** to produce alcohol **B** (Scheme 1, Eq. 1).[7g] The reaction is proposed to generate carbanion **C**, in which the carbonyl carbon becomes nucleophilic (umpolung reactivity) and, finally, **C** captures a proton from water to give **B**.

Carbon–carbon (C–C) bond formations promoted by inversion operators are well-established in organic synthesis.[11] However, it is difficult to construct a tertiary alcohol via umpolung reactivity; one of the few examples is the SmI_2 promoted C–C bond formation of α-keto esters/amides reported by Fukuzawa et al.[12] We thought that C–C bond formation would be possible when the appropriate carbon electrophiles are captured by **C** in lieu of the protons supplied by water (Scheme 1, Eq. 2). Formation of a quaternary carbon via umpolung reactivity is unprecedented within the scope of photoinduced electron-transfer reactions of DMBI-H. In this Letter, we disclose the allylation of various benzoyl substrates by photoinduced electron-transfer with DMBI-H.

We conducted a photoreaction (λ >280 nm, 500 W Hg–Xe lamp) using benzophenone **1a** and 2-(*p*-anisyl)-1,3-dimethylbenzimidazoline **2a**, capturing the resultant species in situ with allyl bromide in acetonitrile at room temperature for 1 h. Then, α-allyl adduct **3a** was obtained in 54% yield (Table 1, entry 1). While the reaction of benzaldehyde **1b** gave **3b**, albeit in low yield (entry 2), acetophenone **1c** was inactive (entry 3). Notably, the reaction of methyl benzoylformate **1d** gave allylated mandelate **3d** in good yield



Scheme 1. The photo-reduction of a benzophenone derivative via umpolung reactivity.

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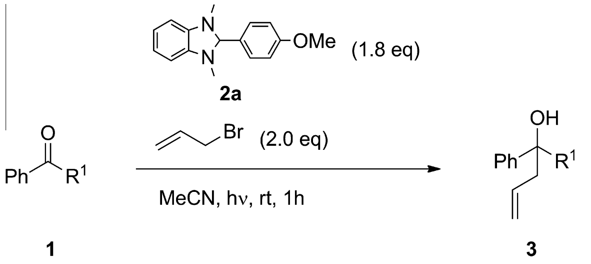
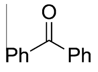
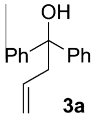
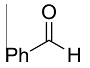
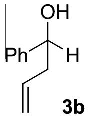
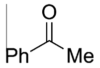
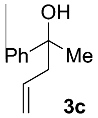
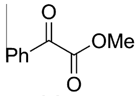
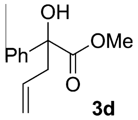
Table 1
A photo-allylation reaction of benzoyl compounds **1** and DMBI-H **2a** with allyl bromide[a]

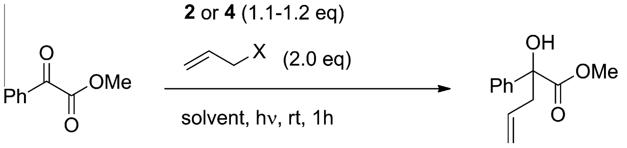


Entry	Benzoyl compound	Product	Yield[b] (%)
1	 **1a**	 **3a**	54
2	 **1b**	 **3b**	20
3	 **1c**	 **3c**	0
4	 **1d**	 **3d**	86

[a] Typical procedure: a solution of **1** (0.2 mmol), **2a** (0.36 mmol), and allyl bromide (0.4 mmol) in acetonitrile (4 mL) was irradiated at room temperature under an argon atmosphere for 1 h.

[b] Isolated yield.

Table 2
Reaction conditions for the photo-allylation reaction of **1d** and **2** or **4** with allyl halides[a]

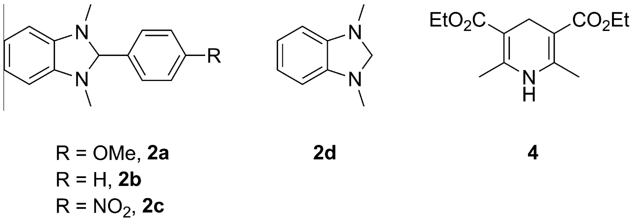


Entry	X	Solvent	**2** or **4**	Yield[b] (%)
1	Br	MeCN	**2a**	76
2[c]	Br	MeCN	**2a**	0
3	Cl	MeCN	**2a**	14
4	I	MeCN	**2a**	31
5	Br	CH_2Cl_2	**2a**	63
6	Br	THF	**2a**	42
7	Br	toluene	**2a**	48
8	Br	EtOAc	**2a**	52
9	Br	DMF	**2a**	40
10	Br	DMSO	**2a**	0
11	Br	*i*-PrOH	**2a**	Trace
12	Br	MeCN	**2b**	59
13	Br	MeCN	**2c**	0
14	Br	MeCN	**2d**	38
15	Br	MeCN	**4**	0

[a] Typical procedure: a solution of **1d** (0.2 mmol), **2** or **4** (0.22–0.24 mmol), and allyl halides (0.4 mmol) in solvent (4 mL) was irradiated at room temperature under an argon atmosphere for 1 h.

[b] Isolated yield.

[c] Without light, 14 h.

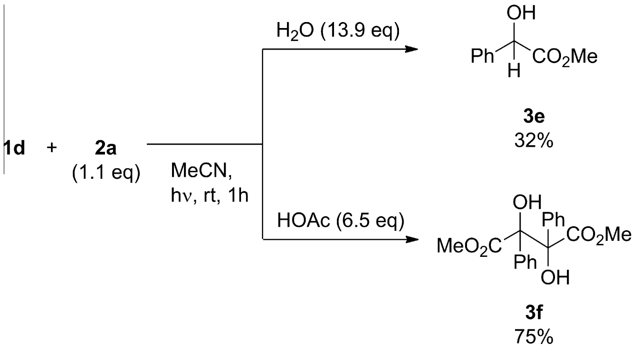


R = OMe, **2a**
R = H, **2b**
R = NO_2, **2c**

2d

4

Figure 1. A series of DMBI-H **2a**–**d** and Hantzsch ester **4**.



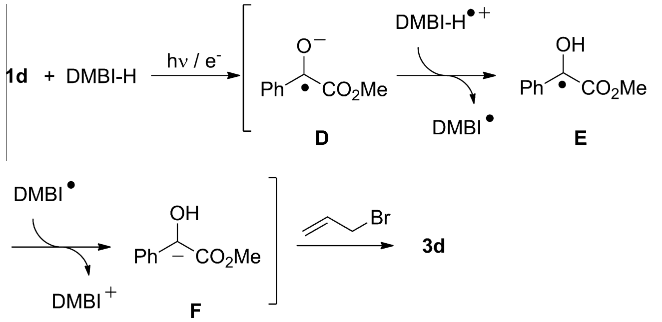
Scheme 2. A photoreaction of **1d** and **2a** with a proton donor.

(entry 4). Mandelate derivatives are useful in various fields of chemistry, such as organic synthesis,[13] biochemistry,[14] and inorganic chemistry,[15] and α-substituted mandelate derivatives are important units in several biologically active natural products and versatile synthetic intermediates.[16] Thus, we decided to examine the photoreaction of benzoylformates in detail.[17]

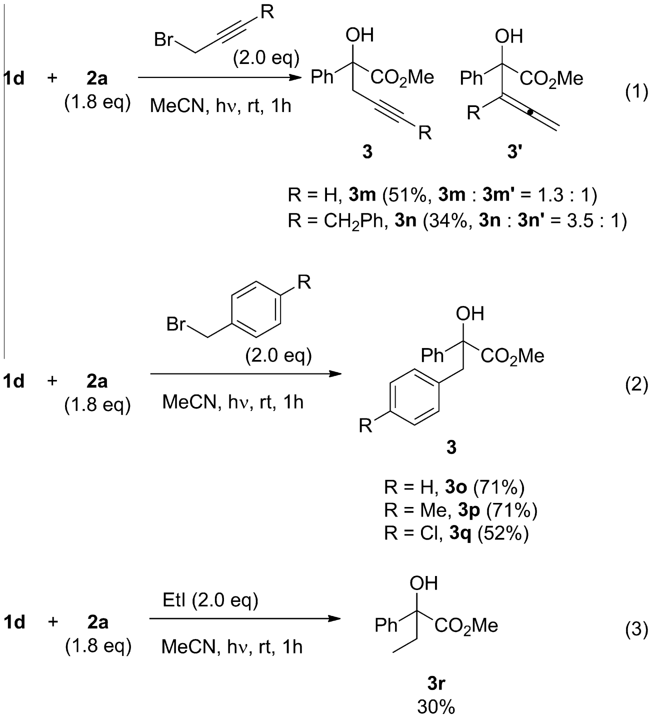
First, we conducted a photoreaction between **1d** and **2a** in the presence of allyl halides to form the desired products (Table 2, entries 1–4). When the quantity of DMBI-H was less than 1.8 equiv shown in Table 1, **3d** was still obtained in good yield (entry 1). Without light, the reaction was not able to proceed (entry 2). Additionally, the use of allyl chloride greatly decreased the yield of **3d** (entry 3) and the reaction of **1d** with allyl iodide produced **3d** in 31% yield (entry 4).

Next, different solvents were explored to discover those suitable for the photo-allylation reaction (Table 2, entries 5–11). While irradiation in dichloromethane, THF, toluene, ethyl acetate, and DMF produced **3d** in moderate yields (40–63% yields) (entries 5–9), no reaction proceeded in DMSO (entry 10). The origin of this unexpected effect caused by DMSO is unclear. Isopropanol was also ineffective, possibly due to interfering proton transfer in the radical ion pairs by this protic solvent (entry 11). Thus, acetonitrile was found to be optimal among the solvents studied.

We also examined the steric and electronic effects of the 2-substituent of DMBI-H by using a series of DMBI-H derivatives **2a**–**d** and the applicability of Hantzsch ester **4**, the most recognized organic hydride donor in organic synthesis,[3] (Fig. 1) in the photo-allylation reaction of **1d** and allyl bromide (Table 2, entries 12–15). While 2-phenyl substituted **2b** was moderately effective, giving **3d** in 59% yield (entry 12), 2-*p*-nitrophenyl substituted **2c** did not display any of the desired reactivity (entry 13). Using less sterically hindered **2d**,[9] the yield of **3d** was unexpectedly decreased to 38% yield (entry 14). It is considered that the generated intermediate, DMBI radical or DMBI radical cation from **2d**, cannot be stabilized in the absence of 2-aryl substituent. In addition, **2d** was discovered to be rather unstable in air. Notably, **4** did not produce **3d** at all (entry 15).



Scheme 3. A proposed mechanism for a photo-allylation reaction.



Scheme 4. The photo-addition reaction of **1d** with various electrophiles.

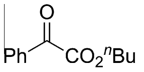
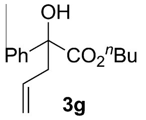
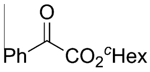
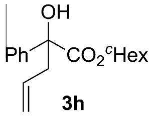
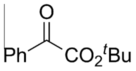
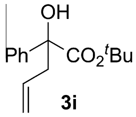
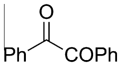
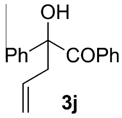
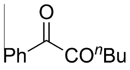
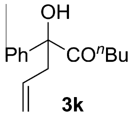
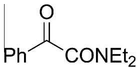
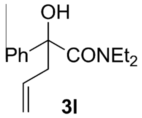
In order to explore the nature of the intermediate for the photoreaction of **1d** and **2a**, allyl bromide was replaced by proton donors (Scheme 2). While the reaction of **1d** with water gave alcohol **3e**, an addition of acetic acid produced 1,2-diol **3f**. These results were similar to those of the reactions reported in the literature,[7g] that alcohol **B** was a major product from **A** in the presence of water (Eq. 1 in Scheme 1) while benzopinacol was exclusively obtained upon using acetic acid.

On the basis of the observations described above, we propose a plausible mechanism for the reaction of **1d** and DMBI-H with allyl bromide (Scheme 3). The reaction pathway begins with a photoinduced electron-transfer in which initially formed radical anion **D** abstracts a proton from DMBI-H radical cation (DMBI-$H^{\cdot+}$) to give the radical **E**.[18] The subsequent electron transfer between **E** and DMBI radical (DMBI$^{\cdot}$) generates carbanion **F**,[19] in which the carbonyl carbon becomes nucleophilic (umpolung reactivity). Finally, **F** reacts with allyl bromide to produce **3d** while **F** is protonated by water to give **3e** in the absence of allyl bromide. If acetic acid exists, **D** is protonated by acetic acid instead of DMBI-$H^{\cdot+}$ to give **E** which dimerizes to produce **3f**.

We then applied the optimized conditions (**1**:**2a**:allyl bromide = 1:1.8:2.0) to a variety of benzoylformates and other types of benzoyl compounds (Table 3). When the reactions with *n*-butyl ester **1g**, cyclohexyl ester **1h**, and *t*-butyl ester **1i**, were performed under the same conditions, the respective α-allyl adducts, **3g**, **3h**, and **3i**, were obtained in good to excellent yields (entries 1–3). Next, the reactions of α-diketones, such as benzil **1j** and 1-phenyl-1,2-dioxohexane **1k**, resulted in the formation of **3j** and **3k** in 48% and 56% yields, respectively (entries 4, 5). The reaction of **1k** proceeded regioselectively, with the *n*-butyl carbonyl remaining intact in **3k**. *N*,*N*-Diethylbenzoylformamide **1l** was completely unreactive (entry 6). Thus, either properly electron withdrawing or conjugated substituents adjacent to benzoyl are necessary to promote the reactions.

To further explore the nucleophilic reactivity of the proposed anionic intermediate **F** (Scheme 3), we examined the reaction of **1d** with various electrophiles (Scheme 4).[20] The reaction of **1d** with propargyl bromide under the optimized reaction conditions gave 51% yield of **3m** as a mixture of α- and γ-adduct (1.3:1) (Eq. 1). When 1-bromo-4-phenyl-2-butyne (simply adding a terminal substituent to propargyl bromide) was used as the electrophile, a 34% yield of **3n** as a mixture of α- and γ-adduct (3.5:1) was obtained. Notably, α-adducts were preferentially formed in the above reactions, particularly when the S_N2' pathway was hindered by the terminal substituents. Next, we chose several benzyl bromide derivatives as electrophiles (Eq. 2). Reaction of **1d** with benzyl bromide gave benzyl adduct **3o** in 71% yield. Addition of *p*-methylbenzyl bromide produced **3p** in 71% yield. Further, the reaction of *p*-chlorobenzyl bromide resulted in the formation of **3q** in 52%

Table 3
Photo-allylation reactions with electron withdrawing or conjugative benzoyl compounds **1**[a]

Entry	Benzoyl compound	Product	Yield[b] (%)
1	 **1g**	 **3g**	94
2	 **1h**	 **3h**	85
3	 **1i**	 **3i**	88
4	 **1j**	 **3j**	48
5	 **1k**	 **3k**	56
6	 **1l**	 **3l**	0

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[a] Typical procedure: a solution of **1** (0.2 mmol), **2a** (0.36 mmol), and allyl bromide (0.4 mmol) in acetonitrile (4 mL) was irradiated at room temperature under an argon atmosphere for 1 h.

[b] Isolated yield.

yield. Finally, it was found that the use of iodoethane gave **3r** in 30% yield (Eq. 3), while bromoethane was unreactive in this system.

In conclusion, we have demonstrated a novel C–C bond formation reaction of benzoylformate derivatives initiated by a photoinduced electron-transfer with DMBI-H. This is the first successful application of DMBI-H to photoinduced C–C bond formation. Although not fully elucidated, the reaction mechanism proposed involves the coupling of halide-bearing alkylating agents and hydroxyl methyl anions; the reactivity of these anions must be properly tuned by adjacent substituents. This process enacts the C–C bond formation between an electrophile and a polarity inverted carbonyl carbon of a substrate (umpolung reactivity). This mild method allows to avoid using reactive or strongly basic reagents. Future investigations will explore other potential reactions using DMBI-H.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.10.028.

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