# Divergent Photocatalytic Reactions of α-Ketoesters Under Triplet Sensitization and Photoredox Conditions

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**ABSTRACT:** The long-lived triplet excited states of transition metal photocatalysts can activate organic substrates via either energy- or electron-transfer pathways, and the rates of these processes can be influenced by rational tuning of the reaction conditions. The characteristic reactive intermediates that are generated by each of these activation modalities, however, are distinct and can exhibit very different reactivity patterns. Herein, we show that the photocatalytic reactions of benzoylformate esters with alkenes can be directed towards either Paternò–Büchi cycloadditions under conditions that favor energy transfer or allylic functionalization reactions under superficially similar conditions that favor electron transfer. These studies provide a framework for designing other divergent photocatalytic methods that produce different sets of reaction outcomes under photoredox and triplet sensitization conditions.

The development of new photocatalytic reactions has recently reemerged as an important theme of research in synthetic chemistry.1 The photocatalysts that have most commonly been utilized for these methods to date belong to a family of Ru and Ir polypyridyl complexes with several features that make them ideal for synthetic applications, including strong absorption in the visible range, excellent chemical stability, and predictable tunability across a wide range of excited-state redox potentials and triplet-state energies.<sup>2</sup> Most importantly, these complexes undergo efficient intersystem crossing to produce long-lived triplet excited states that can initiate useful organic transformations via either electron-transfer (photoredox) or energy-transfer (triplet sensitization) mechanisms. Though the same photocatalytic triplet excited state is responsible for both pathways, the reactive intermediates that are generated by each are different and exhibit distinctive reactivity patterns. The optimization of photocatalytic reactions, therefore, often requires careful tuning of reaction conditions to ensure that one pathway is favored to the exclusion of the other.<sup>3</sup> The mechanistic diversity available to photochemical reactions, however, might also offer an opportunity to engineer divergent reactions that give markedly different chemical outcomes under superficially similar conditions. This goal would be valuable because reactions that produce significant structural diversity using a small set of simple reactants can facilitate the discovery of compounds with new chemical and biological properties.

Photoreactions of carbonyl compounds have been an important topic of study throughout the history of organic photochemistry, and the mechanisms of their reactions have been extensively investigated.4 Among the oldest and best-known photocycloaddition reactions is the Paternò-Büchi reaction, which classically involves the reaction of excited-state aryl ketones with alkenes to afford structurally complex oxetane products.<sup>5</sup> As a starting point for our investigations, we examined the photocatalytic reaction of benzoylformate esters. Neckers has explored the photochemistry of these compounds and demonstrated that they are excellent reactants for Paternò-Büchi cycloadditions.<sup>6</sup> The triplet energies of benzoylformate esters have been reported to be ~62 kcal/mol;<sup>7</sup> we proposed, therefore, that irradiation of methyl benzoylformate(1) and tetramethylethylene (2) in the presence of a fluorinated Ir(III) complexes with a high triplet-state energy would generate long-lived triplet 1\* via Dexter energy transfer (Scheme 1, left). Subsequent [2+2] cycloaddition via the standard stepwise biradical mechanism of the Paternò-Büchi reaction would then afford oxetane 3a. Indeed, upon irradiation of 1 and 2 in acetonitrile with 465 nm LEDs in the presence of 1 mol% [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dtbbpy)]BArF<sub>1</sub><sup>8</sup> Paternò-Büchi cycloadduct (3) was obtained in 74% yield.

Our laboratory has a long-standing interest in the use of Lewis acid co-catalysts to increase the driving force for photoinduced electron transfer to carbonyl-containing substrates.<sup>9</sup> We imagined that an appropriate Lewis acid could accelerate electron transfer to ketoester substrate 1, outcompeting the rate of energy transfer (Scheme 1, right). The resulting Ir(IV) complex could then oxidize electron-rich alkene 2 to the corresponding radical cation (2<sup>-+</sup>). Deprotonation would afford an allylic radical (5) that could generate product either by combination with the persistent Lewis acid

Scheme 1. Divergent outcomes of triplet sensitization and photoredox reactions of benzoylformate esters



stabilized ketyl radical  $([Y]-1^{-})^{10}$  or via a Lewis acid catalyzed addition to another equivalent of ketoester.<sup>11</sup> After a brief screen of Lewis acid co-catalysts, we found that the addition of 15 mol%  $Y(OTf)_3$  and 20 mol% phenanthroline ligand to conditions otherwise identical to those used for the Paternò–Büchi reaction resulted in the formation of 51% allylic functionalization products as a 3:1 mixture of regioisomers (**4a** and **4a**'), in addition to significant amounts of the oxetane cycloadduct.

Table 1. Optimization studies for Paternò-Büchi cycloaddition.ª

Ĵ	OMe Me Me 1	mol% photocatalys	t o-	oMe	
Ph	↓ + ↓ − O Me Me	blue LED 16 h	Ph''' MeO <sub>2</sub> C	''Me Me	
1	2		3a		
entry	Photocatalyst <sup>b</sup>		solvent	yield	
1	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy	7)]BArF (60)	MeCN	74%	
2	[Ir(Fppy)2(dtbbpy)]PF6(	(53)	MeCN	40%	
3	[Ir(ppy) <sub>2</sub> (dMeObpy)]PF	6(57)	MeCN	5%	
4	[Ir(ppy)2(dtbbpy)]PF6(4	9)	MeCN	6%	
5	[Ir(dF(CF3)ppy)2(dtbbpy	7)]BArF	$CH_2Cl_2$	81%	
6	[Ir(dF(CF3)ppy)2(dtbbpy	7)]BArF	toluene	92%	
$7^{\rm c}$	[Ir(dF(CF3)ppy)2(dtbbpy	/)]BArF	toluene	97%	
<b>8</b> <sup>d</sup>	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy	/)]BArF	toluene	0%	
9	none		toluene	15%	

<sup>a</sup> Reactions conducted using 0.1 mmol 1, 0.5 mmol 2, 1 mol%  $[Ir(dFCF_3ppy)_2(dtbbpy)]BArF$ , and 5 mL solvent and irradiated with a 16 W LED lamp (465 nm) for 16 h unless otherwise noted. Yields were determined by <sup>1</sup>H NMR analysis. <sup>b</sup> Values in parentheses represent the photocatalyst triplet energies in kcal/mol. <sup>c</sup> Reaction conducted in 1.5 mL toluene. <sup>d</sup> Reaction conducted in the dark.

The observation that the partitioning of the reaction between Paternò-Büchi and allylic functionalization pathways could be influenced by reaction conditions was intriguing, and we elected to optimize each of these processes independently. First, Table 1 summarizes the results of studies to improve the yield of the former process. As expected for a triplet sensitization reaction, the yield of Paternò-Büchi product is highest using high triplet energy photocatalysts (entries 1-4). Also consistent with a triplet mechanism is the relative insensitivity of the reaction towards the polarity of the solvent (entries 5-7), with the highest yields observed in toluene. The yield is increased at higher concentrations (entry 7). Control experiments show that no product is observed in the absence of light (entry 8); however, a slow Paternò-Büchi reaction was observed in the absence of photocatalyst, which results from a tailing of the absorption of 1 into the visible region (entry 9). Nevertheless, product formation in this reaction is dominated by the photosensitized reaction pathway.

Table 2 summarizes an investigation of the scope of this photosensitized Paternò-Büchi cycloaddition. We first examined the scope with respect to the ketoester reaction component. Ester moieties bearing potentially reactive functional groups including alkenes (3d), alkynes (3e), halides (3f), and azides (3g) are well-tolerated. The identity of the arene substituent could also be easily modified with various electron-donating and -withdrawing substituents (3h-**30**), although *ortho* substituents retard the reaction somewhat (**3p**). Heteroaryl groups are also tolerated (3q and 3r). The scope with respect to the alkene was also examined. The reaction was fastest with relatively electron-rich alkenes, consistent with the oxyl radical character of the  $n\pi^*$  triplet ketone intermediate, although disubstituted aliphatic alkenes afforded reasonable yields of the oxetane cycloadduct (3s and 3t). In all cases, the regioselectivity of the reaction could be predicted by considering the stability of the intermediate 1,4-diradical expected from the conventional stepwise mechanism of the Paternò–Büchi cycloaddition (3u–3x).



<sup>a</sup> Reactions conducted using 0.5 mmol **1**, 2.5 mmol **2**, 1 mol% [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dtbbpy)]BArF, and 7.5 mL toluene and irradiated with a 16 W LED lamp (465 nm) for 16 h unless otherwise noted. <sup>b</sup> Reaction conducted using 0.5 mol% [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dtbbpy)]BArF. <sup>c</sup> Reaction conducted for 24 h.

As a further validation of the triplet mechanism of this photoreaction, we wondered if other fundamental photoreactions of  $n\pi^*$  triplet ketones could be accessed using the conditions optimized for the Paternò–Büchi cycloaddition. We targeted the Norrish–Yang photocyclization<sup>12</sup> of *ortho*-methyl benzoylformates<sup>13</sup> to access benzofused cyclobutanes that are important structural elements of bioactive drugs and natural products.<sup>14</sup> Indeed, a variety of *ortho*-methyl benzoylformates undergo smooth transformation to the benzocyclobutenol products **6a–6h** (Table 3).

Table 3. Norrish type II reactions under energy-transfer conditions.ª



<sup>a</sup> Reactions conducted using 0.5 mmol ketoester, 1 mol%  $[Ir(dFCF_3ppy)_2(dtbbpy)]BArF$ , and 7.5 mL toluene and irradiated using a 16 W LED lamp (465 nm) for 16 h.

We next undertook studies to optimize the photoredox allylic functionalization process (Table 4). We speculated that the product distribution might be diverted completely towards allylic functionalization by appropriately tuning the identity of the photocatalyst and Lewis acid co-catalyst to maximize the rate of photoredox activation and minimize the rate of energy transfer. First, a screen of alternate ligands for  $Y(OTf)_3$  revealed that a slightly more electron-deficient

5-chlorophenanthroline ligand afforded somewhat improved yields of the allylic functionalization product (entries 1–3). We next examined photocatalysts with lower triplet energy and more negative excited state reduction potentials that might further improve the yield of this reaction (entries 4–7). Indeed,  $[Ir(ppy)_2(dMeObpy)]PF_6$  gave exclusively the allylic functionalization product in 89% yield (entry 7). Control experiments indicated that the photocatalyst, Lewis acid co-catalyst, and light were all required for the formation of the allylic functionalization product (entries 8–10).

Table 4. Optimization studies for allylic functionalization

			L L	OH Me		
Ph	DMe +	15 mol% Y(OTf 30 mol% ligano 1 mol% photocata	) <sub>3</sub> Phuếng d MeO <sub>2</sub> C alyst	+ M	, <sup>Me</sup> e <b>4a</b>	
" 1	Me Me	blue LED MeCN, 16 h	Ph'' MeO <sub>2</sub> t	OH Me	× 4a'	
entry	photocatalyst		ligand	yield	r.r.	
1	$[Ir(dF(CF_3)ppy)_2($	dtbbpy)]BArF	phen	51%	3:1	
2	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (	dtbbpy)]BArF	bpy	32%	4:1	
3	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (	dtbbpy)]BArF	5-Cl-phen	58%	4:1	
4	$[Ru(bpy)_3](PF_6)_2$		5-C-lphen	19%	4:1	
5	Ir(ppy)3		5-Cl-phen	78%	4:1	
6	[Ir(Fppy)2(dtbbpy)	$]PF_{6}$	5-Cl-phen	85%	4:1	
7	[Ir(ppy)2(dMeObp	y)]PF6	5-Cl-phen	89%	4:1	
8	none		5-Cl-phen	1%		
9 <sup>b</sup>	[Ir(ppy)2(dMeObp	y)]PF6	none	2%		
10 <sup>c</sup>	[Ir(ppy)2(dMeObp	$(y)]PF_6$	5-Cl-phen	0%		

<sup>a</sup> Reactions conducted using 0.1 mmol **1**, 0.5 mmol **2**, 1 mol% photocatalyst, 15 mol%  $Y(OTf)_3$ , 30 mol ligand, and 1.5 mL MeCN and irradiated with a 16 W LED lamp (465 nm) for 16 h unless otherwise noted. Yields were determined by <sup>1</sup>H NMR analysis. <sup>b</sup> Reaction conducted without  $Y(OTf)_3$ . <sup>c</sup> Reaction conducted in the dark.

Table 5. Allylic functionalization scope studies.<sup>a</sup>



<sup>a</sup> Reactions conducted using 0.5 mmol 1, 2.5 mmol 2, 1 mol%  $[Ir(ppy)_2(dMeObpy)]PF_{6}$ , 15 mol%  $Y(OTf)_3$ , 30 mol% 5-Cl-phen, and 7.5 mL toluene and irradiated with a 16 W LED lamp (465 nm) for 16 h unless otherwise noted. Values in parentheses represent the ratio of regioisomers. <sup>b</sup> Reaction conducted using 1 mol%  $[Ir(Fppy)_2(dtbpy)]PF_{6}$ . <sup>c</sup> Reaction conducted for 24 h. <sup>d</sup> Reaction conducted for 32 h.

Scope studies exploring the generality of this allylic functionalization are summarized in Table 5. All of the benzoylformates examined in the Paternò–Büchi reaction performed well in this transformation but afforded the allylic functionalization product to the exclusion of the previously observed oxetanes (4a-4p). In general, we obtained relatively modest regioselectivity for the formation of the tetrasubstituted olefin product over the 1,1-disubstituted alkene isomer. However, those benzoylformates bearing bulky *ortho* substituents gave better selectivities (4p-4v). Importantly, in these cases, we observed no trace of the Norrish–Yang cyclization products.

Scheme 2. Support for a photoredox mechanism.



Several lines of evidence support the contention that the allylic functionalization reaction involves a photoredox process. First, cyclic voltammetry performed with benzoylformate **1** showed a quasi-reversible reduction wave at -1.28 V vs SCE. The addition of  $Y(OTf)_3$  and phen results in a positive shift to -0.70 V vs. SCE, which is easily within the range accessible by the excited states of both  $[Ir^*(dFCF_3ppy)_2(dtbbpy)]^+(-0.89$  V vs SCE)^8 and the more strongly reducing  $[Ir^*(ppy)_2(dMeObpy)]^+(-1.26$  V vs SCE). Second, this mechanism predicts that the oxidation of tetramethylethylene (+1.45 V vs SCE) by the oxidized  $[Ir(ppy)_2(dMeObpy)]^{2+}$  catalyst (+1.21 V vs SCE) would be slightly endergonic by 5.5 kcal/mol. Consistent with this expectation, less-electron-rich

trisubsitutted alkenes such as 7 (+1.98 V vs SCE)<sup>15</sup> fail to give any C–H functionalization products (Scheme 2A). On the other hand, electron-rich methallylsilane **8** (+1.24 V vs SCE)<sup>16</sup> participates readily in this reaction to afford Sakurai addition product **9** in 90% yield (Scheme 2B).

In summary, we have shown that divergent reactivity is accessible in the photocatalytic reaction of benzoylformates with alkenes. Under conditions that favor energy transfer, the triplet-state benzoylformate undergoes smooth Paternò–Büchi cycloaddition to afford complex oxetane scaffolds. Under photoredox conditions, on the other hand, the same starting materials undergo selective transformation to allylic functionalization products. These results offer a valuable demonstration that the ability to rationally design systems that favor either photoredox or energy transfer mechanisms offers a means not only to impact the rate of useful photocatalytic transformations but also to rationally alter their chemical outcomes as well.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures, full spectroscopic data for all new copounds (PDF).

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## ACKNOWLEDGMENT

We dedicate this paper to Prof. Ilhyong Ryu on the occasion of his 70<sup>th</sup> birthday. We are grateful to Katie Rykaczewski and Prof. Corinna Schindler for sharing unpublished data. Funding for this project was provided by the NIH (GM095666). NMR and MS facilities at UW–

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