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Visible-Light-Initiated Manganese-Catalyzed Giese Addition of Unactivated Alkyl Iodides to Electron-Poor Olefins

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Herein, we report a mild protocol for direct visible-light-initiated Giese addition of unactivated alkyl iodides to electron-poor olefins (Michael acceptors) with catalysis by decacarbonyl dimanganese, $Mn_2(CO)_{10}$, an inexpensive earth-abundant-metal catalyst. This protocol is compatible with a wide array of sensitive functional groups and has a broad substrate scope with regard to both the alkyl iodide and the Michael acceptor.

Modular organic reactions that form C(sp³)–C(sp³) bonds facilitated by traceless activation groups are a useful addition to the medicinal chemistry toolbox and have accelerated the discovery of new therapeutics.¹ One such reaction is the Giese addition, in which an electron-deficient alkene is attacked by a nucleophilic alkyl radical.² Classic Giese reactions using alkyl iodides as the alkyl radical source often require a tin reagent, which can limit their substrate scope and chemoselectivity.^{2,3} With the rapidly growing interest in the use of photoredox catalysis in organic synthesis,⁴ there have been several reports of visible-light-mediated photoredox Giese reactions with carboxylic acids,⁵ alkyltrifluoroborates,⁶ alcohols,⁷ alkyl bromides,⁸ and organotrimethylsilanes⁹ as the alkyl radical sources (Scheme 1a).¹⁰ In addition, Ryu described a protocol for Giese reaction with alkyl iodides under a Pd/light system using SolarBox (1500 W of xenon lamp in a box).¹¹ Although these reactions allow access to diverse products, most of the previously reported protocols require a precious-metal catalyst (Ir or Ru) and are limited in scope with respect to the alkyl radical source. Therefore, it would be a significant advance if the expensive Ir and Ru catalysts could be replaced with an inexpensive, earth-abundant 3d transition metal, such as Mn, and if the substrate scope could be expanded to widely available organic compounds commonly used as building blocks in medicinal chemistry, such as alcohols and alkyl iodides. However, a

challenge is posed by the fact that the excited state of typical photoredox catalysts cannot be efficiently quenched by unactivated alkyl iodides (ca. -1.67 V vs. SCE for ethyl iodide) to generate alkyl radicals.¹²

Therefore, we became interested in exploring the possibility of a visible-light-initiated manganese-catalyzed Giese reaction. Mn₂(CO)₁₀, an inexpensive and readily available decacarbonyl complex of an earth-abundant metal, can homolyze to form a manganese-centered radical, [·Mn(CO)₅], upon irradiation with visible light,¹³ and the radical can selectively abstract the iodide atom from an alkyl iodide to furnish an alkyl radical with concomitant formation of Mn(CO)₅I.¹⁴ For successful catalytic turnover, the active catalyst, [·Mn(CO)₅], would have to be regenerated from Mn(CO)₅I under the reaction conditions. Giese reactions via such a process would be independent of the reduction potential of the photoredox catalyst and would differ from all of the photoredox Giese reactions shown in Scheme 1a. Herein we disclose the successful development of a protocol for efficient visible-light-initiated Giese reactions of unactivated alkyl iodides with catalysis by Mn₂(CO)₁₀ via a unique mechanism (Scheme 1b). The scope of the reaction was extended to alkyl iodides generated from alcohols, which further demonstrates the versatility of our protocol.

a) Current visible-light-mediated Giese reaction:



photoredox catalyst Ir/Ru

b) This work: visible-light-mediated Giese reaction using unactivated alkyl iodides

EWG +
$$\mathbf{R} - \mathbf{I} \xrightarrow{\text{Mn[0]}} \mathbf{Wn} \rightarrow \mathbf{R} \xrightarrow{\text{EWG}}$$

inexpensive, abundant metal (Mn) catalyst Scheme 1. Visible-light-mediated Giese reactions to form C–C bonds.

Table 1. Optimization of reaction conditions.^a

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1	+ HE (1.5 equiv), solvent 36 W blue LED, r 2	(0,1 M) .t.	3 3
entry	photocatalyst	solvent	yield (%) ^b
1	Mn ₂ (CO) ₁₀	DMSO	96 (92°)
2 ^d	Mn(CO)₅I	DMSO	82
3 ^e	[Ru(bpy) ₃](PF ₆) ₂	DMSO	NR
4 ^e	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	DMSO	NR
5	Mn ₂ (CO) ₁₀	CH₃CN	83
6	Mn ₂ (CO) ₁₀	MeOH	87
7	Mn ₂ (CO) ₁₀	DMA	34
8 ^f	Mn ₂ (CO) ₁₀	DMSO	NR
9	_	DMSO	NR
10 ^g	Mn ₂ (CO) ₁₀	DMSO	NR
11 ^h	Mn ₂ (CO) ₁₀	DMSO	80

^aGeneral conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.6 mmol), photocatalyst (0.03 mmol), Hantzsch ester (HE, 0.45 mmol), and solvent (3 mL) under Ar atmosphere. ^bDetermined by ¹H NMR spectroscopy using dibromomethane as an internal standard. NR = no reaction. ^cIsolated yield. ^dCatalyst loading increased to 0.06 mmol. ^eCatalyst loading reduced to 0.003 mmol. ^fPerformed in the absence of light. ^gPerformed in the absence of HE. ^hReaction mixture irradiated for 5 min and then kept in the dark for 24 h.

We began our evaluation of Mn₂(CO)₁₀ as a catalyst for visiblelight-induced Giese addition by using iodocyclohexane (2, 2.0 equiv) and benzyl acrylate (1, 1.0 equiv) as substrates (Table 1). We were delighted to find that in the presence of 10 mol % of Mn₂(CO)₁₀ and Hantzsch ester (HE) as a reductant, irradiation of a DMSO solution of 1 and 2 with a 36 W blue LED at room temperature afforded an excellent yield of addition product 3 (entry 1). Notably, Mn(CO)₅I could also mediate this reaction, affording 3 in 82% yield (entry 2), which confirms that the active catalyst, [·Mn(CO)₅], was generated by visible-light irradiation of Mn(CO)₅I. The reaction failed to proceed if Mn₂(CO)₁₀ was replaced with a Ru or Ir photocatalyst (entries 3 and 4). Other solvents (acetonitrile, methanol, and N,Ndimethylaniline) gave lower yields than DMSO (entries 5-7). Control experiments showed that the reaction did not occur in the absence of light, Mn₂(CO)₁₀, or HE (entries 8–10). Unlike typical photocatalysts, the Mn catalyst did not require a photon for turnover (entry 11).14,15 However, continuous irradiation was necessary for high efficiency, likely because the precatalyst, $Mn_2(CO)_{10}$, was in equilibrium with the active catalyst, [·Mn(CO)₅]. Also noteworthy is that unactivated primary, secondary, and tertiary alkyl bromides and alkyl chlorides, as well as aryl iodides, showed no reactivity.

With the optimized reaction conditions in hand, we studied the scope of the reaction with respect to the unactivated alkyl iodide (Table 2). We found that a wide range of primary alkyl iodides reacted with 1 to give the desired products in moderate to good yields. For example, linear alkyl iodides afforded 4–7 in 63–73% yields. We were pleased to find that primary alkyl iodides bearing various functional groups (chloride, iodide, trifluoromethyl, ethyl ester, and trimethylsilyl) were amenable to the reaction conditions, giving good yields of 8–13, respectively. Benzyl iodide, phenylethyl iodide, and phenylpropyl iodide were also suitable substrates, giving 14, 15, and 16 in 29%, 77%, and 71% yields, respectively. The

low yield of **14** may be due to the lower activity of <u>benzyl radical</u>. Notably, the Giese reaction of 4-iodophenylethyb iodide, which has an iodoaryl moiety, proceeded chemoselectively at the C(sp³)–I bond to furnish **17** (68% yield). Remarkably, sunlight, the main component of which is visible light, gave **17** in almost the same yield (62%) as that obtained upon irradiation with a 36 W blue LED. Unactivated secondary alkyl iodides generate more-stable radicals than primary iodides and therefore gave higher yields of the corresponding products (**18–24**). Finally, the use of *tert*-butyl iodide enabled direct construction of compound **25** (82% yield), which has a quaternary carbon. Likewise, this protocol provided access to **26**, a compound bearing an adamantyl moiety, which is often used by medicinal chemists to enhance the druglike qualities of lead

Table 2. Sub	strate scope	with respect	to the alk	yl iodide. ^a
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compounds without increasing their toxicity.¹⁶



^aReactions were performed on a 0.3 mmol scale under the optimized conditions shown in Table 1. Isolated yields are given.

Next, we tested this new Giese reaction protocol with a variety of Michael acceptors and several alkyl iodides (Table 3). The mild reaction conditions were found to be compatible with a range of functional groups (esters, an alcohol, amides, imides, ethers, and a sulfone), providing a variety of handles for subsequent synthetic manipulations. Specifically, as far as acrylate-based acceptors, unsubstituted acrylates and α -alkyl acrylates were well tolerated, giving **27–33** in 34–95% yields. A cyclic ester acceptor gave the corresponding product (**34**) in 41% yield. In addition, other electrophilic olefins (alkylidene malonate, maleimide, phenyl acrylamide, and phenyl vinyl sulfone) furnished the corresponding conjugate adducts (**35–41**) in moderate \cdot to good yields (39–72%). Taken together, the results shown in Tables 2 and 3 demonstrate the robustness of this protocol.

To demonstrate the practicality of our method, we extended the reaction to alkyl iodides generated from alcohols. Gratifyingly, we found that pretreatment of naturally occurring secondary alcohols L-menthol and steride with I_2 generated the corresponding iodoalkanes, which could then be subjected to our standard Giese reaction conditions to furnish conjugate adducts **42** and **43**, respectively, in moderate yields (Scheme 2a).

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^aReactions were performed on a 0.3 mmol scale under the optimized conditions shown in Table 1. Isolated yields are given.

In addition, the protocol was amenable to scale up: the reaction of **1** with **44** carried out on a 4.0 mmol scale under sunlight was complete within 6 h and gave **17** in 56% yield (Scheme 2b). Iodide **17** smoothly underwent Suzuki coupling with arylboronic acids to provide moderate to good yields of the corresponding products (**45–47**).



Scheme 2. Applications of the protocol.

Having explored the substrate scope and utility of the reaction, we turned our attention to the mechanism (Scheme 3). When a radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 1,1-diphenylethylene, was present in a reaction mixture containing 1 and 2, the formation of 3 was completely inhibited; instead the product of cyclohexyl radical trapping, 1-(cyclohexyloxy)-2,2,6,6tetramethylpiperidine (48), was detected by mass spectrometry (Scheme 3a). To confirm the involvement of radical species (Scheme 3b), we carried out a radical clock experiment: reaction of (iodomethyl)cyclopropane (50) with ethyl acrylate (49) gave 1,2disubstituted cyclopentane 51 in 36% yield. The reaction of 6-iodo-1-hexene (52) and 1 gave 9:1 mixture of 53a and 53b in 57% yield via a 5-exo radical cyclization. These experiments clearly point to a radical pathway. Finally, to confirm the source of the hydrogen atom in the product, we performed two deuterium-labeling experiments (Figure S6). Although the reaction of 1 and 2 in DMSO d_6 resulted in a coupled product containing no deuterium, the use





Scheme 3. Mechanistic experiments.

On the basis of our experimental observations and literature reports, we propose the mechanism depicted in Scheme 4. First, $Mn_2(CO)_{10}$ is homolyzed to $[\cdotMn(CO)_5]$ upon irradiation with the blue LED. Subsequent iodine abstraction from iodocyclohexane (2) generates nucleophilic radical species **A** and $Mn(CO)_5I$; this abstraction step is effectively irreversible owing to the difference in bond dissociation energy between the Mn–I bond of $Mn(CO)_5I$ (67 kcal/mol) and the C(sp³)–I bond of iodocyclohexane (60 kcal/mol).¹³ Radical **A** then adds to Michael acceptor **1** via a Giese-type pathway to afford radical intermediate **B**. This intermediate abstracts a hydrogen from the 4-position of the HE to give product **3** and a dienyl radical, which reacts with $Mn(CO)_5I$ to regenerate the active catalyst, $[\cdotMn(CO)_5]$.



Scheme 4. Proposed mechanism

Conclusions

In conclusion, we have developed a protocol for visible-lightinitiated Giese reactions involving unactivated alkyl iodides with catalysis by $Mn_2(CO)_{10}$, an inexpensive complex of an earthabundant metal. This versatile protocol tolerates a wide range of functional groups and has a broad scope with regard to both the alkyl iodide and the Michael acceptor. The reaction was also extended to alkyl iodides generated from alcohols, further demonstrating the versatility of our method. Moreover, unlike the tin hydride catalyzed reaction originally reported by Giese, this reaction was chemoselective for a C(sp³)–I bond over C(sp³)–X (X = Br, Cl) bonds and C(sp²)–I bonds. We believe that this novel protocol will facilitate the development of clinical drug candidates.

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Conflicts of interest

There are no conflicts to declare.

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inexpensive, abundant metal (Mn) catalyst

Visible-light-initiated Giese addition of unactivated alkyl iodides to electron-poor olefins with catalysis by decacarbonyl dimanganese, Mn₂(CO)₁₀ was reported.