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COMMUNICATION

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Catalyst-free Decarboxylation and Decarboxylative Giese Additions of Alkyl Carboxylates through Photoactivation of Electron Donor-acceptor Complex

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Abstract. We report herein a catalyst-free method to perform decarboxylative conjugated addition and hydrodecarboxylation of aliphatic N-(acyloxy)phthalimides (redox active esters, RAEs) through photoactivation of electron-donor-acceptor (EDA) complex with Hantzsch ester (HE) in N,N-dimethylacetamide (DMA) solution. The reactions present a green method to decarboxylatively construct carbon-carbon bond and to perform hydrodecarboxylation with broad substrate scope and functional group tolerance under mild blue light irradiation condition without recourse of popularly used photoredox catalysts.

Keywords: Decarboxylation; Giese Additions; Photoactivation; Redox Active Ester; EDA complex

Decarboxylative carbon-carbon bond construction[1] and efficient decarboxylation[2] are transformations still receiving intensive developments in synthetic community, because of the easy accessibility, abundance, and environmentally benign properties of aliphatic carboxylic acids for green organic synthesis.[3] Besides the atom- and step-economic methods to utilize carboxylic acids directly,[4] the traceless activation group strategy that uses N-(acyloxy)phthalimide (so-called redox active esters or RAEs),[5] which can be easily installed through condensation reaction,[5c] offered the other convenient way to perform various decarboxylative transformations.[6] The majority of the developed methodologies for decarboxylative carbon-carbon bond formation utilized either transition-metal complexes as catalyst under thermal condition[7] or photoredox catalysts[8] to activate RAEs, especially for decarboxylative conjugated additions.[9] Recent studies revealed that RAEs could be efficiently activated through formation of electron-donor-acceptor complex with an electron donor species under irradiation.[10] The electron-donor-acceptor complex can be a transient encounter complex, which is formed in equilibrium in solution through weak non-covalent interactions,[11] such as Coulombic interaction, hydrogen bonding, and π-π□stacking, which are heavily affected by solvation. With our interest in development of inexpensive methodologies to use aliphatic carboxylic acids in organic synthesis,[12] we conceived that decarboxylative conjugated addition with Michael acceptors and hydrodecarboxylation could be performed with a electron donor substrate such as Hantzsch ester (HE) under mild irradiation condition using blue LEDs. As depicted in Figure 1, an encounter complex of RAE and HE is photoactivated to induce inner sphere electron transfer to decarboxylatively generate alkyl radical. The alkyl radical can be effectively trapped by an olefin acceptor to form a new carbon-carbon bond followed by further hydrogen transfer from oxidized HE to deliver conjugate addition product and pyridinium salts. Hydrodecarboxylation can also be achieved in the absence of olefin coupling partner.

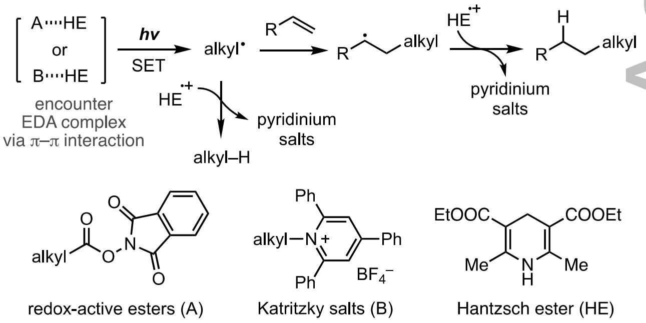
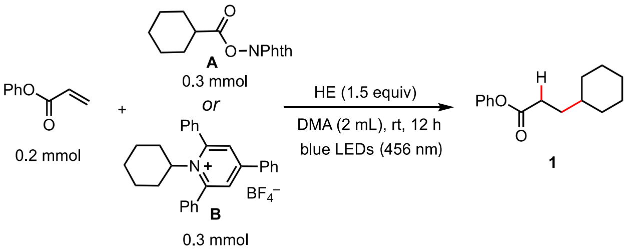


Figure 1. Working hypothesis of decarboxylative and deaminative conjugate addition through photoactivation of encounter EDA complex.

Herein we reveal a simple reaction system composed of RAE (1.5 equiv), HE (1.5 equiv), and olefin acceptor (1.0 equiv) in N,N-dimethylacetamide solvent (DMA) under irradiation of blue LEDs effectively delivers Giese type conjugate addition[13] products with broad substrate scope of both carboxylates and olefins. This method is also applicable to deaminative conjugate addition of primary aliphatic amine-derived Katritzky salt.[14,15] Selection of DMA as solvent is a key to achieve high reaction efficiency and broad reaction scope. It is noteworthy that Overman and co-workers reported that a tertiary RAE (1-methylcyclohexane-1-carboxylate) reacted with butanone and acrylonitrile in moderate yields (50 – 60%) in the absence of a photoredox catalyst.[16] The method presented herein offers an environmentally benign and economic method to perform decarboxylative addition and hydrodecarboxylation, and demonstrated the synthetic utility of photoactivation of electron-donor-acceptor complex (EDA complex) with broad substrate scope without using expensive photocatalyst.

Table 1. Optimization of reaction conditions.[a]

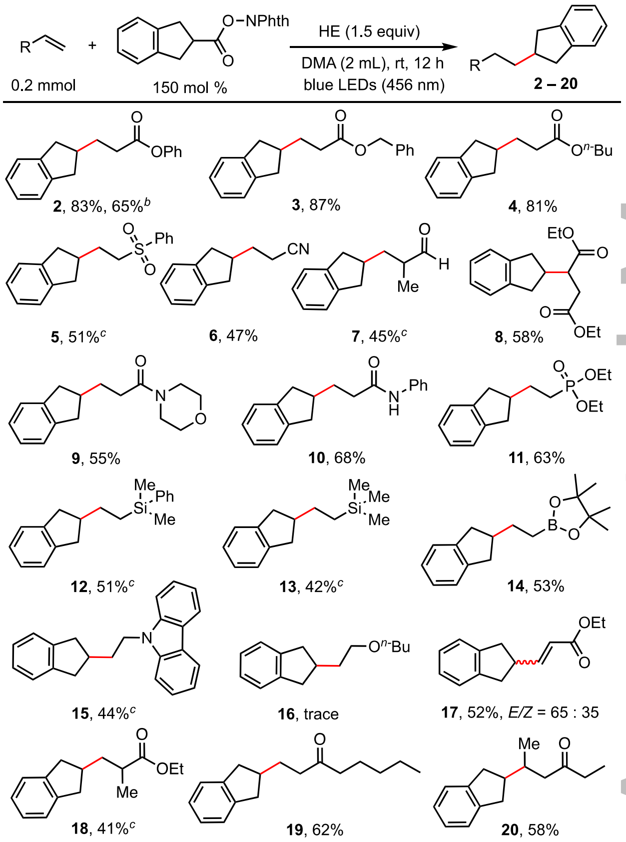


Entry	Variations from condition above	Yield [%]
1	**A**, none	91(88[b])
2	**B**, none	85
3	**A**, DMF instead of DMA	68
4	**A**, THF instead of DMA	42
5	**A**, CH_3CN instead of DMA	33
6	**A**, DCM instead of DMA	18
7	**A**, TTMMS instead of HE	trace
8	**A**, BNAH instead of HE	25
9	**A**, 1,4-CHD instead of HE	n.r.
10	**A**, 390 nm instead of 456 nm	65
11	**A**, 427 nm instead of 456 nm	81
12	**A**, 440 nm instead of 456 nm	89
13	**A**, 467 nm instead of 456 nm	82
14	**A** or **B**, without HE	n.r.
15	**A**, HE (1.2 equiv)	71
16	**A**, HE (2 equiv)	86
17	**A**, H_2O (1 equiv)	85
18	**A** or **B**, under air	trace
19	**A** or **B**, in dark	n.r.
20	Cy-Cl/Br/I instead of **A**	n.r.

[a] Reaction condition: olefin (0.2 mmol), electrophiles (0.3 mmol), HE (0.3 mmol) in DMA (2 mL), irradiated by 40 W blue LEDs (456 nm) at room temperature for 12 h under argon atmosphere. Yield determined by GC using diphenylmethane as an internal standard. [b] Isolated yield. TTMMS = Tris(trimethylsilyl)silane. BNAH = 1-benzyl-1,4-dihydronicotinamide. 1,4-CHD = 1,4-cyclohexadiene.

The optimized reaction condition is shown in Table 1, entry 1. Irradiation of a mixture of phenyl acrylate (0.1 mmol), N-(cyclohexanecarbonyl)phthalimide (0.15 mmol), and HE (0.15 mmol) in DMA (2.0 mL) by blue LEDs (456 nm) under room temperature (25 ± 3 °C) for 12 h delivered Giese type addition product (**1**) in 91% yield. The same reaction condition is also applicable for deaminative Giese addition using Katritzky salts (entry 2, see Supplementary Information for key parameters of deaminative addition).[15] Solvent is a key parameter for this reaction as solvation heavily affects molecular assembly through weak non-covalent interaction to form encounter complex for photoactivation (entries 3–6). N,N-dimethylacetamide (DMA) was found to be the optimal solvent, while the yield significantly decreased when N,N-dimethylformamide (DMF) was used (entry 3). Tetrahydrofuran (THF), acetonitrile, dichloromethane (DCM) used as solvent resulted in much lower yields.

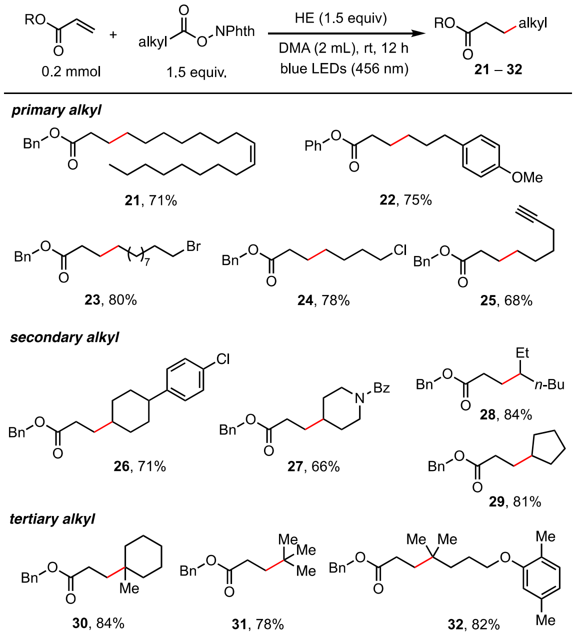
Table 2. Scope of decarboxylative conjugated addition with respect to olefins.[a]



[a] Reaction condition: alkenes (0.2 mmol), RAEs (0.3 mmol), HE (0.3 mmol) in DMA (2 mL), irradiated by 40W blue LEDs (456 nm) at room temperature for 12 h under argon atmosphere. Isolated yield. [b] The corresponding Katritzky salt was used instead of RAE and yield was determined by GC analysis using diphenylmethane as an internal standard. [c] RAEs were used in 0.4 mmol.

Electron donor reagents other than HE, such as tris(trimethylsilyl)silane (TTMMS), 1-benzyl-1,4-dihydronicotinamide (BNAH), and 1,4-cyclohexadiene (1,4-CHD) were tested and were all incompetent (entries 7–9). The wavelength length of light source is a crucial parameter in irradiation-induced reactions. As shown in entries 10-13, using purple LEDs of wavelength of 390 nm resulted in reduced yield. Other irradiation sources with wavelengths of 427 nm, 440 nm, and 467 nm were competent light sources that resulted in good yield (>80%). Hantzsch ester (HE) is absolutely necessary for both decarboxylative and deaminative additions (entry 14), and reducing the amount of HE to 1.2 equivalent resulted in reduced yield (entries 15 and 16). The reaction is not sensitive to water (entry 17) but is highly sensitive to oxygen. Reaction exposed to air produced only trace amount of desired product (entry 18). Irradiation by LED light is essential for the reactivity (entry 19). Alkyl halides that do not form absorbing EDA complex with HE could not be activated by this method (entry 20). Critically speaking, the necessity of stoichiometric amount of HE to form absorbing EDA complex is a disadvantage of this method regarding to atom economy.

Table 3. Scope of decarboxylative conjugate additions with respect to different aliphatic carboxylic acids.[a]

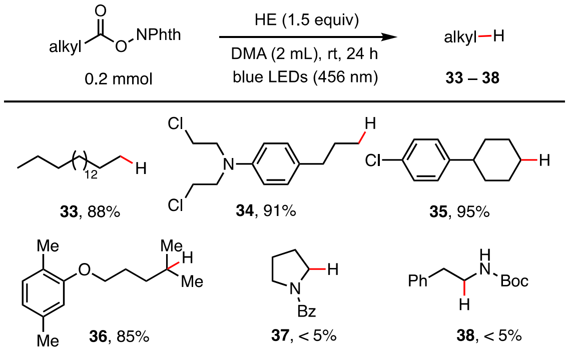


[a] Reaction condition: olefines (0.2 mmol), RAEs (0.3 mmol), HE (0.3 mmol) in DMA (2 mL), irradiated by 40 W blue LEDs (456 nm) at room temperature for 12 h under argon atmosphere. Yield of isolated product.

The scope of Giese type addition reaction regarding to olefin part is demonstrated in Table 2. Indan-2-carboxylic acid derived RAE was chosen as model substrate for easily tracing the product under thin layer chromatography. A broad scope of olefins exhibited as amenable substrates, including α,β-unsaturated ester (**2**–**4**, **18**), sulfone (**5**), nitrile (**6**), aldehyde (**7**), amide (**9**, **10**), phosphate (**11**), and ketone (**19**). Maleate was also suitable substrate (**8**). The reaction also worked well with vinyl silane and vinyl pinacol boronate (**12**–**14**), albeit in moderate yields. N-vinyl carbazole was amenable substrate to deliver N-alkylated carbazole in moderate yield (**15**), while vinyl alkyl ether did not afford the desired addition product probably due to the competitive radical oligomerization of vinyl ether (**16**). Ethyl propiolate afforded β-alkylated acrylate as stereoisomeric mixture (**17**). Substituents on both α– and β– positions were tolerated (**7**, **8**, **18**, **20**).

The reaction scope regarding to aliphatic carboxylic acid derived RAEs is demonstrated in Table 3. Primary alkylation, secondary alkylation, and tertiary alkylation using RAEs all proceeded smoothly in good yields. A *cis*-alkene structure in oleic acid was full preserved (**21**). Alkyl bromide (**23**), alkyl chloride (**24**), and terminal alkyne (**25**), which are useful coupling units in cross-coupling chemistry,[17] were well tolerated under this metal-free condition. Amino acid derived RAEs were not amenable under the optimized reaction conditions.

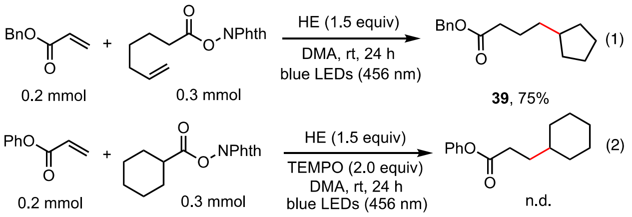
Table 4. Decarboxylative reduction of RAEs using HE.[a]



[a] Reaction condition: RAEs (0.2 mmol), HE (0.3 mmol) in DMA (2 mL), irradiated by 40 W blue LEDs (456 nm) at room temperature for 24 h under argon atmosphere. Yield of isolated product.

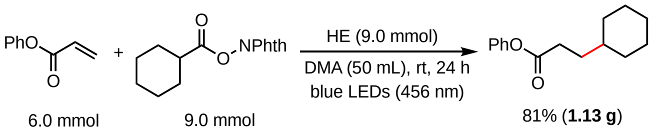
We noticed in many entries of decarboxylative addition in Table 2 and Table 3, the moderate yields were due to formation of competitive reduction product by hydrogen abstraction of alkyl radical with oxidized HE (Figure 1). We realized that besides decarboxylative addition to forge carbon-carbon bond, the method also provides an efficient way for hydrodecarboxylation of aliphatic carboxylic acids in the absence of olefin coupling partners. Compared with Barton decarboxylation,[18] which requires handling of toxic and smelly tin and thiol reagents, the metal-free method through visible light activation of EDA complex present a user-friendly and operationally simple way for reductive decarboxylation. Primary, secondary, and tertiary carboxylic acids-derived RAEs all decarboxylated smoothly to deliver the reduction products in high yields (Table 4, **33**–**36**).

Interestingly, amino acid derived RAEs (**37**, **38**) were not compatible substrates, probably because hydrogen bonding of amide with HE disturbs the formation of encounter EDA complex through π-π assembly for productive photoactivation.



Scheme 1. Evidence for radical decarboxylation.

Radical clock experiment[19] (Scheme 1, eq. 1) and experiment using radical scavenger (Scheme 1, eq. 2) unambiguously proved radical decarboxylation process. The scalability of this method is demonstrated by a gram-scale synthesis in good yield (Scheme 2).



Scheme 2. Gram-scale synthesis.

UV-vis absorption spectrum of the reaction mixture was measured to provide information on formation of EDA complex. As shown in Figure 2a, a mixture of RAE (**A**) and HE in DMA with a concentration identical to the reaction condition exhibits a strong bathochromic shift compared with the absorption of each substrate alone. The absorption band (red line) is considered to belong to the formation of an EDA complex, and extends to wavelength longer than 500 nm. Concentration plays an important role, as a diluted solution (1/10 of the concentration of the reaction mixture) showed blue-shifted absorption band. This observed dilution effect on hypsochromic shift of absorption band could be ascribed to the inhibition of association process to form EDA complex. Selection of solvent is crucial for photoreaction proceeding through encounter EDA complex, as solvation may heavily affect the transient formation of EDA complex. As shown in Figure 2b, the UV-vis absorption spectra measured in DCM (a poor solvent afforded desired product in 18% yield in Table 1) showed hypsochromic shift of all absorption bands compared with spectra measured in DMA, which suggests that the encounter EDA complex does not form effectively in DCM.

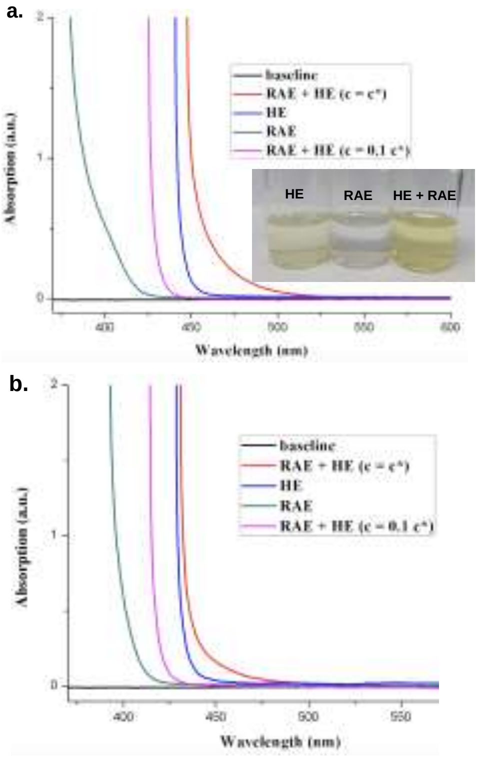


Figure 2. UV-vis spectra**.** (a) UV-vis spectra measured in DMA solvent. Inset photo shows the appearance of reactant solution under reaction concentration. (b) UV-vis spectra measured in DCM solvent. Concentration of each substance in UV-Vis measurement is identical to the concentration used in reactions (c*).

In conclusion, a catalyst-free method for hydrodecarboxylation and decarboxylative Giese addition reaction based on photoactivation of RAEs/HE encounter EDA complex is discovered. Solvation effect that heavily affects the formation of encounter EDA complex is find to be crucial for the high reactivity and substrate generality. The reaction exhibits high efficiency and broad substrate scope, and offers a green and sustainable method to used biomass-derived aliphatic carboxylic acids in organic synthesis.

Experimental Section

General Procedure

Olefins (1.0 equiv, 0.2 mmol) (when solid), redox-active esters (0.3 mmol), HE (0.3 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, olefins (1.0 equiv, 0.2 mmol) (when liquid) and anhydrous DMA (2 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with blue LEDs (456 nm, distance app. 3.0 cm from the bulb), maintained at approximately room temperature by a desk fan in the air-conditioned room of 25°C for 12 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

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[15] Duing the scope investigation of this work Aggarwal and co-workers reported the deaminative conjugate addition using same strategy, so the scope of

deaminative conjugate addition was not further demonstrated in this paper. For deaminative conjugate addition using similar strategy, see: J. Wu, P. S. Grant, X. Li, A. Noble, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2019**, *58*, 5697–5701; *Angew. Chem.* **2019**, *131*, 5753–5757.

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