## **ORGANIC CHEMISTRY**

# Photocatalytic decarboxylative alkylations mediated by triphenylphosphine and sodium iodide

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Most photoredox catalysts in current use are precious metal complexes or synthetically elaborate organic dyes, the cost of which can impede their application for large-scale industrial processes. We found that a combination of triphenylphosphine and sodium iodide under 456-nanometer irradiation by blue light-emitting diodes can catalyze the alkylation of silyl enol ethers by decarboxylative coupling with redox-active esters in the absence of transition metals. Deaminative alkylation using Katritzky's N-alkylpyridinium salts and trifluoromethylation using Togni's reagent are also demonstrated. Moreover, the phosphine/iodide-based photoredox system catalyzes Minisci-type alkylation of N-heterocycles and can operate in tandem with chiral phosphoric acids to achieve high enantioselectivity in this reaction.

he power of light-induced electron transfer for catalytic organic synthesis (1–8) has been demonstrated by the remarkable recent progress in photoredox catalysis (9, 10). The photoredox catalysts in current use are mostly precious metal complexes (11–15) and synthetically elaborate organic dyes (16), which have charge-separated excited states (17–19) accessible by absorption of visible light (Fig. 1A). Photoinduced intermolecular charge transfer through assembly of donor and acceptor molecules by noncovalent interactions is a well-known process in photochemistry (Fig. 1A), which may not require each substrate (donor or acceptor) to absorb at the desired wavelength individually (20, 21). Such irradiation-induced intermolecular charge transfer is applied in organic photovoltaics (22) and traditional photochemistry (23) but is seldom used as a principle to construct a catalytic redox cycle for organic synthesis.

We posited that a photoredox catalytic cycle based on light-induced intermolecular electron transfer without direct excitation of the catalyst and substrates could obviate the need for expensive dyes. Specifically, we targeted light-induced intermolecular electron transfer from sodium iodide to an aliphatic redox-active ester (RAE) (24–26) to induce radical decarboxylation controllably and thereby deliver an alkyl radical useful in organic synthesis (Fig. 1B).

# Simulations of charge transfer energetics

Sodium iodide is known to reduce aryl bromide and triflate to the respective aryl radicals for the aromatic Finkelstein reaction, but only under high-energy ultraviolet (UV) irradiation (27, 28). Through density functional theory (DFT) calculations (see supplementary materials), we estimated that electron transfer from sodium iodide to the RAE N-(cyclohexanecarbonyl)phthalimide is endergonic by 56.2 kcal/mol, but only by 44.3 kcal/ mol in the presence of triphenylphosphine (PPh<sub>3</sub>) because of the favorable formation of the Ph<sub>3</sub>P-I• radical (calculated to be exergonic by 11.9 kcal/ mol) (29, 30). A Ph<sub>3</sub>P-I• species was observed by electron paramagnetic resonance spectroscopy in the 1970s (30). Theoretical calculations (see supplementary materials) and natural bond orbital analysis suggest a reduction potential of 0.69 V versus saturated calomel electrode (SCE), and spin densities delocalized across I and P are 0.44 and 0.42, respectively (Fig. 1B). The calculations also suggested that complexation of NaI and PPh<sub>3</sub> is exergonic in acetonitrile through the cation- $\pi$  interaction (exergonic by 4.6 kcal/mol). The assembly of NaI and PPh<sub>3</sub> with the RAE N-(cyclohexanecarbonyl)phthalimide to form a charge transfer complex (CTC) via coulombic interaction is calculated to be exergonic by 3.8 kcal/mol

A В NPhth alkyl\* SET alky (-NPhth) || 0 in metal complex in organic dye spin location (RAE) 0.44 ΔG D 0.42 intramolecular CT Nal 56.2 kcal/mol Nal-PPh3 44.3 kcal/mol Ph (alkyl = cyclohexyl) + e-E (Ph<sub>3</sub>P-I•/PPh<sub>3</sub>+I<sup>-</sup>) iodide/phosphine redox cycle = 0.69 V vs SCE С non-covalent interactions intermolecular CT RAE Ph Fig. 1. Redox catalysis based on light-induced Na Na intermolecular electron transfer from sodium Nal iodide to redox-active ester. (A) Light-+ PPh<sub>3</sub> induced intramolecular charge transfer (CT) and light-induced intermolecular donor (D)-acceptor (A) charge transfer through  $\Delta G^{\dagger}$  (w/o PPh<sub>3</sub>) = 86.5 kcal/mol self-assembly via noncovalent interactions. (0.0 kcal/mol) (-3.8 kcal/mol) L, ligand; M, metal. (B) Estimated Gibbs  $\Delta G^{\dagger}$  (w/ PPh<sub>3</sub>) = 61.2 kcal/mol energy change of intermolecular electron

to aliphatic *N*-(acyloxy)phthalimide (NPhth) to deliver an alkyl radical, and a possible iodide/phosphine redox cycle. (**C**) Photoactivation of assembled complex of *N*-(acyloxy)phthalimide with Nal and PPh<sub>3</sub> through coulombic and cation- $\pi$  interactions. SET, single electron transfer.

transfer from Nal and Nal/PPh3 component

(Fig. 1C). The energy barrier of the electron transfer process from iodide to the phthalimide moiety was estimated to be 61.2 kcal/mol using Marcus theory, within 1.5 kcal/mol of the photon energy that 456-nm blue LEDs can provide. The analogous electron transfer process in the absence of PPh<sub>3</sub> must overcome a higher barrier of 86.5 kcal/mol (Fig. 1C; see supplementary materials). Further computational studies on the excited state of the CTC assigned the So-to-S1 excitation to electron transfer from iodide to the  $\pi^*$  orbital of the phthalimide moiety with an excitation energy of 2.85 eV, which corresponds to a wavelength of 436 nm (fig. S3). On the basis of the above theoretical analysis, we explored a simple combination of NaI and PPh3 as a photoredox catalyst for decarboxylative alkylation reactions (31, 32).

### Investigation of key reaction parameters

The optimized reaction conditions for decarboxylative alkylation using NaI/PPh<sub>3</sub> are shown in Fig. 2. Decarboxylative cyclohexyl addition to trimethyl[(1-phenylvinyl)oxy]silane delivered  $\alpha$ -cyclohexylacetophenone in 82% yield under blue LED irradiation of 20 mole percent (mol %) PPh<sub>3</sub> and 150 mol % NaI in acetonitrile (see table S1 for details of optimization) (*33, 34*). The reaction requires further desilylation by a base to form the  $\alpha$ -alkylated ketone. Because NaI is so inexpensive, it was used in superstoichiometric quantity (1.5 equivalent) both as electron-transfer catalyst and base to trap the trimethylsilyl (TMS) cation.

Extremely pure (99.999%) NaI without any metal contamination was tested and gave the same results observed with the commonly available reagent-grade material (purity >99.0%). The results of testing other alkali halides are shown in Fig. 2A. Lithium and potassium iodide were much less effective than NaI, and a soluble quaternary ammonium iodide was entirely ineffective. The observed alkali metal cation effect revealed that the sodium cation has an important role in the electron transfer activation step, as indicated by DFT study in Fig. 1C (formation of the CTC by LiI, NaI, and KI is exergonic by 1.1 kcal/mol, 3.8 kcal/ mol, and 2.9 kcal/mol, respectively, as indicated by DFT calculation). Other sodium halides (fluoride, chloride, and bromide) were also ineffective.

As noted above, phosphine is crucial to facilitate intermolecular charge transfer and stabilizes the iodine radical as a  $R_3P-I$ • species (*30*). Thus, we also screened a series of phosphines with different electronic and steric properties (Fig. 2A, second row). The results showed that the electronic properties of triarylphosphines did not significantly affect the reaction efficiency, as using tris(4-fluorophenyl) phosphine and tris(4-methoxyphenyl)phosphine gave comparable yields. However, highly electrondeficient tris(4-pentafluorophenyl)phosphine was completely ineffective, probably due to its lack of electron-donating capacity to facilitate electron transfer of the iodide salt. The use of tricyclohexylphosphine lowered the yield, as did the sterically bulky triarylphosphine ligand 2-(diphenylphosphino)biphenyl, which likely hindered formation of the CTC (Fig. 2A). All three components—phosphine, sodium iodide,



Fig. 2. Key reaction-controlling parameters of Nal and PPh<sub>3</sub>-catalyzed decarboxylative alkylation. (A) Parameters affecting decarboxylative alkylation of silyl enol ethers. (B) Parameters affecting decarboxylative alkylation of N-heteroarenes. (C and D) UV-Vis absorption spectra of reactant mixtures. Concentration of each substance in UV-Vis measurement is identical to the concentration used in reactions. Me, methyl; TFA, trifluoroacetic acid.

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and irradiation—were essential for the reaction (Fig. 2A). Moreover, addition of 10 mol % of iodine to the reaction mixture entirely suppressed the reaction (*35*). This poisoning effect rules out a productive role for iodine or  $I_3$ <sup>-</sup> in the redox cycle and highlights the important role of PPh<sub>3</sub> in keeping the iodine radical trapped as the putative persistent  $R_3P$ –I• species. The classic CTC  $I_2$ •PPh<sub>3</sub> was also ineffective.

We next explored the dependence of the reaction on irradiation wavelength. Across the spectrum (Fig. 2A and table S1), green LEDs emitting at 520 nm were ineffective, whereas blue and purple LEDs at wavelengths of 456 nm, 440 nm, and 427 nm were comparably effective. Shorter wavelengths than these resulted in lower yields. Investigation of reaction parameters for decarboxylative Minisci-type alkylation (*36*, *37*) of 4-methylquinoline (Fig. 2B) gave results similar to those observed for the alkylation of silyl enol ether (Fig. 2A), except that for the Minisci reaction, both sodium iodide and PPh<sub>3</sub> could be used in catalytic quantities (5 to 20 mol %; see table S4 for a detailed parameter study). Sever-





al commonly used low-boiling solvents, such as trifluoromethyltoluene, acetone, acetonitrile, and dioxane, effectively dissolved 10 mol % of NaI and afforded alkylation products in high yield (>85%). Control experiments showed that for the Minisci alkylation, PPh3, NaI, irradiation, and a Brønsted acid additive to increase the electrophilicity of the N-heteroarene were all essential (Fig. 2B). Once again, addition of 10 mol % of iodine completely suppressed the reaction. The quantum yield of the decarboxylative Minisci alkylation (Fig. 2B) was measured to be 0.15, a value suggesting a closed catalytic cycle rather than a radical chain process initiated by electron transfer (38, 39). Cyclohexyl iodide was not detected in the reaction mixtures of the silyl enol ether or the N-heteroarene, and a control experiment using cyclohexyl iodide as alkylation reagent did not yield any desired alkylation products.

To provide further understanding of the NaI/ PPh<sub>3</sub> photoredox system, we measured UV-visible (UV-Vis) absorption spectra. Reactant concentration effects on the UV-Vis absorption spectrum in a light-induced intermolecular donor-acceptor charge-transfer reaction were reported by Miyake and co-workers for C-S coupling of aryl halides (40). We performed a UV-Vis absorption measurement using a solution of the same concentration as the real reaction mixture (Fig. 2, C and D), from which it was apparent that neither NaI, PPh<sub>3</sub>, nor the combination of NaI and PPh3 has any absorption in the visible region (Fig. 2D). Silyl enol ether and 4-methylquinoline showed absorption features only in the UV (<350 nm). The redox-active ester showed an absorption onset around 390 nm. The mixture of redox-active ester (1) with either silyl enol ether (2) or 4methylquinoline (4) did not show any significant change of the absorption onset compared with redox-active ester (1) alone, which suggests that no intermolecular charge transfer took place. However, an obvious redshift of absorption onset, tailing into the wavelength range of blue LED irradiation, was observed when the NaI/ PPh<sub>3</sub> component was mixed with redox-active ester. This redshift supports the formation of a charge-transfer complex (41, 42) between NaI/ PPh3 and redox-active ester in the reaction mixture (see Fig. 1C).

### Application to alkylation of silyl enol ethers and N-heteroarenes

Next, we explored the reaction scope for ketone synthesis through decarboxylative alkylation of silyl enol ethers (Fig. 3). A broad range of functional groups such as ether (**6**), alkyl chloride (**7**), terminal alkyne (**8**), terminal alkene (**9**), ester (**10**), amide (**12**), sulfide (**23**), aryl fluoride (**27**), aryl bromide (**28**), aryl chloride (**29**), aryl iodide (**30**), trifluoromethyl (**33**), acidic methyl sulfone (**34**), and even aryl pinacol boronate (**43**) proved compatible. Redox-active esters derived from various natural and unnatural amino acids were reactive to give  $\alpha$ -aminoalkylation products in good yields. The scalability of this reaction was demonstrated by preparation of 2.9 g of amino acid derivative **18**. The low cost of this NaI/PPh<sub>3</sub> catalytic

system is appealing for industrial application to large-scale syntheses.

The scope of Minisci-type alkylation (Fig. 4A) spanned redox-active esters derived from secondary (**46**, **49**) and tertiary (**50–53**) aliphatic

carboxylic acids,  $\alpha$ -amino acids (**54–59**),  $\alpha$ -hydroxy acids (**47, 48**), and peptides (**63**) (*36*). The catalyst loading for a gram-scale reaction could be reduced to 5 mol % of NaI and 5 mol % of PPh<sub>3</sub> to give 2.78 g of alkylation product **62** in 80% yield. Besides 4-methyl quinoline, other substituted quinolines were also reactive (**64**, **70**). Alkylation took place on the C4 position of the quinoline ring when C2-substituted quinolines were tested (**65**, **71**). Isoquinolines (**66–68**),



**Fig. 4. Minisci-type decarboxylative alkylation.** (**A**) Scope for Miniscitype decarboxylative alkylation of N-heteroarenes. Reaction conditions: N-heteroarenes (0.2 mmol, 1.0 equiv), redox-active ester (0.3 mmol), Nal (10 mol %), PPh<sub>3</sub> (20 mol %), TFA (0.2 mmol), acetone (2 ml), 15 hours, r.t., 456-nm blue LEDs. Isolated yields are reported. \*PhCF<sub>3</sub> as solvent. †N-heteroarenes (8.0 mmol, 1.0 equiv), redox-active ester (8.8 mmol, 1.1 equiv), Nal (5 mol %), PPh<sub>3</sub> (5 mol %), TFA (8.0 mmol), acetone (40 ml), 15 hours, r.t., 456-nm blue LEDs. ‡(±)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (5.0 mol %) instead of TFA (0.2 mmol). (**B**) Merging Nal/PPh<sub>3</sub> photoredox catalysis with chiral phosphoric acid (PA) catalysis for enantioselective Minisci-type α-aminoalkylation. Reaction conditions: N-heteroarenes (0.1 mmol, 1.0 equiv), redox-active ester (0.15 mmol), Nal (20 mol %), PPh<sub>3</sub> (20 mol %), chiral PA (5.0 mol %), 1,4-dioxane (2 ml), 20 hours, r.t., 456-nm blue LEDs. Isolated yields are reported; enantiomeric excesses were determined by high-performance liquid chromatography (HPLC). (**C**) Scope of enantioselective Minisci-type decarboxylative  $\alpha$ -aminoalkylation by relay of Nal/PPh<sub>3</sub> redox catalysis with chiral anion catalysis. Reaction conditions: N-heteroarenes (0.2 mmol, 1.0 equiv), redox-active ester (0.3 mmol), Nal (10 mol %), PPh<sub>3</sub> (10 mol %), (*R*)-TRIP-PA (5 mol %), 1,4-dioxane (2 ml), 15 hours, r.t., 456-nm blue LEDs. Isolated yields are reported; enantiomeric excesses were determined by HPLC. Absolute stereochemistry of products was assigned by analogy to **73**. \*N-heteroarenes (0.3 mmol), redox-active ester (0.2 mmol). †Nal (20 mol %), PPh<sub>3</sub> (20 mol %), (*R*)-TRIP-PA (10 mol %). Cy, cyclohexyl; Et, ethyl; *t*-Bu, *tert*-butyl; Ac, acetyl; *i*-Pr, isopropyl. Fig. 5. General applicability of Nal/PAr<sub>3</sub> photoredox system. (A) Decarboxylative alkenylation of RAEs. (B) Deaminative alkenylation of Katritzky's N-alkylpyridinium salts. (C) Trifluoromethylation using Togni's reagent. \*Using PPh3 instead of  $P(p-MeO-C_6H_4)_3$ .  $+Using P(p-F-C_6H_4)_3$ instead of P(p-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. ‡Yield measured by <sup>1</sup>H nuclear magnetic resonance using diphenylmethane as internal standard.



Fig. 6. A proposed full catalytic cycle of Nal/PPh<sub>3</sub> photoredox catalysis. Catalytic cycle of decarboxylative alkylation with N-heteroarene is

demonstrated as an example. See fig. S4 for proposed full catalytic cycles for reactions with silyl enol ether and alkene.

or chiral phosphate

phenanthridine (**69**), and pyridine (**72**) were all effective substrates, yielding a variety of alkylated N-heteroarenes of pharmaceutical importance (*43*).

# Merging with chiral Brønsted acid catalysis for enantioselective alkylation

To our excitement, we found that the NaI/PPh<sub>3</sub> redox catalyst could operate synergistically with a chiral Brønsted acid catalyst (44, 45) to achieve asymmetric a-aminoalkylation of N-heteroarenes (Fig. 4B). This enantioselective transformation was reported only recently by Phipps and co-workers (46) using an expensive iridium photoredox catalyst, following from the precedent reported by our group pairing the iridium with achiral phosphoric acid catalysis (36). Here, we combined 20 mol % of NaI/PPh3 with 5 mol % of chiral phosphoric acid in the absence of transition metals. Evaluation of various commercially available chiral phosphoric acids showed that (R)-TRIP-PA [(R)-3,3'-bis(2,4,6-triisopropylphenyl)-1, 1'-binaphthyl-2,2'-diyl hydrogenphosphate] was the optimal choice to deliver (S)- $\alpha$ -aminoalkylated product in 97% yield and 95% enantiomeric excess (ee). Zhou-type spiro-phosphoric acids (47) were also found to be effective, giving comparable yield and enantioselectivity. The absolute configuration of the a-aminoalkylated products was unambiguously determined by x-ray singlecrystal analysis (73). The configuration is switchable by changing the absolute configuration of the chiral phosphoric acid catalyst. A broad scope of natural and unnatural α-amino acid-derived RAEs was applicable to the asymmetric decarboxylative Minisci-type α-aminoalkylation reaction (73-80) to produce various valuable enantioenriched basic heterocycles in high enantioselectivity (Fig. 4C). For quinoline derivatives that did not possess substituents on the 2- or 4-positions, enantioselective alkylation proceeded with C2 selectivity. Besides quinoline, asymmetric decarboxylative C2-alkylations of functionalized pyridines (84-86) were also achieved in high yields and high enantioselectivity. Isoquinoline was reactive to give the  $\alpha$ -aminoalkylation product in high yield, but the enantioselectivity was only 33% ee (see supplementary materials).

Because the noncovalent interaction (cation- $\pi$ interaction, Coulombic interaction, etc.) required for assembly of CTC is rather common, and electron transfer from iodide to many organic molecules is precedented under UV (27, 28) or high-temperature conditions (39), we posited that the iodide phosphine photoredox system should be generally applicable to substrates other than RAEs. Indeed, besides decarboxylative alkenylation using RAEs with 1,1-diphenylethylene (Fig. 5A), we have found that NaI/PAr3 also activates Katritzky's Nalkylpyridinium salts to enable catalytic deaminative alkylation (48) with 1,1-diarylethylene to deliver alkyl Heck-type products (49) (88-91) (Fig. 5B). The NaI/PPh3 system also activated Togni's reagent for photoredox trifluoromethylation of 1,1-diarylethylene and silyl enol ether (92 and 93) (Fig. 5C). For all these reactions, control experiments confirmed the essential roles of NaI, PAr<sub>3</sub>, and irradiation. Solvent plays a crucial role for these transformations [e.g., dimethylformamide (DMF) as solvent is crucial for deaminative alkylation, as the reaction failed in acetonitrile and acetone], probably because noncovalent interactions required for assembling the CTC, such as cation- $\pi$  and electrostatic interactions, are heavily influenced by solvation. Last, a proposed full catalytic cycle of NaI/ PAr<sub>3</sub> photoredox catalysis is illustrated in Fig. 6 by taking Minisci alkylation as an example (see fig. S4 for proposed full catalytic cycles for reactions with silyl enol ether and alkene). After photofragmentation of the CTC, the generated alkyl radical attacks N-heteroarene to form a carbon-carbon bond. The PPh3-I• radical oxidizes the delocalized carbon radical generated after the alkvl radical attacks the  $\pi$  system to regenerate PPh3 and NaI. Generally, the oxidation potentials of delocalized carbon radicals (such as benzylic radical and allylic radical) are lower than the reduction potential of PPh3-I• (0.69 V versus SCE) (50). Thus, the redox potential of PPh<sub>3</sub>-I• is sufficient to close the redox cycle.

We hope the reactions presented above will inspire future research in photoredox catalysis by introducing a tricomponent catalytic system based on a salt, a phosphine, and an electronaccepting substrate to access the CTC without the need of a traditional dye- or metal complexbased photoredox catalyst.

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#### SUPPLEMENTARY MATERIALS

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# Photocatalytic decarboxylative alkylations mediated by triphenylphosphine and sodium iodide

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### Crowdsourcing a chromophore

Photoredox catalysis is widely used to accelerate chemical reactions by channeling the energy in visible light. However, most implementations rely on expensive chromophores to absorb light. Fu *et al.* now show that a pair of cheap components acting in concert can induce these reactions, despite not being strong visible absorbers individually. The combination of sodium iodide and triphenylphosphine allowed photoinduced electron transfer to catalyze a variety of alkylations.

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