Electro-mediated PhotoRedox Catalysis for Selective C(sp³)–O Cleavages of Phosphinated Alcohols to Carbanions

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Abstract: We report a novel example of electro-mediated photoredox catalysis (e-PRC) in the reductive cleavage of C(sp³)–O bonds of phosphinated alcohols to alkyl carbanions. As well as deoxygenations, olefina tions are reported which are E-selective and can be made Z-selective in a tandem reduction/photosensitization process where both steps are photoelectrochemically promoted. Spectroscopy, computation, and catalyst structural variations reveal that our new naphthalene monoimide-type catalyst allows for an intimate dispersive precomplexation of its radical anion form with the phosphinate substrate, facilitating a reactivity-determining C(sp³)–O cleavage. Surprisingly and in contrast to previously reported photoexcited radical anion chemistries, our conditions tolerate aryl chlorides/bromides and do not give rise to Birch-type reductions.

Introduction

Synthetic methodologies involving single electron transfer (SET) are increasingly popular for the facile synthesis or modifications of important organic compounds. PhotoRedox Catalysis (PRC)\[1\] and Synthetic Organic Electrochemistry (SOE)\[2\] lead to easy SET processes, providing notable redox power for various organic transformations under mild conditions. Generally, visible-light PRC generates radical intermediates with good functional group tolerance in a mild manner. However, synthetic applications of PRC in terms of transformations needing highly oxidizing or reducing potentials are limited by the energetic limitations of visible light photons. One solution is to generate photoexcitable radical ions by multi-photon processes.\[3\] Such photoexcited radical ions are highly oxidizing\[3a,b\] or reducing species\[3c–h\], leading to a significantly expanded redox “window” for activating inert substrates. Sacrificial redox additives (e.g. DIPEA) are employed in stoichiometric excesses in consecutive Photo-induced Electron Transfer (conPET) processes to prime catalysts prior to excitation. Their excesses and organic by-products can plague purification steps. In contrast, SOE allows direct access to high, user-controlled redox energy without involving photocatalysts or sacrificial redox additives, offering advantages to net-oxidative/reductive reactions. However, the applied constant current or voltage can cause uncontrollable over-reductions/oxidations to afford by-products. To address the aforementioned limitations in PRC and SOE, organic chemists have recently explored their combination (Scheme 1).\[4\]

Merging the advantages of these two important techniques has made photoelectrochemistry a tool for greener, more challenging and more selective molecular activations.\[5\] Pioneering reports by Xu,\[5b–m\] Lambert,\[5g,h,i,k\] Lin\[5h,j\] and

**Scheme 1.** Previous reductive e-PRC reports involving C(sp²)–X cleavages to afford aryl radicals vs. this work involving C(sp³)–O cleavages to afford alkyl radicals and carbanions. [a] E°red. [b] E₁/₂. [c] Redox potential vs. SCE.
Wickens and Haines have shown that introducing applied potential in photoredox catalysis is not only beneficial for accessing challenging redox reactions, but is also a green replacement for sacrificial redox additives.

Among the various strategies for combining photocatalysis and electrochemistry, the sub-category coined electrochemically-mediated photoredox catalysis (e-PRC) is highly attractive. In addition to turning over “spent” closed-shell photocatalysts, e-PRC can also involve electrochemical generation of open-shell (radical ion) photocatalysts, followed by their photoexcitation to species with ultra-high redox potentials. A seminal report from the Lambert group demonstrated this strategy for super-oxidations of highly electron-poor arenes. In the reductive direction, photoexcited radical anions of dicyananthracene (DCA) and of 2,6-disopropylphenyl-containing naphthalenemonoimide (NpMI) are highly reducing species ($E_{\text{red}}^{\text{cell}} < -3.0 \text{ V vs. SCE}$) that reduce challenging aryl chlorides to their aryl radicals. Even p-chloroanisole was reduced, beyond reach of the photon energy limit of monophotonic PRC and where SOE inevitably leads to dehalogenation via subsequent aryl radical reduction (Scheme 1A). Despite these elegant advances, reductive e-PRC and biphotochemical strategies are still heavily focused on the reductions of aryl halides/pseudohalides through C(sp$^2$)–X bond cleavages to generate aryl C(sp$^2$) radicals in an overall dehalogenation or functionalization with excesses of radical trapping agents.

Inspired by previous reports, we envisioned that phosphinates of aliphatic alcohols ($E_{\text{red}}^{\text{cell}} = -2.2 \rightarrow -2.6 \text{ V vs. SCE}$) could undergo e-PRC reduction to give carbanions (Scheme 1B). Thereby, an electroactivated-PhotoRedox Catalyst (e-PRCat) undergoes cathodic activation and photoexcitation to afford a potent reductant. SET reduction of 1 to its radical anion followed by C(sp$^2$)–O bond cleavage delivers benzyl radical 1′: Its further reduction would enable either an olefination (X = Cl, Br) or a deoxygenation (X = H) process by a mechanism that does not depend on hydrogen atom transfer agents or decarboxylation. Herein, we report the e-PRC reduction of alkyl phosphinates to alkyl(sp$^2$) carbanions for olefination and deoxygenation reactions that proceeds under exceedingly mild conditions, ii) tolerates aryl halides/pseudohalides with similar or more accessible redox potentials than the target alkyl phosphinate moiety.

**Results and Discussion**

To assess the viability of our proposed e-PRC alkyl phosphinate reduction, we employed 2-chloro-1,2-diphenylphosphinate 1a as a model substrate for the olefination reaction (Table 1). By using DCA as an e-PRCat and Zn(+) in the presence of light, we examined the reduction of 1a under blue light irradiation and with different applied constant potentials. A high constant voltage ($U_{\text{cell}} = -3.2 \text{ V}$) used previously for electron-priming DCA to its radical anion for photoexcitation gave notable decomposition, desired product E-stilbene (E-2a) in only 7% yield and a 25% yield of diphenylethane 3a.

| Entry | Substrate | e-PRCat | $U_{\text{cell}}$ [V] | t [h] | Product | Yield [%] |
|-------|-----------|---------|-----------------------|-------|---------|-----------|
| 1     | 1a        | DCA     | -3.2                  | 12    | 2a      | 7%, E-/Z- > 20:1 |
| 2     | 1a        | DCA     | -1.6                  | 12    | 2a      | 7%, E-/Z- > 20:1 |
| 3     | 1a        | DCA     | -1.0                  | 12    | 2a      | n.d.      |
| 4     | 1a        | DCA     | -1.0                  | 24    | 2a      | 7%, E-/Z- > 20:1 |
| 5     | 1a        | DCA     | -1.0                  | 12    | 2a      | n.d.      |
| 6     | 1a        | DCA     | -1.0                  | 12    | 2a      | n.d.      |
| 7     | 1a        | DCA     | -1.0                  | 12    | 2a      | n.d.      |
| 8     | 1a        | NpMI    | -1.6                  | 12    | 2a      | 80%, E-/Z- = 1:1.3 |
| 9     | 1a        | NpMI    | -1.6                  | 48    | 2a      | 78%, E-/Z- = 1:10 |
| 10$^d$| 1d        | DCA     | -1.0                  | 12    | 2d      | n.d.      |
| 11$^d$| 1d        | NpMI    | -1.6                  | 12    | 2d      | trace     |
| 12$^d$| 1d        | “BuO-NpMI | -1.6                | 12    | 2d      | 75%       |
| 13$^d$| 1d        | “BuO-NpMI | -      | 12    | 2d      | n.d.      |
| 14$^d$| 1d        | “BuO-NpMI | -1.6               | 12    | 2d      | n.d.      |
| 15$^d$| 1d        | “BuO-NpMI | -1.6               | 12    | 2d      | <5%       |

[a] n.d. = not detected; yields determined by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. [b] E-/Z- ratios determined by $^1$H NMR spectroscopy. [c] In the dark. [d] Fe cathode.
one-pot NaBH₄ reduction/Cl-P(O)Ph₂ protection (see SI). Here we opted to use Fe instead of RVC as a cheaper, robust cathode material.[10] However, it was quickly identified that DCA and NpMI were ineffective e-PRCats for the majority of phosphinates. For example, cyclic substrate 1d underwent no reaction with these catalysts (entries 10–11). We synthesized *BuO-NpMI as a novel e-PRCat which afforded the desired product 2d in very good yield (entry 12). Control reactions confirmed operation of e-PRC (entries 13–15), while cathode materials greatly impacted the reaction (for detailed optimizations, see SI).[11] Optimal conditions were examined for a range of olefination reactions (Scheme 2). Unsymmetrical Z-stilbenes 2b, 2c were prepared in high yields from the tandem e-PRC reduction/photoelectroisomerism process. Cyclic olefins 2d–2h, rarely synthesized by the Wittig reaction due to the inconvenience of substrate preparations, were prepared in good to excellent (69–83%) yields. Terminal olefin 2i could not be prepared in high selectivity by dehydration of its corresponding tertiary alcohol as such a method inevitably leads to the most substituted olefin,[12] in this case, a tetrasubstituted instead of a terminal olefin.

After the successful preparations of a series of E-styrene derivatives (exclusive isomers) bearing divergent substituents including -Ph (2j), -OBz (2k), -OMe (2l) and -CF₃ (2n) at their arene rings, we questioned whether halogen substituent could be tolerated by our reaction. This is a highly challenging issue, since the reductions of aryl chlorides and bromides by photoexcited radical anions (either e-PRC or conPET-type) are highly efficient and heavily reported as discussed earlier (Scheme 1).[3c–g,5f,h] With this aim, we tested phosphinates bearing either a chloro- or bromo-substituent on their arene. To our delight, aryl chlorides 1o–1q and aryl bromide 1r underwent olefination in moderate to good (39–69%) yields with high or exclusive selectivities for their E- or Z-isomers; only traces of dehalogenated styrenes were observed (>10:1 in favor of olefination for 2p). Compared with products 2o–2p, p-chlorostilbene 2q has a more conjugated p-system and is easier to reduce, yet still gave only traces of dechlorinated product 2a. Substrate 1s, bearing both an alkyl and aryl phosphate,[13] selectively underwent e-PRC reduction of the alkyl phosphate leading only to C(sp³)/O cleavage to afford 2s in good yield. Our method retains reductively labile C(sp³)/O functionality, providing complementary selectivity to a recent report involving a phenothiazine photocatalyst.[13]

Styrene-forming substrates containing longer-chain aliphatic groups or a benzyl group retained high E-isomer selectivity, affording 2t–2v in good to high (62–79%) yields and high selectivities (>10:1 in favor of their E-isomers). Olefin geometry is not impacted by the diastereomeric ratio of phosphate precursors, but by the reaction conditions. For example, although the diastereomeric ratios of phosphate precursors to 2r, 2t and 2v were all >30:1, the E/Z-ratios were 4:1, 10:1 and 20:1 respectively. Hindered olefins derived from carboxycles 1w–1x were formed in high (83–87%) yields. In the synthesis of 2x, our conditions offer an alternative to i) BuLi or Grignard chemistry with expensive bromocyclobutane and ii) expensive Wittig reagents/cyclobutanone, instead starting from commercial, inexpensive

**Scheme 2.** e-PRC reductive olefination scope. [a] for compounds 2a–2q, 2t–2x, X = Cl; for compounds 2r–2s, 2y–2z, 2ae–2ag, X = Br. [b] Isolated yields. [c] E/Z-ratios determined by 1H NMR spectroscopy. [d] Yields in parentheses () are 1H NMR yields from NpMI as an e-PRCat.
cyclobutyl phenyl ketone. Our e-PRC phosphinate reduction offers complementary selectivity to Birch-type photochemical reports involving SET[14] or E₁T[15] Naphthalene-based substrate 1y was well-tolerated, affording 2y in good (62%) yield without Birch-type reduction products. Amide 1x was also well-tolerated, in spite of its free proton and labile heterocycle that would react with strong bases. Although an alkyl phosphinate derived from a non-benzylic alcohol 1aa did not react, alkyl phosphinates derived from aliphatic alcohols were feasible. Allylic substrates 1ab, 1ac derived from naturally-occurring terpenes were found to be sluggish, but afforded dienes 2ab, 2ac in satisfactory (30–33%) yields in a complementary fashion to previous reports that require strong bases[16] or transition metal catalysis.[17]

Demonstrating the utility of our base-free approach, products 2ad–2ag were synthesized from their alkyl p-acetylbenoate precursors. Given the properties of Geraniol and Nootkatone as fragrance oils and cholesteryl benzoate as bases[19] or transition metal catalysis. While conPET photocatalysis of aryl halides/pseudohalides,[3d,g] conPET conditions did not offer complementary selectivity to Birch-type photochemical reductions on the naphthalene and being unaffected by substitution on the aniline. Spectroelectrochemistry of both e-PRCats gave identical UV-vis bands for their radical anions (Figure 1, right) by cyclic voltammetry. Their radical anions are electro-generated with equal efficiency, which is entirely consistent with the spin densities of their radical anions (Figure 1, left) by cyclic voltammetry. Their radical anions are electro-generated with equal efficiency, which is entirely consistent with the spin densities of their radical anions (Figure 1, right) being localized on the naphthalene and being unaffected by substitution on the N-aniline. Spectroelectrochemistry of both e-PRCats gave identical UV-vis bands for their radical.

Concerning the first question, measured reduction potentials (E°red) of the alkyl phosphinates (in good agreement with those calculated by DFT) did not correlate with reactivity (Table 2). Instead, comparison of the C(sp3)–O bond dissociation free energies (BDFEs) of phosphinate radical anions correlated well with reactivity. This corroborated C(sp3)–O cleavage as the rate-limiting step and rationalized i) the unique tolerance of our conditions to aryl halides due to their less exergonic C–X BDFEs (entries 4, 5; 6, 7) and ii) the lack of reactivity of phosphinates derived from non-benzylic/allylic alcohols that require higher temperatures[25] to assist C(sp3)–O cleavage (entries 9, 10).

As to the second question, NpMI and BuO-NpMI had identical redox potentials (E°1/2 = −1.3 V vs. SCE, Figure 1, left) by cyclic voltammetry. Their radical anions are electro-generated with equal efficiency, which is entirely consistent with the spin densities of their radical anions (Figure 1, right) being localized on the naphthalene and being unaffected by substitution on the N-aniline. Spectroelectrochemistry of both e-PRCats gave identical UV-vis bands for their radical.
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Table 3: Lifetimes of neutral and electroreduced \(^{a}\) e-PRCats.

| Entry | e-PRCat | Conditions | \(\lambda_{\text{max}}\) (nm) | \(r\) (ns) | \(E^{\text{corr}}\) (kcal mol\(^{-1}\)) |
|-------|---------|------------|-----------------|--------|-------------------------------|
| 1     | NpMI    | –          | 375/412         | r = 3.2| (S) 75.4                     |
| 2     | NpMI    | –1.6 V, 1 h\(^{a}\) | 452/535 | \(r_1 = 5.4\) \(r_2 = 21.7\) | (ES) 56.6 |
| 3     | \(^{a}\)BuO-NpMI | –          | 375/412         | r = 3.2 | (S) 57.6                    |
| 4     | \(^{a}\)BuO-NpMI | –1.6 V, 1 h\(^{a}\) | 452/548 | \(r_1 = 6.8\) \(r_2 = 19.5\) | (ES) 56.6 |
| 5     | \(^{a}\)BuO-NpMI | –1.6 V, 1 h\(^{a}\) | 452/548 | \(r_1 = 8.1\) \(r_2 = 20.3\) | – |

[a] Electroreduced e-PRCat (2.5 mM in MeCN (0.1 M \(^{+}\)Bu\(_4\)N·PF\(_6\)), diluted 8 /C148.

is a candidate for ES

We calculated the vertical excitation energy of this lowest quartet state with CASSCF (see SI) and found a reasonable agreement with the observed \(\lambda_{\text{max}}\) of luminescence. It is energetically close to the doublet states underlying the 415 nm absorption band so that ISC is plausible.

Miyake similarly found that the putative \(^{3}\)BPI\(^{-}\) was not catalytically active in the Birch SET step. They hypothesized SET from a higher lying excited doublet state \(^{3}\)BPI\(^{-}\) (D\(_0\)) in an anti-Kasha fashion. Consistent with previously reported anti-Kasha photochemistry of doublet excited state photocatalysts,\(^{[8a,14]}\) excitation of the broad absorption of \(^{3}\)[BuO-NpMI] between 650–900 nm (D\(_0\)–D\(_1\)) with 740 nm or 850 nm LEDs gave only traces of D\(_2\).\(^{[29]}\)

Ruling out participation of the first excited state (D\(_1\)), “effective minimum” potentials \(E_{\text{1/2}}\) of \(^{3}\)BuO-NpMI\(^{-}\) (D\(_1\)) at ~3.7 V vs. SCE and \(^{3}\)BuO-NpMI\(^{-}\) (D\(_2\)) at ~3.8 V vs. SCE can be calculated by previously described methods,\(^{[29]}\) easily reaching \(E_{\text{1/2}}\) of all phosphinates herein as well as aryl halides.\(^{[30,31]}\)

A preassembly of a doublet excited state in SET is consistent with aforementioned quenching of the EPR signal (Figure 2).

High-level DFT/MRCI calculations were carried out for \(^{3}\)BuO-NpMI\(^{-}\) to characterize this D\(_0\) state. The computed spectrum (Figure 3, top) is in excellent agreement with the experimental absorption spectrum, especially at the band with \(\lambda_{\text{max}} = 415\) nm comprising two bright \(\pi^*\) states (D\(_0\) — D\(_1\) and D\(_0\) — D\(_{\text{an}}\)). Contrary to the D\(_0\) — D\(_1\) transition around 870 nm, both these excitations transfer electron density from the naphthalene to the N-aniline unit of \(^{3}\)BuO-NpMI\(^{-}\) (Figure 3, bottom). Peasembling of ground state radical anion and substrate could explain (i) photochemistry of ultrashort-lived doublet states\(^{[25]}\) and (ii) faster than rates of diffusion.\(^{[5a]}\)

Preassembly of \(^{3}\)BuO-NpMI\(^{-}\) with 1d being more favorable than that of NpMI\(^{-}\) may explain the reactivity differences of the e-PRCats in effecting C(sp\(^3\)) cleavage following SET, and may rationalize profound shift in the molecular site of reduction compared to previous reports.\(^{[32]}\) However, like Miyake and co-workers, we were unable to find spectroscopic evidence of preassembly by UV-vis or EPR (see SI). While the absence of spectroscopic perturbations does not rule out a preassociation\(^{[33]}\) preassembly could occur at the N-aniline that is spin-disconnected from the naphthalene where the radical anion spin density is localized (Figure 1, right). Spin densities of favorable candidate preassemblies at the N-aniline unit of \(^{3}\)BuO-NpMI\(^{-}\) found by computational geometry optimizations do not differ from that of \(^{3}\)BuO-NpMI\(^{-}\) alone, while a favorable candidate preassembly at the naphthalene unit of \(^{3}\)BuO-NpMI\(^{-}\) does differ (see SI). A preassembly at the N-aniline could also rationalize anti-Kasha photochemistry, since charge transfer to the N-aniline in the D\(_{\text{an}}\) states is proximal to the bound substrate and promotes intermolecular SET upon photoexcitation (Figure 3). In contrast, the charge density of the lowest excited doublet state D\(_1\) remains localized on the naphthalene and is not close to the substrate.

Where spectroscopy offers little insight, a top-down approach varying catalyst structure and examining product yields has proven useful in investigating the mechanisms of reactions involving \textit{in situ}-formed organic electron donors.\(^{[34]}\)

To probe the importance of a preassembly of 1d at the N-aniline of the e-PRCat, we explored the influence of a series of e-PRCats with varying electronics and steric bulk (5a–f, Scheme 6). Compared to NpMI, catalysts with electron donating alkoxy or p-anisole substituents on the naphthalene unit (5a, 5b) gave no reaction. Compared to \(^{3}\)BuO-NpMI, a catalyst with additional alkoxy substituents on the N-aniline...
(5c) gave a lower (41%) yield of 2d. The yield of 2d increased with decreasing steric hindrance at the ortho-positions of the N-aniline (NpMI < 5d < 5e). A decrease in “steric bulk” likely promotes preassociation of radical anion e-PRCat and 1d. In our computational investigations we found multiple stable ground state preassemblies. Geometry optimizations (see SI) converged to pincer-like conformations for all candidates, where two of the substrate’s aryl groups coordinate to the N-aniline of the e-PRCat in a T–π and π–π orientation, respectively. The thermodynamics and kinetics of their formations (see SI) mirror reactivity trends in Scheme 6, corroborating a preassembly between e-PRCat and substrate before photoexcitation.

Conclusion

We report an electro-mediated photoredox catalytic reductions of phosphinates derived from α-chloroketones toward selective olefinations and deoxygenations. This study reports reductive formation of alkyl carbanions via photoexcited radical anions as super-reductants. The selective reduction of C(sp3)–O bonds in the presence of C(sp3)–X bonds was achieved. Reactivity differences of various radical anion photocatalysts and anti-Kasha photochemistry, backed by computational insights, suggest the importance of a close catalyst-substrate interaction for an effective, selective reaction. In this context, our calculations indicate that intramolecular charge transfer in the catalyst radical anion upon photoexcitation promotes SET to the substrate. Photocatalyst-substrate preassemblies such as EDA complexes, non-covalent interactions, hydrogen bonding and ordering of solvent are receiving increasing attention to unveil the next generation of photocatalytic transformations and offer new frontiers in selectivity and efficiency. Further studies into the nature of interactions and structure of preassemblies, as well as catalyst stability, are ongoing.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] Selected reviews on photochemistry: a) Q.-Q. Zhou, Y.-Q. Zou, L.-Q. Lu, W.-J. Xiao, Angew. Chem. Int. Ed. 2019, 58, 1586–1604; Angew. Chem. 2019, 131, 1600–1619; b) L. Marzo, S. K. Pagire, O. Reiser, B. König, Angew. Chem. Int. Ed. 2018, 57, 10034–10072; Angew. Chem. 2018, 130, 10188–10228; c) J. Xie, H. Jin, A. S. K. Hashmi, Chem. Soc. Rev. 2017, 46, 5193–5203; d) N. A. Romero, D. A. Nicewicz, Chem. Rev. 2016, 116, 10075–10166; e) C. K. Prior, D. A. Rankic, D. W. C. MacMillan, Chem. Rev. 2013, 113, 5322–5363.

[2] Selected general reviews on electrochemistry: a) T. H. Meyer, I. Choi, C. Tian, L. Ackermann, Chem. 2020, 6, 2484–2496; b) P. Xiong, H.-C. Xu, Acc. Chem. Res. 2019, 52, 3339–3350; c) S. Tang, Y. Liu, A. Lei, Chem. 2018, 4, 27–45; d) A. Wiebe, T. Gieshoff, S. Möhle, E. Rodríguez, M. Zirbes, S. R. Waldvogel, Angew. Chem. Int. Ed. 2018, 57, 5594–5619; Angew. Chem. 2018, 130, 5694–5721; e) M. Yan, Y. Kawamata, P. S. Baran, Chem. Rev. 2017, 117, 13230–13319.

[3] For selected representative examples, see: a) K. Targos, O. P. Williams, Z. K. Wickens, J. Am. Chem. Soc. 2021, 143, 4125–4132; b) D. Rombach, H.-A. Wagenknecht, Angew. Chem. Int. Ed. 2020, 59, 300–303; Angew. Chem. Int. Ed. 2020, 132, 306–310; c) J. I. Bardagi, I. Ghosh, M. Schmalzbauer, T. Ghosh, B. König, Eur. J. Org. Chem. 2018, 34–40; d) M. Neumeier, D. Sampedro, M. Majek, V. A. de la Peña Oszawa, A. Jacobi von Wangelin, R. P. Ruiz, Chem. Eur. J. 2018, 24, 105–108; e) L. Zeng, T. Liu, C. He, D. Shi, F. Zhang, C. Duan, J. Am. Chem. Soc. 2016, 138, 3958–3961; f) I. Ghosh, B. König, Angew. Chem. Int. Ed. 2016, 55, 7676–7679; Angew. Chem. 2016, 128, 7806–7810; g) I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, Science 2014, 346, 725–728; h) H. Li, X. Tang, J. H. Pang, X. Wu, E. K. L. Yeow, J. Wu, S. Chiba, J. Am. Chem. Soc. 2021, 143, 481–487; For full reviews, see: i) F. Glaser, C. Kerzigg, O. S. Wenger, Angew. Chem.
For relevant reviews on electrode materials, see: a) A. M. Barham, B. König, Angew. Chem. Int. Ed. 2020, 59, 10266 – 10284; Angew. Chem. 2020, 132, 10350 – 10370; j) M. Schmalzbauer, M. Marcon, B. König, Angew. Chem. Int. Ed. 2021, 60, 6270 – 6292; Angew. Chem. 2021, 133, 6338 – 6363.

For a full review on the combination of photoredox catalysis and organic electrochemistry: a) J. P. Barham, B. König, Angew. Chem. Int. Ed. 2020, 59, 11732 – 11747; Angew. Chem. 2020, 132, 11828 – 11844; For highlights, see: b) J. Liu, L. Lu, D. Wood, S. Lin, ACS Cent. Sci. 2020, 6, 1317 – 1340; c) L. Capaldo, L. L. Quadri, D. Raveli, Angew. Chem. Int. Ed. 2019, 58, 17508 – 17510; Angew. Chem. 2019, 131, 17670 – 17672; d) Y. Y. Pu, Y. Guo, J.-S. Zhong, Y. Yuan, K.-Y. Ye, Org. Chem. Front. 2020, 7, 131 – 135.

For recent examples on homogeneous photoelectrochemistry, see: a) S. Wu, J. Zaraukas, M. Domatski, P. S. Hitzfeld, V. Butera, D. J. Scott, J. Rebbein, A. Kuma, E. Thybaud, J. Hauer, J. P. Barham, Org. Chem. Front. 2021, 8, 1132 – 1142; b) P. Xu, P.-Y. Chen, H.-C. Xu, Angew. Chem. Int. Ed. 2020, 59, 14275 – 14280; Angew. Chem. 2020, 132, 14381 – 14386; c) X.-L. Lai, X.-M. Shu, J. Song, H.-C. Xu, Angew. Chem. Int. Ed. 2019, 59, 10626 – 10632; Angew. Chem. 2019, 132, 10713 – 10719; d) L. Niu, C. Jiang, Y. Liang, D. Liu, F. Bu, R. Shi, H. Chen, A. D. Chowdhury, A. Lei, J. Am. Chem. Soc. 2020, 142, 17693 – 17702; e) Y. Qiu, A. Schernjevitch, L. H. Finger, L. Ackermann, Angew. Chem. 2020, 26, 3241 – 3246; f) N. G. W. Cowper, C. P. Chernowsky, O. P. Williams, Z. K. Wickens, J. Am. Chem. Soc. 2020, 142, 2093 – 2099; g) H. Huang, Z. M. Strater, T. H. Lambert, J. Am. Chem. Soc. 2014, 136, 1698 – 1703; h) H. Kim, H. Kim, T. H. Lambert, S. Lin, J. Am. Chem. Soc. 2020, 142, 2087 – 2092; i) H. Huang, T. H. Lambert, Angew. Chem. Int. Ed. 2019, 59, 658 – 662; Angew. Chem. 2019, 132, 661 – 662; j) W. Zhang, K. L. Carpenter, S. Lin, Angew. Chem. Int. Ed. 2019, 59, 409 – 417; Angew. Chem. 2020, 132, 417 – 425; k) H. Huang, Z. M. Strater, R. Rauch, J. Shee, T. J. Sisto, C. Nuckolls, T. H. Lambert, Angew. Chem. Int. Ed. 2019, 58, 13318 – 13322; Angew. Chem. 2019, 131, 13452 – 13456; f) F. Wang, S. S. Stahl, Angew. Chem. Int. Ed. 2019, 58, 6385 – 6390; Angew. Chem. 2019, 134, 6451 – 6466; m) H. Yan, Z. W. Hou, H.-C. Xu, Angew. Chem. Int. Ed. 2019, 58, 4592 – 4595; Angew. Chem. 2019, 131, 4640 – 4643.

For reviews on benzyl radicals to benzylic anions by PRC: a) K. Donabauer, B. König, Acc. Chem. Res. 2021, 54, 242 – 252. For examples of electrochemical reports: b) W. Zhang, S. Lin, J. Am. Chem. Soc. 2020, 142, 20661 – 20670; c) L. Jiu, J. C. Sui, Y. Lai, S. Lin, J. Am. Chem. Soc. 2020, 142, 21272 – 21278; For the reduction potential of a benzylic radical: d) J. Grimshaw, Electrochemical Reactions and Mechanisms in Organic Chemistry, Elsevier, Amsterdam, 2000, pp. 89 – 157.

The alkane product likely forms via high-voltage-mediated C–H bond reduction, see: X. Liu, R. Liu, J. Qiu, X. Cheng, G. Li, Angew. Chem. Int. Ed. 2020, 59, 13962 – 13967; Angew. Chem. 2020, 132, 14066 – 14071.

For a full review on homogeneous photocatalysis and organic electrochemistry, see: a) A. M. Couper, D. Fletcher, F. C. Walsh, J. Chem. Rev. 1990, 90, 837 – 865; b) D. M. Heard, A. J. J. Lennox, Angew. Chem. Int. Ed. 2020, 59, 18866 – 18884; Angew. Chem. 2020, 132, 19026 – 19044.

For reviews on photosensitized TTET isomerizations of alkenes see: a) T. Ganicz, W. Staiciycz, Materials 2009, 2, 9 – 128; b) G. Mishra, A. K. Srivastava, Polym. Bull. 2007, 58, 351 – 358; c) N. Casirrueta, V. García, A. Arias, I. Moggio, R. Ziolo, A. Ponce, V. González, J. E. Hale, J. L. Flükiger, T. Cooper, J. Mater. Chem. 2012, 22, 3770 – 3780; d) M. Misra, A. K. Srivastava, Colloid Polym. Sci. 2008, 286, 445 – 451; K. Nilles, P. Theato, Eur. Polym. J. 2007, 43, 2091 – 2092.

This can only be an estimation for measurements at rt. Cryogenic experiments. 2.45 eV) as SET reduction of the formation of reaction and were superior to graphite felt, but redox potential differences between are not the final page numbers!
In Ref. [30a], an attempt to determine the lifetime of $^1[N$-arylnaphthalimide$]^+$ in MeCN by transient absorption spectroscopy led to rapid bleaching, suggesting solvent redox processes.

π-stacking interactions were implicated by DFT to explain selective reduction of arenes over aliphatic esters by photoexcited neutral electron donors: E. Doni, B. Mondal, S. O’Sullivan, T. Tuttle, J. A. Murphy, J. Am. Chem. Soc. 2013, 135, 10934–10937.

Hunter and Sanders claimed π–π stacking rarely leads to notable UV-vis perturbations, advocating the participation of σ–π stacking in favorable edge-to-face binding: C. A. Hunter, J. K. M. Sanders, J. Am. Chem. Soc. 1990, 112, 5525–5534.

When the reaction was attempted with the N-phenyl derivative (N-Ph NpMI, with no para- or ortho-substitution), no product was observed. We confirmed this was not due to solubility differences, both catalysts are fully soluble in reactions and solubility limits of N-Ph NpMI and N-BuO-NpMI are 62.5 mM and 250.0 mM in MeCN, respectively. Instead, we presume a certain degree of electron richness is required in the N-aniline moiety to render it sufficiently reductive in its higher order charge transfer excited doublet state.

Selected reviews: a) C. G. S. Lima, T. de M. Lima, M. Duarte, J. K. M. Sanders, J. Am. Chem. Soc. 2013, 135, 10934–10937.

Selected examples: a) N. Berg, S. Bergwinkl, P. Nuernberger, D. Horinek, R. M. Gschwind, J. Am. Chem. Soc. 2021, 143, 724–735; b) F. Burg, T. Bach, J. Org. Chem. 2019, 84, 8815–8836.

While this manuscript was in press, a complementary e-PRC reductive cleavage of C(sp$^2$)/C=O bonds was disclosed: C. P. Chernowsky, A. F. Chmiel, Z. K. Wickens, Angew. Chem. Int. Ed. 2021, DOI:10.1002/anie.202107169; Angew. Chem. 2021, DOI:10.1002/ange.202107169.
Beyond C(sp³)–X cleavage: We report reductive cleavages of C(sp³)–O bonds of phosphinated alcohols to alkyl carbanions by electro-mediated photoredox catalysis. Deoxygenations as well as E- or Z-selective olefinations are reported. Surprisingly, reactions tolerate C(sp²)–X cleavages such as aryl halides. Radical ion catalyst-substrate preassembly is key in enabling reactivity and overturning conventional redox chemoselectivity.