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Recent advances in phosphoranyl radical-mediated deoxygenative functionalisation

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Alcohols and carboxylic acids have been established as versatile building blocks in the assembly of various carbon frameworks. The deoxygenative functionalisation is one of the most attractive approaches for the conversion of these abundant materials into high-value products. However, the direct deoxygenative transformation under mild conditions has long been a challenging task in organic synthesis due to the lack of efficient methods for the activation of strong C–O bonds (102 kcal mol^{-1}). Recently, the strategy of visible light photocatalytic phosphoranyl radical fragmentation provides a novel and powerful platform for C–O, N–O and S═O bond activation. This highlight mainly discusses recent breakthroughs in phosphoranyl radical-mediated deoxygenative functionalisations of alcohols, carboxylic acids, oximes and sulfoxides with a particular emphasis on reaction scopes and mechanism.

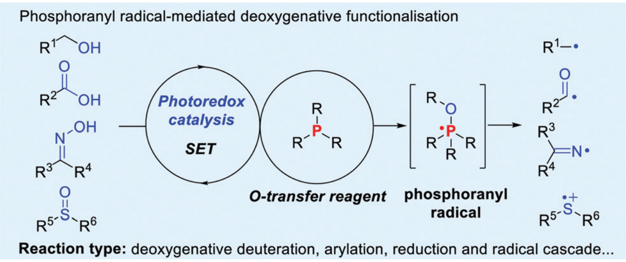
1. Introduction

Deoxygenative reactions are fundamental reactions in organic and biological synthesis, which have attracted considerable interest from synthetic chemists.[1] In this context, the direct deoxygenative functionalisations of alcohols, carboxylic acids, oximes and sulfoxides have long been elusive transformations. Several challenges are associated with the deoxygenative process, most notably the relatively high bond strength of C–O, N–O and S═O bonds.[2] Representative strategies for deoxygenative transformations of these compounds mainly rely on distinct preactivated steps to generate new reactive functional groups, or the use of some strong nucleophiles and reductants.[3] From a sustainable point of view, the exploration of novel and efficient strategies for the direct deoxygenative transformation of alcohols, carboxylic acids, oximes and sulfoxides is still highly desirable.

The phosphoranyl radical fragmentation strategy has been esteemed as an efficient method for deoxygenative reactions.[4] Typically, the phosphoranyl radical-mediated deoxygenative reactions have been achieved under high-energy UV irradiation or other initiation conditions, such as Bz_2O_2 and $(n\text{-Bu})_3SnH$/AIBN *etc.*[5] Recently, visible light photoredox catalysis has emerged as a preeminent handle for the formation of reactive radicals and radical ions *via* single electron transfer (SET) and energy transfer (ET) pathways.[6] In this context, visible light-induced fragmentation of phosphoranyl radicals provides a novel and powerful platform for the direct activation of C–O, N–O and S═O bonds, delivering a diversity of radical species (Scheme 1). These reactions generally obviate the need for pre-functionalisation steps and radical initiators. This concept has been successfully applied in the deoxygenative deuteration, arylation, reduction and radical cascade reactions. Distinguishing features of these reactions include mild conditions, broad scopes and high efficiency. Very recently, impressive examples on phosphoranyl radical fragmentation reactions have been summarized by Rossi-Ashton.[7] This highlight mainly discusses the recent advances in phosphoranyl radical-promoted deoxygenative technologies, with particular emphasis on reaction scope and mechanism.

2. Deoxygenative functionalisation of carboxylic acids and alcohols

An important breakthrough in this field was achieved by Zhu and Xie *et al.*[8] They developed an elegant deoxygenative



Reaction type: deoxygenative deuteration, arylation, reduction and radical cascade...

Scheme 1 Phosphoranyl radical-mediated deoxygenative functionalisation.

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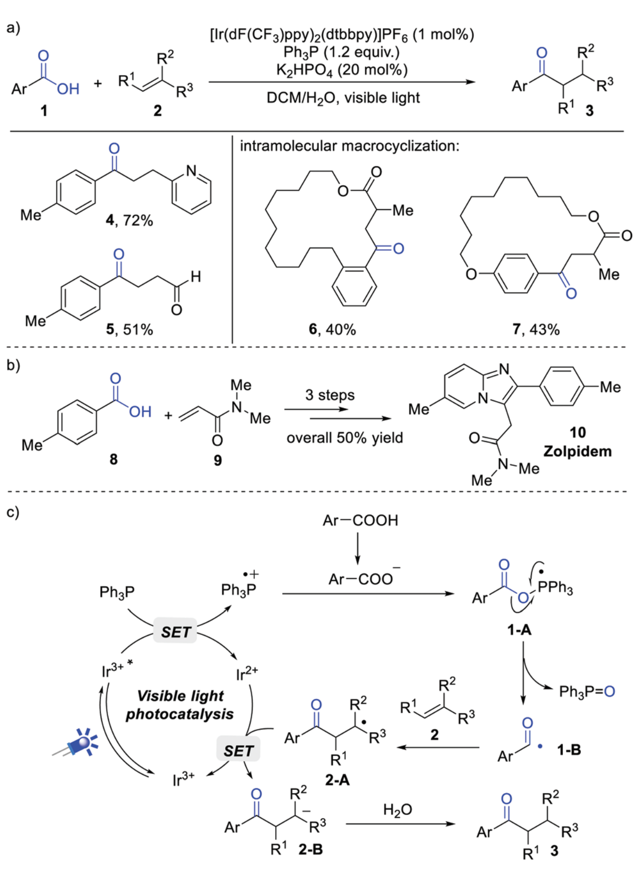
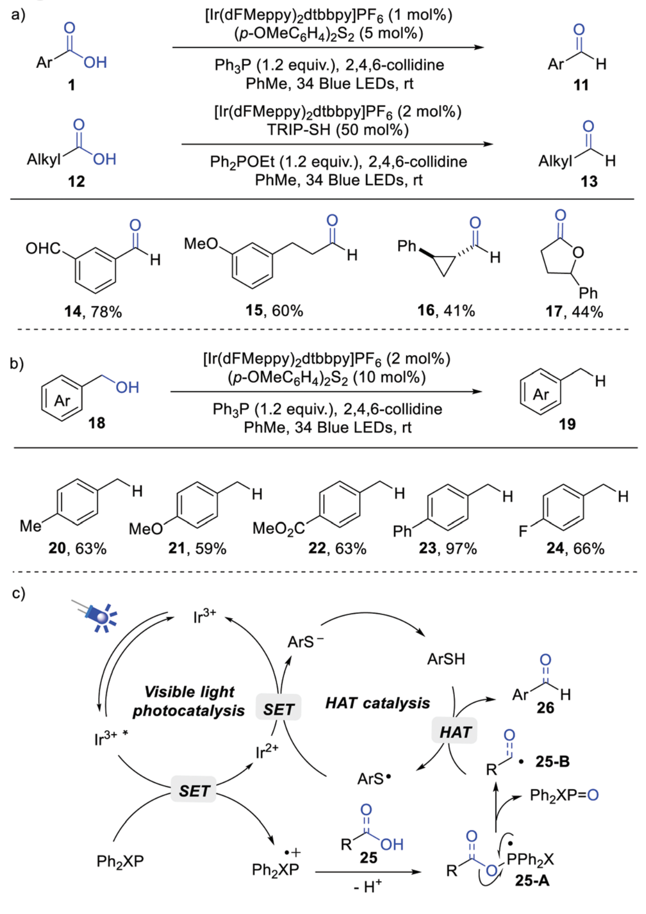
addition of carboxylic acids to alkenes for the synthesis of diverse ketones. In this reaction, triphenylphosphine (Ph_3P) was the optimal O-transfer reagent. A wide range of aromatic carboxylic acids and electron-deficient alkenes were compatible in this reaction, delivering the expected ketones in generally good yields. However, aliphatic carboxylic acids were not suitable in this reaction system. The synthetic potential was demonstrated by the concise synthesis of cyclophanebraced cycloketones (Scheme 2a, **6** and **7**) and the drug zolpidem (Scheme 2b, **10**).

A series of control experiments have been conducted to investigate the reaction mechanism. Stern–Volmer analysis indicated that the excited state of *Ir(III) can be efficiently quenched by Ph_3P. In addition, ^{18}O-labeling experiments revealed that the O-atom of triphenylphosphine oxide ($Ph_3P{=}O$) comes from the carboxylate group rather than H_2O. Radical trapping reaction by 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) demonstrated the intermediacy of an acyl radical during this transformation. Based on these results, a possible mechanism is proposed in Scheme 2c. Initially, the photoexcited *Ir(III) [$E_{1/2}^{\text{red}}$ (*Ir$^{\text{III}}$/Ir$^{\text{II}}$) = +1.21 V *vs.* SCE] was reductively quenched by Ph_3P ($E_{1/2}^{\text{red}}$ = +0.98 V *vs.* SCE) to generate the triphenylphosphine radical cation intermediate. Afterwards, the combination of a Ph_3P radical cation with a carboxylate anion results in a radical intermediate **1-A**, which undergoes a C–O bond cleavage to give the key acyl radical **1-B** and $Ph_3P{=}O$ as the byproduct. The addition of **1-B** to electron-deficient alkenes gives rise to C-based radical **2-A**, followed by a single electron reduction and protonation cascade to give the final products.

Almost at the same time, Doyle, Rovis *et al.* achieved a visible light-induced deoxygenative reduction of carboxylic acids (Scheme 3a).[9] Remarkably, by rationally modifying the phosphine reagent, both aryl and alkyl carboxylic acids can be successfully reduced to the corresponding aldehydes. Ph_3P was used as an efficient O-transfer reagent for the reduction of aryl carboxylic acids. However, it was ineffective for the transformation of aliphatic carboxylic acids. They proposed that a more electron-rich phosphoranyl radical intermediate was generated from Ph_3P and aliphatic carboxylic acid. This electron-rich phosphoranyl radical was susceptible to oxidation, producing a phosphonium species for a rapid acyl transfer reaction. An electron-deficient phosphinite Ph_2POEt proved to be suitable for the reduction of aliphatic acids. Under these reaction conditions, carboxylic acids were selectively reduced even in the presence of other reactive carbonyl groups, which demonstrated the promising potential in precise reductive reactions. Moreover, the intramolecular acyl radical-mediated cyclisa-



Scheme 2 Visible light-induced deoxygenative addition of carboxylic acids to alkenes (a), (b) and proposed mechanism (c).



Scheme 3 Deoxygenative reduction of carboxylic acids (a) and benzylic alcohols (b), and proposed mechanism (c).

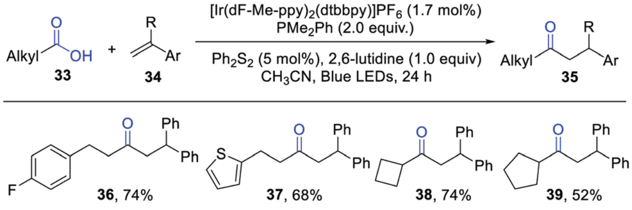
tions of carboxylic acids were also successful, delivering the corresponding lactones and lactams in high efficiency.

Gratifyingly, the current catalytic system can be further applied to the direct reduction of benzylic alcohols without the requirement of preactivation steps (Scheme 3b). Alcohols bearing both electron-rich and deficient groups reacted smoothly in this transformation. In addition, secondary alcohols were also suitable for this reaction, albeit with lower yields. This reaction offers novel avenues for deoxygenative transformations of carboxylic acids and alcohols under mild conditions.

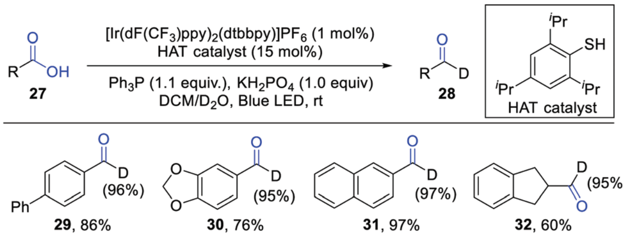
The proposed mechanism is outlined in Scheme 3c. The key phosphoranyl radical **25-A** is generated from the combination of the *in situ* generated Ph_3P radical cation with a carboxylic acid or benzylic alcohol, which proceeds through a β-scission process to give a C-centred radical **25-B** with simultaneous generation of $Ph_2XP{=}O$. The H-atom abstraction of ArSH by radical **25-B** affords the expected product.

Xie and co-workers further developed a phosphoranyl radical-mediated deoxygenative deuteration by combination of visible light photocatalysis and H-atom transfer (HAT) catalysis (Scheme 4).[10] D_2O was used as the deuterium reagent. It should be noted that the direct deuterium-atom abstraction from D_2O by acyl radical intermediates is historically known to be difficult due to the strong bond dissociation energy (BDE) of the O–D bond. The addition of a thiol catalyst is critical for this reaction, which can bridge the energy gap between radical species and D_2O. The proton exchange of a thiol catalyst ($pK_a = 10–17$) with an excess D_2O ($pK_a = 32$) generates a D-labelled thiol, which then reacts with acyl radicals to give the deuterated products. Significantly, both aromatic and aliphatic carboxylic acids were well tolerated in this reaction. For the reaction of aromatic acids, Ph_3P was employed as a good O-atom transfer reagent, while Ph_2POEt proved to be the optimal transfer reagent for aliphatic acids. Various deuterated aldehydes were obtained in generally good yields with high D-incorporation.

In 2019, Doyle *et al.* reported an elegant intermolecular hydroacylation of olefins from aliphatic carboxylic acids by photoredox catalysis (Scheme 5).[11] Key to the success of this reaction is the proper choice of an electron-rich phosphine. The previously used PPh_3 and Ph_2POEt delivered the desired products only in low yields. Subsequent studies demonstrated that the substrate diphenyl ethylene quenched the photoexcited *Ir(III) over two times than PPh_3 or Ph_2POEt, which may inhibit the formation of the key phosphoranyl radical intermediates. Therefore, a more reactive phosphine with lower oxidation potential is essential for this reaction. Dimethyl phenyl phosphine PMe_2Ph turned out to be the best candidate. Under standard conditions, a wide range of aliphatic carboxylic acids reacted smoothly with styrenes, furnishing the desired dialkyl ketones in high efficiency. Importantly, this protocol was successfully performed on a 10 mmol scale under solvent-free conditions.



Scheme 5 Visible light-induced intermolecular hydroacylation of olefins.

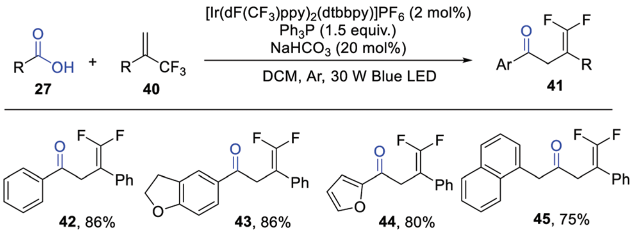


Scheme 4 Phosphoranyl radical-mediated deoxygenative deuteration.

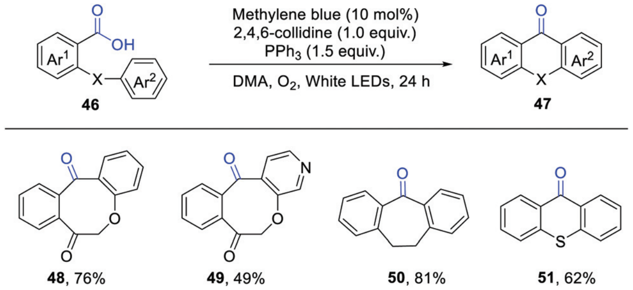
Shortly after these studies, the group of Wang extended this concept to a visible light photocatalytic deoxygenation/radical addition/defluorination cascade reaction of carboxylic acids with α-trifluoromethyl alkenes for the construction of γ,γ-difluoroallylic ketones (Scheme 6).[12] Consistent with the work of Zhu and Xie, the aliphatic carboxylic acids failed to give the expected products. Notably, phenylacetic acids performed smoothly in this protocol. This reaction features mild conditions, good functional group tolerance and broad substrate scope, which can be further applied in the late-stage modification of some biologically important molecules, such as adapalene and indometacin.

An intramolecular deoxygenative acyl radical cyclisation of aromatic carboxylic acids has been developed by Chu, Sun and co-workers (Scheme 7).[13] They employed methylene blue (MB) as an efficient photosensitizer and O_2 as a green oxidant. When Ph_2POEt was used instead of PPh_3, a slightly lower yield was observed. Mechanistic studies indicated the intermediacy of acyl radicals, which were generated *via* the β-scission of phosphoranyl radical intermediates. This protocol provides a straightforward access to diversely functionalised dibenzocycloketones.

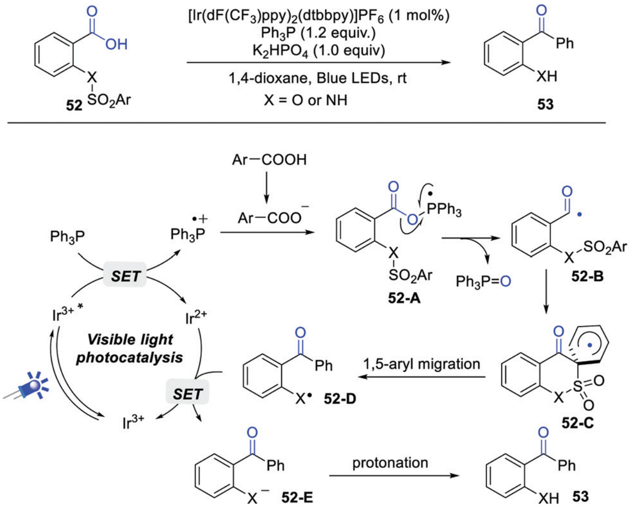
In 2019, Zhu and Xie *et al.* described an interesting deoxygenative arylation of aryl carboxylic acids *via* acyl radical-mediated 1,5-aryl migration (Scheme 8).[14] Under the standard conditions, a wide range of *o*-amino and *o*-hydroxy diaryl ketones can be obtained in satisfying yields. Importantly, the



Scheme 6 Photocatalytic deoxygenation/defluorination reaction.



Scheme 7 Deoxygenative acyl radical cyclisation of aromatic carboxylic acids.

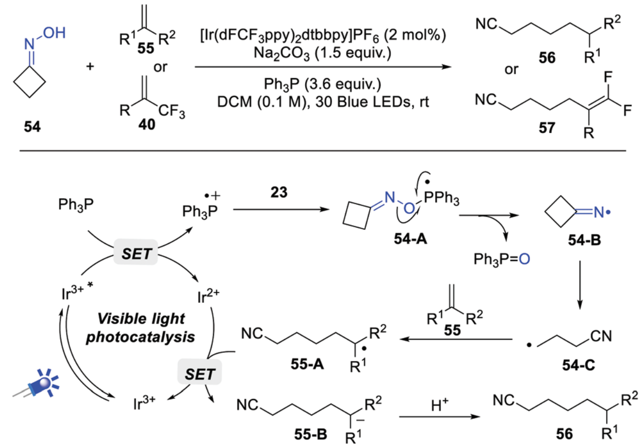


Scheme 8 Visible light-induced deoxygenative arylation of carboxylic acids.

current reaction can be successfully scaled up to 5 mmol. This reaction begins with the generation of Ph_3P radical cation *via* a single electron oxidation of Ph_3P by photoexcited *Ir(III), which reacts with the carboxylate anion to give intermediate **52-A**. Subsequently, the selective C–O bond scission of **52-A** forms an acyl radical **52-B**, which undergoes a sequential intramolecular 1,6-*ipso* addition and 1,5-aryl migration process to deliver radical **52-D**. Finally, the reduction of radical **52-D** generates intermediate **52-E**, followed by a protonation process gives the desired product. The quantum yield (Φ = 0.39) indicated that the radical chain pathway is less likely. The results of DFT calculations further demonstrated the thermodynamic and kinetic feasibility of this reaction.

3. Deoxygenative transformation of oximes

Iminyl radicals represent one of the most important nitrogen-centered radicals, which have been widely applied in the convenient construction of C–N bonds. Historically, these iminyl radicals are generated from the corresponding α-*N*-oxyacids, *O*-acyl and *O*-aryl hydroxylamines.[15] However, the direct generation of iminyl radicals from simple oximes is largely unexploited. Very recently, Yang, Chen and Xiang *et al.* achieved an impressive iminyl radical reaction of strained cycloketone oximes *via* phosphoranyl radical-mediated N–O bond activation (Scheme 9).[16] PPh_3 was the optimal O-transfer reagent, while *n*-Bu_3P resulted in a lower yield. Upon the irradiation by 30 W blue LEDs, various cyclobutanone oximes and alkenes or α-trifluoromethyl alkenes coupled smoothly, furnishing the elongated cyano products in good yields.



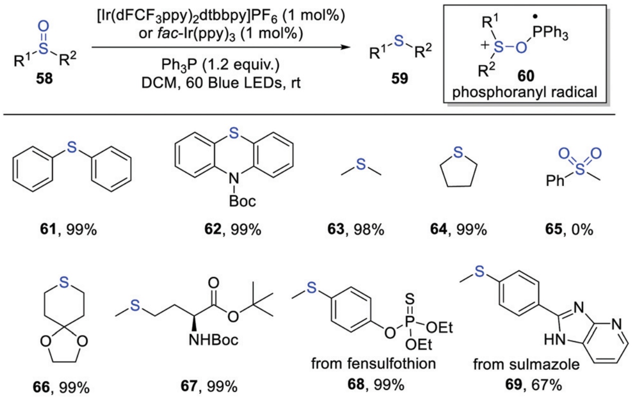
Scheme 9 Phosphoranyl radical-mediated N–O bond activation.

On the basis of control experiments, a possible reaction pathway is outlined in Scheme 9. Under photocatalytic conditions, the phosphoranyl radical **54-A** is firstly formed *via* a polar/SET crossover process. The selective N–O bond cleavage of **54-A** delivers the key iminyl radical **54-B**, which undergoes a rapid β-fragmentation to give a cyanoalkyl radical **54-C**. Subsequently, the radical addition of **54-C** to alkenes gives a new C-based radical **55-A**, which performs a sequential single electron reduction and protonation process to give the final products. The quantum yield of this reaction revealed that a radical long-chain pathway is unlikely to be involved in current protocol.

4. Deoxygenative reduction of sulfoxides

The selective reduction of sulfoxides to sulfides is an important reaction in organic synthesis. Established methods generally require the use of metal hydride reagents, phosphorus and halide ions *etc.*, which often suffer from harsh reaction conditions and limited substrate scopes.[17]

In 2020, Rossi-Ashton, Unsworth and Taylor *et al.* developed an elegant photocatalytic deoxygenation of sulfoxides for the synthesis of sulfides *via* phosphoranyl radical-mediated S–O bond activation (Scheme 10).[18] The key phosphoranyl radical **60** is formed *via* a polar nucleophilic addition of sulfoxide to the phosphine radical cation. By using oxidizing and reducing photocatalysts, the authors developed several complementary



Scheme 10 Visible light-induced deoxygenation of sulfoxides.

reaction conditions for this deoxygenative reaction. The attractive features of this transformation are mild conditions, good functional group tolerance and simple operation. A wide range of sulfoxides worked well in this process, providing the corresponding sulfides in excellent yields. Moreover, the synthetic utility was further demonstrated by the late-stage deoxygenation of some biologically active molecules, such as fensulfothion and sulmazole. However, the sulfone substrates were not suitable for this reaction. This protocol provides an alternative and efficient means to the reduction of sulfoxides under mild conditions. Mechanistic studies suggested a radical chain pathway of this reaction.

5. Summary

Recently, visible light-induced phosphoranyl radical fragmentation strategies have been successfully applied in the direct activation of C–O, N–O and S=O bonds under mild conditions. Phosphoranyl radicals proved to be the key intermediates in these reactions, which undergo a selective β-scission process to generate reactive radical species. By using this novel strategy, various deoxygenative deuteration, arylation, reduction and radical cascade reactions have been developed for the efficient synthesis of valuable products and late-stage functionalisations of natural products, agrochemical and drug molecules. Notable features of these reactions include mild conditions, broad scope and simple operation. We hope this highlight paper will encourage further development of new reactions in this field.

Conflicts of interest

There are no conflicts to declare.

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