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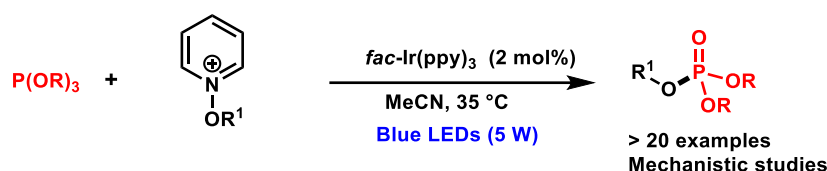
Visible Light–Mediated Access to Phosphate Esters

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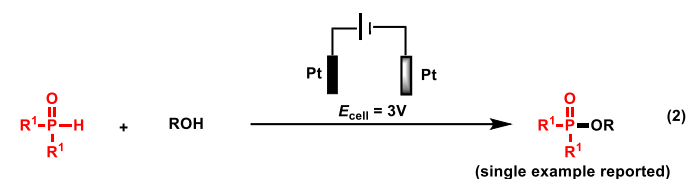
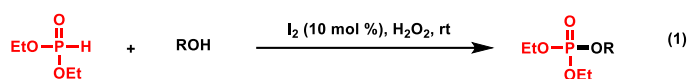


ABSTRACT: we report herein a practically simple visible–light photocatalytic approach for the synthesis of a large variety of phosphate esters through the combination of N–alkoxy–pyridinium salts and phosphites under mild conditions. The scope of the reaction is broad and was successfully applied to the synthesis of biologically relevant structures. Quantum yield measurement, as well as EPR experiments, allowed the suggestion of a reasonable reaction mechanism.

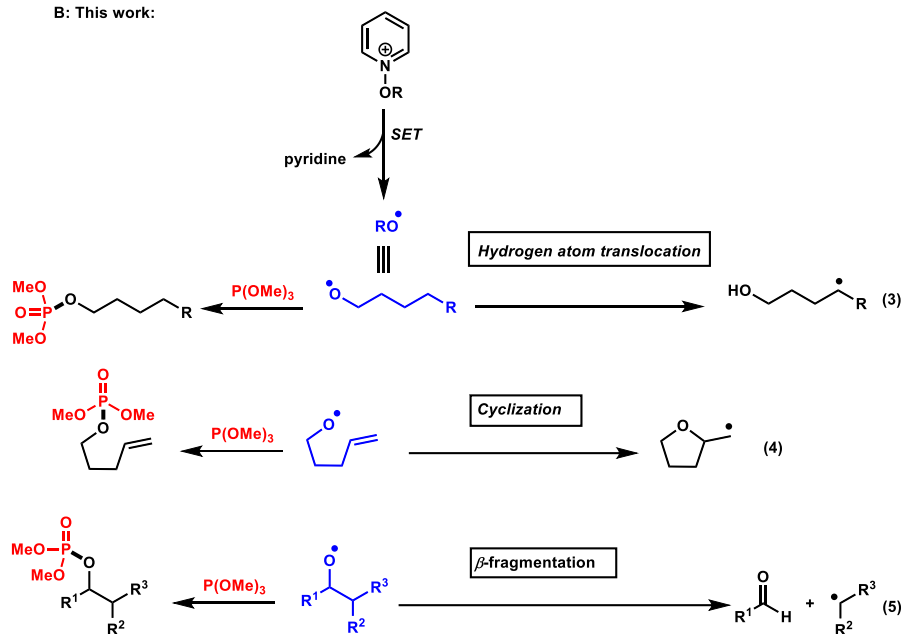
Phosphate esters are useful structural scaffolds that besides their frequent use in organic synthesis and catalysis are part of natural molecules such as carbohydrates, steroids, nucleic acids and coenzymes. They are furthermore essential in the biochemical regulation of protein–protein interactions and the ATP–based energy conversion in living organisms.¹ It is not surprising, therefore, that synthesis of those molecules has been and still is the subject of intensive investigations both in academia and industry. Traditionally, access to phosphate esters can be achieved through nucleophilic attack at phosphorus by treatment of alcohols with phosphorus halides.² However, because of the moisture sensitivity and toxicity of the latter, efforts in providing synthetic alternatives to this method are relevant. In this context, Prabhu and colleagues reported an elegant phosphorylation of alcohols using molecular iodine as a catalyst and H₂O₂ as an oxidant (Scheme 1, eq. (1)).³ The proposed mechanism postulates the catalytic generation of the highly electrophilic phosphoryl iodide that reacts with an alcohol to give the desired phosphate ester. Although efficient, the stoichiometric use of a H₂O₂ remains a limitation of this methodology due to its incompatibility with many group functionalities. Importantly, a sustainable approach for the synthesis of phosphinates has been accomplished electrochemically by reaction of various secondary phosphine oxides with alcohols (Scheme 1, eq. (2)).⁴ However, only a single phosphate ester has been synthesized by this approach in a rather moderate yield (30 %). Another route to access phosphate esters consists of the addition of alkoxy radicals to phosphites that typically are rapidly deoxygenated to generate alkyl radicals and phosphate. This approach has for instance been applied by Barton in the photochemical synthesis of steroid–based phosphate esters.⁵ However, this approach has not seen a large application in synthesis despite detailed physical organic investigations of these reactions provided by Bentrude *et al.*⁶ This might be attributed to a lack of methods enabling generation of alkoxy radicals under mild conditions.

Scheme 1. (A) Reported Approaches for the Synthesis of Ester Phosphates. (B) Current work.

A: Selected previous work:



B: This work:

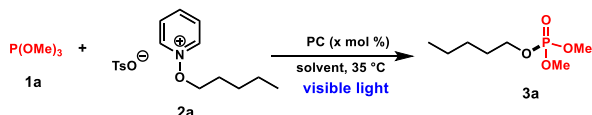


Inspired from these seminal studies and based on the remarkable development of photoredox catalysis as an efficient approach to generate various radical species under mild conditions,⁷ we postulated that synthesis of phosphate esters can be achieved photocatalytically.

Design plan: To this end, we focused on the use of *N*-alkoxy pyridinium ions, which have been shown to be privileged precursors for the generation of alkoxy radicals.⁸ Because the addition of those radicals to phosphites are well-known to be irreversible and diffused-controlled ($> 10^9 \text{ M}^{-1} \text{ s}^{-1}$),⁶ possible alkoxy fragmentations (eq. (3–5)),⁹ and possible Minisci reaction of generated carbon radicals with the pyridinium salts can be encountered.¹⁰

Because $(\text{MeO})_3\text{P}$ (**1a**) is known to be a very reactive and selective trap for the allyloxy radical,¹¹ we started our investigation by testing its reactivity with the pyridinium (**2a**) under photocatalytic conditions. Pyridinium ions were prepared in one step by reaction of pyridine-*N*-oxide with the alkyltosylates, following a protocol reported by Hong.¹⁰

Table 1. Optimization of the Photocatalytic Reaction of Trimethylphosphite 1a with the *N*-alkoxy pyridinium 2a.^a



entry ^a	Photocatalyst (PC)	catalyst loading (%)	solvent	3a, yield [%] ^b
1	Ru(bpy) ₃	5	MeCN	65
2	Eosin Y	5	MeCN	67
3	Rose Bengal	5	MeCN	63
4	<i>fac</i> -Ir(ppy) ₃	5	MeCN	82

5	–	–	MeCN	traces
6	<i>fac</i> -Ir(ppy) ₃ ^c	5	MeCN	72
7	<i>fac</i> -Ir(ppy) ₃ ^d	5	MeCN	80
8	<i>fac</i> -Ir(ppy) ₃	2	MeCN	81
9	<i>fac</i> -Ir(ppy) ₃	2	EtOAc	78
10	<i>fac</i> -Ir(ppy) ₃	2	CH ₂ Cl ₂	77
11	<i>fac</i> -Ir(ppy) ₃	2	DMF	47
12	<i>fac</i> -Ir(ppy) ₃	2	MeOH	75
13	<i>fac</i> -Ir(ppy) ₃	2	Toluene	75
14	<i>fac</i> -Ir(ppy) ₃	2	THF	56

^a Reaction conditions: trimethylphosphite **1a** (0.3 mmol, 3 equiv), *N*-alkoxyppyridinium tosylate **2a** (0.1 mmol, 1 equiv), solvent (1 mL), blue LEDs (5W), 15 h. ^b NMR yields are determined from ³¹P NMR spectroscopy using tributyl phosphate as internal standard. ^c trimethylphosphite **1a** (0.1 mmol, 1 equiv), *N*-alkoxyppyridinium tosylate **2a** (0.1 mmol, 1 equiv). ^d trimethylphosphite **1a** (0.1 mmol, 1 equiv), *N*-alkoxyppyridinium tosylate **2a** (0.3 mmol, 3 equiv).

As depicted in Table 1, when **1a** (3.0 equiv) was mixed with **2a** (1.0 equiv) in acetonitrile in the presence of 5 mol% of either Ru(bpy)₃ (65%, entry 1), Eosin Y (67 %, entry 2) or Rose Bengal (63 %, entry 3) a good conversion of about 65% of the phosphate ester **3a** was obtained in all cases. This conversion is raised up to 82% when the strong reductive *fac*-Ir(ppy)₃ was employed as a photocatalyst under the same conditions (entry 4), whereas only traces of **3a** were detected in the absence of a photocatalyst (entry 5).

Having identified *fac*-Ir(ppy)₃ as a suitable catalyst for the reaction, we next investigated the stoichiometry of the reaction and showed that while the conversion of **3a** drops to 72% (entry 6) when equimolar amounts of **1a** and **2a** are used, 80% of **3a** is formed in excess of **2a** (3 equivalents of **2a** over one equivalent of **1a**) (entry 7).

Interestingly, the photocatalyst loading can be decreased to 2 mol % without affecting the efficiency of the reaction (81%, entry 8). With this catalyst loading (2 mol %), a screening of solvent was performed (entries 9–14) and acetonitrile showed the best results.

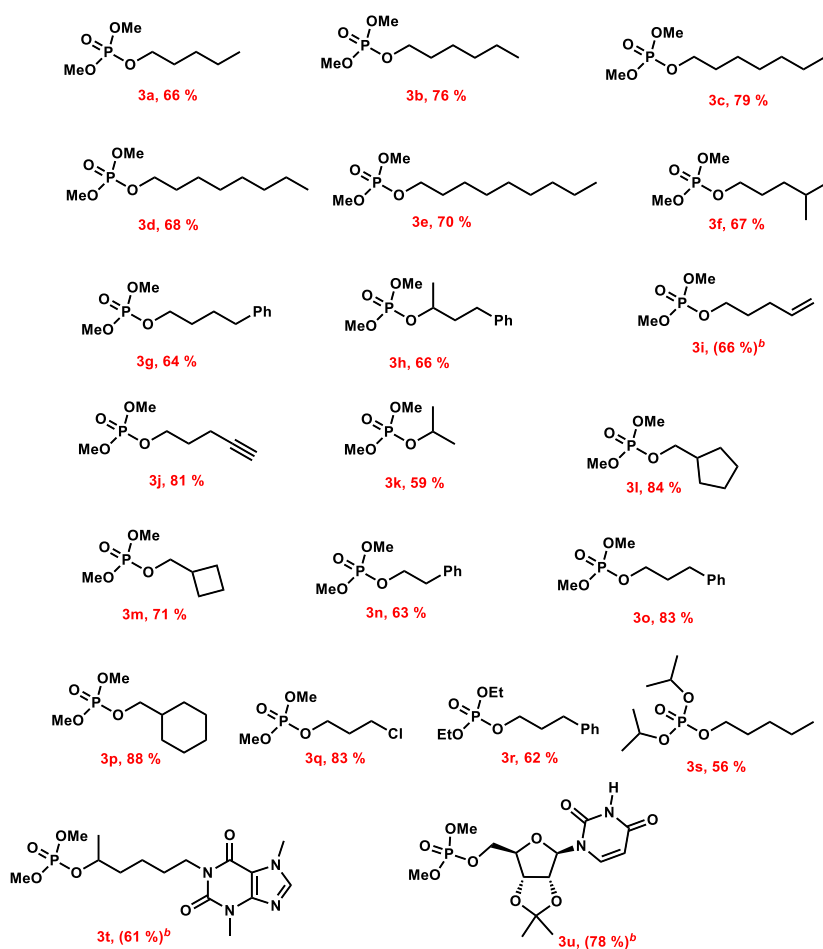


Figure 1. Scope of the Photocatalytic Phosphate Synthesis.^a

^a Reaction conditions: trimethylphosphite **1a** (1.2 mmol, 3 equiv), *N*-alkoxy pyridinium tosylate **2a** (0.4 mmol, 1 equiv), *fac*-Ir(ppy)₃ (2 mol%), CH₃CN (4 mL), blue LEDs (5W), 15 h. ^b Reaction conditions: trimethylphosphite **1a** (4 mmol, 10 equiv), *N*-alkoxy pyridinium tosylate **2a** (0.4 mmol, 1 equiv), *fac*-Ir(ppy)₃ (2 mol%), CH₃CN (4 mL), blue LEDs (5W), 15 h.

In order to explore the scope of the photoreaction, we first tested the reaction of trimethylphosphite **1a** with various pyridinium salts under the optimized conditions. As shown in Figure 1 and in agreement with Bentrude's observations,¹¹ radical addition of the alkoxy radicals to **1a** is faster than the 1,5-hydrogen atom transfer and the phosphate esters **3a–3g** have been obtained in good to excellent yields (64–79%).¹² It should be mentioned that no trace of the Minisci adduct, resulting from the radical addition of the alkyl radical, formed through radical translocation of the alkoxy radical, to the *N*-alkoxy pyridinium salt **2a** (Supporting Information, page S6).

Interestingly, phosphate **3h**, resulting from initial addition of a secondary alkoxy radical with **1a** and subsequent fragmentation was obtained in good 66% yield.

Equally important, phosphate esters bearing alkene and alkyne groups **3i,j** have also been isolated in good yields, 66 and 82%, respectively. Here again, the oxygen radical attack is faster than the intramolecular cyclization.¹³ Additionally, eight phosphates **3k–3q** derived from the reaction of ordinary oxygen-centered radicals and **1a** have been isolated in good to excellent yields (59–88%).

The reaction proceeds also with other phosphites such as triethyl- and triisopropyl-phosphites and the corresponding phosphate esters have been obtained in good yields (62 and 56%, respectively).

To demonstrate the synthetic utility of the developed methodology, phosphonation of a naturally-relevant caffeine phosphate ester (**3t**) has been obtained in fair yields (61%). Finally, our strategy is also amenable for the synthesis of 5'-phosphate nucleoside **3u**, which was obtained in good 78% yield.

To gain more insight about the reaction mechanism, we employed spin trapping/electron paramagnetic resonance (ST/EPR) experiments to characterize possible radicals formed during our photocatalytic reactions.¹⁴ In this context, we first combined the pyridinium salt **2a** with the photocatalyst (*fac*-Ir(ppy)₃) in the presence of *N*-tert-Butyl- α -phenylnitron (PBN) as a spin trap in tert-butylbenzene under blue light irradiation. As depicted in Figure 2, a triplet of doublets because of the hyperfine couplings with the nitrogen nucleus ($a_N = 14.3$ G) and

with the proton in α position to the nitroxide nitrogen ($a_H = 2.2$ G) was observed. Because these values are in good agreement with those reported by Dagousset *et al.* for the spin adduct (MeO-PBN),¹⁵ the structure of the detected radical could be assigned to **4a-PBN**, resulting from the addition of the alkoxy radical **4a** to PBN (Figure 2).

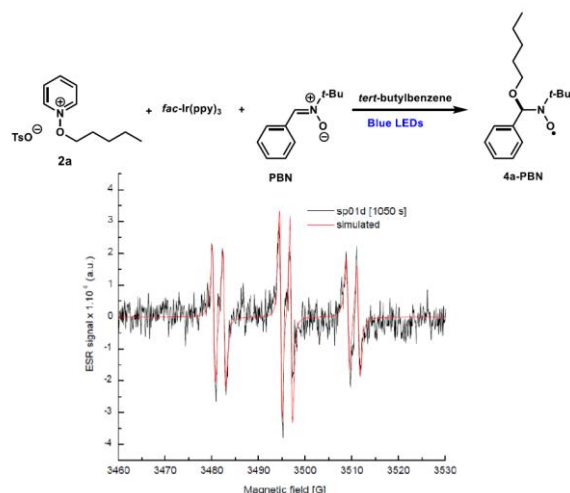


Figure 2. EPR spectrum of the reaction between pyridinium ion **2a** in the presence of *fac*-Ir(ppy)₃ and the spin trap (PBN) in *tert*-butylbenzene under blue light irradiation ($\lambda_{\max} = 420$ nm).

The low reduction potential of **2a** (-0.95 V/SCE) reported by Hong agrees with as a favorable reduction process.¹⁰ Phosphorus centered radicals are detected but the PBN (use for its light stability) cannot give more insight on the structure of the radical center due to its indirect spin trap character. Therefore, this radical can be tentatively proposed as **5** (Figure 3). Another proof of this mechanism is the release of methyl radical from the well-known fragmentation of tetra-coordinate phosphorus radical. The fact that the methyl radical is the only carbon radical observed indicates the selectivity of this process (path (a)) compared to the competitive process (path (b)) (Figure 3). This result was furthermore supported by ³¹P NMR spectroscopy of the photocatalytic reaction of **1a** with **2a**, where the phosphate ester **3a** was observed as a major product (85%) and only 11% of **6** was detected in the crude mixture (Figure S5, Supporting Information, page S7).

To gather more mechanistic information, quantum yield of the reaction has been determined by actinometry and found to be 8.05, which is indicative of a radical chain mechanism.

Taken together, a proposed reaction mechanism is depicted in Figure 3. It starts with the excitation of *fac*-Ir(ppy)₃ with blue light to generate the highly reductive excited state [*fac*-Ir(ppy)₃]^{*} ($E_0^* = -1.73$) that can easily reduce the pyridinium ion (**2**) to form the alkoxy radical (**4**). Because reactions of the latter with phosphites (**1**) are diffusion-controlled, they form phosphoranyl radicals (**5**) prior to fragmentations. A subsequent fast β -scission leads to the formation of the phosphate ester (**3**). Alternatively, the phosphoranyl radical (**5**) can be oxidized either by [*fac*-Ir(ppy)₃]^{*} or the pyridinium salt (**2**) to form the phosphonium ion (**7**). Based on the quantum yield measurement, the second scenario is more likely. Finally, Arbuzov reaction between the pyridine, formed upon reduction of (**2**), and (**7**) leads to the formation of the desired phosphate ester (**3**) and *N*-methylpyridinium (**9**), which has been detected by NMR spectroscopy.

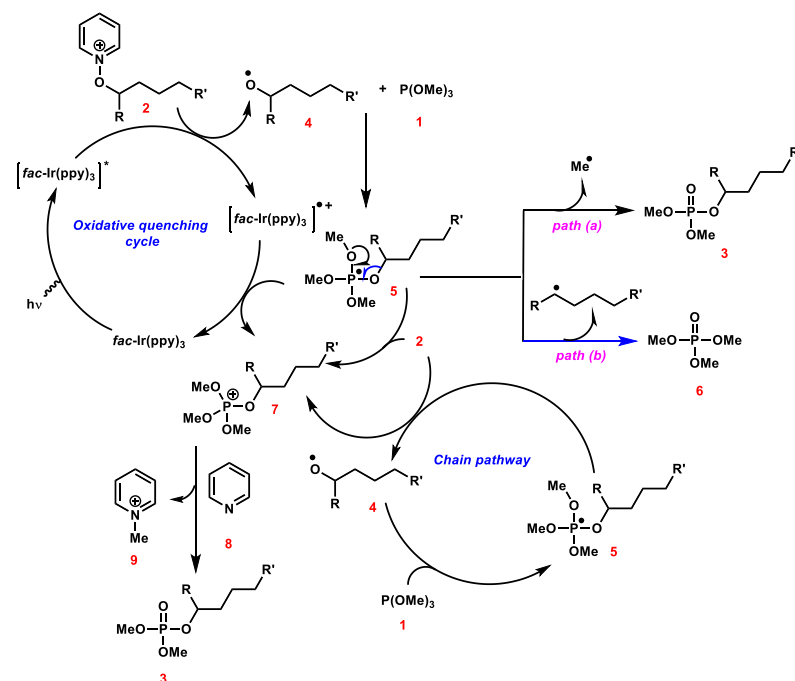


Figure 3. Proposed Mechanism for the Photocatalytic Synthesis of Phosphate Esters from the reaction of *N*-alkoxyppyridinium ions with Phosphites.

This work demonstrates a new synthetic application of *N*-alkoxyppyridinium ions as efficient generators of alkoxy radicals that can intercept with phosphites to lead to a facile access to phosphate esters. The scope is broad and can be applied in late stage phosphonation of complex structures. Interesting, mechanistic investigations, including EPR, NMR and quantum yield experiments allowed the suggestion of a reasonable reaction mechanism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, full spectroscopic data, and copies of ^1H , ^{13}C and ^{31}P NMR for all new compounds

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DEDICATION

Dedicated with respect and admiration to Prof. François Terrier.

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