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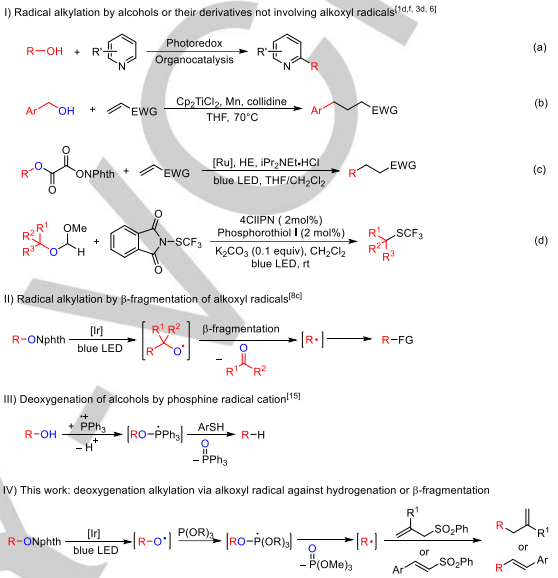
Alkylation of Allyl/alkenyl Sulfones by Deoxygenation of Alkoxyl Radicals

Jia-Bin Han, Ao Guo and Tang Xiang-Ying*

Abstract: *A challenging deoxygenation of alkoxyl radicals from readily accessible alcohol derivatives was developed, affording facile synthesis of functionalized alkenes with good functional group tolerance under mild reaction conditions. Since alkoxyl radicals can easily undergo β-fragmentations or hydrogen abstractions, this new strategy for deoxygenation of alkoxyl radicals is highly valuable. Moreover, mechanistic studies revealed that the electron-neutral phosphine acts as the deoxygenation reagent.*

Alcohols, as one of the most abundant feedstock chemicals, are ubiquitous in drugs and natural products, thus convertion of alcohols or their derivatives to other functionalized moleculars is of high value. Especially, the radical transformation of alcohols has gained much attention in recent years. To date, great achivements have been made in using alcohols[1] or their derivatives, such as xanthate[2], oxalate[3], benzoate[4], phosphate[5], and ethers[6] as alkylation agents. MacMillan and co-workers reported an elegant Minisci reaction under photoredox catalysis with simple alcohols as alkylation agents (Scheme 1, Ia).[1d] Suga and Ukaji disclosed a low-valent titanium-mediated radical conjugate addition of electro-deficient alkenes with benzyl alcohols as benzyl radical sources (Scheme 1, Ib).[1f] In Addition, Overman and coworkers developed an efficient radical alkylation using oxalates as alkylation agents under photoredox catalysis (Scheme 1, Ic).[3d] Recently, Zhu and Xie reported an efficient method for trifluoromethylthiolation and difluoromethylthiolation of tertiary alcohols through selective cleavage of tertiary C(sp^3)–O ether bonds in methoxymethyl protected tertiary alcohols (Scheme 1, Id).[6] However, to the best of our knowledge, a general alkylation protocol via alkoxyl radical generated from alcohols or their derivatives remains a challenge.[5]



Scheme 1. Alcohols or their derivatives as alkylation agents. Nphth = phthalimido, HE = Hantzsch ester.

The alkoxyl radical is a versatile reactive intermediate in many organic transformations and biologic processes.[7] It has been well established that alkoxyl radical can easily undergo β-fragmentations,[8] hydrogen abstractions,[9] or addition to unsaturated bonds.[10] Whereas, reactions involving alkoxyl radicals were always hampered by the instability of alkoxyl radical precursors or harsh reaction conditions.[9a, b, 10a, 11] Thanks to the recent development of visible-light catalysis,[12] the generation of alkoxyl radicals has been realized in mild conditions with excellent functional group tolerance.[9c-g, 10b] Chen and Meggers disclosed the generation of alkoxyl radicals under photoredox catalysis and the subsequent δ-selective functionalization after 1,5-hydrogen atom transfer (HAT). [9c, d] Zuo and co-workers reported a similar 1,5-HAT strategy in which alkoxyl radicals were generated from simple alcohols.[9g] Recently, Chen reported a donor-acceptor complex enabled alkyl radical generation from β-fragmentation of the alkoxyl radical (Scheme 1, II).[8c] Very recently, Dagousset reported the synthesis of ethers via alkoxyl radicals generated from *N*-alkoxypyridinium salts under photoredox catalysis.[10b] Although great achievements involving alkoxyl radicals have been made recently, reactions involving alkoxy radicals against hydrogen abstraction or β-fragmentation are rarely reported.[13] To

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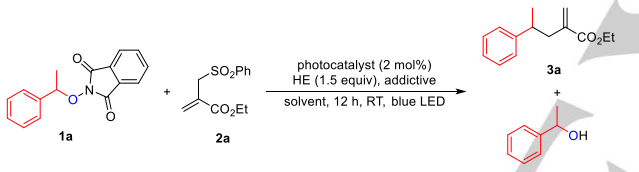
this regard, the direct deoxygenative alkylation using alcohol substrates is highly desirable.

We speculated that if a rapid deoxygenation took place before the intrinsic β-fragmentation or hydrogen abstraction, an innovative alkylation method by deoxygenation of alkoxyl radical would be rationally realized. Because most alkoxyl radical precursors could be readily prepared from cheap and abundant alcohols, [9c,d, 10a,b] this method would be highly practical and valuable. Very recently, Schmidt disclosed an anti-markovnikov alkene hydroamination via phthalimidyl radicals, which was accessed from phosphite promoted radical deoxygenation of *N*-hydroxyphthalimide.[14] Doyle disclosed a novel deoxygenative hydrogenation of benzylic alcohols by phosphine radical cation (Scheme 1, III).[15] Encouraged by these reports and other studies[13,17], we envisioned that phosphine would complete such process due to strong P-O bond strength (148 kcal/mol for $P(O)(OEt)_3$).[18] Herin, we wish to report a novel deoxygenative alkylation of allyl/alkenyl sulfones from readily accessable *N*-alkoxyphthalimides under visible light (Scheme 1, IV).

Table 1. Screening of reaction conditions.



1a 2a 3a 3a'

entry[a]	photocatalyst	additive	**1a**/**2a**/PR_3	Yield[b] (**3a**/**3a'**, %)
1	**Ir-I**	$P(OEt)_3$	1/2/2	44/32
2	**Ir-II**	$P(OEt)_3$	1/2/2	18/54
3	**Ir-III**	$P(OEt)_3$	1/2/2	24/51
4	**Ir-IV**	$P(OEt)_3$	1/2/2	22/60
5	**Ru-I**	$P(OEt)_3$	1/2/2	0/6
6	**Ru-I**	$P(OEt)_3$	1/2/2	2/3
7	Eosin Y	$P(OEt)_3$	1/2/2	5/6
8	**Ir-I**	$P(OMe)_3$	1/2/2	50/25
9	**Ir-I**	$P(O^iPr)_3$	1/2/2	35/47
10	**Ir-I**	$P(OPh)_3$	1/2/2	14/45
11	**Ir-I**	$P(OMe)Ph_2$	1/2/2	0/95
12	**Ir-I**	$P(OH)(OEt)_2$	1/2/2	0/82
13	**Ir-I**	PPh_3	1/2/2	13/27
14[c,d]	**Ir-I**	$P(OMe)_3$	1/2/2	56/22
15[c,e]	**Ir-I**	**$P(OMe)_3$**	**1/3/8**	**83 (80)/8**
16	—	$P(OEt)_3$	1/2/2	4/7

[a] Reaction condition: **1a** (0.2 mmol), **2a**, PC (2 mol%), Hantzsch ester (0.3 mmol), and 1,4-dioxane (2.0 mL) stirred at RT under irridation of 3W blue LED for 12 h. [b] Yields were determined by GC analysis with n-dodecane as an internal standard. [c] PC (1 mol%). [d] MTBE (2 mL). [e] MTBE (4 mL). **Ir-I**: $Ir[(dtb\text{-}bpy)(ppy)_2](PF_6)$; **Ir-II**: $Ir[bpy((dF(CF_3)ppy)_2](PF_6)$; **Ir-III**: $Ir[(dtb\text{-}bpy)((dF(CF_3)ppy)_2](PF_6)$; **Ir-IV**: $Ir(ppy)_3$; **Ru-I**: $Ru(bpy)_3Cl_2$; **Ru-II**: $Ru(bpy)_3(PF_6)_2$.

To test our hypothesis, we first investigated the deoxygenative alkylation of ally sulfone with alcohols as alkoxyl radical precursors in the presence of oxidants such as hypervalent iodine reagents or $Mn(OAc)_3$.[19] Unfortunately, only trace amount of desired products could be obtained. We then chose *N*-alkoxyphthalimides as alkoxyl radical precursors.[8b,9a-c,13] In the presence of 2 mol% of **Ir-I**, Hantzsch ester, and $P(OEt)_3$, the reaction in 1,4-dioxane under the irradiation of 3 W blue LED proceeded smoothly to afford the desired product **3a** in 44% yield together with 32% yield of **3a'** resulting from H abstraction (Table 1, entry 1). Other photocatalysts were observed to be less effective than **Ir-I** (Table 1, entries 2-7). It is worthnoting that the choice of phosphines was crucial to the product distritution. $P(OMe)_3$ was found to be more efficient than $P(OEt)_3$ and $P(O^iPr)_3$ (Table 1, entries 1 and 8-9). To our surprise, the reactions using PPh_3 or $P(OPh)_3$ produced much diminished yields, and this result was quite different from some recent related works[13,17] (Table 1, entries 10 and 13). When $P(OMe)Ph_2$ or $Ph(OH)(OEt)_2$ was employed, **3a'** was given in high yield but no **3a** was not obtained (Table 1, entries 11 and 12). Further screening of reaction conditions revealed that 1 mol% of **Ir-1** was enough for this reaction, and MTBE was proved to be better solvent than 1,4-dioxane (Table 1, entry 14). To further improve the yield of **3a**, 8 equiv of $P(OMe)_3$ was required to suppress the H abstraction process, giving **3a** in to 83% yield with only 8% yield of **3a'** obtained. In addition, low concentration of reactants gave good yield of **3a** (Table 1, entry 15). Control experiments demonstrated Hantzsch ester, photocatalyst, and blue LED were all necessary in this reaction (Table 1, entry 16. For details, see SI).

With the optimized reaction conditions in hand, we sought to investigate the scope of alcohol derived *N*-alkoxyphthalimides. As demonstrated in Scheme 2, a broad array of *N*-alkoxyphthalimides could serve as alkylation agents in this deoxygenative alkylation reaction. Deoxygenation of alkoxyl radicals generated from 1-arylethan-1-ol derivatives occurred smoothly to afford the 1,1-disubstituted alkenes in moderate to good yields (**3b**-**3h**, 50%-90%). *N*-alkoxyphthalimides with electron-donating groups, such as Me, OMe on the phenyl ring afforded better yields than *N*-alkoxyphthalimides with electron-withdrawing groups (**3b** and **3c** vs **3d**-**3h**). It is worth noting that the halide substituents on the phenyl ring were compatible under the reaction conditions (**3e**-**3g**). Ethyl group adjacent to the alkoxyl radical did not impede the deoxynation process, giving desired product **3i** in 77% yield. 1,1-Disubstituted alkenes with an indane, chromanone and furan skeleton could also be obtained in moderate and good yields (**3j**-**3l**). Benzyl alcohol derived *N*-alkoxyphthalimides bearing alkyl, alkynyl, phenyl, halide, trifluoromethoxyl, cyanide, and ester groups were also suitable substrates for this reaction, providing the 1,1-disubstituted alkenes in 34-79% yields (**3m**-**3u**). In addition, **3m** could be

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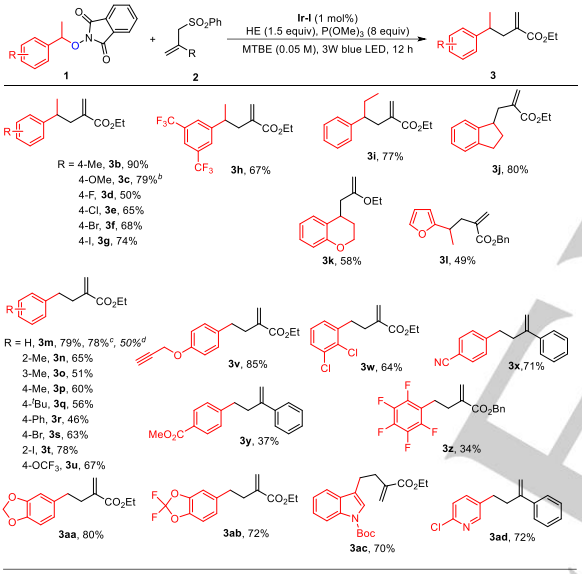
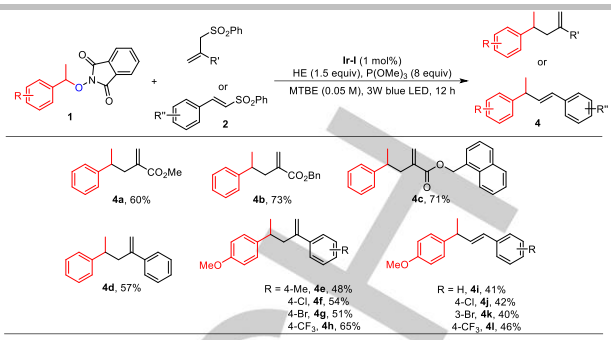
obtained in 78% and 50% yield if performing the reaction on 2 and 5 mmol scale. It was found that the position of the substituents on the phenyl rings had small influence on the reaction. N-aryloxylphthalimide with *m*-Me on the phenyl ring gave the product in slightly lower yield (**3o** vs **3n** and **3p**). Notably, the efficiency of this reaction was not hindered by *ortho* substituents on the phenyl ring (**3n**, **3t**, **3w**, and **3z**). Moreover, 2,3,4,5,6-pentafluorophenyl group was not active in this reaction, provided **3z** in 34% yield probably due to low nucleophilicity of the radical intermediate. Similar result was also observed in the case of **3y**. Piperonyl and difluoromethylated piperonyl alcohol derived *N*-alkoxyphthalimides went through the reaction smoothly to give **3aa** and **3ab** in good yields. Notably, indole- and pyridine-containing heterocycle substrates were both successful alkylation agents, delivering allylation adducts **3ac** and **3ad** in 70% and 72% yield, respectively.

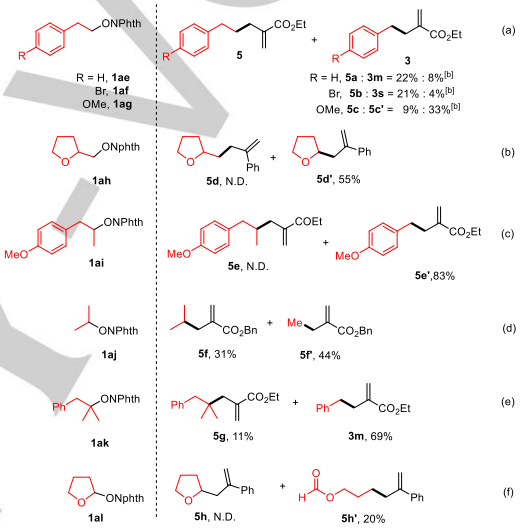


Scheme 2. Scope with respect to *N*-alkoxyphthalimides. Reaction condition: **1** (0.2 mmol), **2a**, **Ir-I** (1 mol%), Hantzsch ester (0.3 mmol), $P(OMe)_3$ (1.6 mmol) and MTBE (4.0 mL) stirred at RT under irridation of 3W blue LED for 12 h. *b* 1,4-dioxne in stead of MTBE. *c* 2.0 mmol scale. *d* 5.0 mmol scale.

We next sought to evaluate the generality of this deoxygenative alkylation reaction with respect to allyl/alkenyl sulfones. As shown in Scheme 3, a wide range of allyl/alkenyl sulfones were sucessfully alkylated under the typical reaction conditions. Allyl sulfones bearing a methyl-, benzyl- and naphthalene benzyl-carboxylic esters are suitable for this reaction, giving the desired products in moderate yields (**4a**-**4c**). Allyl sulfones bearing aromatic groups were also suitable reaction partners, providing phenyl substituted alkenes in 48-65% yields, in which electron-deficient allyl sulfones provided higher yields (**4d**-**4h**). Vinyl sulfones were also suitable radical acceptors, giving aryl substituted styrenes in acceptable yields (**4i**-**4l**).



Scheme 3. Scope with respect to allyl/alkenyl sulfones. Reaction condition: **1** (0.2 mmol), **2** (0.6 mmol), **Ir-I** (1 mol%), HE (0.3 mmol), and $P(OMe)_3$ (1.6 mmol) stirred in MTBE (4 mL) under the irridation of 3W blue LED for 12 h.



Scheme 4. Deoxygenation vs β-fragmentation with respect to *N*-alkoxyphthalimides. [a] Reaction condition: **1** (0.2 mmol), **2** (0.6 mmol), **Ir-I** (1 mol%), Hantzsch ester (0.3 mmol), $P(OMe)_3$ (1.6 mmol) and MTBE (4.0 mL) stirred at RT under irridation of 3W blue LED for 12 h. [b] ^1H NMR yield with CH_2Br_2 as an internal standard.

After demonstrating that benzoxyl radicals could be smoothly deoxygenated in this reaction, we wondered if this deoxygenation strategy could be extended to other alkoxyl radicals. It was found that 2-phenyl-ethanoxyl radical was deoxygenated in a much low efficiency, providing **5a** in only 22% yield, together with the generation of small amount of **3m** (8%). The substituents have dramatic influence on the deoxygenation process. β-Fragmentation of 2-aryl-ethanoxyl radical with *para*-Br substituent was easily suppressed, whereas β-fragmentation of 2-aryl-ethanoxyl radical with *para*-OMe substituent occurred more rapidly (**5b**, **3s** and **5c**, **5c'**). This could be attributed to the stability of the benzyl radical generated from β-fragmentation (Scheme 4a), which can also explain the product distribution in the reactions (Scheme 4b-4c).[20] While in the case of isopropanol derived *N*-alkoxyphthalimides, β-fragmentation was more favored

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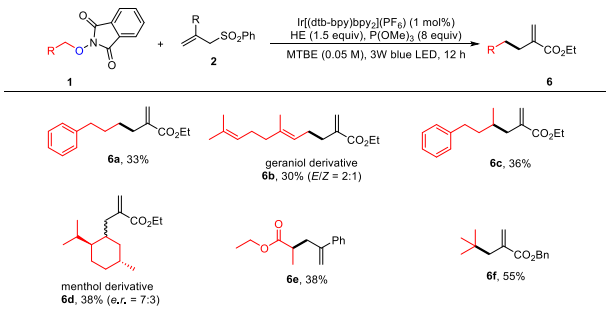
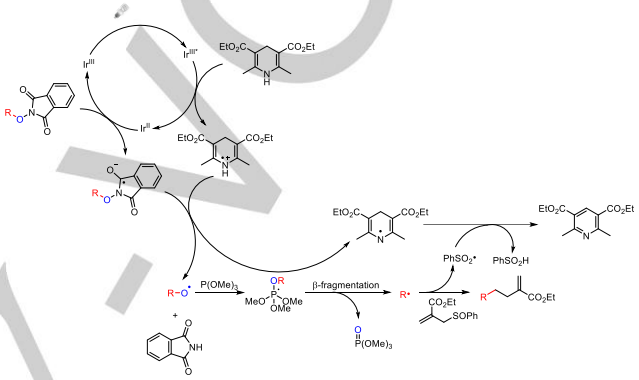
than deoxygenation (Scheme 4d). It is interesting that alkoxyl radical generated from **1al** could also undergo β-fragmentation to afford ring opening product **5h'** (Scheme 4f).[21]



Scheme 5. Scope with respect to *N*-alkoxyphthalimides. Reaction condition: **1** (0.2 mmol), **2** (0.6 mmol), **Ir-I** (1 mol%), Hantzsch ester (0.3 mmol), $P(OMe)_3$ (0.8 mmol) and MTBE (4.0 mL) stirred at RT under irridation of 3W blue LED for 12 h.

It was found that aliphatic alcohols derived *N*-alkoxyphthalimides could be successfully employed in our reaction, affording the corresponding olefines (Scheme 5). Unlike the reaction of 2-phenyl-ethanoxyl radical, 3-phenyl-propanoxyl radical was deoxygenated by $P(OMe)_3$, providing **6a** in 33% yield with trace product from β-fragmentation observed. Geraniol derived *N*-alkoxyphthalimide could also be used for alkylation, giving the product **6b** as an *E*/*Z* isomer mixture in 30% yield. 4-Phenylbutan-2-ol derived *N*-alkoxyphthalimide provided 36% yield of the desired product **6c**. Moreover, menthol derived *N*-alkoxyphthalimide is also a successful alkylation agent in our reaction and product **6d** was obtained in 38% yield. α-Carbonyl radical was also generated by this deoxynative strategy, affording **6e** in 38% yield. *t*-Butyl radical was obtained in the presence of $P(OMe)_3$, and desired product **6f** was produced in 55% yield with a little methylated product detected by ^{1}H NMR.

A Stern−Volmer quenching experiment was performed to exploit whether $P(OMe)_3$ or Hantzsch ester is the real quencher of the photoexited state of $[Ir(dtb\text{-}bpy)(ppy)_2](PF_6)$ (For details, see SI). As expected, hantzsch ester successfully quenched $*[Ir(dtb\text{-}bpy)(ppy)_2](PF_6)$, while $P(OMe)_3$ was not able to decrease the intensity of $*[Ir(dtb\text{-}bpy)(ppy)_2](PF_6)$. Based on Stern−Volmer quenching experiment and recent studies,[8c,9c-d] a plausible mechanism was proposed as shown in Scheme 6. Ir^{III} is activated upon being exposed to blue LED to give $Ir^{III}*$, and then reduced by Hantzsch ester to afford Ir^{II}.[9c, 22] The resulting Ir^{II} species can reduce *N*-alkoxyphthalimide by single electron transfer to give *N*-alkoxyphthalimide anion, which is further protonated by Hantzsch ester radical cation to facilitate a homolytic N-O bond cleavage with formation of an alkoxyl radical and phthalimide.[8c,9c] This alkoxyl radical can easily undergo β-fragmentation or hydrogen abstraction, while in the presence of $P(OMe)_3$, alkoxyl radical was added to $P(OMe)_3$ to form a phosphoranyl radical which could easily undergo β-scission to give an alkyl radical.[16] This alkyl radical then reacts with allyl/alkenyl sulfones to furnish the product and benzenesulfonyl radical by an addition-elimination sequence.[23] The benzenesulfonyl radical abstract a hydrogen radical from Hanzstch ester radical, through the persistent radical effect, to form $PhSO_2H$ and pyridine species to furnish the catalytic cycle.[9d, 24]



Scheme 6. Proposed mechanism.

In summary, we have developed a general strategy for alkylation reactions via deoxygenation of alkoxyl radical generated from *N*-alkoxyphthalimide. A wide range of *N*-alkoxyphthalimides derived from benzyl alcohols serves well as alkylation agents to react with allyl/alkenyl sulfones. Moreover, *N*-alkoxyphthalimides from alkyl alcohols can also be functionalized by our protocol. The synthetic usefullness of this deoxygenation strategy has been demonstrated through the functionalization of natural occurring products, such as geraniol and menthol. Further investigations to understand the mechanism more deeply and expansion of the substrate scope is ongoing in our lab.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkoxyl radical • deoxygenation • photoredox catalysis • alkenes • radical alkylation

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A challenging deoxygenation of alkoxyl radicals from readily accessible alcohol derivatives is described, affording facile synthesis of synthetic valuable alkenes with good functional group tolerance under mild reaction conditions. Since alkoxyl radicals can easily undergo β-fragmentations or hydrogen abstractions, this new strategy for deoxygenation of alkoxyl radicals is of high significance.

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