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Organic Photoredox Catalysis for the Oxidation of Silicates: Applications in Radical Synthesis and Dual Catalysis

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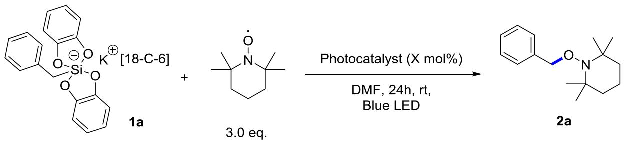
Metal free photooxidation of alkyl bis(catecholato)silicates with the organic dye, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN), allows the smooth formation of alkyl radicals. The latter can be efficiently engaged either with radical acceptors to provide homolytic addition products or in photoredox/nickel dual catalysis reactions to obtain cross-coupling products.

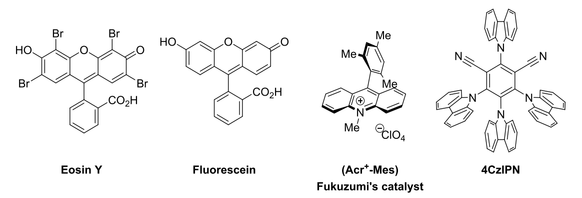
Visible-light photoredox catalysis[1] has emerged as a powerful strategy to generate radical species replacing more and more tin-mediated or stoichiometric redox methodologies.[2] Many opportunities are now available to access all kinds of C-centered radicals, based whether on photooxidative or photoreductive processes.[1] In this context, we and subsequently the group of Molander showed recently that the photooxidation of alkyl bis(catecholato)silicates[3] is a very convenient source of alkyl radicals. This process constitutes a significant advance with advantageous features compared to the photooxidation of carboxylates[4] and trifluoroborates,[5] which is limited to stabilized alkyl radicals[4,5] (allylic, benzylic and α-heterosubstituted radicals). In contrast, given their lower oxidation potential, alkyl bis(catecholato)silicates offer more scope. So far, their effective oxidation has only been described with photocatalysts based on expensive metals[3] (Ir, Ru). Alternatively, we have sought to explore more sustainable processes using easily accessible organic dyes.[6] In a preliminary study,[3b] it was found that only the highly oxidizing Fukuzumi acridinium photocatalyst[6a] showed some activity, limited to allylic and benzylic silicates. In 2012, Adachi et al. described a family of carbazoyl dicyanobenzenes as light-harvesters for organic light-emitting diodes.[7] Among them, 1,2,3,5-tetrakis-(carbazol-yl)-4,6-dicyanobenzene (4CzIPN) displayed promising features for photoredox catalysis: a high photoluminescence quantum yield (94.6%) and a long life-time at the excited state (5.1 µs). Recently, Zhang et al. reported the redox properties of this photosensitizer[8] and the given value for the oxidative potential of the photoexcited 4CzIPN ($E_{1/2}^{*}$(4CzIPN/[4CzIPN]$^{-}$)=+1.35 V vs SCE) augured well for a possible photooxidation of alkyl bis(catecholato)silicates ($E_{1/2}$(Ox/red)=+0.3 to~+0.9 V vs SCE).[3a] We thus decided to assess this reactivity with a series of alkylsilicates and the cheapest photocatalyst 4CzIPN ($0.06/mmol for carbazole, $2.2/mmol for tetrafluoroisophthalonitrile[9]) in both radical synthesis and dual catalysis.

The ability of 4CzIPN to oxidize benzylsilicate **1a** in spin trapping experiments with TEMPO, acting both as radical trap and presumably also as sacrificial electron acceptor, was first explored (Table 1).[3,5] The reaction was performed in a 0.1 M DMF solution under blue LEDS irradiation (477 nm) with **1a** (0.3 mmol), TEMPO (0.9 mmol) and the organic dye (10 mol%). Only Fukuzumi acridinium (Acr^{+}-Mes) and 4CzIPN gave the expected TEMPO adduct **2a** in 66% and 92% yields respectively.[3b] Furthermore, the catalytic loading in 4CzIPN could be diminished down to 1 mol% without any erosion of the yield (entry 5). These preliminary results excited our interested in further uses of 4CzIPN.

Table1 Spin-trapping experiments with TEMPO: screening of organic photocatalysts with benzylsilicate **1a**



Entry	Photocatalyst (mol%)	Yield (%)
1	Eosin Y (10 mol%)	0
2	Fluorescein (10 mol%)	0
3	Acr^{+}-Mes (10 mol%)	66
4	4CzIPN (10 mol%)	92
5	**4CzIPN (1 mol%)**	**94**



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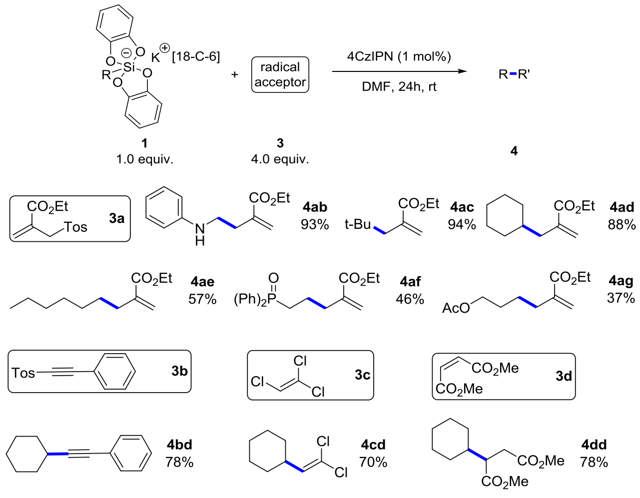
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Therefore, we engaged various alkylsilicates **1** in a series of diagnostic radical addition experiments (Table 2). Using first allylsulfone **3a**, we surmised the following catalytic cycle.[3a] Photoexcited 4CzIPN* would oxidize the alkylsilicate derivative via a SET mechanism leading to the [4CzIPN]$^-$ anion and a hypervalent 5-coordinate silicon radical. Upon homolytic fragmentation of the C-Si bond, the generated C-centered radical would add to allylsulfone **3a**, providing a β-sulfonyl radical which after fragmentation liberates the allylation adduct and a tosyl radical. A SET step would regenerate the photocatalyst and give a sulfinate anion.

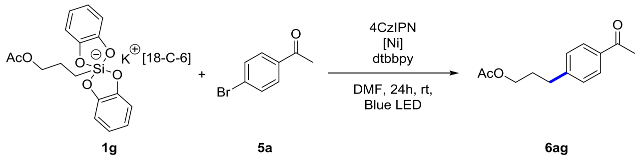
Based on this catalytic cycle, allylation adducts were obtained in excellent yields for stabilized radicals (**4ab**, **4ac**) and secondary radical (**4ad**), to moderate yields for primary radicals (**4ae**, **4af**, **4ag**) (Table 2). Interestingly, silicate **1f** furnished the carbon allylation adduct, without fragmentation of the Ph$_2$PO radical.[10] Encouraged by these results, we engaged cyclohexylsilicate **1d** in various radical reactions like alkynylation,[11] vinylation[11] and Giese-type reaction leading efficiently to products **4bd**, **4cd** and **4dd**. It should be noted that similar additions can be performed by photocatalytic reduction of alkyl halides or related precursors but they generally rely on activated substrates or very special functions.[12]

Table 2 Reaction of silicates with various radical acceptors



Zhang et al. also reported[8] the first examples of the use of 4CzIPN as photocatalyst in photoredox/nickel dual-catalyzed[13] cross-coupling reactions of aminocarboxylates and benzyltrifluoroborates with arylbromides. In the same vein, we planned to extend this mixed photoorganic/metallic dual-catalysis to alkylsilicates.[14] Thus, a mixture of 4’-bromoacetophenone **5a** with acetoxypropylsilicate **1g** in the presence of 4CzIPN (2 mol%), NiCl$_2$.dme (5 mol %) and 4,4’-di-tert-butyl-LED) for 24 hours at rt. In these conditions, an excellent 81% yield of coupling product **6ag** was observed (Table 3). Furthermore, we were able to reduce the catalytic loading in photocatalyst and nickel to 1 mol% and 2 mol% respectively, giving **6ag** in 83% isolated yield (entry 3). However, decreasing the amount of alkylsilicate drastically affected the yield of the reaction (entry 5). Interestingly, no product was observed when a Ni(0) (Ni(COD)$_2$) precatalyst was tested (entry 4). This finding suggests a catalytic cycle starting from a Ni(II) species as previously described by Johannes et al.[15]

Table 3 Screening of reaction conditions for photoredox/nickel dual-catalyzed cross-coupling

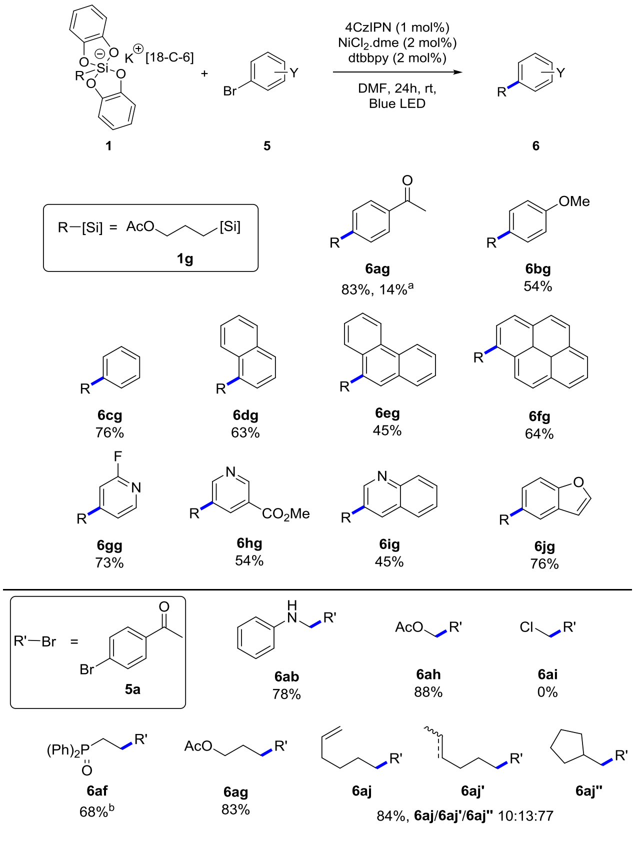


Entry	Silicate (nb eq.)	4CzIPN loading	Nickel source/loading	Yield (%)
1	1.5	2 mol %	NiCl$_2$.dme 5 mol%	81%[a]
2	1.5	2 mol %	NiCl$_2$.dme 3 mol%	77%[a]
3	**1.5**	**1 mol %**	**NiCl$_2$.dme** **2 mol%**	**79%**[a] **(83 %)**[b]
4	1.5	2 mol %	Ni(COD)$_2$ 3 mol%	0%
5	1.2	1 mol %	NiCl$_2$.dme 2 mol%	57%[a]

[a] ^{1}H NMR yield with butadiene sulfone as internal standard , 0.3 mmol scale. [b] Isolated yield.

The scope of this reaction was investigated focusing initially on the influence of aryl ring substitution (Table 4). A better yield was observed with an electron neutral (**6cg**) or an

Table 4 Reaction of silicates with various aryl bromides

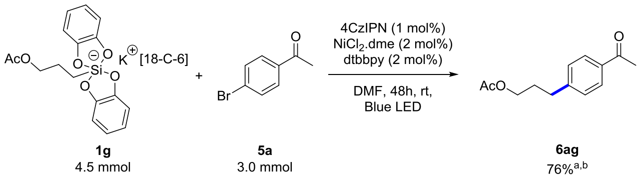


[a] Experiment realized with 4’-chloroacetophenone. [b] Yield determined in a mixture with ethyldiphenylphosphine oxide (15% of byproduct).

electron withdrawing group (**6ag**) than with a methoxy substituted substrate (**6bg**). Polyaromatic substrates also gave the expected products (**6dg**-**6fg**) in good to moderate yields. Moreover, when 4'-chloroacetophenone was engaged the yield of the reaction dropped dramatically (from 83% to 14% of **6ag**). This highlights the importance of the oxidative addition step, in accordance with the postulated mechanism.[13,14] Heteroaryl bromides can also act as electrophilic partners. Pyridines (**6gg** and **6hg**), quinoline (**6ig**) or benzofuran derivatives (**6jg**) provided coupling products in moderate to good yields. In addition, the compatibility of several types of alkylsilicates was explored with 4'-bromoacetophenone. An assortment of key functions such as amine (**6ab**), ester (**6ah** and **6ag**) or phosphine oxide (**6af**) was well tolerated in the reaction conditions. In all cases, products were obtained in good to fair yields regardless of the stability of the generated C centered radical. Concerning silicate **1f** as before, no product derived the generation of a P-centered radical was observed.[10,16] Not surprisingly, chloromethylsilicate **1h** did not give the desired product (**6ha**). Finally, the reactivity of hex-1-enylsilicate **1j** was examined with 4'-bromoacetophenone and resulted in a mixture of products **6ja**, **6j'a** and **6j''a** in a 10/13/77 ratio and 82% overall yield. Here, the intermediate 5-hexenyl radical would directly react to provide product **6ja** and **6j'a** resulting from post-isomerization of **6ja**.[17] Interestingly, the formation of the major product **6j''a** implies a 5-exo-trig cyclization step prior to the coupling process.

In order to illustrate the versatility of 4CzIPN as photocatalyst for this type of dual catalysis, a scale-up experiment was accomplished using acetoxypropylsilicate **1g** and 4'-bromoacetophenone. The reaction conditions were the same as previously except the reaction time. Indeed, after 24 h of reaction, only 63% yield of **6ag** was obtained, which could be further improved to 76% yield by increasing the reaction time to 48 h (Table 5).

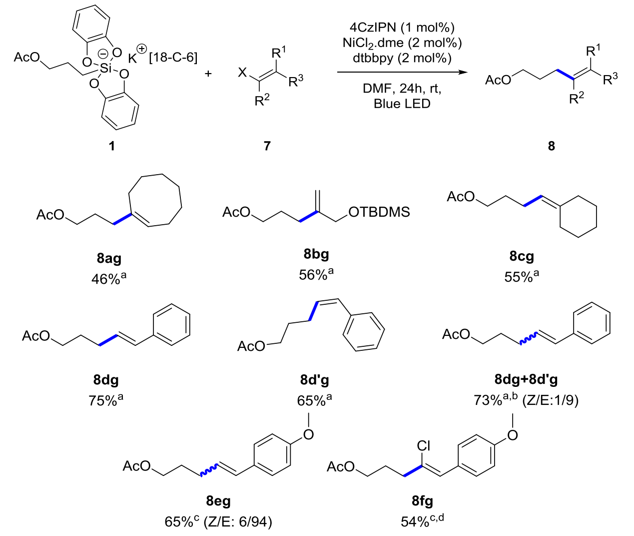
Table 5 Scale-up reaction



[a] 7% of the starting material recovered. [b] 63% obtained after 24h of reaction

Finally, a series of alkenyl bromides was treated under the dual catalysis conditions (Table 6). Unactivated alkenyl bromides were converted to their corresponding products in moderate yields (**8ag**-**8cg**). However, activated alkenyl bromides such as styryl bromide, styryl chloride, and β-gem-dichlorostyrene gave fair to good yields of coupling products, respectively **8dg** and **8d'g**, **8eg** and **8fg**.

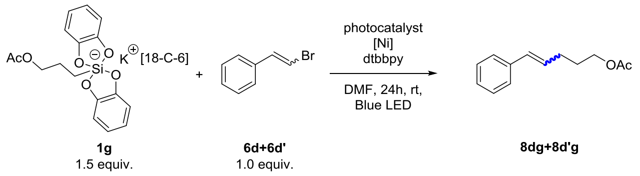
Table 6 Reaction of silicates with alkenyl halides



[a] Alkenyl bromide used as substrate. [b] Starting from a mixture of diastereoisomer Z/E: 15/85. [c] Alkenylchloride used as substrate. [d] Reaction performed during 48 hours.

Concerning β-bromostyrene **6d**/**6d'**, complete retention of the double bond geometry was observed when using each pure isomer. Same result was observed starting from the commercial mixture of both isomers (ratio Z/E: 15/85). It was interesting to compare this finding with the metallic photocatalysts $Ru(bpy)_3(PF_6)_2$ and $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (Table 7). Previously reported conditions[3c,14b] led to the expected products **8dg**,**8d'g** in 75% (Z/E: 15/85) yield with ruthenium and 90% (Z/E: 33/67) with iridium (Table 7, entries 2 and 3). We also verified that the reaction does not follow a pure radical vinylation mechanism involving an addition–β-elimination tandem. However, only traces of products (**8fd** and **8fd'**) were obtained when running the reaction in the absence

Table 7 Comparison of experimental conditions for photoredox/nickel dual-catalysis with β-bromostyrene



Entry	Photocatalyst (mol %)	Nickel source (mol %)	Yield (E/Z)
1	4CzIPN (1 mol%)	NiCl$_2$.dme (2 mol%)[a]	73%[b] (90/10)
2	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	NiCl$_2$.dme (3 mol%)[a]	75%[b] (85/15)
3	$[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (2 mol%)	$Ni(COD)_2$ (3 mol %)[a]	93%[b] (2/1)
4	4CzIPN (1 mol%)	No nickel	<5%[a]
5	4CzIPN (1 mol%)	No nickel	S.M.[b,c] (65/35)
6	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	No nickel	S.M.[b,c] (85/15)
7	$[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (2 mol%)	No nickel	S.M.[b,c] (40/60)

[a] Nickel catalyst and 4,4'-di-tert-butyl-2,2'-bipyridine engaged in a 1/1 ratio. [b] Starting from a commercial mixture of diastereoisomer E/Z: 85/15. [c] Experiment performed without silicate.

of nickel salt and dtbbpy ligand (entry 4) which precluded the exclusive radical pathway. Isomerization of β-bromostyrene in the presence of a photosensitizer has been already reported.[18] Control experiments were realized in the absence of nickel catalyst and silicate and showed that the bromide slightly isomerized in the presence of 4CzIPN (E/Z 65:35) compared to an E/Z ratio of 40:60 with the iridium complex (entries 5 and 7). In this case, a heavy atom effect, brought by the bromide atom would easily give access to the triplet state[19] of the styryl derivatives which promotes the isomerization. In contrast, no isomerization was observed with the ruthenium complex (entry 6) probably due to the lower energy state of the photoexcited $[Ru(bpy)_3]^{2+*}$. Thus, even if this organic-dye can act as a photosensitizer of β-bromostyrene, the oxidation process of silicates is faster than the photoisomerization of the substrate. Therefore, stereoselective alkenyl-alkyl cross-coupling are also workable.

In conclusion, all these results demonstrate that 4CzIPN is as efficient as metal based photocatalysts for the photooxidation of alkyl bis(catecholato)silicates. The generated radicals can be engaged efficiently with radical acceptors and also in organic photoredox/nickel dual-catalysed processes with (hetero)aryl halides and alkenyl halides affording in that case alkene derivatives with high stereoselectivity. Requiring only a low catalytic loading (1 mol%), 4CzIPN opens very exciting perspectives for more sustainable photoredox catalysis.

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