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Synthesis of Aliphatic Amides through a Photoredox Catalyzed Radical Carbonylation Involving Organosilicates as Alkyl Radical Precursors

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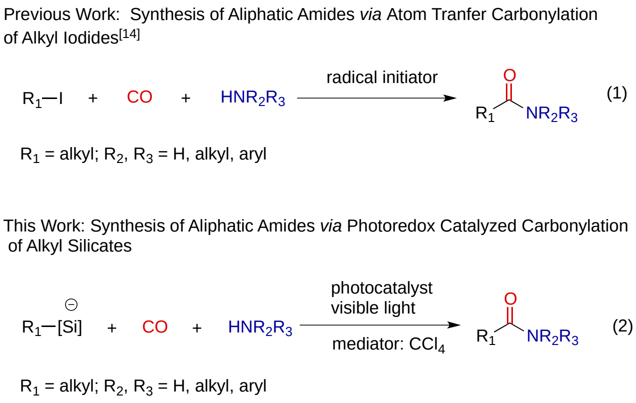
Abstract. Alkyl radicals, from primary to tertiary, formed by photocatalyzed oxidation of organosilicates, are involved efficiently in radical carbonylation with carbon monoxide (CO), in the presence of various amines and CCl_4, leading to a variety of amides in moderate to good yields.

Keywords: Carbonylation; multi-component reaction; photooxidative catalysis; radical/polar; silicates

Introduction

Visible-light photoredox catalysis has changed the scene of radical chemistry[1,2] by notably involving new reactants. Among them, a class of relatively low oxidation potential of alkyl (bis)catecholatosilicates[3] have recently proven to be efficient radical precursors, as shown by some of us[4] and Molander[5] as well as other groups.[6] They are interesting for their ease of synthesis from the corresponding alkoxysilane or trichlorosilane and for their ability to generate unstabilized primary alkyl radicals, under photoredox-catalyzed conditions, whether in the presence of classical Ru(II) or Ir(III) photocatalysts or even with an organic dye.[4a-c] The nucleophilic radicals thus formed can be readily engaged in C-C bond formation by addition to various species such as activated alkenes[4d], allylsulfones,[4d] imines[7] or recently heteroarenes[8] and N-acylhydrazone[9] or by nickel catalyzed cross coupling reactions.[4d,5,6a,6c]

Multicomponent radical reactions have great potential in organic synthesis,[10] in which carbon monoxide (CO) can be incorporated to install a carbonyl function through the formation of acyl radical intermediates.[11,12] Recently, we reported a photoredox catalyzed carbonylation of alkyl (bis)catecholatosilicates by using 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyano-benzene (4CzIPN) as photocatalyst and in the presence of alkenes and allylsulfones which leads to of variety of functionalized ketones and represents one of the first radical carbonylation under a photooxidative regime.[13] Aiming at extending this process to trivalent derivatives, we examined the possibility to develop a new synthesis of aliphatic amides. Carbonylative synthesis of aliphatic amides has been achieved by radical/ionic or radical/transition metal hybrid carbonylation of alkyl iodides (Scheme 1, eq 1).[14,15] Based on the known halogenation of acyl radicals by homolytic substitution, we surmised that adding a chlorinating agent like CCl_4 could *in situ* generate acyl chlorides which would then react with an amine to lead to amides (Scheme 1, eq 2).[16] We herein report that various aliphatic amides could indeed be synthesized from alkylsilicates under mild visible-light irradiation in metal-free conditions using 4CzIPN photocatalyst and carbon tetrachloride as a mediator.

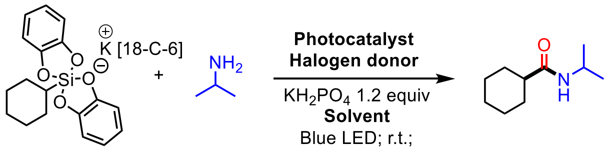


Scheme 1. Previous and present concepts for synthesis of aliphatic amides based on radical carbonylation

Results and Discussion

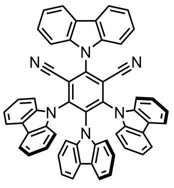
We chose to test the desired formation of amide using cyclohexyl bis(cathecolato)silicate **1a** in the presence of isopropylamine **2a**, CO, and 4CzIPN as photocatalyst in a series of model experiments. The latter were carried out in a stainless-steel autoclave equipped with two quartz glass windows that serve as a pressure-durable apparatus during light irradiation (15 W blue LED, see Supporting Information for details). The results are summarized in Table 1. Our first attempt consisted of the irradiation of **1a**, **2a**, 4CzIPN (1 mol%) and KH_2PO_4 (1.2 equiv) in DMF under a CO pressure of 80 atm during 24 h. While expected amide **3a** was obtained in less than 5% (Table 1, entry 1), a significant improvement of the yield of **2a** up to 24% was observed in the presence of CCl_4, which would work as chlorine atom donor and mediator of the reaction (Table 1, entry 2).[17] The reaction using $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ as photocatalyst gave **3a** in 15% yield (Table 1, entry 3). When the reaction was carried out under a lower CO pressure (40 atm), the yield was decreased to 20% (Table 1, entry 4). The use of the less nucleophilic solvent THF instead of DMF improved the yield of **3a** to 51% (Table 1, entry 5). To our delight, with a longer reaction time of 48 h, we were able to obtain the product **3a** in 81% yield (Table 1, entry 6). $CBrCl_3$, a bromine atom donor, was also found to work (Table 1, entry 7) but remained less efficient than CCl_4. Although KH_2PO_4 is not required for the reaction to occur, it was found to increase significantly the yield of the reaction (Table 1, entry 8). ^1H NMR data also shown that the reaction is cleaner in the presence of KH_2PO_4, avoiding the formation of small amounts of undesired by-products.

Table 1. Optimization of the reaction conditions [a]

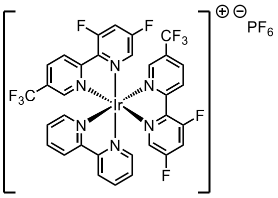


Entry	Catalyst	Donor	Solvent	CO (atm)	Time (h)	Yield **3a**[b]
1	4CzIPN	none	DMF	80	24	< 5%
2	4CzIPN	CCl_4	DMF	80	24	24%
3	[Ir][c]	CCl_4	DMF	80	24	15%
4	4CzIPN	CCl_4	DMF	40	24	20%
5	4CzIPN	CCl_4	THF	80	24	51%
6	4CzIPN	CCl_4	THF	80	48	81%[d]
7	4CzIPN	$CBrCl_3$	THF	80	48	75%
8	4CzIPN	CCl_4	THF	80	48	52%[e]

[a] Conditions: potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate (**1a**, 0.3 mmol, 1 equiv), isopropylamine (**2a**, 2 equiv), photocatalyst (1 mol%), KH_2PO_4 (1.2 equiv), CO (40-80 atm), solvent (7 mL), irradiation by blue LED lamp (425 nm) for 24-48 h. [b] Determined by ^1H NMR using acetanilide as an internal standard. [c] $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$. [d] Isolated yield. [e] Without KH_2PO_4.

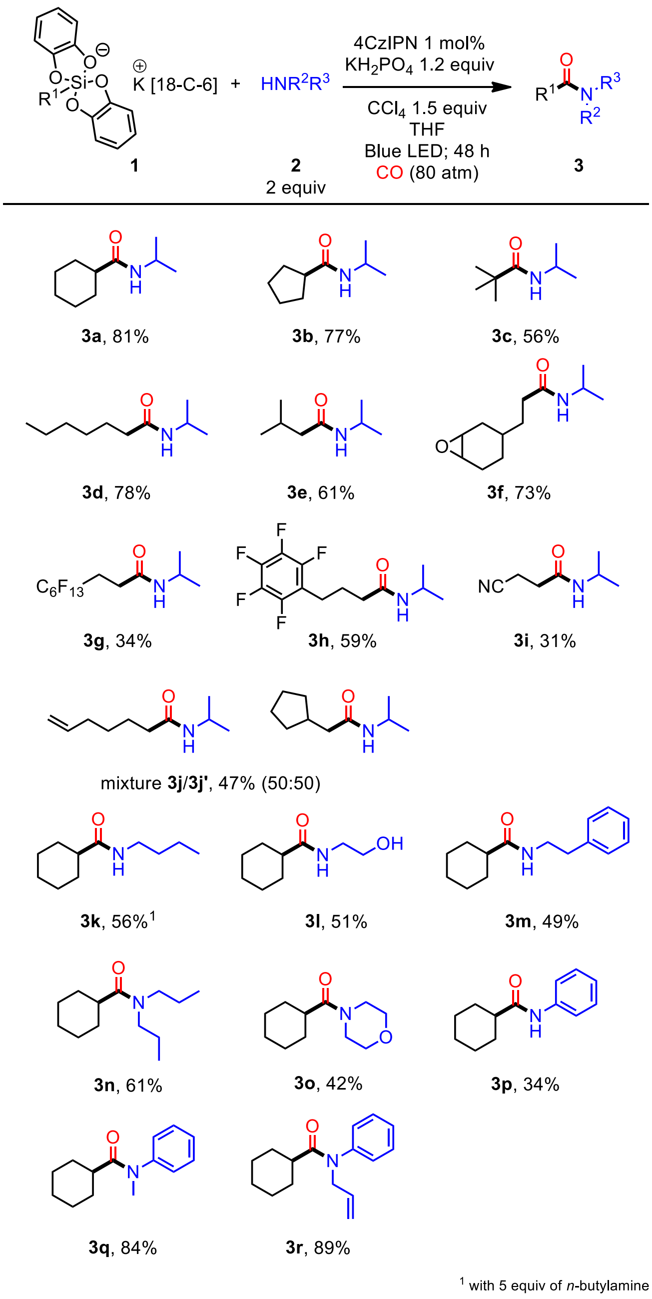


4CzIPN



$[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$

These promising results in hands, we applied this protocol to a series of alkyl bis(catecholato)silicates **1** and results are summarized in Scheme 2. Similar to cyclohexyl silicate **1a**, cyclopentyl silicate **1b**, gave



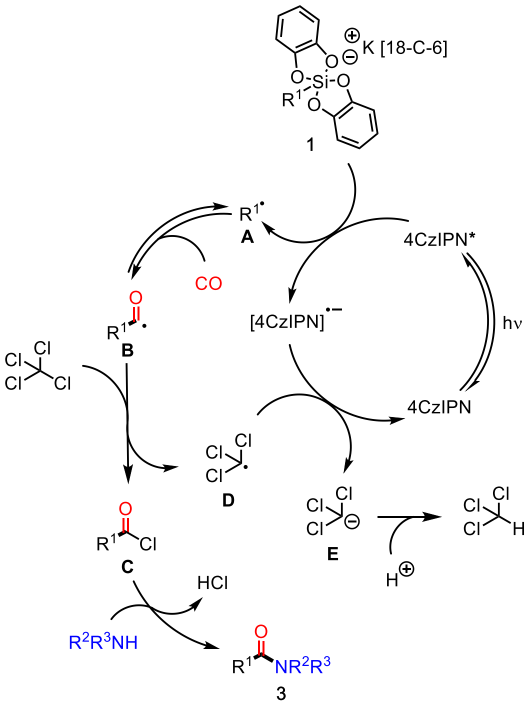
Scheme 2. Scope of the multicomponent reaction leading to amides **3**

the corresponding amide **3b** in 77% yield. Even the highly hindered *tert*-butyl silicate **1c** gave the corresponding amide **3c** in a satisfactory yield of 56%. The reaction of primary alkyl silicates **1d** and **1e** gave **3d** and **3e** in 78% and 61% yield, respectively. Knowing from these results that primary, secondary, and tertiary alkyl silicates worked well for this reaction, we next focused on the compatibility of various functional groups toward this process. The reaction of **1f**, bearing a sensitive epoxy ring was well tolerated and delivered a good yield of the corresponding amide **3f** (73%). A propyl silicate substituted by a pentafluorobenzene ring **1h** furnished the corresponding amide **3h** in 59% yield while perfluorohexyl-substituted ethyl silicate **1g** also gave the corresponding amide, albeit in low yield (34%). The amide product **3i**, bearing a nitrile functionality, was also obtained in low yield (31%). When the reaction of 5-hexenyl silicate **1j** was tested, an equimolar mixture of amides, uncyclized **3j** and cyclized **3j'**, were obtained in 47% total yield, which is consistent with our previous report on ketone synthesis.[13]

We then investigated the viability of a larger scope of nucleophile amines in this carbonylative amide synthesis. The results are also summarized in Scheme 2. The reaction of **1a** with the primary amine *n*-butylamine provided the desired amide **3k** in 36% yield and no double acylation was observed. This yield could be increased to 56% by using 5 equiv of *n*-butylamine. In the case of 2-aminoethanol as nucleophile, amide **3l** was obtained in 51% yield as the sole product. Of note, no addition of the less nucleophilic alcohol to form the corresponding ester was observed. Amide **3m** was obtained in 49% yield from **1a** and 2-phenylethylamine. We also checked if the reaction could occur when using a secondary amine. The reaction of di-*n*-propylamine with cyclohexylsilicate **1a** furnished amide **3n** in good yield (61%). More modest yields were obtained from morpholine (**3o**, 42%) and aniline (**3p**, 34%). Interestingly, however, the yield was substantially increased up to 84% of desired amide **3q** when the more nucleophilic *N*-methylaniline was used instead. In the case of the *N*-allyl-substituted aniline, the reaction was even more successful, leading to amide **3r** in an excellent yield of 89%.

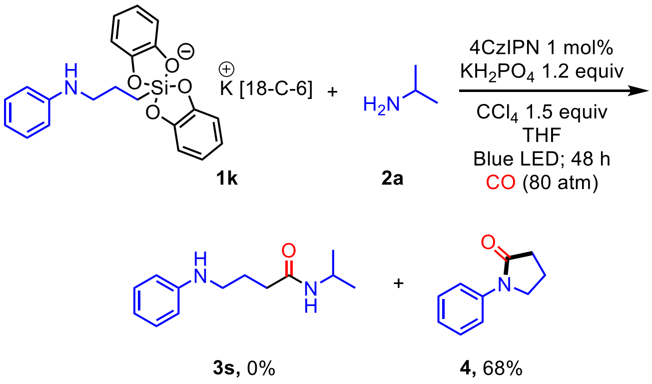
Based on our previous study[13] and literature reports,[12,16] a plausible mechanism is proposed on Scheme 3. The preliminary step is the excitation of the photocatalyst 4CzIPN by blue LED light. 4CzIPN*[18] has a long lifetime at the excited state (5.1 µs) and is also a very good oxidant ($E_{1/2}$(4CzIPN*/[4CzIPN]$^{\cdot-}$) = +1.59 V vs. SCE),[4b,19,20] which allows efficient single electron transfer from organosilicates (Eox < 1 V vs. SCE)[4d] to generate the reduced dye [4CzIPN]$^{\cdot-}$ and, after homolytic cleavage of the Si-C bond, the radical intermediate **A**.[4-8] C-centered radical **A** would react with CO to form the corresponding acyl radical **B**, which after chlorine abstraction from CCl_4, generates acyl chloride **C** *in situ* and radical intermediate **D**. An acyl chloride of type **C** was detected by ^1H NMR in the crude product of a reaction using n-hexyl silicate **1d** and conducted in the regular conditions except no amine was present.[21]

Acyl chloride **C** is then trapped by the amine to form the desired amide **3**. Furthermore, ^1H NMR monitoring of the crude mixture showed a chloroform peak suggesting us that $[4CzIPN]^{\cdot -}$ reduces radical **D** to its anionic form **E**, allowing as well the regeneration of the photocatalyst 4CzIPN in its ground state, and **E** would be protonated by KH_2PO_4 or by the protonated amide to form chloroform as by-product.



Scheme 3. Proposed mechanism

We then applied the present protocol to study the inter- vs intramolecular competition in the amide formation. Interestingly, when we used aniline bearing silicate **1k** in the presence of 2 equiv of isopropylamine **2a,** the intramolecular reaction occurred preferentially and only the pyrrolidinone **4** was obtained in 68% yield (Scheme 4).



Scheme 4. Synthesis of *N*-phenyl-γ-butyrolactam **4** from 3-(phenylamino)propane silicate **1k**.

Conclusion

In summary, we have achieved a metal-free synthesis of aliphatic amides from a photoredox-catalyzed radical carbonylation of alkylsilicates with CO in the presence amines, in which CCl_4 works as excellent mediator. Thanks to the use of a wide range of alkyl bis(catecholato)silicates and amines, a large scope of aliphatic amides could be obtained in a multicomponent process. We are now examining the feasibility of the formation of other acyl derivatives under photooxidative regimes as well as other multicomponent reactions.

Experimental Section

Please see the Supporting Information for general experimental considerations.

Typical procedure for the synthesis of silicates 1

To a stirred solution of catechol (10.05 mmol, 1.11 g) in dry methanol (20 mL) was added 18-C-6 (5.00 mmol, 1.32 g). After dissolution of the crown ether, the trimethoxycylohexylsilane (5.09 mmol, 1.04 g) was added, followed by a 30% solution of potassium methoxide in methanol (5.05 mmol, 1.18 g). The reaction mixture was stirred for 3 hours and the solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at -20°C overnight. The crystals were collected by filtration, washed with diethyl ether and dried under vacuum to afford silicate **1a** (2.44 g, 77%) as a light brown solid.

Synthesis of 4CzIPN

The 4CzIPN has been synthesized following a previous reported procedure.[1] To a 100 mL flask was added NaH (60% in mineral oil) (15.0 mmol, 606 mg) in THF (40 mL). Carbazole (10.0 mmol, 1.68 g) was added slowly to the mixture. After 30 min of stirring at room temperature the tetrafluoroisophtalonitrile (2.00 mmol, 406 mg) was added and the mixture was stirred at room temperature for 20 hours. A brown/yellow precipitate progressively appeared. The solid was successively washed with water and ethanol. The crude product was dissolved in the minimum of CH_2Cl_2 and crystallized by addition of hexane to give 4CzIPN as a yellow solid (1.17 g, 74% yield).

Typical procedure for the photoredox-catalyzed radical carbonylation of silicates with amines

In a stainless-steel autoclave was added potassium [18-crown-6] bis(catecholato)-cyclohexylsilicate **1a** (0.301 mmol, 189.7 mg), KH_2PO_4 (0.370 mmol, 50.4 mg) and 4CzIPN (1mol%, 0.003 mmol, 2.5 mg). THF was added (14 mL), followed by isopropylamine (0.595 mmol, 51 μL) and carbontetrachloride (0.455 mmol, 44 μL). The autoclave was flushed 3 times under CO atmosphere and the reaction mixture was irradiated with blue LEDs (425 nm) under 80 bar CO pressure at r.t. during 48 h. The reaction was diluted with diethyl ether (50 mL), washed with an aqueous saturated K_2CO_3 solution (20 mL x 2 times), water (20 mL x 2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified to afford *N*-isopropylcyclohexanecarboxamide **3a** (41.6 mg, 82%) as a yellow solid.

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FULL PAPER

Synthesis of Aliphatic Amides through a Photoredox Catalyzed Radical Carbonylation Involving Organosilicates as Alkyl Radical Precursors

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