Heterogeneous Visible-Light Photoredox Catalysis for α -Aminoalkyl Radical Additions, Allylations and Heteroarylations

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ABSTRACT: A protocol for the photooxidative activation of α -silylamines and α -amino acids for desilylative and decarboxylative additions, allylations and heteroarylations in the presence of graphitic carbon nitride (g-C₃N₄) was developed. The procedure has broad scope and provides the desired products in high yields. The heterogeneous nature of the g-C₃N₄ catalytic system enables easy recovery and recycling as well as the use in multiple runs without loss of activity. The photoredox catalyzed reactions can also be conducted in continuous photo flow fashion and scaled up to gram-scale. Thus, the stable and readily available polymeric g-C₃N₄ provides an alternative to homogeneous photosensitizers for the generation of valuable radical intermediates for applications in synthesis and catalysis.

KEYWORDS: Carbon Nitride, Visible-light photocatalysis, Heterogeneous photocatalyst, α -Aminoalkyl radical, Continuous flow

INTRODUCTION

During the last decades, homogeneous visible light photoredox catalysis using metal complexes or organic molecules as sensitizers has become a powerful tool for the development of new and valuable transformations in organic synthesis.¹ Nevertheless, the development of heterogeneous photoredox catalysis,² which exhibits the inherent advantage of easy catalyst separation and recyclability, is highly desirable and of great interest from the industrial point of view. The solid polymeric graphitic carbon nitride (g-C₃N₄)³ is readily accessible by the pyrolysis of inexpensive precursors including cyanamide, urea or guanidine,⁴ and shows an appropriate electronic band structure with a band gap of 2.7 eV⁵ which allows its use for a wide variety of applications in the area of water splitting optical sensing, and visible-light photocatalysis. So far, applications are mainly limited to photoredox oxidations⁶ and oxidative couplings⁷ under aerobic conditions. Inspired by the possibility to reductively activate O₂ for the generation of highly reactive superoxide radical anions ($\cdot\text{O}_2^-$) through a one-electron photoreduction, the application of g-C₃N₄ towards other reducible substrates such as alkyl halides or trifluoromethanesulfonyl chlorides has been accomplished.⁸

However, to the best of our knowledge, the application of g-C₃N₄ in photooxidation, for the generation of reactive α -aminoalkyl radicals has not been reported.^{9–11}

Figure 1. g-C₃N₄ as heterogeneous photoredox catalyst for the generation of α -aminoalkyl radicals generated by photooxidation.

Herein we report the application of g-C₃N₄ to the generation of α -tertiary- and α -secondary-aminoalkyl radicals from α -silylamines and α -amino acids, respectively (Figure 1) under visible light irradiation. In combination with different acceptors we demonstrate the excellent compatibility of g-C₃N₄ in several photoredox catalyzed transformations including desilylative and decarboxylative additions to α,β -unsaturated compounds, desilylative and decarboxylative allylation and desilylative heteroarylations. Notably, the g-C₃N₄ catalyst shows very good recyclability and can be reused in multiple runs. Due to its heterogeneous nature, the reaction can also be con-

ducted in a recyclable continuous flow photoreactor on a gram-scale.

RESULTS AND DISCUSSION

$g\text{-C}_3\text{N}_4$ was prepared by the pyrolysis of readily available and inexpensive guanidine hydrochloride according to a previously reported protocol (SI). Initial experiments focused on the application of $g\text{-C}_3\text{N}_4$ as heterogeneous photooxidation catalyst for the generation of α -amino radicals from silylamines. The desilylative addition of α -silylamine **1a** to 2-cyclohexenone **2a** was selected as model reaction.^{1b} After a systematic evaluation of the reaction parameters (see Supporting Information), we found that the reaction of **1a** and **2a** in the presence of $g\text{-C}_3\text{N}_4$ under visible light irradiation in methanol proceeds well, yielding the desired product **3a** in 95% yield (Table 1, entry 1).

Table 1. Optimization of the Reaction Conditions^a

entry	PC	base (x equiv.)	t (h)	yield (%) ^b
1	$g\text{-C}_3\text{N}_4$	CsF (2.0)	17	95
2	-	CsF (2.0)	30	-
3 ^c	$g\text{-C}_3\text{N}_4$	CsF (2.0)	30	-
4	TiO ₂	CsF (2.0)	30	-
5	BiVO ₄	CsF (2.0)	30	-
6	$g\text{-C}_3\text{N}_4$	-	30	-
7	$g\text{-C}_3\text{N}_4$	CsF (0.2)	17	90
8	$g\text{-C}_3\text{N}_4$	Li ₂ CO ₃ (0.2)	17	66
9	$g\text{-C}_3\text{N}_4$	Na ₂ CO ₃ (0.2)	17	70
10	$g\text{-C}_3\text{N}_4$	NaOAc (0.2)	17	77
11	$g\text{-C}_3\text{N}_4$	LiCl (0.2)	17	84
12 ^d	$g\text{-C}_3\text{N}_4$	CsF (2.0)	30	92

^aReaction conditions: **1a** (0.13 mmol), **2a** (0.1 mmol), $g\text{-C}_3\text{N}_4$ (10 mg), CsF (0.2 mmol), MeOH (1 mL), 12W blue LEDs. ^bYields determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. ^cNo light. ^dWhite light.

To verify the role of $g\text{-C}_3\text{N}_4$, control experiments were conducted. No conversion was observed in the absence of $g\text{-C}_3\text{N}_4$ or light, which unambiguously proved the catalytic activity of $g\text{-C}_3\text{N}_4$ (Table 1, entries 2 and 3). We also tested other classical heterogeneous photoredox catalysts such as TiO₂ or BiVO₄ which are often used in light-mediated oxidation reactions.^{2c,12} However, no reactivity was observed (Table 1, entries 4 and 5), demonstrating the exceptional photocatalytic effectiveness of $g\text{-C}_3\text{N}_4$ not only for the generation of α -aminoalkyl radicals through the photooxidation process, but also for oxidative quenching of the resulting radical intermediate to close the catalytic

cycle. Notably, the use of CsF as base also played a crucial role for this transformation as the reaction did not proceed in the absence of base (Table 1, entry 6). Use of substoichiometric amounts of CsF as well as evaluation of other bases did not result in further improvement.

Table 2. $g\text{-C}_3\text{N}_4$ Photocatalyzed Desilylative Addition of α -Silylamines^a

3a, 92%	3b, 90%	3c, 88%
3d, 51%	3e, 82%	3f, 81%
3g, 81%	3h, 75%	3i, 65%
3j, 74%	3k, 68%	3l, 83%
3m, 68%	3n, 81%	3o, 78%, 13:1 d.r.
3p, 88%	3q, 61%	3r, 71%
3s, R ³ = H, 96% ^b	3t, R ³ = OMe, 83% ^b	3u, R ³ = Me, 96% ^b
3v, R ³ = F, 92% ^b	3w, 88% ^b	

^aReaction conditions: **1** (0.26 mmol), **2** (0.2 mmol), $g\text{-C}_3\text{N}_4$ (20 mg), CsF (0.4 mmol), MeOH (2 mL), 12W blue LEDs. Yields after isolation. ^b11W white light, acetonitrile/H₂O (20/1) as solvent in the absence of CsF.

With the optimal reaction conditions in hand, the substrate scope of the $g\text{-C}_3\text{N}_4$ photocatalyzed desilylative addition of α -silyl amines was investigated (Table 2). Variation of the electronic properties of the aromatic ring of **1** (R^1 = aryl, R^2 = Me) had no effect on the reactivity and the products **3a-h** were obtained in good yields. The *N*-isopropyl and *N*-benzyl derivatives **ii** and **ij** as well as diaryl amine **ik** and *N*-trimethylsilylmethyl dihydroquinoline **il** were applicable in this reaction and the corresponding products **3i-l** were isolated in good to high yields. Next, a variety of α,β -unsaturated compounds was evaluated under the optimized conditions. The reaction of **1a** with 3-methylcyclohexenone, cyclopentenone and 2-methyl-cyclopentenone proceeded smoothly to give the corresponding products **3m-o** in 68-83% yield. 4H-chromen-4-one and furan-2(5H)-one also underwent the reaction well, affording the corresponding products **3p** and **3q** in 88 and 61% yield. Importantly, an acyclic ketone was also tolerated, providing the corresponding γ -amino ketone product **3r** in 71% yield. Moreover, acrylonitrile derivatives exhibited excellent reactivity, affording products **3s-w** in high yields (83-96%).

Motivated by the excellent activity of $g\text{-C}_3\text{N}_4$ in the desilylative additions, we questioned whether it would be possible to activate more easily available α -amino acids to generate secondary amine derived alkyl radicals through a decarboxylation process.^{1h}

Pleasingly, under similar reaction conditions, the decarboxylative addition of 2-(phenylamino)acetic acid **4a** to cyclohexenone **2a** proceeded smoothly to deliver the desired product **5a** in 79% yield (Table 3). In contrast, α -silyl-secondary-amines exhibited only moderate reactivity to give the corresponding product **5a** in 45% yield. Subsequently, the generality of the $g\text{-C}_3\text{N}_4$ photocatalyzed addition of α -amino acids was surveyed. Introducing substituents such as methyl, fluoro or chloro groups in the *para*-position of the benzene ring of **4a** did not considerably affect the yield of **5b-d**. 2-(Phenylamino)propanoic acid (**4e**) and 4-(methylthio)-2-(phenylamino)butanoic acid (**4f**) are also applicable in this reaction, giving the corresponding products **5e** and **5f** in 54% and 71% yield, respectively. Additionally, application of a series of cycloenones, 4H-chromen-4-one, furan-2(5H)-one and acyclic enone, delivered the corresponding products **5g-l** in good to high yields.

Next, we also examined the efficiency of $g\text{-C}_3\text{N}_4$ -photocatalytic desilylative allylation and decarboxylative allylation. Allylic sulfone **6a** was smoothly converted to the corresponding allylation products **7** and **8** in 83 and 74% yield, respectively (Scheme 1). Desilylative reaction exhibited higher reactivity. In a competition experiment, 1 eq. **6a** was reacted with 1 eq. **1a** and 1 eq. **4a**. The major desilylative product **7** (76% yield) was obtained along with trace amount of the decarboxylative product **8**.

Table 3. $g\text{-C}_3\text{N}_4$ Photocatalyzed Decarboxylative Addition of α -Amino Acids^a

$ \begin{array}{c} R^1 \quad R^2 \\ \quad \\ R^1\text{NH} - \text{CH} - \text{COOH} \quad + \quad R^3 \quad R^6 \\ \quad \\ H \quad R^4 \end{array} \xrightarrow[\text{CsF, MeOH}]{g\text{-C}_3\text{N}_4, \text{Blue LEDs}} \begin{array}{c} R^1 \quad R^2 \quad R^6 \\ \quad \quad \\ R^1\text{NH} - \text{CH} - \text{CH} - \text{CH} - R^5 \\ \quad \quad \\ H \quad R^3 \quad R^4 \end{array} $

5a , 79% (45%) ^b	5b , 75%	5c , 70%

5d , 71%	5e , 54%, 1:1 d.r.	5f , 71%, 1:1 d.r.

5g , 65%	5h , 78%	5i , 73%, 2.6:1 d.r.

5j , 68%	5k , 78%	5l , 53%

^aReaction conditions: **4** (0.2 mmol), **2** (0.26 mmol), $g\text{-C}_3\text{N}_4$ (20 mg), CsF (0.4 mmol), MeOH (2 mL), 12W blue LEDs. Yields after isolation. ^bYield obtained using the corresponding α -silyl-secondary-amine as radical precursor.

Scheme 1. $g\text{-C}_3\text{N}_4$ Photocatalyzed Allylations

Following the heterogeneous photoredox catalyzed desilylative and decarboxylative additions, we further attempted the desilylative heteroarylation^{1f} (Table 4). With respect to the scope in this coupling reaction, five-membered heteroaryl chlorides including benzoxazole, benzothiazole, and benzimidazole-derived scaffolds were found to function as suitable substrates, affording the corresponding α -heteroaryl amines in high yields (**10a-c**, 80-92% yield). Moreover, monocyclic thiazole **9d** was also well-tolerated, delivering **10d** in 72% yield.

Table 4. $g\text{-C}_3\text{N}_4$ Photocatalyzed Desilylative Heteroarylations.^a

^aReaction conditions: **1a** (0.4 mmol), **9** (0.2 mmol), $g\text{-C}_3\text{N}_4$ (20 mg), CsF (0.4 mmol), MeOH (2 mL), 12W blue LEDs. Yields after isolation.

To further illustrate the practicability of the heterogeneous photoredox catalyzed protocols, a recycling procedure was established. $g\text{-C}_3\text{N}_4$ was recovered after reaction and subsequently reused. As shown in Figure 2, the catalyst maintains its high photocatalytic activity when applied in the desilylative addition of α -silylamine **1a** to acrylonitrile **2u**.

Figure 2. Evaluation of the Catalyst Recycling.

Prompted by the result of good catalyst recyclability, we decided to conduct this reaction in continuous flow. Using a column, glass beads, silica gel and the $g\text{-C}_3\text{N}_4$ catalyst, we built a simple and recyclable continuous-flow photoreactor (Scheme 2; for details, see the Supporting Information).

After optimization of the flow reaction conditions, the model reaction shown in Table 1 could be successfully conducted in continuous flow even on a gram-scale, giving the desired product **3a** in 85% yield (1.1 g). Compared

to the batch reaction, the use of a continuous flow reactor resulted in shortening of the reaction time.

Scheme 2. Simplified scheme of the flow reactor. V = volume of the filled reactor, l = length of the filled column, d_{in} = internal diameter of the column, F = flow rate, t_r = residence time. 6 mmol-scale, 85% yield (1.1 g) of **3a**.

Regarding the reaction mechanism, owing to the structural and electronic properties of $g\text{-C}_3\text{N}_4$ with a band gap of 2.7 eV and a decisive bandgap adsorption at about 420 nm,^{3,5,13} visible-light irradiation leads to the efficient separation of photogenerated electron-hole pairs. One electron oxidation of α -silylamine or α -amino acid by the photogenerated hole of $g\text{-C}_3\text{N}_4$, followed by desilylation or decarboxylation process, generates an α -tertiary or α -secondary-aminoalkyl radical (see Figure S3 in the Supporting Information). Subsequently, the radical adds to the C=C bond of cyclohex-2-enone or allylic sulfone to form radical intermediates, which subsequently undergo one electron reduction by photogenerated electron of $g\text{-C}_3\text{N}_4$ and further protonation or loss of tosyl group, delivering the corresponding addition products or allylic amines and the regenerated neutral $g\text{-C}_3\text{N}_4$ catalyst. For the heteroarylation reaction, the α -tertiary-aminoalkyl radical adds to the heteroaryl chloride to form a nitrogen radical, which further undergoes one electron reduction and loss of Cl^- , affording the corresponding cross-coupling product. The base CsF traps the silyl cation and acts as Lewis base in the desilylative reactions. In the decarboxylative reactions, the reactive species are the carboxylate anions and the base plays the crucial role in their formation.¹⁴

CONCLUSIONS

In summary, we have demonstrated for the first time that the readily available $g\text{-C}_3\text{N}_4$ can act as an effective photoredox catalyst for desilylative and decarboxylative additions, allylations and heteroarylations. The newly established methods have a broad substrate scope, high yields and use mild reaction conditions. The heterogeneous nature of the reaction system enables the recovery and reuse of the catalyst without loss of reactivity. The

reaction can also be conducted in continuous flow fashion, even on a gram-scale using a simple and reusable continuous-flow photoreactor, which illustrates the practicability of this heterogeneous photocatalysis protocol. Importantly, the newly developed heterogeneous photooxidations may also be applicable to the recently established dual photoredox/metal catalysis protocols in that the often more expensive homogeneous photocatalyst can be replaced by polymeric carbon nitride.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures and full characterization of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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