Carbon Nitride Photoredox Catalysis Enables the Generation of the Dioxolanyl Radical for Conjugate Addition Reactions

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Carbon Nitride Photoredox Catalysis Enables the Generation of the Dioxolanyl Radical for Conjugate Addition Reactions

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ABSTRACT: Graphitic carbon nitride (g-C_3N_4) is used as photocatalyst in the Giese reaction of dioxolane and wide variety of electron-deficient olefins. The catalyst is shown to be reusable over five cycles with no changes in catalyst composition, morphology and characteristics were observed by scanning electron microscopy, elemental analysis, infrared spectroscopy, and powder X-ray diffraction.

Visible light photoredox catalysis has emerged as a powerful tool in synthetic chemistry over recent years.[1-3] The Harnessing of light and its conversion to chemical energy presents a tremendous opportunity to create sustainable methodology. The most common approaches prescribe transition-metal complexes based on [Ru] or [Ir] along with organic dyes. Recent studies demonstrate that it is increasingly possible to employ heterogeneous photocatalysts, such as polymeric graphitic carbon nitride (g-C_3N_4), in a range of reactions.[4-16] We have been interested in developing methods that enable convenient introduction of protected formyl units onto non-aromatic substrates.[17] Herein, we report the development of a photoredox-Giese reaction mediated by carbon nitride for the introduction of dioxolane as a formyl surrogate under metal-free conditions (Scheme 1). Irradiation of a mixture consisting of g-C_3N_4, dioxolane, and a wide range of Michael acceptors, such as ethylidene malonates, diesters, sulfones, ketones, imides, lactones, butynoate/propiolate, anhydrides, and Meldrum's acid derivatives, to afford the respective adducts.
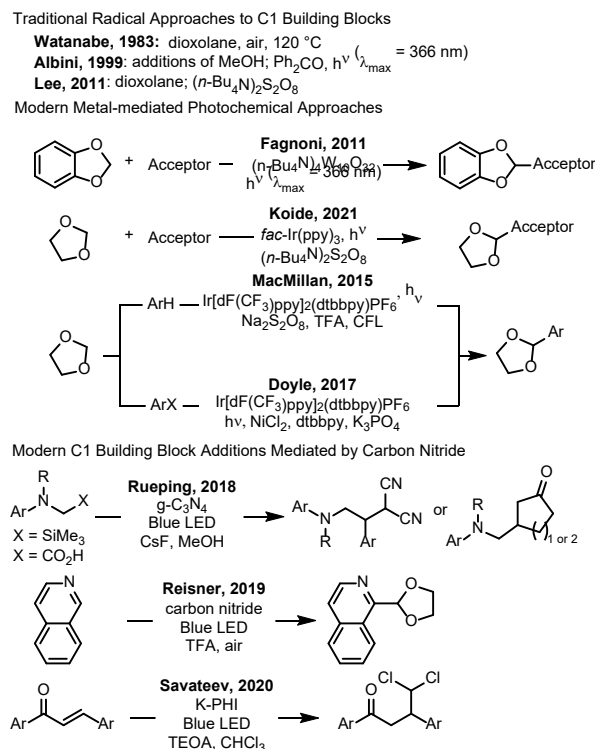
Scheme 1. Addition of Dioxolane to Acceptors Mediated by g-C_3N_4 under Blue LED Irradiation.
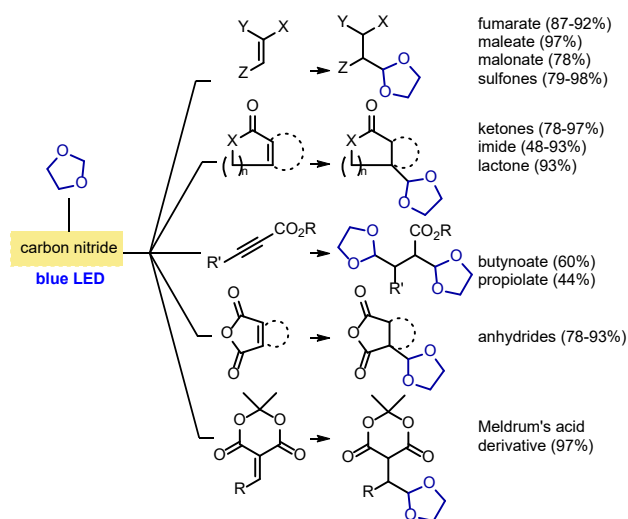
Methods for the introduction of aldehydes in organic molecules are highly sought after, as they are among the most versatile functional groups.[18-22] Industrially, approaches employing syngas (CO/H$_2$) are widely used and lead to direct formylation. These processes prescribe the use of hazardous gases at elevated temperatures and pressures, and thus typically require specialized equipment and precautions. A number of surrogates have been investigated as alternatives for use in research laboratory applications.[23-32]

1,3-Dioxolane is a commodity chemical annually produced in kilo-ton quantities as it is used in polymer synthesis as well as a cleaning agent and paint stripper. Earlier approaches to produce the dioxolanyl radical relied on ultraviolet light irradiation in the presence of ~0.5 equiv benzophenone as sensitizer, leading

Scheme 2: Dioxolane and other C1 Building Blocks.

Traditional Radical Approaches to C1 Building Blocks
Watanabe, 1983: dioxolane, air, 120 °C
Albini, 1999: additions of MeOH; Ph$_2$CO, h$^\nu$ (λ_{max} = 366 nm)
Lee, 2011: dioxolane; (n-Bu$_4$N)$_2$S$_2$O$_8$

Modern Metal-mediated Photochemical Approaches

Modern C1 Building Block Additions Mediated by Carbon Nitride

to adducts along with benzopinacol by-products (Scheme 2).[33] The use of excess (n-Bu$_4$)$_2$S$_2$O$_8$ has been reported to lead to generation of dioxolanyl radical that undergoes trapping by a variety of acceptors.[34] In 2011, Fagnoni reported that Michael acceptors underwent addition by dioxolane in the presence of tetrabutylammonium decatungstate salt as photocatalyst under UV irradiation.[35] Further investigations by Koide showed that dioxolane addition mediated by persulfate is activated in the presence of an iridium photocatalyst and visible light irradiation.[36] More recently, MacMillan[37] and Doyle[38] independently used iridium-based visible light photoredox catalysis to generate active radical species which were employed in Minisci-type reactions and in Ni-catalyzed coupling reactions with aryl chlorides, respectively. The more recent approaches have in common the use of metal-based photoredox catalysts.

Graphitic carbon nitride is obtained by thermal condensation of urea, dicyandiamide, or melamine. It is composed of linked tri-s-triazine units forming a conjugated two-dimensional polymer (Scheme 3).[39-44] The polymer possesses high thermal (up to 600 °C in air) and chemical stability (against acids, bases, and organic solvents). It also provides a material with electronic structure possessing a medium band gap of 2.7 eV, enabling visible light photoexcitation.

Scheme 3: Synthesis of g-C$_3$N$_4$.
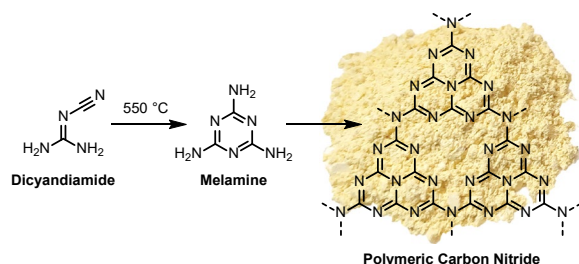
Carbon nitride and its modifications have been extensively studied in photochemical hydrogen generation, water oxidation, carbon dioxide reduction, and organic pollutant degradation; its use in organic synthesis is, however, still underexplored.[4,16,45] Its use has been largely focused on aryl coupling reactions as a photocatalyst often employing nickel co-catalysts. Rueping has recently reported the aminoalkyl radical addition mediated by graphitic carbon nitride photoredox catalysis (Scheme 2).[6] Reisner demonstrated a Minisci coupling of heteroarenes with alcohols, amides, and ethers with cyanamide functionalized carbon nitride.[46] Employing structurally related potassium poly(heptazine imide) (K-PHI), Savateev synthesized γ,γ-dichloroketones from the corresponding enones by addition of dichloromethyl radicals generated from chloroform.[47] In connection with our earlier investigations involving activation of Cu on g-C₃N₄ for Ullman-type amine coupling reactions,[48] we became interested in examining the use of g-C₃N₄ as a photoredox catalyst with dioxolane in the presence of electron deficient acceptors.

We began studying the Giese reaction with emphasis on simplicity and convenience. As previously reported, g-C₃N₄ was readily prepared by calcination of dicyandiamide at 550 °C.[48-51] In preliminary experiments, 2 mg g-C₃N₄ enabled the functionalization of 0.15 mmol diethyl fumarate (**2a**) in 5 mL 1,3-dioxolane (**1**) upon irradiation with blue LEDs (Table 1). These conditions proved particularly practical, as they require few reagents and only a quick workup. Owing to the heterogeneous nature of the reaction, g-C₃N₄ can simply be filtered off by means of a syringe filter or filter paper, depending on the reaction scale. Further purification includes concentration of the reaction mixture and flash column chromatography. Notably, no aqueous workup is needed, saving not only time but also tolerating water-labile functional groups.

Table 1: Exploration of Reaction Conditions[a]

| Entry	Variation from Standard Conditions	Yield[b]
1	None	84%
2	No g-C₃N₄	28%[c]
3	dark	0%
4	20 min irradiation, then dark	33%
5	Dioxolane:MeCN (1:3) as solvent	24%
6	0.1 M concentration[d]	43%
7	*fac*-Ir(ppy)₃ as photocatalyst[e]	78%
8	Ru(bpy)₃(PF₆)₂ as photocatalyst[e]	75%
9	[Acr-Mes](ClO₄) as photocatalyst[e]	40%

[a]Reactions were conducted on a 0.15 mmol scale. [b]Yields were determined by gas chromatography using dodecane (0.5 equiv.) as an internal standard. [c]Yield improved to 45% when irradiated overnight. [d]Reaction was performed on the same scale with less solvent. [e]1 mol% homogeneous photocatalyst loading.

Control studies showed that dioxolane can also react without additional catalyst, which has been previously shown for reactions under UV light.[52-54] It proceeded only sluggishly and even upon prolonged irradiation did not

achieve useful yields (entry 2). When left in the dark, the reaction completely shut down (entry 3). Irradiation of the reaction for 20 minutes gave product (33%, determined by GC); however, yield did not increase further upon standing in the dark further demonstrating the requirement for light (entry 4). It was observed that changing the solvent to a mixture of dioxolane and acetonitrile (entry 5), as well as increasing the concentration of **2a** to 0.1 M (entry 6) decreased the rate of the reaction. When compared to state-of-the-art homogeneous [Ir] or [Ru] photocatalysts, g-C$_3$N$_4$ demonstrated similar activity (entries 7 and 8). By contrast, it afforded better yield in comparison to [Acr- Mes](ClO$_4$) photocatalyst, which furnished adduct in 40% yield (entry 9).

We next set out to investigate the scope of the carbon nitride mediated Giese reaction. To ensure complete conversion of the starting materials, the reactions were run on lower concentrations (0.02 M) and the samples were irradiated for 12 hours unless noted otherwise. We found that fumarates and maleates react equally well (**3a** – **3c**, Scheme 4), whereby the more sterically encumbered dimenthyl fumarate reacted slower than its methyl and ethyl analogues. Malonate and Meldrum's acid derivatives **2d** and **2e** were also employed as starting materials with the corresponding acetals isolated in 78 and 97% yield, respectively. Cyclohexenone adduct **3f** and cylopentenone adduct **3g** were obtained in 88 and 78% yield. Interestingly, cyclohexenone (**2f**) reacts only slowly requiring longer reaction times (24 h) for full conversion. Chromones **3h** – **3j** proved amenable towards dioxolane radical addition, thereby showcasing that aryl chlorides and bromides were well tolerated which opens the possibility for further functionalization of the product in these positions. Interestingly, electron-deficient alkynes are also susceptible for addition of dioxolane, furnishing the doubly substituted esters **3k** and **3l**. Substrates containing lactone and imide groups were also tolerated, and the corresponding products (**3m** – **3o**) were obtained 48 to 93% yield. Vinyl sulfones also underwent radical addition of dioxolane furnishing **3p** and **3q** (98 and 79% yield).

Scheme 4: Substrate scope.
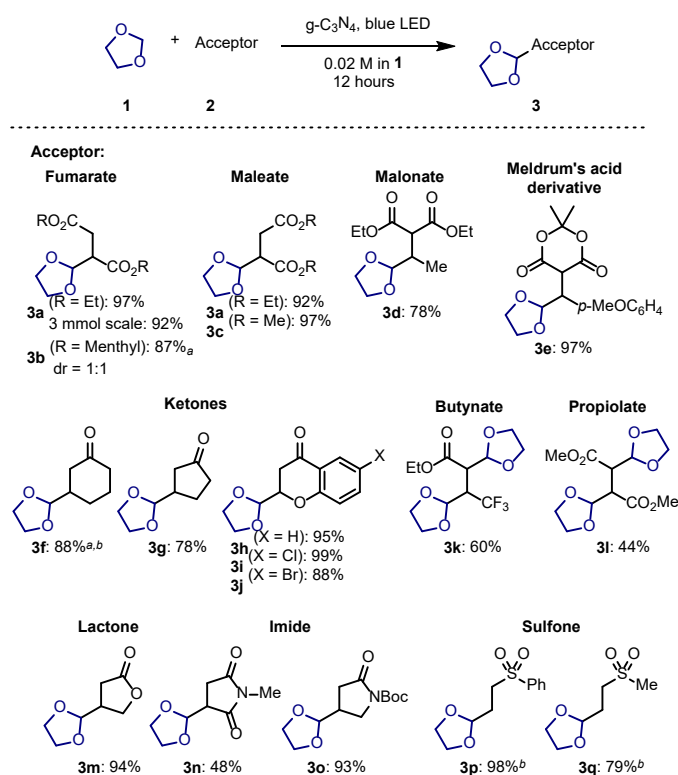
Reaction conditions: dioxolane (15 mL), olefin acceptor (0.3 mmol), g-C$_3$N$_4$ catalyst (5 mg), blue LED for 12 h. The yields correspond to isolated yields. [a]The reaction mixture was irradiated for 24 hours. [b]Reaction was performed on a 0.2 mmol scale.

A particularly interesting class of acceptors are carboxylic acid anhydrides.[55-58] While their highly electrophilic nature facilitates addition reactions to these substrates, it also makes them more susceptible to subsequent reactions such as hydrolysis.[59] Interestingly, substrates, such as **2r** and **2s** were also well-tolerated in the reaction (Scheme

5). Thus, the addition of dioxolane mediated by g-C$_3$N$_4$ furnished adducts **3r** and **3s** in 78 and 93% yield, respectively. It is important to note that because the work-up procedure is a simple filtration and does not prescribe aqueous wash the anhydride products are conveniently isolated.

Scheme 5: Reactions with Anhydrides.
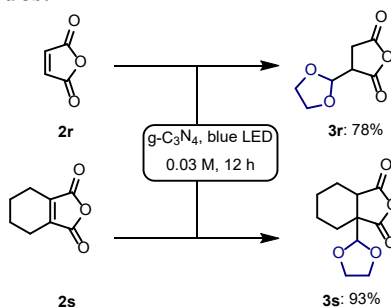
We next studied the stability of the photocatalyst by carrying out investigations in which g-C$_3$N$_4$ was recycled and analyzed. The addition reactions of dioxolane (**1**) to 3 mmol diethyl fumarate (**2a**) under blue LED irradiation for 14 h were conducted multiple times with reuse of the same carbon nitride. Filtration of the reaction mixtures allowed recovery of solid catalyst, which in turn was washed with ethyl acetate, dried under vacuum at ambient temperature, and reused. The yield after each cycle was determined by GC with dodecane as internal standard. As shown in Figure 1, the yield of **3a** averages to 91±2% over the course of five catalytic cycles.

The outcome of the recycling experiment encouraged us to evaluate the physical properties of fresh and recovered g-C$_3$N$_4$. Catalyst morphology was examined by scanning electron microscopy (SEM) as shown in Figure 2a-c. Comparison of the images for fresh catalyst in Figure 2a with catalyst isolated after one (Figure 2b) and five (Figure 2c) reaction cycles show that rough and coarse texture has not been altered over the sequence of transformations. Elemental analyses (C, N, and H) of the recovered graphitic carbon nitride at the same time points further substantiate the stability of the material (Figure 2d) with no major changes in composition observed.

The structural integrity of the catalyst was corroborated by FT-IR spectroscopic analysis (Figure 2e).[60] The signature breathing mode of triazine units was retained at 800 cm^{-1}, along with multiple bands between 1200 and 1600 cm^{-1}, corresponding to characteristic *N*-heterocycles. It is noteworthy that the vibrations above 3000 cm^{-1} are retained, characteristic for secondary and primary amine N–H stretching vibrations. These occur on the surface of g-C$_3$N$_4$ and thereby are potentially susceptible to modification over the course of the reaction. The fact that these are unchanged further highlights the stability of g-C$_3$N$_4$.
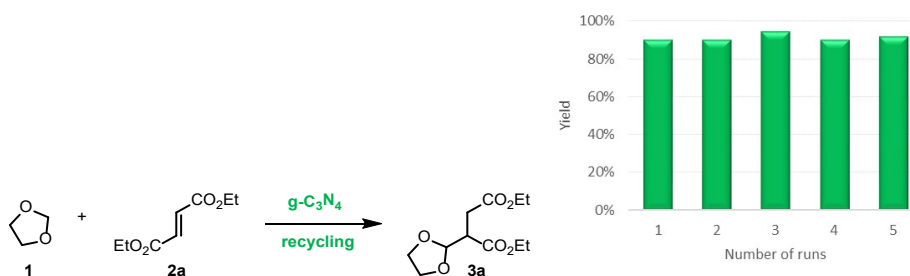
Figure 1: Evaluation of g-C$_3$N$_4$ recycling. Reactions were run on a 3 mmol scale for 12 h. Yields were determined by GC with dodecane (0.5 equiv.) as an internal standard.
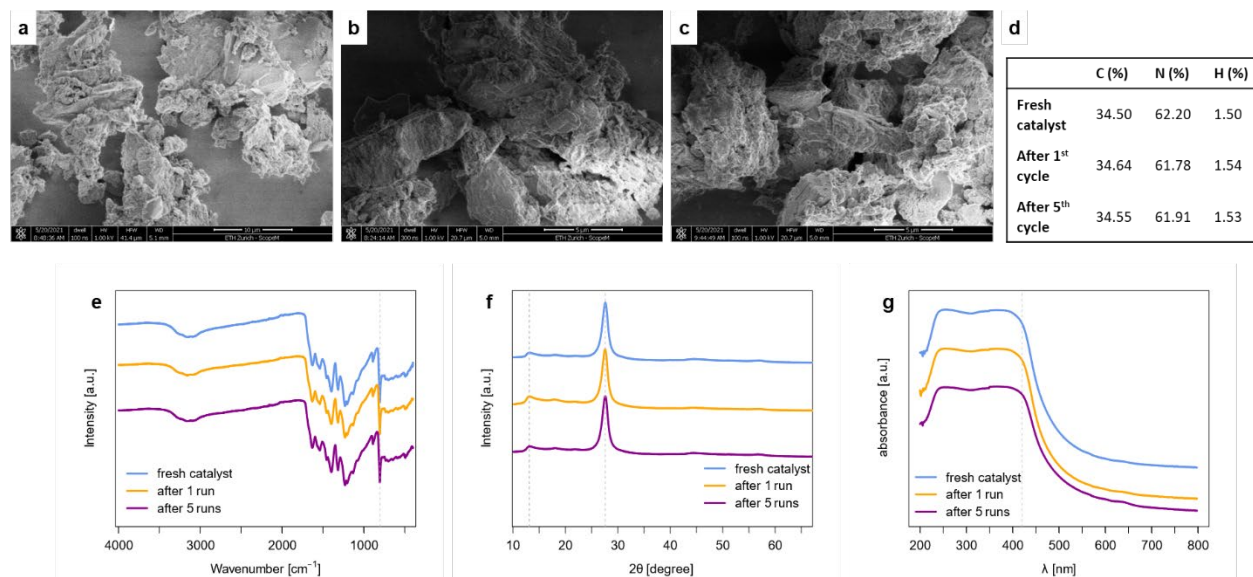
Figure 2: Analysis of new and recovered g-C$_3$N$_4$. Top: (a) SEM images of the fresh catalyst, (b) after one cycle, and (c) after five cycles; (d) elemental analysis; (e) FT-IR spectra, and (f) powder X-ray diffraction pattern, and (g) UV-Vis absorption spectra of the fresh and recycled catalyst.

The powder X-ray diffraction (XRD) patterns of g-C$_3$N$_4$ isolated from various runs in the recycling experiments are shown in Figure 2f. In all three samples, the catalyst displays two distinct peaks at 13.1 ° and 27.6 ° which is consistent with previously reported values.[61] The former peak corresponds to the (100) plane, indicating an in-planar repeat motif with a spacing of 6.74 Å. The latter, main peak is attributed to the (002) plane and originates from the stacking of the conjugated aromatic system with 3.23 Å. UV-Vis absorption spectra (Figure 2g) for fresh and recycled materials show the typical absorption patterns with a strong band gap adsorption at about 420 nm which is consistent with the pale yellow color. Taken together, the comparison of characterization data between the fresh and recycled g-C$_3$N$_4$ clearly demonstrates the durability and stability of the heterogeneous organic semiconductor photocatalyst.

In summary, we have demonstrated the use of g-C$_3$N$_4$ as a photocatalyst in the Giese reaction of dioxolane to a wide variety of electron-deficient olefins. This report represents the first use of graphitic carbon nitride for the convenient generation of dioxolanyl radical for conjugate addition reactions. The transformations constitute the synthetic equivalent of formyl radical additions in protected form. In comparison to extant methods, the approach we describe uses inexpensive g-C$_3$N$_4$ as an alternative to metal catalysts, such as [Ir] or [W]. Following complete conversion, simple filtration of the heterogeneous mixture cleanly removes the graphitic carbon nitride as the only other component of the reaction. The stability of the catalyst was investigated, and it was shown that the activity remains constant over five cycles and that no changes in catalyst composition, morphology and characteristics were observed by scanning electron microscopy, elemental analysis, infrared spectroscopy, and powder X-ray diffraction.

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