Photochemistry Hot Paper

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A Visible-Light-Mediated Synthesis of Carbazoles**

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Carbazole, discovered over 100 years ago,[1,2] is a privileged heterocyclic motif whose electronic and structural features have allowed its derivatives to find numerous applications. In addition to its abundance in natural products[3] and bioactive molecules,[4] carbazole has been a key motif in the development of organic light-emitting materials because of its wide band gap, high luminescent efficiency, and flexibility to modify its parent skeleton.[5] It has been found to be particularly useful in the preparation of highly efficient light-emitting[6] and charge-transporting/host materials.[7]

Recently, catalytic transition-metal-based syntheses of carbazoles, involving oxidative pathways through N activation, have become increasingly attractive (Figure 1). These

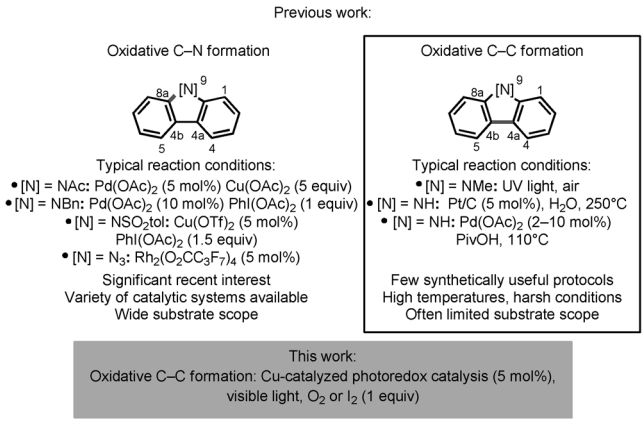

Figure 1. Synthetic strategies toward carbazoles.

synthetic methods utilize the formation of a C–N bond (C8a→N9) as the final step in the formation of the carbazole nucleus. Such oxidative pathways typically exploit a Pd- or Cu-based catalyst system in combination with a stoichiometric oxidant (either Cu salts or hypervalent iodine reagents) and have been used with a wide variety of substrates.[8] Disappointingly, relatively little progress has been made in the alternative retrosynthetic disconnection of a C–C bond (C4a→C4b) for the synthesis of carbazoles from diarylamines. In contrast to the C–N bond formation strategies, only one oxidative Pd-catalyzed C–C bond-forming route toward carbazoles has been reported with a synthetically useful substrate scope, albeit with high reaction temperatures and under highly acidic conditions (PivOH as solvent).[9a] While other C–C bond-forming strategies, such as an oxidative Pt-catalyzed C–H activation[9b] and a UV-light-mediated Mallory-type reaction,[10,11] have been described, the methods have not been further developed into robust synthetic methods.

Photoredox catalysis[12] for oxidative C–C bond coupling would be an attractive synthetic method for the synthesis of carbazoles from the corresponding di- or triarylamines, and would benefit from direct access to these amines through relatively mild cross-coupling methods.[13] When compared to other oxidative C–C bond-forming routes to carbazoles, the photoredox strategy would employ lower temperatures and avoid the use of high-energy UV light. Herein, we describe a photoredox oxidation, utilizing visible light and a continuous-flow strategy to transform arylamines into functionalized carbazoles.

We initially used the common sensitizer $[Ru(bpy)_3](PF_6)_2$ to promote the synthesis of carbazoles from di- or triarylamines (Table 1, entries 1 and 2). While no reaction was observed with diphenylamine (**1**) as substrate,[14] triphenylamine (TPA, **2**) was converted to **4** to some extend (27% yield of isolated product). We next turned our attention to Cu-based complexes that have been previously reported as sensitizers in photoredox transformations and in which the bisphosphine and diamine ligands influence the photophysical properties of the sensitizers (Table 1).[15] In addition to the low cost of these complexes, they can be rapidly screened using an in situ synthesis.[15] The investigated Cu^I-based sensitizers were formed in situ by sequential addition of a bisphosphine ligand, such as Xantphos, and a diamine ligand, such as 2,9-dimethyl-1,10-phenanthroline (dmp), to a $[Cu(MeCN)_4]BF_4$ precursor to afford Cu-based complexes, such as **5**. The Cu-based sensitizer **5** (formed in situ) catalyzed the formation of *N*-phenyl carbazole **4** from **2** in 56% yield (Table 1, entry 3). The reaction was conducted in the dark at reflux, to examine whether any thermal activation was possible,[16] but formation of **4** was not observed. Utilizing other phosphine or amine ligands for the sensitizer, such as combinations of DPEphos **7** or the diamine 2,2′-bipyrazine (bpz, **9**),[17] had no beneficial effect on the reaction (Table 1, entries 5–7). Finally, the reaction was performed for 14 days under optimized conditions, resulting in carbazole **4** in an excellent yield of 85% (Table 1, entry 5). Despite the promising yields obtained in the synthesis of carbazole **4**, the long reaction times prohibited a time-efficient screening for optimized reaction conditions or an investigation of the

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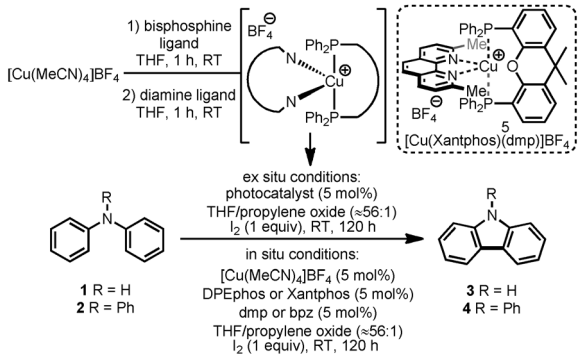
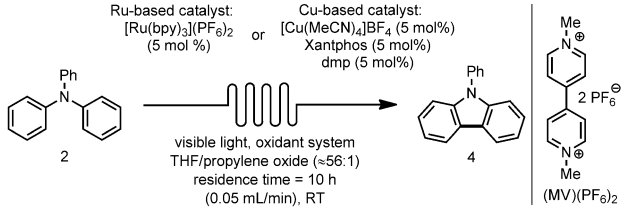
Table 1: Optimization of photocyclization of aryl amines to carbazoles.



Entry	Photocatalyst	R	Yield [%]	Recovered **1** or **2** [%]
1	$[Ru(bpy)_3](PF_6)_2$	H	0	>99
2	$[Ru(bpy)_3](PF_6)_2$	Ph	27	69
3[a]	$[Cu(Xantphos)(dmp)]BF_4$	Ph	56[b]	44
4[c]	$[Cu(Xantphos)(dmp)]BF_4$	Ph	85	0
5	$[Cu(DPEphos)(dmp)]BF_4$	Ph	14	61
6[a]	$[Cu(Xantphos)(bpz)]BF_4$	Ph	32	40
7[a]	$[Cu(DPEphos)(bpz)]BF_4$	Ph	30	47

Unless stated otherwise, reactions were performed using the discreet preformed catalyst. [a] Catalyst formed in situ. [b] Repeating the reaction at reflux instead of using visible light did not afford any product. Purging the mixture with N_2 before and during the reaction lowered the yield to 24%. [c] Reaction was left for 14 days. bpy = 2,2′-bipyridine.

Table 2: Optimization of the photocyclization of arylamines to carbazoles using a continuous-flow reactor.



Entry	Catalyst system	Oxidant system	Yield [%]	Recovered **2** [%]
1	Cu	I_2 (1 equiv)	75	0
2	Cu	O_2 (1 atm)	55	3
3	Cu	$(MV)(PF_6)_2$ (15 mol%) O_2 (1 atm)	65	0
4	Ru	I_2 (1 equiv)	53	14
5	Ru	O_2 (1 atm)	16	27
6	Ru	$(MV)(PF_6)_2$ (15 mol%) O_2 (1 atm)	22	21

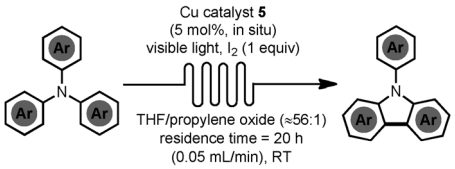
[a] In the absence of light, 94% of **2** was recovered. [b] In the absence of Cu-based catalyst and with an excess of I_2 (5 equiv), **4** was isolated in only 16% yield (61% of **2** was recovered).

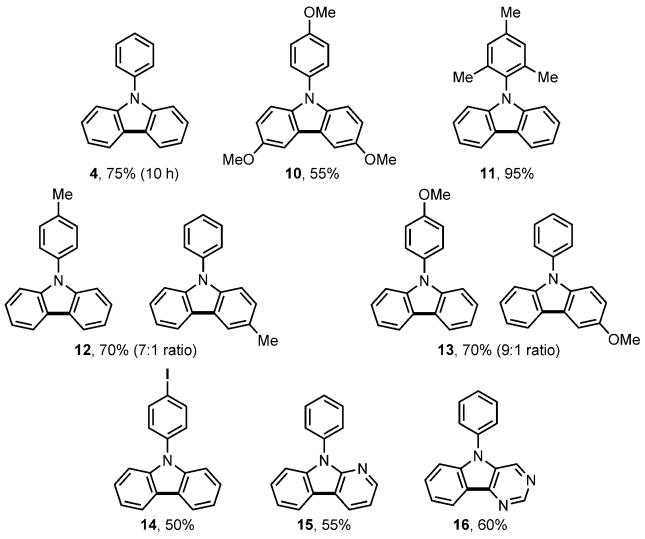
substrate scope. Consequently, photoreactions in a batch reactor (round-bottom flask) were abandoned and replaced by reactions conducted in a continuous-flow reactor.

The most important advantages of using a continuous-flow reactor for synthetic photochemistry[18] is the ability to dramatically increase the exposure of the reaction mixture (surface area) to ambient light or a focused-light source. During the optimization of the continuous-flow reaction, both the Cu-based sensitizer **5** (formed in situ) and the Ru-based sensitizer $[Ru(bpy)_3](PF_6)_2$ were surveyed with various oxidant systems (Table 2). In addition, the flow rate was chosen to target a residence time of 10 hours (0.05 mL min^{-1}, interior diameter of tubing 0.5 mm, a 12-fold reduction in reaction time from the batch reactor). The transposition of the reaction conditions from batch to continuous flow for the synthesis of **4** from **2** proceeded smoothly with Cu-based sensitizer **5** to afford carbazole **4** in 75% yield of isolated product (3.3 mg h^{-1}; Table 2, entry 1). The oxidant (I_2) could be replaced by an O_2 atmosphere, but with slightly lower yields (55% yield of isolated carbazole **4**; Table 2, entry 2). The cyclization of **2** was also performed with methyl viologen (MV) derivative $MV(PF_6)_2$ as a catalytic oxidant (Table 2, entry 3), whose use with Ru-based sensitizers has been well documented.[19] When the photocatalytic formation of **4** was investigated with $MV(PF_6)_2$, O_2, and Cu-based sensitizer **5**, **4** was isolated in 65% yield. When the Ru-based sensitizer was used with I_2 as oxidant, **4** was isolated in a 53% yield (Table 2, entry 4). Once again, switching to O_2 or $MV(PF_6)_2$ and O_2 afforded the product in lower yields, and recovered starting material **2** when compared to I_2 as oxidant system (Table 2, entries 5 and 6).

With these optimized conditions in hand, with which the model triphenylamine afforded the desired carbazole **4** in 75% yield (Table 2, entry 1), the scope of the synthesis of carbazoles was investigated (Table 3). Assuming an oxidative mechanism, electron-rich triarylamines were initially

Table 3: Synthesis of carbazoles from triarylamines.





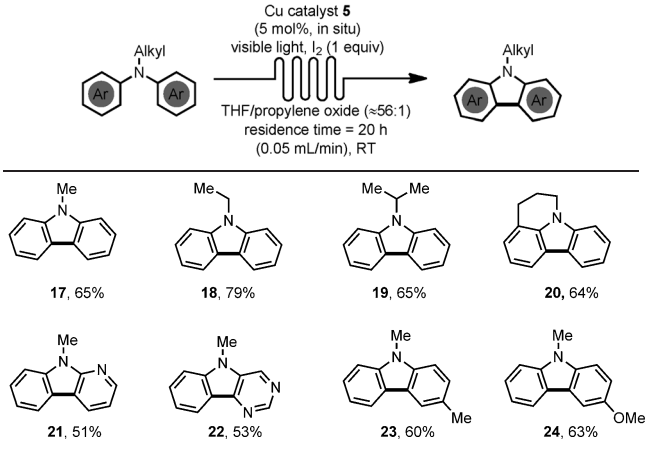
explored. The symmetrical carbazole **10**, which bears three methoxy groups, was isolated in good yield (55%), but the formation of some unwanted by-products was also observed (very electron-rich triarylamines with low oxidation potential, such as derivative **10** (0.52 V vs. SCE), could undergo dimerization, oligomerization, or other unwanted oxidation pathways). Photoredox cyclization afforded the mesityl-substituted carbazole **11** in excellent yield (95%).

Next, the photocyclization of unsymmetrical substrates was investigated. The photocyclization of *N*-tolyl- and *N*-anisyl-substituted derivatives afforded the desired isolated carbazoles **12** and **13** in identical yields of 70%. Interestingly, the carbazoles **12** and **13** were isolated as constitutional isomers in a ratio of 7:1 and 9:1, respectively. In the major isomers, the electron-rich *N*-tolyl and *N*-anisyl rings were not incorporated in the carbazole nucleus, but were instead in an "*exo*" position to the carbazole skeleton. Similar selectivity was observed in the photocyclization of an iodine-containing triarylamine, where the corresponding carbazole **14**, in which the iodide substituent provides a convenient handle for further functionalization, was isolated in 50% yield.

In contrast, the synthesis of carbazoles with precursors that contain electron-poor heterocyclic aromatic groups afforded the corresponding carbazoles as a single constitutional isomer in which the heteroaromatic ring was incorporated into the carbazole framework. Gratifyingly, the pyridine-containing carbazole **15** and the pyrimidine-containing carbazole **16** were isolated in good yields of 55%[20] and 60%, respectively, despite the fact that the inclusion of nitrogen atoms in the aromatic rings of diphenylamines increases their oxidation potentials.[21] More detailed and thorough mechanistic and experimental work is necessary before the origins of the selectivity in the photocyclization can be properly elucidated.

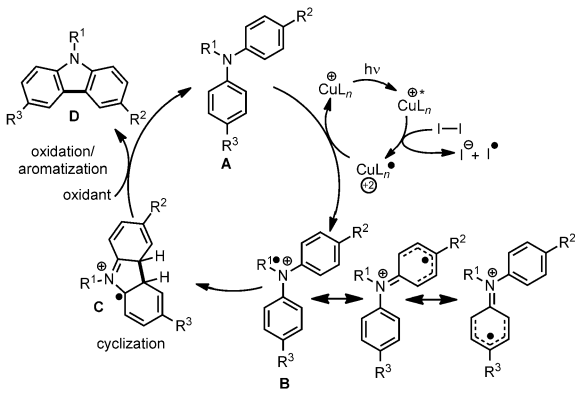
The synthesis of *N*-alkyl-bearing carbazoles was also investigated using the photoredox process catalyzed by Cu-based sensitizer **5** (Table 4). Although the oxidation potential of *N*-methyl-*N*,*N*-diphenylamine is slightly lower (0.84 V vs. SCE) than that of **2** (0.98 V vs. SCE),[22] we expected that the Cu-based sensitizer **5** would promote the oxidation of *N*-methyl-*N*-*N*-diphenylamine.[23] The cyclization of this compound under the optimized conditions led to *N*-methyl-substituted carbazole **17** in 65% yield, and demethylated carbazole was not observed.[24]

Table 4: Synthesis of carbazoles from diarylamines.



The cyclization of other *N*-alkyl-bearing diarylamines was also examined. Both *N*-ethyl- and *N*-isopropyl-bearing carbazoles were isolated in good yields: **18** was obtained in 79% yield and **19** in 65% yield.[25] The photocyclization to form complex tetracyclic heterocycles was also investigated, and polycyclic carbazole derivative **20** was isolated in 64% yield (23% of the starting amine was also recovered). The synthesis of unsymmetrically substituted carbazoles was also possible. The 3,9-dimethyl carbazole **23** was isolated in 60% yield. Similarly, 3-methoxy-9-methylcarbazole **24** was isolated in 63% yield. In addition, the synthesis of heterocyclic motifs was demonstrated. The *N*-methyl α-carboline derivative **21** and the pyrimido[5,4-b]indole derivative **22** were isolated in 51% and 53% yield, respectively.

A possible mechanism for the conversion of an arylamine **A** into a representative carbazole **D** is outlined in Scheme 1. The excited Cu-based sensitizer $[Cu(Xantphos)(dmp)]^{+*}$ could promote the reduction of I_2 to generate the radical



Scheme 1. Possible mechanism for the photoredox cyclization of aryl amines to carbazoles.

dication $[Cu(Xantphos)(dmp)]^{+2}$. Subsequent oxidation of the di- or triarylamine by single-electron transfer (SET) would afford the radical cation **B**.[26] It is possible that such a radical could exist as a result of delocalization throughout the pendant aromatic substituents. The preference for the radical to be localized in one or another aromatic ring (labeled with the substituents R^2 and R^3, Scheme 1) could be responsible for the observed selectivities for different constitutional isomers (Table 3). It should also be noted that under electrochemical oxidation conditions, unstable radical cations such as **B** often participate in an irreversible dimerization and loss of protons to form dimers and oligomeric materials.[27] In contrast, the photoredox cyclization reported herein preferentially proceeds through intramolecular C–C bond formation (**B**→**C**), and a second oxidation via an iodide radical ($I^{\bullet}\rightarrow I^{-}$); molecular oxygen or iodine would be necessary for re-aromatization. The oxidation could be mediated by the sensitizer or by another equivalent of the terminal oxidant. Such an oxidative

quenching mechanism[28] could be supported to a certain extend when considering the relatively similar yields obtained in both the cyclizations of **2** using O_2 and $MV(PF_6)_2$ as alternate oxidants (Table 2, entries 2 and 3). The latter oxidant is well precedented to act in oxidative quenching photoredox processes.[19]

The Cu-based sensitizer $[Cu(Xantphos)(dmp)]BF_4$ has been exploited in the development of a visible-light-mediated photoredox synthesis of carbazoles. The novel photochemical protocol allows the synthesis of carbazoles through C–C bond formation, which remains an underexplored synthetic route to carbazoles compared to other C–N bond-forming strategies. The reaction rates were greatly accelerated through the use of continuous-flow conditions. Triarylamines could be converted to *N*-aryl-bearing carbazoles (50–95%), and a variety of tertiary diarylamines could be converted to *N*-alkyl-bearing carbazoles (51–79%). A variety of interesting carbazoles could be prepared, including some heterocyclic skeletons that have found use in medicinal chemistry. While a more detailed photophysical evaluation of the Cu-based sensitizer **5** is needed before direct comparisons with popular Ru-based systems can be made, this study emphasizes one advantage of the Cu-based systems. In contrast to the well-defined Ru-based catalysts, complexes such as **5** can be rapidly screened using an in situ synthesis, and modification of the bisphosphine and diamine ligands have been shown to dramatically alter the photophysical properties of the resulting complex.[15] The ability to quickly prepare sensitizers with varying properties may accelerate further discoveries in the area of photoredox catalysis. Future work is aimed at developing improved sensitizers for the synthesis of heterocycles, and obtaining more detailed mechanistic data, including photophysical data on the Cu-based sensitizers, quenching experiments, as well as investigating issues of selectivity in the cyclization of complex substituted systems.

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