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PAPER

Visible-Light-Promoted Intramolecular C–H Amination in Aqueous Solution: Synthesis of Carbazoles

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An effective and operationally simple protocol is reported for the synthesis of versatile carbazoles. With water as co-solvent, visible-light rather than various metals is used to facilitate conversion of readily available 2-azidobiphenyls under mild conditions. Various functionalized bioactive natural alkaloids, such as glycoborine, clausine C, clausine L, clausine H and clauszoline K were synthesized efficiently with nitrogen as sole byproduct. The reaction could be performed in water, acidic or alkaline buffer solutions, showing its potential for applications in biochemistry.

Introduction

The carbazole structural unit occurs in a large number of biologically active natural and synthetic compounds, pharmaceutical ingredients,[1] and organic functional materials [2] (Figure 1). Protocols to access these *N*-heterocycles have relied on transformations of pre-existing functional groups,[1a-c, 3] which can result in some unnecessary steps to generate the functionalized starting materials. Recent efforts in the synthesis of carbazoles to circumvent this functional group manipulation have made great achievements.[3,4] One of the simplest and most straightforward approaches is the catalytic dehydrogenative C-H/N-H coupling of 2-aminobiphenyls.[5] Either transition-metal catalysts or oxidants are necessary, which reduces the functional group tolerance due to the tight coordination ability of transition metals or the further oxidation reactions.

Azides as amino group sources in C–H amination have unique advantages,[6] such as ease of preparation, performance under non-oxidative and non-basic conditions, and generation of N_2 gas as the sole by-product. Thus, intramolecular C–H amination of 2-azidobiphenyls has become one of most important green methods for the synthesis of N–H carbazoles (Scheme 1A).[7-11] Through intrinsically prone to decomposition, 2-azidobiphenyls can be directly transformed into carbazoles at high temperature but this wastes power and has low functional group tolerance (Method a).[7] Decomposition by means of UV[8] and laser flash[9] irradiation have also been reported, but these publications focused on mechanistic studies and failed to put the method into practice because of the impediments of the harsh reaction conditions, unavoidable side products like diazo and ring-opened compounds (Method b). Recently, various transition-metal catalytic methods instead of high temperature heating or UV have been well developed but any noble metal must be carefully removed from the final product prior to biological studies and the tight coordination ability of transition metals reduces the functional group tolerance (Method c).[10] In our continuing research on C–H amination reactions[12] with water as solvent,[10h,13] water plays a unique role, including promotion of C–H activation,[13] assisting the absorption of the acidic side products[13a] and an unusual reaction selectivity[13b]. In this paper, we report a visible-light-promoted reaction with water as co-solvent for the synthesis of versatile carbazoles from 2-azidobiphenyls with high yield, good tolerance of functional groups, wide

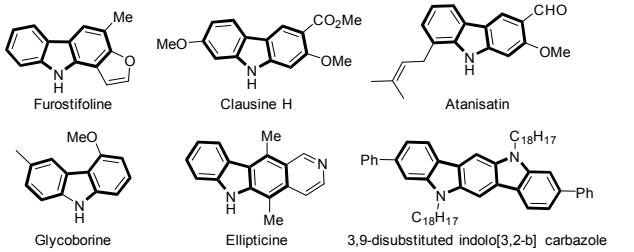

Figure 1. The carbazole motif in biologically active alkaloids and functional materials

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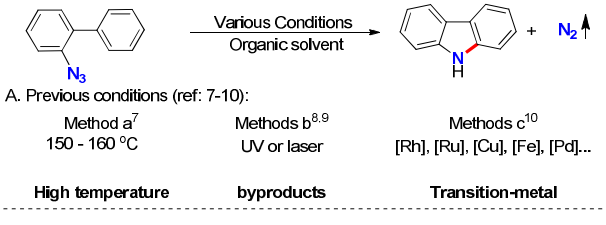
applications and N_2 as essentially the only by-product (Scheme 1B).[14,15]

Results and discussion

We began our investigation by screening the substrate, 2-azidobiphenyl in the presence of a fluorescent lamp as a source of visible light (Table 1).[8i] The initial results were unsatisfactory, because either the low yield or the side products were produced [8,9] under different organic solvents (entries 1-6). A clean reaction was achieved in the presence of water as the solvent (entry 7). Water has not been used previously in the photodecomposition reactions of azides. Under these conditions, carbazole (**2a**) is obtained from **1a** in 45% yield.

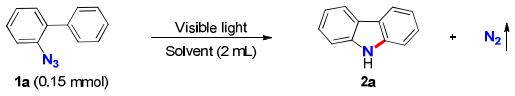


Scheme 1. Synthetic methods for carbazoles from 2-azidobiphenyls

Analysis based on ^{1}H NMR revealed that 54% of starting material (**1a**) was left unchanged. However prolongation of the reaction time or changes in the power of the irradiation failed to improve the yield (entries 8-9) possibly because of the poor solubility of **1a** in water. Screening a variety of water co-solvents (entries 10-13), revealed that a water/acetone mixture, assisted by of silica gel[16] gives yields as high as 80% (entries 14-16). Under these conditions, side-products such as diazo or ring-opened products which are usually unavoidable in photochemistry,[8] were not found. **2a** was not observed without visible light irradiation (entry 17).

With the optimized reaction conditions, we next explored the scope and generality of this method (Table 2).[17] Various substrates with a substituent in the azidophenyl ring were examined. Substrates containing either electron-donating groups (EDG) (**2b**-**d**) or electron-withdrawing groups (EWG) (**2e**-**i**) in the azidophenyl ring reacted smoothly under the standard

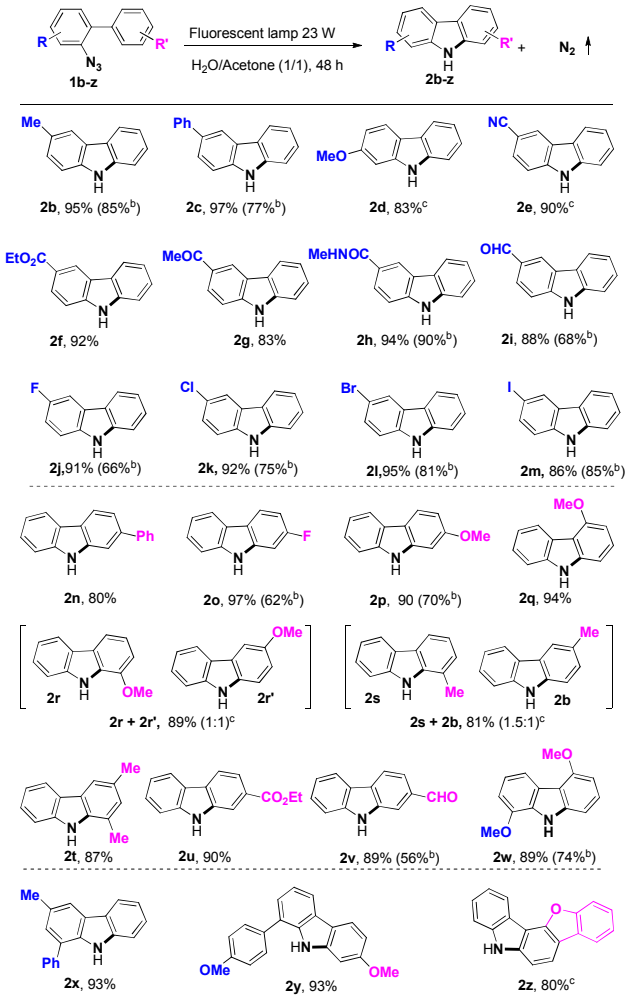
Table 1. Optimization of Reaction Conditions. [a]



Entry	Solvent	Time(h)	Yield [%][b]
1	Toluene	18	28
2	CCl_4	18	44
3	MeOH	18	49
4	MeCN	18	40
5	THF	18	60
6	DMF	18	42
7	H_2O	18	45(54)
8	**H_2O**	**36**	**60(39)**
9[c]	H_2O	36	45(54)
10[d]	H_2O/Acetone = 1/1	36	75(24)
11[e]	H_2O/MeOH = 1/1	36	64(35)
12[e]	H_2O/DCM = 1/1	36	58(40)
13[e]	H_2O/CH_3CN = 1/1	36	78(21)
14[e]	**H_2O/Acetone = 1/1**	**36**	**80[f](19)**
15[e]	H_2O/Acetone = 10/1	36	67(22)
16[e]	H_2O/Acetone = 1/10	36	75(23)
17[g]	H_2O/Acetone = 1/1	36	<5

[a] Visible light: Fluorescent lamp 23 W, 28 °C to 32 °C,. [b] Yield of **2a** was determined by ^{1}H- NMR, recovered yield of **1a** was determined by ^{1}H NMR and is shown in brackets. [c] Fluorescent lamp 18 W. [d] Solvent (1.5 mL/1.5 mL). [e] Solvent (1.5 mL/1.5 mL), silica gel 15 mg. [f] Isolated yield of **2a** by column chromatography. [g] Without irradiation.

Table 2. Scope of 2-Azidobiphenyl[a]



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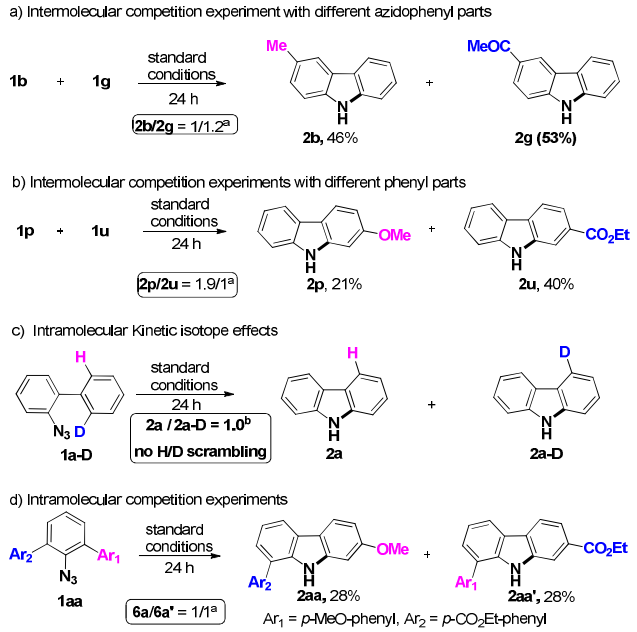
[a] Standard conditions unless otherwise noted: 0.15 mmol **1**, fluorescent lamp 23 W, H_2O / Acetone (1.5mL/1.5 mL), silica gel 15 mg, 28 °C to 32 °C, 48 h, isolated yield based on 100% conversion or the conversion shown in brackets. [b] Conversion. [c] 4 days.

conditions, giving desired carbazoles in high yields. Functional groups commonly used in organic synthesis, such as ester, cyano, carbonyl and aldehyde as well as acylamino groups are tolerated. For the substrate 2-azido-5-nitro-1,1'-biphenyl, less than 5% conversion was observed. The reaction of 2-azidobiphenyl bearing halogen atoms in the azidophenyl ring provides the corresponding halogenated carbazoles (**2j**-**m**) in good to excellent yields, and this provides more options for further conversions of products. Next, substrates with substituents in the unsubstituted phenyl ring of 2-azidobiphenyl (**2n**-**w**) were examined. The phenyl rings substituted with EDG groups such as methyl, methoxyl and EWG groups such as ester and aldehyde are tolerated. When there is a substituent in the *m*-position of this phenyl ring, a mixture of products (**2r**/**r'**, **2s**/**b**) is obtained in good yield but with low regioselectivity. These



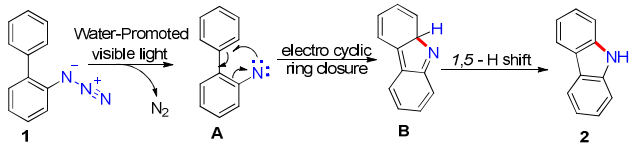
[a] The ratio of products was determinated by mixture ^{1}H NMR. [b] P_H/P_D was determinated by both ^{1}H NMR and GCMS.

Scheme 2. Competitive Experiments

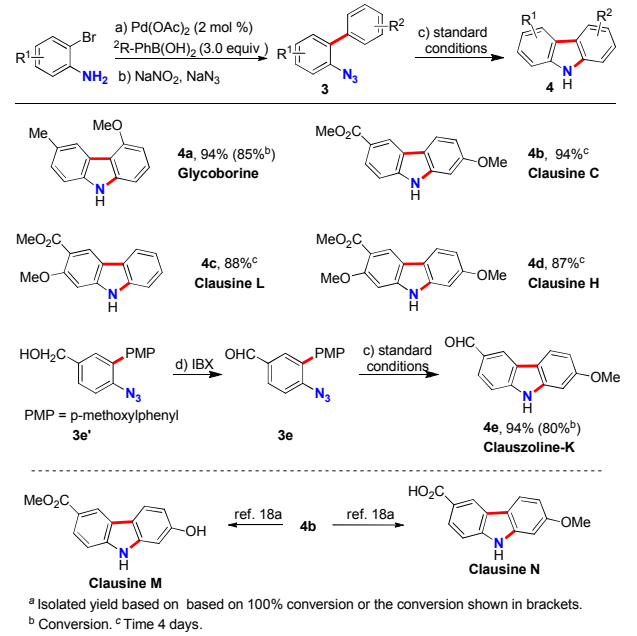
observations are consistent with previous reports on metal-catalyzed processes.[10b] In particular, sterically hindered substrates can be successfully converted to target products (**2x-y**). 1-Heteroaryl-2-azidoarenes are tolerated under the reaction condititions, producing **2z** and showing that this method has potential application to the synthesis of heteroarene fused carbazoles, such as furostifoline (Figure 1). However, few desired product was observed when 3-azido-4-phenylpyridine was used as substrate.

In order to study the mechanism of the reaction, we first performed several competition experiments (Scheme 2). In the intermolecular competitive reaction, there is a slight difference between EDG (**1b**) and EWG (**1g**) substituents in the azidophenyl ring (Scheme 3a). When the competing reaction between the substrate with EWG (**1p**) and that with EDG (**1u**) in the phenyl ring is performed, the compound with EWG in the phenyl ring predominates (Scheme 3b), indicating that the reaction may not proceed through electrophilic C–H amination. We analyzed potential kinetic isotope effects by examining the reaction of monodeuterated aryl azide (**1a**-D) (Scheme 3c). No isotope effect was observed in this reaction which is same as that in the non-catalytic thermal reaction[7], indicating the visible-light-promoted process may have a similar rate-determining step, namely extrusion of N_2.[18] In the intramolecular competing reaction of the aromatic azide **1aa**, which has a phenyl group with both EWG and EDG substituents in the *ortho* position, two isomers were formed in equal amounts. This result suggests again that the extrusion of N_2 is the rate-determining step.

Based on the above results and earlier research on photo-decomposition of azides,[8,10,18] we propose the following mechanism (Scheme 3). The azide (**1**) is transformed to a nitrene



Scheme 3. Proposed mechanism



[a] Isolated yield based on based on 100% conversion or the conversion shown in brackets. [b] Conversion. [c] Time 4 days.

Scheme 4. Synthesis of carbazole alkaloids[a]

intermediate (**A**) by release of N_2 under visible light. Then the intermediate (**B**) is formed rapidly by electrocyclic ring closure.

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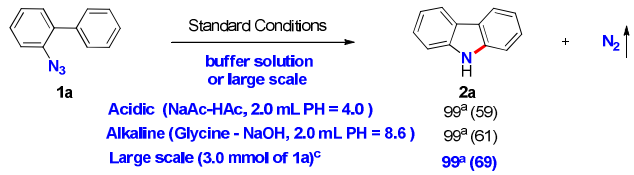
Through a [1, 5] H-shift, **B** is transformed to the final product (**2**)by tautomerization.

Inspired by the good functional group tolerance of this reaction, we attempted to synthesize a series of bioactive natural carbazoles. As shown in Scheme 4, 2-aminobiaryls, ideal precursors of 2-azidobiaryls were synthesized from the commercially available substituted 2-bromoanilines and substituted phenylboronic acid using Suzuki reactions (step a, see Supporting Information).[19] Without purification, the resulting 2-aminobiaryls were converted to 2-azidobiphenyls in moderate to good yields using traditional diazotization reaction conditions (step b, see Supporting Information). Using our standard conditions, the obtained 2-azidobiphenyls were converted to carbazoles smoothly (step c). Based on this simple and general synthetic procedure, various natural alkaloids were obtained in high yields,[20] including the anti-HIV drug glycoborine (**4a**),[21] clausine C (clauszoline-L) (**4b**),[22] clausine L(**4c**),[23] clausine H (**4d**)[24] and clauszoline K (**4e**). It should be noted that these compounds could be easily converted to other nature alkaloids. For example, clausine C can be easily converted into clausines M and N by known methods.[20a]

In order to investigate the potential applications in biochemistry of this reaction, several experiments were



[a] Isolated yield of **2a** based on conversion (shown in bracket). [c] **2a** (64%) and **1a** (25%) were seperated by washing with n-hexane.

Scheme 5. Large scale reaction or the reaction performed in acidic or alkaline buffer solutions

performed. As can be seen in Scheme 5, this has little influence on yield and no decomposition products were observed either in acidic buffer solution or in alkaline buffer solution. When the large scale reaction was performed, the desired product **2a** was still achieved in a reasonable yield (69%). It was noted that **2a** and **1a** could be separated by washing with n-hexane (see the details in ESI).

Conclusions

In summary, we have developed a light-promoted and metal-free intramolecular (Sp^2)-H amination of readily available 2-azidobiphenyls. This transformation is practical and has wide application as demonstrated by the preparation of various bioactive carbazole alkaloids. We anticipate the method, with its mild conditions, clean reactions, environmentally friendly and exceptional atom economy may have extensive application in biochemistry and synthetic chemistry.

Experimental

Substrate **1** (0.15 mmol), silica gel 15.0 mg, H_2O (1.5 mL) and acetone (1.5 mL) were added to a 15 mL glass vial equipped with a stirring bar. The solution was stirred for 48 h at a distance of ~1 cm from a 23 w fluorescent lamp. Then, the solution was diluted with 5 mL of water and 5 mL of CH_2Cl_2 and the phases were separated. The aqueous phase was extracted with an additional of CH_2Cl_2 (3 × 5 mL), and the combined organic phases were washed with water (2 × 5 mL). The organic phase was dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash chromatography on silica gel to give the desired product **2**.

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Conflicts of interest

There are no conflicts to declare.

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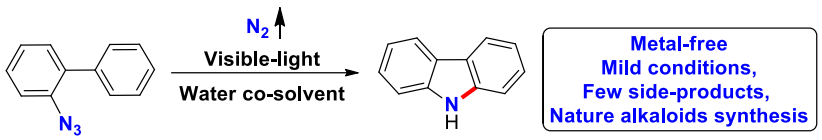

Visible light rather than various metals is reported to promote the synthesis of various carbazoles from readily available 2-azidobiphenyls under mild conditions.