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Facile Synthesis of Carbazoles via a Tandem Iodocyclization with 1,2-Alkyl Migration and Aromatization

Jia Wang,[†] Hai-Tao Zhu,[§] Yi-Feng Qiu,[†] Yuan Niu,[†] Si Chen,[†] Ying-Xiu Li,[†] Xue-Yuan Liu,[†] and Yong-Min Liang*[,†,‡]

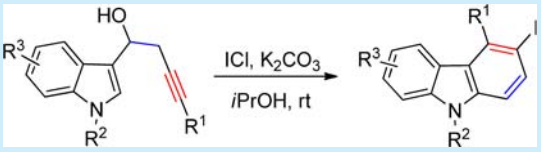
[†]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

[‡]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou, 730000, P. R. China

[§]Shannxi Key Laboratory of Phytochemistry, Baoji University of Arts and Sciences, Baoji 721013, China

Supporting Information

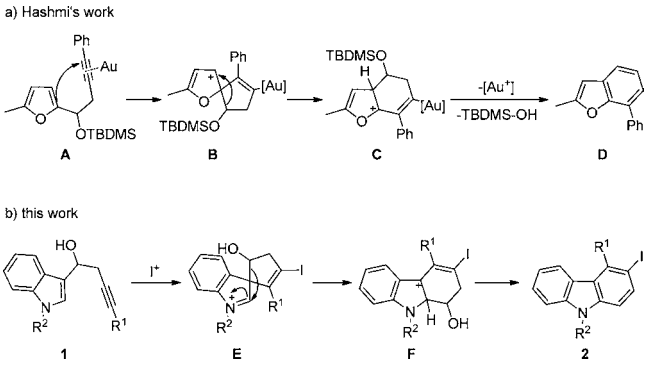
ABSTRACT: A strategy for the synthesis of iodocarbazoles through a tandem iodocyclization with migration and aromatization is presented. This sequential cascade process is concisely conducted at room temperature and in a short time. Moreover, the obtained halides can be further applied to palladium-catalyzed coupling reactions, which act as the important intermediates for building other valuable compounds.



Rearrangement[1] and migration[2] reactions as features in the chemistry field have been the focus of considerable attention for chemists; these could build surprising and unexpected structures. Meanwhile, many compounds that are difficult to synthesize by conventional methods could be gained easily by rearrangement or migration reactions.[3] In recent years, electrophilic cyclization of nucleophiles with an alkyne[4] or allene[5] has proved to be one of the most interesting subjects in organic chemistry and has been widely used to construct carbocycles[6] and heterocycles.[7] Nevertheless, few examples of sequential tandem iodocyclization to form iodocarbazole have been reported until now. Furthermore, carbazoles are important heteroaromatic compounds, which not only show various pharmacological activities, such as anticancer,[8] antimicrobial,[9] antipsychotic,[10] and antimitotic,[11] but also serve as building blocks for potential electroluminescent materials due to their special electrical, thermal, and optical properties.[12] As a result of the remarkable importance of functionalized carbazoles and their derivatives across many fields, much attention has been paid to the development of new methods for the synthesis of carbazoles. Among many useful procedures to construct carbazoles, synthetic pathways of forming a benzene ring from indoles are particularly attractive.[13] Although great achievements have been made to prepare carbazoles, seeking alternative methods for the construction of a carbazole-fused indole via a tandem iodocyclization with migration and aromatization is highly desirable.

In 2011, Hashmi's group described an interesting formation of benzo[*b*]furans from 3-silyloxy-1,5-enynes (Scheme 1).[14] This reaction is generally believed to go through a stepwise mechanism. The 2-position attacks the alkyne induced by the gold catalyst to form a 5-*endo-dig* cyclization **B**, then a Wagner−Meerwein shift delivers intermediate **C** with a more stable carboxonium ion. Finally, the product **D** is afforded by deprotonation and elimination of silanol. The same principles subsequently were also applied to other heterocycles,[15] and it could be shown that spirocyclic intermediates do not always have to be involved.[16] Encouraged by this achievement and in the context of our ongoing interest in iodocyclization,[17] we envisioned that the substrates **1** containing an indole moiety could undergo a similar migration reaction to give intermediate **F**, which could undergo aromatization to form iodocarbazole **2**. Importantly, the starting materials could be synthesized through classic and mature reactions under the mild conditions. Herein, we report a concise and effective method for the synthesis of iodocarbazoles via a 1,2-shift and aromatization.

Scheme 1. Migration Reactions and Aromatization



Our initial study began with 1-(1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol (**1a**) with 2.0 equiv of ICl in *i*PrOH (4 mL) at room temperature. To our delight, the desired product 3-iodo-9-methyl-4-phenyl-9*H*-carbazole (**2a**) was isolated in

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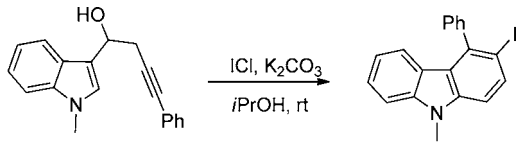
41% yield after 0.5 h (Table 1, entry 1). With the addition of K_2CO_3 (1.0 equiv), product **2a** was gained in 66% yield (entry 2). By increasing the amount of ICl to 3.0 equiv, the yield of **2a** dramatically increased to 89%. However, further increasing the amount of ICl to 3.5 equiv gave a slightly lower yield of **2a** (entry 4). After screening a series of solvents such as CH_3CN, CH_2Cl_2, CH_3COCH_3, THF, EtOH, and *n*-PrOH, we found that *i*PrOH was the best (entries 3 and 5−10). Regretfully, other electrophiles including I_2 and IBr gave unsatisfactory yields of the desired products (entries 11−12). Afterward, the study of bases showed that Na_2CO_3, KOH, and K_3PO_4 could not give a superior yield (entries 13−15). In addition, prolonging the reaction afforded the same result as before (entries 3 and 16). From the series of detailed investigations mentioned above, the combination of 1.0 equiv of **1a**, 3.0 equiv of ICl, and 1.0 equiv of K_2CO_3 in *i*PrOH at room temperature for 0.5 h was determined as the optimum reaction conditions.

Table 1. Optimization Studies on the Rearrangement of 1a[a]



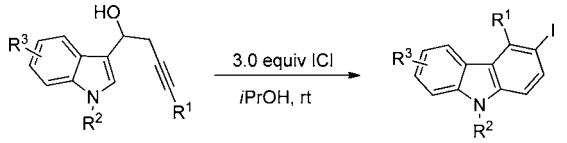
1a **2a**

entry	solvent	electrophile (equiv)	base (1.0 equiv)	time (h)	yield[b] (%)
1	*i*PrOH	ICl (2.0)	none	0.5	41
2	*i*PrOH	ICl (2.0)	K_2CO_3	0.5	66
3	***i*PrOH**	**ICl (3.0)**	**K_2CO_3**	**0.5**	**89**
4	*i*PrOH	ICl (3.5)	K_2CO_3	0.5	87
5	CH_3CN	ICl (3.0)	K_2CO_3	0.5	17
6	CH_2Cl_2	ICl (3.0)	K_2CO_3	0.5	22
7	CH_3COCH_3	ICl (3.0)	K_2CO_3	0.5	24
8	THF	ICl (3.0)	K_2CO_3	0.5	23
9	EtOH	ICl (3.0)	K_2CO_3	0.5	72
10	*n*-PrOH	ICl (3.0)	K_2CO_3	0.5	83
11	*i*PrOH	I_2 (3.0)	K_2CO_3	0.5	41
12	*i*PrOH	IBr (3.0)	K_2CO_3	0.5	45
13	*i*PrOH	ICl (3.0)	Na_2CO_3	0.5	88
14	*i*PrOH	ICl (3.0)	KOH	0.5	50
15	*i*PrOH	ICl (3.0)	K_3PO_4	0.5	87
16	*i*PrOH	ICl (3.0)	K_2CO_3	1.0	89

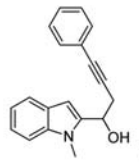
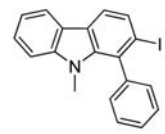
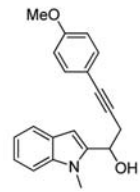
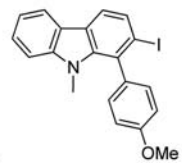
[a]All reactions were run under the following conditions, unless otherwise indicated: 0.20 mmol of **1a**, 3.0 equiv of ICl, and 1.0 equiv of base in 4 mL of solvent were stirred at room temperature. [b]Yields of isolated products.

To investigate the generality and the scope of this migration and aromatization reaction, various 1-(1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol derivatives were subjected to the above-mentioned conditions, as summarized in Table 2. The reactions of substrates **1b−1e** bearing the electron-donating aromatic groups (R^1) at the alkynyl carbon resulted in the corresponding products **2b−2e** in excellent yields (entries 2−5). The structure of the representative product **2e** was determined by X-ray crystallographic analysis (Figure 1). Subsequently, we designed compounds **1f−1i** with electron-withdrawing aromatic groups (R^1) and obtained the desired products **2f−2i** in good yields (entries 6−9). Remarkably, in contrast to product **2e**, the yield of **2i** decreased with the increase of electronegativity on the substituent R^1 group (entry 5 vs 9). This might be due to the electron-withdrawing substituents impairing the activity of the alkyne group. In the meantime, the product **2j** was obtained in 83% yield. However, substrate **1k** only led to **2k** in 37% yield for the weak nucleophilicity of the aliphatic alkyne. It is noteworthy that the yields of **2l** and **2m** decreased successively with electron waning on the substituent R^2. This should be attributed to the electron-rich substituent on R^2 enhancing the nucleophilicity of the 3-position, which is the most nucleophilic position of the indole system.[18] In particular, substrate **1n** with an electron-withdrawing substituent (Ts) on R^2 failed to afford the corresponding product **2n**, owing to the reduced nucleophilicity of the 3-position (entry 14). The reactions also worked well with substrates **1o−1r** with electron-donating or -withdrawing substituents on R^3, furnishing the expected

Table 2. Synthesis of Iodocarbazoles of 2[a]



1 **2**

entry	substrate (R^1, R^2, R^3)	products	yield[b] (%)
1	R^1 = Ph, R^2 = Me, R^3 = H	**2a**	89
2	R^1 = *o*-MePh, R^2 = Me, R^3 = H	**2b**	89
3	R^1 = *m*-MePh, R^2 = Me, R^3 = H	**2c**	91
4	R^1 = *p*-MePh, R^2 = Me, R^3 = H	**2d**	91
5	R^1 = *p*-OMePh, R^2 = Me, R^3 = H	**2e**	92
6	R^1 = *o*-FPh, R^2 = Me, R^3 = H	**2f**	71
7	R^1 = *m*-FPh, R^2 = Me, R^3 = H	**2g**	73
8	R^1 = *p*-FPh, R^2 = Me, R^3 = H	**2h**	71
9	R^1 = *p*-ClPh, R^2 = Me, R^3 = H	**2i**	76
10	R^1 = *p*-OHPh, R^2 = Me, R^3 = H	**2j**	83
11	R^1 = Me, R^2 = Me, R^3 = H	**2k**	37
12	R^1 = Ph, R^2 = Bn, R^3 = H	**2l**	83
13	R^1 = Ph, R^2 = H, R^3 = H	**2m**	75
14	R^1 = Ph, R^2 = Ts, R^3 = H	**2n**	trace[c]
15	R^1 = Ph, R^2 = Me, R^3 = 5-Me	**2o**	78
16	R^1 = Ph, R^2 = Me, R^3 = 6-Me	**2p**	78
17	R^1 = Ph, R^2 = Me, R^3 = 5-Cl	**2q**	81
18	R^1 = Ph, R^2 = Me, R^3 = 6-Cl	**2r**	80
19	R^1 = 2-thienyl, R^2 = Me, R^3 = H	**2s**	82
20	R^1 = 1-naphthyl, R^2 = Me, R^3 = H	**2t**	88
21	 **1u**	 **2u**	68
22	 **1v**	 **2v**	82

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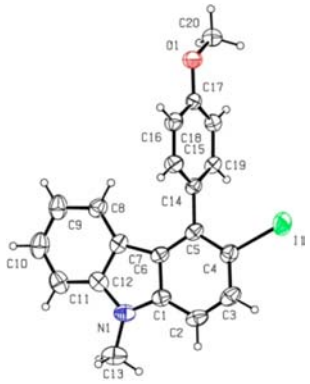
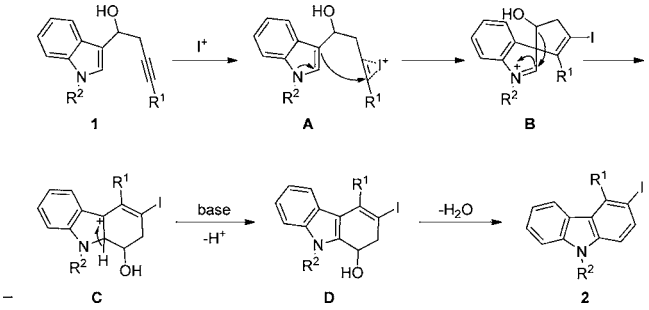


Figure 1. Solid state molecular structure product of **2e**.

products **2o**−**2r** in good yields. Meanwhile, the substrate **1s** with thienyl and **1t** with naphthyl afforded the corresponding products **2s** and **2t** in 82% and 88% yields, respectively. In addition, the products **2u** and **2v** were obtained with migration and aromatization with the alkynyl chains attached to the α-position of indoles. The structure of the representative product **2v** was determined by X-ray crystallographic analysis (see the Supporting Information).

On the basis of the above observations, the following mechanism was proposed and outlined in Scheme 2. The

Scheme 2. Proposed Reaction Mechanism

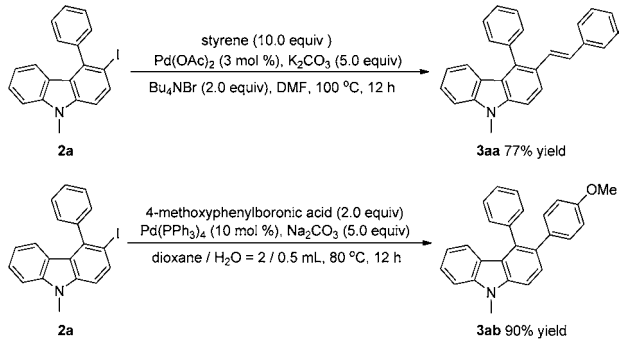


alkyne moiety was first activated by an iodide cation, and the reactive species **A** was attacked by the highly nucleophilic 3-position of the indole ring to give spirocyclic cationic intermediate **B**. Subsequently, the 1,2-shift from the 3- to 2-position occurred to form the intermediate **C** with a more stable carboxonium ion. Afterward, rearomatization of the indole by deprotonation delivered **D** and an aromatization by elimination of water attained the desired product **2**. Such aromatization in related reactions has been reported.[19]

As shown in Scheme 3, the iodocarbazole compound **2a** can be further elaborated by using various palladium-catalyzed processes. The Heck coupling[20] and Suzuki coupling[21] of **2a** afforded the corresponding products **3aa** and **3ab** in 77% and 90% yields, respectively.

In conclusion, a new and mild protocol for the synthesis of iodocarbazoles has been established. This method integrates the tandem iodocyclization, 1,2-shift on the indoles, and aromatization and opens new perspectives for future research. Foremost, the resulting iodocarbazole is readily elaborated to more products by using known organopalladium chemistry which may be essential intermediates for the synthesis of delicate and sophisticated natural products. Further studies on expanding this strategy are currently underway.

Scheme 3. Palladium-Catalyzed Coupling Reactions



■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectral data, and CIF for all new compounds are provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01590.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: liangym@lzu.edu.cn.

Notes

The authors declare no competing financial interest.

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