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Regioselective Cyclization of (Indol-3-yl)pentyn-3-ols as an Approach to (Tetrahydro)carbazoles

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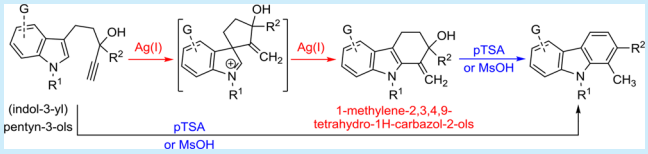
Supporting Information

ABSTRACT: An acid-catalyzed, highly regioselective cycloisomerization as well as dehydro-cyclization of (indol-3-yl)pentyn-3-ols has been reported for the selective synthesis of tetrahydrocarbazoles and carbazoles. This process is mild and found to be very general in terms of structural diversity of substrates. Utilizing the strategy, an efficient synthetic approach for the functionalized frameworks of carbazomycins A−D has also been developed.



Propargylic alcohols are unique building blocks with the association of two functional groups, i.e., alkyne and hydroxyl.[1] They undergo various useful transformations in organic synthesis, utilizing either an alkyne or hydroxyl or both of them. Chemo- and regioselective reactions of propargylic alcohols will greatly expand their chemistry and provide access to attractive synthetic strategies for novel functionalization. However, development of these selective strategies is extremely challenging, in particular the acid-mediated transformations of propargylic alcohols due to the inherent reactivity of propargylic alcohols (alkyne and alcohol together) as a single functional group rather than two.

Indole and its derivatives are very important heterocyclic compounds used in various fields such as pharmaceuticals, materials, and agrochemicals.[2] They have also been employed as synthetic building blocks in organic synthesis. Among various indole derivatives, carbazoles are ubiquitously found in many natural products,[3] bioactive molecules, drugs,[4] and organic materials (Figure 1).[5] Many synthetic methods exist for the generation of these tricyclic frameworks.[6] Furthermore, functionalized tetrahydrocarbazoles have been employed as anti-HPV agents, NPY-1 antagonists, androgen receptor modulators, and DP1 antagonists and have attracted attention in organic synthesis and medicinal chemistry.[7] They are also key structural frameworks of many alkaloids, such as alstoscholarine and gilbertine.[8] Despite these important properties, there is no strategy in the literature for the simultaneous and selective synthesis of both of these carbazole systems.

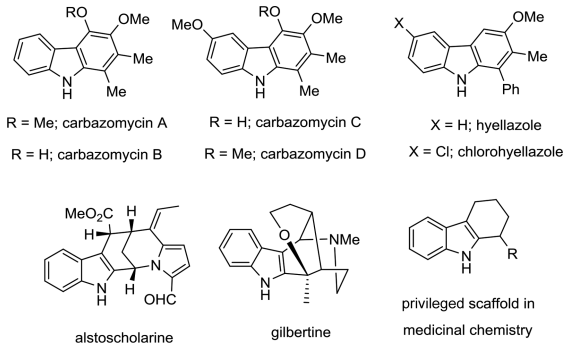
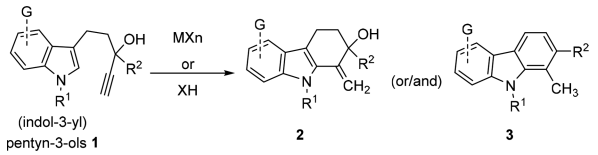


Figure 1. Representative examples of carbazole natural products.

In this context, herein we disclose a strategy for the selective generation of tetrahydrocarbazoles and carbazoles from (indol-3-yl)pentyn-3-ols using Ag(I)[9] and pTSA, respectively. This strategy involves chemo- and regioselective intramolecular cyclizations between indole and propagylic alcoholic units embedded within (indol-3-yl)pentyn-3-ols under π-catalysis.[10] According to our design (Scheme 1), it would be possible to chemo- and regioselectively activate the alkyne present in the propargylic alcohol unit of the (indol-3-yl)pentyn-3-ols **1** toward the 6-*exo*-*dig* cyclizaion by employing a suitable acid catalyst. This would result in the formation of either tetrahydrocarbazoles **2** or carbazoles **3**.

Scheme 1. Design for a Regioselective Cyclization of (Indol-3-yl)pentyn-3-ols



To verify our hypothesis, we started the investigation with (indol-3-yl)pentyn-3-ol **1a**. Treatment of **1a** with MsOH (1.3 equiv) in CH_2Cl_2 at 0 °C to rt (Table 1, entry 1) resulted in an exclusive formation of a completely aromatized 1,2-dimethylcarbazole derivative **3a** in 72% yield after 25 h. Formation of **3a** can be explained via a 6-*exo*-*dig* ring closure followed by a dehydration−aromatization cascade (see Scheme 5 for proposed mechanism). Employing TfOH and *p*TSA (entries 2 and 3) gave the same

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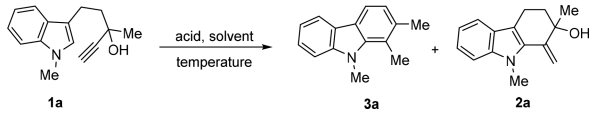
Table 1. Discovery and Optimization Study



1a 3a 2a

entry	acid	equiv	solvent	temp (°C)	time (h)	product	yield (%)[a]
1	MsOH	1.3	CH_2Cl_2	0 →rt	25	**3a**	72
2	TfOH	1.3	CH_2Cl_2	0 →rt	3	**3a**	55
3	pTSA	1.3	CH_2Cl_2	0 →rt	29	**3a**	50
4	pTSA	1.3	CH_2Cl_2	55	3	**3a**	93
5	pTSA	0.5	CH_2Cl_2	55	6.5	**3a**	91
6	pTSA	0.25	CH_2Cl_2	55	8	**3a**	94
7[b]	pTSA	0.15	CH_2Cl_2	55	32	**3a**	68
8[c]	pTSA	0.25	EtOAc	55	72	**3a**	50
9[d]	pTSA	0.25	CH_3CN	55	72	**3a**	29
10	$BiCl_3$	1.3	CH_2Cl_2	0 →rt	24	**3a**	41
11	$BF_3.Et_2O$	1.3	CH_2Cl_2	0 →rt	24	**3a**	50
12	$AgNO_3$	1.3	CH_2Cl_2	0 →rt	4.25	**2a**	80
13	AgOTf	1.3	CH_2Cl_2	0 →rt	10 min	**2a**	87
14	AgOTf	0.25	CH_2Cl_2	0 →rt	20 min	**2a**	89
15[e]	AgOTf	0.15	CH_2Cl_2	0 →rt	35	**2a**	65
16	$Cu(OTf)_2$	1.3	CH_2Cl_2	0 →rt	24	**2a**	62

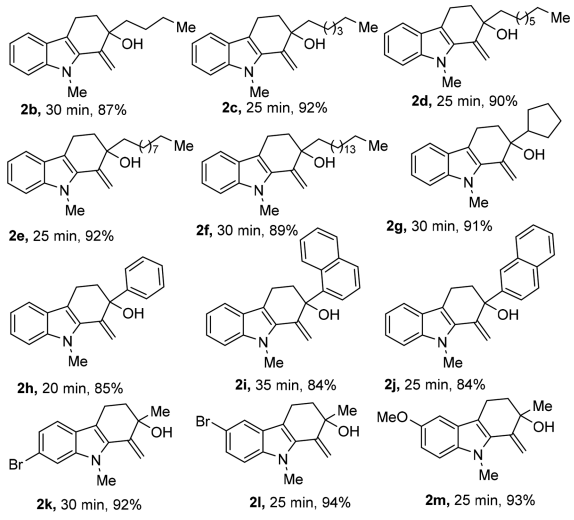
[a]Yields are after chromatographic purification. [b]28% of **1a** [c]30% of **1a** [d]40% of **1a** [e]22% of **1a** was recovered, respectively.

product **3a** without any improved yield. However, an increase in temperature to 55 °C with *p*TSA (1.3 equiv) accelerated the reaction (3 h) and afforded an excellent yield (93%) of **3a**. It was found that 0.25 equiv of *p*TSA is highly suitable to provide **3a** in 94% yield with an 8 h reaction time (Table 1, entries 5 and 6). A further decrease in the amount of *p*TSA (0.15) resulted in an incomplete conversion even after 32 h at 55 °C (entry 7). In solvents such as ethyl acetate and acetonitrile (entries 8 and 9), the reaction was found to be very slow. After heating for 72 h at 55 °C, only 70% and 60% of the respective conversion of **1a** was observed along with the poor yields (50% and 29%) of **3a**.

Next we screened various Lewis acids to see their activation mode toward propargylic alcohol present in **1a**. Both $BiCl_3$ and $BF_3{\cdot}Et_2O$ (entries 10 and 11) resulted in the formation of only the carbazole **3a**. To our surprise, employing transition-metal-based catalysts $AgNO_3$, AgOTf, and $Cu(OTf)_2$ (Table 1, entries 12–16) resulted in the tetrahydrocarbazole **2a** in excellent yields (up to 89%) via a 6-*exo-dig* cyclization process. There was no detection of any traces of the aromatized product **3a**. Among the three catalysts 0.25 equiv of AgOTf in CH_2Cl_2 at 0 °C (entry 14) gave the best yield (89%) of **2a** within 20 min of reaction time. It is noteworthy that no detection of any traces of products arising either from 5-*exo-tet* (via hydroxyl group displacement) or from 7-*endo-dig* cyclizations was observed in all the above instances. Hence this reaction is highly chemo- (alkyne vs hydroxyl) and regioselective (on alkyne).

Having the optimized conditions for the formation of both carbazoles (Table 1, entry 6) as well as tetrahydrocarbazoles (Table 1, entry 14), we next focused on understanding the generality of these transformations. Initially, generation of tetrahydrocarbazoles has been investigated (Scheme 2). Various aliphatic propargylic alcohols **1b–g** upon subjection to standard

Scheme 2. Scope Study for the Formation of 1-Methylene-2,3,4,9-tetrahydro-1*H*-carbazol-2-ols with AgOTf[a]

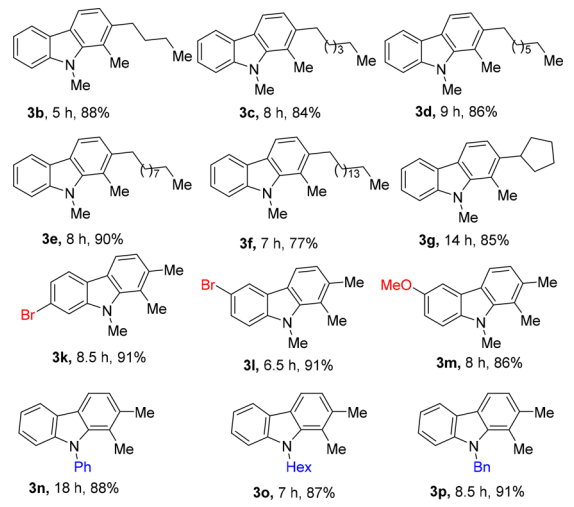


[a]Reaction conditions: **1** (1 equiv), AgOTf (0.25 equiv), CH_2Cl_2, 0 °C to rt.

reaction conditions (AgOTf (0.25 equiv), CH_2Cl_2, 0 °C to rt) underwent the expected 6-*exo-dig* cyclization to afford the corresponding tetrahydrocarbazoles **2b–g** in excellent yields (87–92%) in a short reaction time (25–30 min). Aryl-propargylic alcohols **1h–j** have also been successfully employed in this transformation to generate the polycyclic products **2h–j** in excellent yields (up to 94%). Propargylic alcohols possessing various substituents on indole ring **1k–m** efficiently underwent the transformation and afforded the functionalized tetrahydrocarbazole derivatives **2k–m**. In none of the cases we observed the formation of carbazole derivatives (via dehydration) or products via other competing pathways (5-*exo-tet* or 7-*endo-dig*).

Subsequently, the same (indol-3-yl)pentyn-3-ols **1b–g** were utilized for the generation of a library of structurally novel, 1,2-disubstituted carbazole derivatives **3b–g** in excellent yields (Scheme 3). For this transformation, *p*TSA (0.25 equiv) in dichloromethane at 55 °C was employed as the standard

Scheme 3. Scope Study for the Formation of Carbazoles with pTSA[a]



[a]Reaction conditions: **1** (1 equiv), *p*TSA (0.25 equiv), CH_2Cl_2, 55 °C.

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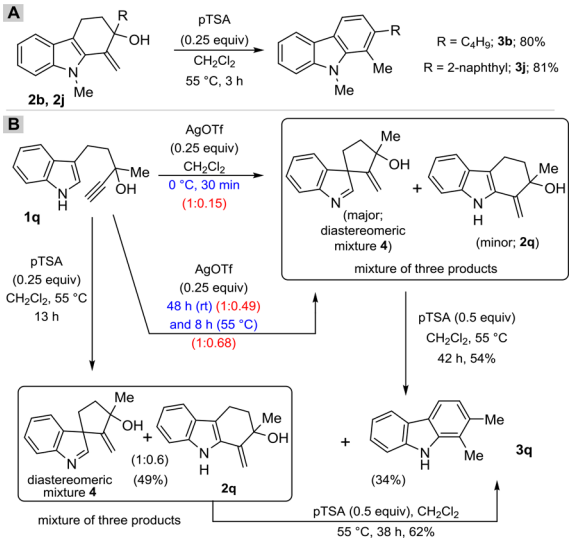
conditions (Table 1, entry 6). Structurally divergent, 1,2-dimethylcarbazoles **3k**–**m** were also obtained when we employed substrates with propargylic alcohols carrying a methyl group, against various substituted indole derivatives. The 1,2-dimethylcarbazoles are ubiquitously found in many bioactive carbazole natural products such as carbazomycins A–D. Different *N*-protecting groups such as *n*-hexyl, phenyl, and benzyl (**1n**–**p**) were also found to be compatible under standard reaction conditions to provide access to 1,2-dimethylcarbazoles **3n**–**p**.

In order to delineate the mechanistic details of this process, we performed a few control experiments (Scheme 4). When

Scheme 4. Control Experiments

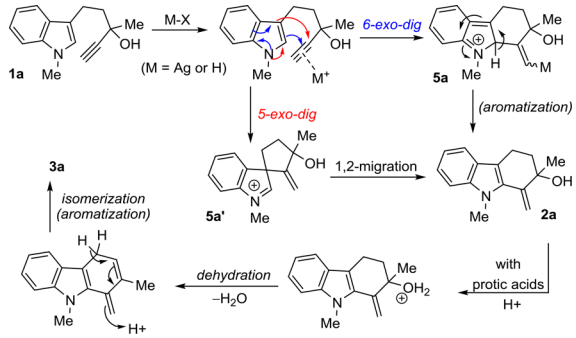


tetrahydrocarbazoles **2b** and **2j** were treated with *p*TSA (0.25 equiv) in dichloromethane at 55 °C, the corresponding carbazoles **3b** and **3j** were obtained in 80% and 81% respective yields after 3 h. This observation supports the intermediacy of the 1-methylene-2,3,4,9-tetrahydro-1*H*-carbazol-2-ols during the formation of carbazoles (Scheme 4A).

Further, to differentiate two possible pathways for the formation of 1-methylene-2,3,4,9-tetrahydro-1*H*-carbazol-2-ols, i.e., 5-*exo-dig* followed by 1,2-migration[11] vs 6-*exo-dig*, we chose an unprotected indole derivative **1q** as the model substrate (Scheme 4B). When **1q** was treated with AgOTf at rt, after 30 min, an inseparable (~1:0.15) mixture resulted of three compounds, two diastereomeric spiro-compounds **4** vs tetrahydrocarbazole **2q** in 77% yield. The same reaction when performed at rt gave a (1:0.49) mixture of **4** vs **2q** after 48 h. Further heating of this mixture at 55 °C for 8 h resulted in only a 1:0.68 mixture. These observations reveal that the conversion of **4** to **2q** is very slow in the presence of AgOTf. This mixture upon subjection to reaction with pTSA, at 55 °C, gave the carbazole derivative **3q** in 54% yield after 36 h. On the other hand, **1q** upon treatment with pTSA, after 13 h at 55 °C, gave an inseparable (~1:0.6) mixture (49%) of three products **4** and **2q** along with separable carbazole derivative **3q** (34%), whereas after 36 h an exclusive formation of the carbazole **3q** resulted in 62% yield. These observations suggest that both 5-*exo-dig* cyclization followed by 1,2-migration and direct 6-*exo-dig* cyclization contribute to the formation of the tetrahydrocarbazole derivatives.

Based on the above observations, we propose a possible mechanistic pathway (Scheme 5). Initially, the Brønsted or Lewis acid activated alkyne **1a** will undergo either a 5-*exo-dig*-cyclization

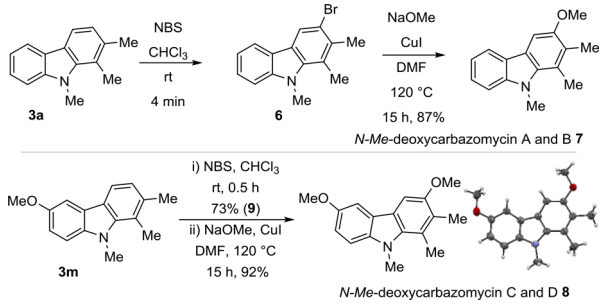
Scheme 5. Possible Mechanism



via C-3 position or a 6-*exo-dig*-cyclization via the C-2 position of the appended indole. These two processes will generate corresponding iminium ions, a 2-methylenespiro[cyclopentane-1,3′-indol]-3-ol **5a** or a 1-methylene-2,3,4,9-tetrahydro-1*H*-carbazol-2-ol **5a′** respectively. Rearomatization of both **5a** and **5a′** (via 1,2-migration) would result in the tetrahydrocarbazole **2a**. In the presence of a Brønsted acid (such as pTSA), **2a** may undergo dehydration–aromatization to yield the carbazole derivative **3a**.

Finally, to highlight the synthetic utility of our strategy, an efficient approach to functionalized frameworks of natural products cabazomycin A–D (Scheme 6) was undertaken.[12] We

Scheme 6. An Approach to Carbazomycins A–D



chose two 1,2-dimethylcarbazole derivatives **3a** and **3m** as the starting materials for this purpose. Treatment of **3a** with *N*-bromosuccinimide (NBS) in chloroform at rt for 4 min gave the 3-bromocarbazole **6** in 71% yield.[13a] Subsequent reaction of **6** with NaOMe in the presence of CuI and DMF at 120 °C generated the 3-methoxycarbazole **7** in 87% yield, which is the *N*-Me-4-deoxycarbazomycins A and B.[13b] Further, this two-step synthetic strategy has also been employed for the efficient conversion of **3m** to *N*-Me-4-deoxycarbazomycins C and D **8** via the bromide **9**. In addition to the spectroscopic characterization, the structure of **8** was unambiguously assigned on the basis of single crystal X-ray diffraction analysis[14] (CCDC 1584984) (Scheme 6).

In conclusion, we have developed highly regioselective cyclizations of (indol-3-yl)pentyn-3-ols under Lewis as well as Brønsted acid catalysis, for the selective synthesis of (tetrahydro)-carbazoles. To the best of our knowledge, this is the first report on the exploration of the reactivity of (indol-3-yl)pentyn-3-ols. This process is mild and very general in terms of the structural novelty of substrates. Further, this strategy has been extended to the efficient synthesis of functionalized frameworks of carbazole natural products, carbazomycins A–D.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00042.

General experimental procedures, characterization data including copies of ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1584984 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(14) Further details are given in the table on p 36 of the Supporting Information.

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