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Dehydrogenative [2 + 2 + 1] Heteroannulation Using a Methyl Group as a One-Carbon Unit: Access to Pyrazolo[3,4-*c*]quinolines

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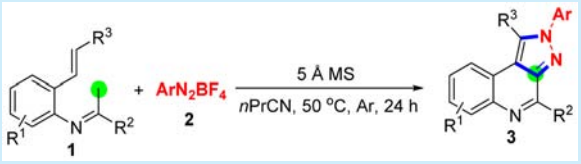
Supporting Information

ABSTRACT: A practical and straightforward access to pyrazolo[3,4-*c*]quinolines by molecular sieve mediated dehydrogenative [2 + 2 + 1] heteroannulation of *N*-(*o*-alkenylaryl)imines with aryldiazonium salts is described using a sp^3-hybrid carbon atom as a one-carbon unit. The reaction enables the formation of three new chemical bonds, a C−C bond and two C−N bonds, in a single reaction and features simple operation and excellent functional group tolerance.

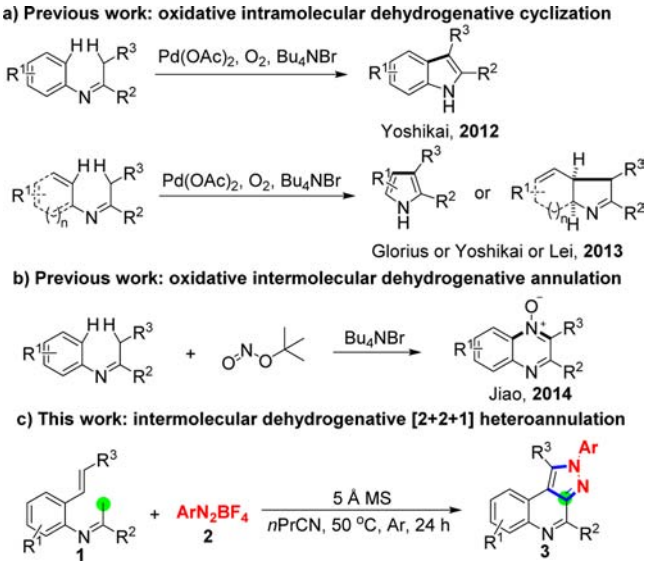


Pyrazoloquinolines,[1,2] including pyrazolo[3,4-*c*]quinolines,[2] are important *N*-heterocycles that are widely distributed in numerous natural products, pharmaceuticals, and synthetic materials. Accordingly, pyrazoloquinoline synthesis has unarguably become an importantly common task in chemical science. Traditionally, the pyrazoloquinoline frameworks are constructed by two common types of transformation:[1,2] one involves the one-step construction of a pyrazole rings onto a pre-existing aromatic ring, such as indoles and quinolines,[2a−g] and the other are multistep reactions which started from anilines.[2a,b,h−n] Therefore, the development of more efficient methods, especially straightforward strategies from simple starting materials, for assembling the pyrazoloquinoline skeletons would be interesting.

Transformation of imines and enamines represents an important and indispensable tool in chemistry for the construction of complex molecules and especially assembly of diverse nitrogen-containing heterocycles.[3] Accordingly, many useful annulation strategies for the imine and enamine transformations are known,[3,4] such as the Povarov reaction,[4a−c] the Bischler−Napieralski reaction,[4d,e] the Hantzsch reaction,[4f,g] the Paal−Knorr reaction,[4h] and the Nenitzescu reaction.[4i,j] In recent years, attractive annulation methods that harness a C−H functionalization process have been established,[5,6] but examples relying on imines as the starting materials are rare.[6]

In 2012, the Yoshikai group first employed common *N*-arylimines to access indoles through Pd-catalyzed oxidative intramolecular linkage of an aryl C(sp^2)−H bond and an alkyl C(sp^3)−H bond (Scheme 1a).[6b] Subsequently, a similar version using allylimines has been independently reported by three groups, which enable linkage of a vinyl C(sp^2)−H bond and an alkyl C(sp^3)−H bond to produce pyrroles (Scheme 1a).[6c−e] Very recently, the group of Jiao reported a different intermolecular [5 + 1] annulation strategy for the synthesis of quinoxaline *N*-oxides by metal-free radical dehydrogenative *N*-incorporation of simple *N*-arylimines through C(sp^2)−H and C(sp^3)−H bond functionalization, which offers a conceptually new breakthrough for expanding new transformations of imines in heterocycle synthesis (Scheme 1b).[6f] In light of these achievements and our interest in the development of the annulation reactions involving C−H functionalization,[7] we envisioned that both the methyl C(sp^3)−H bonds and the alkenes in the *N*-(*o*-alkyenylaryl)imines may be trapped by viable 2π components in new annulation reactions to afford important heterocyclic compounds. Herein, we report a new molecular sieve[6c,d,8] mediated dehydrogenative [2 + 2 + 1] heteroannulation of *N*-(*o*-alkenylaryl)imines with aryldiazo-

Scheme 1. Dehydrogenative Annulation



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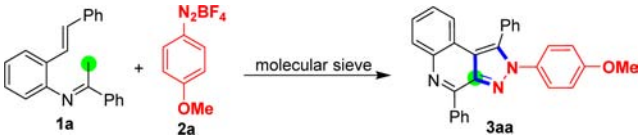
nium tetrafluorobrorates[9] for the synthesis of pyrazolo[3,4-*c*]quinolines, in which a methyl C(sp^3)−H bond in *N*-(*o*-alkyenylaryl)imines served as a one-carbon unit to react with both a C−C double bond and a N−N double bond and results in the formation of three new chemical bonds in a single reaction (Scheme 1c).

Our investigations were initiated with reaction of imine **1a** and 4-methoxyphenyldiazonium tetrafluorobrorate (**2a**) for reaction condition optimization (Table 1). Treatment of imine

Table 1. Screening of Optimal Conditions[a]



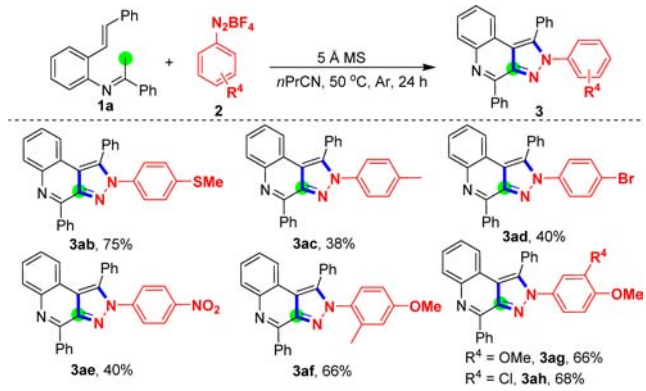
entry	molecular sieves (mg)	solvent	temp (°C)	yield[e] (%)
1[b]	4 Å MS (400)	*n*PrCN	50	15
2	4 Å MS (400)	*n*PrCN	50	68
3		*n*PrCN	50	0
4	3 Å MS (400)	*n*PrCN	50	15
5	5 Å MS (400)	*n*PrCN	50	70
6	5 Å MS (600)	*n*PrCN	50	60
7	5 Å MS (200)	*n*PrCN	50	18
8[c]	5 Å MS (400)	*n*PrCN	50	63
9[d]		*n*PrCN	50	7
10	5 Å MS (400)	MeCN	50	23
11	5 Å MS (400)	toluene	50	5
12	5 Å MS (400)	*n*PrCN	30	55
13	5 Å MS (400)	*n*PrCN	80	20

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), molecular sieves (MS), solvent (2 mL), 24 h in argon. Some byproducts, including 2-styrylaniline and 1-phenylethanone from the decomposition of the C═N bond in **1a**, were observed by GC−MS analysis. [b]$Pd(OAc)_2$ (5 mol %) and nBu_4NBr (2 equiv) under O_2. [c]Na_2CO_3 (40 mg) was added. [d]Na_2CO_3 or $CaCO_3/Na_2CO_3$ (3:1); 40 mg or 400 mg) was added. [e]Isolated yield.

1a with substrate **2a**, 4 Å molecular sieves (MS), $Pd(OAc)_2$, and nBu_4NBr in *n*PrCN under O_2 at 50 °C afforded the desired dehydrogenative [2 + 2 + 1] heteroannulation product **3aa** in a 15% yield (entry 1).[6c−e,10] Extensive screen of the catalytic systems revealed that the molecular sieves were the real catalyst: in the presence of 4 Å molecular sieves alone the reaction was successfully performed under Ar, giving **3aa** in 68% yield (entry 2). However, the reaction could not take place in the absence of molecular sieves (entry 3). Inspired by the results, other types of molecular sieves were examined (entries 4 and 5): While 3 Å molecular sieves showed a lower catalytic activity than 4 Å molecular sieves, 5 Å molecular sieves had activity identical with 4 Å molecular sieves. Therefore, we employed 5 Å molecular sieves to investigate other reaction parameters (entries 6−13). We found that either a higher or a lower amount of 5 Å molecular sieves had a negative effect on the annulation reaction (entries 6 and 7). Owing to the basic property of 5 Å molecular sieves, the basic effect on the reaction was tested, and it was found to effect the annulation reaction (entries 8 and 9). When the reaction of imine **1a** with substrate **2a** and 5 Å molecular sieves was carried out in the presence of Na_2CO_3 (40 mg), the yield of **3aa** was decreased from 70% to 63% (entry 8). Notably, in the absence of molecular sieves the reaction could also deliver **3aa** using a base alone (Na_2CO_3 or a mixture of $CaCO_3/Na_2CO_3$), albeit with lower yields (entry 9). We found that other solvents, such as MeCN and toluene, displayed a lower reactivity than *n*PrCN (entries 10 and 11). A screen of the effect of reaction temperature revealed 50 °C as the best choice for the heteroannulation reaction (entries 5, 12, and 13).

Under the optimal conditions, imine **1a** was subjected to various aryldiazonium tetrafluorobrorates **2b−h** (Scheme 2).

Scheme 2. Variation of the Aryldiazonium Tetrafluoroborates 2[a]



[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.6 mmol), molecular sieves (MS; 400 mg), *n*PrCN (2 mL), 50 °C, 24 h in argon.

We found that several substituents, namely SMe, Me, Br, NO_2, MeO, and Cl, on the aryl ring of substrates **2** were well-tolerated, and their electronic nature affected the reaction. Whereas substrate **2b** with a strong electron-donating *p*-MeS group was exposed to imine **1a** and 5 Å molecular sieves, resulting in the formation of pyrazolo[3,4-*c*]quinoline **3ab** in 75% yield, the respective substrates **2c−e** with a *p*-Me, a *p*-Br, or a *p*-NO_2 group showed diminished reactivity, delivering **3ac−ae** in lower yields. Interestingly, substrates **2f−h** with both one strong electron-donating MeO group and another group, including Me, MeO, and Cl, were converted to **3af−ah** in good yields. Unfortunately, (*E*)-1-phenyl-*N*-(2-vinylphenyl)ethan-1-imine, (*E*)-2-((*E*)-oct-1-en-1-yl)-*N*-(1-phenylethylidene)-aniline, and (*E*)-N-(2-((*E*)-2-(cyclohex-1-en-1-yl)vinyl)-phenyl)-1-phenylethan-1-imine were not suitable substrates for the reaction.

We next turned our attention to exploring the substrate scope of the dehydrogenative [2 + 2 + 1] heteroannulation protocol with regard to *N*-(*o*-alkenylaryl)imines **1** in the presence of (4-methoxyphenyl)diazonium tetrafluorobrorate (**2a**) and 5 Å molecular sieves (Scheme 3). Initially, the substitution effect at the terminal alkene of imines was investigated. Substitution of the imines **1b−g** with either electron-rich aryl groups (MeC_6H_4, $MeOC_6H_4$, and naphthalen-1-yl) or electron-deficient aryl groups (Br and Cl) at the terminal alkene displayed high reactivity and resulted in the formation of **3ba−ga** in moderate yields. Notably, imine **1h** with a heteroaryl group (4-methylthiazol-2-yl) was viable to produce the desired product **3ha** in good yield. We found that the optimal conditions were compatible with imine **1i** having an electron-withdrawing group (CO_2Me), giving **3ia** in 70% yield. Gratifyingly, reaction of the imines **1j−m** substituted at the 4-position of the aromatic ring in the *N*-(*o*-alkenylaryl) moiety successfully provided **3ja−ma** with 61−68% yields. An array of imines **1n−s** with diverse substituted aryl groups, such as 4-

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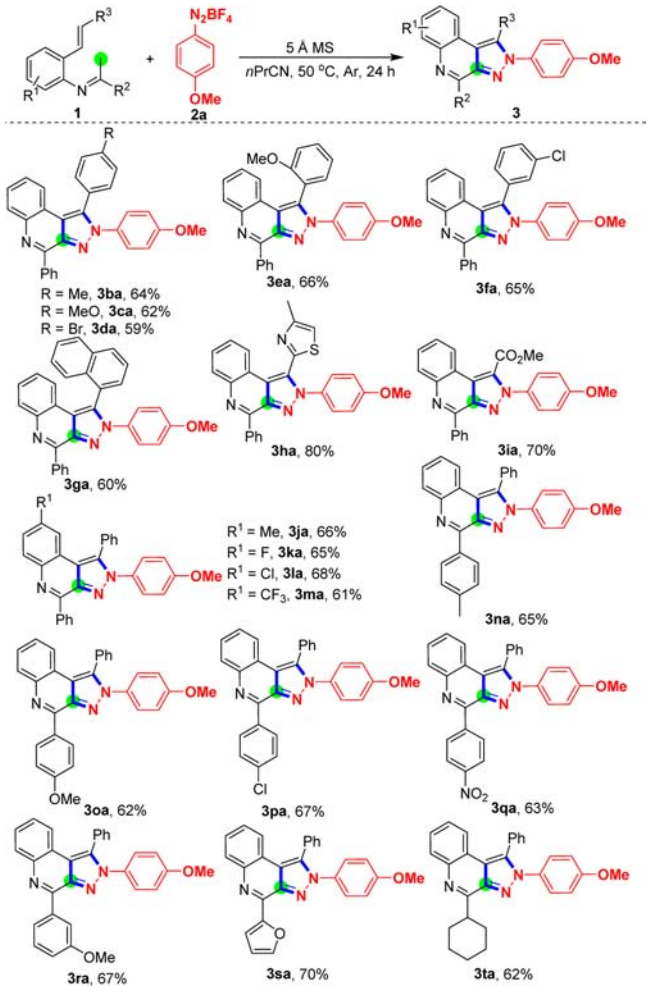
Scheme 3. Variation of the *N*-(*o*-Alkenylaryl)imines 1



MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 3-$MeOC_6H_4$, and furan, were suitable substrates to assemble **3na**−**sa** in high yields. Importantly, the dehydrogenative [2 + 2 + 1] annulation protocol was applicable to aliphatic imine **1t** with a cyclohexyl group at the 1 position, giving **3ta** in 62% yield.

Generally, molecular sieves including 5 Å MS are used as solid bases to trigger the reactions, such as dehydrogenation of alcohols, isomerization of olefins, Knoevenagel condensation, Michael addition reaction, and transesterification.[8] On this basis, the mechanism outlined in Scheme 4 was proposed for

Scheme 4. Possible Mechanisms

the dehydrogenative [2 + 2 + 1] heteroannulation reaction.[5−8] In the presence of basic 5 Å molecular sieves, isomerization of imine **1a** readily occurs to produce intermediate **A**. Intermediate **A** sequentially undergoes the [2 + 2 + 1] cycloaddition with ArN_2^+, which is generated from ArN_2BF_4 with the aid of molecular sieves, to afford intermediate **B**. Finally, isomerization and dehydrogenation of intermediate **B** give the desired product **3**.

In summary, we have developed a new molecular sieve-mediated dehydrogenative [2 + 2 + 1] heteroannulation reaction of *N*-(*o*-alkenylaryl)imines with aryldiazonium tetrafluorobrorates[8] for the straightforward synthesis of pyrazolo[3,4-*c*]quinolines, in which a sp^3-hybrid carbon atom acted as a one-carbon unit. The reaction enabled the formation of three new chemical bonds, a C−C bond and two C−N bonds, in a single reaction and featured a simple operation and an excellent tolerance of a broad range of functional groups. Work on the detailed mechanistic study and application of the heteroannulation strategy is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00618.

Descriptions of experimental procedures for compounds and analytical characterization (PDF)

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Notes

The authors declare no competing financial interest.

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