Organic &
Biomolecular Chemistry

ROYAL SOCIETY
OF CHEMISTRY

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/d0ob00702a

Arylation of indoles using cyclohexanones dually-catalyzed by niobic acid and palladium-on-carbons†

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Received 3rd April 2020,
Accepted 5th May 2020

DOI: 10.1039/d0ob00702a

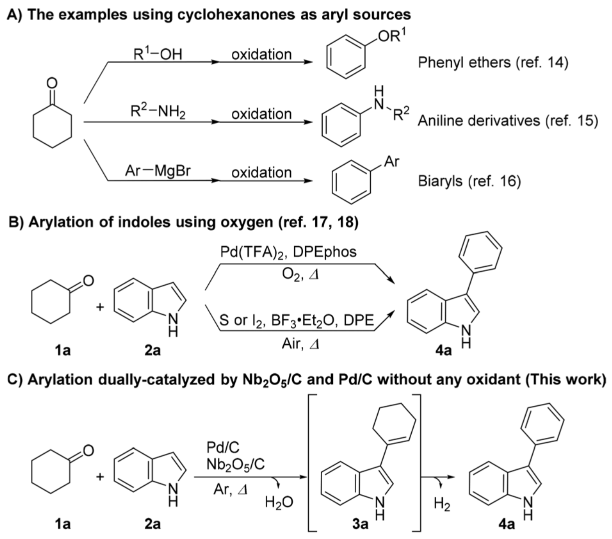
rsc.li/obc

3-Arylindoles were easily constructed from indoles and cyclohexanone derivatives using a combination of catalytic niobic acid-on-carbon (Nb_2O_5/C) and palladium-on-carbon (Pd/C) under heating conditions without any oxidants. The Lewis acidic Nb_2O_5/C promoted the nucleophilic addition of indoles to the cyclohexanones, and the subsequent dehydration and Pd/C-catalyzed dehydrogenation produced the 3-arylindoles. The additive 2,3-dimethyl-1,3-butadiene worked as a hydrogen acceptor to facilitate the dehydrogenation step.

Introduction

Aryl-substituted indoles are fundamental backbones of natural products, functional materials, agrochemicals and pharmaceutical agents.[1] Among them, various synthetic methods of 3-arylindole derivatives, possessing bioactivities, such as the HMG-CoA reductase inhibitor, COX-2 inhibitor, antimicrobial activity, *etc.*,[1c–h] have been developed.[2–17] The Pd-catalyzed direct arylations of indoles using the pre-activated arenes[2–8] (aryl halides,[3] aryl boronic acids,[4] aryl carboxylic acids,[5] diaryliodonium salts,[6] aryl triflates,[7] and arylhydrazines[8]) resulted in the generation of wastes based on the pre-functionalized moieties that have been widely developed. The direct oxidative cross-coupling of arenes with indoles using Pd catalysts has also been accomplished.[9] The Cu-catalyzed 3-arylindole synthesis using diaryliodonium salts[10] and the *t*-BuOK-mediated method using aryl halides[11] has been developed. Additionally, aryl diazonium salts were also applied as a coupling partner of indoles in the presence of a photoredox catalyst.[12] The readily available cyclohexanone derivatives have been recently utilized as arene sources generating only water as waste.[13–16] Namely, the nucleophilic attack of alcohols, amines, or Grignard reagents on cyclohexanones, dehydration, and oxidative aromatization by using organic oxidants [*e.g.*, phthalimide-*N*-oxyl, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and I_2] or Pd catalysts gave the corresponding phenyl ethers,[14] aniline derivatives[15] or biaryls[16] (Scheme 1A). As a similar concept, a homogeneous palladium catalyst was adapted for the oxygen oxidative aromatization step of the 3-arylindole synthesis from the cyclohexanones and indoles as substrates[17] (Scheme 1B). Furthermore, the combination of a stoichiometric Lewis acid and an excess amount of oxidants, such as sulfur and I_2, was also applied to the 3-arylindole synthesis.[18]

In addition, niobic acid (Nb_2O_5), possessing both Brønsted and Lewis acidities,[19,20] has been used as a catalyst for the esterification,[20e] amidation,[20i] imidation,[20j] cyclic imide synthesis,[20h] cellulose hydrolysis,[20b] sulfide oxidation,[20d] and furfural synthesis.[20a,c,f,g] Nb_2O_5-supported-on-carbon (Nb_2O_5/C) was useful due to its easy handling and separation from the



Scheme 1 Arylations using cyclohxanones.

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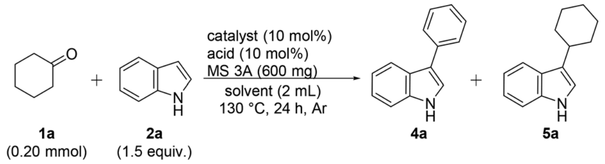
† Electronic supplementary information (ESI) available: Experimental procedure, copies of ^1H, ^{13}C, NMR spectra, of new compounds. See DOI: 10.1039/d0ob00702a

reaction mixture and utilized as a promotive additive in the palladium-on-carbon (Pd/C)-catalyzed hydrogenative debenzylation of *N*-benzyl amines.[21] We have also reported that Pd/C efficiently catalyzed the dehydrogenative aromatization of cyclohexene derivatives.[22] We now demonstrate the 3-arylindole synthesis from cyclohexanone (**1a**) and indole (**2a**) dually-catalyzed by Nb_2O_5/C and Pd/C (Scheme 1C). The acidity of Nb_2O_5/C promoted the nucleophilic addition of **2a** to **1a**, and the following dehydration to the intermediate (**3a**) and the Pd/C-catalyzed dehydrogenation of **3a** gave **4a**.

Results and discussion

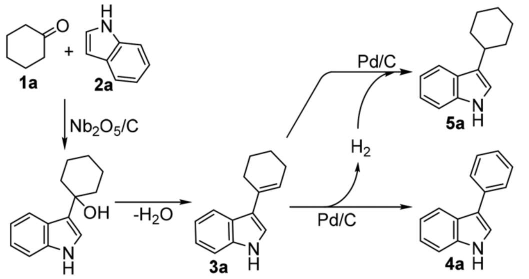
The desired coupling reaction of cyclohexanone (**1a**; 0.2 mmol) and indole (**2a**) could proceed by the combination of 10% Pd/C and 10% Nb_2O_5/C in toluene in the presence of molecular sieves (MS) 3A at 130 °C to give 3-phenylindole (**4a**) in 45% yield and 3-cyclohexylindole (**5a**) as a by-product in 55% yield after 24 h (Table 1, entry 1). Meanwhile, the independent use of Pd/C or Nb_2O_5/C led to the low yields of **4a** as well as **5a** (entries 2 and 3), and the reaction without MS 3A also caused the low yield of **4a** (entry 4). Pt/C or Rh/C instead of Pd/C as a combined catalyst of Nb_2O_5/C was less effective (entries 5 and 6). The use of $FeCl_3$ or $AlCl_3$ as homogeneous Lewis acids or trifluoroacetic acid (TFA) as a Brønsted acid instead of Nb_2O_5/C was also inadequate (entries 7–9). While the desired reaction proceeded in *o*-xylene instead of toluene to give **4a** in a relatively lower yield (entry 10), DMSO, DMF, 1,4-dioxane or H_2O was ineffective as a solvent (entries 11–14).

Table 1 Optimization of the synthesis of 3-phenylindole



Entry	Transition metal cat.	Acid	Solvent	Yield[a] (%) 4a	Yield[a] (%) 5a
1	10% Pd/C	10% Nb_2O_5/C	Toluene	45	55
2	10% Pd/C	—	Toluene	10	Trace
3	—	10% Nb_2O_5/C	Toluene	Trace	40
4[b]	10% Pd/C	10% Nb_2O_5/C	Toluene	18	54
5	10% Pt/C	10% Nb_2O_5/C	Toluene	20	42
6	10% Rh/C	10% Nb_2O_5/C	Toluene	29	58
7	10% Pd/C	$FeCl_3$	Toluene	13	24
8	10% Pd/C	$AlCl_3$	Toluene	19	26
9	10% Pd/C	TFA	Toluene	31	55
10	10% Pd/C	10% Nb_2O_5/C	*o*-Xylene	32	38
11	10% Pd/C	10% Nb_2O_5/C	DMF	0	0
12	10% Pd/C	10% Nb_2O_5/C	DMSO	0	0
13	10% Pd/C	10% Nb_2O_5/C	1,4-Dioxane	0	0
14[b]	10% Pd/C	10% Nb_2O_5/C	H_2O	0	0

[a] The yield was determined by ^1H NMR using 1,2-methylenedioxybenzene as an internal standard. [b] Without MS 3A.



Scheme 2 A plausible 3-arylation reaction mechanism of the indole with cyclohexanone.

Nb_2O_5/C initially promotes the nucleophilic addition of **2a** to **1a** due to the appropriate acidity, and the following dehydration gives **3a**, which undergoes the Pd/C-catalyzed dehydrogenation to produce **4a** (Scheme 2). H_2 is generated during the transformation of **3a** to **4a**, resulting in the undesired Pd/C-catalyzed hydrogenation of **3a** to **5a**, as shown in Table 1, entry 1. Alternatively, the hydrogen transfer[23] (disproportionation) between the intermediates **3a** generates **5a** together with a cyclohexadiene intermediate. Subsequently, the cyclohexadiene intermediate transforms into **4a** *via* the Pd/C-catalyzed dehydrogenation.

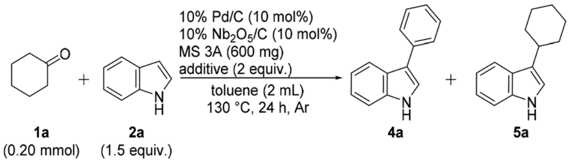
The addition effect of the hydrogen acceptor was next examined to avoid the formation of the by-product **5a** *via* the hydrogenation of **3a** by *in situ* generated H_2, as shown in Scheme 2 (Table 2). The addition of methyl acrylate or acetophenone was not much different from the yield of **4a** (entries 1 and 2) without the additives (Table 1, entry 1). The addition of benzaldehyde or *N*,*N'*-dicyclohexylcarbodiimide (DCC) was harmful to the formation of **4a** (entries 3 and 4). Styrene could be a hydrogen acceptor to improve the yield of **4a**, and the formation of hydrogenated ethylbenzene was detected (entry 5). Specifically, the formation of **4a** efficiently proceeded (78% yield) in the presence of 2,3-dimethyl-1,3-butadiene, even though the generation **5a** was not completely suppressed (entry 6). The mixture of Nb_2O_5/C, Pd/C and MS 3A was recovered after reaction under optimal conditions (entry 6) and used in next run (entry 7). Consequently, **4a** and **5a** was obtained in 35% and 30% yield, respectively. Meanwhile, the scale-up reaction using 5 mmol of **1a** also provided **4a** in a satisfactory yield (entry 8). The reaction conditions under oxygen atmosphere without hydrogen acceptor slightly improved the yield of **4a** (entry 9 *vs.* Table 1, entry 1).

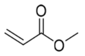
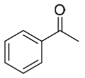
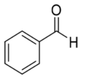
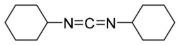
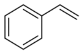
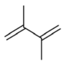
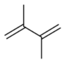
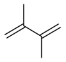
The applicable scope of the cyclohexanone derivatives to the present reaction was investigated with or without 2,3-dimethyl-1,3-butadiene as the hydrogen acceptor since the influence of 2,3-dimethyl-1,3-butadiene significantly depended on each substrate (Table 3). The 4-methyl, 4-phenyl and 3-phenyl cyclohexanone derivatives (**1b–1d**) could be aryl sources to produce the corresponding 3-arylindole derivatives (**4b–4d**) in moderate to good yields in the presence of 2,3-dimethyl-1,3-butadiene (entries 1, 3 and 5), while the reactions without 2,3-dimethyl-1,3-butadiene caused relatively lower yields (entries 2, 4 and 6). 4-*tert*-Butyl cyclohexanone (**1e**) could react with **2a** under both with or without 2,3-dimethyl-1,3-butadiene to give the desired product (**4e**) in 41% or 55% yield (entries 7 and 8). However, 2-methyl cyclohexane (**1f**) was not applicable probably due to steric repulsion around the nucleophilic attack position of **1f** (entries 11 and 12).

Various indoles were also applicable for the present 3-arylindole synthesis as substrates (Table 4). 5-Methyl, 5-methoxy, 5-fluoro, and 7-methyl indole derivatives (**2b–2d**, **2f**) were coupled with cyclohexanone (**1a**) to give the corresponding 3-phenylindoles (**4f–4h**, **4j**) in moderate yields (entries 1–6 and 9–10). 5-Ester-substituted indole (**2e**) was converted to indole derivative (**4i**) in low yield under the conditions without 2,3-dimethyl-1,3-butadiene (entries 7 and 8). The *N*-methyl and *N*-benzyl indoles (**2g** and **2h**) were also transformed into the corresponding 3-phenylindole derivatives (**4k** and **4l**; entries 11–14).

The use of pyrrole (**6**) instead of indoles in the arylation using cyclohexanone (**1a**) in the presence of Pd/C and Nb_2O_5 without 2,3-dimethyl-1,3-butadiene could provide 2 or 3-arylpyrrole (**7**), although the yields were unsatisfactory (Scheme 3). The addition of 2,3-dimethyl-1,3-butadiene resulted in no generation of **7**. When using pyrrole (**6a**), 2-phenylpyrrole (**7a**) was obtained (Scheme 3). On the other hand, *N*-methyl and *N*-benzyl pyrroles (**6b** and **6c**) reacted at their 3-positions to give the corresponding 3-phenylpyrrole derivatives (**7b** and **7c**). Nucleophilic attack of pyrroles usually proceeds at their 2-positions.[24] Intriguingly, the 3-positions of **6b** and **6c** were functionalized. The details of different reactivities are unclear.

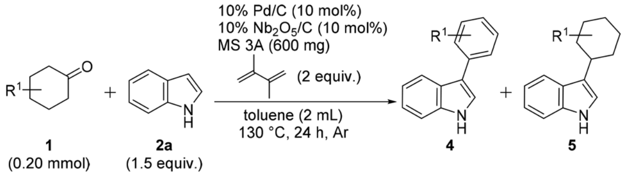
Table 2 Addition of hydrogen acceptors



Entry	Additive	Yield[a] (%) 4a	Yield[a] (%) 5a
1		45	1
2		49	2
3		Trace	3
4		20	4
5		62	5
6		78	6
7[b]		35	30
8[c]		67[d]	7
9[e]	—	52	48

[a] The yield was determined by ^1H NMR using 1,2-methylenedioxybenzene as an internal standard. [b] The recovered mixture of Pd/C, Nb_2O_5/C and MS 3A after the reaction in entry 6 was used. [c] 5 mmol of **1a** was used. [d] Isolated yield. [e] Under oxygen atmosphere.

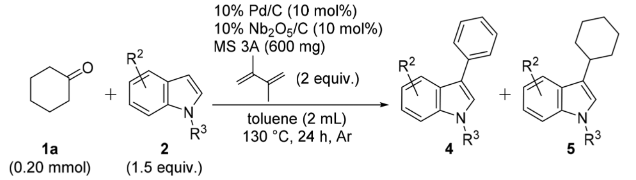
Table 3 The substrate scope of cyclohexanone derivatives



Entry	R^1	Yield[a] (%) 4	Yield[a] (%) 5
1	4-Me (**1b**)	**4b**: 51	**5b**: —
2[b]		**4b**: 44	**5b**: 46
3	4-Ph (**1c**)	**4c**: 64	**5c**: —
4[b]		**4c**: 40	**5c**: Trace
5	3-Ph (**1d**)	**4d**: 60	**5d**: Trace
6[b]		**4d**: 48	**5d**: Trace
7	4-*tert*-Bu (**1e**)	**4e**: 41	**5e**: Trace
8[b]		**4e**: 55	**5e**: 43
9	2-Me (**1f**)	No reaction	
10[b]		No reaction	

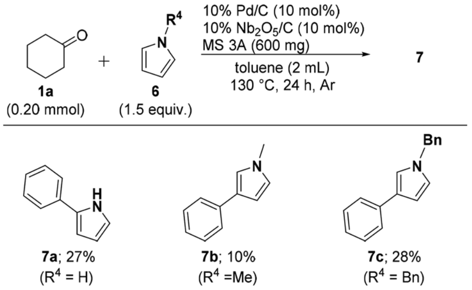
[a] Isolated yield. [b] Without 2,3-dimethyl-1,3-butadiene.

Table 4 The substrate scope of indoles



Entry		R^2	R^3	Yield[a] (%) 4	Yield[a] (%) 5
1	**2b;**	5-Me	H	**4f**: 50	**5f**: 15
2[b]				**4f**: 45	**5f**: 51
3	**2c;**	5-OMe	H	**4g**: 42	**5g**: 13
4[b]				**4g**: 45	**5g**: 48
5	**2d;**	5-F	H	**4h**: 32	**5h**: —
6[b]				**4h**: 45	**5h**: 52
7	**2e;**	5-CO_2Me	H	No reaction	
8[b]				**4i**: 12	**5i**: 12
9	**2f;**	7-Me	H	**4j**: 38	**5j**: —
10[b]				**4j**: 45	**5j**: 55
11	**2g;**	H	Me	**4k**: 72	**5k**: Trace
12[b]				**4k**: 47	**5k**: 42
13	**2h;**	H	Bn	**4l**: 27	**5l**: —
14[b]				**4l**: 30	**5l**: Trace

[a] Isolated yield. [b] Without 2,3-dimethyl-1,3-butadiene.



Scheme 3 Phenylpyrrole synthesis using pyrroles and cyclohexanone.

Conclusions

We have accomplished the Nb$_2$O$_5$/C and Pd/C-catalyzed 3-arylindole synthesis using indoles and cyclohexanone derivatives as aryl sources. The catalysts can be directly used without pre-activation and any additional oxidants, and the reaction only produces water and hydrogen as by-products. Since heterogeneous catalysts are easily removable from the reaction mixture, it is valuable from the viewpoint of green sustainable chemistry. 3-Cyclohexylindoles (**5**) as by-products also possess useful backbones for anti-HCV drugs.[25] Therefore, the presented environmentally-friendly method to construct 3-arylindoles as well as 3-cyclohexylindoles can be effectively utilized in various chemical fields.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the N.E. Chemcat Corporation for the kind gift of the various metal on carbon catalysts. This study was partially supported by a Takeda Science Foundation (for Y. S.).

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