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Platinum-group-metal-on-carbon catalyzed dehydration of tertiary alcohols and its application to the one-pot synthesis of aromatics

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Catalytic dehydration of alcohols remains a challenge in organic synthesis, and olefin products are important synthetic precursors because of their high reactivity. Platinum-group-metal-on-carbon catalysts (such as Ru/C and Pd/C) are commercially available and widely utilized as heterogeneous, green, and sustainable catalysts in various organic reactions. However, examples of their application to the catalytic dehydration of alcohols have not been reported. Herein, we demonstrate the Ru/C-catalyzed dehydration of tertiary (*tert*) alcohols in toluene under thermal conditions. Ru/C also potentially exhibits oxidative activity. Therefore, a tandem reaction involving the Ru/C-catalyzed dehydration of *tert*-benzylic alcohols, a Diels–Alder reaction, and subsequent oxygen oxidation was developed to afford highly functionalized aromatic products. Additionally, a one-pot synthesis of biaryls from 1-arylcyclohexanols as *tert*-alcohol substrates was successfully developed *via* Pd/C-catalyzed dehydration and subsequent dehydrogenation in H₂O. These green and sustainable synthetic approaches based on novel heterogeneous dehydration methodologies are valuable for the construction of diverse functional materials.

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Introduction

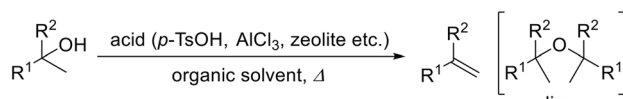
Olefin compounds are important precursors for the introduction of various functional groups in organic synthesis because of their high reactivity (halogenation, hydroboration, reduction, oxidation, *etc.*). Therefore, the development of efficient and environmentally friendly methods for the synthesis of olefins is expected to play a crucial role in advancing process chemistry and drug discovery research. Among these methods, the dehydration of easily prepared or abundant alcohols, including those derived from biomass, remains a challenging issue for accessing valuable olefins.¹ Because the elimination ability of hydroxyl groups in alcohols is comparatively low, the E2 elimination process, which involves pre-functionalization (mesylation, acetylation, *etc.*), is often utilized to enhance the leaving-group ability of hydroxyl groups and subsequent addition of a base. However, E2 elimination leads to the generation of various wastes derived from methanesulfonyloxy and acetoxy groups, as well as bases, and requires a stepwise process under basic conditions. Although the Burgess reagent² is well known to facilitate the dehydration of alcohols under neutral reaction conditions, a stoichiometric amount of reagent is required,

resulting in the generation of an equivalent amount of waste. From this viewpoint, catalytic dehydration is regarded as an efficient and straightforward method that suppresses dimerization as a side reaction. Acidic catalysts¹ (Brønsted acids, Lewis acids,³ acidic ionic liquid gels,⁴ and solid acids⁵ such as zeolites and metal oxides (Al₂O₃, *etc.*)) have been utilized for the dehydration of alcohols under heating conditions (Fig. 1A). Re₂O₇ and CH₃ReO₃ have been explored as heterogeneous metal oxides to catalyze the dehydration of various secondary (*sec*) and tertiary (*tert*) alcohols, and mechanistic insights have also been obtained (Fig. 1B).⁶ The Re₂O₇-catalyzed method overcomes low selectivity (formation of olefins and dimers) and limited functional-group tolerance, which are potential disadvantages of conventional metal oxide catalysts. However, in the dehydration of benzylic alcohols, only substrates bearing strong electron-withdrawing groups (*e.g.*, NO₂) on the aromatic ring are not acceptable. In a recent study, a selective dehydration method for *tert*-alcohols was developed using a combination of triphosgene and 4-dimethylaminopyridine.⁷

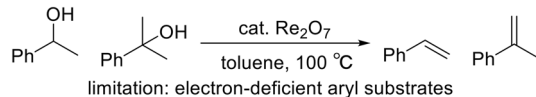
Platinum-group metals on carbon (Pd/C, Ru/C, Pt/C, *etc.*) are commercially available heterogeneous catalysts and are frequently utilized in green and sustainable organic synthesis, including hydrogenation,⁸ dehydrogenation (oxidation),⁹ and deuteration.¹⁰ However, to the best of our knowledge, there are no reported examples of alcohol dehydration using platinum-group-metal-on-carbon catalysts.

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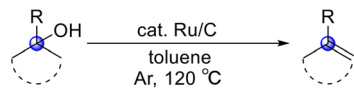
(A) Acid-catalyzed dehydration



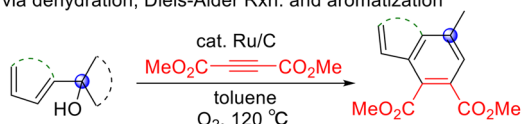
(B) Rhenium-catalyzed dehydration

(C) (This work) Ru/C- or Pd/C-catalyzed dehydration of *tert*-alcohols

(i) Dehydration



(ii) Tandem synthesis of aromatics via dehydration, Diels-Alder Rxn. and aromatization



(iii) Biaryl synthesis from 1-arylcyclohexanol via dehydration and dehydrogenation

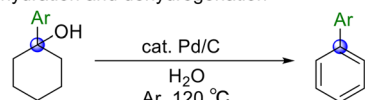


Fig. 1 Dehydration of alcohols to olefins.

We hypothesized that platinum-group metals supported on carbon could be used for the dehydration of alcohols because the supported metal species are partially oxidized to various metal oxide forms, which may possess catalytic activity for dehydration. Herein, we demonstrate the Ru/C-catalyzed dehydration of easily prepared *tert*-alcohols in toluene under heating conditions (Fig. 1C-i). Platinum-group-metal-on-carbon catalysts also potentially possess oxidative activity toward cyclohexene derivatives.⁹ Therefore, the present dehydration method can be extended to the tandem synthesis of aromatics *via* the sequential dehydration of *tert*-benzylic alcohols, a Diels-Alder reaction, and oxidative aromatization (Fig. 1C-ii). Furthermore, the Pd/C-catalyzed dehydration of 1-arylcyclohexanols, followed by dehydrogenation in H₂O, provided the corresponding biaryl products (Fig. 1C-iii). Highly functionalized aromatics and biaryls are important compounds for pharmaceutical and electronic applications.

Results and discussion

First, catalyst efficiencies were screened for the dehydration of 1-phenylcyclohexanol (**1a**; 0.25 mmol) as a *tert*-alcohol in H₂O at 120 °C in 6 h (Fig. 2A). As expected, Ru/C catalyzed the dehydration of **1a** to give the olefin product 1-phenylcyclohexene (**2a**) in 20% yield, while 65% of **1a** remained unchanged (entry 1). Rh/C also exhibited catalytic activity; however, the yield of **2a** was low (entry 2). Meanwhile, the use of Pd/C and Pt/C provided biphenyl **3a** in moderate yields, and a reduced product (**4a**) was also

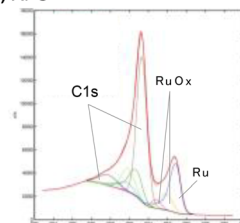
(A) Catalyst and solvent efficiencies in the reaction of 1-phenylcyclohexanol (**1a**) as a *tert*-alcohol

entry	M/C	solvent	yield (%)			
			1a	2a	3a	4a
1	Ru/C	H ₂ O	65	20	trace	0
2	Rh/C	H ₂ O	86	13	trace	0
3	Pd/C	H ₂ O	trace	trace	36	53
4	Pt/C	H ₂ O	trace	0	38	45
5	Ir/C	H ₂ O	quant.	0	0	0
6	Ru/C	toluene	trace	99	0	0
7	Ru/C	<i>n</i> -heptane	trace	99	0	0
8	Ru/C ^[a]	toluene	trace	98	0	0
9	C ^[a]	toluene	98	trace	0	0
10	Ru/C ^[b]	toluene	trace	91	0	0
11	Pd/C	toluene	20	0	30	50
12	Pt/C	toluene	0	0	38	62

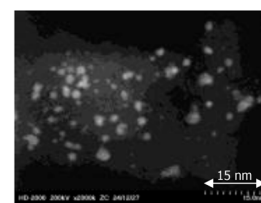
[a] used after washing with H₂O and MeOH and drying.[b] 10.9 mmol of **1a** was used. Reaction time is 3 h.

(B) XPS and STEM analysis of fresh Ru/C

(i) XPS

Ru(0) : RuO_x = 68 : 32 (%)

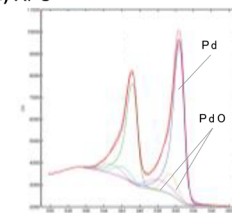
(ii) STEM



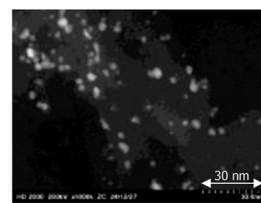
particle size; ave. 1.6 nm

(C) XPS and STEM analysis of fresh Pd/C

(i) XPS

Pd(0) : PdO_x = 77 : 23 (%)

(ii) STEM



particle size; ave. 2.3 nm

Fig. 2 Ru/C-catalyzed dehydration and Pd/C-catalyzed dehydration followed by dehydrogenation.

obtained (entries 3 and 4). Biphenyl **3a** could be produced *via* dehydration followed by dehydrogenation, and the H₂ generated during the dehydrogenation process acted as a reductant for **1a** or **2a** to afford **4a** (further investigation is described later; see Fig. 5). The use of Ir/C did not lead to any reaction (entry 5). In the Ru/C-catalyzed dehydration, changing the solvent from H₂O to toluene or *n*-heptane dramatically improved the reaction efficiency, affording **2a** in 99% yield (entries 6 and 7). Because acidic by-products can contaminate platinum-group-metal-on-carbon catalysts during industrial manufacturing, Ru/C was washed with H₂O and MeOH, and the washed Ru/C was used for the dehydration of **1a** in toluene (entry 8). Consequently, no loss of reactivity was observed, affording **2a** in 98% yield.



This result indicates that the reaction proceeds without metal leaching. However, the reaction using used Ru/C led to low yield (first run: 99% yield of **2a** for 6 h (Fig. 2A, entry 6), second run: 64% yield of **2a** for 24 h). The reason is unclear at this stage.

Encouraged by the successful proof of concept shown in Fig. 2, the substrate scope was investigated for the Ru-catalyzed dehydration of *tert*-alcohols in toluene (Fig. 3A). Solubilities of substrates in toluene are higher than those in heptane. Therefore, the scope of substrates was investigated in toluene. Using 1-arylcycloalkanols, the four-membered substrate decomposed to give the desired product (**2b**), whereas the dehydration of 1-phenylcyclopentanol (five-membered ring) and 1-phenylheptanol (seven-membered ring) proceeded efficiently to afford the corresponding cycloalkene products (**2c** and **2d**) in high yields. Additionally, 1-arylcyclohexanols bearing electron-donating and electron-withdrawing substituents (OMe, OPh, OH, CF₃, CO₂Me, and halogen) on the aryl ring were efficiently transformed into the corresponding dehydrated products (**2e–2o**). Other cyclohexene derivatives (**2p–2s**) were also obtained from the corresponding *tert*-alcohols. Linear alcohols (**1t–1y**) and cyclic alcohols (**1z–1ah**) bearing heteroatoms and acid-labile groups (TBSO, THPO, acetal, *etc.*) were also compatible with the present Ru/C-catalyzed dehydration. Although heteroatoms can potentially poison platinum-group metals, the dehydration of heteroatom-containing alcohols proceeded efficiently under the present conditions. Under conventional acidic conditions, TBSO-, THPO-, and acetal-protecting groups are typically deprotected; however, these functional groups were well tolerated under the present reaction conditions. Furthermore, whereas 1,2-diol substrates typically undergo pinacol rearrangement to afford carbonyl compounds,^{11,12} double dehydration of diol **1ai** proceeded selectively to give the corresponding diolefin product (**2ai**) under Ru/C-catalyzed conditions. 2-Methyl-1-phenyl-2-propanol (**1aj**), bearing a hydroxyl group at a non-benzylic position, afforded a mixture of regioisomeric olefins (**2aj** and **2aj'**). Similarly, Ru/C-catalyzed dehydration of substrates **1ak–1am** also resulted in mixtures of regioisomers. In these cases, increasing the reaction time did not affect the regioisomeric ratios, indicating that olefin migration to adjacent positions did not occur under the present reaction conditions.

Platinum-group-metal-on-carbon catalysts have been reported to promote the dehydrogenation (oxidation) of *sec*- and primary (*pri*) alcohols in H₂O.^{9d,e} Accordingly, the treatment of *sec*-alcohol 1-(2-naphthyl)ethanol (**5a**) with Ru/C in toluene afforded olefin **6a** (36%), carbonyl compound **7a** (11%), and dimer **8a** (14%) (Fig. 3B-i). In addition, *pri*-alcohol 2-(2-naphthyl)ethanol (**9a**) also underwent dehydration under the reaction conditions (Fig. 3B-ii). In general, the order of reactivity of dehydration under acidic conditions is *tert*- > *sec*- >> *pri*-alcohols.¹ However, selective dehydration of *tert*-alcohol **1t** in the presence of *sec*-alcohol **5a** was difficult to achieve under the present Ru/C-catalyzed

conditions (Fig. 3B-iii). Meanwhile, simultaneous dehydration of *tert*-alcohol **1t** and oxygen-mediated oxidation¹³ of *sec*-alcohol **5a** proceeded smoothly to afford the corresponding olefin (**2t**) and ketone (**7a**) in high yields (Fig. 3B-iv).

As demonstrated in Fig. 3, Ru/C efficiently functioned as a catalyst for the dehydration of *tert*-alcohols. Therefore, further one-pot transformations were investigated (Fig. 4). We proposed that the dehydration of *tert*-alcohol **1** generates reaction intermediate **A**, which can undergo a Diels–Alder reaction^{14,15} with dimethyl acetylenedicarboxylate, followed by thermal isomerization to afford cyclohexadiene intermediate **B**. When this reaction is conducted under atmospheric molecular oxygen, subsequent Ru-catalyzed oxidative aromatization proceeds in a one-pot manner to afford highly functionalized aromatic products **10** from *tert*-alcohol **1**. Substrates bearing furan and thiophene moieties underwent the desired tandem sequence to afford the corresponding polycyclic aromatic products (**10a–10d**) in moderate yields. In addition, *tert*-benzyl alcohol derivatives were successfully converted into the corresponding naphthalene products (**10e–10g**). In the case of **10d**, the further oxidation (aromatization) of the dihydrophenanthrene moiety was not observed. The reason is unclear at this stage.

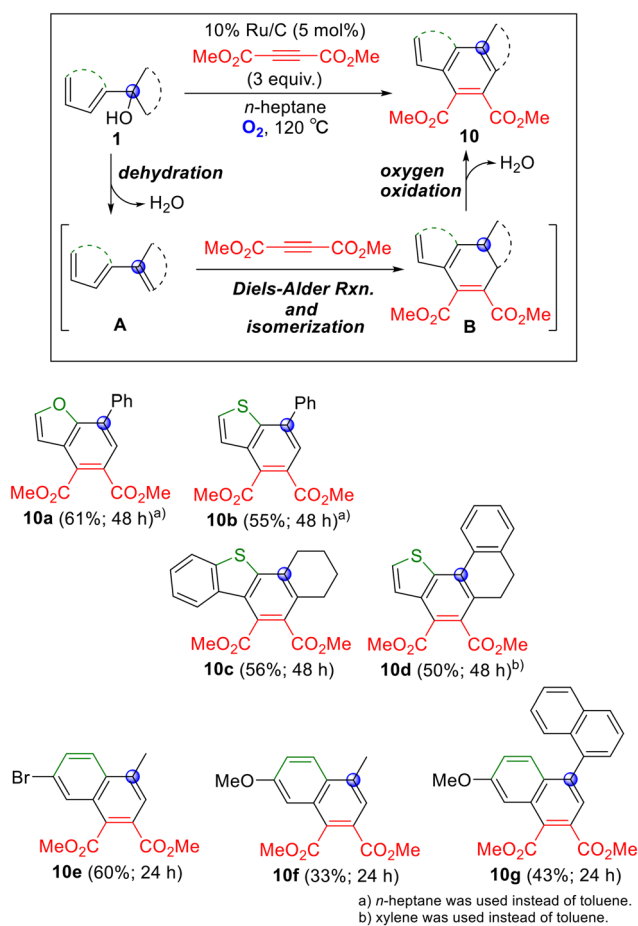
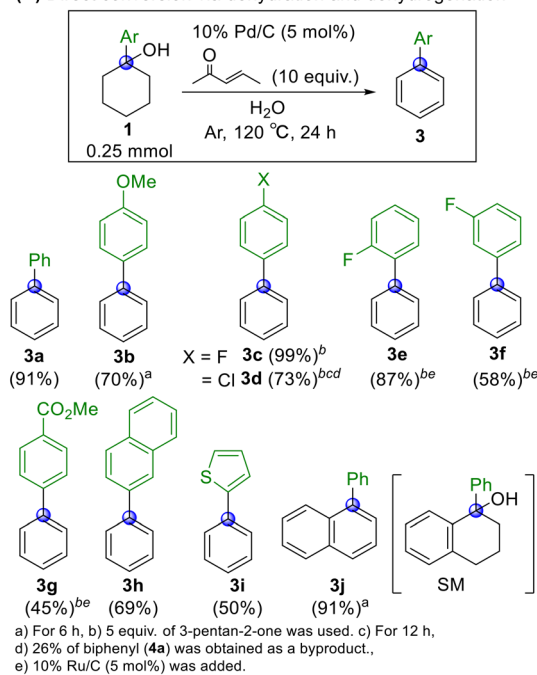


Fig. 4 One-pot synthesis of highly functionalized aromatics via Ru/C-catalyzed dehydration, the Diels–Alder reaction, and oxygen oxidation.



(A) Direct conversion via dehydration and dehydrogenation



(B) Stepwise conversion via dehydrogenation

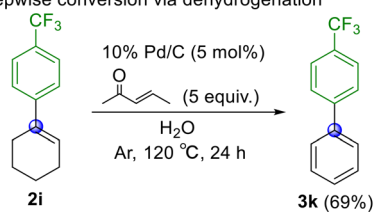


Fig. 5 One-pot biaryl synthesis from 1-arylcylohexanols: construction of benzene rings *via* Pd/C-catalyzed dehydration and dehydrogenation.

In these reactions, by-products arising from competing ene reactions^{15a} following the formation of intermediate **B** were also observed. The reaction under Ar instead of O₂ gave low yield (for example, 42% yield of **10e** was obtained under an Ar atmosphere).

Finally, we developed a method for one-pot biaryl synthesis from 1-arylcylohexanols using a Pd/C catalyst *via* dehydration and double dehydrogenation^{9f} in H₂O as a green solvent. As shown in Fig. 2A, entry 3, the use of Pd/C in H₂O afforded a mixture of biaryl **3a** and the reduced side product **4a**. Compound **4a** was generated by the hydrogenation of **1a** or **2a** using the H₂ produced during the dehydrogenation of **2a** to **3a**. Therefore, the addition of 3-penten-2-one as a hydrogen acceptor effectively suppressed the formation of the reduced side product **4a**, affording **3a** in 91% yield (Fig. 5-A) (screening of hydrogen acceptors is described in the SI).¹⁶ To the best of our knowledge, this is the first example of 3-penten-2-one being used as a hydrogen acceptor in related reactions. Furthermore, owing to its low boiling point, 3-penten-2-one can be readily removed under reduced pressure. The present biaryl synthesis was applicable to a range of substrates bearing electron-donating and electron-withdrawing substituents (OMe, F, Cl, and CO₂Me) on the

aromatic rings, affording the corresponding biaryl products (**3b–3g**). When the dehydration rate was low, the combined use of Pd/C and Ru/C was effective for the formation of products **3e**, **3f**, and **3g**. In reactions employing substrates bearing an aryl chloride, partial cleavage of the Ar–Cl bond occurred, resulting in the formation of biphenyl (**3a**) as a by-product alongside the desired product (**3d**). In addition, naphthyl and thienyl products (**3h** and **3i**) were successfully constructed. Tetrahydro-1-phenyl-1-naphthalenol underwent Pd/C-catalyzed dehydration followed by dehydrogenation to afford 1-phenylnaphthalene (**3j**). Unfortunately, substrates bearing the CF₃ group as a strong electron-withdrawing substituent were not compatible with the one-pot synthesis from 1-arylcylohexanols. However, a stepwise procedure involving Ru/C-catalyzed dehydration to form **2i** (Fig. 3A), followed by Pd/C-catalyzed double dehydrogenation (Fig. 5-B), successfully afforded the biaryl product **3k**.

Conclusions

We discovered that Ru/C and Pd/C, which are commercially available heterogeneous platinum-group-metal-on-carbon catalysts, exhibit dehydration activity toward *tert*-alcohols. The Ru/C-catalyzed dehydration in toluene is applicable to a wide range of substrates. In addition, Ru/C potentially exhibits catalytic activity for the oxidative aromatization of cyclohexene intermediates. Accordingly, tandem reactions involving Ru/C-catalyzed dehydration of *tert*-benzylic alcohols, a Diels–Alder reaction, and oxidative aromatization in toluene under atmospheric molecular oxygen afforded highly functionalized aromatic products. Furthermore, Pd/C-catalyzed dehydration followed by the dehydrogenation of 1-arylcylohexanols in H₂O enabled one-pot access to biaryl products. These green and sustainable transformations, based on the catalytic dehydration of *tert*-alcohols, represent novel and practical approaches for the construction of valuable synthetic intermediates and functional materials.

Author contributions

S. O. performed the synthetic work and wrote the manuscript. Y. S. and R. A. also carried out the synthetic work. S. A. and Y. S. contributed to the conceptualization, writing, review and editing. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available in the supplementary information (SI) of this article.

Supplementary information is available. See DOI: <https://doi.org/10.1039/d6cy00165c>



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