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Straightforward heterogeneous palladium catalyzed synthesis of aryl ethers and aryl amines *via* a solvent free aerobic and non-aerobic dehydrogenative arylation†

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Aryl ethers have been prepared from cyclohexanone derivatives and various alcohols in the presence of a catalytic amount of palladium on charcoal. The formation of an enol ether followed by an aerobic or non-aerobic dehydrogenation reaction, seem to be the key steps of this transformation. In addition, this new method was also adapted for the synthesis of arylamines.

Aryl ethers are employed in diverse domains, like pharmaceuticals, perfumes, cosmetics, paints, and varnishes, and some of them are produced in several ten thousand tons per year.[1] For example, the global production of phenoxyethanol, which is mainly used as a solvent, is around 170 000 t per year.[2]

Over the last century, numerous methods have been developed to synthesize aryl ethers. They can be obtained from epoxides.[3] The Williamson[4] synthesis could be also applied to basic media from halides. The Ullmann[5] and Buchwald–Hartwig[6] coupling reactions are the most described pathways from aromatic halides. Alternative routes using boronic[7] or bismuth[8] coupling partners have also been reported. However, the stoichiometric quantity of the base and the utilization of solvent and toxic substrates in these processes implied the production of a large amount of wastes.

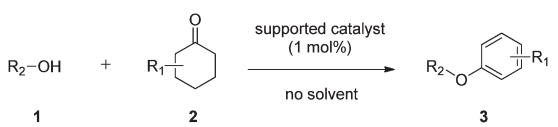
From non-aromatic substrates, the preparation of phenols[9] or anilines[10] was previously described *via* dehydrogenation pathways. Recently, the formation of diarylamines from cyclohexanone using homogeneous palladium catalysis was reported by Deng and co-workers,[11] Li and co-workers,[12] and Yoshikai and co-workers.[13] Maycock and co-workers[14] proposed the synthesis of diarylamines from cyclohexenones promoted by iodine. Moreover, during our study, Li and co-workers[15] described the synthesis of aryl ethers from 2-cyclohexenone in the presence of a stoichiometric amount of $CuCl_2$ in toluene under O_2. In addition, co-oxidant additives (KI and *N*-hydroxyphthalimide) were required when a catalytic amount of copper salts (10 mol%) was introduced, and this method was inefficient with cyclohexanone.

We previously developed acidic conditions to prepare alcohol naphthyl ethers with the recyclable Nafion® catalyst; however this methodology was not efficient enough with phenol derivatives.[16] We also recently described the reductive alkylation of carbonyl derivatives with alcohols and (poly)glycerol (Pd/C, Amberlyst 35, H_2) but aryls were partially reduced under the used conditions.[17] In similar conditions reported by Kita and co-workers[18] and Linder and Gooßen[19] only alkyl ethers were prepared.

Based on our continuous interest in establishing new and eco-efficient processes for etherification reactions which could be applied to glycerol, we report herein a straightforward and palladium-catalyzed direct aerobic and non-aerobic dehydrogenative alkylation of cyclohexanone derivatives with alcohols and polyols, including biosourced glycerol (Scheme 1).

In order to establish a green and safe process, our goal was to develop a solvent-free system, using heterogeneous catalysis and without any additive to facilitate the purification and to limit the production of wastes. In addition, a reaction taking place in an open reactor under air or in a closed system under argon was preferred to avoid the utilization of O_2, considering flammability risks.

At the beginning of our study, cyclohexanone **2a** and hexanol **1a** were used as model substrates in an open reactor,



Scheme 1 Envisaged methodology for the synthesis of aryl ethers by a heterogeneous catalyzed solvent free dehydrogenative arylation using cyclohexanone derivatives, alcohols and biosourced polyols.

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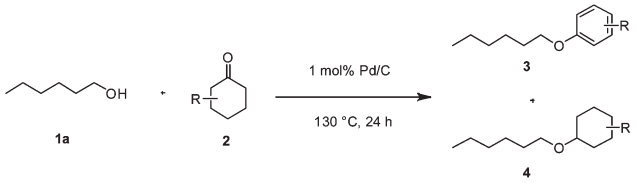
Table 1 Effects of the reactor type, the atmosphere and an additive (1-octene) on the alkylation reaction of hexanol **1a** with cyclohexanone **2a** or α-tetralone **2j**[a]



Entry	Substrate (2)	Reactor type	Additive	Conv.[b] (2, %)	Yield[b] (3, %)	Yield[b] (4, %)
1	 **2a**	Sealed tube (argon)	—	>99	50	50
2[c]	 **2a**	Sealed tube (argon)	1-Octene (1 eq.)	>99	70	30
3	 **2a**	Open reactor (air)	—	>99	99	0
4	 **2j**	Sealed tube (argon)	—	>99	78	<1
5	 **2j**	Open reactor (air)	—	74	58	0

[a] Experimental conditions: molar ratio cyclohexanone **2a**/hexanol **1a** = 1/5, Pd/C (5%) 1 mol%, 130 °C, 24 h. [b] Conversions and the ratio were determined by ^{1}H NMR spectroscopy. [c] Reaction time = 48 h.

without any solvent. First, we supposed that the oxygen from air will play the role of the final oxidant, in order to have an aerobic dehydrogenative arylation. After screening many supported metal catalysts and optimizing the experimental parameters, we found that the desired aryl ether **3a** was obtained in quantitative yield when 1 mol% of Pd/C (5%) was added to a molar ratio cyclohexanone **2a**/hexanol **1a** 1/5 at 130 °C in 24 h. Under these conditions, no by-products were observed.

Several experiments were performed in different reactors in order to propose a mechanism for this transformation. As shown in Table 1, when the reaction was realized in a sealed tube with model substrates cyclohexanone **2a** and hexanol **1a**, the conversion was excellent, but a 50/50 mixture of the aryl ether **3a** and the hydrogenated ether **4a** was obtained (entry 1). This result can be explained by the *in situ* formation of H_2, which can reduce the double bonds of the intermediates before their aromatization. To emphasize this hypothesis, a reaction was performed with 1-octene as an additive and afforded the expected aryl ether **3a** with a better selectivity, in a 70/30 ratio between **3a** and **4a** (entry 2). Moreover, octane was observed confirming the release of H_2 in the medium or in the presence of hydrogen adsorbed on the palladium surface. When the reaction was performed in an open reactor under air, the selectivity was excellent for the desired aryl ether **3a** (entry 3). We may conclude that in an open reactor and in the case of cyclohexanone, O_2 from air consumes hydrogen adsorbed on the palladium surface, affording the desired product in excellent yield. The reactivity of α-tetralone **2j** was compared to cyclohexanone's **2a**: in a sealed tube (entries 1 and 4) the conversion of the ketone was complete but the selectivity toward the desired product was better since 78% of compound **3** were observed. The by-products detected by GC-MS were the deoxygenated starting material, the naphthalene and the naphthol. In an open reactor, the same selectivity was observed, however the conversion was lower after 24 h. As a consequence, reactions performed with tetralone derivatives were realized in sealed tubes, and by increasing the temperature to 150 °C, the conversion was complete after 16 h. The following mechanisms can thus be proposed (Fig. 1).

With cyclohexanone derivatives (**A**), the palladium activates the carbonyl function, leading to the formation of hemiacetal **7** which is dehydrated to form enol ether **8**. Indeed, when the reaction was performed without a catalyst or with 10 wt% of activated charcoal, no conversion was observed, indicating that the palladium catalyst is necessary for the formation of enol ether **8**. Then, this intermediate could be dehydrogenated a first time by the Pd/C catalyst which may be regenerated by O_2 from air. Thus, water is formed as the only by-product. Finally, aryl ether **3** is obtained after a second dehydrogenation reaction of **9**. As described in the literature,[9a] the formation of phenol **5** could be observed in these conditions when less reactive alcohols were used as the substrate as mentioned further in this report. However, and as demonstrated with the results in Table 1 (entries 1 and 2), the oxygen in the air was clearly not necessary to obtain aryl ether **3**, but its presence allows a better selectivity for the aromatic product by reacting quickly with the hydrogen released in the medium, avoiding the hydrogenation reaction leading to hydrogenated ether **4** observed in the sealed tube in 50% yield (Fig. 1, **B**). Indeed, this observation was confirmed when the reaction was started with α-tetralone **2j** as the substrate (entry 4): the reaction afforded the desired aryl ether **3j** with an excellent selectivity

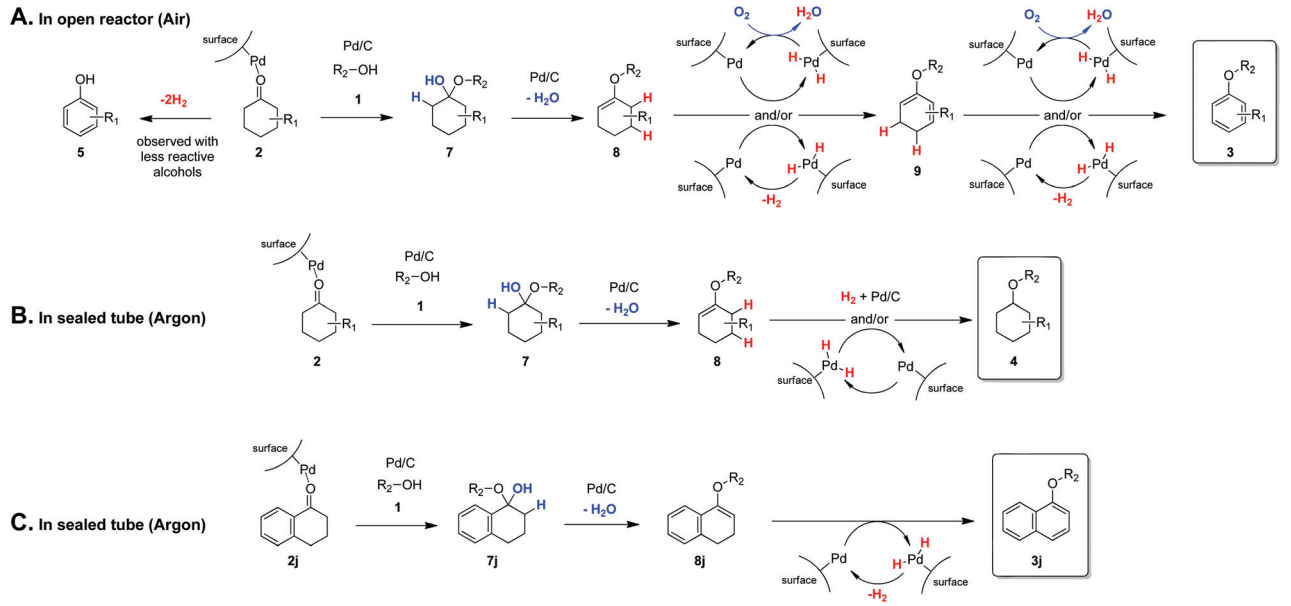
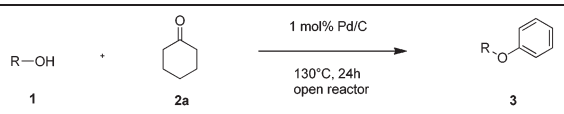


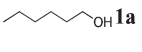
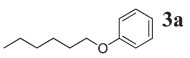
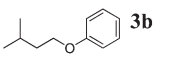
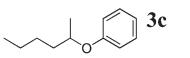
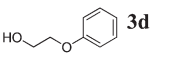
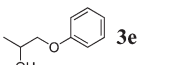
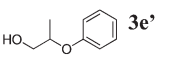
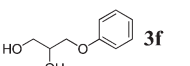
Fig. 1 Proposed mechanisms for (**A**) the dehydrogenative alkylation of cyclohexanone with an alcohol in an open reactor, (**B**) the formation of hydrogenated ether **4** in a sealed tube and (**C**) the dehydrogenative alkylation of a tetralone derivative with an alcohol in a sealed tube.

in a closed system, because in that case only one dehydrogenation reaction has to be performed (Fig. 1, **C**). More precisely, the aromatization of the intermediate enol ether was much faster in the case of α-tetralone **2j** than in the case of cyclohexanone.

To evaluate the scope of this new method, the optimized conditions were first applied for the synthesis of 1-*O*-arylethers by catalytic aerobic dehydrogenative arylation of various alcohols and polyols with cyclohexanone **2a**, without any solvent, as can be seen from the results in Table 2. Aerobic dehydrogenative arylation of hexanol **1a** with cyclohexanone **2a** afforded the corresponding aryl ether **3a** in a good 84% isolated yield (entry 1). When starting with 3-methylbutanol **1b**, the corresponding 1-*O*-phenyl ether **3b** was isolated in 75% yield (entry 2). With a less reactive secondary alcohol 2-hexanol **1c**, the yield of the desired aryl ether **3c** decreased to 34% (entry 3). In this last example, the conversion of the starting cyclohexanone **2a** was still complete, but phenol was observed as the sole by-product of the reaction in 54% NMR-yield. With ethylene glycol **1d**, the conversion was around 92% after 60 h, and 2-phenoxyethanol **3d** was isolated in 43% yield (entry 4). When starting with 1,2-propanediol **1e**, a mixture of regioisomers **3e** and **3e′** was isolated in 40% yield (entry 5). The ratio between 1-*O*-phenyl ether **3e** and 2-*O*-phenyl ether **3e′** was about 61/39. In the two last examples, phenol was also obtained as the sole by-product in 42% and 41% yield, respectively. Finally, with glycerol as the biosourced and available substrate, the desired 3-phenoxypropane-1,2-diol **3f** was isolated in 67% yield, with an excellent regioselectivity since no secondary aryl ether was detected (entry 6). To the best of our knowledge, this is the first successful example of a direct, solvent free arylation of glycerol by a heterogeneous catalysis. Because of the particular reactivity of this natural polyol, the experimental parameters had to be slightly reoptimized, with a longer reaction time and a lower cyclohexanone **2a**/glycerol **1f** molar ratio in order to achieve a complete conversion and thus

Table 2 Aerobic dehydrogenative alkylation of cyclohexanone **2a** with primary alcohols, secondary alcohols and polyols, including glycerol[a]



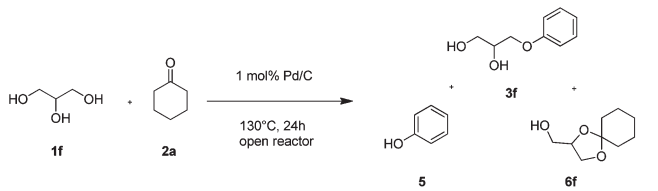
Entry	Substrate (**1**)	Product (**3**)	Conv.[b] (**2a**, %)	Isolated yield (arylether **3**, %)
1	 **1a**	 **3a**	>99	84 (99)[e]
2	 **1b**	 **3b**	>99	75 (96)[e]
3[c]	 **1c**	 **3c**	>99	34 (45)[e]
4[c]	 **1d**	 **3d**	92	43 (48)[e]
5[c]	 **1e**	 **3e**  **3e'**	94	40 (44;[e] ratio **3e**/**3e′** = 61/39)[f]
6[d]	 **1f**	 **3f**	>99	67 (77)[e]

[a] Experimental conditions: molar ratio cyclohexanone **2a**/alcohol = 1/5, Pd/C (5%) 1 mol%, 130 °C, 24 h, open reactor. [b] Conversions were determined by ^{1}H NMR spectroscopy. [c] Reaction time = 60 h. [d] Experimental conditions: molar ratio cyclohexanone **2a**/glycerol **1f** = 1/20, Pd/C (5%) 2 mol%, 130 °C, 60 h, open reactor. [e] ^{1}H NMR yields in parentheses. [f] Ratio between **3e** and **3e′** was determined by ^{1}H NMR spectroscopy.

to increase the yield for aryl ether **3f**. In fact, acetal **6f** was detected as the major compound after a reaction time of 24 h (Scheme 2), phenol **5** and the desired aryl ether **3f** were also identified as minor products. After 60 h, only traces of compound **6f** were detected and the major product was the desired aryl ether **3f**. We may conclude that acetal **6f** was in equilibrium with the intermediate enol ether and the driving force of the reaction was the aromatization leading to ether **3f**, as explained at the beginning of this report. The process in an open reactor was limited by the boiling point of the alcohols (>130 °C) in order to have a good conversion, but the reaction with volatile alcohols is actually under study in the laboratory.

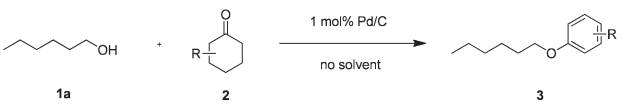
As shown in Table 3, cyclohexanone derivatives were also tested in order to afford functionalized aryl ethers. The dehydrogenative arylation of 3-methylcyclohexanone **2g** afforded aryl ether **3g** in 81% isolated yield (entry 1). With 2-cyclohexenone **2h**, phenyl ether **3a** was isolated in 59% yield (entry 2). When comparing this result with the reaction using cyclohexanone **2a** (Table 2, entry 1), this drop of yield was explained by the formation of phenol as the only by-product of the reaction in 28% yield. This original process was also efficient with tetrahydrothiophen-3-one **2i**, yielding the corresponding hexyloxythiophene **3i** in 56% (entry 3). Finally, this new method was adapted to tetralone derivatives by increasing the temperature to 150 °C in order to reach the complete conversion of the starting material after 16 h and using a sealed tube under an argon atmosphere as the reactor, as explained at the beginning of our report. Besides, working in a sealed tube overcomes the limitation with low-boiling alcohols. When the dehydrogenative arylation was performed with α-tetralone **2j** the desired naphthyl ether **3j** was isolated in an acceptable 67% yield (entry 4). With β-tetralone **2k**, the reaction afforded product **3k** in 80% isolated yield (entry 5). Finally, with a substituted α-tetralone **2l**, the corresponding naphthyl ether **3l** was isolated in 68% yield (entry 6). As explained at the beginning of the report and contrary to cyclohexanone and despite using a sealed tube as the reactor, only traces of hydrogenated ether and naphthol were observed in the last three examples, indicating that the aromatization was faster than the hydrogenation of the intermediate enol ether by the released hydrogen.

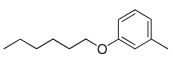
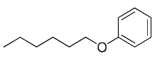
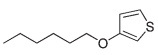
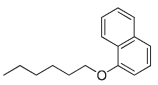
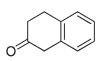
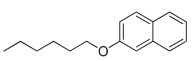
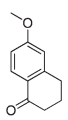
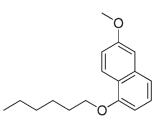
These conditions were also applied to biosourced polyols in order to have access to new molecules with possible surfactant properties, as shown in Table 4. Thus, the reaction with glycerol or diglycerol and α-tetralone **2j** afforded the corresponding naphthyl ethers **3m** and **3n** in 48% and 43% isolated yields, respectively (entries 1 and 2). From β-tetralone **2k**, the desired naphthyl ethers **3o** and **3p** were obtained in 69% and 52% yields (entries 3 and 4). In all these examples, the naphthyl ethers were obtained with an excellent regioselectivity.



Scheme 2 Dehydrogenative alkylation of cyclohexanone **2a** with glycerol **1f** with all detected by-products after a reaction time of 24 h when using the optimized conditions.

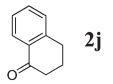
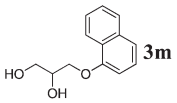
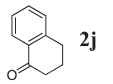
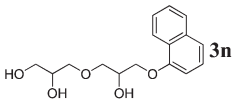
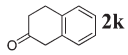
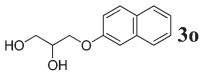
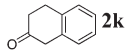
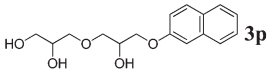
Table 3 Dehydrogenative alkylation of saturated substrate **2** with hexanol **1a**[a]



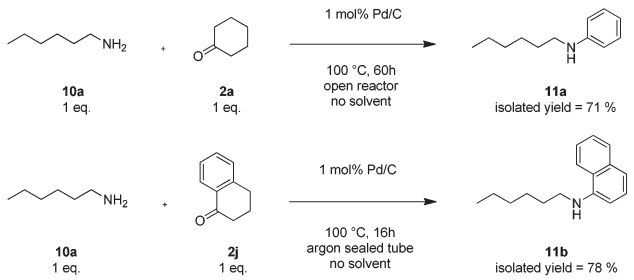
Entry	Substrate (2)	Product (3)	Conv.[d] (2, %)	Isolated yield (arylether 3, %)
1	 **2g**	 **3g**	>99	81 (93)[e]
2	 **2h**	 **3a**	>99	59 (68)[e]
3[b]	 **2i**	 **3i**	>99	56 (59)[e]
4[c]	 **2j**	 **3j**	>99	67 (78)[e]
5[c]	 **2k**	 **3k**	>99	80 (88)[e]
6[c]	 **2l**	 **3l**	>99	68 (74)[e]

[a] Experimental conditions: molar ratio substituted cyclohexanone **2**/hexanol **1a** = 1/5, Pd/C (5%) 1 mol%, 130 °C, 24 h, open reactor. [b] Reaction time = 48 h. [c] Experimental conditions: molar ratio tetralone derivative **2**/hexanol **1a** = 1/5, Pd/C (5%) 1 mol%, 150 °C, 16 h, sealed tube. [d] Conversions were determined by ^{1}H NMR spectroscopy. [e] ^{1}H NMR yields in parentheses.

Table 4 Dehydrogenative arylation of α-tetralone **2k** and β-tetralone **2l** with glycerol **1f** and diglycerol **1o**[a]

Entry	Substrate (2)	Product (3)	Conv.[b] (2, %)	Isolated yield (arylether 3, %)
1	 **2j**	 **3m**	>99	48 (53)[c]
2	 **2j**	 **3n**	>99	43 (47)[c]
3	 **2k**	 **3o**	>99	69 (72)[c]
4	 **2k**	 **3p**	>99	52 (56)[c]

[a] Experimental conditions: molar ratio tetralone derivative **2**/(di)glycerol = 1/5, Pd/C (5%) 2 mol%, 150 °C, 60 h, sealed tube. [b] Conversions were determined by ^{1}H NMR spectroscopy. [c] ^{1}H NMR yields in parentheses.



Scheme 3 Solvent free and Pd-catalyzed dehydrogenative alkylation of cyclohexanone derivatives with hexylamine **10a**. Experimental conditions: molar ratio cyclohexanone derivative/hexylamine **10a** = 1/1, Pd/C (5%) 1 mol%.

Finally, this new solvent free and heterogeneous palladium catalyzed dehydrogenative arylation could be applied for the preparation of aryl amines in a more eco-efficient way by optimizing the experimental parameters (Scheme 3). Indeed, a stoichiometric amount of hexylamine **10a** and cyclohexanone **2a** was reacted in an open reactor with 1 mol% of Pd/C (5%), without any solvent and additive. Under these conditions, the reaction afforded the corresponding arylamine **11a** in a good 71% isolated yield. When starting with α-tetralone **2j**, in a sealed tube, the corresponding naphthylamine **11b** was obtained in 78% isolated yield after 16 h. The scope and limitations of this reaction for amines are under study in our laboratory and will be published further.

Conclusion

In summary, a novel straightforward, solvent free and heterogeneous palladium catalyzed one-step synthesis of aromatic compounds from saturated substrates was developed. This process proposes a new economical, safe and "green" access to a wide variety of functionalized aryl ethers by using alcohols, polyols and substituted cyclohexanones or tetralones as substrates. When using (poly)glycerol as the starting material, new aryl ethers with various hydrophilic/lipophilic balances can be obtained. The key to the reaction mechanism seems to be the formation of an enol ether which is dehydrogenated to afford the final product. This process was successfully generalized for the preparation of arylamines and may be extended to other nucleophiles by slightly adapting the experimental parameters in each case. Besides, the main limitation of this method is the use of a relatively high temperature in an open reactor with cyclohexanone derivatives. For low-boiling alcohols, we are currently working on specific reactors under air pressure in order to overcome this limitation. Further investigations of this transformation are in progress in our laboratory.

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