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Palladium on carbon-catalyzed α -alkylation of ketones with alcohols as electrophiles: Scope and mechanism



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Niklas R. Bennedsen, Rasmus L. Mortensen, Søren Kramer*, Søren Kegnæs*

Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

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1. Introduction

Methods for facile carbon-carbon bond formation are crucial for the synthesis of organic molecules such as pharmaceuticals, agrochemicals, and functional materials [1–4]. Accordingly, the formation of a new $C(sp^3)-C(sp^3)$ bond to the α -carbon of carbonyl compounds, termed α -alkylation, is an important transformation that has received considerable attention [5–10]. Conventional methods for α -alkylation reactions often have problems with undesired waste, e.g. salts from alkyl halides, and require strong metallic bases and cryogenic temperatures. These aspects limit the industrial implementation and decrease the atom efficiency and sustainability of the methodologies [11,12]. Recently, a different strategy where alcohols are used as masked electrophiles, leading to water as the only byproduct, has attracted attention due to its potential as a greener alternative [13-19]. A variety of transition-metals has been implemented as catalysts for the α -alkylation of ketones with alcohols in both homogeneous [20-30] and heterogeneous systems [31-41]. Typically, reaction temperatures above 100 °C and 1-2 mol% catalyst loadings are required.

For homogeneous systems, the reaction mechanism for α -alkylation of ketones with alcohols has been thoroughly examined and the general consensus is that the reactions proceed through a hydrogen-borrowing pathway (Fig. 1) [19,23,26,

ABSTRACT

The α -alkylation of ketones with alcohols represents a green strategy for the formation of crucial carboncarbon bonds since it only produces water as byproduct. In terms of reaction mechanism, the evidence for homogeneous catalysis supports a catalytic hydrogen-borrowing pathway; however, the reaction mechanism has not been investigated for heterogeneous Pd/C catalysts. Here, we report an improved method for α -alkylation of ketones with alcohols using commercially available Pd/C, ubiquitous in organic synthesis labs, as catalyst. The reaction conditions are mild compared to state-of-the-art for both homoand heterogeneous catalysts, and the developed conditions produces quantitative yields for most ketones and alcohols. A hot filtration experiment and recycling of the catalyst supports the heterogeneous nature of catalysis. Importantly, the reaction mechanism is studied for the first time by a combination of stoichiometric experiments and kinetic analyses by in-situ IR (React-IR).

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30,34,42]. The reaction is initiated by dehydrogenation of the alcohol forming the corresponding aldehyde, thus activating it as an electrophile. Next, aldol condensation, which is typically catalyzed by addition of base, reacts the produced aldehyde and the ketone affording an α , β -unsaturated ketone. Finally, the C—C double bond is hydrogenated by the hydrogen originally removed from the alcohol, hence the term "hydrogen-borrowing".

In contrast to the homogeneous reactions, limited mechanistic evidence has been accumulated for α -alkylation of ketones with alcohols using heterogeneous catalysis [37,39,41]. In particular, no thorough mechanistic investigation including kinetics has been performed on α -alkylation of ketones with alcohols using palladium on carbon catalysis. A reaction pathway similar to homogeneous catalysis is tempting to propose; however, it cannot always be assumed that the pathways with homogeneous and heterogeneous catalysts are the same [43,44]. A better understanding of the operating pathways is pivotal for advancement of the field and rational design of future reactions.

In 2005, Cho described the only existing methodology, which includes substrate scope investigation, where commercially available Pd/C is used as catalyst for α -alkylation of ketones with alcohols [31]. The catalytic system used for the reaction between acetophenone and benzyl alcohol (2 equiv) was comprised of 5 mol% Pd/C, 3 equivalents KOH, and 4 equivalents 1-decene in dioxane at 100 °C for 20 h and afforded 66% yield of the corresponding 1,3-diphenylpropan-1-one. Albeit, the use of a commercially available catalyst which is ubiquitous in organic synthesis



^{*} Corresponding authors. E-mail addresses: sokr@kemi.dtu.dk (S. Kramer), skk@kemi.dtu.dk (S. Kegnæs).

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Fig. 1. Hydrogen-borrowing mechanism for α-alkylation of ketones with alcohols.

laboratories is highly convenient, the moderate yield, high catalyst loading, and need for strong base and an additive warrant improvements. Furthermore, no investigation of the reaction mechanism was performed.

Herein, we report a mechanistic investigation of a significantly improved and simplified method for α -alkylation of acetophenones with alcohols using commercially available Pd/C as the catalyst. The individual reaction steps are examined by stoichiometric studies and reaction kinetics is thoroughly investigated by in-situ IR measurements. In addition, the catalyst material is studied by TEM and XPS, and the nature of catalysis is examined by hot filtration and recycling experiments. Finally, based on the mechanistic investigation, a rational solution for future optimization of α -alkylations is suggested.

2. Results and discussion

2.1. Optimization

After an optimization of the reaction conditions on the reaction between acetophenone and benzyl alcohol, the desired product

Table 1

Influence of various reaction parameters on the reaction outcome.



Entry	WIOUIIICations	CONVERSION (%)	field (%)
1	-	100	100
2	No catalyst	6	0
3	Activated carbon	43 ^b	3 ^b
4	10 wt% Pd/C	100	100
5	In air	32	7
6	K ₂ CO ₃	0	0
7	Li ₂ CO ₃	0	0
8	Cs ₂ CO ₃	66	66
9	Et ₃ N	0	0
10	1.0 equiv K ₃ PO ₄	100	100
11	2.0 equiv K ₃ PO ₄	100	100
12	Headspace 3.0 mL	100	100
13	Headspace 2.5 mL	99	99
14	Headspace 2.0 mL	97	97
15	0.125 M	100	100
16	0.50 M	100	100
17	1.0 M	100	100

^a Based on ¹H NMR using 0.5 equivalents of dibenzyl ether as standard.

^b Reaction time was 24 h.

was obtained in a quantitative yield (Table 1, entry 1). The optimized reaction conditions use 1 mol% Pd/C, 1.1 equivalents benzyl alcohol, and 1.5 equivalents of K_3PO_4 in toluene at 80 °C for 6 h. The reaction conditions are slightly milder, but otherwise very similar to those recently reported for a custom-made palladium on carbon catalyst.[38] Control experiments showed that no product is formed in the absence of Pd/C and that activated carbon without palladium leads to highly unselective conversion (entries 2–3). The weight percentage loading of palladium on the carbon does not influence the reaction outcome (entry 4). However, the reaction is sensitive to air and choice of base (entries 5–9). Finally, variations to the K₃PO₄ equivalents, headspace, and concentration were undertaken to ensure that changes to these parameters during a mechanistic investigation was not detrimental to the reaction outcome (entries 10–17).

2.2. Substrate scopes for alcohols and ketones

Having established optimized reaction conditions, the generality of the transformation was assessed by a substrate scope investigation. To ensure one general procedure for all substrates, the reaction time was increased to 24 h. First, acetophenone was reacted with various alcohols (Table 2). Derivatives of benzyl alcohol bearing electron-withdrawing or -donating groups in the paraposition (Me, OMe, CF₃, and F) provided excellent product yields (entries 1–5). In contrast, the use of a secondary benzylic alcohol did not lead to any product formation (entry 6), neither did a secondary aliphatic alcohol, pentan-3-ol (not shown). Although primary aliphatic alcohols reacted more sluggishly than benzylic alcohols, an increase in temperature from 80 °C to 100 °C led to good yields of the corresponding ketone for both heptanol and propanol, respectively (entries 7–8).

Next, a series of acetophenone derivatives were reacted with benzyl alcohol (Table 3). Again, substrates bearing substituents ranging from very electron-donating to very electronwithdrawing (Me, OMe, CF₃, and F) provided excellent yields and selectivity towards the ketone product (entries 1–5). Substitution on the α -carbon of acetophenone decreased the activity but maintained high selectivity towards the ketone product (entry 6). Sterical hindrance in the ortho-position of the acetophenone was well-tolerated (entry 7). Interestingly, under the same reaction conditions, two aliphatic ketones also smoothly underwent α -alkylation with excellent selectivity for the least substituted α -carbon (entries 8–9).

2.3. Recycling and heterogeneity

With regard to the nature of the hydrogen-borrowing catalysis, there are two possibilities: (1) heterogeneous catalysis by palladium nanoparticles or (2) leaching of catalytically active homogeneous species [45,46]. To distinguish between these possibilities, a hot filtration experiment was performed (Scheme 1). In the experiment, inhibition of the catalytic activity occurred when the solid catalyst was removed from the reaction mixture despite the addition of fresh K₃PO₄ (1.5 equiv). This outcome of the hot filtration experiment confirmed the heterogeneous nature of the hydrogen-borrowing catalysis. Accordingly, the developed catalytic system is appropriate for a reaction mechanism study of heterogeneous Pd/C-catalyzed α -alkylation.

Based on the established heterogeneity of the hydrogenborrowing catalysis, the possibility of catalyst recycling was examined. Facile catalyst separation and recycling is an advantage of heterogeneous catalysis in comparison to homogeneous catalysis. Indeed, the Pd/C catalyst was successfully recycled four times for five consecutive reactions (Table 4; see supporting information for procedure). Throughout all consecutive reactions, excellent

Table 2

Substrate scope with respect to the alcohol.



Entry	R^1	R ²	Conversion (%) ^a	Yield (%) ^a
1	Н	Н	100	100
2	Me	Н	100	100
3	MeO	Н	100	100
4	F	Н	100	100
5	CF ₃	Н	98	98
6	F	Me	0	0
7	Me	н	72	72 ^b
8	Me		73	73 ^b

^a Based on ¹H NMR using 0.5 equivalents of dibenzyl ether as standard.

^b Reaction temperature was 100 °C.

Table 3

Substrate scope with respect to the ketone.



Entry	\mathbb{R}^1	R ²	Conversion (%) ^a	Yield (%) ^a
1	Н	Н	100	100
2	Me	Н	100	100
3	MeO	Н	100	100
4	F	Н	100	100
5	CF ₃	Н	100	100
6	Н	Ph	67	52
7	O.		100	100
	Me			
8	0 0		100	100 ^b
	Ме			
9	- Q		100	100 ^c
	Me			

^a Based on ¹H NMR using 0.5 equivalents of dibenzyl ether as standard.

^b Product is 2-cyclohexylethyl phenyl ketone.

^c Product is 1,5-diphenylpentan-3-one.



Scheme 1. Hot filtration experiment on the α -alkylation of acetophenone with benzyl alcohol.

selectivity was maintained, but a decrease in activity was observed at the fourth recycle (from 96% to 60%). The TEM images of the fresh Pd/C catalyst and the Pd/C catalysts which had been recycled four times appeared similar. Both contain Pd nanoparticles with a size of 2–20 nm with a tendency of fewer smaller particles for the recycled compared to the fresh catalyst but few to none larger agglomerates (Fig. 2; additional images in supporting information). Accordingly, particle agglomeration is unlikely to cause catalyst

0.125 mmol



1.1 equiv

Entry	Number of recycles ^a	Conversion (%) ^b	Selectivity (%) ^b
1	0	100	100
2	1	100	100
3	2	100	100
4	3	96	100
5	4	60	100

^a Recycling was performed by extracting the reaction mixture with toluene to remove organic residues from the catalyst. 1.5 equiv fresh K_3PO_4 was added together with a new batch of substrates.

^b Based on ¹H NMR using 0.5 equivalents of dibenzyl ether as standard.

deactivation. The reaction liquid was analyzed by ICP-OES and the palladium content in the reaction liquid was equal or below the blank suggesting that palladium does not leach under our reaction conditions (see supporting information for procedure).

XPS analysis of palladium (3d) for the fresh and recycled catalysts was performed (Fig. 3). The spectrum of palladium for the fresh catalyst indicated the presence of two species with binding energies consistent with Pd and PdO at 335.4 eV and 336.8 eV for the 3d_{5/2} transition, respectively (Fig. 3, left) [47]. The same was observed for the 3d_{3/2} signal at approximately 340 and 342 eV. However, the signals for the PdO species were suppressed strongly and Pd was primarily observed for the recycled catalyst. This observation indicates that PdO was reduced under the reaction conditions, possibly by hydrogen released from benzyl alcohol. The composition of the carbon from the catalyst did not show any difference between the fresh and recycled catalyst (Fig. 3, right). Based on the observation made from XPS, TEM, and ICP, we see a slight change in nanoparticle composition and size, and no palladium is leached during the reaction. However, the effect of change in composition and size of the nanoparticles relative to the deactivation during the recycle study is still only speculative.

2.4. Mechanistic investigation

Finally, we sought to identify the reaction pathway of the developed heterogeneous catalysis system. Potentially, a reaction mechanism similar to the one elucidated for the homogeneous counterparts could be operating (Fig. 1). Accordingly, a series of



Fig. 2. (Left) TEM image of unused Pd/C catalyst. (Right) TEM image of recycled Pd/C that have been used for five consecutive reactions.



Fig. 3. XPS analysis of the fresh Pd/C catalyst and the recycled Pd/C catalyst. (Left) Pd 3d analysis and (right) C 1s analysis of both the fresh and the recycled catalyst.



Scheme 2. Stoichiometric experiments conducted with Pd/C catalyst. (a) Test for alcohol dehydrogenation. (b) Chalcone formation from acetophenone and benzaldehyde under standard reaction conditions. (c) Chalcone hydrogenation using benzyl alcohol as hydrogen donor. (d) Cross-over experiment demonstrating product formation from both a benzylic alcohol and aldehyde under the reaction conditions. A control experiment demonstrated that the use of 2.4 equiv benzyl alcohol under the normal reaction conditions also provides quantitative yield. For all reactions, the yields were determined by ¹H NMR using 0.5 equiv dibenzyl ether as standard. ^aConversion and yield relative to added benzyl alcohol.



Fig. 4. (top) Reaction conditions for React-IR. (bottom) Reaction profile monitored by React-IR.



Fig. 5. Reaction kinetics monitored by React-IR. (a) Same excess experiment. (b) Influence of catalyst loading on reaction rate. (c) First order plot for determination of overall reaction order. (d) Variable time normalization analysis on two different acetophenone concentrations.

experiments were performed to establish the feasibility of the individual steps (Scheme 2). Initially, it was demonstrated that Pd/C is capable of dehydrogenating benzyl alcohol forming benzaldehyde, independent of the presence of K_3PO_4 (Scheme 2a). Next, the quan-

titative formation of chalcone from acetophenone and benzaldehyde was established both under the standard catalytic conditions and in the absence of Pd/C (Scheme 2b). Notably, the chalcone is not reduced due to the lack of a hydrogen donor under these conditions. However, subjecting the chalcone to the reaction conditions in the presence of benzyl alcohol as hydrogen donor leads to facile reduction of the C–C double bond and oxidation of benzyl alcohol (Scheme 2c). Finally, a cross-over experiment between acetophenone, benzaldehyde, and CF₃-labelled benzyl alcohol demonstrated that both the benzylic alcohol substrate and benzaldehyde can form product under the standard catalytic conditions (Scheme 2d). In addition, the observation of significant amounts of unlabeled benzyl alcohol indicates that the alcohol dehydrogenation is reversible. Overall, these results are consistent with the hydrogen-borrowing mechanism illustrated in Fig. 1, thus such a reaction mechanism is also likely to be operating under the heterogeneous catalytic conditions developed here.

After having demonstrated the feasibility of the individual steps under the catalytic conditions, we investigated the reaction kinetics using in-situ IR spectroscopy (React-IR). Initially, a 1.25 mmol scale version of the reaction between acetophenone and benzyl alcohol was monitored up to 90% conversion (Fig. 4). Supporting the stoichiometric experiments, both benzaldehyde and chalcone were observed during the reaction, albeit in low concentrations. At 20 min and at 3 h, the yields of the compounds detected by React-IR correspond to those detected by ¹H NMR.

Based on the reaction profile, the system appeared wellbehaved and suitable for further kinetic analyses. The acetophenone consumption was chosen as a measure for the rate. First, a same excess experiment was performed (Fig. 5a) [48]. The almost perfect overlay of the time-adjusted same excess experiment indicates that there is no product inhibition or deactivation in the ratelimiting step. Interestingly, varying the Pd/C catalyst loading from 0.5 to 2.0 mol% had no influence on the reaction rate (Fig. 5b). Accordingly, the hydrogen-borrowing cycle does not contain the overall rate-limiting step, suggesting that the aldol condensation is rate-limiting.

Plotting the acetophenone consumption in a first order plot produced a straight line up to 90% conversion (Fig. 5c). Thus, the overall reaction order is either first order or at least pseudo-first order. Variable time normalization analysis at two different acetophenone concentrations clearly demonstrated a first order dependence on acetophenone concentration (Fig. 5d; see supporting information for fitting to other orders) [49]. This is again consistent with the aldol condensation being rate-limiting. However, unless deprotonation of acetophenone is rate-limiting, generally, an overall second order reaction would be expected. Nonetheless, the detected, constant steady-state concentration of benzaldehyde (Fig. 4) could lead to an observed overall pseudo-first order reaction, even if addition of the enolate to the aldehyde is rate-limiting. In either case, the rate of the reaction only depends on the concentration of acetophenone with the experimental rate law being: rate = k[ketone].

3. Conclusions

In summary, we have described an improved methodology for commercially available Pd/C-catalyzed α -alkylation of ketones with alcohols. The reaction conditions are mild, and most ketones and alcohols afford quantitative yields. The simple procedure and use of a catalyst which already can be found in any synthesis laboratory makes the method highly convenient and widespread use is predicted. Importantly, the first mechanistic study on this catalyst system was performed. Based on a combination of stoichiometric experiments and reaction kinetics, a catalytic hydrogenborrowing mechanism analogous to homogeneous catalysis is supported. Surprisingly, the Pd/C-catalyzed hydrogen-borrowing cycle is very fast, even with only 0.5 mol% Pd/C, while the rate-limiting step was found to be the base-catalyzed aldol condensation. It is likely that the slow aldol condensation is the reason that elevated reaction temperatures are required for both homogeneous and heterogeneous α -alkylation of ketones with alcohols. These observations indicate that it might be possible to lower the reaction temperature in general for α -alkylation of ketones with alcohols by addition of improved catalysts for the aldol condensation step.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.01.034.

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