

A palladium-catalyzed route for α -alkylation of ketones by primary alcohols

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Abstract

Ketones react with primary alcohols in dioxane at 100 °C in the presence of a catalytic amount of Pd/C and KOH along with 1-decene as a sacrificial hydrogen acceptor to give the corresponding coupled ketones in moderate to good yields. The catalytic pathway seems to be proceeded via a sequence involving initial oxidation of primary alcohols to aldehydes, cross aldol condensation, and regioselective reduction. © 2005 Elsevier B.V. All rights reserved.

Keywords: α -Alkylation; Hydrogen acceptor; Ketones; Palladium catalyst; Primary alcohols

1. Introduction

It is known that α -alkylation of ketones has a wide availability from the viewpoint of carbon–carbon σ bond formation [1]. In connection with this report, besides conventional α -alkylation of ketones, which is generally achieved by the coupling between nucleophilic enolates (enolate equivalents) and electrophilic alkylating agents, several transition metal-catalyzed versions have also been attempted because of the efficiency of reaction and the versatility of substrate [2,3]. During the course of our ongoing studies on ruthenium catalysis, it has been recently found that carbonyl compounds are coupled with primary alcohols in the presence of a ruthenium catalyst [4,5]. The coupling of ketones **1** with primary alcohols **2** preferentially afforded coupled ketones **3** (Scheme 1, route a) [4] or coupled secondary alcohols **4** (Scheme 1, route b) [5] according to the molar ratio of **2** to **1** [6,7]. In close relation with route a of Scheme 1, Ishii and co-workers have also reported an iridium-catalyzed α -alkylation of ketones with primary alcohols [8]. It was suggested by both groups that the α -alkylation of ketones with primary alcohols proceeds via an initial oxidation of primary alcohols to aldehydes

followed by aldol condensation between the starting ketones and aldehydes to form α,β -unsaturated ketones and regioselective reduction of the latter by $[\text{Ru}]\text{H}_2$ generated in the initial oxidation stage. Upon such an intrinsic protocol, this report describes an alternative palladium-catalyzed route for α -alkylation of ketones with primary alcohols by precise tuning of molar ratio of primary alcohols to ketones and the addition of a sacrificial hydrogen acceptor [9].

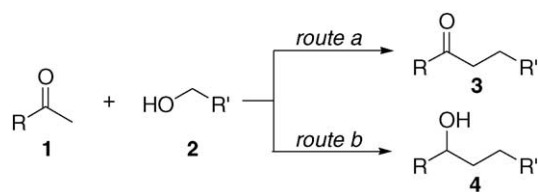
2. Experimental

2.1. General

¹H and ¹³C NMR spectra were recorded on Varian Unity Plus 300 (300 MHz for ¹H NMR; 75.5 MHz for ¹³C NMR) and Bruker Avance Digital 400 (400 MHz for ¹H NMR; 100 MHz for ¹³C NMR) spectrometers using TMS as an internal standard. Infrared spectra were recorded on Mattson Galaxy 7020A FT-IR spectrophotometer. Mass spectra were obtained on a Shimadzu QP-1000 spectrometer. GLC analyses were carried out with Shimadzu GC-17A (FID) equipped with CBP10-S25-050 column (Shimadzu, a silica fused capillary column, 0.33 mm \times 25 m, 0.25 μm film thickness) using N₂ as carrier gas. The isolation of pure products was carried out via column (silica gel 60, 70–230 mesh, Merck) and thin

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Scheme 1.

layer (silica gel 60 GF₂₅₄, Merck) chromatography. Commercially available organic and inorganic compounds were used without further purification and dioxane was purchased from Junsei (extra pure grade).

2.2. Typical procedure for palladium-catalyzed α -alkylation of ketones by primary alcohols

A mixture of **1a** (0.120 g, 1 mmol), **2a** (0.148 g, 2 mmol), 5% Pd/C (0.106 g, 0.05 mmol), KOH (0.168 g, 3 mmol) and 1-decene (0.561 g, 4 mmol) in dioxane (3 mL) was placed in a 5 mL screw-capped vial and allowed to react at 100 °C for 40 h. The reaction mixture was filtered through a short silica gel column (ethyl acetate-hexane = 1:1) to eliminate inorganic salts. To the extract was added appropriate amount of undecane as an internal standard and analyzed by GLC for the determination of the conversion of **1a** and the yield of **5**. Removal of the solvent left a crude mixture, which was separated by thin layer chromatography (silica gel, ethyl acetate-hexane = 1:5) to give coupled ketone **3a** (0.132 g, 75%). The products prepared by the above procedure were characterized spectroscopically as shown below.

1-Phenylhexan-1-one (**3a**) [10]: colorless oil; IR (neat) 1690 cm⁻¹ (C=O); ¹H NMR (300 MHz, CDCl₃) δ 0.91 (*t*, *J* = 7.2 Hz, 3H), 1.34–1.40 (m, 4H), 1.69–1.74 (m, 2H), 2.96 (*t*, *J* = 7.5 Hz, 2H), 7.42–7.48 (m, 2H), 7.52–7.58 (m, 1H), 7.94–7.98 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 13.9, 22.5, 24.0, 31.5, 38.5, 128.0, 128.5, 132.8, 137.0, 200.6 (C=O); MS *m/z* (relative intensity) 176 (*M*⁺, 9), 105 (100).

1-Phenyl-octan-1-one (**3b**) [11]: colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 0.88 (*t*, *J* = 6.8 Hz, 3H), 1.29–1.37 (m, 8H), 1.69–1.78 (m, 2H), 2.96 (*t*, *J* = 7.4 Hz, 2H), 7.43–7.48 (m, 2H), 7.52–7.57 (m, 1H), 7.94–7.97 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 14.0, 22.6, 24.3, 29.1, 29.3, 31.7, 38.6, 128.0, 128.5, 132.8, 137.1, 200.6 (C=O).

5-Methyl-1-phenylhexan-1-one (**3c**) [12]: colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 0.90 (d, *J* = 6.6 Hz, 6H), 1.22–1.30 (m, 2H), 1.52–1.66 (m, 1H), 1.69–1.79 (m, 2H), 2.93 (*t*, *J* = 7.4 Hz, 2H), 7.41–7.46 (m, 2H), 7.50–7.56 (m, 1H), 7.93–7.97 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 22.1, 22.4, 27.8, 38.5, 38.7, 127.9, 128.4, 132.7, 137.0, 200.3 (C=O).

4-Methyl-1-phenylpentan-1-one (**3d**) [13]: colorless oil; IR (neat) 1688 cm⁻¹ (C=O); ¹H NMR (400 MHz, CDCl₃) δ 0.94 (d, *J* = 6.0 Hz, 6H), 1.60–1.66 (m, 3H), 2.95 (*t*, *J* = 7.5 Hz, 2H), 7.42–7.46 (m, 2H), 7.51–7.55 (m, 1H), 7.94–7.97 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.5,

27.9, 33.3, 36.6, 128.1, 128.5, 132.8, 137.1, 200.7 (C=O); MS *m/z* (relative intensity) 176 (*M*⁺, 3), 105 (100).

4-Methyl-1-phenylhexan-1-one (**3e**) [14]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.87–0.93 (m, 6H), 1.15–1.26 (m, 1H), 1.35–1.46 (m, 2H), 1.50–1.59 (m, 1H), 1.73–1.81 (m, 1H), 2.88–2.95 (m, 2H), 7.43 (*t*, *J* = 7.5 Hz, 2H), 7.51–7.54 (m, 1H), 7.95 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.7, 19.4, 29.7, 31.3, 34.6, 36.7, 128.4, 128.9, 133.2, 137.5, 201.1 (C=O).

1,5-Diphenylpentan-1-one (**3f**) [15]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.67–1.83 (m, 4H), 2.66 (*t*, *J* = 7.0 Hz, 2H), 2.97 (*t*, *J* = 7.0 Hz, 2H), 7.15–7.19 (m, 3H), 7.25–7.28 (m, 2H), 7.41–7.45 (m, 2H), 7.51–7.55 (m, 1H), 7.92–7.94 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 23.9, 31.0, 35.7, 38.3, 125.7, 127.9, 128.2, 128.3, 128.5, 132.8, 136.9, 142.2, 200.2 (C=O); MS *m/z* (relative intensity) 238 (*M*⁺, 62), 105 (100).

1,3-Diphenylpropan-1-one (**3g**) [16]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 3.06 (*t*, *J* = 7.6 Hz, 2H), 3.28 (*t*, *J* = 7.6 Hz, 2H), 7.17–7.54 (m, 8H), 7.94 (d, *J* = 7.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 30.1, 40.4, 126.1, 128.0, 128.4, 128.5, 128.6, 133.0, 136.9, 141.3, 199.2 (C=O).

1,5-Diphenylpentan-3-one (**3h**) [17]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.69 (*t*, *J* = 7.5 Hz, 4H), 2.87 (*t*, *J* = 7.5 Hz, 4H), 7.11–7.31 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 29.7, 44.4, 126.0, 128.2, 128.4, 140.9, 209.0 (C=O); MS *m/z* (relative intensity) 238 (*M*⁺, 72), 105 (100).

1,7-Diphenylheptan-3-one (**3i**) [4]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.53–1.64 (m, 4H), 2.38 (*t*, *J* = 7.0 Hz, 2H), 2.59 (*t*, *J* = 7.0 Hz, 2H), 2.69 (*t*, *J* = 7.5 Hz, 2H), 2.87 (*t*, *J* = 7.5 Hz, 2H), 7.06–7.19 (m, 6H), 7.22–7.28 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 23.3, 29.7, 30.9, 35.7, 42.8, 44.2, 125.7, 126.0, 128.2 (x2), 128.3, 128.4, 141.1, 142.1, 210.0 (C=O).

1-Phenyldecane-5-one (**3k**) [4]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (*t*, *J* = 7.0 Hz, 3H), 1.20–1.35 (m, 6H), 1.52–1.65 (m, 4H), 2.34–2.42 (m, 4H), 2.61 (*t*, *J* = 7.0 Hz, 2H), 7.11–7.19 (m, 3H), 7.24–7.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.4, 23.4, 23.5, 31.0, 31.4, 35.7, 42.5, 42.8, 125.7, 128.3, 128.4, 142.2, 211.4 (C=O).

1-Phenyl-octan-3-one (**3l**) [17]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (*t*, *J* = 7.0 Hz, 3H), 1.18–1.33 (m, 4H), 1.51–1.59 (m, 2H), 2.35 (*t*, *J* = 7.5 Hz, 2H), 2.70 (*t*, *J* = 7.8 Hz, 2H), 2.88 (*t*, *J* = 7.8 Hz, 2H), 7.16–7.18 (m, 3H), 7.23–7.28 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.3, 22.9, 23.9, 30.2, 31.8, 43.4, 44.6, 126.5, 128.7, 128.9, 141.6, 210.7 (C=O).

4-Methyl-1-phenylhexan-3-one (**3m**) [18]: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.83 (*t*, *J* = 7.3 Hz, 3H), 1.03 (*t*, *J* = 7.0 Hz, 3H), 1.30–1.41 (m, 1H), 1.60–1.70 (m, 1H), 2.38–2.46 (m, 1H), 2.72–2.77 (m, 2H), 2.89 (*t*, *J* = 7.8 Hz, 2H), 7.17–7.19 (m, 3H), 7.27 (*t*, *J* = 7.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 12.1, 16.2, 26.3, 30.1, 43.2, 48.4, 126.4, 128.7, 128.8, 141.8, 214.2 (C=O).

2-Benzyl-1,2,3,4-tetrahydronaphthalen-1-one (**3n**) [19]: pale yellow viscous oil; ¹H NMR (400 MHz, CDCl₃) δ

Table 1
Optimization of conditions for the reaction of **1a** with **2a**

Run	2a/1a	KOH (mmol)	1-Decene (mmol)	Conversion ^{a,b} (%) of 1a	Yield (%)		
					3a	4a	5a ^a
1	3	1	–	84	18	22	28
2	3	2	–	97	4	40	36
3	3	3	–	98	1	48	40
4	1	3	–	86	37	28	18
5	1	1	–	67	15	8	26
6 ^b	3	3	–	100	3	53	Trace
7	1	3	2	68	53	Trace	Trace
8	2	3	2	86	62	8	4
9	2	3	4	84	75	0	0

Reaction conditions: **1a** (1 mmol), 5% Pd/C (0.05 mmol), dioxane (3 mL), 100 °C, for 40 h.

^a Determined by GLC.

^b In the absence of dioxane.

1.72–1.82 (m, 1H), 2.06–2.13 (m, 1H), 2.63 (dd, $J = 13.6$ and 9.5 Hz, 1H), 2.70–2.77 (m, 1H), 2.84–2.97 (m, 2H), 3.49 (dd, $J = 13.6$ and 4.0 Hz, 1H), 7.19–7.23 (m, 4H), 7.28–7.31 (m, 3H), 7.42–7.46 (m, 1H), 8.07 (d, $J = 7.0$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 27.6, 28.5, 35.6, 49.4, 126.1, 126.5, 127.5, 128.3, 128.7, 129.2, 132.4, 133.2, 140.0, 144.0, 199.3 (C=O); MS m/z (relative intensity) 236 (M^+ , 98), 145 (99), 91 (100).

3. Results and discussion

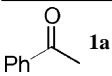

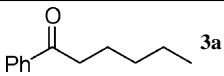
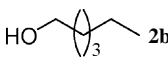
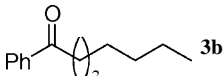
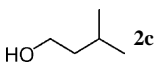
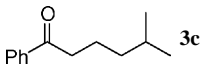
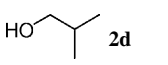
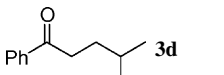
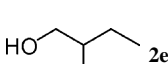
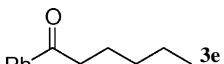

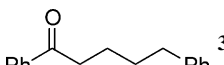
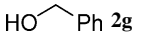
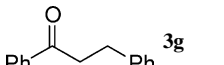
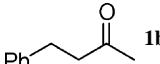
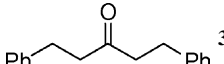
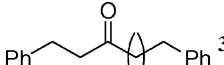
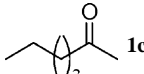
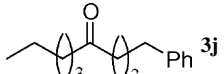
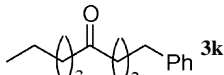
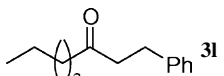
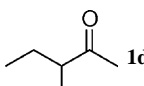
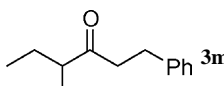
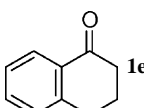
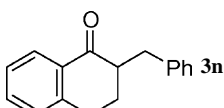
Based on our recent report on ruthenium-catalyzed α -alkylation of ketones with primary alcohols [4], several tentative results for the reaction between acetophenone (**1a**) and butanol (**2a**) are summarized in Table 1. Treatment of **1a** with 3 equiv. of **2a** in dioxane in the presence of a catalytic amount of 5% Pd/C (5 mol%) and KOH (1–3 equiv.) afforded direct transfer hydrogenation product [20], 1-phenylethanol (**5a**) and coupled ketone **3a** and secondary alcohol **4a** (runs 1–3). The amount of KOH was critical for the yield and distribution of coupled products **3a** and **4a**. The yield of **3a** was gradually decreased with the increase in the amount of KOH employed, whereas that of **4a** gradually increased from 22% (1 equiv), 39% (2 equiv), to 48% (3 equiv). The molar ratio of [2a]/[1] also affected the distribution of coupled products, lower molar ratio resulting in preferential formation of coupled ketone **3a** (runs 4 and 5). This could be due to the relative amount of the starting primary alcohol **2a** as hydrogen donor. Performing the reaction in the absence of solvent selectively gave the coupled secondary alcohol **4a** in preference to **3a** without the formation of direct transfer hydrogenation product **5a** (run 6). On the other hand, when 1-decene was further added, the coupled ketone **3a** was obtained nearly as the sole product (run 7). The best result in terms of both overall yield and the selectivity of **3a** to **4a** was best accomplished by further tuning on

the molar ratio [2a]/[1a] and the amount of 1-decene (runs 8 and 9).

Having established reaction conditions, various ketones **1** were subjected to react with primary alcohols **2** in order to investigate the reaction scope and several representative results are summarized in Table 2. Aryl(methyl) ketone **1a** was readily α -alkylated with various primary alcohols (**2a–2f**) having straight and branched alkyl chains to give the coupled ketones (**3a–3f**) in the range of 75–88% yields. With benzyl alcohol (**2g**) under the usual conditions, the coupled ketone **3g** was produced in 45% yield with a considerable amount of coupled secondary alcohol, 1,3-diphenylpropan-1-ol (35% yield). However, shortening the reaction time (for 20 h) gave **3g** (66% yield) selectively in preference to 1,3-diphenylpropan-1-ol (16% yield). As is the case for ruthenium-catalyzed α -alkylation of ketones with primary alcohols, lower reaction rate and yield were observed with alkyl(methyl) ketones (**1b–1d**) under the employed conditions and the alkylation took place exclusively at less hindered methyl position over α -methylene and -methine [21]. On the other hand, it is known that primary and secondary alcohols are readily oxidized to carbonyl compounds in the presence of a palladium catalyst and a base along with an aryl halide [22] and carbon tetrachloride [23] as oxidants. However, treatment of 2-heptanone (**1c**) with **2a** in the presence of 4-bromotoluene in place of 1-decene under the employed conditions afforded 6-undecanone (**3j**) in only 4% yield. Benzo-fused cyclic ketone **1e** which has only methylene reaction site was alkylated with **2g** to give 2-benzyl-1-tetralone (**3n**) in 46% yield, whereas no alkylations occurred with alkyl(aryl) ketones having only methylene reaction site under the employed reaction conditions.

Although the exact scheme is not yet fully understood, a plausible pathway, consistent with the products formed, is depicted in Scheme 2. The pathway seems to proceed via initial oxidation of primary alcohol **2** to aldehyde **6**, which in turn triggers cross aldol condensation with ketone **1** under

Table 2
Palladium-catalyzed α -alkylation of ketones **1** by primary alcohols **2**

Ketones 1	Primary alcohols 2	Coupled ketones 3	Yield (%)
			75
			81
			88
			76
			79
			79
			66 ^a
	2g		57 ^b
	2f		50
	2a		40 ^{b,c}
	2f		40 ^b
	2g		43 ^b
	2g		43 ^b
	2g		46 ^b

All reactions were carried out with **1** (1 mmol), **2** (2 mmol), KOH (3 mmol) and 1-decene (4 mmol) in dioxane (3 mL) at 100 °C for 40 h unless otherwise stated.

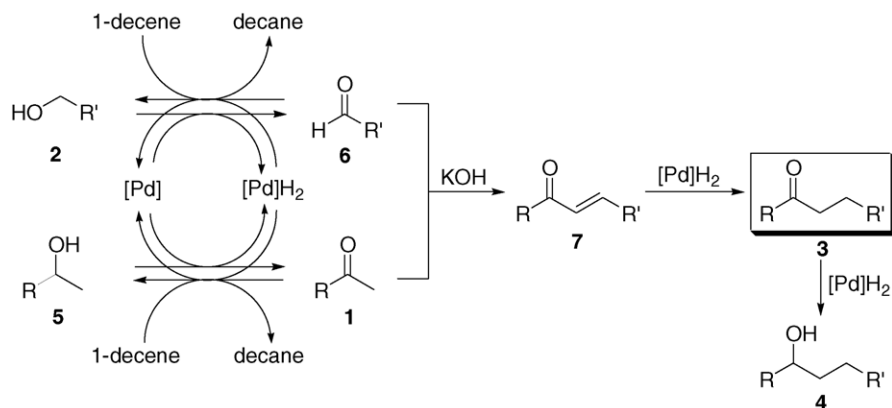
^a For 20 h.

^b [1]/[2] = 2.

^c GLC yield.

KOH to give an α,β -unsaturated ketone **7**. This is followed by hydrogenation to coupled ketone **3** and/or coupled secondary alcohol **4** by a dihydridopalladium species generated in the initial oxidation stage of the alcohol **2** [20]. As shown in the results of Table 1, the addition of 1-decene seems to suppress the formation of direct transfer hydrogenation product **5** and further hydrogenated coupled secondary alcohol **4** by oxidiz-

ing [Pd]H₂ to [Pd] [24]. The formation of **6** seems also to be accelerated by hydrogen transfer from **2** to 1-decene as well as **1** and **7** [25]. It is known that the initial oxidation of **2–6** proceeds via oxidative addition of a palladium to O–H bond and subsequent β -hydrogen elimination and a strong base is used as cocatalyst to promote transition metal-catalyzed transfer hydrogenation [20].



Scheme 2.

4. Conclusion

In summary, it has been shown that ketones undergo α-alkylation with primary alcohols in the presence of a palladium catalyst and a base along with a sacrificial hydrogen acceptor. The preferential direction to coupled ketones or coupled secondary alcohols depends on the molar ratio of starting substrates and whether a sacrificial hydrogen acceptor is added or not.

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