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Ru-MACHO-Catalyzed Highly Chemoselective Hydrogenation of α-Keto Esters to 1,2-Diols or α-Hydroxy Esters

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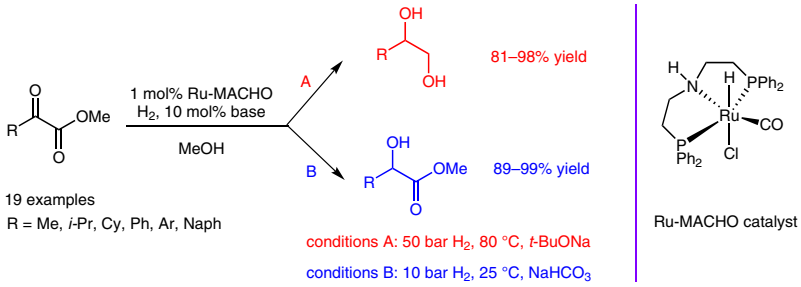

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Abstract A ruthenium pincer catalyst has been shown to be highly effective for the hydrogenation of a wide range of α-keto esters, affording either diols or hydroxy esters depending on the choice of reaction conditions. Strong base, high temperature, and pressure favor the formation of diols whilst the opposite is true for the hydroxy esters.

Key words hydrogenation, α-ketoesters, α-hydroxy esters, diols, ruthenium catalyst

The transformation of ketones and esters into the corresponding alcohols is one of the most important chemical reactions in organic synthesis.[1] Traditionally, production of these chemicals is based on processes using stoichiometric amounts of reducing reagents, such as $LiAlH_4$, $NaBH_4$, and BH_3, which lead to risk in operation and tedious workup.[2] From the viewpoint of both atom economy and practical applications, the direct catalytic hydrogenation of ketones and esters with hydrogen gas affords a clean and efficient route for the preparation of alcohols.[3] Indeed, over the past three decades, the hydrogenation of ketones for the preparation of alcohols has achieved a great deal of success.[4] However, for esters, the hydrogenation is still a challenging task due to their poor reactivity and selectivity.[5] In recent years, excellent catalytic systems have been developed, which are mainly based on pincer complexes containing iron, cobalt, ruthenium, iridium, and osmium, allowing for the hydrogenation of esters under much milder conditions.[6–10] One of the successful examples is Takasago's Ru-MACHO catalyst, which has been applied to the industrial hydrogenation of (*R*)-lactate in a large scale to produce (*R*)-1,2-propanediol.[8f]

Given the importance of 1,2-diols as building blocks in synthetic applications,[11] the pursuit of new methods for their synthesis remains an interesting topic. In the literature, 1,2-diols are synthesized generally by the following methods: osmium-catalyzed dihydroxylation of olefins,[12] diboration of olefins,[13] hydrogenation of α-hydroxy esters[8f] and/or α-hydroxy ketones[14] and/or 1,2-diketones,[15] ring-opening reactions of epoxides,[16] enzymatic reactions,[17] and the reduction of α-keto esters with $NaBH_4$.[18] Among these methods, hydrogenation with H_2 is perhaps the most straightforward, efficient, and atom-economic method. Herein, we report our results on the first hydrogenation of α-keto esters to produce 1,2-diols directly with the Ru-MACHO catalyst. It is noted that by simply changing the base, this catalytic system affords α-hydroxy esters without the formation of diol products.

Initially, we investigated the hydrogenation of α-keto esters with the Ru-MACHO catalyst under the reaction conditions reported by Kuriyama.[8f] Unfortunately, an unsatisfactory chemoselectivity was observed, with the diol **2a** and hydroxy ester **3a** formed in a ratio of 20:80 (Table 1, entry 1). The ratio of **2a**/**3a** increased slightly in favor of **2a** in a prolonged reaction time (Table 1, entry 2). Considering the remarkable impact of base on the catalytic activity in the hydrogenation of ketones and esters,[19] a series of inorganic bases was tested (Table 1, entries 3–7).[20] To our delight, excellent conversion and selectivity for **2a** were achieved with the strong base sodium *tert*-butoxide (Table 1, entry 3). A lower H_2 pressure or temperature did not have much effect on the conversion, but decreased the ratio of **2a**/**3a** (Table 1, entries 8–12). Further experiments demonstrated that decreasing the amount of base improves the ratio of **2a**/**3a** and up to 99:1 was observed (Table 1, entries 13 and 14). However, under the reaction conditions em-

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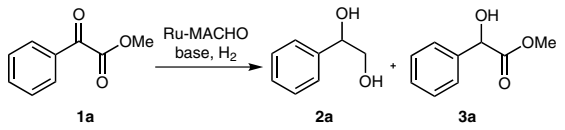
ployed but with a lower catalyst loading of 0.2 mol% and 0.1 mol%, the ratio of **2a**/**3a** decreased to 90:10 (Table 1, entry 15) and 62:38 (Table 1, entry 16), respectively.

Table 1 Optimization of Reaction Conditions for Hydrogenation of α-Keto Ester **1a**[a]



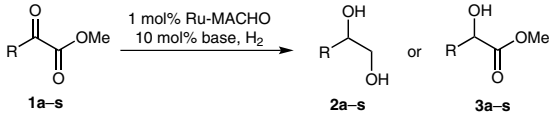
Entry	Base	Temp (°C)	Conversion (%)[b]	**2a**/**3a**[b]
1	MeONa	80	100	20:80
2[c]	MeONa	80	100	23:77
3	*t*-BuONa	80	100	97:3
4	NaOH	80	100	6:94
5	KOH	80	93	0:93
6	*t*-BuOK	80	100	92:8
7	K_2CO_3	80	100	30:70
8[d]	*t*-BuONa	80	100	96:4
9[e]	*t*-BuONa	80	100	92:7
10	*t*-BuONa	60	100	95:5
11	*t*-BuONa	40	100	89:11
12	*t*-BuONa	25	100	77:23
13[f]	*t*-BuONa	80	100	99:1
14[g]	*t*-BuONa	80	100	95:5
15[f,h]	*t*-BuONa	80	100	90:10
16[f,i]	*t*-BuONa	80	100	62:38
17[f,j]	NaOH	25	100	5:95
18[f,j]	KOH	25	91	0:91
19[f,j]	$NaHCO_3$	25	100	0:100
20[f,i,j]	$NaHCO_3$	25	100	0:100

[a] Reaction conditions: **1a** (0.5 mmol), Ru-MACHO (5 umol), base (0.1 mmol), toluene (0.5 mL), 50 bar H_2, 12 h.
[b] The conversion and ratio of **2a**/**3a** were determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[c] The reaction time was 24 h.
[d] The pressure was 30 bar.
[e] The pressure was 10 bar.
[f] With 0.05 mmol base.
[g] With 0.15 mmol base.
[h] S/C was 500.
[i] S/C was 1000.
[j] The pressure was 10 bar.

The chemoselectivity of this catalytic system is strongly affected by the strength of the base. Thus, using a weak base benefited the formation of α-hydroxy esters under the hydrogenation conditions (Table 1, entries 4 and 5).[21] Further studies demonstrated that a weaker base was better, affording excellent chemoselectivity under much milder conditions (Table 1, entries 17–19). In particular, high activity and chemoselectivity were achieved with $NaHCO_3$ at 0.1% catalyst loading and 25 °C (Table 1, entry 20). These results are consistent with ketone reduction being much easier than that of esters.

Based on the optimal reaction conditions, the scope of substrates was explored subsequently and the results are listed in Table 2. In general, most of α-keto esters were fully hydrogenated with a high chemoselectivity, affording either diols under the conditions A or α-hydroxy esters under the conditions B with good to excellent isolated yields. Thus, for substrates **1a**–**k** and hydrogenated diols **2a**–**k** under the reaction conditions A, it was found that the reaction was only slightly sensitive to the substituent position (Table 2, compare entry 3 with entries 4 and 5 and entry 6 with entry 7). For the *para*-substituted esters, the reduction worked equally well for both electron-donating and electron-withdrawing groups (Table 2, entries 2, 3, 6, 8, 10, 11). For disubstituted aromatic substrates **1l**–**o**, the hydrogenation reaction proceeded smoothly, affording excellent isolated yields for both the 2,4-disubstituted substrates (Table 2, entries 12 and 13) and 3,5-disubstituted ones (Table 2, entries 14 and 15). Naphthyl-substituted substrate **1p** and aliphatic substrates **1q**–**s** were both hydrogenated to diol products with high isolated yields (Table 2, entries 16–19).

Table 2 Hydrogenation of α-Keto Esters to Diols and α-Hydroxy Esters[a]



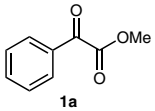
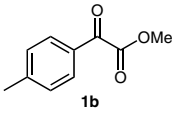
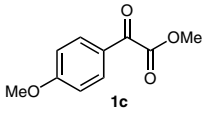
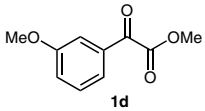
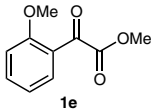
Entry	Substrate	Product **2** (%)[b,d]	Product **3**(%)[c,d]
1	 **1a**	91 (99:1)[e]	98 (0:100)[e]
2	 **1b**	90 (99:1)[e]	95 (0:100)[e]
3	 **1c**	96 (100:0)[e]	99 (0:100)[e]
4	 **1d**	81 (86:14)[e]	98 (2:98)[e]
5	 **1e**	89 (90:10)[e]	91 (3:97)[e]

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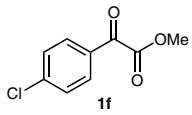
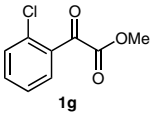
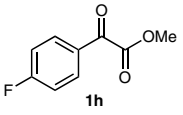
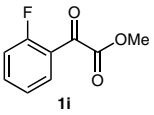
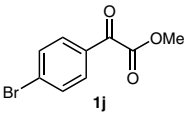
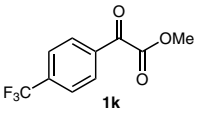
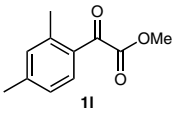
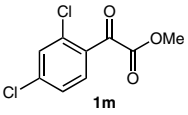
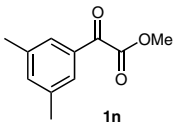
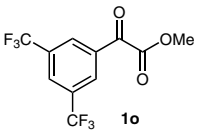
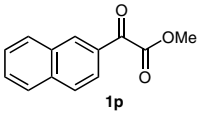
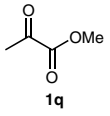
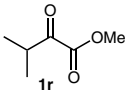
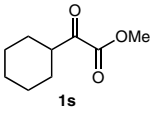
Table 2 (continued)

Entry	Substrate	Product **2** (%)[b,d]	Product **3**(%)[c,d]
6	 **1f**	94 (99:1)[e]	98 (0:100)[e]
7	 **1g**	90 (93:7)[e]	89 (8:92)[e]
8	 **1h**	92 (100:0)[e]	98 (0:100)[e]
9	 **1i**	91 (98:2)[e]	90 (5:95)[e]
10	 **1j**	97 (100:0)[e]	99 (0:100)[e]
11	 **1k**	97 (100:0)[e]	95 (0:100)[e]
12	 **1l**	95 (99:1)[e]	97 (0:100)[e]
13	 **1m**	98 (99:1)[e]	99 (0:100)[e]
14	 **1n**	94 (100:0)[e]	95 (0:100)[e]
15	 **1o**	95 (100:0)[e]	98 (0:100)[e]
16	 **1p**	96 (100:0)[e]	99 (0:100)[e]
17	 **1q**	93 (96:4)[e]	98 (0:100)[e]
18	 **1r**	94 (99:1)[e]	92 (8:92)[f]
19	 **1s**	91 (95:5)[e]	94 (0:100)[e]

[a] The reaction was carried out with 0.5 mmol substrate (**1a**–**1s**), H_2, 0.05 mmol base, MeOH (0.5ml), reaction time 12 h.
[b] Conditions A: 50 bar H_2, *t*-BuONa (0.05 mmol), 80 °C.
[c] Conditions B: 10 bar H_2, $NaHCO_3$ (0.05 mmol), 25 °C.
[d] Isolated yields.
[e] The ratio of **2**/**3**was determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[f] The ratio of **1**/**3**was determined by ^{1}H NMR.

Under the conditions B where a weaker base, lower H_2 pressure, and lower temperature were employed, the substrates **1a**–**s** were all hydrogenated to the α-hydroxy esters **3a**–**s**. Excellent yields were obtained for almost all the substrates examined.

In summary, we have developed an efficient method for the preparation of diol and α-hydroxy esters via the chemoselective hydrogenation of α-keto esters catalyzed by a pincer Ru-MACHO catalyst. It was found that the chemoselectivity can be readily altered by simply varying the reaction conditions, including particularly the strength of the base. Exploration of related chiral pincer catalysts for asymmetric hydrogenation is ongoing in our group.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561971.

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(20) **Typical Procedures for Hydrogenation of α-Keto Esters with Ru-MACHO**

A glass liner containing a stir bar was charged with substrate (0.5 mmol), base (0.05 mmol), Ru-MACHO (5 μmol) and MeOH (0.5 mL) in a glove box. The glass liner was then placed into an autoclave followed by degassing with H_2 three times. The hydrogenation was carried out at 10–50 bar H_2 with stirring at 80 °C for 12–24 h. After the reaction finished, the autoclave was allowed to cool down to r.t. The hydrogen gas was then carefully released in a fume hood, and the solution transferred to a flask with H_2O (2 mL), extracted with CH_2Cl_2 (3 × 5 mL), dried with Na_2SO_4, and concentrated in vacuo to afford the pure product **2a**–**s** or **3a**–**s** (see Supporting Information).

Compound **2a**: 91% yield, white solid; mp 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.38 (m, 5 H), 4.83 (dd, *J* = 3.6, 8.1 Hz, 1 H), 3.76–3.79 (m, 1 H), 3.65–3.70 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 128.7, 128.2, 126.2, 74.8, 68.2 ppm. MS (EI): *m/z* calcd for $C_8H_{10}O_2$ [M + Na]$^+$: 161.0578; found: 161.0561.

Compound **3a**: 98% yield, colorless liquid. ^{1}H NMR (400 MHz,

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$CDCl_3$): δ = 7.33–7.43 (m, 1 H), 5.19 (s, 1 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.3, 138.3, 128.7, 128.7, 126.7, 73.0, 53.2 ppm. ESI-HRMS: *m/z* calcd for $C_9H_{10}O_3$ $[M + Na]^+$: 189.0528; found: 189.0510.

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