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Rhodium(I)- or ruthenium(II)-catalyzed direct coupling of vinyl ketones with aldehydes and the subsequent reduction to give aldol derivatives *anti*-selectively

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Abstract

A vinyl ketone reacts with an aldehyde to give an α-methylene-β-hydroxyalkanone with the concomitant formation of the vinyl ketone dimer in the presence of catalytic amount of $RhH(PPh_3)_4$ or $RuH_2(PPh_3)_4$ under almost neutral conditions. The selectivity of the cross-coupling product is remarkably improved in the presence of an extra mole of aldehyde. This type of cross-coupling is explained by the intermediacy of the transition metal enolate which is formed by the Michael-type addition of M–H to a vinyl ketone. The subsequent hydrogenation of the carbon–carbon double bond of α-methylene-β-hydroxyalkanone proceeds readily to give aldol derivatives in the presence of the catalyst. [Rh(COD)(DPPB)]PF_6, [COD = 1,5-cyclooctadiene, DPPB = 1,4-bis(diphenylphosphino)butane] is the best choice of catalyst and gives aldol derivatives *anti*-selectively. Thus, the two-step operation described provides aldol derivatives by an *anti*-selective route under almost neutral conditions.

Introduction

α,β-Unsaturated ketones are widely used as electrophiles at the carbonyl carbon or the β-carbon. On the other hand, it is difficult to give these compounds a nucleophilic character at the α-carbon. Some viable methods have been proposed to fulfill this requirement, since the introduction of an electrophile to the sp^2-hybridized α-position of α,β-unsaturated ketones is an important operation. Central to the precedented approaches is the three-step procedure composed of (i) Michael-type addition of M–Y to **1**, (ii) attack of an electrophile on **3**, and (iii) elimination of Y–H from **4** as shown in Scheme 1 [1]. Such a strategy, however, requires the inevitable use of an equimolar amount of M–Y which is relatively expensive and/or troublesome to use. On the other hand, an α-acylvinyl carbanion equivalent **5** has

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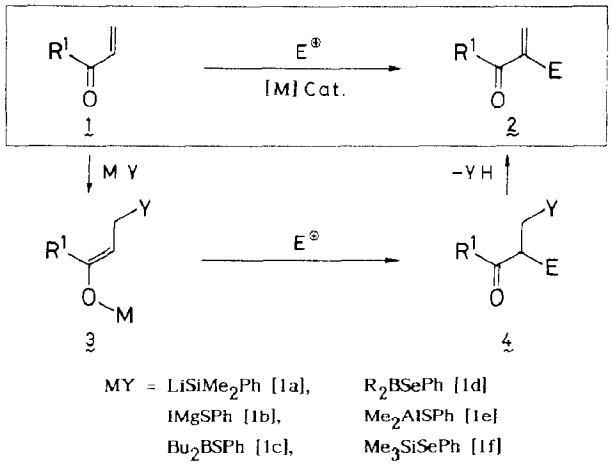
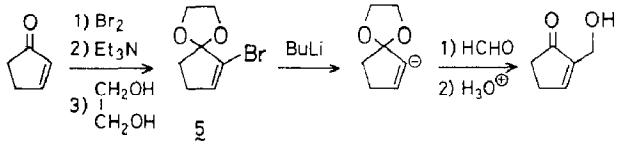


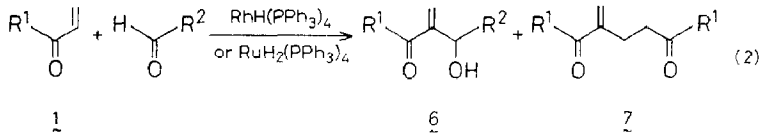
Scheme 1

also been reported, but many steps are required to complete the transformation from the α,β-enone (eq. 1) [2].



(1)

Despite the current widespread upsurge of interest, there are few examples of the selective carbon-carbon bond formations catalyzed by rhodium [3,4] and ruthenium complexes [5]. Recently, we pointed out the putative intervention of a rhodium enolate formed by the Michael-type addition of $RhH(PPh_3)_4$ to an α,β-enone in the synthesis of α-trimethylsilyl ketones [6]. If this type of transition metal enolate has sufficient nucleophilicity for an aldehyde [7], a direct transformation of **1** to **2** can be attained through aldol-type carbon–carbon bond formation with the aid of transition metal complexes under neutral conditions. We describe herein the successful coupling of a vinyl ketone with an aldehyde to give **6** in the presence of $RhH(PPh_3)_4$ or $RuH_2(PPh_3)_4$ as a catalyst precursor.



(2)

1 6 7

Results and discussion

When a mixture of 3-buten-2-one (**1a**) (5 mmol) and propanal (5 mmol) was heated in a sealed tube containing a catalytic amount of $RhH(PPh_3)_4$ (1 mol%) at 105 °C for 2 h, two types of coupling products **6a** and **7a** (**6a**/**7a** = 85/15) were obtained. Exclusion of solvent is crucial in the present reaction to ensure acceptable yields. In fact, when benzene was used as a solvent, the yield of **6a** dropped sharply

Table 1

Coupling reaction of 3-buten-2-one (**1a**) with propanal [a]

Entry	Catalyst [b] (mol%)	Additive [c]	Conditions (°C/h)	Product [d] **6**:**7**	Yield of **6** [e] (%)	Turnover of metal
1	$RhH(PPh_3)_4$ (1.0)	none	105/2	93:7	47	48
2	$RhH(PPh_3)_4$ (0.6)	none	40/40	96:4	17	28
3	$RhH(PPh_3)_4$ (0.9)	EtOH	105/2	90:10	57	62
4	$RhH(PPh_3)_4$ (0.8)	i-PrOH	105/2	93:7	62	74
5	$RhH(PPh_3)_4$ (0.8)	i-PrOH	40/40	97:3	78	92
6	$RhH(PPh_3)_4$ (0.8)	C	105/2	92:8	61	73
7	$RhH(PPh_3)_4$ (0.9)	C	40/20	98:2	83	92
8	$RhH(PPh_3)_4$ (0.9)	D	105/2	93:7	76	86
9	$RhH(PPh_3)_4$ (0.4)	i-PrOH	40/43	97:3	57	157
10	$RhH(PPh_3)_4$ (0.1)	i-PrOH	40/160	97:3	58	457
11	$RhH(PPh_3)_4$ (0.8)	acetone	105/2	90:10	15	18
12	$RhH(PMePh_2)_4$ (1.0)	none	40/20	–	trace	–
13	$RhH(DPPE)_2$ (1.0)	i-PrOH	40/20	–	trace	–
14	$RhH(PPh_3)_3$ (1.0)	i-PrOH	41/40	97:3	56	56
15	A (1.0)	none	105/2	100:0	63 [f]	–
16	B (1.0)	none	110/2	84:16	43	41
17	$RuH_2(PPh_3)_4$ (0.5)	none	40/40	97:3	82	164
18	$RuH_2(PPh_3)_4$ (0.2)	i-PrOH	40/40	97:3	83	365
19	PPh_3 (4.2)	none	40/20	77:23	40 [f]	–

[a] Reactions were conducted on a 5-mmol scale without solvent in a sealed tube using a mixture of **1a**/propanal = 1/2. [b] A: $[Rh(COD)(DPPE)]PF_6/H_2$, B: $RhH(PPh_3)_4$/4 PBu_3. [c] About 20 mol% (based on **1a**) of an alcohol was added. C: 2-methyldiphenylsilylheptan-1-ol, D: 2-trimethylsilylheptan-1-ol. [d] The ratio was determined by capillary GLC analyses (PEG-HT Bonded, 25 m). [e] Isolated yield. [f] Contaminated with an unidentified product.

to 2% even though 3 mol% of $RhH(PPh_3)_4$ had been employed. The predominant formation of **6a** stimulated us to modify further the reaction conditions in order to improve the yield and selectivity of **6a**. We found that the formation of **7a** was appreciably decreased when two equivalents of aldehyde were used. The results are listed in Table 1.

The results show clearly that the lower reaction temperature (40 °C, 40 h) brings about a higher selectivity for **6a** (entries 2, 5, and 7, compared with entries 1, 4, and 6, Table 1); the addition of a small amount of an alcohol increases the yield of **6a** (entries 3–9, compared with entries 1 and 2, Table 1). The turnover number of Rh rose to 457 under similar conditions (entry 10, Table 1). It is well-known that $RhH(PPh_3)_4$ catalyzes the hydrogen transfer from an alcohol to an α,β-enone [8]. Accordingly, the ketone derived from the added alcohol may enhance the cross-coupling. The participation of a ketone, however, was excluded by the experiment in which acetone was used as an accelerator instead of 2-propanol (entry 11, Table 1). Thus the alcohol itself plays an important role in the present cross-coupling reaction.

In contrast to the remarkable catalysis of $RhH(PPh_3)_4$, neither $RhH(PMePh_2)_4$ nor $RhH(DPPE)_2$ [DPPE = 1,2-bis(diphenylphosphino)ethane] was effective as a catalyst for the cross-coupling under similar conditions; almost all the starting materials were recovered (entries 12 and 13, Table 1). The cationic complex, $[Rh(COD)(DPPE)]PF_6$, when activated by hydrogen gas, bubbled through the

solution, was effective for the coupling reaction despite the concomitant formation of an unidentified by-product (entry 15, Table 1).

In contrast to poor results of modified rhodium complexes, the catalysis by $RuH_2(PPh_3)_4$ for this cross-coupling was comparable to that of $RhH(PPh_3)_4$. Moreover, the ruthenium complex gave a high yield of **6a** and a high turnover number of Ru regardless of the absence or presence of an alcohol (entries 17 and 18, Table 1). It should be stressed that the homo-coupling of an aldehyde is not observed at all, although $RuH_2(PPh_3)_4$ is known to be an efficient catalyst for the formation of esters by the Tishchenko-type reaction of aldehydes [9].

It has been reported that triphenylphosphine itself catalyzes the coupling of **1a** with an aldehyde via the phosphonium betaine intermediate [10]; however, the following observations strongly suggest that the rhodium or ruthenium metal itself plays an important role in the reaction catalyzed by transition metal complexes containing triphenylphosphine; (i) the solvent interferes the coupling reaction, (ii) the addition of about 20 mol% of alcohol enhances turnover of catalyst, (iii) the addition of PBu_3 to the catalyst does not affect the reaction [10b,11] (entry 16, Table 1), and (iv) $[Rh(COD)(DPPE)]^+ PF_6^-/H_2$ (entry 15, Table 1) and $RhH(PPh_3)_3$ (entry 14, Table 1), from which the phosphine ligand hardly dissociates, also promote the coupling reaction. Although PPh_3 itself catalyzed the coupling reaction under our conditions, both the yield and the selectivity of **6a** were far lower than the results obtained by the catalysis of $RhH(PPh_3)_4$ or $RuH_2(PPh_3)_4$ (entry 19, Table 1).

Thus, we have extended our coupling reaction to other aldehydes and vinyl ketones under optimum conditions (entries 5 and 17, Table 1). The results are listed in Table 2.

As shown in Table 2, the combination of the aliphatic enone and the aliphatic aldehyde permits smooth coupling in the presence of a catalytic amount of $RhH(PPh_3)_4$ or $RuH_2(PPh_3)_4$. However, the phenyl group introduced into either the α,β-enone or aldehyde appreciably lowers the yield of **6** (entries 6, 13, and 14, Table 2). The steric congestion around the carbonyl group also inhibits the present reaction. In fact, the dimerization of vinyl ketone predominates when the substituent of the aldehyde is relatively bulky (entry 5, Table 2). Although almost similar results are obtained in the reactions catalyzed by the rhodium and the ruthenium complexes, $RuH_2(PPh_3)_4$ gives significantly better results in the reactions of 1-penten-3-one (entry 7, Table 2) and 5-phenyl-1-penten-3-one (entry 14, Table 2) with propanal than the rhodium catalyst.

An interesting feature of this reaction is that carbon–carbon bond formation is attained by the participation of rhodium or ruthenium complexes under almost neutral conditions. At present we have no information on the participation of the metal complex in this step; an intriguing idea is the intermediacy of a metal enolate. In fact, a certain type of rhodium enolate complex has been isolated [12] and the participation of an analogous complex has been suggested for the rhodium-catalyzed isomerization of β-trimethylsilylallyl alcohols [6] and cross-aldol reactions of enol trimethylsilyl ethers [3d–3f,12]. Thus, a putative pathway for the present cross-coupling is shown in Scheme 2; (i) Michael-type addition of M–H to α,β-enone **1** to give enolate complex **8**, (ii) aldol-type addition of **8** to aldehyde to give **9**, (iii) equilibration between **9** and **10**, and (iv) retro-Michael-type elimination of M-H from **10** to give **6**. The selectivity and the yield of **6** are remarkably improved by the

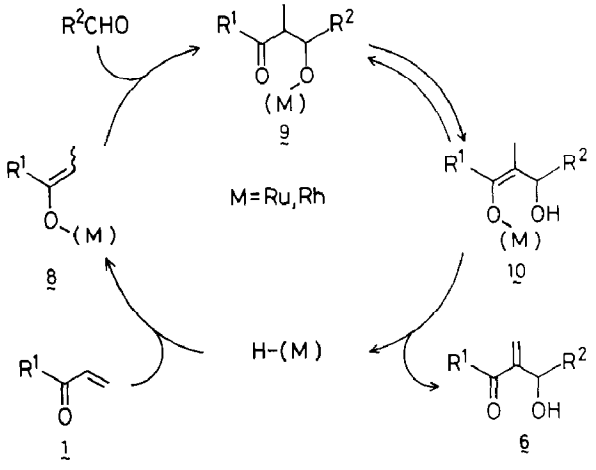
Table 2

Coupling reaction of **1** with aldehydes.

Entry	**1**	R^1	Aldehyde R^2	**6**	$RhH(PPh_3)_4$ [a]		$RuH_2(PPh_3)_4$ [b]	
					Yield [c] (%)	Turnover of Rh	Yield [c] (%)	Turnover of Ru
1	**1a**	Me	Et	**6a**	78 (2)	92	82 (2)	164
2	**1a**	Me	n-C_3H_7	**6b**	61 (3)	45	57 (2)	236
3	**1a**	Me	2-Methylpropyl	**6c**	76 (6)	82	46 (3)	49
4	**1a**	Me	1-Methylethyl	**6d**	70 (9)	74	72 (6)	106
5	**1a**	Me	1-Ethylpentyl	**6e**	14 (42)	10	9 (11)	13
6	**1a**	Me	Ph	**6f**	18 (4)	26	33 (2)	87
7	**1b**	Et	Et	**6g**	14 (0)	36	87 (0)	196
8	**1c**	n-C_5H_{11}	Et	**6h**	63 (0)	36	64 (0)	115
9	**1d**	n-C_8H_{17}	Et	**6i**	70 (0)	97	61 (0)	52
10	**1e**	2-Methylpropyl	Et	**6j**	51 (0)	51	53 (0)	29
11	**1f**	1-Ethylpentyl	Et	**6k**	58 (0)	46	49 (0)	22
12	**1g**	Cyclohexyl	Et	**6l**	79 (0)	65	17 (0)	30
13	**1h**	Ph	Et	**6m**	37 (45)	37	23 (38)	17
14	**1i**	2-Phenylethyl	Et	**6n**	7 (0)	9	54 (0)	40

[a] Reactions were conducted on a 5-mmol scale without solvent in a sealed tube using a mixture of **1**/aldehyde/i-PrOH/$RhH(PPh_3)_4$ = 1/2/0.2/0.01 at 40 °C for 40 h. [b] Reactions were conducted on a 5-mmol scale without solvent in a sealed tube using a mixture of **1**/aldehyde/$RuH_2(PPh_3)_4$ = 1/2/0.01 at 40 °C for 40 h. [c] Isolated yield. Yields of **7** are shown in parentheses.

addition of a small amount of an alcohol in the case of $RhH(PPh_3)_4$. The reason for this is that the added alcohol probably acts as a proton source to accelerate the rate of interconversion in the equilibrium between **9** and **10** or the rate of the elimination of Rh-H from **10**. In contrast to $RhH(PPh_3)_4$, the ruthenium catalyst makes the reaction proceed rapidly without the added alcohol. The formation of the homo-coupling product, **7**, is also explained by the 1,4-addition of **8** of **1**. Thus, the distribution of the products, **6** and **7**, depends on the steric and electronic factors of starting substrates. An appreciable amount of 7 was also formed when a bulky



Scheme 2

aldehyde or activated enone (entries 5 and 13, Table 2) was used. It is known that the β-carbon-bonded ruthenium complex is obtained from the reaction of $RuH_2(PPh_3)_4$ with alkyl methacrylate [13]. However, the formation of **6** and **7** in the reaction of **1** with aldehyde cannot be explained in terms of the intermediacy of an anlogous alkenyl complex.

The structure of **6** is attractive from a synthetic point of view because **6** contains three consecutive carbons functionalized differently. Such functional groups in **6** can be transformed into a variety of others by conventional means. For example, the regio-defined formation of β-hydroxy ketone (**11**) will be effected by the catalytic hydrogenation of the *exo*-methylene group in **6**. Since the methodology of diastereoselection is well established in the catalytic hydrogenation of allylic alcohols [14], the hydrogenation of **6** should open up a new diastereoselective route to aldol derivatives. Thus, the hydrogenation of **6a** was carried out in the presence of various types of transition metal catalyst (eq. 3).

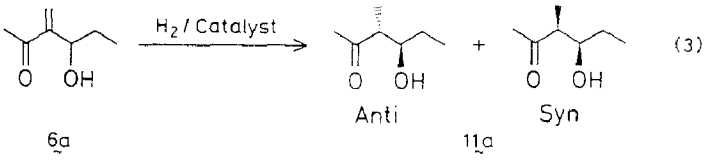


Table 3

Diastereoselective hydrogenation of **6a** [a]

Entry	Catalyst	Solvent	H_2 [b] (kg/cm^2)	Conditions (°C/h)	Conversion [c] (%)	*anti*:*syn* [c]
1	Pd-C (5%)	EtOH	1	25/1	100	67:33
2	$Pd(PPh_3)_4$	C_6H_6	70	25/7	77	59:41
3	$RhCl(PPh_3)_3$	C_6H_6	1	25/1	100	85:15
4	$RhCl(PPh_3)_3$	C_6H_6	70	25/25	25	67:33
5	$RhH(PPh_3)_4$	C_6H_6	1	25/1.5	13	68:32
6	$RhH(PPh_3)_4$	C_6H_6	69	25/14	18	59:41
7	$[Rh(COD)(PMePh_2)_2]PF_6$	CH_2Cl_2	1	25/1.5	0	–
8	[Rh(COD)(DPPE)]PF_6	CH_2Cl_2	1	25/1.5	0	–
9	[Rh(COD)(DPPB)]PF_6	CH_2Cl_2	1	25/2	100	90:10
10	[Rh(COD)(DPPB)]PF_6	CH_2Cl_2	60	25/1	38	89:11
11	[Rh(COD)(DPPB)]PF_6	CH_2Cl_2	65	25/16	100	91:9
12	[Rh(COD)(DPPB)]PF_6	CH_2Cl_2	1	−78/6	0	–
13	[Rh(COD)(DPPB)]BF_4	CH_2Cl_2	1	25/2	100	91:9
14	[Rh(NBD)(DPPB)]BF_4	CH_2Cl_2	1	25/2	85	90:10
15	[Rh(COD)(DPPB)]ClO_4	CH_2Cl_2	1	25/2	100	90:10
16	$RuCl_2(PPh_3)_3$	C_6H_6	1	25/1.5	17	66:34
17	$[Ir(COD)(PMePh_2)_2]PF_6$	CH_2Cl_2	1	25/2	0	–
18	[Ir(COD)(DPPB)]PF_6	CH_2Cl_2	1	25/2	0	–
19	[Ir(COD)(DPPB)]PF_6	CH_2Cl_2	70	25/15	55	65:35
20	$[Ir(COD)(py)(PCy_3)]PF_6$	CH_2Cl_2	1	25/2	20	72:28
21	$[Ir(COD)(py)(PCy_3)]PF_6$	CH_2Cl_2	70	25/2	100	70:30
22	$[Ir(COD)(py)(PCy_3)]PF_6$	CH_2Cl_2	80	−78/6.5	97	70:30

[a] Reactions were conducted on a 1-mmol scale using 1–5 mol% of catalyst. [b] The experiments under high pressure were performed in a 100-ml stainless steel autoclave. [c] Determined by capillary GLC analyses (PEG-HT Bonded, 25 m).

The hydrogenation proceeds smoothly to give **11a**. The structure and diastereochemistry of **11a** was confirmed by comparison of its ^{1}H NMR spectrum with that of an authentic sample [15]. GLC analysis of the product showed that the anti isomer predominates in the presence of a transition metal catalyst. The results are summarized in Table 3. Although the direction taken in the hydrogenation of **11a** coincides with that taken in the reaction of 3-hydroxy-2-methylenecarboxylic esters [16], the stereochemical control in **11a** is more difficult than that of in the esters. The cationic rhodium complexes show an acceptable selectivity for *anti* **11a** (entries 9, 11, 13, and 15, Table 3). It is notable that **11a** is identical to the product obtained from the aldol reaction of 2-butanone with propanal. Thus, the present two-step operation to vinyl ketone offers a facile and attractive alternative to *anti*-selective aldol reactions, since *anti*-selective methods find limited application compared with the *syn*-selective ones.

Experimental

All reactions were carried out under argon or nitrogen. The boiling points are bath temperatures for bulb-to-bulb distillations. IR spectra were recorded on a JASCO IRA-1 or a JASCO IRA-2 spectrometer. Proton NMR spectra were obtained on a JEOL C60HL or Hitachi R-24B instrument using tetramethylsilane as an internal standard. GLC analyses were performed on a Gasukuro Kogyo Model 370 equipped with a flame ionization detector in a fused silica capillary column (PEG-HT bonded, 0.25 mm × 25 m or OV-101, 0.25 mm × 50 m). Tetrahydrofuran (THF) was distilled from sodium metal in the presence of benzophenone, benzene was distilled from sodium metal, and dichloromethane was distilled from phosphorus pentoxide. Benzene and dichloromethane used for catalytic reactions were degassed under vacuum immediately before use.

Hydridotetrakis(triphenylphosphine)rhodium [17], hydridotetrakis(methyldiphenylphosphine)rhodium [18], hydrido[1,2-bis-(diphenylphosphino)ethane]rhodium [19], chlorotris(triphenylphosphine)rhodium [20], hydridotris(triphenylphosphine)rhodium [21], di-μ-chlorotetracarbonyldirhodium [22], dihydridotetrakis(triphenylphosphine)ruthenium [17], dichlorotris(triphenylphosphine)ruthenium [23], tetrakis(triphenylphosphine)palladium [24], and all cationic rhodium [25] and iridium [26] complexes shown in Table 3 were prepared by published procedures. All the aldehydes, 3-buten-2-one (**1a**), and 1-penten-3-one (**1b**) were commercial products and freshly distilled before use. Other α,β-enones **1c–1i** were prepared by PCC oxidation [27] of the relevant allyl alcohols that had been made by the conventional reaction of vinylmagnesium bromide with aldehydes.

*Coupling reaction of **1** with aldehydes*

Procedures for **6a** in the presence of $RhH(PPh_3)_4$, and **6g** in the presence of $RuH_2(PPh_3)_4$ are described as typical examples. Spectral and analytical data of **6** are listed in Table 4.

*4-Hydroxy-3-methylenehexan-2-one (**6a**) [10a]*

A mixture of 264 mg (3.8 mmol) of 3-buten-2-one (**1a**), 484 mg (7.4 mmol) of propanal, 53.2 mg (0.89 mmol, 24 mol% based on **1a**) of 2-propanol, and 36.4 mg

Table 4

Spectral and analytical data for α-methylene-β-hydroxyalkanones (**6**).

Entry	6	B.p. (°C/Torr)	IR (CCl_4) ν(O–H) ν(C=O) (cm^{-1})	δCH–OH	^{1}H NMR (CCl_4) [a] δC=CH [b]	δC=CH [c]	Analysis (Found(calc) (%)) C	H	Formula
1	**6a**	88/2	3525 1665	4.29(t, *J* 5.3, 1H)	5.90(s, 1H)	5.97(s, 1H)	[10a]		
2	**6b**	115/2	3520 1660	4.39(t, *J* 5.2, 1H)	5.98(s, 1H)	6.01(s, 1H)	[10a]		
3	**6c**	115/0.5	3530 1664	4.52(m, 1H)	5.98(s, 1H)	6.07(s, 1H)	69.30 (69.19)	10.35 (10.32)	$C_9H_{16}O_2$
4	**6d**	113/2	3530 1665	4.23(d, *J* 6.1, 1H)	5.94(s, 1H)	6.06(s, 1H)	[10a]		
5	**6e**	131/0.4	3525 1675	4.34(m, 1H)	5.89(s, 1H)	6.00(s, 1H)	72.51 (72.68)	11.22 (11.18)	$C_{12}H_{22}O_2$
6	**6f**	124/0.4	3325 1650	5.52(s, 1H)	5.88(d, *J* 1.4, 1H)	6.05(s, 1H)	[10a]		
7	**6g**	106/2	3520 1662	4.27(t, *J* 6.3, 1H)	5.87(s, 1H)	5.95(s, 1H)	[10b]		
8	**6h**	88/0.3	3520 1670	4.0–4.4(m, 1H)	5.81(s, 1H)	5.90(s, 1H)	[10b]		
9	**6i**	136/0.4	3555 1670	4.22(t, *J* 6.0, 1H)	5.86(s, 1H)	5.95(s, 1H)	74.35 (74.29)	11.62 (11.58)	$C_{14}H_{26}O_2$
10	**6j**	76/1	3480 1668	4.31(t, *J* 5.4, 1H)	5.92(s, 1H)	5.97(s, 1H)	70.40 (70.55)	10.63 (10.66)	$C_{10}H_{18}O_2$
11	**6k**	95/0.4	3500 1645	4.25(t, *J* 5.8, 1H)	5.89(s, 1H)	5.97(s, 1H)	73.62 (73.54)	11.44 (11.39)	$C_{13}H_{24}O_2$
12	**6l**	100/0.7	3500 1655	4.27(t, *J* 6.6, 1H)	5.90(s, 1H)	5.96(s, 1H)	72.56 (72.49)	9.91 (9.95)	$C_{11}H_{18}O_2$
13	**6m**	105/0.8	3525 1660	4.47(t, *J* 6.2, 1H)	5.59(s, 1H)	5.99(s, 1H)	74.82 (74.98)	6.91 (6.86)	$C_{11}H_{12}O_2$
14	**6n**	140/1	3550 1673	4.78(t, *J* 5.7, 1H)	5.86(s, 1H)	5.91(s, 1H)	77.22 (77.03)	8.29 (8.31)	$C_{14}H_{18}O_2$

[a] Shifts are in ppm, coupling constants are in Hz; relative to $SiMe_4$ at 60 MHz and 25 °C. [b] Vinyl proton at *trans* to carbonyl group. [c] Vinyl proton at *cis* to carbonyl group.

(0.032 mmol, 0.8 mol% relative to **1a**) of $RhH(PPh_3)_4$ was placed in a 10-mm ∅ Pyrex tube, under argon. The mixture was cooled and degassed in a vacuum, and the tube was sealed and heated at 40 °C in an oil bath for 40 h. The resulting orange solution was concentrated under reduced pressure, and the subsequent bulb-to-bulb distillaton gave a mixture of products **6a** and **7a** (**6a** : **7a** = 97 : 3, determined by GLC analysis). The crude product was chromatographed on silica gel, with a mixed solvent (hexane/ethyl acetate, 80/20) as eluent, to give 376 mg (78%) of **6a** as a colorless oil. MS *m/e* (relative intensities): 128 (M^+, 1), 127 (1), 113 (15), 110 (21), 100 (16), 99 (100), 95 (14), 87 (2), 85 (7), 81 (3), 75 (2), 71 (6), 70 (7), 67 (17).

The dimer of **1a**, 3-methyleneheptan-2,6-dione (**7a**) [28] (5.3 mg, 2%) was also isolated from the crude mixture. B.p.: 105 °C/2 Torr. IR(CCl_4): 1715, 1675 (C=O) cm^{-1}. ^1H NMR(CCl_4): δ 2.06 (s, 3H, (C=O)CH_3), 2.27 (s, 4H, $-(CH_2)_2-$), 2.47 (s, 3H, =C(C=O)CH_3), 5.75 (s, 1H, =C*H*), 5.89 (s, 1H, =C*H*). MS *m/e* (relative intensities): 140 (M^+, 2), 125 (55), 97 (100), 83 (31).

*5-Hydroxy-4-methyleneheptan-3-one (**6g**) [10b]*

A mixture of 323 mg (3.8 mmol) of 1-penten-3-one (**1b**), 509 mg (8.8 mmol) of propanal, and 19.0 mg (0.017 mmol, 0.4 mol % relative to **1b**) of $RuH_2(PPh_3)_4$ was placed in a 10-mm ∅ Pyrex tube, under argon. The mixture was cooled and degassed in a vacuum, and the tube was sealed and heated at 40 °C in an oil bath for 40 h. The resulting yellow solution was concentrated under reduced pressure, and the subsequent bulb-to-bulb distillation gave 475 mg (87%) of **6g** as a colorless oil.

*Diastereoselective hydrogenation of **6a***

The procedures using [Rh(COD)(DPPB)]PF_6 under atmospheric pressure (entry 12, Table 3) and under a high pressure of hydrogen (entry 14 in Table 3) are described as typical examples.

(1) A solution of 134 mg (1.1 mmol) of **6a** and 28.7 mg (0.037 mmol) of [Rh(COD)(DPPB)]PF_6 in dichloromethane (5 ml) was stirred at room temperature and hydrogen was bubbled through the solution for 2 h. The resulting orange solution was concentrated under reduced pressure, and the subsequent bulb-to-bulb distillation gave 130 mg (95%) of 4-hydroxy-3-methylhexan-2-ones (**11a**) as a colorless oil. B.p.: 100 °C/2 Torr. Anal. Found: C, 64.53; H, 10.79. $C_7H_{14}O_2$ calcd.: C, 64.58; H, 10.84%. IR(CCl_4): 3500 (OH), 1690 (C=O) cm^{-1}. ^1H NMR(CCl_4): δ 1.03 (t, J = 7.6 Hz, 3H, CH_2CH_3), 1.05 (d, J = 7.6 Hz, 3H, $CHCH_3$), 1.6–1.9 (broad m, 2H, CH_2CH_3), 2.59 (q, J = 7.6 Hz, 1H, (C=O)C*H*), 3.4–3.9 (broad m, 2H, C*H*–O*H*).

(2) A solution of 127 mg (1.0 mmol) of **3a** and 35.4 mg (0.045 mmol) of [Rh(COD)(DPPB)]PF_6 in dichloromethane was allowed to react with hydrogen under a pressure of 65 kg/cm^2 at room temperature in a steel pressure bottle (100 ml) containing a glass vessel. The solution was stirred for 16 h, and the resulting orange solution was concentrated under reduced pressure. Subsequent bulb-to-bulb distillation gave 118 mg (92%) of **11a**.

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