Synthesis of Aliphatic Ketones from Allylic Alcohols through Consecutive Isomerization and Chelation-Assisted Hydroacylation by a Rhodium Catalyst

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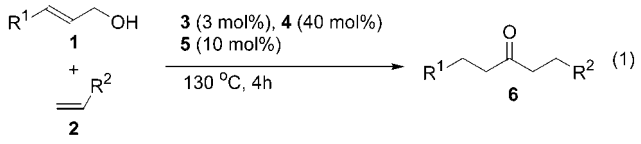
Abstract: An allylic alcohol, utilized as a precursor for an aliphatic aldehyde, reacted with olefins to afford aliphatic ketones in the presence of $RhCl(PPh_3)_3$, 2-amino-4-picoline, aniline, and benzoic acid through a tandem reaction of an isomerization and a chelation-assisted hydroacylation.

Intermolecular hydroacylation is a useful synthetic method for preparing ketones directly from olefins and aldehydes through a transition-metal-catalyzed C−H bond activation.[1,2] We have developed an efficient catalytic system for a chelation-assisted hydroacylation using 2-aminopyridine derivatives, which facilitate C−H bond activation and suppress decarbonylation.[2] While most aromatic aldehydes reacted with olefins to afford the corresponding ketones in high yields under this catalytic system, aliphatic aldehydes suffered from an undesirable side reaction, aldol condensation of aliphatic aldehyde.

In our efforts to solve such a problem in the reaction of aliphatic aldehydes, a primary alcohol was employed as an alternative substrate for hydroacylation instead of an aldehyde, since it could be converted into an aldehyde via hydrogen transfer.[2c] However, the reactivity of aliphatic alcohols in hydroacylation was much lower than that of benzyl alcohol derivatives, which might be ascribed to the unfavorable intermolecular hydrogen transfer from alcohols to olefins. Thus, the use of an allylic alcohol was expected to be advantageous because the transition-metal-catalyzed isomerization of an allylic alcohol into a carbonyl compound is known to be very facile.[3−5] Herein, we report an efficient catalytic system for the synthesis of aliphatic ketones by an isomerization of allylic alcohols and a consecutive chelation-assisted hydroacylation of olefin.

Table 1. Chelation-Assisted Hydroacylation of Olefins (2) with Allylic Alcohols (1) in the Presence of Wilkinson's Complex 3 (eq 1)



entry	alcohols **1** (R^1=)	olefin **2** (R^2=)	product (**6**)	yield (%)[a]
1	**1a** (R^1 = Me)	**2a** (R^2 = *n*-Bu)	**6a**	91
2	**1a**	**2b** (R^2 = *n*-C_6H_{13})	**6b**	86
3	**1a**	**2c** (R^2 = $PhCH_2$)	**6c**	78
4	**1a**	**2d** (R^2 = Cy)[b]	**6d**	83[c]
5	**1b** (R^1 = H)	**2c**	**6e**	77
6	**1c** (R^1 = *cis*-Pr)	**2a**	**6f**	92
7	**1d** (R^1 = *trans*-Pr)	**2a**	**6f**	85
8[d]	**1e** (R^1 = Ph)	**2a**	**6g**	89

[a] All yields are isolated yields except entry 4. [b] Cy = cyclohexyl. [c] GC yield. [d] A small amount of ethylbenzene (ca. 0.5%) and styrene (ca. 1%) were also detected by GC analysis.

In our experiment, allylic alcohols (**1**) reacted with various olefins (**2**, 3 equiv based on **1**) in the presence of $RhCl(PPh_3)_3$ (Wilkinson's complex, **3**), 2-amino-4-picoline (**4**), and benzoic acid (**5**), at 130 °C for 4 h to give alkyl ketones **6** (eq 1). For example, the reaction of crotyl alcohol (**1a**) with 1-hexene (**2a**) afforded 4-decanone (**6a**) in a 91% yield after chromatographic isolation (Table 1, entry 1).

The reaction of other terminal olefins with allylic alcohols also gave the corresponding ketones in good yields as shown in Table 1. In the case of 2-hexenol, *cis*-isomer (**1c**) gave a slightly better yield (92%, entry 6) of 6-dodecanone (**6f**) than *trans*-isomer (**1d**, 85%, entry 7).[6] It is noteworthy that no byproduct such as aldol condensation product was obtained from the reaction of allylic alcohols, whereas aldol condensation was an important side reaction when aliphatic aldehydes were used as substrates for the chelation-assisted hydroacylation. For example, hexanal (**7a**) reacted with **2a** under the same reaction condition to give **6f** in only a 45% yield, and the aldol condensation product, 2-butyl-2-octenal, was obtained in a yield of 22% (based on **7a**).

The most plausible reaction pathway is illustrated in Scheme 1. The first step might be the transition-metal-catalyzed isomerization of **1** to the corresponding aldehyde (**7**), which condenses with **4** to yield aldimine **8**.

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(4) For enantioselective isomerization of allylic alcohols, see: (a) Tani, K. *Pure Appl. Chem.* **1985**, *57*, 1845. (b) Chapuis, C.; Barthe, M.; de Saint Laumer, J.-Y. *Helv. Chim. Acta* **2001**, *84*, 230. (c) Tanaka, K.; Qiao, S.; Tobisu, M.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *122*, 9870. (d) Tanaka, K.; Fu, G. C. *J. Org. Chem.* **2001**, *66*, 8177.

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(6) Other allylic alcohols were purchased from a commercial source as a mixture of isomers.

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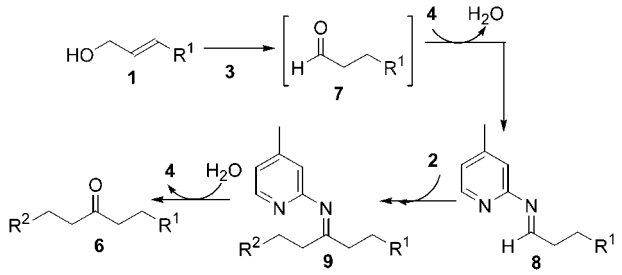
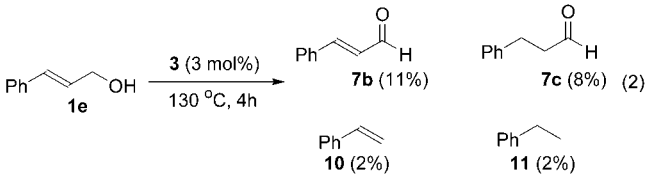
Scheme 1. A Plausible Mechanism for the Transformation of Allylic Alcohol 1 into Ketone 6 through Consecutive Isomerization and Hydroacylation.



Subsequent hydroiminoacylation of **2** with **8**, followed by the hydrolysis of resulting ketimine **9**, give ketone **6** as a final product.

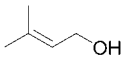
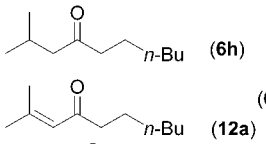
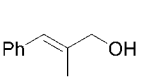
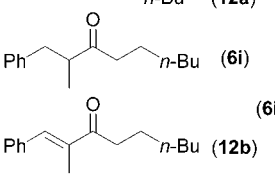
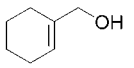
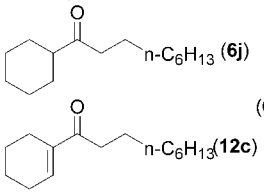
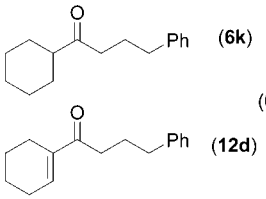
To identify the intermediacy of aldehyde **7** during the transformation of **1** into **6**, the reaction of **1e** under **3** was carried out in the absence of **4** and **5** (eq 2). In this reaction, cinnamaldehyde (**7b**) as well as 2-phenylpropanol (**7c**) were obtained in a 11% and a 8% yield, respectively (determined by GC), along with their respective decarbonylation products, styrene **10** and ethylbenzene **11**. The formation of **7b** implies that the isomerization of **1e** to **7c** might proceed through an α,β-unsaturated aldehyde intermediate as Trost and Kulawiec suggested.[3a,b]



Furthermore, it was found that the reaction of C3- or C2,C3-disubstituted allylic alcohols afforded α,β-unsaturated ketones (**12**) as well as saturated alkyl ketones **6** with slightly decreased reactivities, which might be due to the steric hindrance at the olefinic group that inhibits the intramolecular hydrogen shift (Table 2). The critical influence of the olefin substitution on the isomerization of allylic alcohol has been well documented.[3a,b] When the intramolecular hydrogen shift is inhibited, hydrogens should be transferred to the external olefin to give alkane and α,β-unsaturated ketones **12**. For instance, in the reaction of 1-cyclohexenylmethanol (**1h**) and allylbenzene (**2c**), a small amount of the hydrogenated product of **2c**, propylbenzene, was detected after the reaction (entry 4), while the hydrogenation of olefin was not observed in the reaction of other alcohols (e.g. Table 1, entries 3 and 5).[7]

The decarbonylation of aldehyde is one of the important drawbacks in the isomerization of allylic alcohols to aldehyde,[3g] because it results in the deactivation of the catalyst by forming stable metal carbonyl complexes. Actually, after the reaction depicted in eq 2, a yellow precipitate was obtained and identified as $RhCl(CO)(PPh_3)_2$ (80% based on **3**) by IR spectroscopic analysis.

Table 2. A Hydroacylation of Olefin (2) with Disubstituted Allylic Alcohols[a]

entry	alcohols (1)	olefin (2)	products	yield (%)[b]
1	 (**1f**)	**2a**	 (**6h**) (**12a**)	63 (**6h**/**12a**=88/11)
2	 (**1g**)	**2a**	 (**6i**) (**12b**)	67 (**6i**/**12b**=94/6)
3	 (**1h**)	**2b**	 (**6j**) (**12c**)	64 (**6j**/**12c**=92/8)
4[c]	**1h**	**2c**	 (**6k**) (**12d**)	69 (**6k**/**12d**=91/9)

[a] The reaction was carried out using **1** (0.4 mmol), **2** (1.2 mmol), **4** (0.16 mmol), and **5** (0.04 mmol), in the presence of **3** (0.012 mmol) at 130 °C for 4 h. [b] The yields are isolated yields. The ratios of **6**/**12** were determined by GC. [c] A small amount of propylbenzene was detected by GC.

This result accounts for the low conversion of **1e** into aldehydes in the absence of **4**.[8] Moreover, the resulting rhodium carbonyl complex, $RhCl(CO)(PPh_3)_2$, is also by far less reactive toward chelation-assisted hydroacylation.[9]

Since the accumulation of free aldehyde leads to not only aldol condensation but also decarbonylation, it is very important to keep the net concentration of the aldehyde intermediate low during the whole process. Therefore, aldehyde **7** should be consumed to form aldimine **8** as soon as **7** is generated. Probably, in this reaction, the rate of the formation of intermediate aldehyde might be slower than that of the condensation of aldehyde with **4**.[10]

In this context, the effect of carboxylic acid **5** is also critical because the condensation of aldehyde and **4** is catalyzed by acid.[2e,f] For example, when **1e** was allowed to react with **2a** under the same reaction condition without **5**, the yield of **6g** decreased to 38%, and decarbonylation products **10** and **11** were obtained in a 3% and a 4% yield, respectively (GC yield). The yield of **6g** was only 44% even after the prolonged reaction time (18 h), which might be due to the deactivation of the catalyst through decarbonylation.

(7) Homoallyl alcohols or alcohols bearing a remote olefin from the hydroxyl group exhibited very poor reactivity similar to saturated aliphatic alcohols bearing no olefinic group. For example, *cis*-3-hexenol reacted with **2a** under the same condition to afford **6f** in an isolated yield of 3%, and no reaction occurred with 5-hexenol under this condition. When 1-hexanol was allowed to react with **2a** under the same reaction condition, the yield of **6f** was only 3% (isolated yield).

(8) It should be pointed out that Wilkinson's complex itself has been seldom used as a catalyst for the isomerization of allylic alcohols (see ref 3f), which may be due to the decarbonylation of the resulting aldehyde.

(9) When the reaction of **1e** and **2a** was carried out in the presence of $RhCl(CO)(PPh_3)_2$ instead of **3**, the yield of **6g** was only 9% (isolated yield).

(10) Other 2-aminopyridines were also examined for this reaction, and 2-amino-4-picoline turned out to be the most effective.

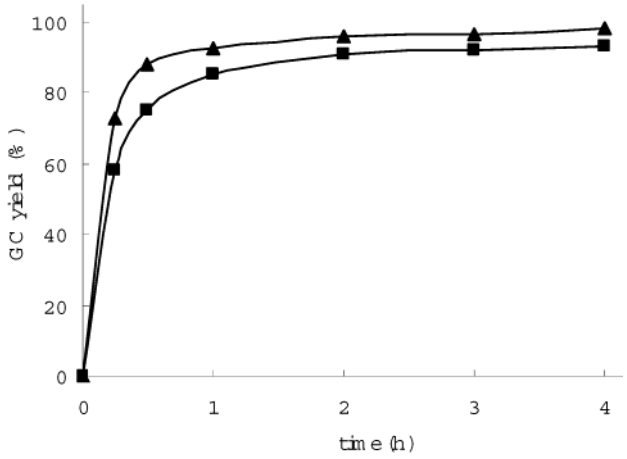


Figure 1. The effect of transimination on the hydroacylation of **2a** with **1a** in the presence of **3** (3 mol %), **4** (40 mol %), and **5** (10 mol %), at 130 °C. The results for the reaction with 50 mol % of **13** (▲) and without **13** (■) are shown.

Table 3. A Chelation-Assisted Hydroacylation of 2 with 1 in the Presence of 13[a]

entry	1	2	time (h)	products (yield, %)[b]
1	**1a**	**2a**	2	**6a** (90)
2	**1a**	**2b**	2	**6b** (94)
3	**1a**	**2c**	2	**6c** (90)
4	**1b**	**2c**	3	**6e** (85)
5	**1c**	**2a**	2	**6f** (96)
6	**1e**	**2a**	2	**6g** (87)

[a] The reaction was carried out using **1** (0.4 mmol), **2** (1.2 mmol), **4** (0.16 mmol), **5** (0.04 mmol), and **13** (0.2 mmol) in the presence of **3** (0.012 mmol) at 130 °C. [b] The yields are isolated yields.

We have previously demonstrated that the reactivity of a chelation-assisted hydroacylation with aldehyde was dramatically improved using a transimination which facilitates the formation of aldimine (e.g. **8** in Scheme 1).[2d,11] Therefore, the effect of transimination was examined for the reaction of **1a** with **2a**, by performing the reaction with or without 50 mol % of aniline **13** (Figure 1).

However, a significant rate enhancement was not observed with the addition of **13**. This result implied that the rate-determining step is not the condensation step of aldehyde and **4**,[2e,f] but the isomerization of allylic alcohol. This result is also in accord with the aforementioned assumption that the isomerization of allylic alcohol might be slower than the condensation of aldehyde with **4**.

Nevertheless, it was beneficial to utilize a transimination technique because the yields of products were slightly increased in the presence of **13** compared with its absence (Table 3). This might be attributed to the more facile condensation of aldehyde with **13** than with **4**, and the consequent retardation of decarbonylation, which gave rise to the deactivation of the catalyst. As shown in Table 3, other allylic alcohols were also allowed to react with olefins under the transimination condition, and afforded corresponding ketones in good yields in a short reaction time compared with the previous reaction condition.

Conclusion

In summary, we have applied an efficient chelation-assisted hydroacylation protocol for the synthesis of aliphatic ketones from allylic alcohols under a catalytic system consisting of Wilkinson's complex, 2-amino-4-picoline, aniline, and benzoic acid. Allylic alcohols were employed as a precursor for aliphatic aldehyde, to prevent aldol condensation, an unfavorable side reaction in hydroacylation with aliphatic aldehyde. In this reaction, the chelation-assistance protocol was also effective in retarding the deactivation of the catalyst through decarbonylation of aldehyde intermediate by forming aldimine.

Experimental Section

General Method. NMR spectra were recorded in $CDCl_3$ at 250 MHz (^{1}H NMR) or 62.5 MHz (^{13}C NMR), and the chemical shift was expressed in ppm relative to TMS. Unless otherwise noted, all allylic alcohols, olefins, and amines used in the experiments were purchased from commercial sources and used as received. Wilkinson's complex ($RhCl(PPh_3)_3$, **3**) was prepared as described in the literature.[12]

Materials. Among allylic alcohols, 2-methyl-3-phenyl-2-propen-1-ol (**1g**) and 1-cyclohexenylmethanol (**1h**) were prepared from α-methyl-*trans*-cinnamaldehyde and 1-cyclohexene-1-carboxaldehyde , using lithium aluminum hydride and purified by column chromatography (SiO_2, *n*-hexane: ethyl acetate = 5:2). All the products are known compounds and are easily identified by ^{1}H NMR, ^{13}C NMR, IR, and mass spectra.

2-Methyl-3-phenyl-2-propen-1-ol (1 g).[13] ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.37−7.19 (m, 5H), 6.52 (s, 1H), 4.19 (s, 2H), 2.03 (br s, 1H), 1.90 (s, 3H).^{13}C NMR (62.9 MHz, $CDCl_3$): δ 137.6, 137.5, 128.8, 128.1, 126.4, 124.9, 68.8, 15.2. IR (neat): 3333, 3023, 2916, 2860, 1600, 1491, 1444, 1070, 1010, 842, 698 cm^{-1}. MS (EI): *m/z* (relative intensity): 148 (M^+, 17), 133 (20), 129 (17), 115 (50), 105 (49), 91 (100), 78 (29), 65 (10), 55 (15), 51 (12), 43 (13).

1-Cyclohexenylmethanol (1h).[14] ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.67 (br s, 1H), 3.97 (s, 2H), 2.94 (br s, 1H), 2.02−1.99 (m, 4H), 1.65−1.58 (m, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 137.3, 122.7, 67.2, 25.4, 24.8, 22.4, 22.3. IR (neat): 3482, 2931, 1717, 1450, 1263, 1096, 1072 cm^{-1}. MS (EI): *m/z* (relative intensity) 112(M^+, 58), 97 (13), 94 (23), 83 (28), 81 (100), 79 (95), 77 (19), 70 (17), 67 (24), 55 (27), 53 (21), 41 (29), 39 (23).

Typical Procedure for a Catalytic Reaction. The Reaction of Crotyl Alcohol (1a) and 1-Octene (2b) (Table 1, entry 2). A screw-capped pressure vial (1 mL) was charged with 28.9 mg (0.400 mmol) of crotyl alcohol (**1a**), 135 mg (1.20 mmol) of 1-octene (**2b**), 17.3 mg (0.160 mmol) of 2-amino-4-picoline (**4**), 4.9 mg (0.040 mmol) of benzoic acid (**5**), and 11.1 mg (0.0120 mmol) of $RhCl(PPh_3)_3$ (**3**). It was stirred for 4 h in an oil bath that was preheated to 130 °C. After the reaction, the mixture was cooled to room temperature and purified by column chromatography (SiO_2, *n*-hexane:ethyl acetate = 5:2) to yield 63.6 mg (86%) of 4-dodecanone (**6b**).

4-Dodecanone (6b).[15] ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.38 (t, J = 7.4 Hz, 2H), 2.37 (t, J = 7.3 Hz, 2H), 1.64−1.53 (m, 4H), 1.27 (br, 10H), 0.94−0.85 (m, 6H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 211.5, 44.7, 42.8, 31.8, 29.4, 29.3, 29.1, 23.9, 22.6, 17.3, 14.0, 13.7. IR (neat): 2958, 2928, 2856, 1715, 1462, 1414, 1375, 1133, 1027, 736 cm^{-1}. MS (EI): *m/z* (relative intensity) 184 (M^+, 4), 141 (55), 99 (22), 86 (71), 71 (100), 58 (73), 43 (72).

Among the products, **6a**,[16] **6c**,[17] **6e**,[18] **6f**,[19] **6g**,[20] **6h**,[21] **6i**,[22] **6j**,[23] **6k**,[24] **12a**,[25] **12c**,[26] and **12d**[27] have already been reported and

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were identified by ^{1}H NMR, ^{13}C NMR, IR, and MS spectra. All new compounds are characterized below.

1-Cyclohexylhexan-3-one (6d). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.39, 2.38 (t, J = 7.7 Hz, J = 7.3 Hz, 4H), 1.71−1.64 (br, 5H), 1.65−1.50 (m, 2H), 1.46 (dt, J = 7.6, 7.4 Hz, 2H), 1.23−1.14 (br m, 4H), 0.91 (t, J = 7.4 Hz, 3H), 0.85−0.80 (br m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 211.6, 44.6, 40.3, 37.2, 33.0, 31.1, 26.5, 26.2, 17.2, 13.7. IR (neat): 2925, 2852, 1715, 1450, 1412, 1372, 1267, 1128, 1040, 888 cm^{-1}. MS (EI): *m*/*z* (relative intensity) 182 (M^+, 10), 139 (30), 121, (100), 96 (94), 87 (60), 81 (35), 67 (25), 58 (76), 55 (69), 43 (76). HRMS (EI): *m*/*z* calcd for $C_{12}H_{22}O$ (M^+) 182.1671, found 182.1684. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.01; H, 12.02.

2-Methyl-1-phenylnon-1-en-3-one (12b). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.52 (d, J = 1.1 Hz, 1H), 7.42−7.31 (m, 5H), 2.80 (t, J = 7.5 Hz, 2H), 2.06 (d, J = 1.3 Hz, 3H), 1.67 (m, 2H), 1.39−1.26 (br m, 6H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 202.7, 176.6, 138.3, 137.4, 136.1, 129.7, 128.4, 37.7, 31.7, 29.1, 25.0, 22.5, 14.0, 13.2. IR (neat): 3057, 3025, 2955, 2928, 2857, 1668, 1626, 1493, 1447, 1366, 1299, 1198, 1058, 1030, 927, 850, 750, 697 cm^{-1}. MS (EI): *m*/*z* (relative intensity) 230 (M^+, 11), 215 (4), 160 (33), 145 (100), 117 (54), 115 (32), 91 (14). HRMS (EI): *m*/*z* calcd for $C_{16}H_{22}O$ (M^+) 230.1671, found 230.1660. Anal. Calcd for $C_{16}H_{22}O$: C, 84.43; H, 9.63. Found: C, 84.42; H, 9.54.

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Supporting Information Available: Copies of ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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