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Ruthenium-Catalyzed Oxidation of Allyl Alcohols with Intermolecular Hydrogen Transfer: Synthesis of α,β-Unsaturated Carbonyl Compounds

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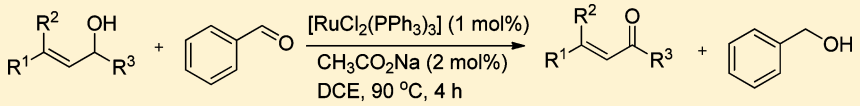
Supporting Information



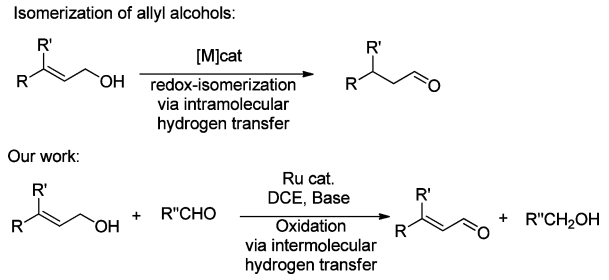
E isomer: R^1, R^2 = aryl, alkyl R^3 = H, alkyl *E* products yield = 83-98%
Z isomer: R^1, R^2 = aryl, alkyl R^3 = H, alkyl *Z* products yield = 93-96%

ABSTRACT: Ruthenium-catalyzed oxidation of multisubstituted allyl alcohols in the presence of benzaldehyde gives enals or enones in good yields. Unlike the commonly reported ruthenium-catalyzed isomerization reaction of allyl alcohols to give saturated ketones, an intermolecular rather than intramolecular hydrogen transfer is involved in this transformation. This reaction offers an efficient, mild, and high-yielding method for the preparation of substituted α,β-unsaturated compounds.

INTRODUCTION

The catalytic redox isomerization is an efficient, useful method for the isomerization of allyl alcohols into the corresponding saturated carbonyl compounds, which represents an atom-economic and elegant shortcut to valuable carbonyl compounds (Scheme 1).[1] In the last few decades, various transition metal complexes of Rh,[2] Ru,[3] Ir,[4] Ni,[5] and Fe[6] have been explored as catalysts for this reaction and an intramolecular hydrogen transfer process have been regarded as a working mechanism.[2a,3a,7] However, the substrate often has a limitation, and the catalytic activity tends to decrease as the degree of substitution of the olefinic bond increases. For instance, allyl alcohols with two substituents at the double bond of primary allyl alcohols required a highly active catalyst to realize such a transformation,[7,8] and the enone intermediate may decoordinate, resulting in a mixture of unsaturated carbonyls and saturated alcohols.

Scheme 1. Metal-Catalyzed Reactions of Substituted Primary Allyl Alcohols



Oxidation of allyl alcohols to the corresponding α,β-unsaturated carbonyl compounds is one of the most common and important reactions in organic chemistry, and numerous useful reagents have been developed.[9] However, many of these methods required stoichiometric quantities of oxidants, which are toxic or hazardous even after the reaction has been completed.[10] From both an environmental and an economical point of view, transition metal-catalyzed transfer hydrogenation has attracted considerable interest because of inexpensive oxidants and mild reaction conditions which tolerate most organic functional groups.[11] Although a variety of transition metal complexes of Ru,[12] Fe,[13] and Ir[14] have been reported as catalysts for secondary alcohols oxidation, among them, there are only a few examples of the oxidation of primary allyl alcohols reported.[12a−c,13] For example, Bäckvall reported the oxidation of hept-1-en-3-ol using the Cp*Ru(II) dimer complex as the catalyst in the presence of actone as the hydrogen acceptor. However, with a simple triphenylphosphine complex of ruthenium, $[RuCl_2(PPh_3)_3]$,[12b] it did not work with the same type of substrate. Herein, we report our preliminary results on the oxidation of allyl alcohols possessing three substituents at the double bond to give enones or enals via sole intermolecular hydrogen transfer in the presence of an aldehyde (Scheme 1).

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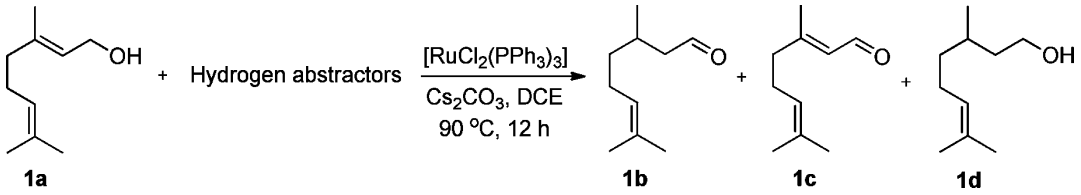
Table 1. Screening of the Hydrogen Abstractors for the Oxidation of Geraniol[a]



entry	hydrogen abstractor	conv. (%)[b]	yield[b] (%) 1b	1c	1d
1	no	92	52	20	20
2[c]	but-3-en-2-one	46	1	44	1
3[c]	hex-1-en-3-one	34	1	32	1
4[d]	benzoquinone	0	0	0	0
5	1-octene	80	26	27	27
6	*n*-butyl vinyl ether	80	28	26	26
7	allyl alcohol	35	1	34	0
8	3-phenylpropanal	75	2	73	0

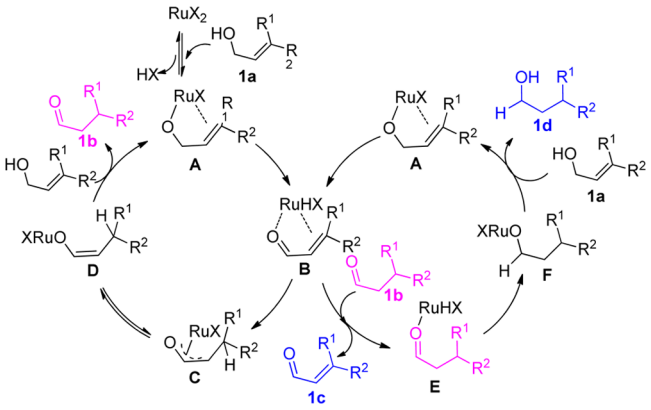
[a]All reactions were carried out with a geraniol (**1a**, 2.0 mmol) at a concentration of 0.5 M at 90 °C for 12 h. Substrate: hydrogen abstractor: $[RuCl_2(PPh_3)_3]$:base = 100:300:2:4. [b]Determined by GC analysis. [c]Reaction time: 24 h. [d]Reaction time: 48 h.

RESULTS AND DISCUSSION

During the investigation of the isomerization of allyl alcohols to give saturated carbonyl compounds via intramolecular hydrogen transfer, geraniol (**1a**) was chosen as the substrate. When $[RuCl_2(PPh_3)_3]$ (2 mol %) was used as a catalyst in the presence of Cs_2CO_3 (4 mol %) after 12 h in DCE at 90 °C, the reaction resulted in 92% conversion of the starting material to give 52% of citronellal (**1b**) as a major product, together with citronellol (**1d**) and citral (**1c**) at a ratio of 1:1 (Table 1, entry 1). These results eloquently proved that intramolecular hydrogen transfer occurred simultaneously with an intermolecular hydrogen transfer. Compound **1d** is either the intermolecular hydrogen transfer product of **1b** or the direct reduced product of **1a** via twice the intermolecular hydrogen transfer.

The mechanism for the redox-isomerization of allyl alcohol to aldehyde had been established as an intramolecular process through competing and labeling experiments (Scheme 2).[15,7,3b,d,2g,h]

Scheme 2. Proposed Catalytic Cycle for the Formation of 1b, 1c, and 1d



First, the Ru−Cl species forms a new Ru−OR species **A** by ligand exchange with the allyl alcohol, subsequently, β-hydrogen elimination yields an α,β-unsaturated aldehyde, which is coordinated to the [Ru−H] species. The [Ru−H] species immediately transfers hydrogen to the C−C double bond of the formed α,β-unsaturated aldehyde, generating a 1,4-hydride addition intermediate **C**, which is in equivilibrium to Ru-enolate **D**. Finally, ligand exchange with the allyl alcohol liberates an enol, which tautomerizes to the saturated aldehyde and regenerates the ruthenium species **A** (left cycle, Scheme 2).

Compound **1c** was formed by decoordination of the formed unsaturated aldehyde from intermediate **B**, probably because of the coordination ability of the unsaturated aldehyde to Ru decreased with the increase of the steric hindrance of the substituted C=C bond. One approach to verify the hypothesis is by performing the isomerization of allyl alcohol **1a** in the presence of a less hindered unsaturated ketone or aldehyde. If this is true, the added less-hindered unsaturated ketone or aldehyde will compete to react with the [Ru−H] species to form the corresponding saturated ketone or aldehyde. As a result, when 3 equiv of but-3-en-2-one were added, dehydrogenated product **1c** together with the saturated ketone butan-2-one, at a ratio of 1:1, was detected by gas chromatography (GC) as the products after prolonging the reaction time to 24 h (Table 1, entry 2). A similar result was obtained when hex-1-en-3-one (3 equiv) was added to the reaction (Table 1, entry 3), albeit with a slightly lower conversion. It was obvious that the addition of an unsaturated ketone, a stronger ligand, decreased the catalytic activity of Ru complexes. This can be ascribed to the competing coordination between allyl alcohol and the added unsaturated ketone. As a result, when benzoquinone (3 equiv), which has an even stronger coordination ability with the metal, was added under the same reaction conditions, even after 48 h, the starting material remained essentially intact (Table 1, entry 4).

If **1d** is the direct reduction product of **1a**, addition of a simple alkene into the reaction will probably suppress the formation of **1d** because of the competitive reduction between **1a** and the added alkene. The fact was that when 1-octene or *n*-butyl vinyl ether was added to the reaction, although the conversion became lower under the same reaction conditions, the formation of **1d** was not suppressed, nor were any reduction products of the alkenes were detected, suggesting that simple alkenes did not serve as the hydrogen abstractors (Table 1, entries 5 and 6). With the addition of 3 equiv of allyl alcohol to the reaction, the formation of **1b** and **1d** was greatly suppressed and **1c** became the overwhelming product together with an equal molar amount

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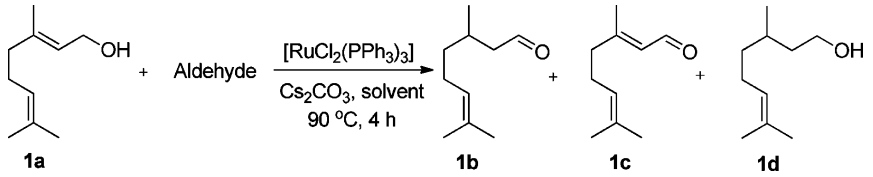
Table 2. Optimization of the Aldehyde and Solvents for the Synthesis of α,β-Unsaturated Aldehyde[a]



entry	solvent	aldehyde	conv.[b] (%)	yield[b] (%) 1b	1c	1d
1[c]	DCE	$(HCHO)_n$	90	23	49	18
2[c]	DCE	CH_3CHO	41	3	33	5
3[c]	DCE	C_3H_7CHO	56	4	50	2
4	DCE	PhCHO	89	3	86	0
5[d]	DCE	PhCHO	69	2	67	0
6[e]	DCE	PhCHO	90	5	73	12
7	PhMe	PhCHO	88	9	75	4
8	1,4-Dioxane	PhCHO	64	6	58	0
9	EtOH	PhCHO	9	1	8	0
10	CH_3CN	PhCHO	54	1	53	0
11	DCE	acetone	5	2	2	1
12	Acetone	no	7	0	5	2
13	Acetone	PhCHO	11	1	8	2
14[c]	DCE	vinyl acetate	48	1	46	1
15[c]	DCE	crotonitrile	30	1	28	1
16[c]	DCE	styrene	78	27	26	25

[a]All reactions were carried out with a geraniol (**1a**, 2.0 mmol) at a concentration of 0.5 M at 90 °C, substrate:aldehyde:$[RuCl_2(PPh_3)_3]$:base = 100:300:2:4. [b]Determined by GC analysis. [c]Reaction time: 12 h. [d]6 equiv of benzaldehyde per mole of substrate was used. [e]1.5 equiv of benzaldehyde per mole of substrate was used.

of 1-propanol, which was produced as detected by GC (Table 1, entry 7). Furthermore, before the consumption of **1a**, the excess of allyl alcohol was transformed to propionaldehyde through redox isomerization, indicating that the aldehyde can serve as a hydrogen abstractor. This was verified by the fact that when 3-phenylpropanal (3 equiv was added), a molar ratio of 1:1 between **1c** and 3-phenylpropan-1-ol was obtained and **1d** was not detected by GC (Table 1, entry 8).

On the basis of our studies, the formation of α,β-unsaturated aldehyde (**1c**) and saturated alcohol (**1d**) is shown in Scheme 2 (right cycle). Competing coordination of **1b** with ruthenium species **B** liberates α,β-unsaturated aldehyde (**1c**) to generate a new ruthenium species **E**, which is then transformed to species **F** by insertion of C═O into Ru−H. Finally, ligand exchange with **1a** liberates **1d** and regenerates the ruthenium species **A**.

Other readily available aldehydes were chosen as hydrogen abstractors to test the efficiency. Formaldehyde was not a good hydrogen abstractor; acetaldehyde and butyraldehyde were better than formaldehyde but were inferior to 3-phenylpropanal. Benzaldehyde proved to be the most effective hydrogen abstractor, and 3 equiv of benzaldehyde was enough for the reaction (Table 2, entries 1−6). Toluene was also a usable solvent, but when the reaction was carried out in a polar solvent, the reaction rate was decreased possibly due to the competitive coordination between the substrate and solvent. Alcohols are not good solvents for this transformation. It can undergo β-hydride elimination and produce other catalytic species (Table 2, entries 7−10).

This reaction is by nature a transfer hydrogenation reaction. As is well-known, acetone is commonly used as a hydride acceptor in transfer hydrogenation reactions; however, when acetone (3 equiv) was added to the reaction, a poor yield of the enone (**1c**) was obtained, and the same poor yield was obtained when we used acetone as the solvent (Table 2, entries 11 and 12). These results are inconsistent with the observation by Bäckvall.[12b] It was probably because of the competing coordination between allyl alcohol and acetone when acetone was used as the solvent. To verify the hypothesis, we conducted the reaction in acetone in the presence of 3 equivlents of benzaldehyde. Not to our surprise, the reaction became very slow, and very low conversion of substrate was observed (Table 2, entry 13). Meanwhile, other commonly used hydrogen acceptors were tested. Styrene did not serve as the hydrogen abstractors; vinyl acetate and crotonitrile were inferior to aldehyde (Table 2, entries 14−16). Apparently, an intermolecular hydrogen transfer reaction in the presence of an aldehyde became easier than intramolecular redox isomerization for allyl alcohols under the catalysis of a Ru catalyst in a nonpolar solvent, and this provided an entry to unsaturated compounds.

To make the reaction more efficient, different bases were also examined for the model reaction, and the results were summarized in Table 3. Sodium carbonate and potassium carbonate gave even better results than cesium carbonate; stronger base like *t*-BuOK and KOH, and weaker base like K_3PO_4, gave poor results. Sodium carboxylates gave better results than other bases. Among all of the sodium carboxylates (RCO_2Na, R = CH_3, *t*-Bu, and Ph) tested, sodium acetate gave the best results, which led to a 98% conversion of **1a** into **1b** (2%) and **1c** (96%) in only 4 h (Table 3, entry 6). Besides $[RuCl_2(PPh_3)_3]$, other catalysts such as $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(benzene)]_2$, and $[RuCl_2(COD)]_n$ were also investigated. No products were detected at all, and the starting material **1a** was recovered. Meanwhile, the influence of catalyst loading and reaction temperature were also investigated. When only 1 mol % of catalyst was used, the desired product (95%) was determined by GC and significant decrease of yield was observed with 0.5 mol % of catalyst (Table 3, entries 11 and 12) and a low reaction temperature (50 °C) also led to significant drop of yield to 65% in 10 h.

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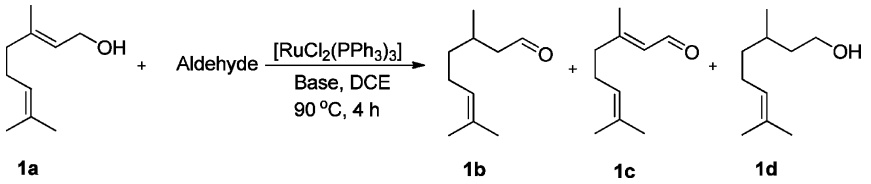
Table 3. Optimization of the Bases for the Synthesis of α,β-Unsaturated Aldehyde[a]

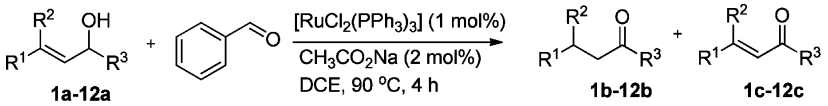


1a 1b 1c 1d

entry	base	conv.[b] (%)	yield[b] (%) 1b	1c	1d
1	K_2CO_3	95	3	92	0
2	Na_2CO_3	98	9	87	2
2	KOH	89	8	79	1
3	*t*-BuOK	81	6	73	1
4	K_3PO_4	98	18	74	6
5	CH_3CO_2K	95	2	93	0
6	CH_3CO_2Na	98	2	96	0
7	CH_3CO_2Li	78	2	74	2
8	*t*-$BuCO_2Na$	55	3	50	2
9	$PhCO_2Na$	72	2	70	0
11[c]	CH_3CO_2Na	97	2	95	0
12[d]	CH_3CO_2Na	80	3	77	0
13[e]	CH_3CO_2Na	67	3	65	0

[a]All reactions were carried out with a geraniol (**1a**, 2.0 mmol) at a concentration of 0.5 M at 90 °C, substrate:aldehyde:[Ru]:base = 100:300:2:4. [b]Determined by GC analysis. [c]1 mol % of $[RuCl_2(PPh_3)_3]$ was used. [d]0.5 mol % of $[RuCl_2(PPh_3)_3]$ was used. [e]Temperature was 50 °C.

Table 4. Synthesis of α,β-Unsaturated Carbonyl Compounds[a]



1a-12a 1b-12b 1c-12c

1a: $R^1 = (CH_3)_2C{=}CH(CH_2)_2$, $R^2 = CH_3$, $R^3 = H$
2a: $R^1 = (CH_3)_3C$, $R^2 = CH_3$, $R^3 = H$
3a: $R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = H$
4a: $R^1 = C_6H_5$, $R^2 = (CH_3)_2CH$, $R^3 = H$
5a: $R^1 = 4\text{-}CH_3C_6H_4$, $R^2 = CH_3$, $R^3 = H$
6a: $R^1 = 4\text{-}CH_3OC_6H_4$, $R^2 = CH_3$, $R^3 = H$
7a: $R^1 = 4\text{-}CF_3C_6H_4$, $R^2 = CH_3$, $R^3 = H$
8a: $R^1 = 2\text{-}CH_3C_6H_4$, $R^2 = CH_3$, $R^3 = H$
9a: $R^1 = (CH_3)_2CH$, $R^2 = C_6H_5$, $R^3 = H$
10a: $R^1 = CH_3$, $R^2 = (CH_3)_2C{=}CH(CH_2)_2$, $R^3 = H$
11a: $R^1 = C_6H_5$, $R^2 = H$, $R^3 = CH_3$
12a: $R^1 = H$, $R^2 = H$, $R^3 = C_6H_5$

entry	substrate	conv.[b] (%)	yield[b] (%) b	c
1	**1a**	97	2	95(93)
2	**2a**	99	3	96(94)
3	**3a**	99	2	97(94)
4	**4a**	97	3	94(91)
5	**5a**	99	3	96(93)
6	**6a**	99	1	98(96)
7[c]	**7a**	85	2	83(80)
8	**8a**	99	2	97(94)
9	**9a**	99	3	96(93)
10	**10a**	95	2	93(90)
11[d]	**11a**	90	10	80(78)
12	**12a**	90	90(88)	0

[a]All reactions were carried out with an allyl alcohol (2.0 mmol) at a concentration of 0.5 M at 90 °C, substrate:aldehyde:[Ru]:NaOAc = 100:300:1:2. [b]Determined by GC analysis. In parentheses, isolated yield of the pure product. [c]Reaction time: 12 h. [d]Reaction time: 24 h.

With the optimized reaction conditions in hand, the scope of the substrates for this transformation was investigated. As shown in Table 4, trisubstituted primary (*E*)-allyl alcohols were evaluated first. Not only aliphatic allyl alcohols, such as **1a** and **2a**, were converted to the corresponding enals in excellent yields but also aromatic substrates were transformed to aryl enals under the same reaction conditions. For aromatic allyl alcohols, the alkyl substituents at the C═C bond did not impose much effect on the reactivity and yields (Table 4, entries 3 and 4), but the substituents at the aromatic ring had an obvious effect on the intermolecular hydrogen transfer reaction (Table 4, entries 5−8). For example, for substrate **7a** with an electron-withdrawing (CF_3) group at the para position of the aromatic ring, the corresponding enone was obtained in only 83% yield after 12 h

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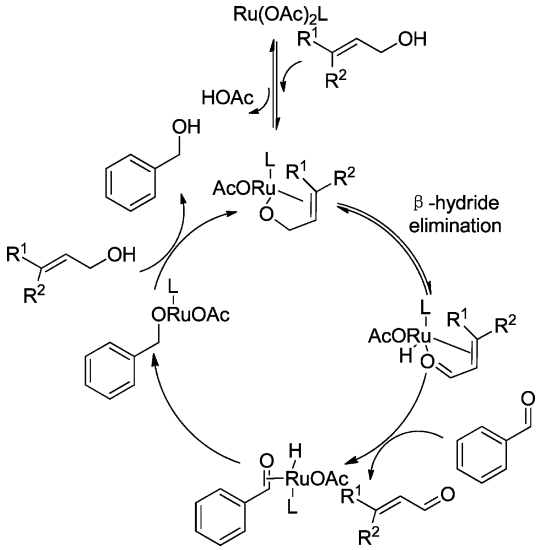
(Table 4, entry 7). The low activity of **7a** was attributed to the decreased coordination ability of the oxygen atom with metal species. Furthermore, trisubstituted primary (*Z*)-allyl alcohols, such as **9a** and **10a**, were also workable substrates under the same reaction conditions (Table 4, entries 9 and 10). To our delight, disubstituted secondary allyl alcohol (**11a**) could be transformed to the corresponding enone in excellent yield (Table 4, entry 11). However, when monosubstituted secondary allyl alcohol (1-phenylprop-2-en-1-ol, **12a**) was tried, the corresponding enones could not be obtained at all; nevertheless, the starting material was transformed to propiophenone by redox-isomerization (Table 4, entry 12). When homoallyl alcohol 1-phenybut-3-en-1-ol was used as substrate, no desired product could be obtained probably because of homoallyl alcohol coordination inferior to benzaldehyde. This implies that the C=C double bond must bind to ruthenium to promote the reaction. To check whether the coordination of the C=C double bond is really necessary, hydrogenated product citronellol (**1d**) was tried and, even after 12 h, the starting material remained essentially intact.

On the basis of the results discussed above, we suggested a mechanism as depicted in Scheme 3. First, the Cl^- of

Scheme 3. Proposed Catalytic Cycle for Intermolecular Hydrogen Transfer of Allyl Alcohols in the Presence of Benzaldehyde



$[RuCl_2(PPh_3)_3]$ was replaced by OAc^- to form $Ru(OAc)_2(PPh_3)_3$ in the presence of NaOAc[16] and then by ligand exchange to give the ruthenium alkoxide species; subsequent β-hydrogen elimination yields α,β-unsaturated aldehyde and a [Ru−H] species, which is still coordinated with the resulted α,β-unsaturated aldehyde. In the presence of a large excess amount of benzaldehyde (relative to the Ru−H species formed), the coordinated α,β-unsaturated aldehyde is replaced by benzaldehyde, which is reduced to the benzyl alcohol. Finally, ligand exchange with allyl alcohol generates the Ru-allyl alkoxide catalytic species.

CONCLUSION

In summary, we have developed a new synthetic method of enals and enones through intermolecular rather than intramolecular hydrogen transfer of allyl alcohols in the presence of an aldehyde. Various substrates could be subjected under the optimized reaction conditions and smoothly transformed into the corresponding enals or enones in high yields.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox, unless otherwise noted. Commercially available reagents were used throughout without further purification, other than those detailed below. Anhydrous EtOH was freshly distilled from Mg. Anhydrous CH_2ClCH_2Cl was freshly distilled from calcium hydride. Anhydrous PhMe and 1,4-dioxane were freshly distilled from sodium. Anhydrous CH_3CN was freshly distilled from anhydrous calcium sulfate. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. The chemical shifts for ^1H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.00 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (300−400 mesh). Flash column chromatography was performed on silica gel (300−400 mesh).

Procedures for Synthesis of Substrates (2a−9a).[21] Triethyl phosphonoacetate (26.9 g, 120 mmol) was added dropwise under nitrogen over a period of 5 min to a stirred suspension of NaH (60% on mineral oil; 4.8 g, 120 mmol) in dry THF (120 mL), and the resulting mixture was stirred for another 0.5 h at 0 °C. A solution of ketone (110 mmol) in dry THF (30 mL) was slowly added to the resulting mixture, and the reaction mixture was heated to reflux overnight. After cooling to room temperature, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After concentration under vacuum, the residue was purified by flash chromatography on silica gel (EtOAc:pentane = 1:40) to afford (*E*)-oate and (*Z*)-oate as colorless oil.

DIBAL-H (40 mL, 1.5 M in toluene) was added to a solution of ester (60 mmol) in THF (100 mL) at −78 °C over a period of 1 h. The reaction mixture was stirred at −78 °C for 1 h and the solution was allowed to reach 0 °C. The solution was quenched with a saturated aqueous solution of NH_4Cl at 0 °C and stirred at room temperature until a white precipitate was formed. The precipitate was filtered through a pad of Celite and washed with Et_2O. The resulting solution was washed with brine and dried over Na_2SO_4. After concentration under vacuum, the residue was purified by flash chromatography on silica gel (EtOAc:pentane = 1:5) as colorless oil.

*(E)-3,4,4-Trimethylpent-2-en-1-ol (**2a**):*[21] Colorless oil: 8.4 g, 60% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 5.46−5.40 (m, 1H), 4.16 (d, J = 6.4 Hz, 2H), 1.64 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 120.5, 59.6, 35.9, 28.7, 12.7.

*(E)-3-Phenylbut-2-en-1-ol (**3a**):*[17] Colorless oil: 8.2 g, 50% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.40 (m, 2H), 7.36−7.30 (m, 2H), 7.29−7.25 (m, 1H), 5.98 (dt, J = 6.4, 1.2 Hz, 1H), 4.37 (d, J = 6.8 Hz, 2H), 2.08 (s, 3H), 1.87 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.7, 137.7, 128.2, 127.2, 126.4, 125.7, 59.8, 16.0.

*(E)-4-Methyl-3-phenylpent-2-en-1-ol (**4a**):*[21] Colorless oil: 9.2 g, 48% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32−7.25 (m, 3H), 7.21−7.16 (m, 2H), 5.49 (t, J = 6.8 Hz, 1H), 4.36 (d, J = 6.8 Hz, 2H), 3.08−2.98 (m, 1H), 1.81 (br, 1H), 1.07 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 142.1, 128.2, 127.5, 127.3, 126.4, 58.6, 29.6, 21.9.

*(E)-3-(p-Tolyl)but-2-en-1-ol (**5a**):*[22] Colorless oil: 9.3 g, 52% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.00 (dt, J = 6.4, 1.2 Hz, 1H), 4.37 (d, J = 6.8 Hz, 2H), 2.84 (br, 1H), 2.39 (s, 3H), 2.08 (d, J = 0.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.8, 137.1, 136.7, 128.8, 125.6, 125.4, 59.6, 20.9, 15.7.

*(E)-3-(4-Methoxyphenyl)but-2-en-1-ol (**6a**):*[22] Colorless oil: 11.8 g, 60% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38−7.33 (m, 2H), 6.89−6.84 (m, 2H), 5.94−5.90 (m, 1H), 4.35 (d, J = 6.8 Hz, 2H), 3.81 (s, 3H), 2.07−2.06 (m, 3H), 1.58 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 137.3, 135.2, 126.8, 124.8, 113.5, 59.9, 55.2.

*(E)-3-[4-(Trifluoromethyl)phenyl]but-2-en-1-ol (**7a**):*[23] Colorless oil: 13.5 g, 57% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.2 Hz,

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2H), 7.48 (d, J = 8.2 Hz, 2H), 6.02 (dt, J = 6.4, 1.2 Hz, 1H), 4.38 (d, J = 6.4 Hz, 2H), 2.08 (s, 3H), 1.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 136.4, 129.2 (q, J = 30.0 Hz), 126.2, 125.8, 125.1 (d, J = 3.4 Hz), 123.1, 59.9, 16.0.

*(E)-3-(o-Tolyl)but-2-en-1-ol (**8a**):*[23] Colorless oil: 7.1 g, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.08 (m, 4H), 5.55 (m, 1H), 4.35 (d, J = 6.4 Hz, 2H), 2.30 (s, 3H), 1.99−1.97 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 139.1, 134.4, 123.0, 128.0, 127.9, 126.7, 125.5, 59.3, 19.6, 18.1.

*(Z)-4-Methyl-3-phenylpent-2-en-1-ol (**9a**):*[21] Colorless oil: 3.9 g, 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.23 (m, 3H), 7.10−7.05 (m, 2H), 5.63 (dt, J = 6.8, 1.2 Hz, 1H), 3.95 (d, J = 6.8 Hz, 2H), 2.60 (m, 1H), 1.57 (s, 1H), 1.03 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.8, 140.4, 128.7, 128.2, 127.0, 123.5, 60.5, 35.9, 21.8.

Preparation of 1-Phenylpro-2-en-1-ol (12a):[18] To the solution of benzaldehyde (1.1 g, 10 mmol) in anhydrous THF (40 mL) was added vinylmagnesium chloride (7 mL, 1.6 M in THF) slowly at −10 °C. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl (40 mL), followed by the addition of 60 mL of ether. The organic phase was washed with brine, dried with anhydrous sodium sulfate, and removed under reduced pressure. The crude product was purified by silica-gel column chromatography (1.3 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.26 (m, 5H), 6.05 (ddd, J = 17.2, 10.0, 6.0 Hz, 1H), 5.38−5.31 (m, 1H), 5.23−5.16 (m, 2H), 2.05 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 140.2, 128.5, 127.7, 126.3, 115.1, 75.3.

Preparation of 1-Phenylbut-3-en-1-ol.[19] To a 50 mL three-necked flask was equipped with a magnetic stirrer, a pressure equalizing dropping funnel, and reflux condenser mounted with a nitrogen source. To the flask were added magnesium (0.3 g, 10 mmol), a small amount of iodine, and 5 mL of ether. To this was added a small amount allyl chloride. The reaction mixture was stirred until the purple iodine color disappeared at room temperature. To this was added 10 mL of a solution of allyl chloride (0.8 g, 10 mmol) slowly at −10 °C. After 30 min, a solution of benzaldehyde (1.1 g, 10 mmol) in 20 mL of ether was added dropwise at such a rate to maintain the internal temperature below −10 °C. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl (40 mL), followed by the addition of 60 mL ether. The organic phase was washed with brine, dried with anhydrous sodium sulfate, and removed under reduced pressure. The crude product was purified by silica-gel column chromatography. 1-Phenylbut-3-en-1-ol was obtained as a colorless oil (1.3 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.30 (m, 5H), 5.84−5.79 (m, 1H), 5.17−5.12 (m, 2H), 4.68 (t, J = 8.0 Hz, 1H), 2.89 (br, 1H), 2.50 (t, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 134.4, 128.2, 127.3, 125.7, 117.9, 73.2, 43.5.

Preparation of (*E*)-1-phenylbut-3-en-2-ol (11a).[20] To a solution of benzaldehyde (5.3 g, 50 mmol) in acetone (125 mL) was added triethylamine (0.5 g, 5 mmol). The reaction mixture was stirred at 45 °C in a 250 mL three-necked flask. After 24 h, the reaction mixture was cooled to room temperature, and a saturated $NaHCO_3$ solution (50 mL) and ethyl acetate (50 mL) were added. After phase separation, the aqueous phase was extracted three times with EtOAc and the organic layer was dried over Na_2SO_4 and concentrated in vacuum to give (*E*)-4-phenylbut-3-en-2-one (6.1 g, 84% yield). Next, to a solution of (*E*)-4-phenylbut-3-en-2-one (4.4 g, 30 mmol) and $CeCl_3{\cdot}7H_2O$ (11.2 g, 30 mmol) in 20 mL of MeOH was added $NaBH_4$ (1.7 g, 45 mmol) over a 10 min period. The reaction mixture was stirred for 1 h at room temperature and then quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ether (3 × 10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, and removed under reduced pressure. The crude product was purified by silica-gel column chromatography (4.0 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.12 (m, 5H), 6.47 (d, J = 16 Hz, 1H), 6.17 (dd, J = 16.0, 6.4 Hz, 1H), 4.43−4.36 (m, 1H), 1.74 (br, 1H), 1.28 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.5, 133.5, 129.0, 128.4, 127.4, 126.3, 68.5, 23.2.

A Typical Procedure for the Oxidation of Allyl Alcohols with Intermolecular Hydrogen Transfer: Synthesis of α,β-Unsaturated Carbonyl Compounds. In a dried Schlenk tube, $[RuCl_2(PPh_3)_3]$ (19.2 mg, 0.02 mmol), CH_3CO_2Na (3.5 mg, 0.04 mmol), and substrate (2 mmol) were dissolved in DCE (4 mL), and then a benzaldehyde (6 mmol) was added into the solution at room temperature. The solution was stirred at 90 °C under nitrogen and monitored by gas chromatography. After completion of the reaction, the solvent was evaporated and the residue was dissolved with EtOAc (5 mL) and water (2 mL). The layers were separated, and the aqueous layer was washed with EtOAc (2 × 2 mL). The combined organic extracts were washed with brine (5 mL) and then dried over Na_2SO_4. After the solvent was evaporated, the crude product was purified by column chromatography over silica gel.

*Citral (**1c**):*[24] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (282.7 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (d, J = 8.2 Hz, 1H), 5.88−5.86 (m, 1H), 5.07−5.03 (m, 1H), 2.23−2.12 (m, 7H), 1.67−1.60 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.3, 163.9, 132.9, 127.4, 122.5, 40.6, 25.7, 25.6, 17.7, 17.6.

*(E)-3,4,4-Trimethylpent-2-enal (**2c**):*[25] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (237.1 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (d, J = 8.0 Hz, 1H), 5.95−5.92 (m, 1H), 2.16 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.6, 171.2, 124.5, 37.8, 28.3, 13.7.

*(E)-3-Phenylbut-2-enal (**3c**):*[26] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (274.6 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (d, J = 7.6 Hz, 1H), 7.56−7.53 (m, 2H), 7.43−7.39 (m, 3H), 6.40 (dq, J = 8.0, 1.2 Hz, 1H), 2.58 (d, J = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.8, 157.2, 140.1, 129.7, 128.4, 126.8, 125.9, 15.9.

*(E)-4-Methyl-3-phenylpent-2-enal (**4c**):*[27] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (318.9 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.26 (d, J = 8.0 Hz, 1H), 7.40−7.18 (m, 5H), 5.91 (d, J = 8.0 Hz, 1H), 3.78−3.71 (m, 1H), 1.24 (d, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 169.8, 139.9, 128.9, 128.2, 127.9, 127.1, 30.2, 22.3.

*(E)-3-(p-Tolyl)but-2-enal (**5c**):*[28] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (297.8 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (d, J = 8.0 Hz, 1H), 7.47−7.43 (m, 2H), 7.23−7.19 (m, 2H), 6.39 (dq, J = 8.4, 2.0 Hz, 1H), 2.54 (d, J = 1.2 Hz, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.9, 157.2, 140.2, 137.1, 129.1, 128.9, 126.1, 125.9, 21.0, 15.8.

*(E)-3-(4-Methoxyphenyl)but-2-enal (**6c**):*[22] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 6:1) to give the compound as oil (338.1 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (d, J = 8.0 Hz, 1H), 7.56−7.49 (m, 2H), 6.94−6.90 (m, 2H), 6.42−6.35 (m, 1H), 3.84 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.1, 161.1, 156.9, 132.1, 127.6, 125.2, 113.9, 55.2, 15.8.

*(E)-3-[4-(Trifluoromethyl)phenyl]but-2-enal (**7c**):*[29] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (342.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (d, J = 7.6 Hz, 1H), 7.68−7.62 (m, 4H), 6.40−6.37 (m, 1H), 2.58 (d, J = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.0, 155.9, 144.1, 131.5 (d, J = 32.2 Hz), 128.4, 126.5, 125.6 (d, J = 3.0 Hz), 118.2, 16.3.

*(E)-3-(o-Tolyl)but-2-enal (**8c**):*[30] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (301.2 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (d, J = 8.0 Hz, 1H), 7.27−7.13 (m, 4H), 7.10 (m, 1H), 6.00−5.93 (m, 1H), 2.47 (d, J = 1.2 Hz, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.9, 160.9, 142.4, 133.4, 130.5, 129.9, 128.1, 126.5, 125.7, 19.6, 19.1.

*(Z)-4-Methyl-3-phenylpent-2-enal (**9c**):*[27] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (323.8 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (d, J = 8.0 Hz, 1H), 7.40−7.36 (m, 3H), 7.23−7.19 (m, 2H), 6.07 (dd, J = 8.0, 1.2 Hz, 1H),

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2.81−2.74 (m, 1H), 1.11 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6, 171.8, 137.5, 128.2, 127.8, 125.9, 36.4, 20.7.

(Z)-3,7-Dimethylocta-2,6-dienal (10c):[31] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (273.8 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (d, J = 8.2 Hz, 1H), 5.89−5.81 (m, 1H), 5.10−5.06 (m, 1H), 2.59−2.53 (m, 2H), 2.21 (q, J = 7.2 Hz, 3H), 1.96 (t, J = 1.2 Hz, 3H), 1.66 (s, 3H), 1.59−1.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.6, 163.7, 133.4, 128.4, 122.1, 32.4, 26.8, 25.4, 24.9, 17.5.

(E)-4-Phenylbut-3-en-2-one (11c):[32] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give the compound as oil (227.9 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.51 (m, 3H), 7.43−7.37 (m, 3H), 6.72 (d, J = 16.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.1, 143.2, 134.1, 130.3, 128.7, 128.0, 126.9, 27.3.

Propiophenone (12b):[33] The crude material was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20:1) to give the compound as oil (235.9 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95−7.93 (m, 2H), 7.54−7.50 (m, 1H), 7.45−7.41 (m, 2H), 2.98 (q, J = 8.0 Hz, 2H), 1.20 (t, J = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 136.8, 132.8, 128.4, 127.8, 31.7, 8.1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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