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Ruthenium-catalysed reductive cleavage of allylic esters with formic acid and triethylamine. Application to short-step synthesis of α-hydroxy acids

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Abstract

Ruthenium-catalysed reductive cleavage reactions of allylic carboxylates and carbonates with formic acid and triethylamine to give olefins were explored. As an application of the ruthenium-catalysed processes, a new synthetic route to α-hydroxy acids has been discovered. The reductive cleavage of allylic esters is considered to proceed through π-allylruthenium intermediates.

Key words: Ruthenium; Catalysis; Reductive cleavage; Allyl; Formic acid

1. Introduction

Among various palladium-catalysed reactions utilizing cleavage of the C–O bond in allylic esters [1–4], reductive cleavage of allylic esters to give terminal olefins with formic acid in combination with tertiary amines provides a convenient means of considerable synthetic utility since the reaction yields terminal olefins in high selectivity under mild reaction conditions [5]. The reaction course in reductive cleavage of allylic acetate (**1**, **2**) has been explained to proceed through formation of π-allylpalladium carboxylate intermediates produced by cleavage of the allylic–oxygen bond as shown in Scheme 1, where M = Pd [6].

In contrast to the wide use of palladium catalysts, examples of catalytic processes with other transition metal complexes involving allyl–O bond cleavage are still limited [7,8]. To find new catalytic processes which may not be achieved with palladium catalysts, we have explored the ruthenium-catalysed reductive cleavage of allylic esters with formic acid. In this paper we describe the results of our exploration which led to finding of a new, convenient catalytic process to give α-hydroxycarboxylic acids [9].

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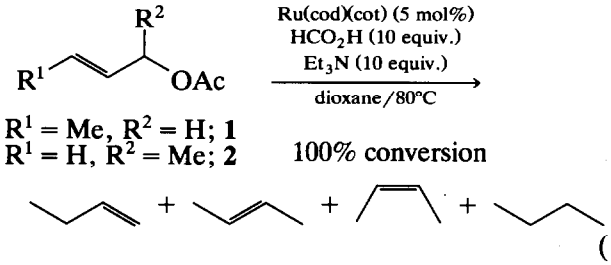
2. Results and discussion

2.1. Ruthenium-catalysed reductive cleavage of allylic esters

Reaction of crotyl acetate (**1**) with formic acid in the presence of Ru(cod)(cot) (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) in dioxane at 80°C caused quantitative cleavage of the allylic acetate to give a mixture of 1-butene, *trans*-2-butene and *cis*-2-butene together with n-butane (eqn. (1), Table 1). The similar reductive cleavage of 1-methyl-2-propenyl acetate (**2**), the isomer of **1**, also gave a mixture of butenes and butane.



R^1 = Me, R^2 = H; **1**
R^1 = H, R^2 = Me; **2**

100% conversion

(1)

The catalytic process can be accounted for in a similar manner to that proposed for the system with palladium catalysts as shown in Scheme 1, where M = Ru. The process is considered to consist of oxidative addition of allylic acetate to a Ru(0) complex to form

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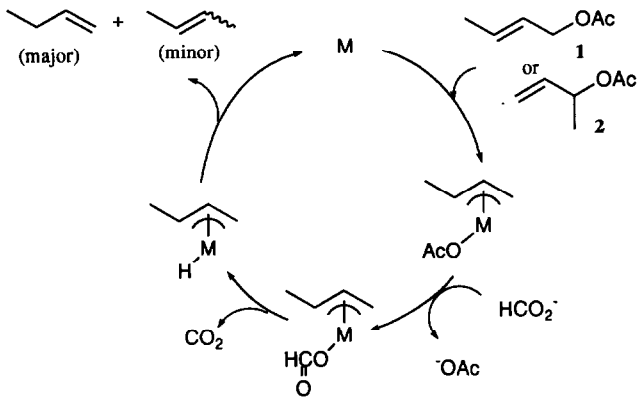
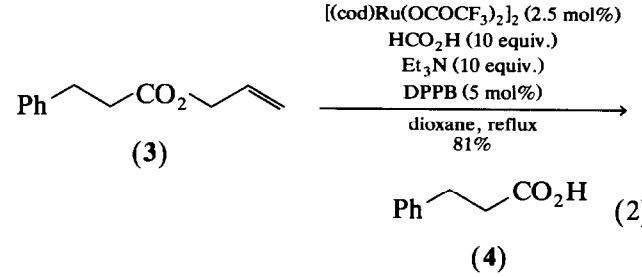


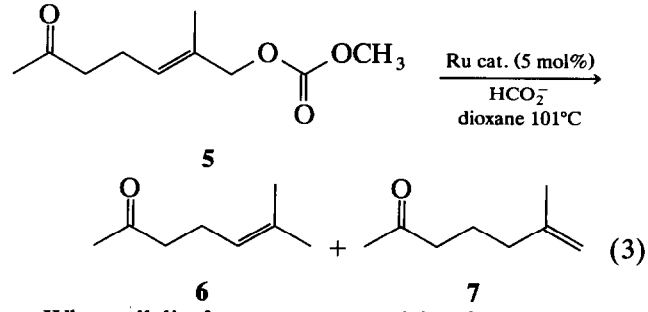
Scheme 1.

the π-allylruthenium acetate, substitution of the acetate ligand with formate anion, decarboxylation of the formate ligand to form a π-allylruthenium hydride and reductive elimination of the allyl and hydride ligands to liberate olefins. Conversion of the allylic acetate was quantitative but the selectivity to give the terminal olefin was lower than for the system with palladium complexes. The selectivity to give 1-butene could be improved by addition of DPPB (1,4-bis(disphenylphosphino)butane) at the expense of the reaction rate. Employment of other phosphines did not work since they caused catalytic decomposition of formic acid as reported by Watanabe and co-workers [10,11].

The ruthenium-catalysed reductive cleavage of allyl carboxylates with formic acid was found to be applicable to reductive cleavage of allyl 3-phenylpropionate (**3**) to the corresponding acid **4** under neutral conditions (eqn. (2)).



Similarly to allylic carboxylates, allylic carbonates also are cleaved by ruthenium catalyst in the presence of formic acid and triethylamine. Decarboxylative cleavage of an allylic methyl carbonate (**5**) with formic acid in the presence of Ru(cod)(cot) gave a mixture of internal olefin **6** and terminal olefin **7** with 93% conversion in a ratio of 83:17 (eqn. (3), Table 2). Combination of formic acid with triethylamine was most suitable for the reduction whereas the use of formic acid alone was not effective (Table 2). Addition of DPPB inhibited the reaction in this case. Ru(cod)(cot) was most effective as the catalyst but $[Ru(cod)(OCOCF_3)_2]_2$ was also applicable, whereas $RuH_2(PPh_3)_4$ was inactive as the catalyst.



When allylic formate was used in place of acetate, quantitative reductive cleavage of the C–O bond in

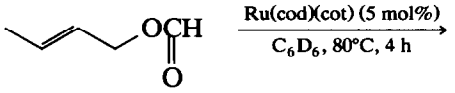
TABLE 1. Ruthenium-catalysed reductive cleavage of allylic acetates with formic acid

Substrate	Phosphine	Ratio			
		1-Butene	*trans*-2-Butene	*cis*-2-Butene	n-Butane
1	–	39	38	7	16
2	–	27	46	18	9
1	DPPB (5 mol%)	81	7	10	2

TABLE 2. Ruthenium-catalysed hydrogenolysis of **5** with formic acid

Ru catalyst	Ligand	Reactants	Conversion (%)	Selectivity **6**:**7**
Ru(cod)(cot)	–	$HCO_2H + Et_3N$	93	83:17
Ru(cod)(cot)	–	HCO_2K	67	55:45
Ru(cod)(cot)	–	HCO_2H	Trace	–
Ru(cod)(cot)	DPPB	$HCO_2H + Et_3N$	Trace	–
$[Ru(cod)(OCOCF_3)_2]_2$	–	$HCO_2H + Et_3N$	85	76:24

allylic formate catalysed by Ru(cod)(cot) proceeded smoothly without adding formic acid (eqn. (4)). The reaction of crotyl formate (**8**) gave a mixture of 1-butene and *cis*- and *trans*-2-butene without producing butane (Table 3). Addition of PPh_3 or DPPB raised the selectivity for the formation of terminal olefin with a considerable decrease in the conversion of **8**.



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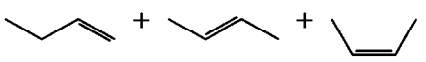
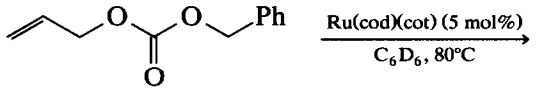


(4)

The decarboxylative cleavage of allyl benzyl carbonate (**9**) in the presence of Ru(cod)(cot) in C_6D_6 at 80°C without formic acid took place quantitatively to give benzaldehyde and propene with evolution of carbon dioxide (eqn. (5)). The reaction is considered to



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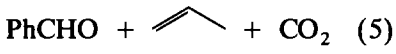


(5)

100% conv.

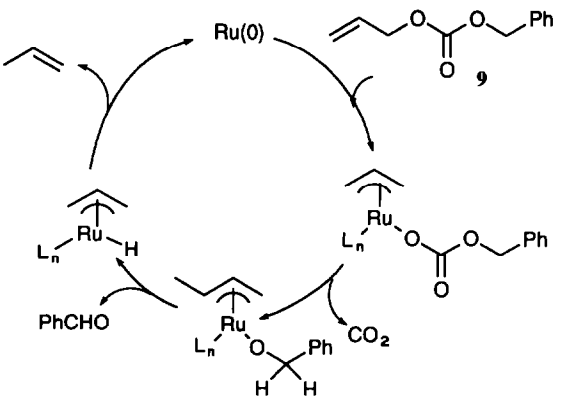
take a route as shown in Scheme 2 involving allyl–O bond cleavage, decarboxylation to give a π-allylruthenium benzyloxide that releases benzaldehyde by β-hydrogen abstraction and reductive elimination of propene to regenerate the Ru(0) complex. In contrast to the benzyl allyl carbonate, the decarboxylative cleavage of allyl ethyl carbonate was very slow and allyl methyl carbonate was unreactive.

Previous studies on the catalytic C–O bond cleavage of alkenyloxiranes have shown that palladium complexes serve as convenient catalysts to give homoallylic alcohols regio- and stereospecifically by reductive cleavage of the oxirane C–O bond. The process has been conveniently utilized in the synthesis of biologically active compounds [12]. Examination of ruthenium complexes as the catalysts in the reaction of the alkenyloxiranes **10** to the homoallylic alcohol **11** revealed that ruthenium complexes had less reactivity and selectivity than palladium catalysts. The reaction was accompanied by formation of byproducts **12** and **13** as shown in eqn. (6). The δ keto ester **12** may have been produced by isomerization of the allylic alcohol [A], which was generated by reductive cleavage of **10**. Compound **13** may have been formed by dehydration of **11**.

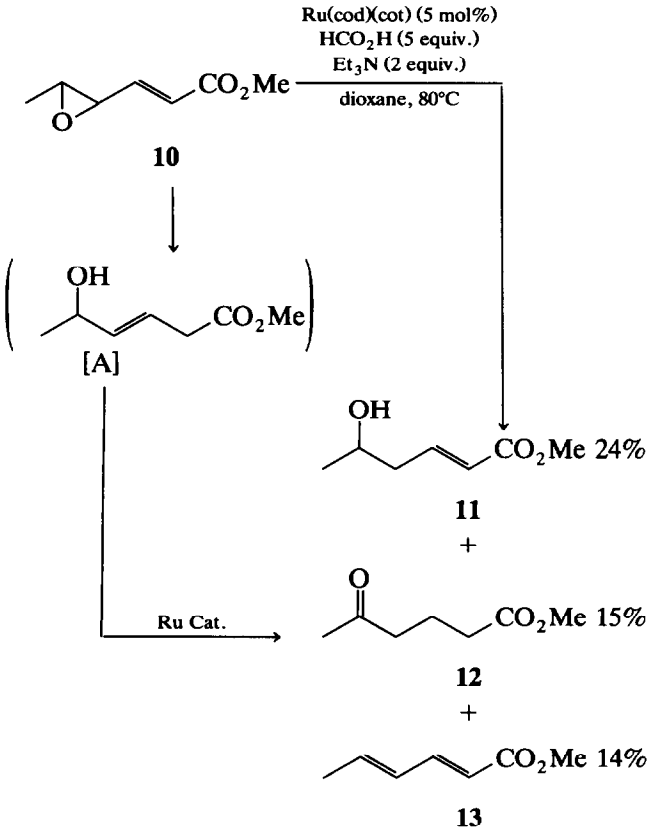
TABLE 3. Ruthenium-catalysed reductive cleavage of crotyl formate (**8**)

Ligand	Conversion (%)	Ratio		
		1-Butene	*trans*-2-Butene	*cis*-2-Butene
–	100	28	62	10
PPh_3 [a]	20	57	36	7
DPPB [b]	23	69	22	9

[a] PPh_3/Ru(cod)(cot) = 3:1.
[b] DPPB/Ru(cod)(cot) = 1:1.



Scheme 2.



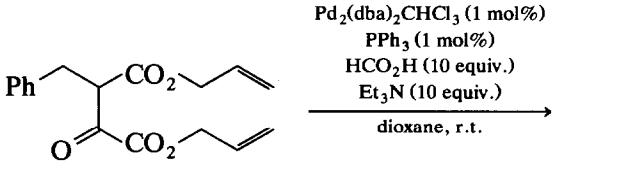
(6)

TABLE 4. Synthesis of α-hydroxycarboxylic acid **16** with some ruthenium catalysts

Ru catalyst	Yield (%)
$[(cod)Ru(OCOCF_3)_2]_2 + 2DPPB$	80
$RuH_2(PPh_3)_3$	69
$RuCl_2(PPh_3)_3$	68
$RuCl_3 \cdot 3H_2O + 3PPh_3$	35
$Ru_3(CO)_{12} + 9PPh_3$	73

2.2. *Synthesis of α-hydroxycarboxylic acids*

We have shown previously that catalytic reductive decarboxylation of diallyl α-oxalylcarboxylates such as **14** using palladium catalysts in combination with formic acid and triethylamine proceeds readily to give α-keto acids in high yields (eqn. (7)) [13]. The process provides



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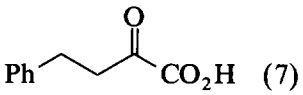
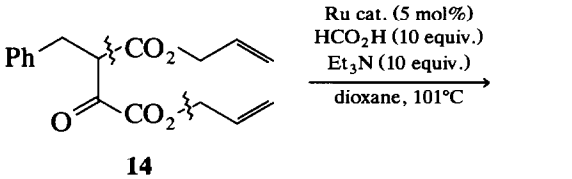


(7)

15

88% Yield

a convenient means of preparing synthetically useful α-keto acids since the starting compounds are readily available in a one-step reaction of allyl carboxylates and diallyl oxalate. Application of ruthenium catalysts instead of palladium to the decarboxylative deallylation of diallyl α-oxalylcarboxylate (**14**) (eqn. (8)) gave α-hydroxycarboxylic acids in good to medium yields, as shown in Table 4 and (eqn. (9)) Table 5. Among



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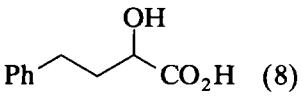

(8)

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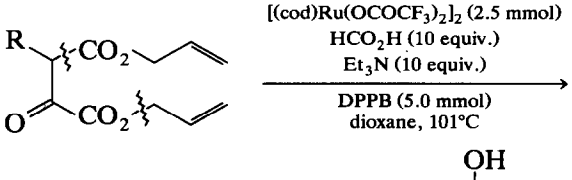
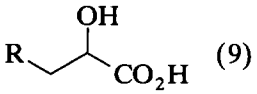
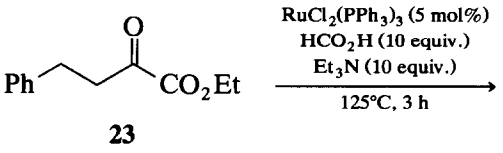




(9)

various catalysts examined, $[Ru(cod)(COCF_3)_2]_2$-DPPB proved to be most effective. The decarboxylative reduction of diallyl α-oxalylcarboxylates to α-hydroxy acids may proceed via the initial formation of α-keto acids as was observed with the palladium catalyst followed by further reduction of the keto group by the ruthenium catalysts. Ruthenium-catalysed hydrogenation of carbonyl compounds to the alcohols with formic acid has already been reported [10]. In fact, treatment of the α-keto ester **23** with $RuCl_2(PPh_3)_3$ in combination with formic acid and triethylamine produced the α-hydroxy acid **24** (eqn. (10)). The one-pot synthesis of α-hydroxy acids from diallyl α-oxalylcarboxylates may be regarded as one advantage of using ruthenium catalysts over palladium catalysts.



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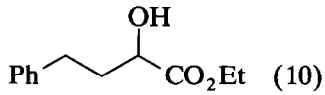
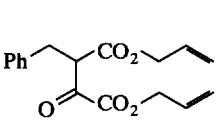
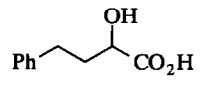
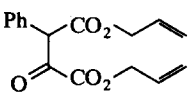
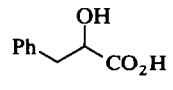
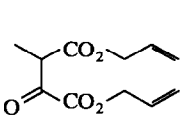
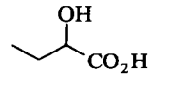
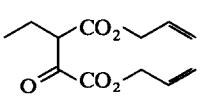
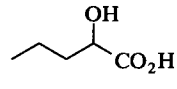


(10)

24

59% yield

TABLE 5. Synthesis of some α-hydroxycarboxylic acids using $[(cod)Ru(OCOCF_3)_2]_2$ with formic acid

α-Oxalylcarboxylate	Product	Yield (%)
 **14**	 **16**	80
 **17**	 **20**	73
 **18**	 **21**	50
 **19**	 **22**	63

3. Experimental details

Unless stated otherwise, experiments were carried out under an argon atmosphere. Infrared spectra were obtained on a Shimadzu IR-400 instrument. ^{1}H NMR spectra were recorded on a Hitachi R-90H spectrometer in benzene-d_6 or $CDCl_3$ at 90 MHz or a JEOL PMX 60 MHz spectrometer in CCl_4 or $CDCl_3$. ^{13}C NMR spectra were recorded on a Hitachi R-90H instrument at 22.5 MHz in $CDCl_3$. ^{1}H and ^{13}C NMR chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (TMS). Ru(cod)(cot) [14], $[Ru(cod)(OCOCF_3)_2]_2$ [15], $RuCl_2(PPh_3)_3$ [16], $RuH_2(PPh_3)_4$ [17] and $Ru_3(CO)_{12}$ [18] were prepared according to the literature. All compounds, except **5**, **14**, **17**, **18** and **19**, are known, and the characterization was achieved by means of ^{1}H NMR and IR spectra. Diethyl ether, tetrahydrofuran (THF) and dioxane were distilled from benzophenone ketyl. Triethylamine (Et_3N) was distilled over calcium hydride. Column chromatography was performed using Wakogel C-200 or C-300.

3.1. General procedure for ruthenium-catalysed reductive cleavage of allylic compounds 1 and 2 with formic acid

A mixture of formic acid (189 μl, 5 mmol) and triethylamine (279 μl, 2 mmol) was added to a solution of Ru(cod)(cot) (16 mg, 50 μmol) in dioxane (5 ml) at room temperature. The allylic acetate **1** or **2** (1.0 mmol) was added to the solution and the mixture was heated at 80°C for 4 h. The end of the reaction was determined by confirming the disappearance of the allylic acetate peaks by gas chromatography. 1-Butene, 2-butenes and butane were determined by gas chromatographic analysis.

3.2. Ruthenium-catalysed reductive cleavage of allyl hydrocinnamate (3) with formic acid and triethylamine

A mixture of formic acid (0.75 ml, 20 mmol) and Et_3N (2.8 ml, 20 mmol) was added to a solution of $[Ru(cod)(OCOCF_3)_2]_2$ (44 mg, 50 μmol) and DPPB (43 mg, 100 μmol) in dioxane at room temperature. To the solution was added allyl hydrocinnamate (**3**) (380 mg, 2 mmol) and the mixture was refluxed for 4 h. Organic acids were extracted with saturated aqueous $NaHCO_3$ solution. To the aqueous solution hydrochloric acid (3 M) was added to acidify the solution. Organic compounds were extracted with diethyl ether and the ethereal extract was concentrated *in vacuo* and the residue was chromatographed on silica gel using hexane–diethyl ether (4:1) as the eluent to give 3-phenylpropionic acid (**4**) as an oil (243 mg, 81% yield): ^{1}H NMR (60 MHz, CCl_4), δ 2.75 (m, 4H, CH_2CH_2), 7.20 (m, 5H, C_6H_5); IR (neat), 3005, 2620, 1684, 1416, 1313, 1209 cm^{-1}.

3.3. Preparation of 6-oxo-2-methyl-2-heptenyl methyl carbonate (5)

SeO_2 (0.53 g, 4.8 mmol) and salicylic acid (2.28 g, 23.8 mmol) were dissolved in CH_2Cl_2 (100 ml), and a solution of tert-butyl hydroperoxide (80%, 23 ml) was added at room temperature. 2-Methyl-2-hepten-6-one (12.0 g, 95.1 mmol) was added to the mixture and the resultant mixture was stirred for 1 h at room temperature. After treatment with dimethyl sulphide for 1 h at room temperature, saturated aqueous $NaHCO_3$ solution was added to the mixture. The mixture was extracted with CH_2Cl_2, and the CH_2Cl_2 solution was washed with saturated NH_4Cl, dried over $MgSO_4$ and condensed *in vacuo*. The residue was chromatographed on silica gel with diethyl ether–hexane (5:95) as the eluent to give 6-oxo-2-methyl-2-heptenol as an oil (3.61 g, 27%).

A mixture of 6-oxo-2-methyl-2-heptenol (2.00 g, 14.1 mmol) and pyridine (3.4 ml, 42.2 mmol) in CH_2Cl_2 (50 ml) was cooled to 0°C. Methyl chloroformate (3.3 ml, 42.2 mmol) was added dropwise and the solution was stirred at 0°C until 6-oxo-2-methyl-2-heptenol disappeared, as confirmed by TLC analysis. After neutralization of the solution with hydrochloric acid (1 M), the organic layer was extracted with diethyl ether. The extract was washed with saturated aqueous $NaHCO_3$ solution and brine and dried over $MgSO_4$. After filtration, the solution was evaporated to dryness. The residue was purified by chromatography on silica gel with diethyl ether–hexane (5:95) as the eluent to give 6-oxo-2-methyl-2-heptenyl methyl carbonate (**5**) as an oil (1.67 g, 57%). ^{1}H NMR (90 MHz, $CDCl_3$), δ 1.58 (s, 3H, CH=C(CH_3)–), 2.13 (s, 3H, CH_3CO), 2.16–2.57 (m, 4H, CH_2CH_2), 3.78 (s, 3H, CH_3O), 4.49 (s, 2H, allyl CH_2), 5.44 (m, 1H, –C*H*=C); ^{13}C NMR (22.5 MHz, $CDCl_3$), δ 13.4, 21.6, 29.5, 42.4, 54.3, 73.0, 128.0, 130.3, 155.3, 207.5; IR (neat), 2916, 1737, 1711, 1436, 1367, 1272 cm^{-1}; GC–MS, m/e = 199 (M − 1).

3.4. General procedure for ruthenium-catalysed reductive cleavage of 6-oxo-2-methyl-2-heptenyl methyl carbonate (5) with formic acid

A mixture of formic acid (0.75 ml, 20 mmol) and Et_3N (2.8 ml, 20 mmol) was added to a solution of Ru(cod)(cot) (5 mol%, 100 μmol) in dioxane (40 ml) at room temperature. To the solution was added 6-oxo-2-methyl-2-heptenyl methyl carbonate (**5**) (400 mg, 2 mmol) and the mixture was refluxed for 27 h. Organic compounds were extracted with diethyl ether and brine, and the ethereal extract was concentrated *in vacuo* to give the residue, which was chromatographed on silica

gel using hexane–diethyl ether (5:1) as the eluent to afford a mixture of 6-oxo-2-methyl-2-heptene (**6**) and 6-oxo-2-methyl-1-heptene (**7**) as an oil. The ratio of **6** and **7** was determined by ^{1}H NMR integration of olefinic protons.

When using HCO_2K, instead of HCO_2H and Et_3N, the salt was treated together with Ru(cod)(cot). ^{1}H NMR (90 MHz, $CDCl_3$), **6**, δ 1.62 (s, 3H, $CH_3(CH_3)C$=), 1.66 (s, 3H, $CH_3(CH_3)C$=), 2.12 (s, 3H, CH_3CO), 2.16–2.55 (m, 4H, CH_2CH_2), 5.07 (m, 1H, –C*H*=); **7**, δ 1.66 (s, –$(CH_3)C$=), 2.12 (s, CH_3CO), 2.16–2.55 (m, 6H, $COCH_2$–, –CH_2– and –CH_2C=), 4.66–4.72 (m, 2H, =CH_2); IR (neat), 2925, 1718, 1457, 1378 cm^{-1}; GC–MS, m/e = 125 (M − 1).

3.5. *Ruthenium-catalysed reductive cleavage of crotyl formate (8)*

To a mixture of Ru(cod)(cot) (3.2 mg, 10.1 μmol) and triphenylphosphine (8.0 mg, 31 μmol) in C_6D_6 (0.4 ml) was added crotyl formate (**8**) (20 mg, 204 μmol) in an NMR tube. The mixture was heated at 80°C for 4 h. The conversion of the reaction was determined by ^{1}H NMR integration. ^{1}H NMR showed the formation of 1-butene and *cis*- and *trans*-2-butene. The ratio was determined by GC analysis.

3.6. *Preparation of methyl (E)-4,5-epoxy-2-hexenoate (10)*

A solution of methyl sorbate (4.5 g, 35.7 mmol) in methanol (50 ml) was added to a solution of Oxone® in water (50 ml) whose pH was adjusted to 6 by adding 1 M KOH. The pH was kept at this value by the addition of 1 M KOH dropwise. The reaction mixture was stirred for 4 h. The organic layer was extracted with diethyl ether, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel using hexane–diethyl ether (9:1) as the eluent to give the alkenyloxirane **10** as an oil (0.758, 16% yield). ^{1}H NMR (60 MHz, CCl_4), δ 1.35 (d, J = 5.0 Hz, 3H, CH_3CH), 2.89 (m, J = 2.0, 5.0 Hz, 1H, CH_3CH–), 3.09 (dd, J = 2.0, 6.5 Hz, 1H, –C*H*–CH=), 3.66 (s, CO_2CH_3), 6.01 (d, J = 15.0 Hz, 1H, =C*H*–CO_2CH_3), 6.70 (dd, J = 15.0, 6.5 Hz, 1H, CH–C*H*=CH); IR (neat), 2953, 1724, 1654, 1438, 1398, 1307, 1261, 1197, 1148, 1018, 978, 407 cm^{-1}.

3.7. *Reductive cleavage of methyl (E)-4,5-epoxy-2-hexenoate (10) with formic acid and triethylamine*

A mixture of formic acid (0.13 ml, 3.52 mmol) and Et_3N (0.20 ml, 1.47 mmol) was added to a solution of Ru(cod)(cot) (11 mg, 35 μmol) in dioxane (40 ml) at room temperature. To the solution was added the alkenyloxirane **10** (100 mg, 0.70 mmol) and the mixture was refluxed for 27 h. Organic compounds were extracted with diethyl ether and brine and the ethereal extract was concentrated *in vacuo*. The products were separated by chromatography on silica gel using hexane–diethylether (5:1) as the eluent to give the homoallyl alcohol **11** (oil, 23.8 mg, 23% yield), ketone **12** (oil, 15.5 mg, 15% yield) and methyl sorbate **13** (oil, 12.6 mg, 14% yield). Characterization of **11–13** was effected on the basis of spectroscopic data.

3.7.1. *Methyl 5-hydroxy-2-hexenoate (11)*

^{1}H NMR (60 MHz, CCl_4), δ 1.15 (d, J = 6.4, 3H, CH_3CH), 2.27 (t, J = 6.2, 2H, –CH_2–), 3.60 (s, 3H, –CO_2CH_3), 3.85 (q, J = 6.2 Hz, 1H, CH_3–C*H*(OH)–), 5.78 (d, J = 15.8 Hz, 1H, =C*H*–CO_2Me), 6.85 (dt, J = 15.8, 6.9 Hz, CH_2–C*H*=CH); IR (neat), 3739, 3650, 3480, 3174, 2978, 2267, 1732, 1667, 1483, 1453, 1400, 1394, 1300, 1233, 1189, 1108, 1000 cm^{-1}.

3.7.2. *Methyl-5-oxo-2-hexenoate (12)*

^{1}H NMR (60 MHz, CCl_4), δ 1.15 (t, J = 6.5 Hz, 2H, $COCH_2$–), 1.78 (t, J = 6.5 Hz, 2H, –$CH_2CO_2CH_3$), 2.05 (s, 3H, CH_3CO), 2.33 (quint, J = 6.5, 2H, –CH_2–), 3.58 (s, 3H, –CO_2CH_3); IR (neat), 2989, 2896, 2256, 1730, 1718, 1476, 1389, 1232, 1169, 1112 cm^{-1}.

3.8. *General procedure for preparation of diallyl α-oxalylcarboxylates (14, 17, 18 and 19)*

To a suspension of sodium hydride (55 wt.%, 40 mmol) and allyl alcohol (940 mmol) in THF (100 ml) was added a mixture of allyl carboxylate (20 mmol) and diallyl oxalate (4.25 g, 25.0 mmol) and the solution was stirred at room temperature for 4 h. Hydrochloric acid (3 M) was added to the solution and the organic layer was extracted with diethyl ether. The combined ether extracts were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel using hexane–diethyl ether (95:5) as the eluent to give diallyl α-oxalylcarboxylate as an oil. The α-oxalylcarboxylate thus obtained was found to be in equilibrium with its enol isomer.

3.8.1. *Allyl 3-allyloxycarbonyl-2-oxo-4-phenylbutanoate (14) and allyl 3-allyloxycarbonyl-2-hydroxy-4-phenyl-2-butenoate (14') (oil, 73%)*

^{1}H NMR (60 MHz, CCl_4), **14**, δ 3.21 (d, J = 6.4 Hz, 2H, PhCH_2–), 4.45 (t, J = 7.0 Hz, 1H, –CH_2CH<), 4.20–4.77 (m, 4H, allyl CH_2 × 2), 4.97–6.10 (m, 6H, –CH=CH_2 × 2), 6.97–7.07 (m, 5H, C_6H_5); **14'**, δ 3.84 (s, 2H, PhCH_2–), 4.20–4.77 (m, 4H, allyl CH_2 × 2), 4.97–6.10 (m, 6H –CH=CH_2 × 2), 6.97–7.07 (m, 5H, C_6H_5), 12.60 (s, 1H, –OH); ^{13}C NMR (22.5 MHz, $CDCl_3$) of the mixture of **14** and **14'**, δ 31.0, 33.1, 55.8, 66.0, 66.3, 67.2, 67.4, 106.7, 118.7, 119.0, 119.7, 120.1,

120.3, 126.0, 126.9, 128.2, 128.3, 128.6, 129.0, 130.4, 130.9, 131.0, 131.1, 137.3, 157.3, 159.8, 162.3, 167.9, 172.7, 188.1; IR (neat) of the mixture of **14** and **14'**, 3451, 3029, 2945, 1732, 1649, 1496, 1455, 1365, 1247, 1091, 990, 938, 750, 700 cm^{-1}; MS of the mixture of **14** and **14'**, $m/e = 302$ (M^+).

3.8.2. Allyl 3-allyloxycarbonyl-2-oxo-3-phenylpropanoate (17) and allyl 3-allyloxycarbonyl-2-hydroxy-3-phenyl-2-propenate (17') (oil, 80%)

^1H NMR (60 MHz, CCl_4), **17**, δ 4.31–4.80 (m, 5H, allyl $CH_2 \times 2$ and PhCH<), 4.90–6.05 (m, 6H, –CH=C$H_2 \times 2$), 6.90–7.31 (m, 5H, C_6H_5); **17'**, δ 4.31–4.80 (m, 4H, allyl $CH_2 \times 2$), 4.90–6.05 (m, 6H, –CH=C$H_2 \times 2$), 6.90–7.31 (m, 5H, C_6H_5), 12.57 (s, 1H, –OH); ^{13}C NMR (22.5 MHz, $CDCl_3$) of the mixture of **17** and **17'**, δ 60.0, 65.8, 66.1, 66.3, 67.1, 108.2, 118.1, 118.8, 119.1, 119.8, 127.6, 127.8, 128.5, 128.8, 129.7, 130.3, 130.5, 131.0, 131.1, 132.4, 159.6, 159.9, 162.1, 167.4, 171.9, 186.1; IR (neat) of the mixture of **17** and **17'**, 3448, 2449, 2363, 1736, 1648, 1610, 1497, 1456, 1424, 1364, 1270, 1230, 1179, 1059, 990, 940, 793, 700 cm^{-1}; MS of the mixture of **17** and **17'**, $m/e = 288$ (M^+).

3.8.3. Allyl 3-allyloxycarbonyl-2-oxo-butanoate (18) and allyl 3-allyloxycarbonyl-2-hydroxy-2-butenoate (18') (oil, 50%)

^1H NMR (60 MHz, CCl_4), **18**, δ 1.35 (d, $J = 7.0$, 3H, CH_3–), 4.12 (q, $J = 7.0$ Hz, 1H, CH_3CH–), 4.40–4.77 (m, 4H, allyl $CH_2 \times 2$), 5.02–6.40 (m, 6H, –CH=C$H_2 \times 2$); **18'**, δ 1.94 (s, 3H, CH_3–), 4.40–4.77 (m, 4H, allyl $CH_2 \times 2$), 5.02–6.40 (m, 6H, –CH=C$H_2 \times 2$), 12.10 (s, 1H, –OH); ^{13}C NMR (22.5 MHz, $CDCl_3$) of the mixture of **18** and **18'**, δ 11.2, 11.6, 48.3, 65.9, 66.0, 66.2, 66.9, 103.6, 118.6, 118.7, 119.3, 119.8, 130.4, 131.0, 131.1, 156.6, 159.9, 162.3, 169.2, 172.9, 189.0; IR (neat) of the mixture of **18** and **18'**, 3466, 3088, 2990, 2946, 2361, 1736, 1660, 1650, 1455, 1380, 1240, 1197, 1120, 1189, 1041, 994, 939 cm^{-1}; MS of the mixture of **18** and **18'**, $m/e = 227$ ($M^+ + 1$).

3.8.4. Allyl 3-allyloxycarbonyl-2-oxo-pentanoate (19) and allyl 3-allyloxycarbonyl-2-hydroxy-2-pentenoate (19') (oil, 48%)

^1H NMR (60 MHz, CCl_4), **19**, δ 0.79–1.19 (m, 3H, CH_3CH$_2$–), 1.68–2.03 (m, 2H, CH_3CH_2–), 4.40–4.73 (m, 4H, allyl $CH_2 \times 2$), 5.97–6.20 (m, 6H, –CH=C$H_2 \times 2$); **19'**, δ 0.79–1.19 (m, 3H, CH_3CH$_2$–), 2.38 (q, $J = 7.0$, 2H, CH_3CH_2), 451–6.20 (m, 10H, allyl $\times 2$), 12.13 (s, 1H, –OH); ^{13}C NMR (22.5 MHz, $CDCl_3$) of the mixture of **19** and **19'**, δ 11.6, 14.6, 19.2, 20.7, 55.5, 65.8, 66.0, 66.3, 67.0, 109.5, 118.7, 118.9, 119.5, 120.0, 130.4, 130.5, 131.1, 131.3, 157.2, 160.1, 162.3, 168.5, 172.9, 188.6; IR (neat), 3466, 3088, 2972, 2881, 1732, 1649, 1456, 1425, 1367, 1238, 1186, 1126, 1098, 1052, 989, 938, 795 cm^{-1}; MS of the mixture of **19** and **19'**, $m/e = 241$ ($M^+ + 1$).

3.9. General procedure for ruthenium-catalysed reductive cleavage of diallyl α-oxalylcarboxylates (14, 17, 18 and 19) with formic acid

A typical procedure is as follows. A mixture of formic acid (0.75 ml, 20 mmol) and Et_3N (2.8 ml, 20 mmol) was added to a solution containing [Ru(cod)-$(OCOCF_3)_2]_2$ (5 mol%, 100 μmol) and DPPB (43 mg, 100 μmol) in dioxane (10 ml) at room temperature. To the solution was added diallyl α-oxalylcarboxylate (2 mmol) and the mixture was refluxed for 4 h. Organic acids were extracted with saturated aqueous $NaHCO_3$ solution. To the aqueous solution hydrochloric acid (3 M) was added to acidify the solution. Organic compounds were extracted with diethyl ether, the ethereal extract was concentrated *in vacuo* and the residue was chromatographed on silica gel using hexane–diethyl ether (4 : 1) as the eluent to give the α-hydroxy acid.

3.9.1. 2-Hydroxy-4-phenylbutanoic acid (16) (solid, 80% yield)

^1H NMR (90 MHz, $CDCl_3$), δ 1.09–2.21 (m, 2H, –CH_2–), 2.77 (t, $J = 7.7$ Hz, 2H, PhCH_2CH$_2$–), 4.23 (dd, $J = 4.6$, 7.5 Hz, 1H, –CH(OH)–), 5.96 (m, 2H, –OH and CO_2H), 7.20 (m, 5H, C_6H_5); IR (KBr), 3453, 2931, 1715, 1496, 1455, 1424, 1098 cm^{-1}.

3.9.2. 2-Hydroxy-3-phenylpropionic acid (20) (solid, 73% yield)

^1H NMR (90 MHz, $CDCl_3$), δ 2.73–3.43 (m, 2H, PhCH_2–), 3.80 (s, 2H, –OH and CO_2H), 4.42–4.63 (m, 1H, –CH(OH)–), 7.24 (s, 5H, C_6H_5); IR (KBr) 3421, 2926, 1719, 1497, 1453, 1216, 1091 cm^{-1}.

3.9.3. 2-Hydroxybutanoic acid (21) (oil, 50% yield)

^1H NMR (60 MHz, CCl_4), δ 0.70–2.30 (m, 5H, CH_3CH$_2$–), 3.85–4.48 (dd, 1H, –CH(OH)–), 6.62 (s, 2H, –OH and CO_2H); IR (neat), 3407, 2971, 1720, 1460, 1215, 1128 cm^{-1}.

3.9.4. 2-Hydroxypentanoic acid (22) (oil, 63% yield)

^1H NMR (60 MHz, CCl_4), δ 0.70–2.17 (m, 7H, CH_3CH$_2$CH$_2$–), 3.85–4.33 (m, 1H, –CH(OH)–), 6.43 (s, 2H, –OH and CO_2H); IR (neat), 3417, 2964, 1731, 1465, 1214, 1133 cm^{-1}.

3.10. Ruthenium-catalysed reduction of ethyl 2-oxo-4-phenyl-butanoate (23)

A mixture of ethyl 2-oxo-4-phenylbutanoate (**23**) (206 mg, 1 mmol), formic acid (10 mmol) and $RuCl_2(PPh_3)_3$

(48 mg, 50 μmol) were placed in a stainless-steel autoclave and the air was replaced with argon. The autoclave was heated at 125°C for 3 h. To the solution was added saturated aqueous $NaHCO_3$ and the organic extracts were washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel using hexane–diethyl ether (9:1) as the eluent to give the ethyl 2-hydroxy-4-phenylbutanoate (**24**) as an oil (59%). 1H NMR (90 MHz, $CDCl_3$), δ 1.28 (t, $J = 7.3$ Hz, 3H, CH_3CH_2–), 2.51–2.93 (m, 4H, CH_2CH_2), 3.83 (m, 1H, –CH(OH)–), 4.00–4.30 (q, 3H, CH_3CH_2OCO), 7.23 (m, 5H, C_6H_5); IR (neat), 3458, 1731, 1603, 1455 cm^{-1}.

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