

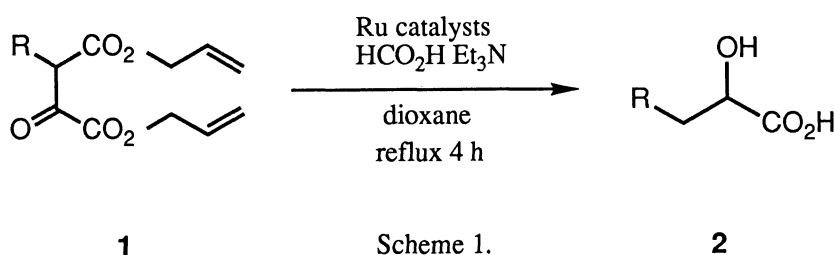
Facile Synthesis of α -Hydroxycarboxylic Acids by Ruthenium-Catalyzed Reduction
of Diallyl α -Oxalylcarboxylates with Formic Acid

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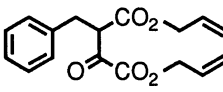
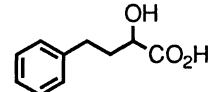
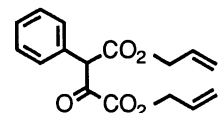
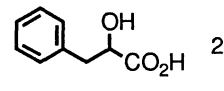
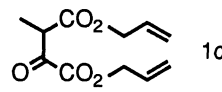
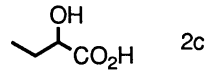
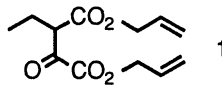
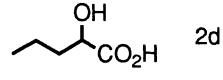
Reaction of diallyl α -oxalylcarboxylates with catalytic amounts of ruthenium
complexes gave α -hydroxycarboxylic acids in good yields.

α -Keto acids and α -hydroxy acids are useful compounds for organic synthesis.¹⁾ Previously we have reported that α -keto acids can be prepared with ease by the palladium-catalyzed decarboxylative hydrogenolysis of diallyl α -oxalylcarboxylates with formic acid.²⁾ Recently we have found that allylic acetate can be reduced to propene with formic acid by ruthenium catalysts.³⁾ Since it is also known that carbonyl compounds can be reduced to alcohols with formic acid by ruthenium catalyst,⁴⁾ we have expected that α -hydroxy acids **2** may be obtained in one step from the α -oxalylcarboxylates using ruthenium catalysts. Herein we wish to report a novel direct synthesis of α -hydroxy acids by ruthenium-catalyzed reduction of diallyl α -oxalylcarboxylates **1** with formic acid (Scheme 1). Since the diallyl oxalylcarboxylates are obtained in one step by the reaction of allyl carboxylates and diallyl oxalate,²⁾ the method described here provides a useful synthetic method for α -hydroxy acids.



Various ruthenium catalysts were used for conversion of **1** to **2** (Table 1). Among them, $\text{Ru}_2(\text{cod})_2(\text{OCOCF}_3)_4$ -1,4-bis(diphenylphosphino)butane (DPPB) was most effective. In a typical experiment, a mixture of formic acid (16.6 mmol) and triethylamine (16.6 mmol) was added to a solution of $\text{Ru}_2(\text{cod})_2(\text{OCOCF}_3)_4$ (0.083 mmol) and DPPB (0.083 mmol) in dioxane (35 ml) at room temperature under argon. Diallyl oxalylcarboxylate **1a** (1.66 mmol) was added to the solution and the mixture was refluxed for 4 h. After the reaction mixture was cooled to room temperature, organic acids were extracted with saturated sodium bicarbonate solution. To this aqueous solution 3 M-HCl (1 M = mol dm⁻³) was added to acidify the

Table 1. Ruthenium-Catalyzed Reduction of Diallyl α -Oxalylcarboxylate a)

Run	Diallyl α -oxalylcarboxylate	Catalyst b)	Product	Yield /%
1	 1a	A	 2a	80
2	1a	B	2a	69
3	1a	C	2a	68
4	1a	D	2a	73
5	1a	E	2a	35
6	 1b	A	 2b	73
7	 1c	A	 2c	50
8	 1d	A	 2d	68

a) Ru catalyst (5 mol%), HCOOH (10 equiv.), Et₃N (10 equiv.) in dioxane under reflux.

b) A: Ru₂(cod)₂(OCOCF₃)₄ + 2dppb B: RuCl₂(PPh₃)₃ C: RuH₂(PPh₃)₄

D: Ru₃(CO)₁₂ + 9PPh₃ E: RuCl₃ + 3PPh₃

solution. Organic compounds were extracted with ether. The ethereal extract was concentrated in vacuo and the residue was chromatographed on SiO₂ with a 3:1 mixture of hexane-ether to give 2-hydroxy-4-phenylbutanoic acid (80%). As shown in Table 1 the other hydroxy acids (**2b-2d**) were obtained in good yields from the corresponding diallyl oxalylcarboxylates (**1b-1d**).

The reaction is considered to proceed via α -keto acids which are obtained similarly in the case of palladium catalyst.²⁾ Further investigation including reaction mechanisms of allylic compounds with ruthenium catalyst is in due course.

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References

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