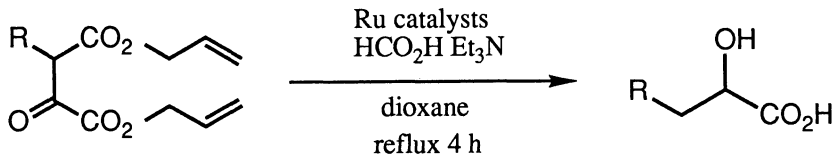
CHEMISTRY LETTERS, pp. 1365-1366, 1992.

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

Isao SHIMIZU,* Masafumi TEKAWA, Yooichiroh MARUYAMA, and Akio YAMAMOTO
Department of Applied Chemistry, School of Science and Engineering,
Waseda University, Okubo 3-4-1, Shinjuku-ku, Tokyo 169

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

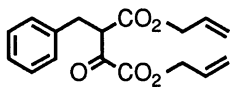
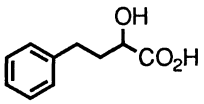
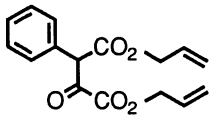
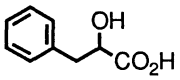
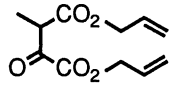
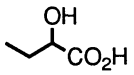
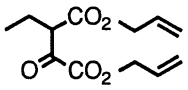
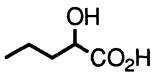
α-Keto acids and α-hydroxy acids are useful compounds for organic synthesis.[1] Previously we have reported that α-keto acids can be prepared with ease by the palladium-catalyzed decarboxylative hydrogenolysis of diallyl α-oxalylcarboxylates with formic acid.[2] Recently we have found that allylic acetate 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.



1 Scheme 1. **2**

Various ruthenium catalysts were used for conversion of **1** to **2** (Table 1). Among them, $Ru_2(cod)_2(OCOCF_3)_4$-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 $Ru_2(cod)_2(OCOCF_3)_4$ (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.), Et_3N (10 equiv.) in dioxane under reflux.

b) A: $Ru_2(cod)_2(OCOCF_3)_4$ + 2dppb B: $RuCl_2(PPh_3)_3$ C: $RuH_2(PPh_3)_4$
D: $Ru_3(CO)_{12}$ + $9PPh_3$ E: $RuCl_3$ + $3PPh_3$

solution. Organic compounds were extracted with ether. The ethereal extract was concentrated in vacuo and the residue was chromatographed on SiO_2 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.

This work was financially suported by the Grant-in-Aid from the Ministry of Education, Science and Culture and the Asahi Glass Foundation for Industrial Technology.

References

1). G. Iwasaki, R. Kimura, N. Numao, and K. Kondo, *Chem. Pharm. Bull.*, **37**, 280(1989).
2). I. Shimizu, T. Makuta, and M. Oshima, *Chem. Lett.*, **1989**, 1457.
3). I. Shimizu, Y. Maruyama, and A Yamamoto, Unpublished results.
4). Y. Watanabe, T. Ohta, and Y. Tsuji, *Bull. Chem. Soc. Jpn.*, **55**, 2441(1982).

(Received March 27, 1992)