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# OXIDATION OF ALCOHOLS WITH ALLYL METHYL CARBONATE BY MEANS OF RUTHENIUM CATALYST

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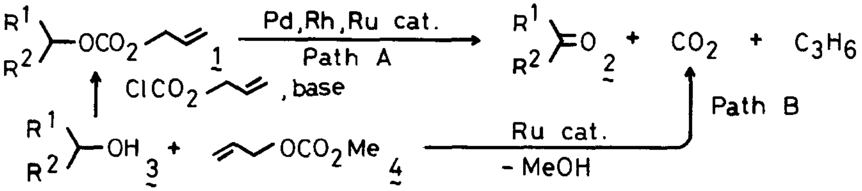
Summary; Ruthenium-catalyzed reaction of secondary or allylic alcohols with allyl methyl carbonate gives ketones or α,β-unsaturated aldehydes.

Oxidation of alcohols is one of the most important reactions in organic synthesis. Generally, chromium compounds such as PCC1) are used as oxidants, but separation of inorganic compounds is usually a problem. Toxicity of chromium compounds is another problem. We have previously reported the palladium-catalyzed decarboxylation-dehydrogenation of allylic carbonates **1** to give ketones or α,β-unsaturated aldehydes **2** (Path A in Scheme 1).2) This reaction is clean and facile since only $CO_2$ and propene are generated as by-products. But turnover of the palladium catalyst was not very high (usually 5-10 times). In our continuing work on the reaction of allylic carbonates, we found that ruthenium catalyst is more effective than the palladium catalyst for the same reaction. Furthermore, we found that direct oxidation of secondary and allylic alcohols **3** with allyl methyl carbonate (**4**) proceeds with ruthenium catalyst (Path B in Scheme 1). Here we wish to report a clean and efficient oxidation of secondary and allylic alcohols with **4** catalyzed by the ruthenium hydride complex, $RuH_2(PPh_3)_4$.

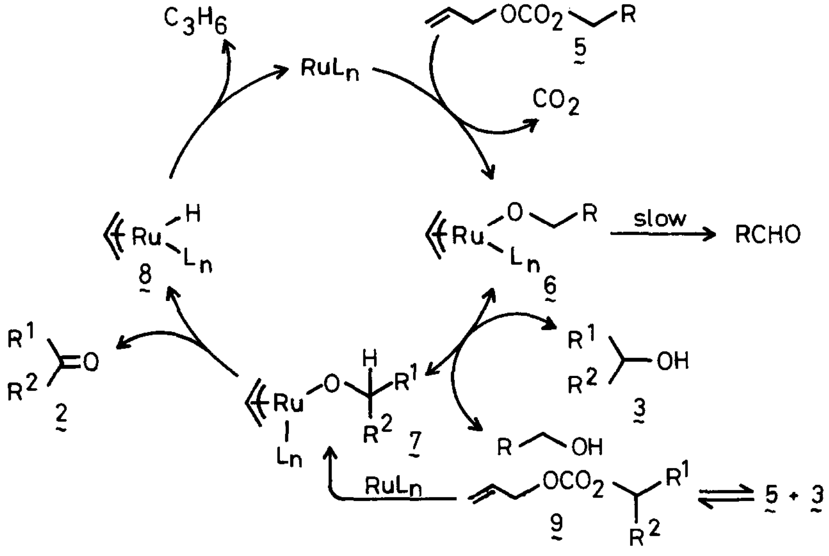
<Scheme 1>



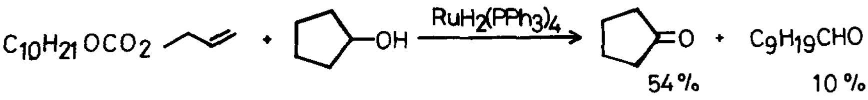
First, we examined catalytic activities of various transition metal complexes for the intramolecular decarboxylation-dehydrogenation of allyl cyclopentyl carbonate. Palladium (86%), rhodium (88%), and ruthenium (93%) catalysts gave cyclopentanone (5) in good yields.3) We also observed an interesting solvent effect. The palladium-catalyzed reaction proceeds only in coordinative solvents such as MeCN or PhCN,2) while rhodium and ruthenium catalyzed reactions proceed smoothly in non-polar solvents such as benzene or toluene.

As we have reported previously, saturated primary alcohols are hardly oxidized with palladium catalyst.2) Ruthenium and rhodium catalysts showed the same tendency. In other words, formation of saturated aldehydes from **1** ($R^1$ = H) is very slow with these catalysts. Thus we speculated that secondary alcohols may be oxidized by the following mechanism (Scheme 2). Oxidative addition of ruthenium(II) species to allyl carbonate of primary alcohol **5**, followed by decarboxylation gives (π-allyl)ruthenium alkoxide complex **6**, which is in equilibrium with **7**, formed by the exchange reaction with secondary or allylic alcohol **3**. Then, β-hydrogen elimination from **7** gives ketone **2** and (π-allyl)-ruthenium hydride complex **8**. Finally, reductive elimination of propene from **8** regenerates the ruthenium catalyst. A possibility of forming the (π-allyl)-ruthenium complex **7** from carbonate **9** by the oxidative addition-decarboxylation of **9** should be ruled out since transesterification of **5** with **3** is extremely slow. Furthermore, allylic carbonates have high reactivity with low-valent transition metal complexes.[3] Thus the mechanism involving the alkoxide exchange reaction of **6** with **3** is reliable in this case. We were pleased to find that reaction of cyclopentanol with allyl decyl carbonate in the presence of the ruthenium catalyst gave cyclopentanol (54%) and decylaldehyde (10%) (<Scheme 3>).[3] When the reaction was carried out using two equivalents of allyl methyl carbonate (**4**), cyclopentanone was obtained quantitatively with 1 mol% of the ruthenium catalyst. With 10 mol% of the palladium catalyst, Pd-black deposited during the reaction and the reaction was not complete (57%). The rhodium catalyst gave a small amount of allyl cyclopentyl ether[4] as a by-product (3%). As for a hydrogen acceptor, allyl methyl carbonate (**4**) is used most conveniently since it gives propene, methanol, and $CO_2$ as by-products. Removal of excess **4** (b.p. 130°C) is also easy. Other allylic compounds such as allyl acetate, allyl phenyl ether, N,N'-dicyclohexyl-O-allylisourea,[5] allyl carbamates,[6] and allyl formate have moderate reactivities in this reaction.

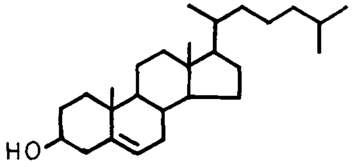
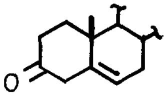
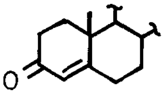
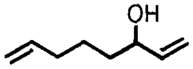
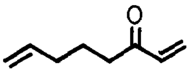
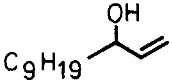
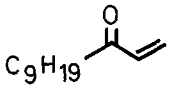
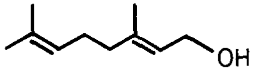
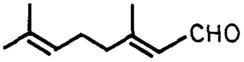
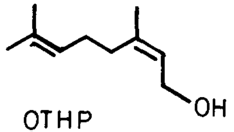
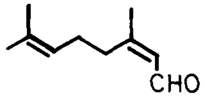
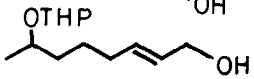
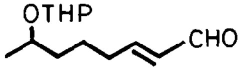
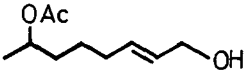
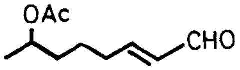
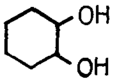
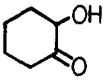
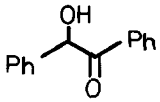
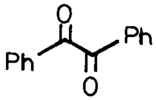
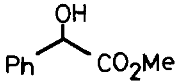
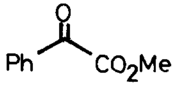
<Scheme 2>



<Scheme 3>



<Table 1> DEHYDROGENATION OF VARIOUS ALCOHOLS WITH ALLYL METHYL CARBONATE (**4**)a)

| RUN | ALCOHOL | TIME(h) | PRODUCT | YIELD(%) |
|---|---|---|---|---|
| 1 |  | 2 | <br> | 52<br>18 |
| 2 |  | 4 |  | 95b) |
| 3 |  | 2 |  | 81 |
| 4c) |  | 3.5 |  | 79<br>E:Z = 96:4 |
| 5c) |  | 3.5 |  | 75<br>E:Z = 1:9 |
| 6c) |  | 8 |  | 85 |
| 7c) |  | 8 |  | 80 |
| 8 |  | 10 |  | 55d) |
| 9c) |  | 24 |  | 98 |
| 10c) |  | 24 |  | 61 |

a) General procedure; A solution of alcohol (1 mmol), allyl methyl carbonate (**4**) (2 mmol), and $RuH_2(PPh_3)_4$ (0.01 mmol) in toluene (5 mL) was refluxed under argon. Then the reaction mixture was filtered through florisil and purified by column chromatography on silica-gel. b) Calculated by GLC analysis. c) 5 mmol of **4** was used. d) The diol was recovered (25%).

Application of the oxidation was examined with various allylic and secondary alcohols using 1 mol% of the ruthenium catalyst. Results are shown in <Table 1>. Cholesterol was converted to 5-cholesten-3-one. But 4-cholesten-3-one was obtained in a considerable amount by thermally induced isomerization. With chromium or manganese compounds, oxidation of secondary allylic alcohols is sometimes difficult because of allylic rearrangement. The ruthenium-allyl carbonate method gave $\alpha,\beta$-unsaturated ketones in good yields (runs 2 and 3). E- and Z- allylic alcohols were converted to the corresponding enals with retention of the configuration (runs 4 and 5). Allylic alcohols which have acid-sensitive functional groups or base-sensitive functional groups underwent smooth oxidation without affecting these functional groups (runs 6 and 7). Reaction of 1,2-diol gave $\alpha$-hydroxy ketone in moderate yields with two equivalents of **4**. Also $\alpha$-hydroxy ketone and ester were converted to the corresponding $\alpha$-dicarbonyl compounds in satisfactory yields with five equivalents of **4** (runs 9 and 10). So far, several methods for ruthenium catalyzed dehydrogenation of alcohols with various hydrogen acceptor have been reported.$^{7)}$ In the present reaction, allyl methyl carbonate (**4**) is used as the hydrogen acceptor which is converted to propene, carbon dioxide, and methanol. Thus reaction is clean and facile. As a stoichiometric reaction, decarboxylation-dehydrogenation-decarbonylation of allyl ethyl carbonate with $RuH_2(PPh_3)_4$ to give $RuH_2(CO)(PPh_3)_3$ has been reported.$^{8)}$

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