

Preliminary communication

A selective synthesis of α -methylene- β -hydroxyalkanones catalyzed by $\text{RuH}_2(\text{PPh}_3)_4$

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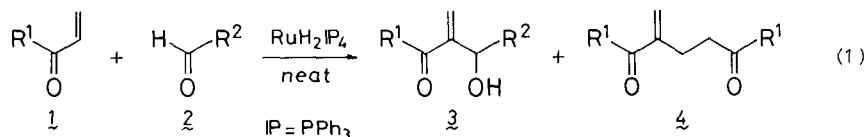
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Abstract

The $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed coupling of vinyl ketones with aldehydes accomplishes the selective synthesis of α -methylene- β -hydroxyalkanones under neutral conditions. A plausible pathway involving possible intermediacy of a ruthenium enolate is proposed.

Despite the current widespread upsurge of interest in the selective reactions catalyzed by ruthenium complexes [1], relatively little attention has been paid to catalytic carbon-carbon bond formation [2]. Neither complex formation nor catalytic reactions involving ruthenium enolates have been reported. We report on the intermediacy of ruthenium enolate in the $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed coupling of a vinyl ketone with an aldehyde to give an α -methylene- β -hydroxyalkanone (3).

When a mixture of 20.5 mmol (1.44 g) of 3-buten-2-one, 54.2 mmol (3.15 g) of propanal, and 0.046 mmol (0.054 g) of $\text{RuH}_2(\text{PPh}_3)_4$ was heated in a sealed tube at 40 °C for 40 h, 3-methylene-4-hydroxyhexan-2-one (3a) [3] and 3-methyleneheptan-2,6-dione (4a) [3] were isolated in yields of 82 and 2%, respectively. The presence of an extra mole of propanal diminished the formation of 4a remarkably (3a/4a 85/15 in the reaction of 3-buten-2-one with an equivalent of propanal). Some other examples are summarized in eq. 1 and Table 1. These results are particularly



surprising because it has been reported that an aldehyde readily dimerizes to give an ester with the aid of a catalytic amount of $\text{RuH}_2(\text{PPh}_3)_4$ even at room temperature [4]. Even the use of an excess of aldehyde here did not give rise to the formation of ester.

Table 1

RuH₂(PPh₃)₄-catalyzed coupling reaction of **1** and **2**^a

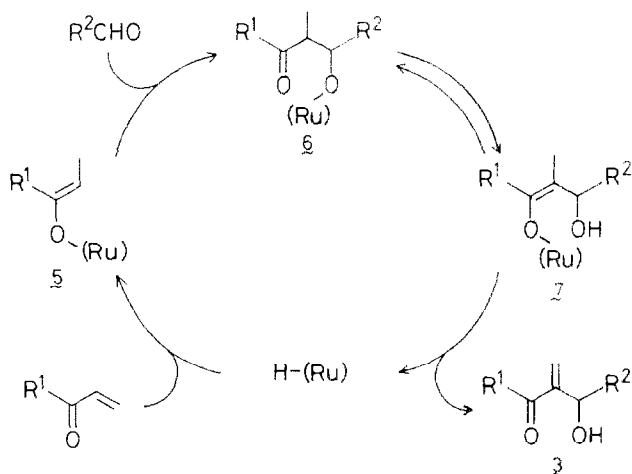
Entry	Vinyl ketone 1	Aldehyde 2	Product		Turnover of Ru
			Yield of 3 ^b (%)	Selectivity ^c (3/4)	
1	3-Buten-2-one	Propanal	82	97/3	164
2	3-Buten-2-one	Propanal	83 ^d	97/3	365
3	3-Buten-2-one	Butanal	57	97/3	236
4	3-Buten-2-one	3-Methylbutanal	46	93/7	49
5	3-Buten-2-one	2-Methylpropanal	72	92/8	106
6	3-Buten-2-one	2-Ethylhexanal	9	45/55	13
7	3-Buten-2-one	2-Ethylhexanal	27 ^d	61/39	31
8	3-Buten-2-one	Benzaldehyde	33	95/5	87
9	1-Penten-3-one	Propanal	87	> 99/1	196

^a Reactions were carried out at 40 °C for 40 h on a 5 mmol scale without solvent in a sealed tube containing 1 mol% (relative to vinyl ketone) of RuH₂(PPh₃)₄ and a mixture of vinyl ketone/aldehyde 1/2. ^b Isolated yield after column chromatography on silica gel and subsequent bulb-to-bulb distillation.

^c The ratio was determined by capillary GLC analyses (PEG-HT Bonded, 25 m column). ^d 2-Propanol (about 20%) was added.

The previous routes to **3** are three-step operations which include Michael type additions of unstable organometals to α,β -enones [5]. Thus, our results are extremely valuable because direct carbon-carbon bond formation is realized at the α -position of vinyl ketones under almost neutral conditions.

It is known that RuH₂(PPh₃)₄ readily activates alkyl methacrylate [6] and aldehyde [3] by oxidative addition with C-H bond cleavage. However, the formation of products **3** and **4** cannot be accounted for in terms of such intermediates. Thus, we propose a nucleophilic interaction of H-(Ru) with vinyl ketone in the first stage of the reaction. Although any direct evidence suggesting the intermediacy of complexes **5**, **6**, and **7** has not been obtained up to the present, the pathway shown in Scheme 1 can be proposed as one plausible route to the product. It entails the



Scheme 1.

formation of enolate complex **5** as a result of Michael type addition of H-(Ru) to **1**, the subsequent aldol type reaction of **5** with aldehyde to give **6**, and 1,4-elimination of H-(Ru) from **7** which is in equilibrium with **6**. While similar coupling also was accomplished by the assistance of $\text{RhH}(\text{PPh}_3)_4$ [7], the addition of 20% of alcohol (typically 2-propanol) was crucial for acceptable yields of **3**. In contrast to the rhodium catalyst, $\text{RuH}_2(\text{PPh}_3)_4$ did not require the presence of alcohol to complete the catalytic cycle. Furthermore, a significant improvement of catalytic activity was observed in the reaction of 1-penten-3-one with propanal (entry 9 in Table 1), in which an unsatisfactory result was obtained for rhodium [7]. Thus the equilibrium between **6** and **7** is attained rapidly enough without the assistance of alcohol. The presence of alcohol also slightly improves the yield of **3** or turnover of Ru (entries 1 and 7 in Table 1).

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