

An unusual dimerization of primary unsaturated alcohols catalyzed by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3^\dagger$

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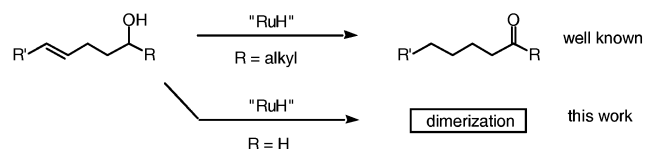
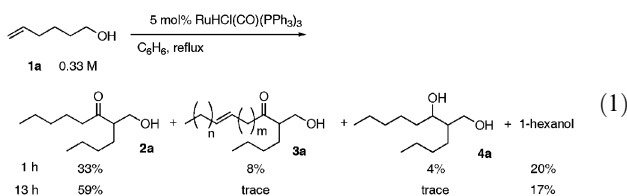
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When primary unsaturated alcohols were treated with a catalytic amount of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ in benzene under reflux, dimerization reactions took place to give α -hydroxy-methyl ketones as major product.

The isomerization of carbon-carbon double bonds, a process catalyzed by metal hydride complexes *via* hydrometalation and subsequent β -hydride elimination, is among the most familiar reactions in transition metal chemistry.¹ Ruthenium hydride complexes are used in such alkene-isomerization reactions,²⁻⁴ in which $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ is the most frequently used catalyst.³ While the isomerization of secondary unsaturated alcohols to the corresponding saturated ketones by HRu-catalysts is known (Scheme 1),⁴ remarkably, to the best of our knowledge, isomerization reactions of *primary* unsaturated alcohols have not been investigated in any detail.^{4a,e,5} In this communication we report that *primary* unsaturated alcohols, when treated with a catalytic amount of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, undergo an unusual dimerization to give α -hydroxymethyl ketones as the major product.

Treatment of 5-hexen-1-ol (**1a**) with $\text{RuHCl}(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, resulted in the isomerization of the C-C double bond to give a mixture of hexenols, while hexanal was formed in only trace amounts with these catalysts. In contrast, when a 0.33 M benzene solution of 5-hexen-1-ol (**1a**) was treated with 5 mol% of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ for 1 h at reflux, a mixture of 5-hydroxymethyl-6-undecanone (**2a**) and the related unsaturated products **3a** were obtained in 33% and 8% yields, respectively (eqn (1)). The crude mixture also contained the saturated alcohol, 1-hexanol and diol **4a**, the reduced form of **2a**.⁶ Interestingly, however, when the reaction time was extended to 13 h, the yield of α -hydroxymethyl ketone **2a** increased to 59%, whereas the yield of **3a** and **4a** diminished to the level of trace amounts. It seems likely that **3a** and **4a** were converted to **2a** under the reaction conditions.



Scheme 1 Ru-H catalyzed reaction of unsaturated alcohols.

Table 1 summarizes results of RuH-catalyzed dimerization of unsaturated alcohols. Dimerization of the isomeric hexenyl alcohols **1b**, **1c**, **1d**, **1e** and **1f** under similar conditions (0.33 M, 5 mol% $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, benzene reflux, 13 h) also occurs to give the same product **2a** in similar yields (entries 1–5). Both *cis* and *trans* isomers underwent a smooth dimerization. On the other hand, no dimerization was observed with the secondary alcohol **1g**, which underwent the isomerization to 3-hexanone (**5**) (entry 6).⁷ Thus, the dimerization of primary hexenols proceeds irrespective of the position or the *E*- or *Z*-geometry of the double bonds.

The reaction of unsaturated alcohol **1i**, which contains a longer substituent at the 3-position, gave the saturated dimer **2i** in 33% yield together with a significant amount of unsaturated dimer **3i**, in which the position of the C-C double bond was dispersed into the longer carbon chain (entry 8). The subsequent treatment of the mixture of **2i** and **3i** with hydrogen and a Pd/C catalyst gave **2i** as the sole dimerization product. The experimental result of **1i**, which was obtained at a low concentration (0.017 M), which is 20 times lower than the standard concentration, is interesting, since decanal (**7**) and an isomeric mixture of decenals **8** were obtained in significant amounts (entry 9). This result proposes that a double bond migration reaction of **1i** would take place to give **7**, whereas allylic alcohol **1i** would also serve as the hydrogen source of transfer hydrogenation to be converted into 2-decenal.^{8,9} Cinnamyl alcohol (**1j**) also underwent dimerization to give a mixture of **2j** and **3j** (entry 10).

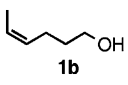
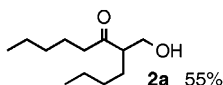
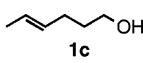
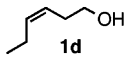
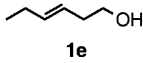
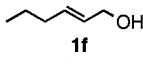
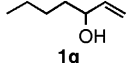
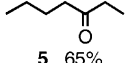
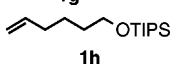
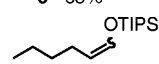
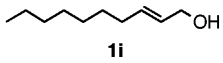
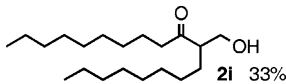
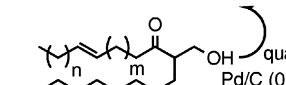
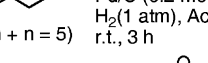

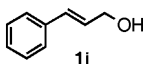
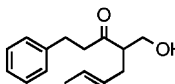
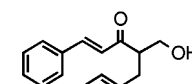
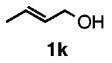
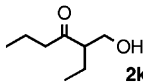
Following up the above observation, we propose a rationale for the dimerization of **1a** to **2a** based on an Ru-aldol reaction¹⁰ and transfer hydrogenation (Scheme 2). Thus, as a consequence of ruthenium hydride-mediated isomerization of a C-C double bond, aldehyde **B** would be formed *via* allylic alcohol **A**. Transfer hydrogenation of **B** with **A** would produce α,β -unsaturated aldehyde **C** and n-hexanol. Hydroruthenation of **C** would produce ruthenium enolate **D**, which then undergoes aldol reaction with **B** to give **F** *via* **E**. Transfer hydrogenation of **F** with **A** provides the dimerization product **2a** and α,β -unsaturated aldehyde **C**. A similar scenario based on aldol reaction of **D** with **C** may account for the formation of unsaturated by-product **3a**.

In summary, we have found that $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ catalyzes the dimerization of unsaturated primary alcohols leading to the

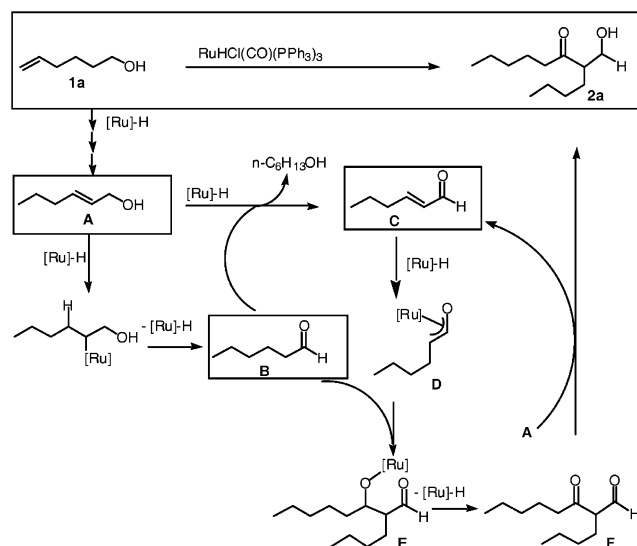
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[†] Electronic supplementary information (ESI) available: Experimental procedure and NMR data. See DOI: 10.1039/b602103d

Table 1 Representative examples of Ru–H catalyzed dimerization of primary unsaturated alcohols^a

Entry	Unsaturated alcohol 1	Products (yield ^b)
1		 2a 55%
2		2a 56%
3		2a 52%
4		2a 58%
5		2a 58%
6		 5 65%
7		 6 79% (E/Z = 29/71) ^c
8		 2i 33%
9 ^d	1i	 2i 19% 3i 4%  7 33%  8 11% (m + n = 5) quantitative Pd/C (0.2 mol%), H ₂ (1 atm), AcOEt, r.t., 3 h
10		 2j 37%  3j 12%
11 ^{e,f}		 2k 41%

^a General Conditions: [1] = 0.33 M, RuHCl(CO)(PPh₃)₃ (5 mol%), C₆H₆, reflux, 13 h. ^b Isolated yield. ^c Determined by ¹H NMR. ^d [1i] = 0.017 M. ^e 10 mol% of RuHCl(CO)(PPh₃)₃ was used. ^f 2-Ethylhexane-1,3-diol was obtained in 13% yield as a by-product.

**Scheme 2** A possible reaction mechanism for the dimerization of **1a**.

formation of α -hydroxymethyl ketones. Formation of ruthenium enolates and aldol reaction with aldehydes was proposed as a rationale to account for the unusual reaction. Further detailed mechanistic studies as well as optimization of the dimerization reaction are currently being pursued in our laboratory.

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