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Reshuffling of Functionalities Catalyzed by a Ruthenium Complex in Water

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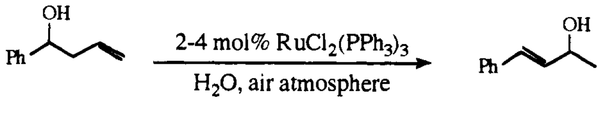
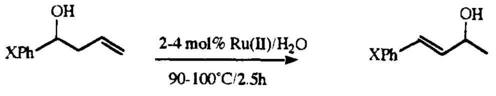
Isomerization of organic compounds through the catalytic activity of transition metals has been used in a variety of organic transformations, such as the isomerization of allylic alcohols to ketones.[1a–p] Isomerization of organic compounds, as in the examples above, usually occurs with some attrition of the functionalities within the molecule.[2] Repositioning the functionalities of olefinic alcohols is a common process encountered in synthesis.[3] Such transformations often require multistep reactions, or strong acids.[4] We report here that, in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$, homoallylic alcohols and allyl alcohols undergo structural reorganization in which both the hydroxyl group and the olefin have been reshuffled.

Stirring a mixture of allylbenzyl alcohol **1** with a catalytic amount of $RuCl_2(PPh_3)_3$ in water at 100 °C for 3 h led to compound **2** virtually as a single product.[5] Previously, Grubbs has shown that homoallylic alcohols form stable complexes with a ruthenium(II) salt in water that are inert toward olefin isomerizations.[1a]



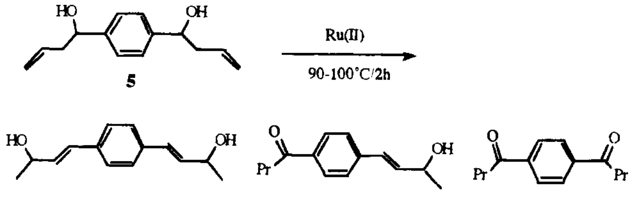
1 **2**

The unusual selectivity of this new process led us to investigate the scope of the reaction. In all cases where a benzylic hydroxyl group was involved (**3a–e**), the corresponding product (**4a–e**) was obtained cleanly under standard reaction conditions. However, no reaction occurred when alkyl substituents were present at the terminal position.[6] The presence of a hydroxyl group (**3e**) does not inhibit the reaction. Such compatibility is further demonstrated by compound **5**, where a double reshuffling product, **6a**, is the predominant product.



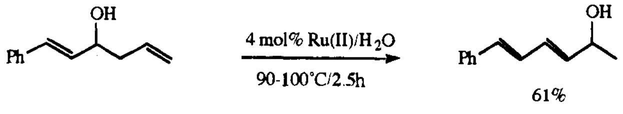
3 **4**

3a, X= 4-Cl-/2h	**4a**, 65%
3b, X= 3-Br-/2h	**4b**, 59%
3c, X= 4-Methyl-/1.5h	**4c**, 75%
3d, X= 4-Mthoxyl-/1.5h	**4d**, 67%
3e, X= 4-HOCH$_2$-/3h	**4e**, 49%



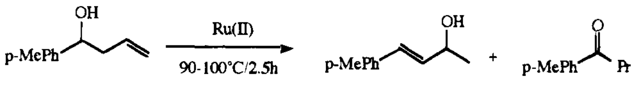
6a (44%) **6b** (19%) **6c** (23%)

In the case of compound **7**, where both an allylic and a homoallylic functional group are involved, the reaction occurs exclusively by rearrangement of the homoallylic group to give the conjugated dienol product **8**. The same reaction of aliphatic homoallylic alcohols leads to the formation of a mixture of several olefinic alcohols, demonstrating a lack of regioselectivity.



7 **8**

The reaction shows a marked dependence on the Ru(II): substrate ratio. Increasing the amount of catalyst results in an increased formation of the phenyl ketone **9**, also an isomerized product.[7]



4c **9**

cat(mol %)	**4c:9**	conversion (%)
2.2	12:1	87
4.5	4.5:1	94
7.0	1.7:1	90
10.0	1.2:1	92

The exact mechanism of this unprecedented catalytic reaction is not yet clear. Initially, a trace amount of acid generated from the catalyst was suspected as being responsible for product

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(1) (a) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224–235. (b) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 2027–2036. (c) Backvall, J. E.; Andeasson, U. *Tetrahedron Lett.* **1993**, *34*, 5459–5462. (d) Smadja, W.; Ville, G.; Georgoulis, C. *J. Chem. Soc., Chem. Commun.* **1980**, 594–595. (e) Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 4133–4136. (f) Nicholson, J. K.; Shaw, B. L. *Proc. Chem. Soc. London* **1963**, 282–283. (g) Tatsumi, T.; Hashimoto, K.; Tominaga, H.; Mizuta, Y.; Hata, K.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1983**, *252*, 105–112. (h) Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 4591–4592. (i) Damico, R.; Logan, T. J. *J. Org. Chem.* **1967**, *32*, 2356–2358. (j) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958–967. (k) Tani, K. *Pure Appl. Chem.* **1985**, *57*, 1845–1854. (l) Alper, H.; Hachem, K. *J. Org. Chem.* **1980**, *45*, 2269–2270. (m) Strohmeier, W.; Weigelt, L. *J. Organomet. Chem.* **1975**, *86*, C17–C19. (n) Baudry, D. S.; Ephritikihne, M.; Felkin, H. *Nouv. J. Chim.* **1978**, *2*, 355–356. (o) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 1566–1570. (p) Goetz, R. W.; Orchin, M. *J. Am. Chem. Soc.* **1963**, *85*, 1549–1550.

(2) For examples of rearrangements of allyl esters, see: Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321. Grieco, P. A.; Tetsuo, T.; Shannon, L. B.; Hideo, T. *J. Am. Chem. Soc.* **1980**, *102*, 7587. Burke, S. D.; Schoenen, F. J.; Nair, M. S. *Tetrahedron Lett.* **1987**, *28*, 4143. *Tetrahedron Lett.* **1987**, *28*, 5655. Grieco, P. A.; Tuthill, P. A.; Sham, H. L. *J. Org. Chem.* **1981**, *46*, 5005. Tamaru, Y.; Yamada, Y.; Ochiai, H.; Nakajo, E.; Yoshida, Z. *Tetrahedron* **1984**, *40*, 1791.

(3) For some examples, see: Overman, L. E.; Campbell, C. B.; Knoll, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 4822. Paquette, L. A.; Ham, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 3025. Ueno, Y.; Sano, H.; Okawara, M. *Synthesis* **1980**, 1011. Marshall, J. A.; Jenson, T. M. *J. Org. Chem.* **1984**, *49*, 1707. Yasuda, A.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1976**, 2621. Yasuda, A.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1757. Bannai, K.; Tanaka, T.; Okamura, N.; Hazato, A.; Sugiura, S.; Manabe, K.; Tomimori, K.; Kurozumi, S. *Tetrahedron Lett.* **1986**, *27*, 6353. Singh, A. K.; Bakshi, R. K.; Corey, E. J. *J. Am. Chem. Soc.* **1987**, *109*, 6187. Clive, D. L. J.; Chittattu, G.; Curtis, N. J.; Menchen, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 770. Zoretic, P. A.; Chambers, R. J.; Marbury, G. D.; Riebiro, A. A. *J. Org. Chem.* **1985**, *50*, 2981. Oehlschlager, A. C.; Mishra, P.; Dhami, S. *Can. J. Chem.* **1984**, *62*, 791. Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers: New York, 1989; p 114 and references cited therein.

(4) Cymerman, J.; Heibron, I. M.; Jones, E. R. H. *J. Chem. Soc.* **1945**, 90.

(5) All new compounds have been fully characterized spectroscopically and their elemental compositions established by combustion analysis and/or high-resolution mass spectroscopy.

(6) Such a result is presumably due to the increased steric effect.

(7) The results were obtained through ^1H NMR measurement of the crude reaction mixture.

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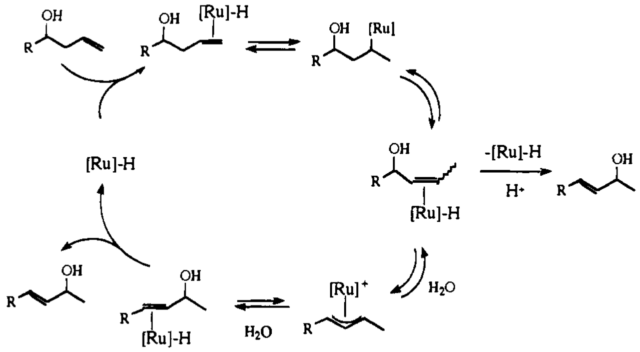
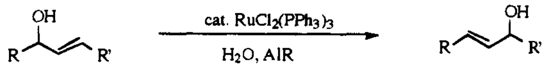


Figure 1. Postulated catalytic cycle for functional group reshuffling in homoallylic alcohols.

formation. However, the pH of the reaction medium shows a value between 5 and 6 both during and at the end of the reaction. As control experiments, we have carried out the same reactions by using aqueous 0.1 N HCl (pH = 1), $RuCl_3$ (pH = 1), or aqueous saturated NH_4Cl as the reaction solvent, as well as using other transition metals, such as $FeCl_2$, $RhCl(PPh_3)_3$, $CoCl_2$, and $CuCl_2$. The corresponding product was not observed in any of these cases. A conjugated diene has also been suspected as being the reaction intermediate. Such a possibility was ruled out because the reaction of 1-phenyl-1,3-butadiene with the ruthenium catalyst did not generate any desired product under the same reaction conditions.

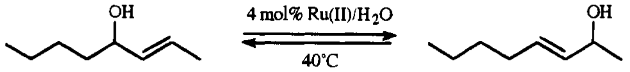
A possible mechanistic explanation (Figure 1) is that the ruthenium complex first coordinates to the olefin and transfers it from a terminal position to an internal position through the usual mechanism,[8,9] providing an allylic alcohol. A π-allyl–ruthenium complex is then formed through carbon–oxygen bond cleavage of the allylic alcohol. Attack of the π-allyl complex by H_2O gives the more stable final product and regenerates the catalyst. Alternatively, carbon–oxygen bond cleavage could also be due to acid catalysis.[10]

To explore this argument, the allylic alcohol intermediates **10** were synthesized. Under reaction conditions the same as or milder than those for the rearrangement of homoallylic alcohols, the allylic alcohols rearranged rapidly to the final product **11** in water. These results indicate that the rate-determining step of the reshuffling of homoallylic alcohols is the initial olefin migration.



10	**11**
R=Ph, R'=Methyl (90%)	R=Ph, R'=Propyl (70%)
R=p-CH3Ph, R'=Propyl (74%)	R=p-CH3OPh, R'=Propyl (89%)
R=p-ClPh, R'=Propyl (65%)	R=m-BrPh, R'=Propyl (72%)

An internal allylic alcohol, where only aliphatic substituents are present, is also reactive. However, the reaction leads to the formation of an approximately 1:1 mixture of starting material **12** and the rearranged product **13**, which implies that an equilibrium has been established.



12 **13**

Irrespective of the exact mechanism, and although the reaction is still limited to benzyl and cinnamyl type alcohols, the use of catalytic amount of a transition-metal complex to selectively reshuffle molecular structures under an environment of water and air opens up many new opportunities both mechanistically and synthetically. The fact that the reshuffled precursors can also be prepared in water by an indium-mediated Barbier reaction[11] further enhances its synthetic versatility.

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(8) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; pp 31–35.

(9) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; pp 188–190.

(10) An allyl alcohol intermediate **9a** was also rearranged by aqueous 0.1 N HCl, giving a result comparable to that by a catalytic amount of the ruthenium catalyst under nearly neutral conditions.

(11) Li, C. J.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 7017–7020.