

HOMOGENEOUS REARRANGEMENT OF UNSATURATED CARBINOLS
TO SATURATED KETONES CATALYZED BY RUTHENIUM COMPLEXES

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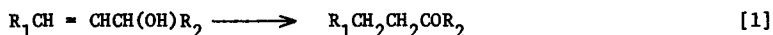
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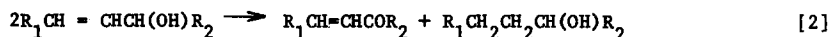
(Received in USA 3 July 1974; received in UK for publication 16 October 1974)

The isomerization of allylic and other unsaturated alcohols to the corresponding saturated aldehydes or ketones (eq. 1) has been accomplished in the presence of a number of catalysts¹.



Reaction [1] can be carried out in acidic or basic media¹, in the presence of metallic copper² and supported palladium³, with iron⁴ or cobalt⁵ carbonyls, as well as, in the presence of some ruthenium (III) salts⁶. However, these methods are of limited practical synthetic value since they require extreme reaction conditions and/or yield substantial amounts of side products in addition to the saturated ketone.

Some ruthenium (II) phosphine complexes are known to catalyze intermolecular hydrogen transfer reactions where alcohols serve as hydrogen donors⁷. Consequently, we have tried several of these complexes⁸ for the intramolecular process, eq. [1], and have found that high yields of the product can be obtained under relatively mild conditions. For example when a 2mM solution of hydrido-chloro-tris(triphenylphosphine)ruthenium (II), (1), in 1-hexene-3-ol was maintained at 110° under nitrogen, a clear reddish-orange solution resulted. After 1 hr. the mixture was found to contain, (via glc analysis), 3-hexanone (92%), 1-hexene-3-one (3.5%) and 3-hexanol (3.5%). The 1-hexene-3-one and 3-hexanol are apparently formed by a disproportionation of 1-hexene-3-ol. This disproportionation reaction can be represented, in general, as shown in eq. [2].



Results of experiments with several other unsaturated alcohols are summarized in the Table.

Table: Isomerization of Unsaturated Alcohols to Saturated Ketones(10 mg RuHCl(PPh₃)₃, 0.5 ml Carbinol Substrate, 1 atm N₂, 110°)

	Carbinol Substrate	Product ^a	% Yield ^b , After 1 hr.
I ^c	CH ₃ CH(OH)CH=CH ₂	CH ₃ COCH ₂ CH ₃	91
II ^c	CH ₃ CH ₂ CH(OH)CH=CH ₂	CH ₃ CH ₂ COCH ₂ CH ₃	92
III	CH ₃ (CH ₂) ₂ CH(OH)CH=CH ₂	CH ₃ (CH ₂) ₂ COCH ₂ CH ₃	92
IV	CH ₃ (CH ₂) ₃ CH(OH)CH=CH ₂	CH ₃ (CH ₂) ₃ COCH ₂ CH ₃	90
V	CH ₃ (CH ₂) ₄ CH(OH)CH=CH ₂	CH ₃ (CH ₂) ₄ COCH ₂ CH ₃	93
VI	<u>CH₂CH₂CH₂CH=CHCH(OH)</u>	<u>CH₂CH₂CH₂CH₂CH₂CO</u>	81 ^d
VII ^c	CH ₃ CH=CHCH(OH)CH ₃	CH ₃ CH ₂ CH ₂ COCH ₃	75 ^d
VIII ^{c,e}	CH ₂ =CHCH ₂ CH(OH)CH ₃	CH ₃ CH ₂ CH ₂ COCH ₃	79 ^d
IX ^c	CH ₃ CH ₂ CH(OH)C≡CH	---	0
X ^{c,f}	CH ₃ CH=CHCH ₂ OH	---	0

a Separation of reaction mixtures was carried out using a 1.8 meter 10% Carbowax 20M on Chromosorb W Column at 70 - 130°. The products were identified on the basis of their spectral properties and by comparison to authentic samples.

b With Carbinol Substrates I - VIII, 7-8% of the disproportionation products (eq. 2) were identified.

c Reaction in sealed tube.

d More than 90% of the product was obtained after 2.5 hours.

e The first step of the isomerization of this compound (i.e. the migration of the double bond from the 1 to 2 position) is approximately 3 times faster than the second step - the formation of the saturated ketone.

f An inactive ruthenium carbonyl complex⁹ is probably formed in the case of primary allylic alcohols.

Experiments with other ruthenium (II)-phosphine catalysts, namely hydridoacetatotris-(triphenylphosphine)ruthenium (II), (2) and dichlorotris(triphenylphosphine)ruthenium (II), (3) gave essentially the same results; however, with (3) almost twice the reaction time used with (1) or (2) was necessary to obtain similar yields of the products.

Although the use of ruthenium (II)-phosphine complexes for reaction [1] enable the use of milder reaction conditions and provide improved product yields over previously used catalysts¹⁻⁶, certain disadvantages are apparent. Although solutions of (1), (2) and (3) are stable to oxygen in unsaturated alcohols, such is not the case in other common solvents (eg. (1), (2) and (3) are sensitive to air when dissolved in benzene). Furthermore, (1) and (2) are fairly unstable in the solid state and must be prepared shortly before use. Recovery of the catalysts, once the isomerization reaction is complete, is very difficult due to their air sensitivity and high solubility in organic solvents. These catalytic systems still yield 7-8% of the undesired intermolecular hydrogen transfer products. Furthermore, none of these catalysts is specific for reaction [1] and they all are more active for common isomerization of C - C double bonds⁸.

We have found that the shortcomings of the ruthenium-phosphine type catalysts are overcome when the recently reported oxotriruthenium acetate complex, $\text{Ru}_3\text{O}(\text{OOCCH}_3)_7$ ¹⁰, (4) is used for reaction [1]. Although (4) is only soluble in polar solvents such as water, low alcohols and dimethylformamide, it does not suffer from any of the above disadvantages. Furthermore, it is considerably more active than (1), (2) or (3).

When 1 ml. of a 2mM solution of (4) in a 1:1 (v/v) mixture of 1-propanol and 1-hexene-3-ol was heated to 85°, a clear green solution resulted, which after 30 minutes was analyzed and found to contain 98% 3-hexanone and less than 1% of the disproportionation products. When the reaction was carried out in a 1:1 mixture of dimethylformamide and 1-hexene-3-ol at 85° the same result was achieved. With other 1-alkene-3-ols similar results were obtained. However, other unsaturated alcohols (eg. substrates VI - X in the Table) were much less reactive under these conditions. Thus, (4) is specifically active towards 1-alkene-3-ol substrates.

Separation of the products and recovery of (4) is very convenient when ethylene glycol is used as a solvent. The resulting ketones, (unlike the carbinol substrates), are essentially insoluble in ethylene glycol and thus separate immediately upon cooling the reaction mixture to room temperature. Upon decantation the product can readily be separated from the solvent which still contains (4). This separated solvent containing (4) can be used for a subsequent catalytic process. The same batch of (4) was used in this way for a number of catalytic cycles without any significant loss in activity.

ACKNOWLEDGEMENT

We thank the National Research Council of Canada and the University of Waterloo for financial support, and Engelhard Industries for the loan of ruthenium.

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