

H-TRANSFER CATALYSIS WITH $\text{Ru}_3(\text{CO})_{12}$

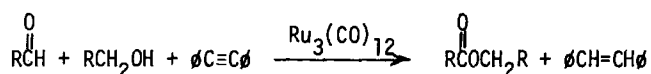
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Summary: $\text{Ru}_3(\text{CO})_{12}$, in the presence of toluene, catalyzes the formation of esters from the following three systems: alcohol + aldehyde, alcohol and aldehyde.

Recently published results¹⁻³ concerning H-transfer reactions catalyzed by mononuclear and by cluster ruthenium complexes prompt us to publish our results.

We have found that $\text{Ru}_3(\text{CO})_{12}$ (a commercially available catalyst) catalyzes fast and selective formation of esters when placed in contact with a mixture of primary alcohol and aldehyde. The reaction requires the presence of an H-acceptor, viz. toluene, and takes place according to the following stoichiometry:



No solvent was used and the reaction was carried out under nitrogen in a glass sleeve in a stainless steel reactor. Qualitative and quantitative analyses were carried out using GC, NMR and MS. Representative results are presented in Table I.

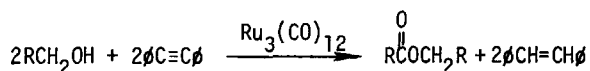
Table I. $\text{RCHO} + \text{RCH}_2\text{OH} \rightarrow \text{RCO}_2\text{CH}_2\text{R}$

<u>R</u>	<u>t(h)</u>	<u>T(C°)</u>	<u>Yield(%)</u>	<u>Turnover Number</u>	<u>Product</u>
ϕ	2	147	72	54	Benzyl benzoate
n-C ₄ H ₉	2	147	78	78	n-Pentyl n-pentanoate

An equimolar mixture of aldehyde, alcohol and toluene was used. The catalyst concentration was 0.3% mol with respect to the combined concentrations of alcohol and aldehyde. Turnover number represents moles of ester produced per mol of catalyst per hour at 2h reaction time. The reactions proceed to complete conversion after 4h. Control experiments indicate no reaction in the absence of the catalyst and a sluggish reaction in the absence of the acceptor. The toluene was converted into a mixture of cis and trans stilbenes which upon prolonged reaction time was quantitatively converted to trans stilbene.

A mixture of benzaldehyde and 1-pentanol, when subjected to the above reaction conditions generates all four possible esters. This implies oxidation of the alcohol to aldehyde under

the reaction condition employed. Indeed, in separate experiments alcohols were converted directly to esters:



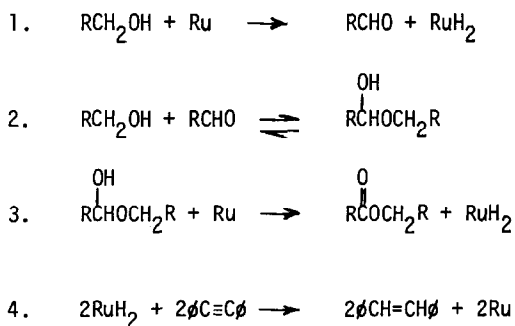
The reaction conditions were identical to those employed in the previous reaction, and the relevant data are presented in Table II.

Table II. $RCH_2OH \rightarrow RCO_2CH_2R$

<u>R</u>	<u>t(h)</u>	<u>T(C°)</u>	<u>Yield(%)</u>	<u>Turnover Number</u>	<u>Product</u>
ϕ	2	147	80	60	Benzyl benzoate
n-C ₄ H ₉	2	147	87	65	n-Pentyl n-pentanoate

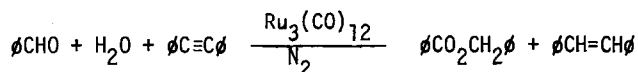
Conversions are complete at 3h reaction time. Similar results were obtained with isobutanol, while 2-butanol was oxidized to 2-butanone. The reaction is fast and selective and seems to be of general nature inasmuch as both benzylic and aliphatic alcohols react at similar rates.

A sequence of steps which may constitute a reasonable catalytic cycle is presented below. Central to the formation of the ester is the intermediacy of a hemiacetal. In the absence of other information Ru and RuH₂ represent two forms of the reactive catalyst.



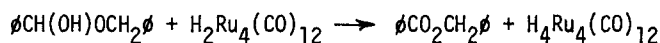
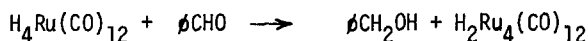
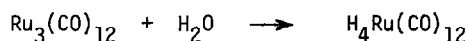
Reactions 1-4 represent the direct conversion of alcohol to ester, while 2-4 represent the conversion of aldehyde + alcohol to ester. The above scheme should be regarded only as a material balance of the catalytic cycle, since it is not known whether some or even all the steps occur on the catalyst, thus ruling out the existence of a free hemiacetal in solution. Only 5% yield of benzyl benzoate was obtained after 20h reaction of PhCHO + PhCH₂OH in the absence of the toluene. It is therefore concluded that the aldehydes are relatively poor H-acceptors.

We further tested the feasibility of the conversion aldehyde \rightarrow ester, and observed the following reaction:



It was carried out under the previously described conditions. The formation of the ester was substantially slower (56% yield at 13h reaction time). Benzyl alcohol, benzoic acid and benzene were detected in small quantities. Formation of the ester could not be detected in the absence of either H_2O or toluene.

It is known⁴ that $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ are generated from $\text{Ru}_3(\text{CO})_{12}$ and water under the reaction conditions used by us. Nevertheless in our system these species can not reduce PhCHO beyond the catalytic level, since catalyst regeneration would require CO. However, a self sustained catalytic cycle generating benzyl benzoate could be envisaged:



This cycle however does not require the intervention of an H acceptor which we find is absolutely essential for the production of the ester. A slow Cannizzaro reaction with subsequent esterification was ruled out by the appropriate control experiment. It is conceivable that additional ruthenium species are involved in this reaction.

Finally, we would like to point out that cyclic hemiacetals, viz. sugars are oxidized to the corresponding lactones heterogenously⁵ with Pt/C, and Rh/C, and homogenously⁶ with $\text{RuH}_2(\text{PPh}_3)_3$ and H-acceptors. With the latter catalyst fast intramolecular disproportionation of furanose and 2-hydroxypyran was also obtained in the absence of an acceptor.⁶ Such disproportionation of 2-hydroxypyran to diol and lactone was also obtained⁷ with $\text{H}_4\text{Ru}_4(\text{CO})_8(\text{PBu}_3)_4$. Numerous H-transfer reactions from primary alcohols^{2,3,7,8,9,10} to various acceptors resulting in formation of aldehydes are catalyzed by mononuclear transition metal complexes. To the best of our knowledge in no case has an intermolecular reaction leading to an ester been observed. Thus, the conversion $\text{PhCH}_2\text{OH} \rightarrow \text{PhCHO}$ was quantitatively obtained⁸ with $\text{RuCl}_2(\text{PPh}_3)_3$ with no ester formation. We believe that the present reaction, aside from its synthetic value,

demonstrates the unique nature of cluster vis-a-vis mononuclear reactivity, and its mechanism is highly interesting.

References

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(Received in UK 13 January 1981)