

FORMATION OF ACRYLIC ESTERS FROM ACROLEIN AND ALCOHOLS
BY RUTHENIUM COMPLEXES

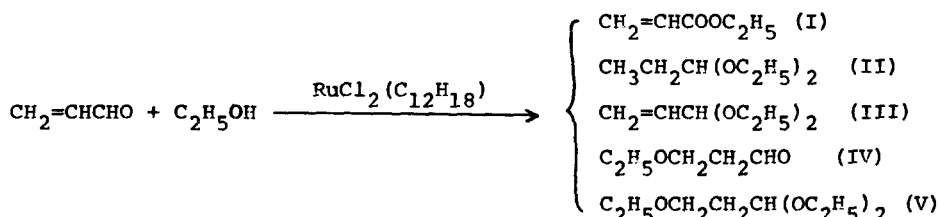
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Direct syntheses of carboxylic esters from aldehydes and alcohols are not known except only a few reports, ie., a Wacker-type reaction by $\text{PdCl}_2\text{-CuCl}_2\text{-O}_2$ ¹⁾, and an oxvesterification reaction by palladium metal in a gas phase.²⁾

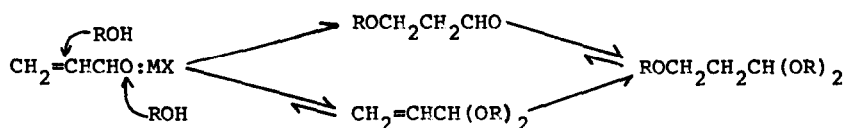
The reaction of acrolein with alcohols in the presence of mineral acids or Lewis acids yields acrolein acetals, β -alkoxypropionaldehydes and their acetals.³⁾ In a previous paper⁴⁾, we have reported that 2-(alkoxymethyl)-penta-2,4-dienal as well as β -alkoxypropionaldehydes is catalytically obtained from acrolein and alcohols in the presence of such metallic compounds as ZnCl_2 , $\text{Pb}(\text{acac})_2$, and CoCl_2 . During the course of our studies on the reaction of acrolein with transition metal complexes⁵⁾, we have now found that acrylic esters and propionaldehyde acetals are directly prepared from acrolein and alcohols by using rhodium, ruthenium and iridium complexes. Other products such as acrolein acetals, β -alkoxypropionaldehydes and their acetals were also found in the reaction mixture.



Complexes such as $\text{RuCl}_2(\text{C}_{12}\text{H}_{18})$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$, $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$, $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$, $\text{RhCl}(\text{PPh}_3)_3$ and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ are effective as the catalyst for the above reaction. Among them, $\text{RuCl}_2(\text{C}_{12}\text{H}_{18})$ is most effective for the formation of ethyl acrylate, but the yield of ethyl acrylate is ca. 10%. Palladium complexes such as $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ and $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ did not yield ethyl acrylate.

Table 1. shows typical results obtained by using $\text{RuCl}_2(\text{C}_{12}\text{H}_{18})$ as catalyst. The presence of oxygen in the reaction increased the yield of ethyl acrylate. Ethyl propionate as well as ethyl acrylate was formed with an increase of reaction temperature, but its yield was very low.

Inoue et al.³⁾ investigated the addition reactions of alcohols to acrolein by Lewis acids and proposed the following reaction scheme from the kinetical studies on the reaction products.



In our reactions, the yields of ethyl acrylate, propionaldehyde diethyl acetal, β -ethoxypropionaldehyde and its acetal increased gradually, while the yield of acrolein diethyl acetal at first increased and then levelled off. These results indicate an analogous scheme for the formation of acrolein diethyl acetal, β -ethoxypropionaldehyde and its acetal. The formation of ethyl acrylate may proceed through an acyl-type complex formed by the oxidative addition of acrolein to the metals, followed by the attack of ethanol. Hydrogen atoms formed in this reaction may be attached to the metals and instantaneously transferred to acrolein to give propionaldehyde acetal.

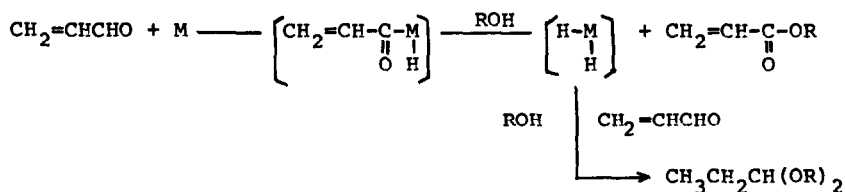


Table 1. The Reaction of Acrolein with Ethanol by $\text{RuCl}_2(\text{C}_{12}\text{H}_{18})$.

Ac/EtOH	I	II	III	IV	V	Conv. of Ac
0.29	10.6%	9.3%	3.6%	18.2%	27.8%	89.2%
A 0.56	8.3	4.9	2.6	28.2	15.2	76.5
0.79	7.7	3.8	2.1	23.6	11.4	65.0
B 0.28	10.4	8.2	7.0	12.4	19.6	76.5
0.28*	5.5	3.5	18.0	3.1	6.9	62.0

A; 60°C, 8 hrs. Cat/EtOH= 0.4 mol%

B; 60°C, 6 hrs. Cat/EtOH= 0.2 mol%, *; reaction under nitrogen

Yields and conversion are based on initial acrolein.

The above mechanism is supported by the fact that treatment of the isolated rhodium-acyl complex, $[\text{RhCl}_2(\text{COC}_2\text{H}_5)(\text{PPh}_3)_2]_2 \cdot 2\text{C}_6\text{H}_6^6$, with ethanol affords ethyl propionate.

Use of propionaldehyde in place of acrolein in the above reactions affords the corresponding ester, ethyl propionate, but its yield is very low compared with that of the ester derived from acrolein.

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