C–O Bond Cleavage in Alkenyl Carboxylates Promoted by Transition-metal Hydrides

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Summary Hydrido complexes of group VIII metals (Fe, Co, Ru, Rh and Pd) promote C–O bond cleavage in vinyl or allyl carboxylates liberating ethylene or propylene and forming the transition-metal carboxylate.

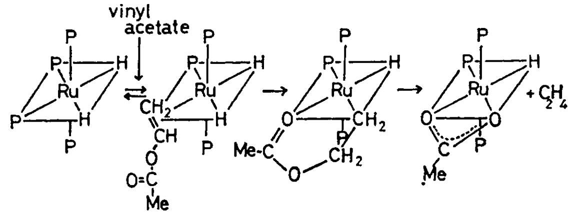
Cleavage of the carbon–halogen bond in alkyl and allyl halides in oxidative addition to low-valent transition-metal complexes is well known and the process has some synthetic applications,[1] but C–O bond cleavage promoted by transition-metal complexes is scarcely known except for a note on the oxidative addition of allyl acetate to a zero-valent molybdenum complex giving an allyl molybdenum acetate complex.[2] We now report cleavage of the C–O bond in alkenyl esters promoted by transition-metal hydrides.

$RuH_2(PPh_3)_4$ (**1**)[3] when treated with vinyl acetate at room temperature liberates 1 mol of ethylene per mol of (**1**) and gives a light brown precipitate. The precipitate was recrystallized from THF–Et_2O and identified as $RuH(O_2CMe)(PPh_3)_3$[4] (**2**) by elemental analysis, i.r., n.m.r., and ^{31}P n.m.r. spectra, m.p., and chemical reactions. No hydrogenation product of vinyl acetate and hydrogen was detected in the reaction mixture.

Allyl acetate when treated with (**1**) gives (**2**) and propylene and the reaction of vinyl propionate with (**1**) gives $RuH(O_2CEt)(PPh_3)_3$ and ethylene in high yields at room temperature. There was no reaction between ethyl acetate and (**1**) at room temperature and the reaction of pentyl acetate at 80° caused decarbonylation. Predissociation of $RuH_2(PPh_3)_4$ in solution producing a co-ordinatively unsaturated species seems necessary to initiate the reaction since $RuH_2(PPh_2H)_4$[5] and $RuH_2(PPh_2Me)_4$,[6] which show little tendency to dissociate in solution (confirmed by n.m.r. spectra) were not reactive with vinyl acetate.

The reaction seems to take place generally with group VIII transition metal hydrides; $FeH_2(N_2)(PPh_2Et)_3$,[7] $CoH(N_2)(PPh_3)_3$,[8] $RuHCl(PPh_3)_3$,[9] $PdH_2[P(C_6H_{11})_3]_2$,[10] and $RhH(PPh_3)_4$[3] readily released ethylene when treated with vinyl acetate . In the reaction of cobalt and iron hydrides with vinyl acetate complete displacement of the tertiary phosphine ligands was observed. The reaction of vinyl acetate with the palladium complex did not proceed quantitatively and partial hydrogenation of liberated ethylene to ethane was observed.

The requirement of a vacant site in the complex coupled with the failure of alkyl esters to react with the transition-metal hydrides suggests that the reaction pathway involves the co-ordination of the carbon–carbon double bond to the vacant site followed by insertion of the olefinic entity into the metal–hydrogen bond and cleavage of the C–O bond liberating ethylene (Scheme).



Scheme

It is significant that this process can be regarded as the reverse process of the production of vinyl acetate from ethylene and acetic acid by the palladium complex.[11]

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