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# CONDENSATION OF ALCOHOLS CATALYSED BY TERTIARY PHOSPHINE TRANSITION METAL COMPLEXES

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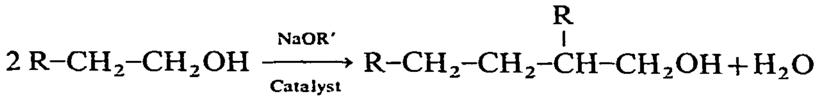
## SUMMARY

The condensation of alcohols catalysed by tertiary phosphine complexes of Rh, Ir, Pt, Ru is reported and discussed.

In the course of our investigations on the synthesis of higher molecular weight alcohols by the so-called Guerbet reaction, we reported that supported metals of Group VIII show outstanding properties as heterogeneous catalysts of this reaction[1,2]:



$$2\,R\text{-}CH_2\text{-}CH_2OH \xrightarrow[\text{Catalyst}]{\text{NaOR}'} R\text{-}CH_2\text{-}CH_2\text{-}\underset{}{\overset{\displaystyle R\atop|}{C}}H\text{-}CH_2OH + H_2O$$

We have extended this catalytic reaction to the homogeneous phase, using soluble complexes of similar metals, with the aim of obtaining a more detailed knowledge of the mechanism and catalytic action of the transition metals in the heterogeneous phase.

TABLE 1

BUTANOL CONDENSATION

(0.3 *M* solutions of sodium butoxide in boiling n-butanol)

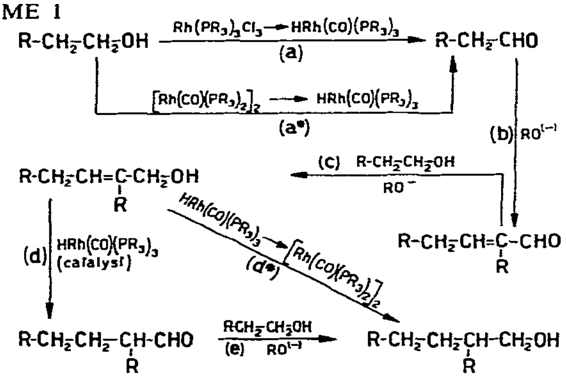
| *Catalytic system* | *Catalyst concentration (mg-atoms metal·l$^{-1}$)* | *Yield (%) dimer formed from the reacted alcohol* | *Initial reaction rate (mmoles alcohol·h$^{-1}$·l$^{-1}$)* |
|---|---|---|---|
| $[Rh(CO)_2Cl]_2+8\,P(C_2H_5)_3$ | 10 | 90 | 120 |
| $RhCl_3{\cdot}3\,H_2O+4\,P(C_4H_9)_3$ | 60 | 85 | 280 |
| $RuCl_3{\cdot}3\,H_2O+4\,P(C_4H_9)_3$ | 10 | 90 | 50 |
| $IrCl_3{\cdot}3\,H_2O+4\,P(C_4H_9)_3$ | 5 | | 20 |
| $Ir(CO)Cl(PPh_3)_2$ | 5 | 90 | 10 |
| $PtCl_2(PPh_3)_2$ | 2 | 45 | 10 |
| $PdBr_2(PPh_3)_2+2\,P(C_4H_9)_3$ | 5 | 0 | 0 |
| $AuCl(PPh_3)$ | 5 | 0 | 0 |

We first tried as catalysts many complexes of Group VIII transition metals with different ligands but, in nearly all cases, metal separation quickly occurred (because of the reducing properties of the boiling sodium alkoxide solutions). Stable low oxidation state complexes which showed a relatively small but sharp catalytic activity were only formed *in situ* with tertiary phosphines as ligands (see Table 1).

The catalytic activity was dependent on the metal and the nature of the tertiary phosphine, the greater activity being usually achieved with alkylphosphines. In particular, the selectivity of the platinum catalysts was low (aldehydes and ketones are formed with hydrogen evolution) and in this case the colour of the solutions slowly turned deep red probably because of the formation of platinum(0) clusters[3].

Generally, all the catalytic systems showed a gradual loss of activity with time, the rhodium and ruthenium catalysts being the more stable from this point of view. Only the $RhCl_3$/trialkylphosphine system has been investigated in detail and as a result of this investigation we propose Scheme 1.

SCHEME 1



The first step (*a*) certainly involves the dehydrogenation of alcohol to aldehyde with consequent reduction of the rhodium complex, firstly to $Rh(CO)(PR_3)_2Cl$[4] and then to a mixture of $[Rh(CO)(PR_3)_2S]_2$ (where S is the solvent) and $HRh(CO)(PR_3)_3$, as already reported[5]. With an excess of alcohol in the alkaline medium an easy crotonisation and a hydrogen transfer to the aldehyde take place [steps (*b*) and (*c*)].

As already reported for the decarbonylation reaction of allylic alcohols[6], we have found experimentally that the unsaturated alcohol which is formed easily isomerises in the presence of the hydridic species $HRh(CO)(PR_3)_3$ to the saturated aldehyde [step (*d*)]. Via a second hydrogen exchange the last intermediate reacts with the excess of alcohol [step (*e*)] to form the final saturated alcohol. It is noteworthy that the low molecular weight aldehyde is continously reformed through steps (*c*) and (*e*).

The direct hydrogenation of the intermediate allylic alcohol must also be considered [step (*d**)] in view of the reactivity of $HRh(CO)(PR_3)_3$ observed under the same conditions in the case of hydrogen transfer to a double bond, even when this is internal[5]. Zerovalent rhodium species of the type $[Rh(CO)(PR_3)_2S]_2$ are thus formed and these readily abstract hydrogen from the excess of alcohol to reform aldehyde and the active catalyst $HRh(CO)(PR_3)_3$ [step (*a**)]. However, these reactions are rather slow compared with the total rate of alcohol condensation and probably do not participate very much in the overall mechanism of catalysis. In fact, the greater stability and activity of rhodium and ruthenium complexes must be attributed to the easy hydrogen abstraction from alcohols by $Rh^{III}$, $Rh^{I}$, $Rh^{0}$, $Ru^{III}$, $Ru^{II}$ complexes to form stable metal hydrides.

Probably low valent metal complexes of platinum and iridium, although they form stable hydride complexes, are not so capable of abstracting hydrogen from alcohols when the hydridic hydrogen is lost as $H_2$ or transferred to an organic substrate.

The complete inactivity of palladium and gold complexes, which do not form stable hydrides but are reduced under our reaction conditions to low valent species[7,8], confirms the necessity of the metal–hydrogen bonds for catalytic activity. Such bonds are probably formed also on the surfaces of supported metals.

## EXPERIMENTAL

Catalytic reactions were performed in boiling alcohols by separating continuously the excess water in a Marcussow apparatus. Reaction rates were followed by VPC determination of the residual alcohol.

Preformed metal complexes were synthesized by well-known methods. In the case of rhodium catalysis, catalytic complexes were in some cases isolated from reaction mixtures by washing with water and removing the alcohol in an inert atmosphere. The complexes[5] were characterized by analysis and infrared spectra.

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