

HOMOGENEOUS AND HETEROGENEOUS HYDROGENATION.

I. Jardine and F.J. McQuillin

Department of Organic Chemistry, University of Newcastle upon Tyne,
Newcastle upon Tyne.

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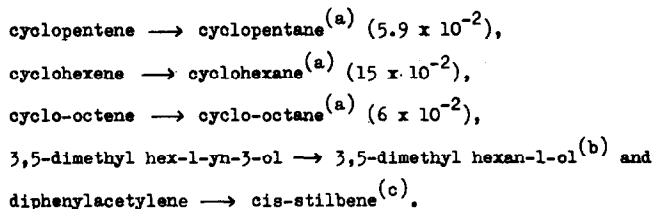
We have indicated that a range of observations relating to catalytic hydrogenation and hydrogenolysis are usefully considered in terms of organometallic intermediates (1, 2). In particular we have presented evidence characterising a chemisorbed olefin as generally very similar to a transition metal-olefin π -complex such as the historic Zeise's salt (1). We were, therefore, interested to examine examples of transition metal hydride complexes, a number of which are known (3) and which have been shown to effect hydrogenation of a few organic substances (4). We were concerned to see how far a soluble hydride will reproduce the phenomena and especially the stereochemistry of the heterogeneous reaction.

The chloroplatinic acid/stannous chloride mixture of Cramer (4(c)) we found rather prone to deposit metallic platinum. The more stable triphenylphosphine complexes (5): $[\text{Ph}_3\text{P}]_4\text{Pt}$, $[\text{Ph}_3\text{P}]_3\text{Pt}$, $\text{cis}-[\text{Ph}_3\text{P}]_2\text{PtCl}_2$, $[\text{Ph}_3\text{P}]_2\text{PtH}_2$ and $\text{trans}-[\text{Ph}_3\text{P}]_2\text{PtHCl}$ failed to catalyse hydrogenation of an olefin as reactive as norbornadiene when shaken with hydrogen in alcohol solution. However, since the hydrido-chloride is known to react with ethylene under pressure (5(c)) the problem is clearly one of ligand displacement. Cramer (4(c)) noted catalysis of the formation of Zeise's salt from chloroplatinic acid in the presence of stannous chloride.

Following this observation we found that the hydriochloride, $[\text{Ph}_3\text{P}]_2\text{PtHCl}$, in presence of stannous chloride (2 mols) in alcohol is an effective catalyst for the homogeneous hydrogenation of norbornadiene to norbornane and of 2,5-dimethyl hex-3-yn-2,5-diol to 2,5-dimethyl hexane-2,5-diol at an appreciable rate.

The triphenylphosphine complexes $[\text{Ph}_3\text{P}]_2\text{Pt}[\text{SnCl}_3]_2$ and $[\text{Ph}_3\text{P}]_2\text{PtClSnCl}_3$ are known (4(c)) and it seems most likely that the reagent in our case is the hydriostannochloride: $[\text{Ph}_3\text{P}]_2\text{PtHSnCl}_3$. The bromo and iodo-complexes (5(c)), $[\text{Ph}_3\text{P}]_2\text{PtHX}$ (X = Br or I) were ineffective with or without added stannous chloride.

With a view to realising a more rapid reaction we turned to ruthenium from the other end of Group VIII. With triphenylphosphine in methanol RuCl_3 was found to catalyse the hydrogenation of norbornadiene with a rate maximum at a ratio of $\text{Ph}_3\text{P}/\text{Ru}^{\text{III}}$ of 6:1. Using $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (10^{-2} m.) with triphenylphosphine (6×10^{-2} m.) in methanol we were able to hydrogenate the following substances (10^{-2} m.):

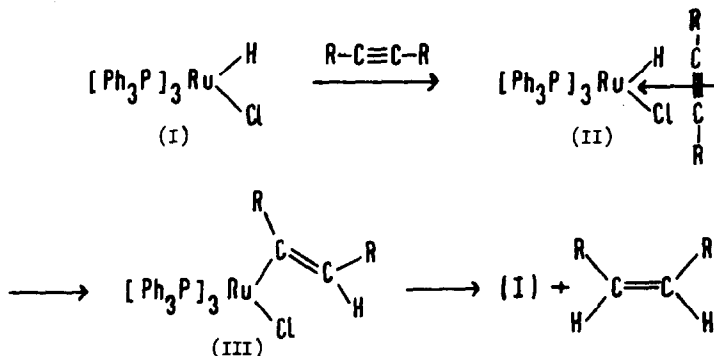


The figures in parenthesis indicate the rate of hydrogen uptake (c.c./min.). The products were identified: (a) by g.l.c., (b) by t.l.c., and (c) by u.v. absorption.

Triphenylphosphine is known (4(e)) to reduce the Ru^{III} halide and to form a series of complexes with the Ru^{II} ion viz. $[\text{Ph}_3\text{P}]_n\text{RuCl}_2$, where $n = 2, 3$ or 4 . Reaction with hydrogen (4(e)) gives a hydriochloride,

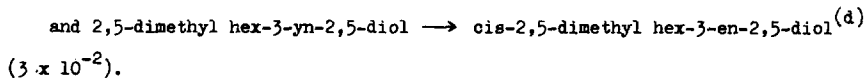
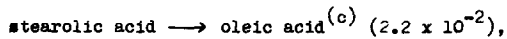
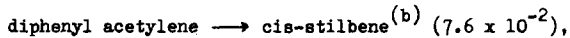
$[\text{Ph}_3\text{P}]_3\text{RuHCl}$ which is regarded as the reagent in our work.

The characterisation of the reduction product of diphenyl acetylene as *cis*-stilbene is of interest. We considered it important, however, to establish that the added hydrogen originates in molecular hydrogen and not from the alcohol solvent. Whilst a reaction sequence:



is reasonable the vinyl ruthenium intermediate (III) might react with a solvated alcohol molecule, and with retention of configuration.

This possibility was excluded by demonstrating hydrogenation of the following substances by shaking with a solution of $[\text{Ph}_3\text{P}]_3\text{RuCl}_2$ ($4 \times 10^{-3}\text{m.}$) in benzene:



The figures in parenthesis indicating the rate of reaction, the concentration of the unsaturated molecule being in this case $3.6 \times 10^{-2}\text{m.}$ i.e. an effectively catalytic reaction. The products were characterised as indicated: (a) by g.l.c., (b) by n.m.r. and u.v. absorption, (c) by n.m.r. and i.r., and

(d) by t.l.c.

These examples also add two further instances of cis-hydrogen addition as in heterogeneous catalysis.

We also examined several iridium complexes, viz: $[\text{Ph}_3\text{P}]_3\text{IrHCl}_2$, $[\text{Ph}_3\text{P}]_3\text{IrH}_2\text{Cl}$, $[\text{Ph}_3\text{P}]_3\text{IrH}_2\text{SnCl}_3$ (6) which, however, are rather too insoluble, and none was found to catalyse hydrogenation of norbornadiene. The difficulty in this case appears, however, to be due to formation of a too stable organo metallic. Norbornadiene with $[\text{Ph}_3\text{P}]_3\text{IrH}_2\text{SnCl}_3$ was found to give an extremely stable product with displacement of the norbornadiene resonances from τ 3.3, 6.4 and 8.0 to τ 4.6, 6.2 and 8.8 with broadening, and with loss of the 2220 cm^{-1} band of the two characteristic Ir-H bands in the infra red at 2220 and 2180 cm^{-1} .

By using a stannochloride in place of triphenylphosphine as ligand we were, however, able to establish a slow hydrogenation of norbornadiene. We found a rate maximum at a ratio of $\text{SnCl}_2/\text{Na}_2\text{IrCl}_6$ of 3.5 corresponding to formation of an Ir^{III} derivative, $\text{Ir}[\text{SnCl}_3]_3$, which however we have not isolated.

The correspondence with the phenomena of heterogeneous hydrogenation shown in these experiments is very close.

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