

Versatility of Palladium Compounds

Carbonylation: Direct Synthesis of Carbonyl Compounds

BY H. M. COLQUHOUN, D. J. THOMPSON AND M. V. TWIGG, Plenum Press, New York, 1991, 296 pages, ISBN 0-306-43747-3, U.S.\$65

The authors have used their experience of industrial catalysis to provide an authoritative and practical account of carbonylation.

The volume deals with the carbonylation of organic compounds, principally mediated by transition metal catalysts but also including relevant reactions which use stoichiometric reagents. The major parts of the book are organised according to the chemical nature of the product. In addition, there are useful sections which deal with mechanistic and practical aspects of carbonylation.

The use of carbon monoxide is proving increasingly useful in organic synthesis and the chapter on practical aspects of carbonylation is a valuable guide to chemists not experienced in handling these materials. It includes valuable details on the properties of carbon monoxide and metal carbonyls, it describes the handling of these materials and also deals with the equipment and procedures required to carry out reactions and isolate the products. The major sections of the book on organic syntheses are organised in a clear and concise way. They contain practical details of selected compounds and point out limitations of particular methodology.

The chapter on aldehydes describes their synthesis from halocarbons using either soluble palladium catalysts or stoichiometric iron reagents. Hydroformylation of alkenes is also discussed with an emphasis on the commercial rhodium catalysts and to a lesser extent cobalt.

The section on ketones describes their synthesis from halocarbons (using iron reagents or palladium catalysts) and from dienes (using palladium, rhodium or cobalt catalysts).

The synthesis of carboxylic acids from alkyl and benzyl halides with palladium-triphenylphosphine or anionic nickel carbonyl catalysts and from vinylic halides using palladium or cobalt catalysts is described. There is discussion of the Monsanto based

rhodium catalyst systems which have become the dominant technology for the carbonylation of methanol to acetic acid. This catalyst is less useful for the carbonylation of higher alcohols where strong acids find some application. Other sources of carboxylic acids are alkynes, diazonium ions (using palladium catalysts) and aldehydes.

The preparation of esters via similar substrates is described, and in addition the hydroesterification of alkenes with carbon monoxide and ethanol using bimetallic catalysts containing platinum or palladium with tin halide as co-catalyst is discussed, as is the carbonylation of organometallic reagents such as Grignard, organothallium, organoboron and organosilicon reagents with palladium or cobalt catalysts.

The Tennessee Eastman rhodium process for the production of acetic anhydride is described along with other routes to acid anhydrides. There are further sections on the synthesis of amides, acyl halides, lactones, lactams and related heterocycles.

A chapter is devoted to decarbonylation where aromatic aldehydes can be useful starting materials. Palladium-on-carbon catalysts have been employed at high temperatures and also homogeneous rhodium systems under less extreme conditions.

The final chapter deals with the preparation and recovery of precious metals catalysts. This includes sufficient detail to enable a qualified chemist to prepare relevant catalysts of interest.

This volume demonstrates that palladium compounds serve as versatile catalysts in organic synthesis involving carbon bond-forming reactions. The authors have provided a good balance between established reactions and emerging chemistry. It should serve as a useful text for synthetic chemists working in a research and development environment.

M.J.H.R.