

# Oxidation in Organic Synthesis

**Organic Syntheses by Oxidation with Metal Compounds**

EDITED BY W. J. MIJS AND C. R. H. I. DE JONGE, Plenum Press, New York, 908 pages, \$138

This book is concerned with the synthetic aspects of oxidation reactions involving metal compounds which are either readily available or easy to prepare. It considers reagents which are both stoichiometric and catalytic. There are a total of 16 chapters, together with a helpful appendix in tabular form which contains a list of substrate and product classes, and gives references to experimental procedures in the preceding chapters. At the end of each chapter representative synthetic procedures are given, including experimental details. The majority of chapters are concerned with transition metal complex reagents, including vanadium, chromium, cobalt, copper, manganese, nickel, silver, thallium, bismuth and cerium. There are, however, three chapters devoted to complexes of ruthenium, palladium and osmium.

Ruthenium tetroxide oxidation is discussed by J. L. Courtney, and the major sections within this chapter deal with mechanism, scope and limitations of reactions, and experimental considerations and procedures. The advantages that ruthenium tetroxide has as a reagent over osmium tetroxide in terms of rigour and versatility are emphasised. In addition to discussing the formation of aldehydes and ketones, acids, imides, sulfoxides and sulphones from various substrates, attention is focused on some more novel organic transformations. These include the formation of esters and lactones from ethers, also oxygen insertion reactions, the oxidation of cycloalkanes, and the formation of quinones and diacids, the latter via the destruction of the aromatic nucleus. Throughout this section comparisons are made with more established oxidants; this should prove useful to practising synthetic organic chemists.

The use of palladium compounds in oxidation transformations is well documented, and S. F. Davison and P. M. Maitlis summarise this in a 31 page review. The oxidation of alkenes, in particular ethylene, is discussed objectively

and problems relating to the formation of acetaldehyde (the Wacker process), vinyl acetate and ethers are discussed. Vinylic substitution reactions and in particular the arylation of olefins and variants of this based around the Heck reaction are described and it is demonstrated that this can result in mild regio- and stereoselective reactions which can be utilised for a wide range of functionalities on the substrate. Other sections deal with aromatic substitution reactions, oxidative aryl coupling, oxidative carbonylations and the oxidation of alcohols. In this chapter it is noted whether the reagent may be used stoichiometrically or catalytically, and limitations to the utility of synthetic routes are discussed.

Osmium tetroxide is one of the oldest metal compounds to be used in the oxidation of organic compounds and its uses, particularly in the hydroxylation of alkenes—where it finds widespread application—are described by H. S. Singh, who also reviews the use of alkene, diene, quinone, pyran and steroidal substrates. In the past, these reactions have been carried out stoichiometrically, but the use of co-oxidants for alkene oxidation is described; this renders the reaction catalytic in osmium. More recent work which improves the scope of osmium reagents and can improve the effectiveness of osmium tetroxide in alkene oxidations is exemplified by the use of alkylimidoosmium reagents and chloramine-T for the formation of aminoalcohols. The use of ferricyanide with catalytic amounts of osmium tetroxide in the synthesis of acids, diacids and hydroxyacids is discussed; a section is devoted to the use of osmium in more complex transformations relevant to biorganic synthesis.

This book should prove a useful addition to departmental libraries, providing an overview of oxidation transformations using metal compounds and demonstrating, in part, the versatility of the platinum metals. M.J.H.R.