Catalysts for Fine Chemical Synthesis

Volume 1

Hydrolysis, Oxidation and Reduction

Edited by

Stan M Roberts and **Geraldine Poignant**
University of Liverpool, UK

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Catalysts for Fine Chemical Synthesis Series Preface

During the early-to-mid 1990s we published a wide range of protocols, detailing the use of biotransformations in synthetic organic chemistry. The procedures were first published in the form of a loose-leaf laboratory manual and, recently, all the protocols have been collected together and published in book form (*Preparative Biotransformations*, Wiley-VCH, 1999).

Over the past few years the employment of enzymes and whole cells to carry out selected organic reactions has become much more commonplace. Very few research groups would now have any reservations about using commercially available biocatalysts such as lipases. Biotransformations have become accepted as powerful methodologies in synthetic organic chemistry.

Perhaps less clear to a newcomer to a particular area of chemistry is *when* to use biocatalysis as a key step in a synthesis, and when it is better to use one of the alternative non-natural catalysts that may be available. Therefore we set out to extend the objective of *Preparative Biotransformations*, so as to cover the whole panoply of catalytic methods available to the synthetic chemist, incorporating biocatalytic procedures where appropriate.

In keeping with the earlier format we aim to provide the readership with sufficient practical details for the preparation and successful use of the relevant catalyst. Coupled with these specific examples, a selection of the products that may be obtained by a particular technology will be reviewed.

In the different volumes of this new series we will feature catalysts for oxidation and reduction reactions, hydrolysis protocols and catalytic systems for carbon–carbon bond formation *inter alia*. Many of the catalysts featured will be chiral, given the present day interest in the preparation of single-enantiomer fine chemicals. When appropriate, a catalyst type that is capable of a wide range of transformations will be featured. In these volumes the amount of practical data that is described will be proportionately less, and attention will be focused on the past uses of the system and its future potential.

Newcomers to a particular area of catalysis may use these volumes to validate their techniques, and, when a choice of methods is available, use the background information better to delineate the optimum strategy to try to accomplish a previously unknown conversion.

S.M. ROBERTS
I. KOZHEVNIKOV
E. DEROUANE
LIVERPOOL, 2002

Preface for Volume 1: Hydrolysis, Oxidation and Reduction

A REVIEW OF NATURAL AND NON-NATURAL CATALYSTS IN SYNTHETIC ORGANIC CHEMISTRY: PRACTICAL TIPS FOR SOME IMPORTANT OXIDATION AND REDUCTION REACTIONS

In this volume we indicate some of the different natural and non-natural catalysts for hydrolysis, oxidation, reduction and carbon–carbon bond forming reactions leading to optically active products. Literature references are given to assist the reader to pertinent reviews. The list of references is not in the least comprehensive and is meant to be an indicator rather than an exhaustive compilation. It includes references up to mid-1999 together with a handful of more recent reports.

The later sections of the book deal with the actual laboratory use of catalysts for asymmetric reduction and oxidation reactions. Most of the protocols describe non-natural catalysts principally because many of the corresponding biological procedures were featured in the sister volume *Preparative Biotransformations*. As in this earlier book, we have spelt out the procedures in great detail, giving where necessary, helpful tips and, where appropriate, clear warnings of toxicity, fire hazards, etc.

Many of the procedures have been validated in the Liverpool laboratories (by GP). Other protocols were kindly submitted by colleagues from the USA, Japan, the UK and mainland Europe. The names of the contributors are given at the start of the corresponding protocol. These descriptions of the recipes also contain references to the literature. In these cases the references point the reader to the more practical aspects of the topic and are meant to complement rather than repeat the references given in the first, overview chapter.

Some of the practicals describe the use of similar catalysts and/or catalysts that accomplish the same task. This has been done purposely to try to get the best match between the substrate described and the one being considered by an interested reader. Moreover when catalysts can be compared, this has been done. Sometimes a guide is given as to what *we* found to be the most useful system in our hands. In this context, it is important to note that, except for polyleucine-catalysed oxidations and the use of a bicyclic bisphosphinite for asymmetric hydrogenation, the Liverpool group had no previous experience in

using the catalysts described herein; we approached the experiments carried out in Liverpool as newcomers in the field.

Thus for the first volume in this series we have performed a selection of oxidation and reduction reactions, arguably some of the most important transformations of these two types, mainly employing non-natural catalysts. In other volumes of this work other catalysts for oxidation and reduction will be featured and, of equal importance, the use of preferred catalysts for carbon–carbon bond formation will be described. In the first phase, therefore, this series will seek to explore the 'pros and cons' of using many, if not most, well-documented catalysts and we will endeavour to report our findings in a non-partisan manner.

We truly hope these procedures will be really valuable for fellow chemists trying out a new catalyst system for the first time. Feedback and further hints and tips would be most welcome.

G. POIGNANT
S.M. ROBERTS
LIVERPOOL, 2002

Abbreviations

Ac	acetyl
Ar	aryl
b.p.	boiling point
BSA	*N,O*-bis-(trimethylsilyl)-acetamide
Bu	butyl
cat	catalyst
CLAMPS	cross-linked aminomethylpolystyrene
DBU	1,8-diazabicyclo[5.4.0]undec–7–ene
DEPT	diethyl tartrate
DIPT	diisopropyl tartrate
DMAP	4-dimethylaminopyridine
DMM	dimethoxymethane
DMSO	dimethyl sulfoxide
EDTA	ethylenediaminetetraacetic acid
ee	enantiomeric excess
eq	equivalent
Et	ethyl
GC	gas chromatography
HPLC	high pressure liquid chromatography
ID	internal diameter
IR	infrared (spectroscopy)
L	ligand
lit.	literature
M	metal
m.p.	melting point
MCPBA *m*-CPBA	*meta*-chloroperbenzoic acid
Me	methyl
MTPA	methoxy-α-(trifluoromethyl)phenylacetyl
NMR	nuclear magnetic resonance
Ph	phenyl
Pr	propyl
psi	pounds per square inch
r.p.m.	rotation per minutes
R_f	retention factor
R_t	retention time

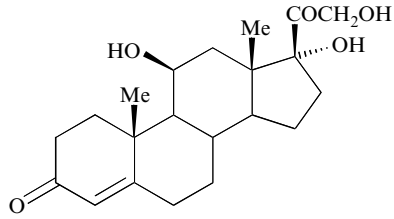
TBHP	*tert*-butyl hydroperoxide
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetramethylsilane
UHP	urea–hydrogen peroxide
UV	ultraviolet
v:v	volume per unit volume

Part I Review

1 The Integration of Biotransformations into the Catalyst Portfolio

CONTENTS

The science of biotransformations has been investigated since the days of Pasteur[1]. However, progress in the use of enzymes and whole cells in synthetic organic chemistry was relatively slow until the 1950s, when the use of microorganisms to modify the steroid nucleus was studied in industry and academic laboratories[2]. Thus conversions such as the transformation of 17α-acetoxy-11-deoxycortisol into cortisol (hydrocortisone) (**1**), using the microorganism



(**1**)

Curvularia lunata to introduce the 11β-hydroxy group directly, helped to revive interest in the application of biological catalysis to problems in synthetic organic chemistry. The momentum was continued by Charles Sih, J. Bryan Jones, George Whitesides and others, until, by the mid-1980s, biocatalysis

was being accepted as a powerful method, especially for the production of optically active products[3]. At this time the whole field was given another boost by Alexander Klibanov at the MIT who showed emphatically (but not for the first time) that some enzymes (especially lipases) could function in organic solvents, thus broadening the substrate range to include water-insoluble substances[4].

For a while, in the early 1990s, the interest in the use of enzymes in organic synthesis increased at an almost exponential rate and two-volume works were needed even to summarize developments in the field[5]. Now, at the turn of the century, it is abundantly clear that the science of biotransformations has a significant role to play in the area of preparative chemistry; however, it is, by no stretch of the imagination, a panacea for the synthetic organic chemist. Nevertheless, biocatalysis is the method of choice for the preparation of some classes of optically active materials. In other cases the employment of man-made catalysts is preferred. In this review, a comparison will be made of the different methods available for the preparation of various classes of chiral compounds[6].

Obviously, in a relatively small work such as this it is not possible to be comprehensive. Preparations of bulk, achiral materials (e.g. simple oxiranes such as ethylene oxide) involving key catalytic processes will not be featured. Only a handful of representative examples of preparations of optically inactive compounds will be given, since the emphasis in the main body of this book, i.e. the experimental section, is on the preparation of chiral compounds. The focus on the preparation of compounds in single enantiomer form reflects the much increased importance of these compounds in the fine chemical industry (e.g. for pharmaceuticals, agrichemicals, fragrances, flavours and the suppliers of intermediates for these products).

The text of this short review article will be broken down into the following sections:

1. Hydrolysis of esters, amides, nitriles and oxiranes
2. Reduction reactions
3. Oxidative transformations
4. Carbon–carbon bond forming reactions.

In each of these areas the relative merits of biocatalysis versus other catalytic methodologies will be assessed. Note that the text is given an asterisk (*) when mention is made of a catalyst for a reduction or oxidation reaction that is featured in the later experimental section of this book.

1.1 HYDROLYSIS OF ESTERS, AMIDES, NITRILES AND OXIRANES

The enantioselective hydrolysis of racemic esters to give optically active acids and/or alcohols (Figure 1.1) is a well established protocol using esterases or lipases. In general, esterases from microorganisms or animal sources (such as