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Foreword

Asymmetric synthesis has been a focal point for much of the most interesting new organic chemistry developed over the past few years. With growing maturity of the topic, there has been increasing realisation of the importance of catalysis, such that a new stereogenic centre in the product is formed by multiplying rather than merely reproducing the chirality of the reactants.

This collection of manuscripts by leading authors in the field of asymmetric catalysis gives a fair cross-section of current activity -the drive towards reactions of near-perfect optical efficiency, towards high catalytic turnover and towards a deeper understanding of reaction mechanisms as a means of developing future catalysts of enhanced effectiveness. The selection emphasises the international character of current work, with contributions from ten different countries. Several of these contributions are from industrial laboratories, underscoring the potential practical importance of the subject.

It might be useful to highlight some of the the most common recurrent themes, in the order of presentation of manuscripts. A continuing goal in catalytic oxidation is the search for suitable catalysts for asymmetric epoxidation of simple olefins, exemplified by Katsuki's contribution. Extensions of the titanium-tartrate procedure for asymmetric epoxidation (Marko, Davies) and pertinent frontier-orbital calculations on this reaction and asymmetric osmylation (Jorgensen) are included. Naruta and Maruyama demonstrate the metalloporphyrin-based enantioselective oxidation of sulphides

Asymmetric hydrogenation, which was the first practically important catalytic asymmetric reaction, still continues to attract substantial attention. The current emphasis on ruthenium catalysts is highlighted by Noyori's synthesis of β-amino acids and Genet's synthesis of both D- and L-threonine. Current developments in ligand design are exemplified by chiral phospholane ligands (Burk) and trans-chelating biphosphines (Ito). Achiwa presents his interpretation of the origin of asymmetry in rhodium hydrogenations. Related catalysts have been applied to catalytic hydroboration of prochiral olefins with catecholborane, represented by the contributions from Hayashi and Burgess. The difficult challenge of asymmetric hydroformylation is taken up by Gladiali and Heil.

Diverse approaches have been made to the catalytic asymmetric synthesis of C-C bonds, with Lewis-acid catalysis the most important strand. Mukaiyama describes further developments of their new silylenol thioester aldol condensation, now under catalytic conditions. Helmchen and Mikami offer new contributions to the catalyic asymmetric Diels-Alder reaction, with diverse Lewis acids, whilst Yamamoto describes the catalysed Claisen rearrangement. Organometallic catalysis is represented by allylic alkylation with palladium complexes. Methodology for effecting the simple enantioselective addition of malonate esters with high optical efficiency is reported by Yamaguchi and Yamagishi, and the successful application of chiral phosphinocarboxylates as ligands by Minami. Phosphines are not essential for the allylic alkylation, and Togni demonstrates the use of palladium-sparteine complexes. Conjugate reduction of unsaturated carbonyl compounds with high catalytic efficiency and high enantioselectivity is reported by Pfaltz, using semicorrin cobalt complexes, and nickel-catalysed enantioselective conjugate alkylation is demonstrated by Bolm.

Inevitably, in a collection of restricted size, some areas will not be given full justice relative to their current significance. The underrepresentation of enzymology in asymmetric synthesis is countered by the contribution from Kellogg, concerning pig liver esterase. The status of heterogeneous catalysis in asymmetric synthesis, which must be an area ready for expansion, is represented by the work of Blaser, applied here to reductive dechlorination.

Much remains to be done before catalytic asymmetric asymmetric synthesis reaches a stable state. Whilst it is possible to achieve high enantiomer excesses in many reactions, others are far from satisfactory. Many reactions based on Lewis acid catalysts are limited by slow turnover, or by mass action which requires conditions where the components are present at high concentration. Organometallic catalysts can be very successful but constrained by narrow substrate specificity, or a requirement for fine tuning with each new substrate. We look forward to a hypothetical Special Issue on this topic in five years time when these problems have been fully addressed.

John Brown.
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