Book Reviews

Organic Synthesis *via* Organometallics (OSM 4, Aachen). Edited by D. Enders, H.-J. Gais, and W. Keim. Vieweg: Braunschweig; 1993, VIII + 223 pp., hardback. DM 84. ISBN 3-528-06481-1.

This book arises from a symposium on 'Organic Synthesis *via* Organometallics' held in Aachen, Germany in July 1992 but the chapters are more than reproductions of the talks given at that meeting. Most of the contributors have put considerable effort into writing clear accounts of their work including extensive referencing to the primary literature. Although phototypeset the book has been produced to a high standard. The area covered is wide including organic synthesis, asymmetric synthesis, organometallic synthesis, new materials, and mechanistic studies.

Several chapters will be of immediate interest to synthetic organic chemists. In 'Stereoselective C–C bond formation with chiral α-substituted organolithium compounds' Hoffmann describes some recent mechanistic and synthetic work using α-bromo-, -seleno-, and -thio-substituted organolithium species. He focuses on the configurational stability of these species and diastereocontrol in their alkylation reactions. Kocienski surveys a further reactivity of α-hetero-metal species in 'Synthetic applications of 1,2-metallate rearrangements'. The stereospecific migratory insertion of α-heterovinylmetallic species into carbon–copper and carbon–boron bonds is illustrated by use in total synthesis and the mechanism of the transformations discussed. In 'Organometallics in synthesis *via* radicals' Giese briefly highlights several recent advances in radical chemistry, including their generation from organocobalt and organoiron species. Bäckvall describes applications of the intramolecular palladium catalysed oxidative 1,4-addition of oxygen and nitrogen nucleophiles across dienes.

The chapter by Crabtree on 'Synthetic applications of mercury photosensitisation' should persuade many readers to find applications for this esoteric sounding method. Irradiation of refluxing organic substrates in the presence of mercury vapour affords dehydrodimers *via* C-H activation. A combination of the selective excitation of the Hg in the gas phase with the selective retention in the liquid of the reaction products avoids side reactions. The use of H atoms from H_2 as the initial radical carriers greatly extends the scope of the reaction.

The topic of asymmetric synthesis inevitably pervades the book. In 'Chiral diamines in asymmetric organic synthesis' Alexakis describes the use of C2-symmetric aminals as control elements for 1,2- and 1,4-additions with excellent results. Shibasaki covers both his work on the asymmetric Heck reaction (intramolecular cyclisation of prochiral systems) and the use of lanthanum 2,2'-dihydroxy-1,1'-binaphthyl complexes as Lewis acids for the nitroaldol reaction. Kaminsky describes the formation of trimers and tetramers of propene with high enantioselectivity using homochiral 1,1'-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium based catalysts.

New materials form the main theme of 'Synthetic aspects of the metal-mediated cyclooligomerization of phosphaalkynes (Regitz) and 'Metal containing compounds: precursors for new reactions and materials' (Roesky). Roesky introduces many unusual metal containing heterocycles including cyclophosphazenes [M–N=PR_2–N=PR_2–N=] and metallacyclosiloxanes [–R_2Si–O–TiXX'–O–]$_2$. The chapter also includes a useful survey of titanium and zirconium imido chemistry. In 'Methylidenetitanacyclobutane vs titanocene-vinylidene – versatile building blocks' Beckhaus describes structural and synthetic studies on these interesting organometallic species.

Mechanistic studies are highlighted in 'Applications of high pressure techniques in mechanistic and synthetic studies of organometallic systems in solution' (van Eldik), 'Cleavage of carbon–hydrogen bond on achiral and chiral transition metal complexes' (Dahlenburg) and 'New developments in zinc-mediated organic synthesis' (van Koten). Brookhart describes how mechanistic studies lead to the development of a class of rhodium based catalysts for the efficient tail–tail dimerisation of methyl methacrylate.

Overall this book provides interesting insights into a wide variety of chemistry, but few will find more than a minority of the subjects directly relevant. It is a 'good read' rather than a volume that will have a long lifetime as a reference work so can be recommended for library rather than personal purchase.

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