Chemical Society Reviews

Volume 25 Issue 3 Pages 155-228 June 1996



Arene-catalysed Lithiation Reactions By Miguel Yus (pp. 155-162)

The lithiation of different substrates in the presence of a catalytic amount of an arene [mainly naphthalene or 4,4'-di-*tert*-butylbiphenyl (DTBB)] allows the easy preparation of organolithium compounds under very mild reaction conditions. Using this methodology, new routes for alkyllithium compounds from non-halogenated materials (allylic alcohols, or their O-silyl or O-mesyl derivatives, alkyl sulfates or phosphates, sulfides, sulfoxides or sulfones and nitriles) as well as oxygen-, nitrogen- and sulfur-containing functionalised organolithium compounds or polylithium intermediates from chlorinated materials or saturated heterocycles (three-, four- and six-membered systems) are developed.

HT

Chiral Discrimination by Modified Cyclodextrins *By Chrisopher J. Easton and Stephen F. Lincoln* (pp. 163–170)

Naturally occuring cyclodextrins show only limited enantioselectivity in their interactions with chiral guests, because they form inclusion complexes in which there is only limited interaction between chiral centres of the cyclodextrin and those of the guest. As the extent of interaction between these groups is increased, as a result of modification to the cyclodextrin, the stereoselectivity is often increased. Additional secondary bonding interactions, complexation to metallocyclodextrins and covalent host–guest interactions all lead to enhanced chiral discrimination.

Through-bond and Through-space Models for Interpreting Chemical Reactivity in Organic Reactions *By Keith Bowden and Edward J. Grubbs* (pp. 171–178)

The relative importance of the two mechanisms considered to be responsible for localised polar substituent effects, *i.e.* the electrostatic field and inductive effects, has been disputed. There are three relatively simple model systems which can assess the reality of these effects. The results appear to be consistently explained by the electrostatic field effect, but not by the inductive effect. Other reactive consequences of the electrostatic field effect are reviewed and computational approaches illustrated.

The Chemistry of Paper Conservation By Vincent D. Daniels (pp. 179–186)

Collectables on paper contain a large number of components of varying degrees of stability. The factors that cause these to deteriorate include oxidation, acid hydrolysis, air pollutants and water. Deacidification is often used by conservators and there are beneficial effects from the introduction of Mg^{2+} and Ca^{2+} ; however, excessive alkalinity must be avoided. There are many mechanisms for the development of discolouration in paper. Several examples of ageing effects of inks and pigments are considered.



Diatomic Molecular Probes for Mid-IR Studies of Zeolites *By A. Zecchina and C. Otero Areán* (pp. 187–198)

Mid-IR spectroscopy of adsorbed probe molecules is a very active research field which contributes to a deepening of our knowledge of the local structure of zeolite active sites, and of the physico-chemical properties of the intrazeolite space. This has strong bearings on the many technological applications of zeolites and of related microporous materials. This review discusses the use of diatomic molecular probes for IR studies of Brønsted and Lewis acidity, structural defects and internal electric fields. Dual acid–base pairs are also considered.

N O



Solid State Metathesis Reaction for Metal Borides, Silicides, Pnictides and Chalcogenides. Ionic or Elemental Pathway By I. P. Parkin (pp. 199–208)

Solid state metathesis reactions offer a rapid, low external energy route to a range of inorganic ceramic materials including nitrides, oxides, pnictides, chalcogenides, silicides and borides. The reactions can be filament or bulk thermally initiated and often proceed with a thermal flash or propagation wave. The reactions can follow either an ionic metathetical or a reductive recombination pathway.

Modelling of Solvent Effects on the Diels–Alder Reaction By C. Cativiela, J. I. García, J. A. Mayoral and L. Salvatella (pp. 209–218)

This review presents a summary of the different approaches used quantitatively to describe solvent effects on Diels–Alder reactions. Basically, two methodologies are considered: on the one hand, empirical models, based on solvent parameter scales and linear regression analyses, and on the other hand, theoretical models, based on quantum chemical and Monte Carlo calculations. It is shown that both approaches lead to similar conclusions, and provide complementary information on these processes.

After the Actinides then what? By Simon A. Cotton (pp. 219-228)



More sophisticated nuclear syntheses, together with more rapid means of separation and detection, have led to the identification of elements with atomic numbers up to 111. Chemical experiments have been carried out for elements 104 and 105 (and are in prospect for 106) indicating them to be members of a 6d transition series. Chemical properties have been predicted for heavier elements but it remains to be seen if stable 'magic number' nuclei with atomic numbers around 114 can be made.

Articles that will appear in forthcoming issues include

A Radical Reappraisal of Gif Reactions M. John Perkins On the Mechanism of the Gif Reaction Derek H. R. Barton INGOLD LECTURE: Reactive Intermediates: Carboxylic Acid Enols and Other Unstable Species A. J. Kresge Photoelectron Spectroscopy in a New Light: Zero Kinetic Energy (ZEKE) Photoelectron Spectroscopy with Coherent Vacuum Ultraviolet Light John W. Hepburn The Changing Face of Arene Oxide-Oxepine Chemistry Derek R. Boyd and Narain D. Sharma New Approaches to Chemical Kinetics Barry Johnson and Stephen K. Scott Assembly and Encapsulation with Self-complementary Molecules Julius Rebek, Jr. Application of Fluorescence Microscopy to a Study of Chemical Problems R. S. Davidson Designing New Lattice Inclusion Hosts Roger Bishop Potential Energy Surface Crossings in Organic Photochemistry Fernando Bernadi, Michael Robb and Massimo Olivucci Specificity and Versatility in Erythromycin Biosynthesis Rembert Pieper, Camilla Kao, Chaitan Khosla, Guanglin Luo and David E. Cane Glutamate and 2-Methyleneglutarate Mutase: From Microbial Curiosities to Paradigms for Coenzymes B₁₂-dependent Enzymes Wolfgang Buckel and Bernard T. Golding Nitrous Acid and Nitrile in the Atmosphere Gerhard Lammel and J. Neil Cape Environmentally Friendly Catalytic Methods James H. Clark and Duncan J. Macquarrie 'Covalent' Effects in 'Ionic' Systems Paul A. Madden and Mark Wilson Non-porphyrin Photosensitisers in Biomedicine Mark Wainwright Scanning Transitiometry Stanislaw L. Randzio