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Book reviews

Organic Syntheses, Vol. 73

Robert K Boeckman (Editor-in-Chief)
Wiley, New York, 1976
353 pages. £29.95
ISBN 0–471–14701–X

Since 1921, *Organic Syntheses* has annually published recommended and tested methods for preparing key organic compounds, and the series will need no introduction to practising organic chemists. Initially decennial, and more recently quinquennial, Collective Volumes are published of the previous issues.

Volume 1 included such simple compounds as alkyl bromides, allyl alcohol, benzoin, diacetone alcohol, thiophenol and triethylamine. Volume 73 appears in the format which would be familiar to the 1921 chemist, but he would be impressed by the emphasis on stereoselectivity, and on rules for safe working and for disposal of chemicals, and by the widespread use of organometallic reagents and intermediates.

The present volume covers 28 compounds (some of which illustrate general methods), including such simple products as 2-cyclohexene-1,4-dione, 3-pyrroline, 1,3,5-cyclo-octatriene, and 4-ketoundecanoic acid, but others which are relatively complex. None of the procedures is for the synthesis of an organometallic compound *per se*, though the preparation of ethynylferrocene is given as an example of the conversion of methyl ketones to terminal acetylenes. Many, however, involve organometallic chemistry.

tert-Butyldimethylsilylation is used to protect the OH group of (4*R*)-(+)- and (4S)-(−)-hydroxy-2-cyclopenten-1-one for use in prostaglandin synthesis, and the 2-methoxymethyl ethers of 1,2,3-triols are prepared by conversion of a substituted allyl alcohol into the (allyloxy)dimethylhydrosilane, then intramolecular ring closure with a $Pt\{(CH_2{=}CHSiMe_2)_2O\}_2$ catalyst to give a 1-oxa-2-silolane, in which the C–Si bond of the ring can be cleaved by hydrogen peroxide.

Cuprous-catalysed conjugate addition of methylmagnesium bromide to a vinyl ketone in the presence of chlorotrimethylsilane gives a silylenolate which is oxidized by *m*-chloroperoxybenzoic acid under basic conditions to give a 1,3-dihydroxy-2-one, and trimethylsilyl azide can be used as a source of nucleophilic azide for the conversion of an epoxide into a 2-azido alcohol.

A number of the reactions involve intermediate lithiation. Thiol esters react with lithium di-isopropylamide ($LiNPr^i_2$; LDA) to give the lithium enolates, which condense with ketones to give β-lactones and thence, by decarboxylation, alkenes. Dibromomethane is lithiated at low temperatures by LDA to give $LiCHBr_2$, which reacts with alkyl iodides RI to give the dibromides $RCHBr_2$; these in turn react with esters in the presence of titanium tetrachloride, zinc and a catalytic amount of $PbCl_2$ to give vinyl ethers by alkylidenation of the carbonyl group.

For the lithiation of the methyl group of a methyl vinyl ketone or of a methylphosphonate, however, lithium hexamethyldisilazide, $LiN(SiMe_3)_2$, gives better yields than does LDA. *sec*-Butyl-lithium lithiates the aromatic ring of *N*-protected indolines, and the vinyl group of methoxymethyl vinyl ethers, but the more reactive *t*-butyllithium is needed for lithiating 2,3-dihydrofuran.

The most useful of H.C. Brown’s many syntheses based on hydroboration of alkenes is that where the alkylborane which is formed is oxidized with alkaline hydrogen peroxide to give the anti-Marknownikoff alcohol. The final step of this procedure has now been improved by carrying out the oxidation instead with sodium perborate, $NaBO_3{\cdot}4H_2O$. The yields and stereoselectivities are as good or better, and the reactant is stable, safe and easily handled.

A soft-cover version of *Organic Syntheses* is now also produced relatively rapidly and cheaply, and sent at no charge to the members of the Organic Division of the American and the French Chemical Societies, the Perkin Division of the Royal Society of Chemistry, and the Society of Synthetic Organic Chemistry of Japan. This hard-back version will join its predecessors in the library as a primary reference source for anyone involved in organic synthesis.

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Chiral Auxiliaries and Ligands in Asymmetric Synthesis

Jacqueline Seyden-Penne
John Wiley, New York, 1995
£55.00; $85.00 737 pp.
ISBN 0471116076

This book contains a state-of-the-art review of the use of chiral auxiliaries for asymmetric synthesis up to 1994. This is a well-timed contribution to a relatively new and exciting field of organic chemistry research which has undergone massive expansion and development over the last decade. It describes the use of chiral auxiliaries, reagents, catalysts and ligands for asymmetyric synthesis, comprehensively covering all aspects of the topic in 11 well-written chapters citing some 1700 primary references. An introduction describing the basic principles governing stereoselection is also included for the benefit of the uninitiated reader. All the principle exponents of this art have highlights of their relevant works included in ordered fashion so that contrast and comparison with other contributions to this field can be readily made. Although originally written in French, the book has been translated

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successfully into English with assistance from Professor D.P. Curran, who has been acknowledged by the author for also making helpful comments and suggestions on some aspects of the chemistry.

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Molecular Modeling of Inorganic Compounds
Peter Comba and Trevor W. Hambley

VCH, Weinheim, 1995
240 pp. £76.00
ISBN 3-527-29076-1

The claim that this book will be invaluable for everyone working in or entering the field of quantitative atomistic-based modelling of inorganic compounds is not far from the truth. An experimental inorganic chemist would have to be exceptional to enter the field solely on the basis of this book plus whatever software seemed appropriate, but most graduate students would find it invaluable for avoiding the common pitfalls as well as writing up the introductory sections of their theses.

The book has three sections: Part I, Theory; Part II, Applications; and Part III, The Practice of Molecular Mechanics, as well as various appendices including a listing of various software and force-fields. The theory section deals with parameterization, generalizing well over the various force-fields and making it clear that molecular mechanics is an interpolative procedure. The sections on various minimization methods and the multiple-minima problems are also good for their emphasis on the limitations and possible problems of such methods, and form a good antidote to the hype that can be associated with commercial modelling packages. An expert on each section could well criticize the level of coverage afforded in less than 50 pages for Part I, but this is compensated for by over 100 references.

The applications section is very wide ranging, covering structural aspects, stereoselectivities, metal-ion selectivity, spectroscopy, electron transfer, electronic effects, bioinorganic chemistry, organometallics, and compounds with *s*-, *p*- and *f*-block elements. A good grasp of the underlying inorganic chemistry is assumed, and so the main emphasis is on reporting the results and commenting critically on the approximations made. This is often quite incisive, and the theme that ‘the quality of the force-field parameters depends on good fitting of carefully chosen experimental data, and that they are not necessarily related to physically meaningful parameters’ is well established. In some more peripheral areas the coverage is rather superficial and degenerates to almost a mere listing of what has been tried on which systems. Nearly 300 references, almost 40% originating in 1990 or later, provide the entry point to most of the fields, which again, in less than 100 pages, are generally given the sort of treatment that will be useful to those in adjacent areas, but may not please all who specialize in a specific application.

The final 20-page section of practical advice on how to apply molecular mechanics to problems involving metal complexes, and how to interpret and use the results, does indeed highlight many of the common pitfalls. Nevertheless, the overall tone of the book is optimistic, and many will be interested and pleased to see how well molecular modelling can perform for carefully chosen problems, even when electronic effects are important.

This book may date more rapidly than similar books in equivalently lively research fields, because molecular mechanics methods fundamentally have to approximate electronic effects (e.g. Jahn–Teller distortions) which tend to be more important in inorganic than organic problems, a theme which is well treated in this book. State-of-the-art studies of many areas of inorganic chemistry may soon be based on quantum mechanics rather than molecular modelling, given recent advances in computer power and in computational methods which treat the electrons explicitly. However, this book is well timed for the many who want to complement their experimental ligand design work with some modelling calculations, and will provide a benchmark for the evolving quantum methods.

The book will be a great help for graduate students in the area, and provide food for thought for the experts. However, although most sections would represent a very high level of doctoral thesis, benefiting from the authors’ evident maturity in the field, there are a disconcerting number of typographical errors, equations poorly or inconsistently defined, and other signs of a rushed production that would not impress most PhD examiners. The price, £76, means that the book’s most avid users are unlikely to buy their own copies.

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