

Handbook of Grignard Reagents

G. S. Silverman and P. E. Rakita (eds)

Marcel Dekker, New York, 1996

736 pages. \$225

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Grignard reagents are of course among the most familiar of organometallic compounds, being covered by elementary as well as advanced textbooks on organic and organometallic chemistry. They continue to be of great academic interest: exactly how does magnesium react with an organic halide, and what species are present in the resulting solution or suspension? They also have important applications — hence the interest of this book to readers of this journal; not only are they important reagents for laboratory-scale organic and organometallic syntheses, but such syntheses are widely used on an industrial scale.

On the positive side, this book contains a tremendous amount of useful information, some of which is not readily available from other sources. On the other hand, the information is not always easy to locate, it is sometimes not presented in a systematic and balanced manner, and there are some surprising omissions. A fundamental weakness is that the book comprises 34 self-contained chapters, by 29 different contributors, with very little cross-referencing, some overlap, and wide variation in depth of treatment. Some assistance is given to the reader by the detailed table of contents, but the index is almost useless.

Part I of the book is a brief Introduction. Part II covers methods of Grignard preparation, including 'traditional' methods, preparations from olefins and acetylenes (by hydrometallation, carbometallation, reactions of dienes with magnesium, etc.) and magnesium activation. Part III is a useful chapter on safe handling practices for industrial Grignard reagents (but without reference to the hazards of metallic magnesium). Part IV covers analyses of Grignard reagents: wet analyses (but there is no reference to the useful Gilman qualitative tests), infrared and Raman spectroscopy, nuclear magnetic resonance and crystal structures. Part V, on mechanisms and structure–reactivity relationships, is very unbalanced. The review on mechanisms of Grignard reagent formation by Hamdouchi and Walborsky is detailed and authoritative, but at 73 pages it is out of proportion with good, but much shorter and inevitably less-detailed, accounts of mechanisms of carbonyl addition and related reactions, structure–reactivity relationships, and the Schlenk equilibrium and its effect on reactivity; then there is a full chapter on the effect of tris(pyrazolyl)hydroborato ligation — interesting, but scarcely mainstream.

The least satisfactory part of the book is Part VI, on general reactions of Grignard reagents. While some of the chapters are good, on the one hand there is too much overlap (for example, between the chapter on nucleophilic addition to unconjugated carbon–carbon multiple bonds

and the one in Part II, referred to above, covering carbometallation); on the other hand, in several chapters the subjects are covered so sketchily as to be uninformative or even misleading. For example, anyone inexperienced in the area, and seeking information on reactions of Grignard reagents with nitriles, would be given no hint of the potential complications of these reactions from the mere half-page devoted to the subject.

Finally, Part VII comprises reviews, generally of a high standard, but again very uneven in terms of length and depth of coverage, on special topics: the Barbier reaction; Grignard reagents as bases; S_N2 versus S_N2' (reactions of allylic compounds, etc.); alkynyl Grignard reagents and their uses; Grignard reagents and silanes; Ziegler–Natta catalysis; and organomagnesium compounds as polymerization initiators.

Anyone hoping to find in this *Handbook of Grignard Reagents* a worthy successor to Kharasch and Reinmuth's classic *Grignard Reactions of Nonmetallic Substances* will be disappointed, and it cannot be recommended as an introduction to the subject. However, it does contain some excellent reviews, and specialists in the area will find it useful to have them collected together.

One final grumble: why, in a book costing \$225, can the publisher not ensure that the structural formulae are of good quality and in a uniform style?

B. J. WAKEFIELD

*Ultrafine Chemicals, Manchester***Principles of Process Research and Chemical Development in the Pharmaceutical Industry**
O. Repič

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xvi + 213 pages. Hard cover £60

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This book is about process and development chemistry — essential topics linking medicinal chemistry with industrial scale-up in the pharmaceutical industry.

The author starts and ends the book with two very important themes in process chemistry. Firstly, the reader is introduced to the safety and economics of industrial scale-up with poignant examples demonstrating that the judicious choice of solvents, catalysts and reaction conditions can markedly influence both the economics and safety of all reactions.

Subsequent chapters cover important considerations in scale-up. These include understanding and troubleshooting impurity profiles and by-product generation, and guidelines for successful asymmetric synthesis taking a known hypocholesteremic agent as an example. This chapter contains examples of organosilicon and organoboron intermediates. Practical methods such as prefer-