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Book Review

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The chemistry of organolithium compounds (two volume set)

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This book is another addition to the excellent 'Patai' series on the *Chemistry of Functional Groups*, which happily continues after more than 40 years, despite the sad death of the series founder in 1998. Zvi Rappoport, who had co-edited many volumes with Saul Patai, has seamlessly taken over editorship of the series, which continues to provide an invaluable source of reference for practising chemists. For this particular volume, Rappoport is joined as co-editor by Ilan Marek, and together they have assembled an impressive team of writers to cover a topic that over the last few decades has grown enormously, to the extent that it now dominates the field of 'reactive' main group organometallic reagents.

The two-volume set is divided into 18 chapters and the volume editors indicate that they hope that three other commissioned chapters, on the dynamic behaviour of organolithium compounds, on chiral alkyllithium amides and on intramolecular carbolithiation reactions, will appear in a future volume. While it is surely the case that these three chapters would have rendered the volumes more complete, what is provided in the existing 18 chapters is still a prodigious amount of information about most aspects of organolithium chemistry.

As usual for this series, the treatment begins with theoretical studies (written by E. D. Jemmis and G. Gopakumar), which includes studies of the nature of the C–Li bond, of structures and energies of organolithium compounds, and of reactions and applications of organolithiums. This is followed by an extremely useful and informative, if somewhat confusingly titled, chapter on 'Lead structures in lithium organic chemistry' (T. Stey and D. Stalke), which is primarily a description of the experimentally determined structures of organolithium compounds, accompanied by a narrative to help the non-expert appreciate the effects of aggregation, complexation, side-chain coordination and other such factors. A short (just 16 pages) chapter on thermochemistry (S. W. Slayden and J. F. Liebman) then serves as a source of reference for data on molar standard enthalpies of formation of organolithium compounds, and as a wise counsel on the limitations of the available data, given that often there is a lack of reliable data on phase transition enthalpies, state of aggregation, etc.

There follow three chapters devoted to specific techniques that can be used to probe the structures of organolithium compounds: solid-state NMR spectroscopy (D. Johnels and H. Günther), mass spectrometry (though the chapter is somewhat misleading given the much broader heading of gas-phase chemistry; C. Denekamp) and vibrational spectroscopy (I. Powel, W. Kiefer and D. Stalke); a chapter on the effects of structural variation on organolithium compounds (M. Charton); and a very useful overview chapter on the analysis of organolithium compounds (J. Zabicky). Together, the first eight chapters provide state-of-the-art insight into the structures of organolithium compounds, the methods of obtaining structural information, and the problems associated with both the acquisition and interpretation of such information.

The remainder of the work comprises 10 chapters devoted to the chemistry of organolithium compounds, notably the methods for their preparation and the reactions they undergo. In particular, Chapters 9–11 supply the fundamental information that is essential for anyone wanting to make use of organolithium reagents. Chapter 9 (F. Leroux, M. Schlosser, E. Zohar and I. Marek) is an erudite synopsis of the major approaches to preparation of organolithiums and provides considerable insight into how to choose the optimal approach. With extensive use of tables (24 of them, many occupying a full page) and references (eight pages of them), the authors have managed to compress the chapter into under 60 pages, but every page is packed with useful information. As befits the importance of directed metallation of aromatic compounds in modern synthetic chemistry, Chapter 10 (J. Clayden) is the longest chapter in the work, running to over 150 pages. It combines information about the metallation step itself with examples of the synthetic uses to which the organolithium reagents so generated are put. With over 500 references it provides broad coverage of this major topic, but the literature is so extensive that it still cannot be comprehensive. Chapter 11 (M. Yus) describes the use of aromatic compounds such as naphthalene and 4,4-di-*tert*-butylbiphenyl (i.e. compounds capable of reacting with lithium metal to form free-radical anions) to catalyse reactions between lithium metal and a whole range of organic substrates capable of generating organolithium species, which are then trapped with appropriate electrophiles. Interestingly, many of these catalysed reactions are faster than their stoichiometric counterparts, possibly pointing to the involvement of dianions as electron carriers, and the field seems to be growing in importance.

The remaining chapters are more specialized. Chapter 12 (K. Tamooka) is on rearrangements of organolithium compounds; Chapter 13 (M. Braun) is on lithium carbenoids; Chapter 14 (H. Yamataka, K. Yamada and K. Tomioka) is on addition of organolithium reagents to double bonds; Chapter 15 (C. Strohmann and D. Schildbach) is on polylithium compounds: syntheses and selected structures; Chapter 16 (R. E. Gawley and I. Coldham) is on α-amino-organolithium compounds; Chapter 17 (D. Hoppe and G. Christoph) is on asymmetric deprotonation with alkyllithium–(−)-sparteine; and Chapter 18 (F. Chemla and E. Vrancken) is on reactivity of oxiranes with organolithium agents. All are extremely valuable sources of information about these topics, but just two will be singled out for particular mention, because of the synthetic potential of the chemistry described. α-Amino-organolithium compounds (Chapter 16) gain importance as a sub-class of organolithium compounds because of the prevalence of nitrogen atoms in natural products and biologically active compounds. The chapter provides an interesting overview of the preparation, stability and reactions of these interesting reagents. Asymmetric deprotonation (Chapter 17) is a topic of the moment, therefore justifying the chapter's 110 pages of thoughtful and informative text.

All in all, then, this is an astonishingly useful set of volumes for anyone interested in synthetic chemistry. The price tag may deter all but the most dedicated from purchasing a personal copy, but it should be a high-priority purchase for any library serving the needs of synthetic organic chemistry. It is a credit to the Patai series.

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