Book Reviews

Active Metals(Preparation, Characterization, Applications). Edited by A. Fürstner. VCH: Weinheim, 1995, 464 pp, hardback. DM 248. ISBN 3 527 29207 1.

According to an old believing, the use of organometallic derivatives in synthetic organic chemistry is still an area reserved to *experts* and thus, only the chemist who has this formation can synthetically use these compounds. The aim of this book is to demystify this wrong principle. Moreover, it shows us that the synthesis and use of these derivatives result, in fact, from the knowledge of the different parameters necessary for the elaboration of these compounds. Indeed, in the first chapter, the description of highly reactive metal powder, known to insert at low temperature into the carbon-halogen bonds, is easily prepared by alkali metal reduction of metal salts. The efficiency of this method is shown on a large variety of substrates. Then, the practical methods for generating polysubstituted allylic barium reagents are described and the subsequent reaction of these anions with electrophiles in regio- and stereoselective way was performed. The main feature of this present strategy is the absence of metallotropic equilibrium of allylic barium at low temperature and the selective reaction of this latter in α-position with complete retention of the stereochemistry of the starting material. The third chapter describes the important new developments in the Mc Murry reaction and this chapter has been divided into four subgroups; a) the Mc Murry alkene synthesis, b) the Mc Murry keto ester coupling, c) the Mc Murry pinacol synthesis and d) the Mc Murry benzyl radical coupling. In the following chapter, the possibilities offered by the use of the sonochemistry for metal activation were elegantly demonstrated. Ultrasound offers inherent advantages compared with other activation agents and the methodology described in this chapter has proven to be safe, quick, easy to produce active materials under mild conditions and allows the metal-assisted reactions in water. The purpose of chapter five is to present the various preparative methods available for the synthesis of polyfunctional organozinc reagents. The low reactivity of zinc organometallics, which was perceived by organic chemists of the first half of this century as a disadvantage, turned out to be a formidable advantage in the concept of selectivity. The remaining reactivity problem can be solved in the presence of the appropriate catalyst to give the alkylated product in good overall yield. Moreover, the use of polyfunctional diorganozincs in asymmetric synthesis using a chiral titanium catalyst gives to this methodology a powerful impact. In chapter 6, the solvated metal atom dispersion method of preparing activated metals in the form of nanoscale particles was exposed and several interesting advantages were pointed out. The development of electrochemical syntheses of transition metals clusters stabilized by tetraalkylammonium or phosphonium salts is described in chapter 7. The salient feature of these types of metal colloid synthesis is in the high yield, absence of undesired side-products such as metal hydrides, easy isolation and in the variation of solubility by the proper choice of ammonium salt. In chapter 8, the magnesium route to active metals as a novel synthesis route for organic and inorganic materials was described and involves as a common characteristic magnesium metal or magnesium compounds in the initial preparative process. By this way, various organomagnesium derivatives were prepared in high chemical yield as well as the preparation of inorganic Grignard reagents and their applications in inorganic synthesis. The following chapter establishes that metals and metal alloys of 10 to 100 nm particle size are accessible through the chemical reduction of metal salts or metal oxides with hydrotriorganoborates. These particles are also of special interest as catalyst for hydrogenation in both the homogeneous and heterogeneous phases. In chapter 10 are delineated the different arguments for and against the immobilization of an activated metal on an inert support and by this way, the criterias which need to be considered for choosing the proper carrier for a particular metal are exposed. Finally, in the last chapter, a conclusive view is given on the actual structure of metal-graphite combinations which are prepared by the reduction of metal halides by C8K in THF solution. The material in this book is a very appropriate summary of the knowledge that anyone involved in organic chemistry who is a nonspecialist in organometallic chemistry might be expected to have. It is highly recommended as a text for PhD students or for professionals who want to have a readable but accurate overview of the organometallic field with recent examples.

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Synthetic Methods of Organometallic and Inorganic Chemistry, Volume 3. By H. H. Karsch. Edited by W. A. Herrmann. Thieme: Stuttgart, 1996, 228 pp, hardback. DM 185. ISBN 3 13 103041 8.

This is the third Volume of a new series that is a modernized, English-language version of a classic German language compendium, Georg Brauer's "Handbuch der Präparativen Anorganischen Chemie". Volumes 1 and 2 were reviewed earlier [*Synthesis* **1996**, 1402; *Synthesis* **1997**, 372], together with general features of the series. This review covers Volume 3, which features a brief introduction and five main chapters: acyclic phosphorus(III) compounds (64 pages), acyclic phosphorus(V) compounds (26 pages), acyclic compounds with two or more phosphorus atoms (50 pages), cyclic phosphorus compounds (32 pages), and arsenic, antimony, and bismuth compounds (26 pages). The introduction includes a reminder on safety precautions, and cross references all phosphorus, arsenic, and bismuth containing compounds in Volumes 1 and 2 – such as the section on "commonly used starting materials" in Volume 1. The chapters within Volume 3 are also completely cross referenced.

Overall, this is an especially timely and topical volume. There is hardly a field of preparative chemistry – from commodity chemicals through fine chemicals to pharmaceuticals – where the design and synthesis of new organophosphorus compounds is not actively being pursued. These efforts include targeting solubilities in aqueous, organic, and fluorous media, and the construction of well-defined chiral environments. Accordingly, the contributions in this volume originate from a broad spectrum of experts, all of whom are leaders in their fields, and vividly convey the breadth of modern group 15 chemistry.

A number of themes run throughout various chapters or the entire volume. For example, the many types of compounds with multiple bonds to phosphorus include phosphaacetylenes and phosphaethenes (first main chapter), diphosphenes and 1,3-diphosphaallene (third chapter), and 1,3-diphosphacyclobutadienes and phosphabenzenes (fourth chapter). The very useful $E(TMS)_3$ reagents (E = P, Ar, Sb, Bi) are described in the first and fifth chapters. It seems somewhat incongruous to find diphosphiranes (diphosphacyclopropanes) in the chapter on acyclic compounds with two or more phosphorus atoms. However, a more rigid standard would fragment many multistep sequences, or scatter contributions from one laboratory.

Noteworthy preparations for the synthetic organic community would include the parent Wittig reagent $Ph_3P{=}CH_2$ and Verkade's highly basic bicyclic tetraaza phosphines. A variety of cyclopentadienyl- and "supermesityl"- substituted phosphorus compounds are also described. Procedures for lithium salts of diphosphaallyl anions are given. A potpourri of transition metal complexes are detailed in passing. The antimony and bismuth compounds that round out the volume are of more specialized interest, but represent an area that could grow considerably over the next decade. The only conspicuous omission is the absence of non-racemic compounds, an important part of contemporary research in this field.

The volume is richly illustrated with detailed renderings of apparatuses, especially for the technically more difficult procedures. It contains a subject index as in previous volumes, and is further enhanced by the inclusion of a formula index. As in any ambitious undertaking of this sort, there are minor oversights. Nonetheless, it is an immensely useful compendium. All readers will want to have the same access to this eight-volume series as they have to "Organic Synthesis", "Fieser and Fieser", and the more recent "Encyclopedia of Organic Reagents".

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