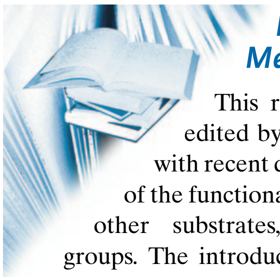
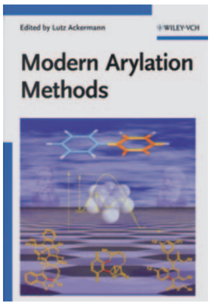


Modern Arylation Methods



Modern Arylation Methods
Edited by Lutz Ackermann.
Wiley-VCH, Weinheim 2009.
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This recently published book edited by Lutz Ackermann deals with recent developments in the area of the functionalization of aromatic and other substrates, specifically by aryl groups. The introduction of aryl groups (or the functionalization of aryl groups if one looks at it the other way) can be regarded as one of the "hot spots" of synthetic chemistry over the last two decades, especially in relation to the discovery and further development of transition-metal-catalyzed reactions. The first chapter contains a rather short, but concise and very readable introduction to the historical development of arylation reactions. Most of the other 14 chapters deal with reactions of the cross-coupling type and direct (C–H) or heteroatom–H arylations in the broadest sense. In addition, arylation reactions that use arynes, free-radical methodology, and photochemistry are discussed. In most of the chapters the literature is reviewed up to the year 2007, in some cases even to 2008, which makes it an up-to-date book.

Following the introduction, in Chapter 2 Littke describes recent advances and trends in transition-metal-catalyzed coupling reactions of relatively inert arenes such as aryl chlorides, tosylates, and fluorides. In addition to the rather dry listing of different catalyst systems, one might wish every once in a while to read some mechanistic explanations, because not all reactions follow the textbook cross-coupling mechanistic scheme. In Chapter 3, Schlummer and Scholz give a very clear description of the palladium-catalyzed arylation of amines (Hartwig–Buchwald reaction) and C–H acidic compounds. The comparable copper-catalyzed arylations of amines and alcohols using boron-based reagents are described by Thomas and Ley in Chapter 4, including details of the different catalyst systems used.

Chapter 5 by Nakamura and Ito deals with the still developing area of transition-metal-catalyzed cross-coupling reactions of aryl compounds with alkyl halides or pseudohalides, where significant advances have been made in recent years. The Sonogashira reaction, reviewed in Chapter 6 by Viciu and Nolan, has already come of age and has become established as the most versatile method for the formation of C(sp)–C(sp^2) bonds. The authors also describe some alternative catalyst systems in addition to the usual ones. In Chapter 7 on the arylation of alkenes, Trepohl and Oestreich give a detailed description of the Mizoroki–Heck and related reactions, including stereoselective versions of the reaction. Chapter 8, by Defieber and Carreira, is concerned with stereoselective catalytic arylations, in particular with addition reactions of aryl groups to carbonyl compounds, which are especially important as the enantioselective arylation of aldehydes and imines gives access to a number of pharmacologically interesting compounds.

The following three chapters are devoted to the transition-metal-catalyzed direct arylation methodology, which has recently attracted tremendous interest because of the possibility to directly functionalize C–H bonds of a substrate without the need for an organometallic coupling reagent. It was an excellent idea to split the topic into three chapters: while Ackermann and Vicente in Chapter 9 summarize direct arylations catalyzed by the late transition metals, excluding palladium, Miura and Satoh deal in depth with palladium-catalyzed direct arylations, especially for the preparation of biaryls (Chapter 10). The mechanistic background of both chapters is then discussed and compared in Chapter 11 by de Mendoza and Echavarren, giving the reader an impression of the diversity of this area.

In the extensive Chapter 12, Chen and Larock provide an update on the use of arynes for the functionalization of arenes. This section turns out to be a treasure trove, as arynes show some interesting reactive properties, so that in some cases they can even serve as alternatives to transition-metal-catalyzed reactions. The final two chapters, Chapter 13 on free-radical arylations by Vaillard, Schulte, and Studer, and Chapter 14 on photochemical arylations by Dichiarante, Fagnoni, and Albini complete the book with interesting contributions on methods in which the focus shifts away from transition metal complexes.

Although many aspects of (modern) arylation methods have already been covered separately by reviews in the primary literature, this book is an important contribution as a very readable and informative compilation of the current state of knowledge. The quality of the chapters is in general high, and the presentation of data in tables and schemes where necessary is very helpful for the reader to obtain a view of the field as a whole. The choice of topics to be covered in a book is, as always, difficult in such a dynamic and fast-growing topic as arylation reactions. However, one might have wished to find a more detailed treatment of cycloaddition reactions for the de novo synthesis of aromatic systems, for example, by the [2+2+2] cycloaddition reaction, which is only mentioned briefly in Chapter 12. The book is recommended to readers who seek an inspiring source of information on the highly topical area of arylation reactions.

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