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Introduction

Polysubstituted benzenes are widely used both in industry and in research laboratories. Regioselective construction of polysubstituted benzenes is usually achieved through the gradual introduction of substituents in the aromatic ring by Friedel–Crafts reaction or similar reactions of electrophilic substitution or through organometallic synthesis. In 1948, Reppe reported the \([2+2+2]\) trimerization of substituted acetylenes in the presence of transition metals to form polysubstituted benzenes (Scheme 1.1) [1].

Transition metal catalyzed cycloaddition reactions enables facile design of blocks of highly functionalized molecules in a single step. Reactions of \([2+2+2]\) cycloaddition of alkynes are an effective method for the formation of substituted arenes and nonaromatic rings, as described in a monograph [2] and reviews [3–9]. However, high regioselectivity and good yield can be achieved using the right choice of reagents and synthetic routes. Another promising methodology consists in the construction of the benzene ring in a \([4+2]\) reaction of conjugated enyne with alkyne in the presence of a Lewis acid [10, 11] or by the transition metal catalyst [2, 12, 13]. More recently, it was shown that the construction of the benzene ring may proceed using dienynes, triynes, and tetryynes [3, 14, 15]. Similar approaches can be used for the creation of naphthalene and other condensed aromatic systems, for example, acenes.

Many articles have been published on the formation of substituted arenes by this type of reaction in the presence of transition metals. The current development of the field of organic synthesis focuses on the design of intermolecular substituted arenes, which makes it possible to control the construction of a precursor in the synthesis of the product.
ALKYNES IN CYCLOADDITIONS

Scheme 1.1

There is a problem of stereoselectivity in the synthesis of arenes by intramolecular [2+2+2] cycloaddition.

The thermal reaction of benzannelation of enediynes, the Bergman cycloaromatization, that occupies a special place, has been intensively studied [16]. These methods include also the less studied Myers–Saito [17] and Schmittel [18] cycloaromatization. Cycloaromatization of enediyne and enyne-allene blocks is described in books [19–23] and reviews (Scheme 1.2) [24–30].

During the study of systems containing (Z)-hex-3-en-1,5-diyne and (Z)-hepta-1,2,4-triene-6-yne blocks, a new methodology of organic synthesis was created, which involved one-pot synthesis of aromatic structures. These comprised β-substituted naphthalenes, linearly fused acenes, fulvene, and indene systems, as well as helical structures, spherical poly-cyclic aromatic hydrocarbons, the building blocks for the construction of fullerenes, and finally, condensed heterocycles containing O, N, and S atoms [26–32]. Polycyclic aromatic hydrocarbons and related compounds containing one or more heteroatoms are important to many areas of chemistry and material science as a basis for new materials [23, 27]. A specific role of diacetylene systems involves fundamentally new approaches to obtaining nanostructures based on cascade reactions.

Scheme 1.2 Intermediate biradicals in the Bergman and Myers–Saito cyclization reactions.
INTRODUCTION

Such syntheses are difficult by classical methods [30–32]. Chemical modifications of triple carbon–carbon bonds in reactions such as nucleophilic addition and cycloaddition lead to a wide range of new heterocycles, that cannot be synthesized by other routes [33–37]. This area of chemistry of acetylene compounds is extremely promising since it complements earlier methods. New methodology for the formation of cyclic systems based on cycloaddition reactions of acetylene units has been described in the recent literature; works published in the years 2000–2012 are considered in detail in Chapter 2.

Many of these reactions have attracted the attention of researchers due to the fact that these processes occur in the body during the application of anticancer drugs containing an enediyne block. Chapter 3 is devoted mainly to the analysis of papers related to the study of the cyclization mechanism. Chapter 4 includes additional material on cycloaddition with acetylenic units or those sourced from acetylenic compounds, leading to the formation of carbo- and heterocycles of different structures. The concluding Chapter 5 includes some recent results.