



Digest paper

Transition metal-free formal [2+2+2] cycloaddition reactions of alkynes



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ARTICLE INFO

Article history:

Received 4 August 2016
 Revised 26 September 2016
 Accepted 21 October 2016
 Available online 24 October 2016

Keywords:

Alkynes
 [2+2+2] cycloaddition
 Cyclotrimerization
 Condensation reactions
 Transition metal-free reactions
 Dehydro-Diels-Alder reactions
 Domino reactions

ABSTRACT

Cyclotrimerization reactions of alkynes and their oligomers with themselves or other heterocumulenes are usually performed by stoichiometric or catalytic mediacy of transition metal complexes. However, a number of transition metal-free variations have appeared, ranging from stepwise cyclizations of alkynes or oligoalkynes under rather drastical reaction conditions to trimeric condensation reactions of ketoalkynes under amine catalysis and finally uncatalyzed cyclizations of oligoalkynes under partially rather mild conditions. Consequentially a range of different reaction conditions and mechanism are involved in these transformations. The presented digest accounts selected examples of such transition metal-free formal [2+2+2] cycloadditions and exemplarily discusses their mechanistic course of action.

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Introduction

The transition metal-catalyzed [2+2+2] cycloaddition reaction has evolved over the last decades into a matured technology for a large range of structurally different mostly aromatic carbocycles and heterocycles [1,2]. Throughout the whole range early as well as late transition metals can be mediated this particular transformation, including a variety of reaction mechanisms with large or only minor similarities. The reaction commemorates its discovery 150 years ago by Berthelot, who observed the (metal-free) uncatalyzed cyclotrimerization of acetylene at rather higher tempera-

tures (400 °C), while Sir Ramsey applied most presumably heterogeneous catalysis to combine acetylene and HCN to form pyridine as one of the products (Fig. 1) [3]. Brought to the stage of catalysis as a highly useful tool for the synthesis of organic molecules first by the work of Reppe et al. (Fig. 1, bottom) [4], subsequent investigations by Vollhardt et al. uncovered the potential for total synthesis [5]. In recent years the inclusion of stereoselectivity into the cyclization by using chiral catalyst systems has added further usefulness to this type of reaction [2a,6]. Ever since especially the members of group 9 of the transition metals (Co, Rh and Ir) are foremost utilized catalyst metals [7].

Due to the expanding application of transition metal-catalyzed cyclotrimerizations extensive computational studies on their mechanisms have been performed, uncovering general mechanistic schemes, which have metallacyclopentadienes as a common

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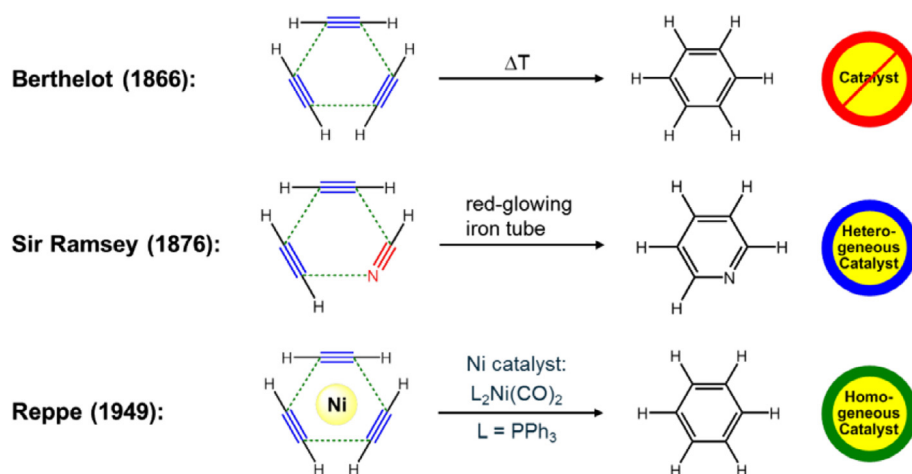


Fig. 1. Historic development of the cyclotrimerization reaction.

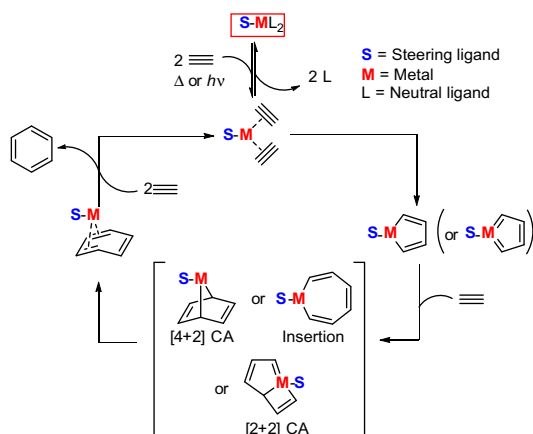
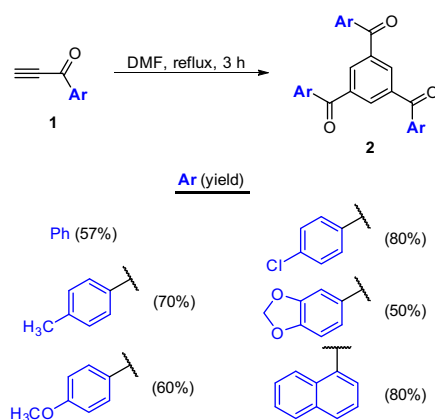


Fig. 2. General catalytic cycle for transition metal-catalyzed [2+2+2] cycloaddition reactions (CA = cycloaddition).

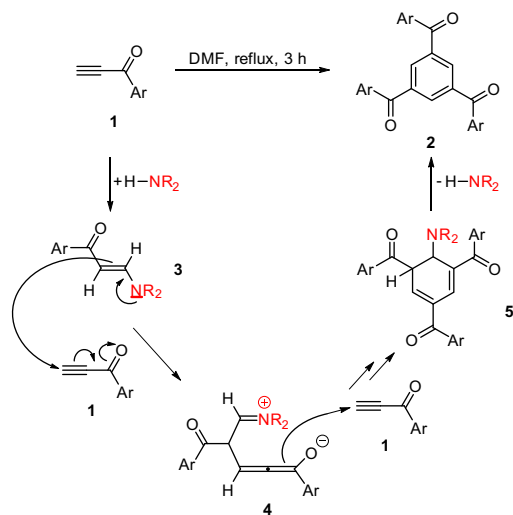
and frequently observed reaction intermediate [8]. However, individual and fine-tuned differences do exist between the different metals on structurally related intermediates. A general mechanistic scheme applicable as a blueprint for many cyclotrimerization reactions of alkynes is depicted in Fig. 2.

However, the initial discovery made by Berthelot, who heated acetylene in a closed vessel and observed the formation of benzene beside other hydrocarbons with higher molecular weight, led to the unveiling of uncatalyzed cyclotrimerization reactions [3]. According to the Woodward-Hoffmann rules this reaction is a thermally allowed [2+2+2] cycloaddition [9]. While the cyclotrimerization of acetylene to yield benzene is highly exothermic (experimental data: $\Delta H^0 = -143$ kcal/mol), the successful reaction requires to overcome a rather large activation barrier of at least 36 kcal/mol [10]. The exact mechanism of the particular reaction with a proposed concerted process of bond connection and the degree of the therefore expected aromatic transition state has been the subject of several theoretical studies [11].

The cyclotrimerization reaction has been experimentally investigated by Vollhardt et al. in their remarkable work on the rearrangement of 1,5,9-cyclododecatriyne to hexaradialene. Here the intramolecular [2+2+2] cycloaddition seems to be the simplest possibility to assemble the aromatic benzene core [12]. The results of their studies including the utilization of ^{13}C -labelled compounds, corroborated the theoretical prediction that direct thermal cyclotrimerizations are not simply feasible reactions.



Scheme 1. Cyclotrimerization of aryl ethynyl ketone yielding triarylbenzenes in DMF.



Scheme 2. Reaction pathway for the amine-mediated cyclotrimerization of aryl ethynyl ketones.

In recent years beside the intense development of transition metal-mediated cycloadditions several possibilities of performing formal [2+2+2] cycloadditions have been reported. The following discussed examples should demonstrate the variety of different

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