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Digest paper

Recent advances in transition-metal-catalyzed asymmetric reactions of diazo compounds with electron-rich (hetero-) arenes

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The transition-metal-catalyzed reaction of diazo compounds with arenes or heteroarenes is an efficient and straightforward approach to functionalize aromatic compounds. This digest summarizes recent progresses on transition-metal-catalyzed asymmetric reactions of diazo compounds with electron-rich (hetero-) arenes, including C–H functionalization, cascade reaction, cyclopropanation, cycloaddition, Buchner reaction and intramolecular dearomatization.

Contents

Introduction

Diazo compounds, featuring two linked nitrogen atoms as a terminal functional group, define a fundamental unit of organic compounds. Studies toward the preparation and transformation of diazo compounds have been going on for over a century, and are still flourishing in modern organic synthesis.[1] Diazo compounds are easily decomposed by late transition-metals (e.g. Cu, Rh, Pd) to generate metal carbenes or carbenoids through extrusion of nitrogen (Scheme 1).[1,2] The highly active metal carbenes generated from diazo compounds easily undergo various transformations, including X-H bond insertion, cyclopropanation, cyclopropenation,

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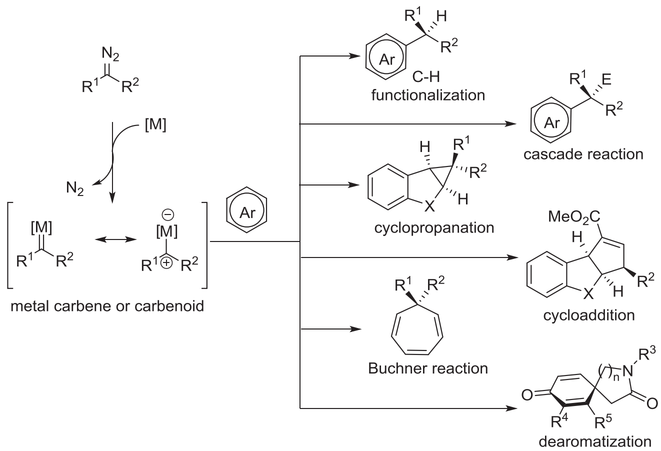


Scheme 1. Outline of the transition-metal-catalyzed reactions of diazo compounds with electron-rich arenes or heteroarenes.

ylide rearrangement and so on. Although the transition-metal-catalyzed carbene transfer reactions have been frequently reviewed,[2] the carbene transfer reactions with electron-rich arenes or heteroarenes have rarely been systematically summarized. In fact, numbers of transformations of diazo compounds with electron-rich arenes or heteroarenes, including C—H functionalization, cascade reaction, cyclopropanation, cycloaddition, Buchner reaction and intramolecular dearomatization can be promoted enantioselectively by transition-metal catalysts (Scheme 1). These reactions can produce useful chiral building blocks from easily accessible starting materials and now become a new growth point in diazo chemistry. To give the interested readers a brief reference, this digest reviewed the significant progress in this field made since 2010. The pioneering attempts before 2010 were referred but not discussed in detail here.

CH functionalization

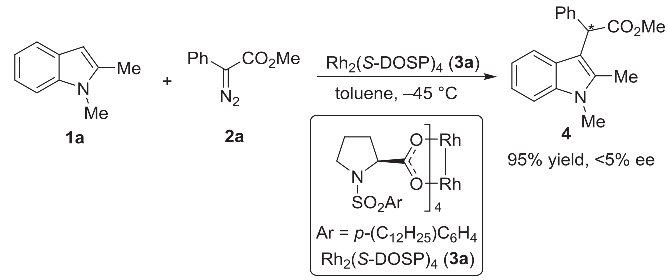
C—H functionalization of electron-rich heteroarenes

Transition-metal-catalyzed direct C—H functionalization of aromatic rings by diazo compounds is a remarkable approach towards functionalized benzenes and heteroarenes. Various strategies and catalysts were disclosed for this transformation in recent decades.[3] This type of reaction generally starts with a nucleophilic attack of the electron-rich arenes or heteroarenes to the in situ generated metal carbene intermediates from diazo compounds.

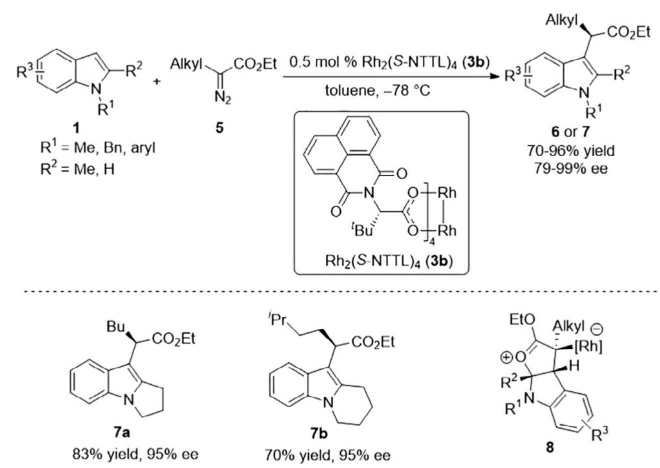
In 2010, Davies and co-workers[4] disclosed a Rh_2(*S*-DOSP)$_4$ (**3a**)-catalyzed C—H functionalization of 1,2-dimethylindole **1a** with methyl phenyldiazoacetate **2a**; however, very poor asymmetric induction (<5% ee) was observed (Scheme 2).

Soon after, Fox and co-workers[5] reported a highly enantioselective C—H functionalization of *N*-protected indoles **1** with α-alkyl-α-diazoesters **5** (Scheme 3). Rh_2(*S*-NTTL)$_4$ (**3b**) was found to be the optimal catalyst, which afforded C3 functionalized indoles **6** in high yields and enantioselectivities across a wide array of substrates. When R^1 and R^2 were tethered, the fused indoles also gave satisfactory results (e.g. **7a** and **7b**). A cyclopropanation/fragmentation pathway for this reaction was ruled out by experimental and computational studies. Alternatively, a mechanism involving a Rh-ylide intermediate **8** with oxocarbenium character was proposed.

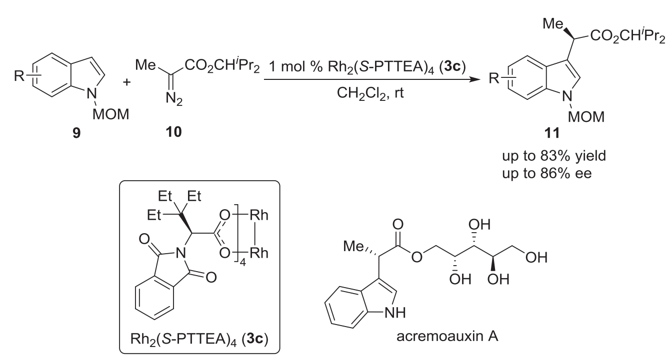
In Fox's study,[5] 2-substituents of indoles (typically, R^2 = Me, Scheme 3) were needed for high enantioselectivity. Hashimoto and co-workers[6] disclosed that Rh_2(*S*-PTTEA)$_4$ (**3c**) exhibited a better performance than **3b** in the C—H functionalization of 2,3-unsubstituted indoles **9** with α-diazopropionates **10** (Scheme 4). Both methoxymethyl (MOM) protecting group on indoles and the 2,4-dimethyl-3-pentyl moiety of the α-diazopropionates were found to be crucial to the reactivity. This reaction enabled the asymmetric synthesis of the (+)-α-methyl-3-indolylacetic acid, a fragment of the plant-growth inhibitor acremoauxin A.



Scheme 2. Rh_2(*S*-DOSP)$_4$-catalyzed C—H functionalization of indoles.



Scheme 3. Rh_2(*S*-NTTL)$_4$-catalyzed C—H functionalization of indoles.



Scheme 4. Rh_2(*S*-PTTEA)$_4$-catalyzed C—H functionalization of 2,3-unsubstituted indoles.

In 2012, Fox and co-works[7] developed a mixed-ligand dirhodium complex Rh_2(*S*-PTTL)$_3$TPA (**3d**) as an efficient catalyst in asymmetric cyclopropanation and cyclopropenantion of α-alkyl-α-diazoesters with olefins and alkynes. In the C—H functionalization of 4-substituted indole **12** with ethyl α-diazobutanoate **5a**, catalyst **3d** was superior to its parent catalyst **3e** in terms of both yield and enantioselectivity (Scheme 5).

Davies and co-workers[8] reported an asymmetric C—H functionalization of indoles **1** with methyl (*E*)-vinyldiazoacetate **14**