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Review

Recent advances of catalytic processes on the transformation of alkynes into functional compounds

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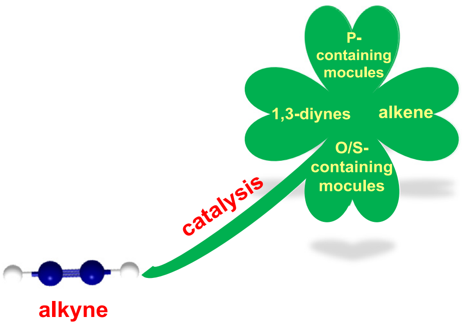
HIGHLIGHTS

- Recent advances on catalytic processes for alkynes transformation are reviewed.
- Processes for hydrogenation, cross coupling and functionalization are discussed.
- Advantages and disadvantages of the processes are systematically compared.
- Development trends for catalytic transformation of alkynes are delineated.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkynes are important raw materials for the generation of a variety of useful organic compounds through the construction of new C—C, C—H or C—X bonds. Although relatively low in thermodynamic reactivity, alkynes can be readily and selectively activated in the presence of functional groups under mild conditions. The activation is done by means of metal or metal-free catalysis through either selective alkyne $C\equiv C$ bond or terminal alkyne C—H bond reactions. From the standpoint of green chemistry, it is desirable to develop catalytic processes for the transformation of alkynes that have the least impact on our environment. In this mini-review, we summarize the progresses of alkyne transformation to functional substances in the past six years, with emphasis on the results generated in our research group: heterocoupling of terminal alkynes into unsymmetrical 1,3-diynes, selective hydrogenation of alkynes with formic acid or hypophosphorous acid, and functionalization of alkynes by O-, P-, or S-containing molecules. The advantages and disadvantages of these processes and the effects of reaction conditions are systematically described. Moreover, the catalysts adopted for these processes are illustrated and compared. Finally, we make a prediction on the processes that have potential for industrial applications in the near future.

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Contents

1. Introduction

As a class of unsaturated hydrocarbons, alkynes containing at least one C≡C triple bond are important raw materials in organic synthesis. Composed of one sigma bond and two π-bonds, a C≡C triple bond is strong: 369 kJ/mol from the σ-bond and 268 and 202 kJ/mol, respectively, from the first and second π-bond, giving C≡C bond strength of 839 kJ/mol. In other words, alkynes are thermodynamically low in reactivity. Nonetheless, they can be readily and selectively activated through selective alkyne C≡C bond or terminal alkyne C—H bond reactions (Ritleng et al., 2002).

In the past decades, the catalytic activation and transformation of alkynes have attracted much attention and much progresses have been made, including alkyne hydrogenation (Crespo-Quesada et al., 2012; Biffis et al., 2016), alkyne coupling (Trost and Cregg, 2015; Trost et al., 2015), and so on (Nakamura and Yamamoto, 2004; Patil and Yamamoto, 2008; Dondoni and Marra, 2014). These developments focus on atom-economic transformation where minimal or no theoretical by-products are formed. For example, Negishi et al. (2010) regarded that the elementometalation-Pd-catalyzed cross-coupling approach is a green route that is high-yield, efficient, selective, economical, and safe for the synthesis of all conceivable types of acyclic alkenes. Alkyne hydrothiolation is also regarded as a powerful protocol for the synthesis of S-containing molecules (Corma et al., 2010; Di Giuseppe et al., 2012; Singh et al., 2013). There are other novel methods or processes reported for alkyne transformation (Chinchilla and Najera, 2013; Zeng and Dong, 2015), many of which are orthogonal to biological condition. These modern catalytic alkyne reactions are much more resource-, time-, and manpower-efficient, and provide an alternative to classical stoichiometric alkyne chemistry. There are a number of recent review papers on alkyne transformation from the viewpoint of organic synthesis (Ackermann, 2013; Luo et al., 2014; Chen et al., 2015a, b,c; Fang and Bi, 2015; Qin et al., 2016). Most recently, Trost and Li edited a book entitled "Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformation", including catalytic isomerization, catalytic cycloaddition, catalytic nucleophilic addition and substitution, catalytic dimerization, and so on (Trost and Li, 2014).

In this review, we summarize the recent progresses on the catalytic transformation of alkynes into functional substances from the viewpoint of chemical engineering and industrial application. The processes and catalysts for alkynes transformation are systematically compared, and the effects of reaction conditions on the transformation are illustrated and discussed. Despite there were many review papers on the functionalization of alkynes into N-containing compounds, we determined that there is a need of one that is focused on heterocoupling, hydrogenation, and reaction of alkynes with organophosphorous compounds. Also, we pay attention to the functionalization of alkynes with S- or O-containing groups.

2. Coupling of terminal alkynes into 1,3-diynes

Symmetrical and unsymmetrical 1,3-diynes belong to an important class of intermediates in organic synthesis, and they are ubiquitous structural motifs in natural products and functional materials (Scheme 1) (Lampkowski et al., 2016; Sindhu et al., 2015; Weng et al., 2012). Moreover, 1,3-diynes are precursors of basic heterocycles. Herein we summarize the recent progresses in the catalytic transformation of alkynes to symmetrical and unsymmetrical 1,3-diynes.

1,3-Diynes could be symmetrical or unsymmetrical according to the substituent groups linked to the sides of the buta-1,3-diyne structure (Scheme 2). Earlier reports were mainly focused on the synthesis of symmetrical diynes. Despite unsymmetrical diynes are common in nature, it is only lately that they received more attention.

2.1. Homocoupling of terminal alkynes into symmetrical 1,3-diynes

Symmetric diynes could be generated simply through the oxidative coupling of the corresponding terminal alkynes (Scheme 3). Glaser, Eglington, and Hay couplings are classical pro-