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Mini-review

Palladium-catalyzed approach to the synthesis of five-membered *O*-heterocycles

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ABSTRACT

In recent decades, a large number of reports related to the synthesis of N, O and S containing heterocycles have appeared owing to a wide variety of their biological activity. The metal catalyzed synthesis of heterocycles is becoming an important and highly rewarding protocol in organic synthesis. This review focuses on the use of palladium as a catalyst for the synthesis of oxygen containing five-membered heterocycles. It describes the formation of different types of heterocyclic rings.

Contents

1. Introduction

Heterocycles form by far the largest of the classical divisions of organic chemistry. Moreover, they are of immense importance not only biologically but also industrially to the functioning of any developed human society [1,2]. Heterocycles are prevalent in various natural products and pharmaceutically active compounds [3,4].

Development of newer approaches for heterocycle syntheses employing efficient and atom economical routes is a popular research area nowadays. Among a variety of new synthetic transformations, transition metal catalyzed reactions are the most attractive methodologies, since those reactions can directly construct multiple substituted molecules from readily accessible starting materials under mild conditions [5–10].

Transition metal catalyzed coupling transformations are now serving as one of the most useful and powerful tools in organic synthesis. Transition metal catalyzed heteroannulation provides a useful and convenient tool for the construction of *O*-heterocycles [11,12].

The development of efficient, rapid and versatile routes for their synthesis has thus become a key area of research. To this end, methods involving transition-metal catalysis have gained prominence [13,14]. Employing such tactic presents a departure from traditional approaches, in which harsh conditions, long reaction times and limited substrate scopes are common.

Heterocyclic synthesis involving transition metal complexes has become of common use in the past decade because a metal-catalyzed reaction can directly build complicated molecules from readily accessible starting materials under mild conditions [15,16]. In this review, we focus on the use of palladium for the construction of various heterocyclic compounds with oxygen heteroatom.

2. Palladium-catalyzed synthesis of five-membered heterocycles with oxygen heteroatom

Among γ-alkylidenebutenolides [17], the highly conjugated lissoclinolide has been prepared through two routes, both elegantly relying on a combination of metal-catalyzed reactions including successive Pd-catalyzed coupling reactions and Ag-catalyzed cyclization. In one synthesis, protected (*E*)-pent-2-en-4-ynol was coupled with methyl

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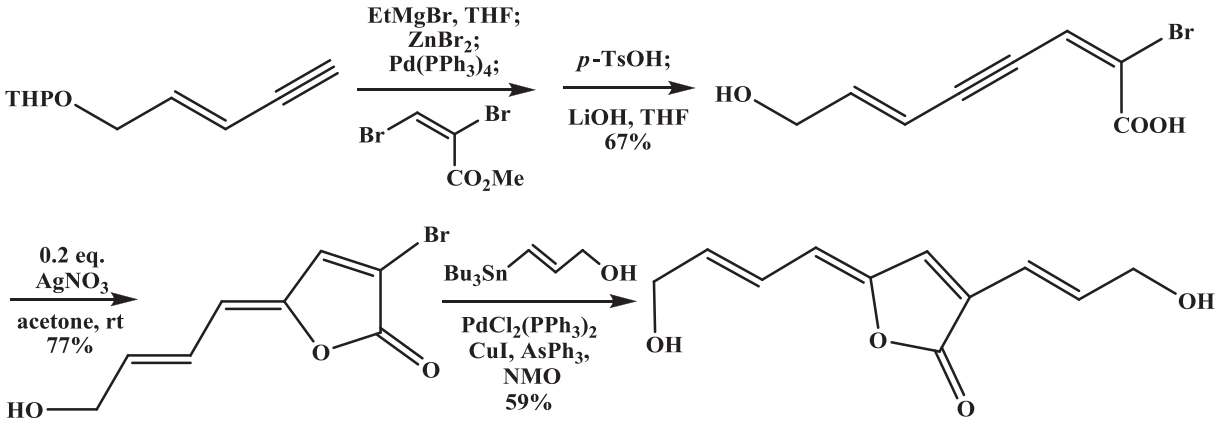
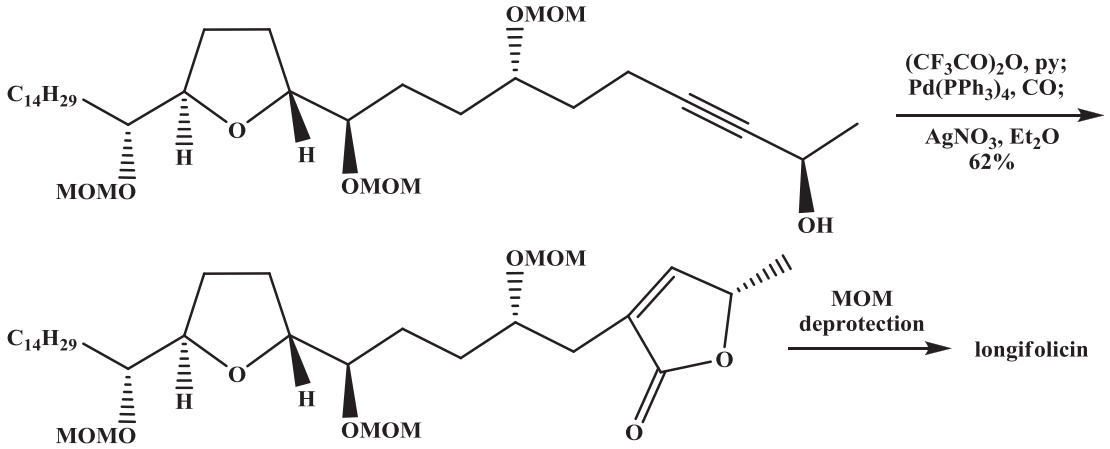


Scheme 1. Synthesis of lissoclinolide.

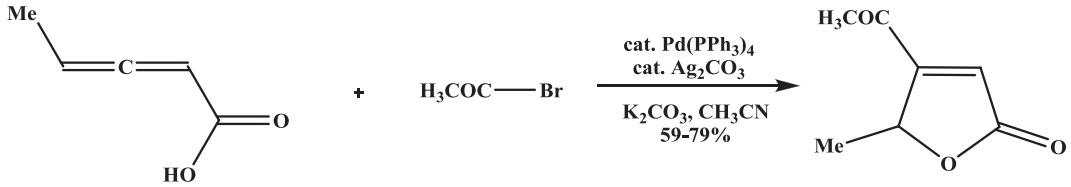


Scheme 2. Synthesis of furanocembrane rubifolide.

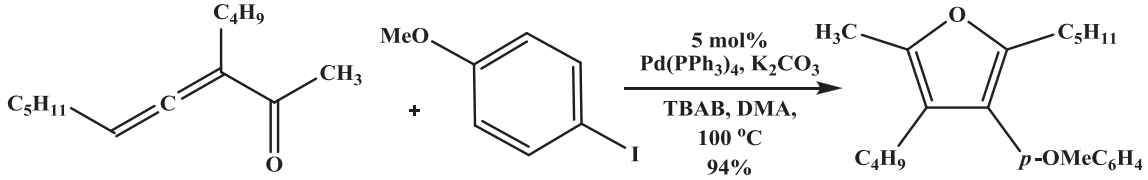
2,3-dibromoprop-2-enoate and the resulting bromodienyneester was converted into the corresponding acid and cyclized with silver nitrate in acetone. The alkylidene bromolactone so formed was then homologated by coupling again, yielding the natural product in only seven steps (Scheme 1) [18,19].

The total synthesis of the enantiomer of the marine furanocembrane rubifolide has been achieved by using this procedure. In order to avoid the lability of the mesylate under the conditions of its formation and isolation, the entire sequence from alcohol to butenolide is the best performed without isolation of any intermediate [20]. The synthesis of the butenolide moiety present in (+)-longifolicin skeleton is also possible following the same procedure (Scheme 2) [21,22].

Pd(0)/Ag(I) co-catalyze cyclizations of aryl halides with 1,2-allenic carboxylic acids. Ag(I) forms a 3-silver-2-butenolide intermediate, which undergoes a transmetalation reaction with R_2PdX followed by reductive elimination to afford butenolide [22,23] (Scheme 3).



Scheme 3. Synthesis of butenolide.



Scheme 4. Synthesis of tetrasubstituted furan.