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MINI-REVIEW ARTICLE

Bromoaldehyde as a Useful Starting Materials for the Synthesis of Various Hetero Cyclic and Carbocylic Molecules by Pd-catalyzed Reaction

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Abstract: This short review presents an overview of the effectiveness of β-bromoaldehyde as synthetic tool in organic chemistry. Few groups have reported significant contributions on β-bromoaldehyde. The aim of our short review was to give an overview of the latest advances in the chemistry of β-bromoaldehyde from their preparation to their transformations and applications in organic synthesis of some heterocyclic and carbocyclic molecules by using palladium-catalyzed reaction.

Keywords: Pyran, intermolecular heck, C-H bond functionalization, palladium, complex, 9 10 dihydrophenanthrene, halovinylaldehydes.

1. INTRODUCTION

This short review presents an overview of the synthesis and applications of both aromatic and vinylbromovinylaldehydes as a starting compound in synthetic organic chemistry. Different groups have reported significant contributions on halovinylaldehydes [1-7]. and our review aims to give an overview of the latest advances in the chemistry of bromoavinylaldehydes , from their synthesis to their applications in carbocyclic and heterocyclic synthesis by using palladium-catalyzed reaction .

Palladium (II) complexes are very important in organopalladium chemistry. They are normally electrophilic, and they are soluble in most of organic solvents, and stable in air. Thus, they are easily stockpiled and handled. The best common organic palladium (II) reactants are electron-dense classes, such as alkynes and arenes. Cyclization by Pd (II)-catalyzed oxidative addition and reductive elimination is a dominant process for building heterocyclic. This method usually comprises the addition of a covalent molecule to a Palladium (0) complex, with the cleavage of the covalent bond and oxidation of Pd (0) to Pd (II) to give an organopalladium (II) halide or triflate complex. The σ-bonded type, once formed, commonly undergoes speedy insertion of an unsaturated species. Successive reductive elimination to afford the preferred heterocyclic and Palladium (0), which reenters the catalytic cycle directly, in contrast to Palladium (II)-catalyzed reactions, which commonly need an additional reoxidation step. The mechanistic pathway of this reaction has been reviewed [8-15]. The Pd-catalyzed cyclization of aryl, vinyl halides or triflates comprising adjacent alkenes, alkynesdienes, and arenes through oxidative addition and reductive elimination reactions provides a very valuable approach to a wide range of oxygen and another heterocyclic [16-27] Here we have discussed the synthesis of various heterocyclic and carbocyclic molecules by palladium-catalyzed reaction starting from β-bromoaldehyde.

2. SYNTHESIS OF 2-BROMO-CYCLOHEXENECARBALDEHYDES

The first reported bromoaldehyde was synthesized by Arnold and Holy starting from cyclohexanone following a formerly developed method by Arnold and Zemlicka for the preparation of chlorovinyl aldehydes [28] using Vilsmeier-Haack type reagent PBr_3 in DMF in place of $POCl_3$ (Scheme **1**). This method is high yielding method for the synthesis of β-bromovinyl aldehydes to date.

3. METHODS OF SYNTHESIS OF CARBOCYCLIC AND HETEROCYCLIC COMPOUND STARTING FROM β-BROMOALDEHYDE

We have developed a universal synthetic route for constructing a fused pyran ring system and tetracyclic pyran moiety by Pd-catalyzed β-hydride elimination and by C-H activation [29, 30]. First, vinylbromoaldehyde **1** was reduced to vinyl bromoalcohols **2** by reacting with $NaBH_4$ in CH_3CN (Scheme **2**). Then, the precursors O-allylated (**3**)/methallylated (**4**) products were synthesized by the reaction of alcohol **2** with allyl bromide/methallyl bromide in the presence of NaH in THF at 0°C.

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