



Reduction of α,β -unsaturated carbonyl compounds by palladium(II) and nickel(II) complexes having nitrogen-containing ligands

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ABSTRACT

Catalytic reduction reactions of α,β -unsaturated carbonyl compounds by palladium(II) and nickel(II) complexes with *N,N*-dimethylamine borane are studied. Palladium and nickel complexes with nitrogen donor ligands such as 2,2'-bipyridine (bpy) and *N,N'*-tetramethylethylenediamine are found to be effective catalysts. In the case of [Pd(bpy)Cl₂] selective double bond reduction is observed. Comparative results of palladium(II)- and nickel(II)-catalysed reactions are presented.

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1. Introduction

Sodium borohydride is commonly used as reducing agent for reduction of carbonyl compounds. Its efficacy and selectivity towards reduction reactions can be enhanced by various metal catalysts [1–9]. The main problem in borohydride reduction is its slow degradation. It also forms insoluble borides when reacted with different metal salts. For these reasons, organoboranes are used as alternative reducing agents in many organic reactions [10]. Boranes may have also versatile reactivities; for example, palladium-catalysed reactions of borane [11–20] are used for borylation of aryl halides [21]. Boranes in the form of ammonia–borane are of interest, as they have high densities of replaceable hydrogens [19,20]; hydrogen release can be controlled by thermal or catalytic [21] means. We report here the reactivity of nickel and palladium complexes-catalysed hydrogenation reactions of *N,N*-dimethylamine borane with various unsaturated carbonyl compounds. For catalytic reactions the complexes [Ni(bpy)Cl₂] [21], [Ni(TMEDA)Cl₂], [Pd(TMEDA)Cl₂] [22] and [Pd(bpy)Cl₂] (where bpy = 2,2'-bipyridine and TMEDA = *N,N'*-tetramethylethylenediamine) are used.

2. Experimental

The α,β -unsaturated carbonyl compounds were prepared by standard procedures. The *N,N*-dimethylamine borane was purchased from Sigma–Aldrich and used as obtained. The [Ni(bpy)Cl₂] [21] and [Pd(TMEDA)Cl₂] [22] were prepared by reported procedures. The complexes [Ni(TMEDA)Cl₂] and [Pd(bpy)Cl₂] were prepared by refluxing corresponding metal chlorides with 1 equiv. of ligand in methanol (dry) for 2 h followed by removal of solvent under reduced pressure.

2.1. Reduction of α,β -unsaturated carbonyl compounds

In a typical reaction, to a well-stirred solution of α,β -unsaturated carbonyl compound (1 mmol) and [Ni(bpy)Cl₂] (25 mg, 0.1 mmol) in methanol (2 ml) Me₂HNBH₃ (90 mg, 1.5 mmol) was added in small portions. The reaction mixture was kept in an oil bath at 70 °C for 9 h. The course of the reaction was monitored by checking TLC of the reaction mixture from time to time. After 9 h the reaction was stopped and the solvent was removed under reduced pressure. To the paste obtained water was added and the mixture was extracted with diethylether. Diethylether was removed from the crude product and the product was then purified by column chromatography [silica gel, eluent used was hexane/ethylacetate]. The compounds **A**, **B**, and **C** as in Scheme 1 were characterized by recording GC–mass spectra and comparing their ¹H NMR and IR spectra with those of authentic samples.

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Similar reactions were carried out with palladium catalyst by using 1 mol% of catalyst with respect to the α,β -unsaturated carbonyl compound (1 mmol) with Me_2HNBH_3 (1.5 mmol). The reaction conditions and time are optimized by monitoring the reactions through TLC by varying time, temperature, and the amount of the catalysts.

3. Results and discussion

3.1. General discussion

Reduction reaction of α,β -unsaturated carbonyl compounds [21] can occur in different ways as illustrated in Scheme 1. It may lead to different products such as (i) allylic alcohol (A), resulting from attack of a hydride on the carbonyl group, (ii) saturated carbonyl compound (B), resulting from the hydrogenation of the double bond and (iii) saturated alcohol (C) resulting from the reduction of double bond as well as the carbonyl group [7]. We have studied these reactions of α,β -unsaturated carbonyl compounds by Me_2HNBH_3 in the presence of nickel, palladium, and copper catalysts. The results are discussed under different sections.

3.2. Nickel-catalysed hydrogenation reactions

It is already observed that these products formation are affected by solvent, metal ion and type of hydrogenation agent used [21]. In the present study we have found that α,β -unsaturated carbonyl compounds [22] react with N,N -dimethylamine borane in the presence of a catalytic amount of $[\text{Ni}(\text{bpy})\text{Cl}_2]$. The reaction does not take place without the metal catalyst under comparable condition. For example 3-phenylprop-2-ene-1-al reacted with N,N -dimethylamine borane in the presence of $[\text{Ni}(\text{bpy})\text{Cl}_2]$ to give corresponding saturated and unsaturated alcohols as shown in Scheme 2.

The reaction is applicable to α,β -unsaturated ketones and it is found that in these reactions saturated ketones are formed exclusively (Scheme 3).

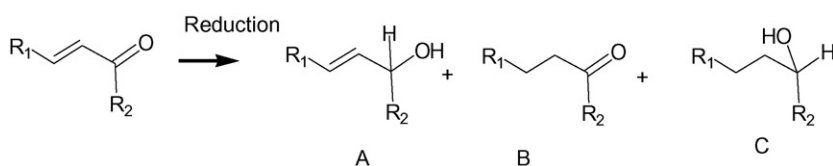
Several α,β -unsaturated compounds were reduced by N,N -dimethylamine borane and a catalytic amount of $[\text{Ni}(\text{bpy})\text{Cl}_2]$. The results are listed in Table 1.

3.3. Palladium-catalysed hydrogenation

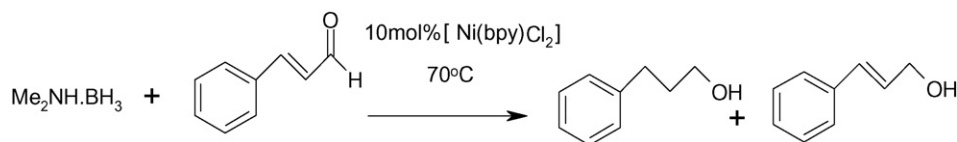
In a similar way to nickel-catalysed hydrogenation reactions, catalytic hydrogenation reaction of α,β -unsaturated carbonyl compounds by $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ and $[\text{Pd}(\text{bpy})\text{Cl}_2]$ is studied. 3-Phenyl-2-propenal reacts with N,N -dimethylamine borane in the presence of 1 mol% of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ to give corresponding saturated and unsaturated alcohols. A series of palladium-catalysed reduction reactions of α,β -unsaturated carbonyl compounds was done and the results along with the reaction conditions are listed in Table 2. The reaction of cinnamyl alcohol with N,N -dimethylamine borane with catalytic amount of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ gives exclusively 3-phenylpropanol. The reaction of 1-phenyl-3-naphthylprop-2-en-1-one with N,N -dimethylamine borane and a catalytic amount of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ gives the saturated ketone. It is also observed that the $[\text{Pd}(\text{bpy})\text{Cl}_2]$ can cause similar catalytic reactions and reduction of chalcone with N,N -dimethylamine borane in the presence of 1 mol% of $[\text{Pd}(\text{bpy})\text{Cl}_2]$ gives exclusively double bond reduced product (type B in Scheme 1). Similar carbon–carbon double bond reduction is observed with a few other substrates listed in Table 2.

3.4. Copper(II)-catalysed hydrogenation

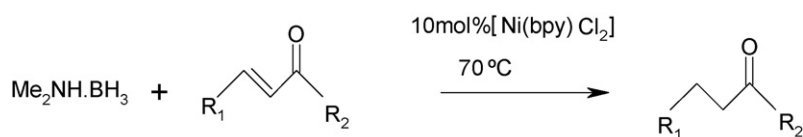
The borohydrides and boranes are known to reduce palladium(II) and nickel(II) salts to their zero oxidation states [21]. The $\text{Pd}(0)$ and $\text{Ni}(0)$ has d^{10} -electronic configuration and are effective hydrogenation catalysts. Thus, a metal complex having d^{10} -electronic configuration may be suitable for hydrogenation reactions. The copper(II) formate complexes with borohydrides are good reducing agents for carbonyl compounds including carbon dioxide [23]. In such reactions copper(II) undergoes reduction to copper(I); and copper(I) has d^{10} -electronic configuration, being an active catalyst. Reduction reactions of few α,β -unsaturated car-



Scheme 1.



Scheme 2.



Scheme 3.

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