



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

Partha P. Jana, Rupam Sarma, Jubaraj B. Baruah *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

ARTICLE INFO

Article history:

Received 23 October 2007

Received in revised form 5 April 2008

Accepted 10 April 2008

Available online 18 April 2008

Keywords:

N,N-Dimethylamine borane

α,β -Unsaturated carbonyl compounds

Nickel catalyst

Palladium catalyst

Reduction reactions

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.

© 2008 Elsevier B.V. All rights reserved.

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.

* Corresponding author. Tel.: +91 361 2582311; fax: +91 361 2690762.
E-mail address: juba@iitg.ernet.in (J.B. Baruah).

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).

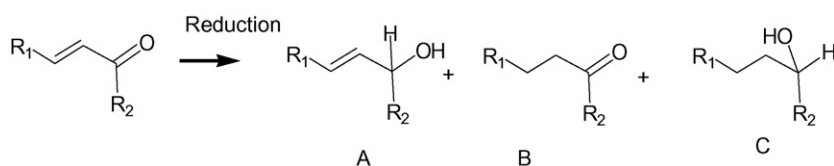
Several α,β -unsaturated compounds were reduced by *N,N*-dimethylamine borane and a catalytic amount of $[\text{Ni}(\text{bpy})\text{Cl}_2]$. The results are listed in Table 1.

3.3. Palladium-catalysed hydrogenation

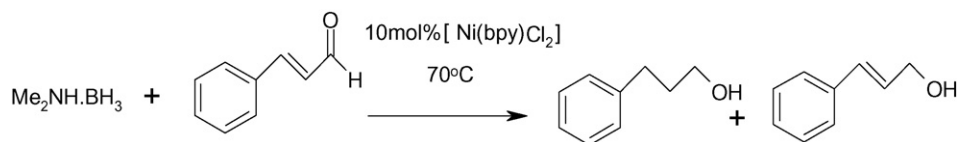
In a similar way to nickel-catalysed hydrogenation reactions, catalytic hydrogenation reaction of α,β -unsaturated carbonyl compounds by $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ and $[\text{Pd}(\text{bpy})\text{Cl}_2]$ is studied. 3-Phenyl-2-propenal reacts with *N,N*-dimethylamine borane in the presence 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

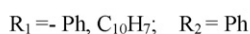
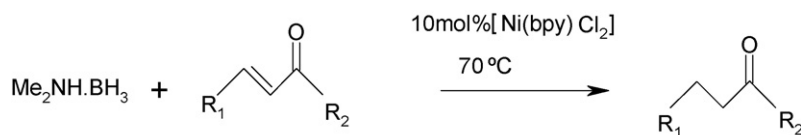
The borohydrides and boranes are known to reduce palladium(II) and nickel(II) salts to their zero oxidation states [21]. The Pd(0) and Ni(0) has d^{10} -electronic configuration and are effective hydrogenation catalysts. Thus, a metal complex having d^{10} -electronic configuration may be suitable for 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.

Table 1Reduction of α,β -unsaturated carbonyl compound by *N,N*-dimethylamine borane and by $[\text{Ni}(\text{bpy})\text{Cl}_2]$ as catalyst (10 mol%) at 70 °C

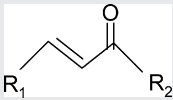
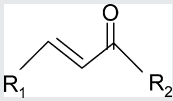
Entry number	Substrate 	Time (h)	Ratio of A:B:C (as in Scheme 1)	Isolated yield (%)
1	$\text{R}_1 = \text{C}_6\text{H}_5, \text{R}_2 = \text{H}$	9	50:0:50	94
2	$\text{R}_1 = \text{C}_6\text{H}_5, \text{R}_2 = \text{C}_6\text{H}_5$	8	0:100:0	86
3	$\text{R}_1 = \text{C}_{10}\text{H}_7, \text{R}_2 = \text{C}_6\text{H}_5$	9	0:100:0	88
4	$\text{R}_1 = p\text{-OMe-C}_6\text{H}_4, \text{R}_2 = \text{CH}_3$	9	0:100:0	98
5	$\text{R}_1 = p\text{-OMe-C}_6\text{H}_4, \text{R}_2 = p\text{-OMe-C}_6\text{H}_4$	9	0:100:0	74

Table 2Reduction of α,β -unsaturated carbonyl compounds with *N,N*-dimethylamine borane

Entry number	Substrate 	Time (h)	Ratio of A:B:C (as in Scheme 1)	Isolated yield (%)
1	$\text{R}_1 = \text{C}_6\text{H}_5, \text{R}_2 = \text{H}$	9	25:0:75	85
2	$\text{R}_1 = \text{C}_6\text{H}_5, \text{R}_2 = \text{C}_6\text{H}_5$	8	0:0:100	80
3	$\text{R}_1 = \text{C}_{10}\text{H}_7, \text{R}_2 = \text{C}_6\text{H}_5$	9	0:100:0	96
4	$\text{R}_1 = p\text{-OMe-C}_6\text{H}_4, \text{R}_2 = p\text{-OMe-C}_6\text{H}_4$	9	0:0:100	71
5	$\text{R}_1 = \text{C}_6\text{H}_5, \text{R}_2 = \text{C}_6\text{H}_5$	6	0:100:0	96 ^a
6	$\text{R}_1 = \text{C}_{10}\text{H}_7, \text{R}_2 = \text{C}_6\text{H}_5$	6	0:100:0	94 ^a

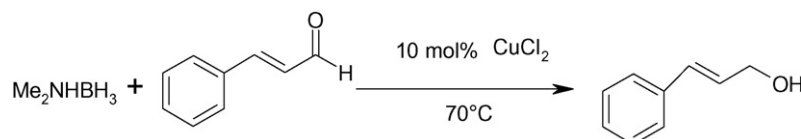
In all cases 1 mol% of $\text{Pd}(\text{TMEDA})\text{Cl}_2$ at 70 °C was used unless stated.^a 1 mol% of $[\text{Pd}(\text{bpy})\text{Cl}_2]$ catalyst was used.

bonyl compounds by *N,N*-dimethylamine borane in the presence of copper(II) salts are studied in the expectation that a copper hydride complex will be formed and would catalyse the reduction reactions. It is found that the reaction of cinnamaldehyde with *N,N*-dimethylamine borane with CuCl_2 gives the corresponding unsaturated alcohol in poor yield (~40%). The reaction is shown in Scheme 4. The reaction is found to be limited to aromatic α,β -unsaturated aldehydes. To confirm that copper(I) complexes are formed in such reactions, copper(II)nitrate is allowed to react with *N,N*-dimethylamine borane in the presence of triphenyl phosphine. This reaction led to the formation of $[\text{Cu}(\text{PPh}_3)_2\text{NO}_3]3\text{H}_2\text{O}$ with evolution of hydrogen gas. The complex $[\text{Cu}(\text{PPh}_3)_2\text{NO}_3]3\text{H}_2\text{O}$ can be alternatively prepared by the reaction of copper(II) nitrate with excess of triphenyl phosphine in alcohol without the borane [24].

3.5. Comparison of reduction reactions by amine borane with different metal catalysts

Significant differences are observed in the reactivity between $[\text{Ni}(\text{bpy})\text{Cl}_2]$ and $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$. For example the reaction of cinnamaldehyde with *N,N*-dimethylamine borane in the presence of a catalytic amount of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ gives saturated:unsaturated alcohols in a 75:25 ratio; whereas a similar reaction with $[\text{Ni}(\text{bpy})\text{Cl}_2]$ as catalyst gives saturated:unsaturated alcohols in a 50:50 ratio. The catalytic reduction reactions by $[\text{Pd}(\text{bpy})\text{Cl}_2]$ are comparable in selectivity with $[\text{Ni}(\text{bpy})\text{Cl}_2]$; but the former catalyst is more active, giving a high yield under mild conditions. The reaction of cinnamyl alcohol with

N,N-dimethylamine borane in the presence of $[\text{Ni}(\text{bpy})\text{Cl}_2]$ or $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ gives 3-phenylpropanol. For this reaction only 1 mol% of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ catalyst is required as against 10 mol% of nickel catalyst. The reaction of α,β -unsaturated ketone with *N,N*-dimethylamine borane in presence of $[\text{Ni}(\text{bpy})\text{Cl}_2]$ catalyst, only the carbon-carbon double bond is reduced. So it is a good catalyst for the hydrogenation of the carbon-carbon double bond of α,β -unsaturated ketones. A control experiment showed that 1,5-bis-(4-methoxyphenyl)penta-1,4-dien-3-one (1 mmol) on reaction with *N,N*-dimethylamine borane (3 mmol) in the presence of $[\text{Ni}(\text{bpy})\text{Cl}_2]$ (10 mol%, 70 °C, 6 h), only one double bond is reduced to give 1,5-bis-(4-methoxyphenyl)pent-1-en-3-one, whereas this reaction with $[\text{Pd}(\text{bpy})\text{Cl}_2]$ led to reduction of 1,5-bis-(4-methoxyphenyl)penta-1,4-dien-3-one in an unspecific manner. The reduction of α,β -unsaturated ketones with *N,N*-dimethylamine borane in the presence of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ is found to be substrate dependent. In the catalytic reactions by $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ either saturated carbonyl compound or a mixture of saturated carbonyl compound and saturated alcohol is formed. As far as the selectivity is concerned, both Ni and Pd has advantages as well as disadvantages. Multiple numbers of products are formed in the case of $[\text{Pd}(\text{TMEDA})\text{Cl}_2]$ as catalyst, whereas $[\text{Ni}(\text{TMEDA})\text{Cl}_2]$ gives selective products. However, $[\text{Pd}(\text{bpy})\text{Cl}_2]$ is more effective and selective also. These reactions are limited to α,β -unsaturated carbonyl compounds; substrates such as acetophenone, cinnamyl esters, cyclo-octenes are not reactive towards all the catalysts studied here, except $[\text{Pd}(\text{bpy})\text{Cl}_2]$. $[\text{Pd}(\text{bpy})\text{Cl}_2]$ acts as catalyst for reduction of acetophenone, benzophenone and cinnamyl ester to the corresponding alcohols in varying yields from

**Scheme 4.**

30 to 80%. In the case of aromatic aldehyde [Pd(bpy)Cl₂] is an excellent catalyst for transformation to benzylic alcohols; for example 1 mol% [Pd(bpy)Cl₂] can convert 4-butylbenzaldehyde (1 mmol) with *N,N*-dimethylamine borane (1 mmol, 70 °C, 6 h) to 4-*tert*-butylbenzyl alcohol in a quantitative yield. Aliphatic aldehyde such as nonanaldehyde reacts with *N,N*-dimethylamine borane in the presence of [Pd(bpy)Cl₂] catalyst in refluxing methanol to give the corresponding alcohol in a poor yield. Thus, the product selectivity and cost effectiveness are to be carefully chosen to achieve selective hydrogenation reactions.

References

- [1] T.J. Clark, C.A. Russell, I. Manners, *J. Am. Chem. Soc.* 128 (2006) 9582.
- [2] M. Hudlicky, *Reductions in Organic Chemistry*, Ellis Howood Ltd., Chichester, 1986.
- [3] B.C. Ranu, A.R. Das, *J. Org. Chem.* 56 (1991) 4796.
- [4] D.H. Appella, Y. Moritani, R. Shintani, E.M. Ferreira, S.L. Buchwald, *J. Am. Chem. Soc.* 121 (1999) 9473.
- [5] Y. Tohru, O. Yuhki, I. Taketo, *Chem. Lett.* (1998) 1129.
- [6] H. Werner, R. Vicha, A. Gissibl, O. Reiser, *J. Org. Chem.* 68 (2003) 10166.
- [7] A.H. McManus, P.J. Guiry, *Chem. Rev.* 104 (2004) 4151.
- [8] J.C. Fuller, S.M. Williamson, B. Singaram, *J. Fluorine Chem.* 68 (1994) 265.
- [9] B. Tamami, N. Goudarzian, *J. Chem. Soc., Chem. Commun.* (1994) 1079.
- [10] N.T. Strande, S.S. Shafer, S.H. Kyle, T.A. Evans, P. Arthasery, S.L. McKay, *Abstracts of Papers, 234th ACS National Meeting, Boston, MA, United States, August 19–23, 2007 (CHED-221)*.
- [11] S.S. White, H.C. Kelly, *J. Am. Chem. Soc.* 92 (1970) 4203.
- [12] J. Chen, K.A. Wayman, M.A. Belshe, M. Dimare, *J. Org. Chem.* 59 (1994) 523.
- [13] A.M. Salunkhe, E.R. Burkhardt, *Tetrahedron Lett.* 38 (1997) 1519.
- [14] H.C. Brown, M. Zaidlewics, P.V. Dalvi, *Organometallics* 17 (1998) 4202.
- [15] H.C. Brown, J.V.B. Kanth, M. Zaidlewicz, *J. Org. Chem.* 63 (1998) 5154.
- [16] F.R. Alexandre, D.P. Pantaleone, P.P. Taylor, I.G. Fotheringham, D.J. Agxer, N.J. Turner, *Tetrahedron Lett.* 43 (2002) 707.
- [17] A. Togni, L.M. Venanzi, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 497.
- [18] K.D. Sugi, T. Nagata, T. Yamada, T. Mukaiyama, *Chem. Lett.* (1997) 493.
- [19] A. Gutowska, L. Li, Y. Shin, C.M. Wang, X.S. Li, J.C. Lineham, R.S. Smith, B.D. Kay, B. Schmid, W. Shaw, M. Gutowski, T. Autrey, *Angew. Chem. Int. Ed. Engl.* 44 (2005) 3578.
- [20] M. Jacoby, *Chem. Eng. News* 83 (2005) 42.
- [21] J.G. Handique, A. Purkayashtha, J.B. Baruah, *J. Organomet. Chem.* 620 (2001) 90.
- [22] A. Purkayashtha, J.B. Baruah, *J. Mol. Catal. A: Chem.* 198 (2003) 47.
- [23] C. Bianchini, C.A. Ghilardi, A. Meli, S. Midollini, A. Orlandini, *J. Organomet. Chem.* 248 (1983) C13.
- [24] R.-N. Yang, T.-X. Li, X.-Y. Hu, D.-M. Jin, Y.-A. Sun, B.-S. Luo, *Chin. J. Struct. Chem.* 19 (2000) 126.