Bull. Chem. Soc. Ethiop. 2005, 19(1), 149-152.
Printed in Ethiopia
ISSN 1011-3924

SHORT COMMUNICATION

PALLADIUM-CATALYSED TRANSFER HYDROGENATION OF ALKENES IN THE PRESENCE OF ZINC POWDER AND VARIOUS ORGANIC ACIDS

I.B. Masesane[1*] and P.G. Steel[2]

[1]Department of Chemistry, University of Botswana, P/Bag UB 00704, Gaborone, Botswana
[2]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

(Received July 31, 2004; revised September 10, 2004)

ABSTRACT. Catalytic transfer hydrogenation using palladium(II) chloride, zinc powder and various organic acids proved effective for the reduction of a variety of alkenes at ambient temperature and atmospheric pressure. The method was found to be convenient, economical and uses a stable nonpyrophoric catalyst.

KEY WORDS: Catalytic transfer hydrogenation, Hydrogenation of alkenes, Palladium(II) chloride, Zinc powder, Organic acids, Nonpyrophoric catalyst

INTRODUCTION

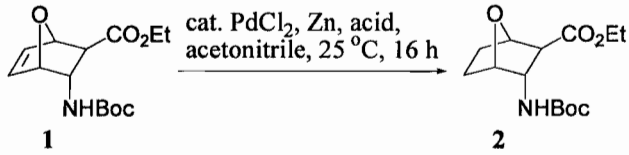
Catalytic transfer hydrogenation is a promising method for the reduction of various functional groups which avoids some of the technical and safety concerns associated with using compressed hydrogen gas [1]. The ammonium formate/Pd-C system has proven to be an effective reagent for the reduction of the azides to amines, nitriles to methyl groups, carbonyls to alcohols, nitro compounds to the corresponding amines and alkenes to alkanes [2]. The limitation of this system is that it is applicable only with ammonium formate or formic acid as the H-donors. In this paper we describe a convenient method for the reduction of different alkenes using catalytic palladium(II) chloride, Zn powder and various organic acids.

RESULTS AND DISCUSSION

As part of a broader synthetic program, we have been exploring the use of oxanorbornene adducts derived from the Diels Alder reaction of ethyl (E)-3-nitroacrylate and furan as intermediates in the synthesis of a range of hydroxylated cyclohexyl β-amino acids [3-5]. While studying the palladium-catalysed reductive ring-opening reactions of oxabicyclic alkenes in the presence of Zn powder and benzoic acid as described by Cheng [6], we noted that oxanorbornene adduct **1** exclusively led to its saturated derivative **2**. Control experiments indicated that no reaction occurred in the absence of zinc powder, benzoic acid or palladium(II) chloride. In an attempt to understand this reduction reaction, a series of organic acids were tested for the reduction of **1** using palladium(II) chloride as the catalyst in the presence of Zn powder. The results in Figure 1 show that the organic acid used does not influence the yield of the reaction. Formic acid, acetic acid, ammonium acetate and benzoic acid afforded **2** in excellent yields. When inorganic acids (HCl and NH_4Cl) were used as hydrogen donors no reaction was observed.

*Corresponding author. E-mail: MASESANE@mopipi.ub.bw

It was conceivable that Pd/C could be used as the catalyst instead of the more expensive palladium chloride. Treatment of adduct **1** with catalytic amount of Pd/C, zinc powder and formic acid afforded adduct **2** in 97% yield. Interestingly, when either benzoic acid or acetic acid was used as the hydride source in the Pd/C catalysed transfer hydrogenation, no reaction was observed.

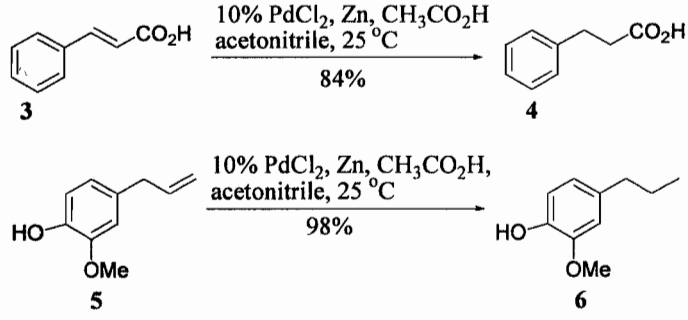


1 **2**

Entry	Organic acid	Isolated yield (%)
1	HCO_2H	96
2	CH_3CO_2H	94
3	$CH_3CO_2NH_4$	97
4	$PhCO_2H$	93

Figure 1. Palladium-catalysed transfer hydrogenation of adduct **1** in various acids.

The $PdCl_2$-catalysed transfer hydrogenation reaction was extended to other alkenes of diverse structures. The reaction of cinnamic acid **3** with acetic acid in the presence of 10% $PdCl_2$ and zinc in acetonitrile at 25 °C for 16 h afforded 3-phenylpropanoic acid **4** [7] in 84% yield (Figure 2). In a similar way, eugenol **5**, having a terminal and non-activated double bond reacted with acetic acid in the presence of Pd(II) catalyst and zinc powder to afford 2-methoxy-4-propylphenol **6** in 98% yield (Figure 2). It is noteworthy that no reaction occurred when the reduction reaction of cinnamic acid **3** was repeated without the acetic acid and this observation is consistent with that made by Arterburn and co-worker [7].



3 **4**

5 **6**

Figure 2. Palladium-catalysed transfer hydrogenation of **3** and **5**.

The catalytic transfer hydrogenation reaction described above is thought to proceed by first reduction of palladium(II) to palladium(0) by the zinc powder. Oxidative addition of the organic acid to the palladium(0) affords a palladium(II) hydride species [6, 8] which then acts as the reducing agent (see Figure 3).

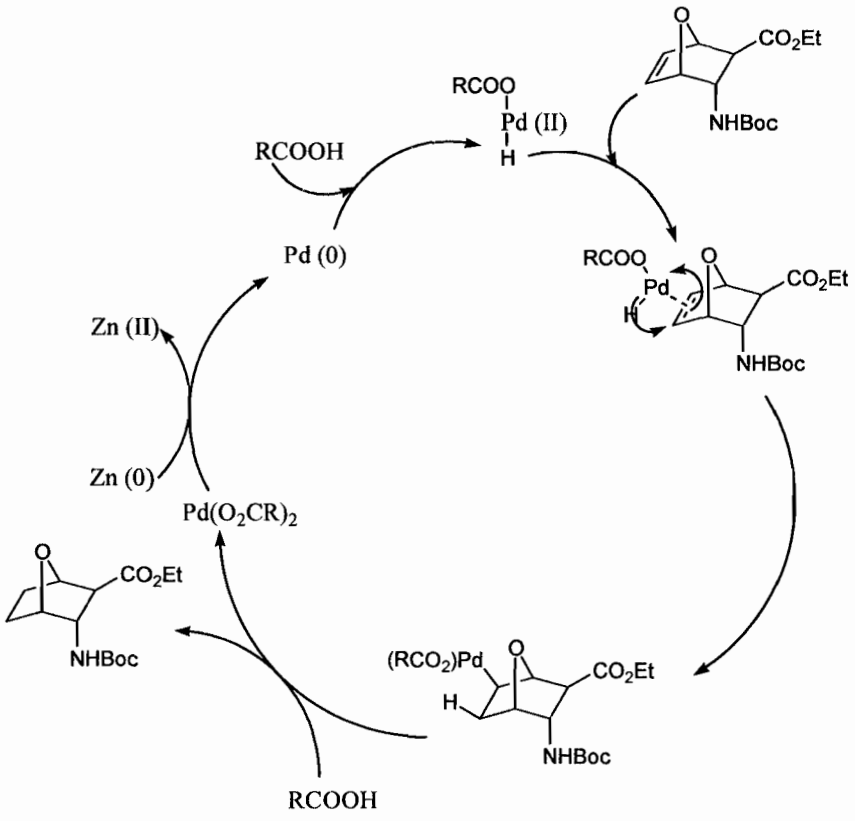


Figure 3. Catalytic cycle for palladium catalysed transfer hydrogenation.

In conclusion, we demonstrated a new and simple palladium(II) chloride catalysed transfer hydrogenation procedure for alkenes in the presence of various organic acids and zinc powder. Future work in this area will include using chiral ligands or optically pure organic acids test the asymmetric version of the catalytic reaction.

EXPERIMENTAL

Typical procedure. To a stirred solution of alkene **1** (400 mg, 1.40 mmol) in acetonitrile (20 cm^3) at room temperature was added $PdCl_2$ (25 mg, 0.14 mmol), zinc powder (275 mg, 4.2 mmol) and acetic acid (0.24 cm^3, 4.2 mmol). The reaction mixture was stirred for 16 h and then filtered. The filtrate was concentrated and dissolved in ethyl acetate and a saturated solution of $NaHCO_3$ (except when the substrate was an unsaturated organic acid. In such a case, column chromatography [stationary phase: silica gel 60 (0.040-0.063 mm)], eluting with a 7:3 mixture of petroleum ether:ethyl acetate was used to purify the product). The layers were then separated and the aquoeus layer was washed three times with ethyl acetate. The organic layers were combined and concentrated under reduced pressure to give the product.

Compound 2. White solid (377 mg, 94%), m.p. 92-94 °C; ν_{max} (KBr disk): 3346 (br), 2992, 1739, 1709, 1523 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 1.26 (3H, *t*, J = 7.2 Hz, $OCH_2C\underline{H}_3$), 1.43 (9H, *s*, $OC(C\underline{H}_3)_3$), 1.84 (4H, *m*, H-5 and 6), 2.14 (1H, *d*, J = 5.0 Hz, H-2), 4.17 (2H, *q*, J = 7.2 Hz, $OC\underline{H}_2CH_3$), 4.22 (1H, br, H-3), 4.72 (2H, br, H-1 and 4), 5.40 (1H, br, NH); δ_C (125 MHz, $CDCl_3$): 14.1 ($OCH_2\underline{C}H_3$), 30.0 (C-5 and 6), 28.3 ($OC(\underline{C}H_3)_3$), 55.0 (C-2), 56.2 (C-3), 61.1 ($O\underline{C}H_2CH_3$), 78.3 and 79.6 (C-1 and 4), 80.1 ($O\underline{C}(CH_3)_3$), 155.2 (NCO_2), 172.0 ($CO_2C_2H_5$); *m/z* (EI): 285 (M^+), 57 (100%); Anal. calcd. for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.12; N, 4.91%. Found: C, 58.23; H, 8.07; N, 4.74%.

Compound 6. Yellow oil (459 mg, 89%), ν_{max} (KBr disk): 3450, 2959, 1607, 1516 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 0.95 (3H, *t*, J = 7.6 Hz, $C\underline{H}_3CH_2CH_2$), 1.63 (2H, *m*, $CH_3C\underline{H}_2CH_2$), 2.53 (2H, *t*, J = 7.6 Hz, $CH_3CH_2C\underline{H}_2$), 3.87 (3H, *s*, OCH_3), 5.55 (1H, *s*, OH), 6.70 (2H, *m*, H-3 and H-6), 6.85 (1H, *d*, J = 7.2 Hz, H-5); δ_C (100 MHz, $CDCl_3$): 14.1 ($\underline{C}H_3CH_2CH_2$), 25.1 ($CH_3\underline{C}H_2CH_2$), 38.0 ($CH_3CH_2\underline{C}H_2$), 56.1 (OCH_3), 111.3 (C-3), 114.3 (C-5), 121.2 (C-6), 134.9 (C-4), 143.7 (C-2), 146.5 (C-1); *m/z* (EI^+): 166 (M^+, 43%), 137 (100%).

ACKNOWLEDGEMENTS

This work was supported by the University of Botswana and the University of Durham. We thank Dr A.M. Kenwright for assistance with NMR experiments and Dr M. Jones for mass spectra.

REFERENCES

1. Johnstone, R.A.W.; Wilby, A.H.; *Chem. Rev.* **1985**, 85, 129.
2. Ram, S.; Ehrenkaufer, R.E. *Synthesis* **1988**, 91.
3. Bunnage, M.E.; Ganesh, T.; Masesane, I.B.; Orton, D.; Steel, S.G. *Org. Lett.* **2003**, 5, 239.
4. Masesane, I.B.; Steel, P.G. *Synlett* **2003**, 735.
5. Masesane, I.B.; Steel, P.G. *Tetrahedron lett.* **2004**, 45, 5007.
6. Li, L.; Rayabarapu, D.K.; Nandi, M.; Cheng, C. *Org. Lett.* **2003**, 5, 1621.
7. Arterburn, J.B.; Pannala, M.; Gonzalez A.M.; Chamberlin, R.M. *Tetrahedron Lett.* **2000**, 41, 7847.
8. Trost, B.M. *Chem. Eur. J.* **1998**, 4, 2405.