HYDROGENATION CATALYST FOR REDUCTION OF BENZALDEHYDES AND ALCOHOL

T.Adinaveen[1], P.Ganapathy[2], M.Deepa[3], V.S.Sangeetha[4]

Assistant professor,

[1]Department of chemistry ,Dhanalakshmi Srinivasan College of Arts & Science for Women(Autonomous)

Perambalur

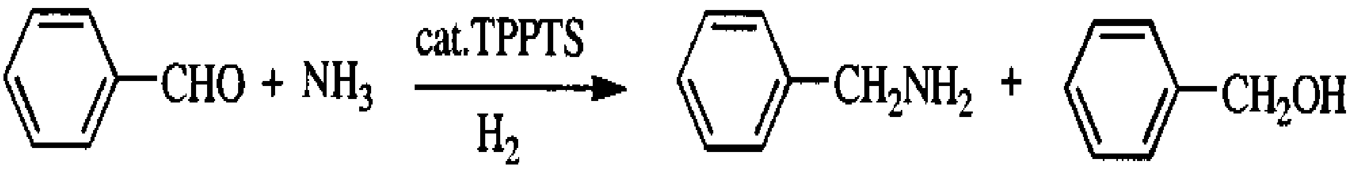
ABSTRACT

The superior reduction reaction of amineoffered 68% yield and time stability of successful product benzyl amine yield is 42% with acids or ammonium salt. The pre catalyst$[Rh(cod)Cl]_2$ on reduction realized in bimetallic medium. Rh and Irmetalsthe acid catalyst compressed the reduction of CO group. 95% of selective benzylamine are identified product compared with expected amine (30%)

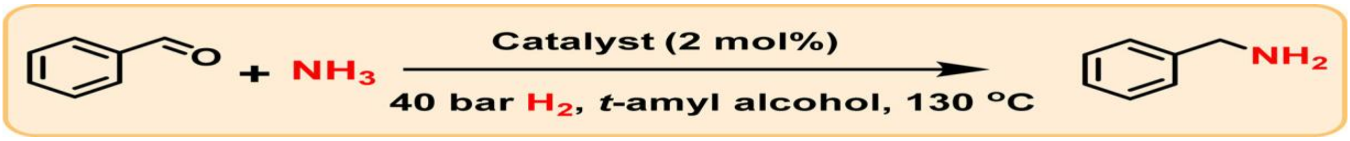
KEYWORDS: Aerobic oxidation processes, MTBE,THF,TPPTS, bimetallic catalyst as Rh/Ir.

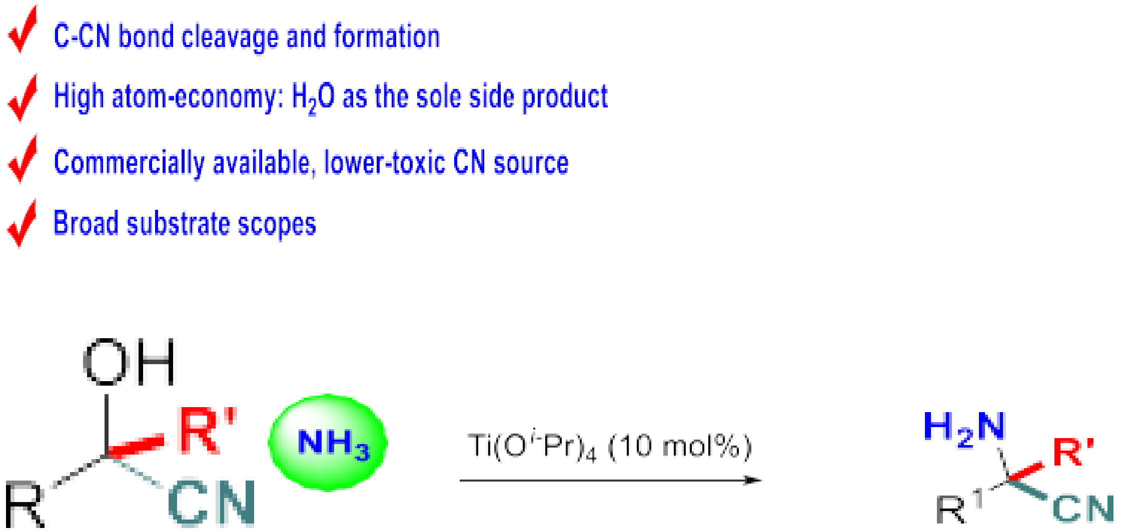
1° 2° alcohols

Amination of Aldehyde Using Ammonia



Amination of ketone Using Ammonia





. Amination of Alcohols Using Ammonia

In d block metal complexes, amination of carbonyl compounds with aqueous ammonia involved at reductive methods.The amino group introduced into an organic molecule the catalyzed hydration of nitrilesmetals. Aerobic oxidation processes based on product recyclable catalysts to accomplish the efficient oxidation of alcohols with molecular oxygen or air as the final oxidant.2 Along this line, pd3 pt4 ,Ag5 , Ru6 and copper7 have achieved..The synthesis of primary amines via reduction the corresponding carbonyl compounds with aqueous ammonia is suitable for soluble transition metal complexes such as Ru, Rh,Ir. Up to an 86% yield and a 97% selectivity for benzylamineswas suitable in the case of various benzaldehydes by using a Rh-catalyst selected with water-soluble phosphine and ammonium acetate. The expected result gotted from aliphatic aldehydes, using a bimetallic catalyst as Rh/Ir. .

AminationOfAldehyde using Ammonia

$C_6H_5CHO+NH_3 \rightarrow C_6H_5CH_2NH_2+C_6H_5CH2OH$

Table 1.Reductive Amination of Benzaldehyde

catalyst, mol %	Organic solvent	temperatur e °C	TPPTS,mo l%	NH4OAc, mol %	primary amine	Alcohol	selectivity: primary aminevs
[Ir(cod)Cl]2, 0.1*c*	MTBE	135	6.4	0	6	66	8
[Ir(cod)Cl]2, 0.1	MTBE	135	2.6	5	42	9	49
[Ir(cod)Cl]2,0.1/[Rh(cod)Cl]2,0.025	MTBE	135	6.4	5	84	14	83
[Rh(cod)Cl]2, 0.025	**MTBE**	**135**	**5.2**	**50**	**64**	**4**	**94**
[Rh(cod)Cl]2, 0.025	MTBE	135	2.6	5	48	8	86
[Rh(cod)Cl]2, 0.05	MTBE	135	2.6	5	80	11	88
[Rh(cod)Cl]2, 0.05	**THF**	**135**	**1.2**	**50**	**86**	**3**	**97**
[Rh(cod)Cl]2, 0.05	THF	135	2.6	5	19	33	37

Reductive Amination of Substituted 2^0,3^0 alcohol

Alcohol→Aldehyde +ketone

1^0 ,2^0 alcohol+ ammonia →1^0 amine

2^0,3^0 alcohol+ ammonia → aminonitrile

catalyst, mol %	Organic solvent	temperature, °C	TPPTS,mol %	Ammonium acetate mol %	primary amine	Alcohol	selectivity: primary aminevsalcohol, %
Ti(OiPr)4,10	toluene	135	2.6	2.6	25	-	25
Ti(OiPr)4,10	MeOH	135	2.6	2.6	-	-	-
Ti(OiPr)4,10	TBME	135	2.6	0	38	66	64

General Procedure s

(1) **.** In a typical experiment (Table 1,),benzaldehyde (30 mmol), [Rh(cod)Cl]2 (0.05 mol %), TPPTS (1.5 mol%), ammonium acetate (55 mol %), 30% aqueous NH3 (20 mL), and freshly distilled THF (20 mL) are utilizesed under an argon atmosphere into a 160 mL stainless steel autoclave equipped with a magnetic stirrer and temper- ature-controlled heating. The autoclave is turn off, flushed once with hydrogen gas, and pressurized to 65 bar of H_2, and the reaction takes place for 2 h at a temperature of 135 C (total pressure at 135 C was ca.100 bar). After the reaction, the autoclave cooled and

slowly depressurized. The organic layer wastranferred, and the aqueous phase has reacted with NaOH (0.5 g) and extracted with THF (2 10 mL). Bis- (methoxyethyl) ether (5 mL) to the combined organic phases, and the mixture was tested by gas chromatography. All aldehydes as well as synthesized amines and corresponding alcohols are commercially available., selective benzaldehyde and products are determined by comparison with authentic samples by GC (column: cross-linked 5% PH ME Siloxane, 30 m 0.25 mm 0.25 μm, all products are identfiedbyGC-MS.

Various substrate such as aldehyde ketone ester were have interest on industrials. The liquidsphase , multi phase immobilized on supported for industrial development expanding ionic liquds.in reduction of amine reaction, aldehyde with NH3 as homogenous catalysis.47% of octylamine from octanal of bimetallic Rh/Ir catalyst are utilized47% of pentylamine with n-petanol

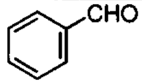
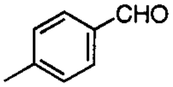
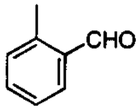
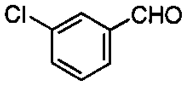
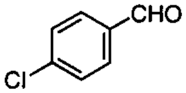
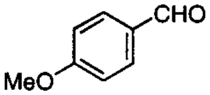
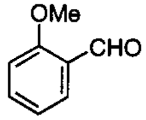
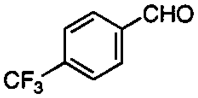
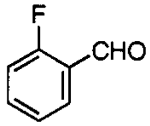
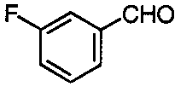
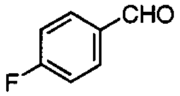
(1) hexylamineissaved to45%byusing toluene solvent at 150^{0}c

the aromatic aldehyde have attactedconsiderable attention as PrimaryAmines are selected as mainproduct with high selectivesthe chemo selectives and enatioselectivites of ionc liquids with excellent yields at room temperature were noted in chemical production. The traditional organic solvents are benzene,, methanol, MTBE, gave as PrimaryAmines as Primaryproduct withhigh selectivities .

side product of aromatic alcohol with as PrimaryAmines by using Rh(COd)cl2 catalyst with the condition of TPPTS AND NH3/H2 frombenzalehyde..

commonly electron donating group from aldehyde give selective PrimaryAmines 65-85%..while chlorine,fluorine.CF3 as electron withdrawing group gave low yield 33-78%

Ammonia is one of the most easiest nitrogen source by the industrial .

substrate	yield **1** %	yield **2** %	Selectivity **1** vs. **2** alcohol, %
	86	3	97
	75	4	95
	65	7	90
	55	8	87
	78	9	90
	77	4	95
	85	3	97
	33	5	87
	58	9	87
	62	11	85
	62	14	82

. . **General Procedure** s

benzaldehyde (0.034 mol), 25% aqueous ammonia (20 mL), NH3/benzaldehyde (8:1), org/aq solution (1:1), H2 (65 bar), time (2h). *b*Yields are foudby GC analysis with bis(methoxyethyl) ether. *c*Time) 10 h. *d* Octanoic acid was produced instead of NH4OAc. On the basis of the successful demonstration of iridium as a hydrogenation catalyst for the reduction of isolated imines, we explored the applicability of iridium complexes as precatalysts for the reductive aminationof benzaldehyde with ammonia for the synthesis of primary amines. Unfortunately, low selectivity (8%) for the expected amine is noted with [Ir(cod)Cl]2 as a catalyst precursor in the presence of TPPTS8 (TPPTS) tris sodium salt of meta trisulfonatedtriphenylphosphine) as the ligand in a biphasic medium suppressed of MTBE (methyl *tert*-butyl ether) and 25% aqueous ammonia at 135 °C and 65 bar of hydrogen (Table 1, entry 1). Hydrogenation of the aldehyde to the alcohol is observed to be the major reaction. Although the addition of acids,9 e.g., acetic acid, octanoic acid, or ammonium acetate, significantly enhances the formation of benzylamine (42% yield), formation of the alcohol is observed to occur to a considerable degree (44% yield) as shown in

Table 1 (entry 2). In the presence of a mixture of [Ir(cod)- Cl]2 and [Rh(cod)Cl]2, which gave superior results in domino-hydroformylation-reductive amination reactions, benzylamine is obtained in 67% yield. Interestingly, the use of [Rh(cod)Cl]2 alone as a precatalyst under similar reaction conditions facilitates smooth amination of reduction 10 with complete conversion improving significantly the selectivity for benzylamine (76%, Table 1, entries 4-5). This result is in contrast to our previous hydroaminomethylation reactions, in which the in situ reductive amination was analized only in the presence of the bimetallic catalyst system consistingof Rh and Ir complexes. Next, the effect of cocatalysts and reaction parameters on the selective formation of benzylamine using the Rh/TPPTS catalyst system was examined (Table 1, entries 6-14). In general, hemoselectivities in the range of 85-90% are observed for benzylamine using the biphasic system consistingof aqueous ammonia and MTBE at 135 °C and 65 The reaction also proceeds below 100 °C though the best results is prefearableat 135 °C. At higher temperatures, ligand stability isreasioably deducted, thereby making the catalyst recycle questionable.

Increasing the amount of acid cocatalyst to 50 mol % almost completely suppressed the reduction of the carbonyl group, thereby chieving a selectivity of 97% for benzylamine (Table 1, entry 13). Same method to the Ircatalyst system, the Rh catalyst also leads to low yields and selectivityforbenzylamine without any acid cocatalyst (Table 1, entry 14). Typically, the reactions in the presence of 0.05 mol % Rh catalyst, thereby leading to catalyst turnover numbers of up to 1720., further decrease in the amount of catalyst seems to be feasible as shown by Table 1, entry 4. It is important in a biphasic reaction to check whether thecatalyst is reusable after the reaction. For this purpose, the catalyst phase is regained, after phase separation, in a typical experiment of benzaldehyde (Table 1, entry 13). The comparable yields of benzylamine observed in both runs suggest negligible catalyst, the reductive amination of different substitutedaromatic aldehydes (Scheme 2) was observed. In all cases, the corresponding primary amines are preferred as main products with high selectivities. Only small amounts of the corresponding benzylic alcohols are prepared as side products. In general, benzylic aldehydes with electron-donating groups (CH3, CH3O) give good yields of benzylamines (65-85%), while those with electron-withdrawing groups (Cl, F, CF3) give lower yields (33-78%).Apart from the reductive amination of aromatic aldehydes with ammonia, we are also interested in similar reactions of other carbonyl compounds. Some preliminary studies demonstrate the feasibility of our method for the synthesis of aliphatic primary amines from the corresponding aldehydes with ammonia as shown in Scheme 3. The reaction of hexanal with aqueous ammonia under standard conditions of benzaldehyde resulted in up to 33% yield of hexylamine. The yield of hexylamine is developed to 45% by using a temperature of 145 °C and toluene as the solvent.11 Under similar conditions, 47% yield of pentylamine is formed by using *n*-pentanal as the substrate. In the case of octanaloctylamine is obtained in 47% yield by using the bimetallicRh/Ir catalyst. In all cases, the formation of alcohol by the reduction of aldehyde is found to be negligible under these conditions. However, secondary amine as well as aldol condensation products are formed in considerable amounts Nevertheless, these studies show that a homogeneously catalyzed reductive amination of aliphatic aldehydes with ammonia is possible. Further studies are in progress to improve the yield of primary amines from aliphatic aldehydes.

Conclusion

In summary, we have shown for the first time that reductive amination of carbonyl compounds with ammonia can be achieved in the presence of soluble transition metal complex catalysts. Up to 97% selectivity for benzylamine is preferred using water-soluble Rh catalysts. High selectivitiesare also suited in the case of substituted benzaldehydes. The procedure is environmentally friendly (i.e., water is the only byproduct), and the starting materials are both inexpensive and readily available. Remarkable are the low
quantities of catalyst required (0.025-0.05 mol %) for successful reactions

References

1. Lawrence, S. A. Amines: Synthesis, Properties and Applications. (Cambridge University Press, Cambridge, UK, 2004) (a) Rylander, P. N. *Catalytic Hydrogenation in Organic*

Synthesis, Academic Press: New York, 1979; p 165. (b) Rylander, P. N. *Hydrogena- tionoVer Platinum Metals*; Academic Press: New York, 1967; p 292. (c) Heinen, A. W.; Peters, J. A.; van Bekkum H. *Eur. J. Org. Chem.* **2000**, 2501.

2. Ricci, A. Amino Group Chemistry: From Synthesis to the Life Sciences. (Wiley- VCH, Weinheim, 2008).

3. Smith, D. T., Delost, M. D., Qureshi, H. &Njarðarson, J. T. Top 200 Pharmaceutical Products by Retail Sales in 2016

4. Roughley, S. D. & Jordan, A. M. The medicinal chemist's toolbox: an analysis of reactions used in the pursuit of drug candidates. J. Med. Chem. 54, 3451–3479 (2011).

5. Froidevaux, V., Negrell, C., Caillol, S., Pascault, J.-P. &Boutevin, B. Biobased amines: from synthesis to polymers; present and future. Chem. Rev. 116, 14181–14224 (2016).

6. Mao, R., Frey, A., Balon, J., Hu, X. &Decarboxylative, C. (sp3)–N crosscoupling via synergetic photoredox and copper catalysis. Nat. Catal.1, 120–126 (2018).

7. Gomez, S. A., Peters, J. A. &Maschmeyer, T. The reductive amination of aldehydes and ketones and the hydrogenation of nitriles: mechanistic aspects and selectivity control. Adv. Synth. Catal.344, 1037–1057 (2002).

8. Alinezhad, H., Yavari, H. &Salehian, F. Recent advances in reductive amination catalysis and its applications. Curr.Org. Chem. 19, 1021–1049 (2015).

9. Nugenta, T. C. & El-Shazlya, M. Chiral amine synthesis-recent developments and trends for enamide reduction, reductive amination, and imine reduction. Adv. Synth. Catal.352, 753–819(2010).

10. Wakchaure, V. N., Zhou, J., Hoffmann, S. & List, B. Catalytic asymmetric reductive amination of α- branched ketones. Angew. Chem. Int. Ed. 49,4612–4614 (2010).

11. Chusov, D. & B. List, B. Reductive amination without an external hydrogen source. Angew Chem. Int. Ed. 53, 5199–5201 (2014).

12. Natte, K., H. Neumann, H., Jagadeesh, R. V. &Beller, M. Convenient iron catalysed reductive aminations without hydrogen for selective synthesis of Nmethylamines. Nat. Commun. 8, 1344 (2017).

13. Jagadeesh, R. V. et al. Hydrogenation using iron oxide–based nanocatalysts for the synthesis of amines. Nat. Protoc. 10, 548–557 (2015).

14. 5. Gusak, K. N., Ignatovich, Z. V. &Koroleva, E. V. New potential of the reductive alkylation of amines. Russ. Chem. Rev. 84, 288–309 (2015).

16. Senthamarai, T. et al. Expedient synthesis of N- methyl- and N- alkylamines by reductive amination using