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# Synthesis of 1-[(6-chloropyridin-3-yl)methyl]imidazolidin-2-imine

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## ABSTRACT

*Imidacloprid is reduced by activated Fe in conc. HCl to obtain a dis-nitro imidacloprid, and further characterized by IR, PMR and LC-MS/MS spectral analysis.*

**Key words:** Imidacloprid, dis-nitro imidacloprid, nitro reduction, yellowish crystalline.

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## INTRODUCTION

Numerous methods of homogeneous and heterogeneous catalytic hydrogenations have been reported. The heterogeneous hydrogenation catalysts offer several advantages over homogeneous hydrogenation catalyst with respect to easy recovery and recycling of the catalysis as well as the minimization of undesired toxic wastes. The various processes are used for the reduction of nitro compounds have been reported. R. H. Khan [1] is used tellurium powder in aqueous methanolic ammonium chloride. Takehito Tsukinoki and Hirohisa Tsuzuki [2] synthesized anilines with zinc metal and  $\text{NH}_4\text{Cl}$  in water. D. G. Desai et al [3] and Yugang Liu et al [4] reduced nitroarenes with  $\text{FeS-NH}_4\text{Cl-CH}_3\text{OH-H}_2\text{O}$  and  $\text{Fe-NH}_4\text{Cl}$  system. D. Channe Gowda et al [5-8] used different catalytic sources Pd/C, Ni, Zn and Mg which selectively reduce nitro compound in presence of other reducible groups like ethenes, ethynes, nitriles, carbonyl compounds, acids, alcohols and acetones and developed the hydrazinium monoformate [9,10] as the hydrogen donor to complete the reaction within 2-10 minutes at a room temperature. All the compounds reduced by Raney Ni/ $\text{N}_2\text{H}_4\cdot\text{HCOOH}$  and Zn/ $\text{N}_2\text{H}_4\cdot\text{HCOOH}$  in good yields (90-95%). P. Haldar and V. V. Mahajani [11] reported the reaction at a temperature between 35-85°C with ammonium formate as a hydrogen donor and propan-2-ol as solvent using Pd/C as a catalyst. P. Selvam et al [12-15] have reported the chemo and regionselective reduction of nitroarenes over NiHMA (nickel-incorporated hexagonal mesoporous aluminophosphate molecular sieves), FeHMA, CoHMA, NiMCM-41. While F, -Cl, -Br, -OH, -CN, -CH<sub>3</sub>, -OCH<sub>3</sub>, -NH<sub>2</sub> groups could be tolerated during the reaction. Radha V. Jayaram et al [16,17] reported the catalytic transfer hydrogenation of aromatic nitro compounds on  $\text{LaMO}_3$  (M= Mn, Fe, Co, Cr, Al). Sachin

Sonavane and Radha Jayaram [18] reported the catalytic hydrogenation of nitroarenes with propan-2-ol and KOH/NaOH over the mixed metal oxides, such as  $\text{ZrO}_2\text{-NiO}$ ,  $\text{ZrO}_2\text{-CoO}$  and  $\text{ZrO}_2\text{-Fe}_2\text{O}_3$ . Further, D. Channe Gowda *et al* [19-20] have reported the reduction of nitro compounds by hydrazine hydrate over zinc and magnesium. The reduction of nitro compounds can be accomplished with a commercial zinc or magnesium dust within ten minutes. Pramod Kumbhar *et al* [21] and Auer *et al* [22] reduced aromatic nitro compounds with hydrazine hydrate over Mg-Fe hydrotalcite and Fe-Mg-Al hydrotalcite. M. Kumarraja and K. Pitchumani [23] reduced nitroarenes by hydrazine in faujasite zeolites using nonpolar solvent. Ravi Kanth *et al* [24] have reduced nitroarenes on  $\text{Al}_2\text{O}_3$  support in presence of sodium hydrogen sulphide under microwave conditions. Wang Lei *et al* [25] reported the reduction of aromatic nitro compounds with metallic tellurium in near-critical water [26]. Elemental iron has also been shown to reduce azo and nitro compounds at high rates to the corresponding aromatic amine counterparts [27]. The number of aromatic nitro compounds has been reduced by the use of activated Fe in conc. HCl. The method of reduction employed by Jenkins, McCullough and Booth, which has been used successfully, this method has been found to be desirable because of the chief materials and undesired chlorinated products [28].

In mammalian systems the 'magic nitro' group of imidacloprid has been postulated to be reduced to nitrosoguanidine and aminoguanidine and then cleaved to the guanidine and urea derivatives. The parent molecules of the nitrosoguanidine would be further converted to a non-toxic urea metabolite via more toxic dis-nitro intermediate, by unknown liver enzymes. LC-MS TOF spectrum of the pseudo molecular ions ( $m/z + \text{H}^+$ ) of imidacloprid and its presumptive dis-nitro, nitrosoguanidine 211  $m/z$  and urea 212  $m/z$  metabolites [29]. The nitro reduction pathway of imidacloprid yields all or most of the -NNO, -NNH<sub>2</sub>, -NH, and -urea series of metabolites [30]. Several attempts have been made to identify the photolysis products from the 254 nm irradiation of imidacloprid to N-NHOH, N-NH<sub>2</sub> and finally N-H, the dis-nitro metabolites [31]. Proposed route for the degradation of imidacloprid promoted by zero-valent metals (Fe, Sn, Zn) in acidic aqueous solution [32].

Hence we thought it proper to reduce imidacloprid to obtain dis-nitro imidacloprid as a target compound by using simple and chief method, Fe in conc. HCl.

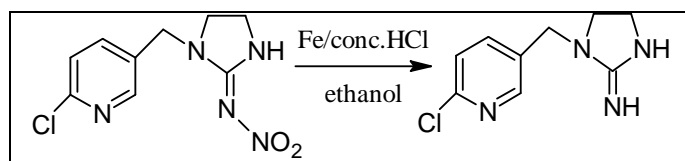


Fig 1: Scheme of synthesis for dis-nitro imidacloprid

## MATERIALS AND METHODS

**General:** All compounds were checked for their purity by TLC. Structures of the synthesized compounds have been confirmed on the basis of LC-MS/MS (Agilent 1200 series HPLC system (Agilent technologies, USA) hyphenated to an API-4000 Q-Trap mass spectrometer, Applied Biosystems, MDS Sciex, Canada), <sup>1</sup>H NMR (Avance II-300, Bruker) and FT-IR (Perkin Elmer

Spectrum one) spectral analysis. The scheme of synthesis of target compound is shown in fig.1. The physical data of all the synthesized compounds are given below.

**1-[(6-Chloropyridin-3-yl)methyl]imidazolidin-2-imine (Dis-nitro imidacloprid) (2).** The solution of imidacloprid (12.75 gm, 0.05 mole) in 30 ml of alcohol, a finely powdered activated Fe metal in the proportion of 1:2 mole (5.59 gm, 0.10 mole) was added, followed by the addition of 40 ml conc. HCl. The reaction mixture was refluxed with constant stirring for 10 h. After completion of the reaction, the reaction mixture filtered while hot to remove unreacted Fe metal. Filtrate was then cooled and neutralized with conc. NaOH to get a yellowish crystalline product separated by filtration. This was then purified by recrystallization in ethanol to get yellowish crystalline product. Yielded 80%, m.p 245<sup>0</sup>C IR (KBr)  $\nu_{\max}$ : 3233, 3083, 2923, 1690 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) :  $\delta$ , 3.55 (s, 2xCH<sub>2</sub>), 4.62(s, CH<sub>2</sub>), 7.36(d, J=8.2 Hz, Py1H), 7.74(dd, J1= 7.5 Hz, J2= 2.5 Hz, Py1H), 8.21(s, NH), 8.32(s, Py1H) ppm. LC-MS/MS (m/z): 211, 193, 175, 169, 133, 126, 84.

## CONCLUSION

The process of nitro reduction of imidacloprid is monitored by using Fe in conc. HCl. It is observed that the removal of nitro compound during the process of reduction gave dis-nitro imidacloprid as a yellowish crystalline compound. This method of reduction is simple, rapid as the product is easily separated from the reaction mixture.

## REFERENCES

- [1] R. H. Khan, *J. Chem. Research*, **2000**, **31**, 290-291.
- [2] T. Tsukinoki, H. Tsuzuki, *Green Chemistry*, **2001**, **3**, 37-38.
- [3] D. G. Desai, S. S. Swami, S. K. Dabhade, M. G. Ghagare, *Synthetic Communications*, **2001**, **31**(8), 1249-51.
- [4] Y. Liu, Y. Lu, M. Prashad, O. Repic, T. J. Blacklock, *Adv. Synth. Catal.*, **2005**, **347**, 217-19.
- [5] D. Channe Gowda, B. Mahesh, *Synthetic Communications*, **2000**, **30**(20), 3639-44.
- [6] K. Abiraj, G. R. Srinivasa, D. Channe Gowda, *J. Chem.*, **2005**, **58**, 149-51.
- [7] D. Channe Gowda, A. S. Prakasha Gowda, A. R. Baha, Shankare Gowda, *Synthetic Communications*, **2000**, **30**(16), 2889-95.
- [8] D. Channe Gowda, B. Mahesh, Shankare Gowda, *Indian Journal of Chemistry*, **2001**, **40**, 75-77.
- [9] Shankare Gowda, B. K. Kempe Gowda, D. Channe Gowda, *Synthetic Communications*, **2003**, **33**(2), 281-89.
- [10] Shankare Gowda, D. Channe Gowda, *Tetrahedron*, **2002**, **58**, 2211-13.
- [11] P. Haldar, V. V. Mahajani, *Chemical Engineering Journal*, **2004**, **104**, 27-33.
- [12] P. Selvam, S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram, *Tetrahedron Letters*, **2004**, **45**, 2003-07.
- [13] S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram, P. Selvam, *Applied Catalysis B: Environmental*, **2003**, **46**, 155-63.
- [14] S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram, P. Selvam, *Tetrahedron Letters*, **2002**, **43**, 8527-29.
- [15] S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram, *Organic Letters*, **2002**, **4**(24), 4297-4300.
- [16] A. S. Kulkarni, R. V. Jayaram, *Applied Catalysis A: General*, **2003**, **252**, 225-30.

- [17] A. S. Kulkarni, R. V. Jayaram, *Journal of Molecular Catalysis A: Chemical*, **2004**, 223, 107-10.
- [18] S. U. Sonavane, R. V. Jayaram, *Synthetic Communications*, **2003**, 33(5), 843-49.
- [19] Shankare Gowda, D. Channe Gowda, *Indian Journal of Chemistry*, **2003**, 42B, 180-83.
- [20] G. R. Srinivasa, K. Abiraj, D. Channe Gowda, *Indian Journal of Chemistry*, **2003**, 42B, 2885-87.
- [21] P. S. Kumbhar, J. Sanchez-Valente, Jean Marc M. Millet, F. Figueras, *Journal of Catalysis*, **2000**, 191, 467-73.
- [22] S. M. Auer, J.-D. Grunwaldt, R. A. Koppel, A. Baiker, *Journal of Molecular Catalysis A: Chemical*, **2000**, 139, 305-13.
- [23] M. Kumarraja, K. Pitchumani, *Applied Catalysis A: General*, **2004**, 265, 135-39.
- [24] S. Ravi Kanth, G. Venkat Reddy, V. V. V. N. S. Rama Rao, D. Maitraie, B. Narsaiah, P. Shanthan Rao, *Synthetic Communications*, **2002**, 32(18), 2849-53.
- [25] W. Lei, L. Pin-Hua, J. Zhao-Qin, *Chinese Journal of Chemistry*, **2003**, 21, 222-24.
- [26] Q-x. Shi, R-w. Lv, Z-x. Zhang, D-f. Zhao, Advances in Heterogeneous Catalytic Transfer Hydrogenation of Aromatic Nitro Compounds, The Proceedings of the 3rd International Conference on Functional Molecules, pp-54-58.
- [27] J. R. Perey, B. L. Lubenow, P. C. Chiu, D. K. Cha, Electrochemical Methods for Wastewater and Potable Water Treatment, Symposia Papers Presented Before the Division of Environmental Chemistry American Chemical Society Boston, MA August **2002**, 18-22, 42 (2), 534-36.
- [28] S. E. Hazlet, C. A. Dornfeld, *J. Am. Chem. Soc.*, **1944**, 66 (10), 1781-82.
- [29] G. Pandey, S. J. Dorrian, R. J. Russell, J. G. Oakeshott, *Biochemical and Biophysical Research Communications*, **2009**, 380, 710-14.
- [30] K. A. Ford, J. E. Casida, *Chem. Res. Toxicol.*, **2006**, 19, 1549-56.
- [31] A. F. Lagalante, P. W. Greenbacker, *Analytica Chimica Acta.*, **2007**, 590, 151-58.
- [32] R. P. Lopes, Ana P. F. M. de Urzedo, Cle´sia C. Nascentes, R. Augusti, *Rapid Commun. Mass Spectrom.*, **2008**, 22, 3472-80.