Microwave Assisted reduction of Aromatic Nitro Compounds with Ammonium Chloride and Zinc dust

Jassim Mohammed Abdullah Mohammed Mahmood Suliman
College of Environmental , Mosul University
Salem Jassim Mohammed
College of Science, Mosul University

(NJC)

(Recevied on 11/1/2011) **(Accepted for publication 10/ 7/2011)**

Abstract

A fast, easy and rapid environmentally friendly method for the reduction of aromatic nitro compounds to their corresponding amines in good yield and short time is developed by using microwave irradiation, in the presence of zinc dust ammonium chloride and solvent free condition.

الخلاصة

تم تطوير طريقة سريعة وسهلة وصديقة للبيئة لاختزال مركبات النترو الاروماتيه إلى الأمينات الاروماتيه وبزمن تفاعل قصير وناتج عالي وذلك باستخدام تقنية المايكروويف وبوجود مـسحوق الخارصـين وكلوريـد الامونيـوم وبدون مذيب .

Introduction

During the last decades microwave irradiation has became an increasingly valuable tool in organic chemistry, since it is a simple and easy technique, applicable to a large Varity of organic synthesis [1-3].Thus, a large number of organic reactions that require heat can be carried out under microwave irradiation to give higher yields than conventional methods after short time under mild conditions

Aromatic amines are an important class of organic compounds, frequently used as key intermediates in the synthesis of pharmacy products, dye stuff and polymers[4].Various methods have been reported the synthesis of aromatic amines[5,6],from the corresponding nitro compounds. The methods employed are generally metal-acid catalysed reduction [7-9].However these methods have one or more limitation, either it needs strong acidic medium, high temperature and organic solvents in recent years, metal mediated reactions have wide scope in organic synthesis. Hydrazine hydrate, diammonium hydrogen phosphate, ammonium formate are usually used as hydrogen donor in the presence of heterogenous catalysts such as activated

zinc, copper, Rany nickel and ferric chloride. The reaction usually conducted in refluxing condition ,organic solvent and in most cases require several hours[10-12]

The aim of this work was to develop environmentally acceptable, simple method for reduction of aromatic nitro compounds using low cost commercial zinc dust and ammonium chloride under microwave irradiation and solvent free condition.

Experimental

All the aromatic nitro compounds used were either Fluka or Aldrich chemical products without further purification. Melting points were determined using electro thermal 9300 melting point apparatus and are uncorrected. IR Spectra were recorded by Bruke 96565 Spectroscopy as (KBr disk). UV Spectra were recorded on Shimadzu (UV-1600) UV-Visible Spectrophotometer using methanol as a solvent.

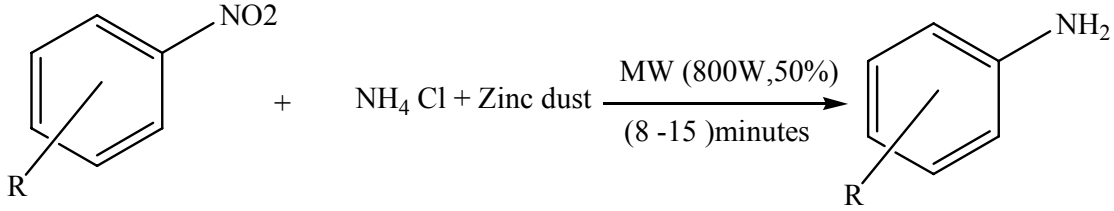
General procedure

Aromatic nitro compounds(5mM),Zinc dust (0.25 g) and ammonium chloride (10mM) in 5 ml water were mixed thoroughly in a small beaker size 25ml .Then the reaction solid mixture was placed in aCALTRNIC,MW G748,GMBH microwave oven(800W)for domestic at 50% power level for(8-15 min.), the progress of the reaction was monitored by checking the solubility of the solid reaction mixture product in dilute HCl, when all the organic solid dissolved, filtered to separate Zinc dust, neutralize the aqueous solution, separate the solid by filtration and recrystallized from an appropriate solvent(aqueous Ethanol).

Result and Discussion

The reduction of aromatic nitro compounds to the corresponding aromatic amines, in the presence of zinc dust ammonium chloride solvent free and under microwave irradiation was completed within 8-15 minutes. The course of the reaction was monitored by checking the solubility of the solid product in aqueous HCl. The workup of the reaction products isolation and purification were easy Thus all the compounds reduced ,Table(1) by this system were obtained in good to excellent yield (82-95%) .All the products were identified and characterized by comparison of their ,mp. IR and UV absorption spectra with that reported in literatures [17,19-22], Tables (1and 2).

The general scheme and condition of the reaction are shown in scheme 1.



R= P-OCH_3 ,m- NH_2, o-CH_3, m- OCH_3,o-NH_2, p-NH_2, p-CH_3,p-Br ,p-Cl

(Scheme 1)

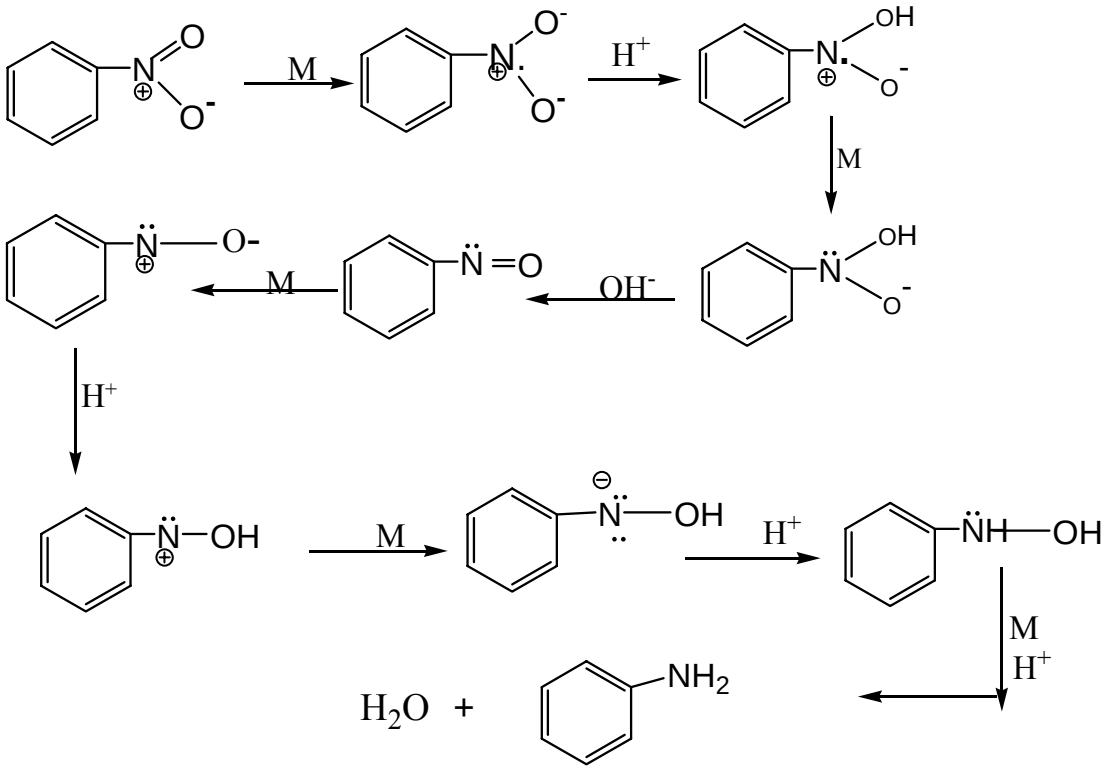
Control experiments were carried out using two of the nitro compounds with ammonium chloride with out zinc dust under microwave irradiation did

not yield the desired aromatic amine products.

The advantage of the present method is that all the reductions could be carried out in the presence of air and not requires a nitrogen atmosphere.

The obvious advantages of the microwave method over the conventional reduction methods are The reduction is easy to operate under simple experimental condition completed within short time with high yield of the substituted aromatic amines. Avoidance of using organic solvents and strong acid medium and Less expensive materials used.

The general expected mechanism [18] of the reduction of aromatic nitro compounds using metal powder and hydrogen promoter like ammonium chloride formic acid, hydrazine, ---etc, as shown in scheme 2.

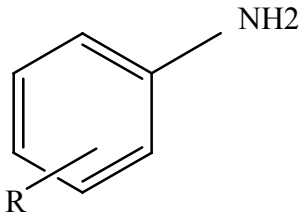


(Scheme 2)

Structural assignment of these products are strongly supported by physical and spectral data .The IR spectra showed characteristic absorptions at the range (3285-3384 cm^{-1})for symmetrical NH ,(3335-3445 cm^{-1}) for asymmetrical NH ,at the range (3040-3134 cm^{-1}) due to CH-Ar group ,and the range (1600-1630 cm^{-1}) for aromatic system .Finally C-N group are shown in the range (1079-1290 cm^{-1}). The UV spectra showed ג max (MeOH) at the range (210 – 293 nm) for all the products .

Finally, we concluded that aeries of substituted aromatic amines have been synthesized using domestic microwave oven. The reaction time has been brought down from hours to minutes ,resulting higher overall yields ,these comparing very favorably with alternative methodology [5,6,11,12] .

Table1: Physical data of the Aromatic Amines (2a-i)



Compounds No.	R	m.p.(ºc) found (lit.)	Yield %	Time of reaction (minutes)
2a	p-OCH3	55-57 (56-57)	93	10
2b	m-NH2	65-66 (64-65)	95	11
2c	o-OH	174-175 (173-174)	86	10
2d	m- OH	120-122 (121-123)	92	15
2e	o- NH2	99-101 (102-104)	84	10
2f	p- NH2	142-144 (139-141)	93	12
2g	p- CH3	44-46 (44-45	93	15
2h	p-Cl	71-73 (70-71)	92	8
2i	p- Br	63-65 (65-66)	95	10

Table 2: **Spectral data for aromatic amines (2a-2)**

COMPDS NO.	IR (KBR)					UV (MEOH)
	NH_2	C=C	CH-Ar	C-N	others	
2a	3340 3425	1630	3050	1135	-------	240
2b	33203 380	1605	3098	1079	--------	218
2c	3285 3335	1610	3055	1268	3450 for OH	282
2d	3300 3370	1600	3040	1172	3433 for OH	293
2e	3285 3390	1620	3125	1290	---------	210
2f	3300 3375	1620	3130	1175	---------	205
2g	3350 3430	1630	3134	1083	----------	238
2h	3384 3445	1610	3097	1172	----------	242
2i	3370 3418	1623	3065	1183	---------	245

References

1- J.T.Tierney; P.Lindstrom; Microwave-assisted organic synthesis; Blackwell: Oxford,UK,**2005**

2 - A.Loupy,Microwave in organic synthesis;Wiley-VCH:Weinheim,Germany,**2006**

3- p. Lindstrom, J, Tierney; B. Wathey ; J. Westman ,.***Tetrahedron*** ,2001**,57**, 9225-9283.

4- S.Ram, R. E. Ehrenkaufer ; *Tetrahedron Lett*. 1984,**25**, 3415.

5- F. Yuste; J.L.; f.walls, ***Tetrahedron Lett***.; 1982, **23**, 147.

6-R.E.lyle; J. L., LaMattina; Synthesis,**1974**,726.

7- H.O.House, Modern Synthesis Reaction ,2ndEd. ;Benzamin Inc. U.S.,**1972**

8- C. A. Merlic, B. Quinn, ***J.Org.chemistry***,1995,**60**,3365.

9- R. A. Johnstone, A. H. Willy, I. D.Entwistle;***Chem.Rev***.,1985,**85,** 129.

10- L.Wang,L.Pin-Hua,J.,Zhao-Qin,;***Chines J. Chem. Rev***.,1985,**21**,222.

11- B.W.,Yoo,S.K..Hwang, J.W.Choi,; ***Synth. Commun***.,2003,**33**,2985.

12-K. Bhaumik, K.G. Akamanchi , ***Can.J.Chem***.;2003,**81**,197.

13- F.Ragaini,S. Cenini,M. Gasperini;***J.Mol.Cat***.,2003,**74,**51.

14- D.G.Desai ,S.S.Swani,S.K. Dabhade,M.G.,Ghagare;***Synth.Commun.,*** 2001,**31**,1249.

15- D.C.Gowda,B.Mahesha,A. Gowda,***Indian,J.,Chem***.,2001,**40B**,75-77.

16- S. Amit, R., Brindaban, ***J. Org. Chem***., 2008**,73(17)**,6867-6870.

17- K. A. Kumer, K. S., Shruthi, N., Nagaraja, C.Gowda,E-Journal of Chemistry,**2006**,**5(4),**914-917.

18- B., Raju, R. Ragul, B. N., Sivasankar; ***Indian Journal of Chemistry***,2009, **48B**,1315-1319.

19- A.I.Vogel,Text Book of practical Organic Chemistry,5th Ed. Addison Wesly Longman Limited,UK,,**1977**.

20- The Merch Index,11thEd.;Merch co.,Inc.,,USA,**1989**

21- Hand Book of fine chemicals Aldrich, **2007**

22- K., Abiraj; S. Gowda;C.H.,Gowda; Synth.React.***Inorg.Met.Org.Chem***., 2002,**32(8)**,1409-1417.