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Microwave Assisted Iodination of Aromatic Amines by Using Iodineand Iodic Acid Combination as a Iodinating agent

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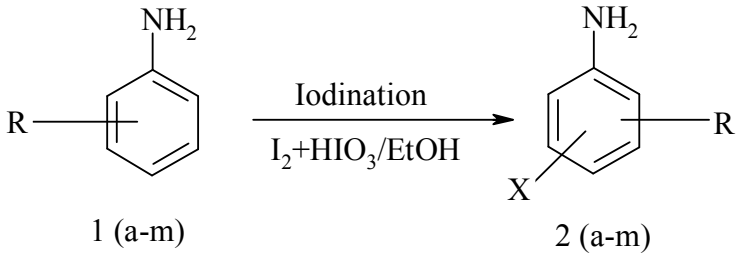
Abstract : A fast and simple method for the oxidative iodination of aromatic amines either under microwave irradiation or conventional method is reported, iodine and iodic acid combination as a iodinating agent in solvent ethanol is described. A combination of iodine and iodic acid has been found to be an excellent reagent for efficient iodination of aromatic amines. The attractive feature of microwave methods are simple experimental procedure, short reaction time and pure iodoproducts.Thus, method is mild and ecofriendly.
Key Words: Aniline, Iodine, Iodic acid, Microwave, Iodoanilines**.**

Introduction

Iodobenzene derivatives are useful in the synthesis of organic and biochemistry.[1] Iodo compounds are also reported to posses antifungal and antibacterial activity.[2] Iodination of aromatic compounds has been carried out by using molecular iodine along with strong oxidising agent such as nitric acid[3], sulphuric acid[4], iodic acid[5], sulphur trioxide[6] and hydrogen peroxide[7]. Recently iodination methods have been intensively developed using iodinium donating systems such as iodine monochloride,[8] iodine–di–iodine-pentaoxide,[9] murcury-II oxide iodine,[10] iodine-F-TEDA-[1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo [2,2,2] octane-bis-(tetrafluoroborate)][11] iodine silver sulphate,[12] iodine mercury salt,[13] NaOCl – NaI,[14] iodine/ $Na_2S_2O_8$,[15] Benzyl trimethyl ammonium dichloroiodate,[16] urea hydrogen peroxide[17] and iodine and iodic acid.[18]
Bis (pyridine) Iodonium (I) Tetra fluoroborate CF_3SO_3H [19] , iodine $(NH_4)_2S_2O_8$-$CuCl_2$-Ag_2SO_4[20]
However some of these reagents are hazardous and toxic.

Considering importance of iodoaromatic in organic synthesis, we are reporting first time synthesis of some iodoanilines by iodination of substituted anilines using iodine and iodic acid combination as reagent and ethanol as solvent under microwave irradiation method. In conventional method [21] for iodination, substituted aniline and iodine was dissolved in ethanol. Iodic acid dissolved in minimum amount of water added at 40°C and solution stirred for 2 h. Separated solid was filtered ,washed with sodium thiosulphate solution and then with water and crystallised from ethyl alcohol.
In microwave accelerated method, substituted aniline and iodic acid were dissolved in ethanol. Iodic acid dissolved in minimum amount of water was added and solution irradiated for 2 min. Separated solid was filtered,washed with sodium thiosulphate solution and then water and crystallised from ethyl alcohol. Microwave assisted iodination completes within 2 min. where as conventional method completes within 2 h.
Structures of the products were confirmed by compairing melting point with authentic samples or by an elemental analysis and spectral data.
The attractive features of microwave methods are simple experimental procedure, short reaction time and pure iodoproducts. Thus, method is mild and ecofriendly.

Scheme:



1 (a-m) 2 (a-m)

Where, R=H,NO_2,Cl,CH_3,COOH and X = Iodine

Experimental

Melting points (uncorrected) were determined in open capillary tubes. The purity of compounds was checked by TLC using silica gel G. The I.R. spectra (Nujol) were recorded on a Perkin-Elmer Spectrophotometer and ^{1}HNMR Spectra were recorded on Gemini 300-MHz instrument in $CDCl_3$ as solvent and TMS as an internal standard. The mass spectra were recorded on an automated Finningan MAT1020c mass spectrometer using ionization energy of 70 ev. LG make (450W) micro oven was used.

General Procedure for Iodination of substituted aromatic amines in solvent ethanol by conventional method.

An appropriate amines (0.05 mol.) and iodine (0.04 mol.) was dissolved in ethyl alcohol. Iodic acid (0.01 mol.) dissolved in water (1 ml.) was added with stirring within a period of 5 min. and then the reaction mixture was stirred for 2 h. at room temperature, solid product separate out. It was treated by sodium thiosulphate to remove unreacted iodine. Solid obtained was filtered and crystallized from ethyl alcohol.

General Procedure for iodination under microwave irradiation:

A mixture of aniline (0.05 mol.) and iodine (0.04 mol.) was dissolved in ethanol, iodic acid (0.01mol) dissolved in water (1.0 ml) was added. The flask was placed in a microwave oven (450 W) and irradiated for 20 s six times (total 2 min.) with short interval of time for cooling to avoid evaporation of solvent. The reaction mixture on cooling solid product separates out. Solid obtained was filtered, washed with sodium thiosulphate solution followed by water and crystallised from ethyl alcohol.

4-Iodo-2-nitroaniline[22] 2a: yield 84%. mp 118 ^{o}C (lit. mp 122^{o}C) IR (cm^{-1}): 3379 (NH). 1669, 1554 (C=C).^{1}HNMR ($CDCl_3$) δ :6.1 (s,2H,-NH_2), 6.7 (d,1H, 6Ar-H). 7.6 (d,1H,5Ar-H), 8.45 (s,1H,3Ar-H) Mass: 254 (M^+100), 234 (15), 218 (06), 170 (12) 91 (4), 64 (05)

2-Iodo-5-nitroaniline[23] 2b: yield 80%. mp 118^{o}C (lit. mp 120^{o}C) IR (cm^{-1}): 3355(NH). 1611, 1550 (C=C).^{1}HNMR ($CDCl_3$) δ 4.0 (s,2H,NH_2), 7.0 (d,1H,3ArH), 7.34(d,1H,4ArH), 7.76 (s,1H,6ArH).

2-Iodo-4-nitroaniline[24] 2c: yield 85%. mp 114^{o}C (lit. mp 116^{o}C) IR (cm^{-1}): 3308 (NH), 1620, 1580 (C=C).^{1}HNMR ($CDCl_3$), δ :4.80 (s,2H,-NH), 6.65 (d,1H, 6Ar-H). 8.05(d,1H,5Ar-H), 8.45 (s,1H,3Ar-H).

2,6-di-Iodo-4-nitroaniline[25] 2d: yield 82%. mp 250^{o}C, (lit. mp 250^{o}C) IR (cm^{-1}): 3379 (NH), 1621, 1554 (C=C).

2-chloro-4-Iodo-aniline[17] 2e: yield 80%. mp 68^{o}C (lit. mp 70^{o}C) IR (cm^{-1}): 3323-3336 (NH), 1614, 1477 (C=C).^{1}HNMR ($CDCl_3$) δ :4.0 (s,2H,-NH_2), 6.25 (d,1H, 6Ar-H), 7.30 (s,1H,5Ar-H), 7.55 (s,1H,3Ar-H).

5-chloro-2-Iodo-aniline[23] 2f: yield 85%. mp 59^{o}C, (lit. mp 58^{o}C), IR (cm^{-1}): 3338(NH), 1610, 1589 (C=C).^{1}HNMR ($CDCl_3$) δ :4.21 (s,2H,-NH_2), 7.4-8.2 (m,3H, Ar-H).

4-chloro-2-Iodo-aniline[25] 2g: yield **9**0%. mp 40^{o}C (lit. mp 39^{o}C) IR (cm^{-1}): 3358 (NH), 1620 (C=C).

2,6 di-Iodo-4-methylaniline[23] 2h yield **92**%. mp 118^{o}C, (lit. mp 120^{o}C), IR (cm^{-1}): 3319(NH). 1610, 1578 C=C).^{1}HNMR ($CDCl_3$) δ :2.2 (s,3H,-CH_3), 4.25(s,2H, NH_2), 7.5 (s,2H,2,6 Ar-H), Mass: 359 (M^+100), 205 (18), 154 (40), 153 (20) 127 (02), 76 (03).

4-amino-3-Iodo benzoic acid[26] 2i: yield **78**%. mp 255^{o}C, (lit. mp 258^{o}C) IR (cm^{-1}) :3377(NH), 1616, 1568 (C=C). ^{1}HNMR ($CDCl_3$) δ :4.2 (s2H,-NH), 6.45 (d,1H, 6Ar-H), 7.40 (d,1H,5ArH) 7.92 (s,1H,3ArH).

4-amino-3,5-di-Iodo benzoic acid[23] 2j: yield **75**%. mp 254°C, (lit. mp 254°C), IR (cm^{-1}):3345(NH), 1609, 1546 (C=C). ^{1}HNMR ($CDCl_3$) δ :4.65 (s,2H,-NH), 7.85(s,2H, 3,5Ar-H).

2-amino-5-Iodo benzoic acid[25] 2k: yield **82**%. mp 208°C, (lit. mp 208°C) IR (cm^{-1}) : 3377(NH), 1616, 1658 (C=C). ^{1}HNMR ($CDCl_3$) δ:4.2 (s,2H,-NH), 6.45 (d,1H, 6Ar-H), 7.40 (d,1H,5ArH) 7.92 (s,1H,3ArH).

2-amino-6-Iodo-4-nitro Toluene[23] 2l yield **80**%. mp 77°C, (lit. mp 78°C) IR (cm^{-1}): 34.46(NH). 1627, 1504 (C=C).^{1}HNMR ($CDCl_3$) δ :2.26 (s,3H,-CH_3), 3.92(s,2H, NH), 7.15 (s,1H,2Ar-H), 7.45 (s,1H,4 Ar-H).

2,6-Dichloro, 4-Iodoaniline[23] 2m: yield 84%. mp 80 °C, (lit. mp 80°C) IR (cm^{-1}): 3355, (NH) 1611, 1550 (C=C).^{1}HNMR ($CDCl_3$) δ :3.7(s,2H,-NH), 7.5 (s,2H, 3,5 Ar-H). Mass: 288 (M^+60), 259 (04), 143 (100), 118 (98), 91 (60), 65 (40),39, (45).

Result and Discussion

In our laboratory, we have devised a simple and efficient method for preparing of substituted iodo aromatic amines under microwave irradiation or conventional heating by using iodine and iodic acid combination as a iodinating agent. For the microwave assisted reactions, the reacton times were always shortened, simple experimental procedure and pure iodoproducts . Thus, the method is mild and ecofriendly.

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