Reduction of aryl nitro compounds to azoarenes and/or arylamines by Al/NaOH in methanol under ultrasonic conditions

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Abstract

Arylnitro compounds are reduced to the corresponding azoarenes and/or arylamines by aluminium metal in the presence of sodium hydroxide in methanol in high yields under influence of power ultrasound (35kHz) at 25°C. © 2004 Published by Elsevier B.V.

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1. Introduction

Reactions using ultrasound are more convenient than those by traditional methods and hence a large number of them are now been carried out under the influence of ultrasound, where in yields are high and the reaction gets accelerated. As mentioned in our earlier report [1], reductions of nitroarenes by Al/NH4Cl to the corresponding amines is an important transformation since many aromatic amines exhibit biological activity and find a multitude of industrial applications, being intermediates for the syntheses of dyes, photographic, pharmaceutical and agro chemicals.

Recent investigations on reduction by heterogeneous and homogeneous catalysts indicate that, aromatic nitro compounds are reduced by metal-mediated reactions into aryl amines by a variety of reagents such as, In/FeCl3/H2O [2], Te-near critical water temperature [3], Raney Ni/NH4Cl [4], Mg/N2H4 [5], Zn/N2H4 [6], Mg/HCOONH4 [7], Ru3(CO)12/chelating dimines [8], FeS/NH4Cl/CH3OH/H2O[9], Sm/NH4Cl [10], nanosized activated metallic iron powder in water [11], and Zn/NH4Cl in ionic liquids [12]. Each of these methods has its own advantages and limitations. On the other hand, reports on controlled reduction of nitroarenes to give intermediate products like azoarenes with glycol in presence of sodium metal [13], NaBH4/DMSO [14], or azoxyarenes with NaBH4/BiCl3 [15], and hydrazoarenes with Raney Ni/N2H4 [16] are also found in the literature.

2. Experiments

2.1. Material and Instruments

All nitro compounds were purchased from BDH and Merck, all the solvents used were distilled and dried before use. Reactions were monitored by TLC and GC–MS by comparison with authentic samples. Yields refer to the isolated products after purification by silica gel chromatography. Melting points/boiling points were taken in open capillaries using paraffin bath and are uncorrected. The IR and GC–MS spectra of the starting compounds and the products were recorded on a Nicolet 400D FT–IR Spectrophotometer and Shimadzu GC–MS QP 5050A respectively. All the reactions were carried out using Julabo, USR-3 German and Sidilu–Indian
make sonic baths working at 35kHz (constant frequency) maintained at 25°C by constant circulation of water.

2.2. General experimental procedure for reduction of nitroarenes at 35kHz

Nitroarene (10mmol), aluminium foil (82mg, 30mg cut into small pieces) and methanol (10ml) were placed in a two necked 50ml round bottom flask and sodium hydroxide (8g, 20 mmol) was added. The contents were sonicated in a sonic bath working at 35kHz (constant frequency), maintained at 25°C by circulating water. A vigorous exothermic reaction ensued with rapid development of yellow–orange coloration (attributed to the formation of the azoxy, azo or hydrazo compounds). The reaction was continued till they showed absence of the starting nitroarene in the reaction mixture, the progress of which was monitored by TLC [eluent: EtOAc–petroleum ether (60–80°C)], and by GC–MS. Later the reaction was quenched by adding water and then the organic compound was extracted by diethyl ether (2×25ml). The combined ether extract was washed with dil.HCl and neutralized with sat. NaHCO3. The extract was then dried over anhydrous K2CO3 and ether was removed on a rotavap. The product after drying under vacuum was identified by comparison of the mp/bp, IR spectrum with the authentic sample and GC–MS spectral analysis. Wherever a mixture was obtained, separation of the products was done by silica gel chromatography, using 10% acetone in pet. ether (40–60°C) as eluent.

3. Results and discussion

In this paper we report the results of reduction of nitroarenes to azoarenes and/or anilines by readily available inexpensive Al metal, in the presence of NaOH, in methanol as solvent. At reflux conditions (60–65°C), we observe facile reduction of nitroarenes into azoxy and azo compounds, which are further reduced into the corresponding hydrazoarenes and then into amines on continuing the reaction for prolonged time. It is also found that the reaction gets accelerated appreciably under the influence of ultrasound in a bath (35kHz). The reaction is schematically represented in Scheme 1.

The reaction conditions were optimized by carrying out the reduction of nitrobenzene with aluminium/NaOH. The progress of the reaction i.e., appearance of azoxybenzene from nitrobenzene, its disappearance and formation of azobenzene was monitored by TLC, GC–MS and also by working up small aliquots of the reaction mixture taken out at regular time intervals. In the case of p-nitroaniline, p-phenylenediamine was observed. In order to understand the mechanism of the reaction and to standardize the conditions, the reaction of different substituted nitroarenes with Al/NaOH in methanol was carried out in parallel experiments at reflux temperature of the solvent and under the influence of ultrasound in a bath (35kHz). The results of the experiments are summarized in Table 1.

Several interesting features of the reduction are apparent from Table 1. Substituents like –Cl, –NH2, –CH3, –OCH3, –OH, –COOH are not affected under the above reaction conditions. Electron withdrawing substituents such as –COOH, enhance both the initial reduction to azoxy compound and further reduction to azo and finally to amines. For such cases the reactions are relatively rapid and require less time for completion and afford good yields of amines (entries 11 and 12), p- and o-chloronitrobenzenes are also converted to azo derivatives (entries 2 and 3). Electron-releasing groups, on the other hand, retard the reaction to varying degrees, depend upon their donating ability and require relatively more time for completion of the reaction (entries 4 to 10). o- and m-Nitrotoluenes are reduced to the corresponding azo and amine derivatives (entries 6 and 7), o-nitroanisole affords the corresponding azoxyarene and amine derivatives (entry 8). o- and p-nitroanilines, p-nitroanisole, o-nitrophenol are completely converted to the corresponding amines (entries 4, 5, 9 and 10). The reactions take 7–18h for completion at reflux temperature of the solvent, and the yields of the products are found to be 3–5% less than that under the influence of ultrasound. However, nitrosobenzene, aryl-hydroxylamine or hydrazobenzene were not detected in these reactions.
4. Conclusion

We have developed a simple and convenient method for the preparation of azoarenes and/or aryl amines by the reduction of nitroarenes using inexpensive, readily available and abundant Al metal in the presence of NaOH in methanol under the influence of ultrasound. From the GC–MS spectral analysis it is clear that the reduction proceeds through the formation of azoxy, azo and probably hydrazoarene intermediates to give aryl amines. In our opinion, the present method of reduction of nitroarenes into azoarenes and/or aryl amines is superior to some of the existing methods of reduction which employ expensive reagents as discussed above.

References