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Ultrasonics Sonochemistry 13 (2006) 42–46

Ultrasonics SONOCHEMISTRY

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A comparative study and development of an improved method for the reduction of nitroarenes into arylamines by Al/NH_4X (X = Cl, Br, I) in methanol under ultrasonic conditions

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Received 13 July 2004; received in revised form 27 November 2004; accepted 16 December 2004
Available online 5 March 2005

Abstract

Nitroarenes were shown by us earlier to undergo reduction when treated with Al/NH_4Cl in methanol under sonic conditions to give anilines in high yields [D. Nagaraja, M.A. Pasha, Tetrahedron Lett. 40 (1999) 7855]. Now, a comparative study has been carried out and an efficient and improved procedure for this reduction by using Al/NH_4X (X = Cl, Br, I) is reported. A plausible mechanism of the reaction is envisaged.

Keywords: Aluminium; Ammonium halides; Nitroarenes; Arylamines; Reduction; Hydrogen transfer; Ultrasound

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1. Introduction

Ultrasound has been used extensively in organic syntheses. Compared to traditional methods, it is more convenient and hence a large number of organic reactions have been reported in the past three decades [1,2]. Ultrasound is beneficial in one or more ways like accelerating a chemical reaction, uses less purified or cruder reagents, initiating reactions without the need of additives or catalysts, avoids forcing conditions like high temperature and high pressure, and for simplifying the reaction by reducing the number of steps, hence, makes a reaction cost effective which matches with 'green chemistry' protocols. Under sonic conditions, the yields are high and the reactions occur in shorter reaction durations.

Reduction of nitroarenes into anilines on the other hand is an important transformation since many aromatic amines exhibit biological activity and find a multitude of industrial applications being intermediates for the synthesis of dyes, photographic, pharmaceutical and agricultural chemicals [3].

Although a large number of methods for the reduction of aromatic nitro compounds have been developed [4], many of these are incompatible with other functional groups in the substrate. Recent investigations on reduction of functional groups by heterogeneous and homogeneous catalysts indicates that, aromatic nitro compounds are reduced by metal-mediated reactions into aryl amines by a variety of reagents, some of them are In/$FeCl_3/H_2O$ [5], Te/near critical water temperature [6a], Te/NH_4Cl [6b], Ni/NH_4Cl [7], $Ru_3(CO)_{12}$/chelating diimines [8], FeS/$NH_4Cl/CH_3OH/H_2O$ [9], Sm/NH_4Cl [10], nanosized activated metallic iron powder in water at 210 °C [11], Zn/NH_4Cl in ionic liquids [12], Mg/$HCOONH_4$ [13a], Mg/N_2H_4 [13b] and Zn/N_2H_4 [13c]. The reported methods have their own advantages and limitations. For example, some of the systems require longer duration and works at reflux temperature of the solvent or at higher temperatures, expensive metals like indium, tellurium, samarium and ruthenium carbonyls are used for the reaction. Hydrazine hydrate is toxic in

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doi:10.1016/j.ultsonch.2004.12.008

nature and ionic liquids are expensive. Further, Raney Ni is flammable in presence of air and presents considerable hazards during handling.

2. Experiments

2.1. Material and instruments

All nitro compounds were purchased from BDH and Merck. Solvents used were commercially available and distilled before use. Reactions were monitored by TLC by comparison with authentic samples. Yields refer to the isolated products after purification by basic alumina chromatography. The IR and GC–MS spectra of the starting compounds and the products were recorded on NICOLET 400D FT-IR Spectrophotometer and SHIMADZU GC–MS 5050 respectively. All the reactions were studied using JULABO, USR-3 German and SIDILU Indian make sonic baths working at 35 kHz (constant frequency) at 25 °C.

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

A mixture of nitrobenzene (0.123 g, 10 mmol), aluminium foil (0.082 g, 30 mg atom cut into small pieces) and ammonium bromide (0.58 g, 60 mmol) in methanol (10 ml) were placed in a two necked 50 ml round bottom flask. The contents were sonicated in a sonic bath working at 35 kHz (constant frequency) maintained at 25 °C by circulating water. The progress of the reaction was monitored by TLC [eluent: 5% EtOAc-pet. ether (60–80 °C)] and by GC–MS technique. The reaction mixture was filtered through a celite pad, washed with little ether and quenched by adding little water, extracted with diethyl ether (3 × 20 ml). The combined ether extract was washed with dil. HCl and the acidic washings were combined, neutralized with sat. $NaHCO_3$ and then extracted with diethyl ether (2 × 20 ml). The ethereal extract was then dried over anhyd. K_2CO_3 and the solvent distilled out on a rotavap. The product after drying under vacuum was identified to be aniline by comparison of the bp, TLC and with IR spectrum of the authentic sample. Aniline in its ^1H NMR spectrum showed a multiplet between 6.5 and 7.0 δ for 5H (aromatic) and a singlet at δ 7.3 for 2H ($-NH_2$); its IR showed N–H stretch at υ 3359 cm^{-1} and in its MS *m/e* 93 (M^+), 66, 65 ion peaks were observed.

2.3. General experimental procedure for the reduction of nitroarenes under silent condition at 65 °C

A mixture of nitrobenzene (0.123 g, 10 mmol) and ammonium bromide (0.58 g, 60 mmol) in methanol (10 ml) taken in a two necked 50 ml round bottom flask were stirred on a preheated oil bath maintained at 65 °C. The reaction was initiated by the addition of aluminium foil (0.082 g, 30 mg atom cut into small pieces). The progress of the reaction was monitored by TLC [eluent: 5% EtOAc-pet. ether (40–60 °C)]. After completion of the reaction (1.15 h), the reaction mixture was filtered through a celite pad, washed with little ether and quenched by adding little water. The organic matter was then extracted into diethyl ether (3 × 20 ml). The combined ether extract was washed with dil. HCl and the acidic washings were combined, neutralized with sat. $NaHCO_3$ and then extracted with diethyl ether (2 × 20 ml). The ethereal extract was then dried over anhyd. K_2CO_3 and the solvent distilled out on a rotavap. The crude thus obtained was purified by basic alumina chromatography using 5% acetone in light petroleum as an eluent to get aniline.

3. Results and discussion

In our earlier report [1], we have described the reduction of nitroarenes by Al/NH_4Cl to the corresponding amines. Recently, we have reported the cleavage of azoarenes into arylamines by Al/NH_4Br [14], and the reduction of nitroarenes into azoarenes and/or arylamines by Al/NaOH in methanol [15] under sonic conditions. In continuation with our work on the development of novel reagents for the reduction of functional groups in organic synthesis, we wish to report a comparative study on the reduction of nitroarenes into arylamines by aluminium metal in the presence of different ammonium halides. In this paper we are reporting an improved procedure for the reduction of different substituted nitroarenes into arylamines by Al/NH_4Br within 20 min in high yields under the influence of ultrasound as shown in Scheme 1.

As reported by us earlier, the reduction of nitroarenes with Al/NH_4Cl takes a long time (6–24 h) for completion under normal condition and under the influence of ultrasound, the reaction is reasonably faster (3 h). In order to have a meaningful comparison on the rate and the course of the reaction, as the ammonium halides show variation in their reactivity when we go down in a period in the periodic table, the reaction of various substituted nitroarenes by aluminium in the presence of NH_4F, NH_4Cl, NH_4Br and NH_4I in methanol was taken up. In a typical experiment, 10 mmol of nitrobenzene was treated with 30 mg atoms of Al metal and

$$R\text{-}NO_2 \xrightarrow[))))\ \ 20\ \text{min}]{Al/NH_4Br} R\text{-}NH_2$$

R = aryl

Scheme 1.