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# Selective reduction of azoarenes into arylamine(s) by aluminium / $NH_4Br$ under sonic conditions

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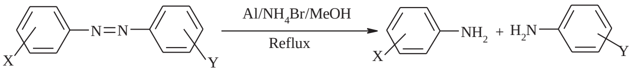
Azoarenes, both symmetrical and unsymmetrical are cleaved into arylamine/s by aluminium metal and ammonium bromide in refluxing methanol with high yields. The rate of the reaction is greatly accelerated by irradiating at 35 kHz in a sonic bath maintained at 25 °C.

**Keywords**: selective reduction, azo compounds, aluminium metal, ammonium bromide

In recent years, the applications of ultrasound radiation in organic synthesis are increasing very rapidly, due to advantages such as short reaction time, suppression of side products, less polluting processes of sonication and excellent yields.[1] The reactions under influence of ultrasound meet green chemistry protocols. Pioneering work on the synthesis of arylamine/s is reported by various methods including In /$FeCl_3/H_2O$,[2] Te–near critical water temperature,[3] Raney Ni/$NH_4Cl$,[4] Mg/$N_2H_4$,[5] Zn/$N_2H_4$,[6] Zn/$N_2H_4.HCO_2H$,[7] $Ru_3(CO)_{12}$/chelating diimines,[8] FeS/$NH_4Cl/CH_3OH/H_2O$,[9] Sm/$NH_4Cl$,[10] nanosised activated metallic iron powder in water,[11] and Zn/$NH_4Cl$ in ionic liquids.[12] Owing to their broad spectrum of biological activity arylamines find a multitude of industrial applications as intermediates in the synthesis of dyes, pharmaceuticals, photographic and agricultural chemicals.[13]

Earlier reports reveal that, catalytic hydrogenation has been used for the reduction or reductive cleavage of azoarenes into amines, and systems such as $HCO_2NH_4$/10% Pd–C,[14] Mg/$HCO_2NH_4$,[15] $N_2H_4$/Raney Ni or Pd/C,[16] have been employed. Some of these systems require longer reaction times (~ 20–40 h) for completion at a reflux temperature and the use of expensive catalysts.

In our earlier work we have used inexpensive readily available metals such as Al or Zn in the presence of ammonium salts for the reduction of different functional groups under various reaction conditions.[17-20] We have now found that azoarenes substituted by either electron withdrawing or electron donating groups can be conveniently and selectively reduced to aniline/s by Al/$NH_4Br$ in MeOH at reflux, however, the reaction takes about 2 h for completion. As the rates of the reactions are accelerated under the influence of ultrasound the present reaction is carried out in a sonic bath working at 35 kHz and found to go to completion within 30 min. The products are obtained in high yields as shown in Scheme 1.



X OR Y = -H, -Cl, -OH, $-OCH_3$, -COOH, $-CH_3$, $-NH_2$, $-N(CH_3)_2$

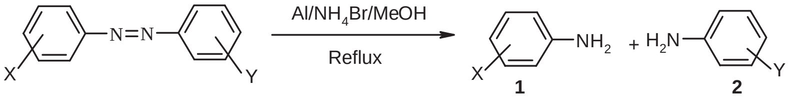
**Scheme 1**

In a typical experiment, 10 mmol of azobenzene in methanol (10 ml) was taken in a two-necked round bottom 50 ml flask, treated with 30 mmol of aluminium metal (cut into small pieces) and 30 mmol of ammonium bromide. The contents were then subjected to ultrasound in a sonic bath working at 35 kHz maintained at 25 °C, after the completion of the reaction (30 min, TLC), the product was worked up to give aniline 90% yield. 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 ($-N\underline{H_2}$), its IR showed N–H stretch at ν 3359 $cm^{-1}$ and in its MS *m/e* 93 ($M^+$), 66, 65 ion peaks were observed.

In order to standardise the reaction and verify the suitability of the conditions for the reduction of other azoarenes, the reaction of different substituted azo compounds was carried out with Al/$NH_4Br$ in refluxing methanol and under the influence of ultrasound at 35kHz and the results are presented in Table 1.

The cleavage of azo compounds under the influence of ultrasound goes to completion in a short time with aluminium metal instead of expensive platinum or palladium, Pd/C, Raney nickel, *etc*, without adverse consequences. The yields in all the reactions are quantitative and the products are found to be pure; this procedure will therefore be of simple and

**Table 1** Reduction of azoarenes into aniline(s) by Al/$NH_4Br$ in MeOH at reflux and under the influence of ultrasound at 35 kHz



| Entry | Substrate |  | Product[a] |  | Reflux |  | Yield/%[b] |  | Melting point (°C) found |
|---|---|---|---|---|---|---|---|---|---|
|  | X | Y | X | Y | /h | /min | **1**, | **2** |  |
| 1. | -H | -H | -H | -H | 2 | 15 | 90, | – | 186[c] |
| 2. | 2-OH | 2-OH | 2-OH | -OH | 1.66 | 15 | 80, | – | 174[c] |
| 3. | 4-$NH_2$ | –H | 4-$NH_2$ | -H | 1.75 | 15 | 85, | 90 | 146, 186[c] |
| 4. | 4-$N(CH_3)_2$ | 2-COOH | 4-$N(CH_3)_2$ | 2-COOH | 2 | 10 | 85, | 90 | 53, 146 |
| 5. | 3- $CH_3$ | 3-$CH_3$ | 3-$CH_3$ | 3-$CH_3$ | 2 | 15 | 90, | – | 203[c] |
| 6. | 2-$CH_3$ | 2-$CH_3$ | 2-$CH_3$ | 2-$CH_3$ | 2 | 15 | 90, | – | 200–202[c] |
| 7. | 3,4-Cl | 3,4-Cl | 3,4-Cl | 3,4-Cl | 2 | 20 | 85, | – | 72 |
| 8. | 2-$OCH_3$ | 2-$OCH_3$ | 2-$OCH_3$ | 2-$OCH_3$ | 2 | 15 | 90, | – | 226[c] |

[a] Characterised by $^1H$ NMR, IR and GC–MS spectral analysis.
[b] Isolated by chromatographic separation and/or purification.
[c] Boiling point (690 torr).

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convenient use, especially in cases where rapid, mild and selective reduction or cleavage of substituted azoarenes into aniline/s is required.

In conclusion, we have developed an improved procedure for the selective reduction of nitroarenes into anilines by using inexpensive, readily available and abundant Al metal in the presence of $NH_4Br$ in methanol, under the influence of ultrasound. In our opinion this method is superior to some of the existing methods of reduction, which employ expensive and hazardous reagents as discussed above.

## Experimental

All azo compounds and ammonium bromide were purchased from BDH and Merck, or prepared according to standard procedures reported earlier[21] and all the solvents were dried before use. Reactions were monitored by TLC by comparison with authentic samples. Yields refer to the isolated yields of the products after purification by silica gel chromatography. Melting points/boiling points were taken in open capillaries using a paraffin bath and are uncorrected. $^1$H NMR, IR and GC–MS spectra of the products were recorded on a 90 MHz Bruker Spectrometer, 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 sonic baths working at 35 kHz (constant frequency) maintained at 25 °C by constant circulation of water.

*General experimental procedure for reduction of nitroarenes at 35 kHz*: A suspension of the azo compound (1.82 g, 10 mmol), 30 mmol of aluminium metal (cut into small pieces) and ammonium bromide (0.98 g, 20 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. A vigorous exothermic reaction ensued with rapid development of yellow-orange coloration. The reaction was continued until there was an absence of the starting azo compounds in the reaction mixture. The progress 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 ($2 \times 25$ ml). The combined ether extract was washed with dil.HCl and neutralised with sat. $NaHCO_3$. The extract was then dried over anhydrous $K_2CO_3$ and ether was removed on a rotary evaporator. The product after drying under vacuum was identified by comparison of the m.p./b.p., 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.

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