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Ammonium chloride mediated reduction of azo compounds to hydrazo compounds

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The reduction of azo compounds with magnesium powder as catalyst in the presence of ammonium chloride at room temperature in methanol leads to hydrazo compounds.

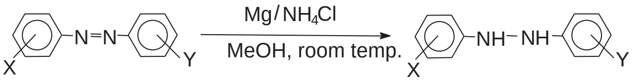
Keywords: azo compounds, ammonium chloride, magnesium powder, hydrazo compounds

Reductive cleavage of azo and azoxy benzenes continues to be used in connection with structural determinations of azo dyes.[1] There are some methods available in the literature for the conversion of azo compounds to hydrazo compounds [2-6] and reductive cleavage of azo compounds to corresponding anilines.[7] The conversion of azo compounds to hydrazo compounds requires longer reaction times and employs expensive and pyrophoric catalysts such as Pd–C,[2] Raney Ni.[3] In addition, if the azo compounds contain reducible or hydrogenolysable groups like halogen or nitrile, then systems like 10% Pd–C/$HCOONH_4$[8] and 10%Pd–C/triethylammonium formate [9] reduce the nitrile group to a methyl group and remove the halogen from aromatic rings. Moreover, poor yields were reported during the reduction of azo compounds to hydrazo compounds.

Recently, we have reported the utility of magnesium[10] for deblocking of some commonly used protecting groups in peptide synthesis. The application of ammonium chloride for the reduction of azides to amines has been reported.[11] We now report a rapid and selective reduction of azo compounds to the corresponding hydrazo compounds by using magnesium powder as a catalyst in the presence of ammonium chloride at room temperature in methanol media as depicted in Scheme 1. Many primary and secondary functional groups such as halogens, –OH, $–OCH_3$, –COOH, $–CH_3$ and $–COCH_3$ are tolerated.

The reduction of azo compounds to hydrazo compounds in the presence of magnesium powder and ammonium chloride at room temperature was completed within 3–10 min. The course of reaction was monitored by TLC. The products were obtained in good yields (90–95%) and the products were characterised by comparison of their melting points, TLC and IR spectra with authentic samples. The disappearance of a strong absorption band between 1630 and 1575 cm^{-1}due to –N = N– stretching and the appearance of strong absorption band between 2290 and 2440 cm^{-1}due to the –NH–NH– group, clearly showed that azo compounds have been reduced to hydrazo compounds and moreover, that there was no reductive cleavage of azo compounds to anilines at room temperature, even after several hours of reaction.

A control experiment was carried out using azo compounds with ammonium chloride in the absence of catalysts, but it did not yield the desired product. Furthermore, an attempted reduction of an azo compound using catalysts in the absence of ammonium chloride did not yield the desired product. In order to obtain optimum reduction condition, a number of trials with a range of solvents, which are commonly employed for reduction reactions were carried out. Methanol was found to be the best solvent as far as the solubility of substrate and rate of reaction is concerned. To interpret the role of methanol, the reaction was carried out for several hours in the absence of ammonium chloride and it fails to give any reduced product indicating clearly that methanol serves only as a solvent.



X or Y = -H, halogen, -OH, $-OCH_3$, -COOH, $-CH_3$

Scheme 1

The reduction of azo compounds to hydrazo compounds by using magnesium in the presence of ammonium chloride systems are more effective than earlier systems like hydrazine/10% Pd–C[2] and hydrazine/ Raney Ni.[3] The methods mentioned earlier required longer reaction time and employ expensive and pyrophoric catalysts, but low cost magnesium powder in presence of ammonium chloride systems easily reduced azo compounds to hydrazo compounds in less than ten minute at room temperature, Thus, this system provides a useful alternative for the reduction of azo compounds to hydrazo compounds instead of expensive systems like palladium or Raney nickel without affecting other reducible or hydrogenolysable substituents. The yields were virtually quantitative and the resulting products were analytically pure. This procedure, therefore is of general utility, especially in case of where a rapid, mild and selective reduction is required.

Experimental

Reduction of azo compounds to hydrazo compounds. general procedure: A suspension of the azo compound (2g), magnesium powder (1g) in methanol or in any suitable solvent (10 ml or requisite amount) and ammonium chloride (2g) was stirred under a nitrogen atmosphere at room temperature. After the completion of the reaction (monitored by TLC or by the disappearance of the colour of the starting material), the reaction mixture was filtered through a Celite pad and washed with solvent. The combined filtrates and washings were evaporated under vacuum. The residue was taken into 15 ml chloroform or diethyl ether, washed twice with 15 ml saturated brine solution and finally with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed with a rotary evaporator. Subsequently, the products were purified either by preparative TLC or column chromatography. After purification, the products were characterised by elemental analyses, IR spectra and the melting points were compared with authentic samples.

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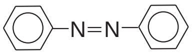
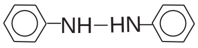
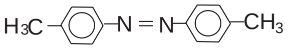
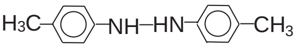
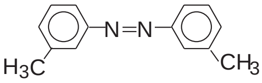
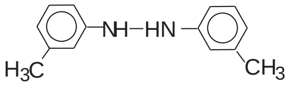
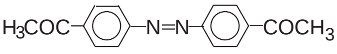
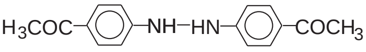
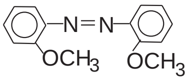
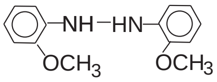
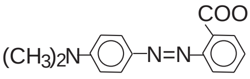
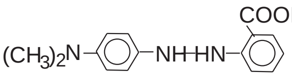
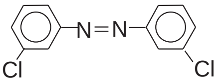
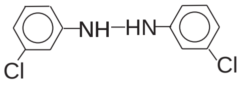
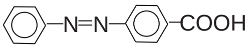
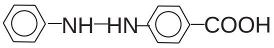
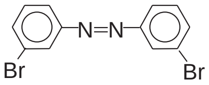
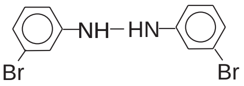
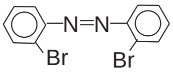
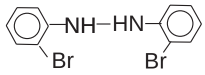
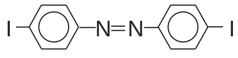
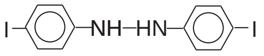
Table 1 Reduction of azo compounds to hydrazo compounds by using magnesium and ammonium chloride[a]

Entry no.	Substrate	Product	Duration /min	Yield /%[b]	Melting point/°C	
					Found	Literature
1			5	90	125-–26	127[12]
2			3	92	133–135	134[12]
3			5	90[c]	Oil	38[12]
4			6	87	83–85	86[12]
5			6	90	98–100	102[12]
6			5	60[c,d]	Oil	–
7			5	90	89–92	90–94[13]
8			10	65[c,d]	176–177	–
9			7	91	106–107	107–108[14]
10			9	89	96–98	97–98[13]
11			6	75[c]	162–164	–

[a] More than 15 azo compounds are converted to hydrazo compound, only representative examples are given.
[b] Isolated yields are based on single experiment and the yields were not optimised.
[c] Satisfactory elementary analysis is obtained for these compounds.
[d] The low yield is due to water soluble nature of these compounds, but TLC analysis shows more than 90% reduction.

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