A facile reduction of azoxyarenes with hydrazine hydrate/magnesium: formation of different products under different reaction conditions

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Azoxyarenes on treatment with hydrazine hydrate in presence of magnesium turnings in methanol undergo reduction. The reactions have been carried under microwave irradiation as well as at reflux to give the corresponding hydrazoarenes and azoarenes as reduced products. The reactions are very fast and give excellent yields of the products. Substituents like OCH_3, OC_2H_5 and Cl are unaffected.

Keywords: azoarenes, azoxyarenes, hydrazine hydrate, hydrazoarenes, magnesium turnings

The reduction of azo and azoxyarenes has received a good deal of attention in recent years since reduction of –N–N– multiple bonds is an important type of reaction in connection with structural determination of azodyes.[1] Hydrazoarenes on the other hand, have received little attention due to their tendency towards aerial oxidation, Benzidine rearrangement can occur in acidic medium or further reduction into anilines can occur where it is difficult to obtain only hydrazoarenes. Reports are available in the literature for the reduction of azoxy and azoarenes to hydrazoarenes which include systems like Raney-Nickel/NH_2NH_2, Pd/NH_2NH_2 and Mg/NH_4Cl.[2-6] Reagents have also been developed for the reductive coupling of nitroarenes such as Al/KOH in methanol[7] and a complex of the coenzyme dihydrolipoamide and iron(II).[8]

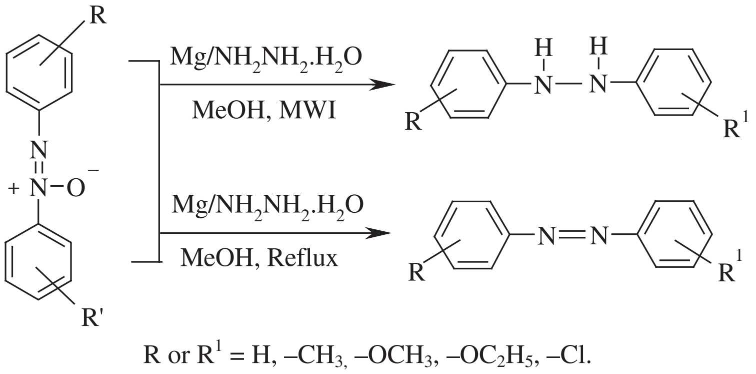
Azoarenes on the other hand have generated attention for their wide applications in the dye industry and have ability to be used in optical switching and image storage technology. Finally that azoarenes have drawn wider interest is evident from the fact that their various uses have been the subject of publication.[9]

Hydrazine hydrate is a reductant in organic syntheses that has been found to be useful in the synthesis of amines and has proved to be a potent reagent in several organic transformations. Hydrazine has been used in the catalytic hydrogenation of nitroarenes into anilines in the presence of a number of catalysts. In our laboratory, we are working on organic transformations employing easily available reagents in combination with inexpensive metal such as Al and Zn and, we have already reported the selective reduction of aromatic nitro and azo compounds with different reagents under various conditions.[10]

Microwave irradiation (MWI) has emerged as a powerful technique to promote a variety of chemical reactions. Microwave reactions are attractive in offering reduced pollution and offer low cost together with simplicity in processing and handling. Introduction of microwave technology assures safe and easy experimental procedures and has gained acceptance and popularity among the synthetic chemistry community. Undoubtedly, microwave assisted reactions are going to be highly important in future organic transformations. The growing number of publications in microwave synthesis includes virtually all types of chemical reactions.[11]

In continuation of our work on the use of hydrazine hydrate in functional group transformations,[12-14] we now report the reduction of azoxyarenes into hydrazoarenes and azoarenes by hydrazine hydrate in presence of magnesium metal [see CAUTION in Experimental section.]. It has been found that 99–100% hydrazine hydrate in methanol under microwave irradiation is an exceedingly convenient system to achieve the transformation of substituted azoxyarenes into the corresponding hydrazoarenes (Scheme 1), which are summarised in Table 1.

The reaction proceeds smoothly and is completed within 1.5–2 min without affecting substituents like OCH_3, OC_2H_5 and Cl. Hydrazoarenes that are obtained are of high purity. Further, to compare the reaction at different conditions with microwave irradiation, the reactions were performed by stirring at room temperature and at reflux with same substrates, which afforded hydrazoarenes after 24 h at 25 °C. The course of this reaction was monitored by TLC by taking an aliquot of the reaction mixture throughout the reaction time and there was no evidence for the formation of an azoarene intermediate. At reflux, azoarenes are recovered within 10 min but not hydrazoarenes. Azoxyarenes generally display a strong absorption bands in the region between 1630 and 1575 cm^{-1} of the IR spectra due to –N=N– stretching



R or R^1 = H, $-CH_3$, $-OCH_3$, $-OC_2H_5$, –Cl.

Scheme 1

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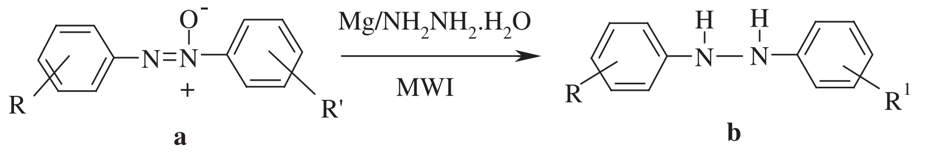
Table 1 Reduction of azoxyarenes into hydrazoarenes by Mg/hydrazine hydrate in methanol under microwave irradiation



Entry	Substrate		Product[a]		yield[b]/%	M.p/°C	
	R	R′	R	R′		Found	Lit[15]
1	H	H	H	H	90	126	126
2	2-CH$_3$	2′-CH$_3$	2-CH$_3$	2′-CH$_3$	90	16–166	165
3	3-CH$_3$	3′-CH$_3$	3-CH$_3$	3′-CH$_3$	90	37	38
4	4-CH$_3$	4′-CH$_3$	4-CH$_3$	4′-CH$_3$	90	133–134	134
5	2-OCH$_3$	2′-OCH$_3$	2-OCH$_3$	2′-OCH$_3$	90	102–103	102
6	2-OC$_2$H$_5$	2′OC$_2$H$_5$	2-OC$_2$H$_5$	2′OC$_2$H$_5$	85	88	89
7	4-Cl	4′-Cl	4-Cl	4′-Cl	89	124	123–124

[a] Products were characterised by the comparison with TLC, melting point and IR spectra of authentic samples. [b] Isolated yields.

which could not be observed in the products. These showed a strong absorption band between 2290 and 2240 cm^{-1} due to the –NH–NH– group clearly indicating the conversion of azoxyarenes into hydrazoarenes. The trend of disappearance of absorption band between 1630 and 1575 cm^{-1} of the IR spectra is noticed in all the hydrazoarenes prepared by our procedure. Table 2 lists the results of the conversion of various azoxyarenes into the corresponding azoarenes at reflux.

In conclusion, we have demonstrated the synthesis of hydrazoarenes and azoarenes from azoxyarenes with hydrazine hydrate in presence of magnesium metal as a catalyst without affecting the reduction of other reducible substituents. The reaction may be considered as simple from a practical point of view.

Experimental

All azoxyarenes are either commercial grade or prepared according to standard procedures[15] and purified before use. Hydrazine hydrate and other solvents were purchased from Merck and BDH and were purified and dried prior to use. Yields refer to the isolated yields of the products after purification by column chromatography using 60–120 mesh silica gel with a suitable eluent. Melting points were obtained by the capillary method and are uncorrected. Analytical TLC was performed on precoated aluminum plates with Merck silica gel 60 F-254 as the adsorbent. The developed plates were air dried and irradiated with UV light. GC analysis was performed on a SHIMADZU GC-MS QP 5050A instrument. IR spectra were recorded on NICOLET 400D FT-IR Spectrometer.

CAUTION: Hydrazine hydrate is toxic and corrosive and appropriate precautions must be taken.

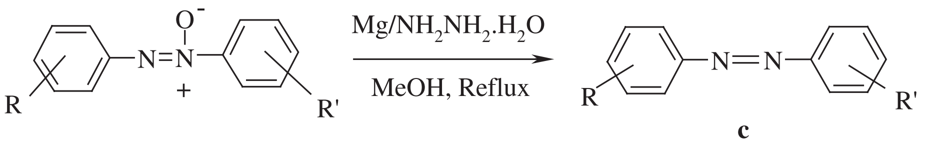
General procedure **1**

A mixture of azoxybenzene (0.2 g, ~1 mmol), hydrazine hydrate (99–100%, 0.5 ml) and magnesium turnings (0.24 g, 10 mg atom) in methanol (5 ml) was taken into a Pyrex cylindrical tube and irradiated in a commercial microwave oven (unmodified, LG, Little Chef, MS-194W, 230V~50 Hz working at 160 W) for 1.5–2 min and then poured into 100g of crushed ice. The solid obtained was filtered, dried and recrystallised from 95% ethanol to get desired hydrazobenzene (0.175 g, 95 %, mp 126 °C).

General procedure **2**

The same substrates and quantities used in the general procedure **1** were taken in a round-bottomed flask and the contents were refluxed with continuous stirring. After the completion of the reaction (10 min, monitored on TLC or by the appearance of colour of azoarenes which are almost all coloured compounds), the reaction mixture was filtered through a celite pad and washed with a little diethyl ether. The organic matter was taken into ether by extracting twice with 15 ml of diethyl ether. The combined ether layer was washed successively with saturated brine solution and water, dried over anhydrous sodium sulfate and then the solvent was removed under a vacuum. The product thus obtained was purified (wherever required) by silica gel column chromatography with a suitable eluent system, and characterised to be the azoarene by its mp and IR spectra.

Table 2 Reduction of azoxyarenes into azoarenes by Mg/hydrazine hydrate in methanol at reflux



Entry	Substrate		Product[a]		Yield[b]/%	M.p/°C	
	R	R′	R	R′		Found	Lit[15]
1	H	H	H	H	91	67–68	68
2	2-CH$_3$	2′-CH$_3$	2-CH$_3$	2′-CH$_3$	90	55	55
3	3-CH$_3$	3′-CH$_3$	3-CH$_3$	3′-CH$_3$	90	54–55	54–55
4	4-CH$_3$	4′-CH$_3$	4-CH$_3$	4′-CH$_3$	91	145–146	144–145
5	2-OCH$_3$	2′-OCH$_3$	2-OCH$_3$	2′-OCH$_3$	90	142–144	143
6	4-OCH$_3$	4′-OCH$_3$	4-OCH$_3$	4′-OCH$_3$	90	159–161	160
7	4-OC$_2$H$_5$	4′-OC$_2$H$_5$	4-OC$_2$H$_5$	4′-OC$_2$H$_5$	90	156–158	157–159
8	2-Cl	2′-Cl	2-Cl	2′-Cl	89	137–138	137
9	3-Cl	3′-Cl	3-Cl	3′-Cl	89	100–101	101
10	4-Cl	4′-Cl	4-Cl	4′-Cl	90	185–187	185

[a]Characterised by IR spectral analysis, TLC and on GC with authentic samples. [b] Isolated yields.

Characterisation data of compounds [**b**(**1–7**)]

b1: ^{1}H NMR ($CDCl_3$) δ (ppm): 6.65–7.40 (m, 10H, $2C_6H_5$); MS (*m/z*): 184(M^+).

b2: ^{1}H NMR ($CDCl_3$) δ (ppm): 2.40 (s, 6H, $2CH_3$); 6.65–7.42 (m, 8H, $2C_6H_4$); MS (*m/z*): 212(M^+).

b3: ^{1}H NMR ($CDCl_3$) δ (ppm): 2.42 (s, 6H, $2CH_3$); 6.68–7.45 (m, 8H, $2C_6H_4$); MS (*m/z*): 212(M^+).

b4: ^{1}H NMR ($CDCl_3$) δ (ppm): 2.40 (s, 6H, $2CH_3$); 6.70–7.50 (m, 8H, $2C_6H_4$); MS (*m/z*): 212(M^+).

b5: ^{1}H NMR ($CDCl_3$) δ (ppm): 3.85 (s, 6H, $2CH_3$), 6.60–7.60 (m, 8H, $2C_6H_4$); MS (*m/z*): 244(M^+).

b6: ^{1}H NMR ($CDCl_3$) δ (ppm): 1.42 (t, 6H, $2CH_3$), 4.00 (q, 4H, $2CH_2$), 6.68–7.50 (m, 8H, $2C_6H_4$); MS (*m/z*): 272(M^+).

b7: ^{1}H NMR ($CDCl_3$) δ (ppm): 7.45–8.00 (m, 8H, $2C_6H_4$); MS (*m/z*): 252 (M^+).

Characterisation data of compounds [**c**(**1–10**)]

c1: ^{1}H NMR ($CDCl_3$) δ(ppm): 7.35–7.85 (m, 10H, $2C_6H_5$); MS (*m/z*): 182 (M^+).

c2: ^{1}H NMR ($CDCl_3$) δ(ppm): 2.40 (s, 6H, $2CH_3$), 7.40–7.85 (m, 8H, $2C_6H_4$); MS (*m/z*): 210 (M^+).

c3: ^{1}H NMR ($CDCl_3$) δ(ppm): 2.38 (s, 6H, $2CH_3$), 7.38–7.80 (m, 8H, $2C_6H_4$); MS (*m/z*): 210 (M^+).

c4: ^{1}H NMR ($CDCl_3$) δ(ppm): 2.42 (s, 6H, $2CH_3$), 7.30–7.85 (m, 8H, $2C_6H_4$); MS (*m/z*): 210 (M^+).

c5: ^{1}H NMR ($CDCl_3$) δ(ppm): 3.88 (s, 6H, $2CH_3$), 7.10–8.00 (m, 8H, $2C_6H_4$); MS (*m/z*): 242 (M^+).

c6: ^{1}H NMR ($CDCl_3$) δ(ppm): 3.94 (s, 6H, $2CH_3$), 7.10–8.05 (m, 8H, $2C_6H_4$); MS (*m/z*): 242 (M^+).

c7: ^{1}H NMR ($CDCl_3$) δ(ppm): 1.42 (t, 6H, $2CH_3$), 4.05 (q, 4H, $2CH_2$), 6.90–8.10 (m, 8H, $2C_6H_4$); MS (*m/z*): 270 (M^+).

c8: ^{1}H NMR ($CDCl_3$) δ(ppm): 7.42–7.90 (m, 8H, $2C_6H_4$); MS (*m/z*): 250 (M^+).

c9: ^{1}H NMR ($CDCl_3$) δ(ppm): 7.35–7.85 (m, 8H, $2C_6H_4$); MS (*m/z*): 250 (M^+).

c10: ^{1}H NMR ($CDCl_3$) δ(ppm): 7.45–8.05 (m, 8H, $2C_6H_4$); MS (*m/z*): 250 (M^+).

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