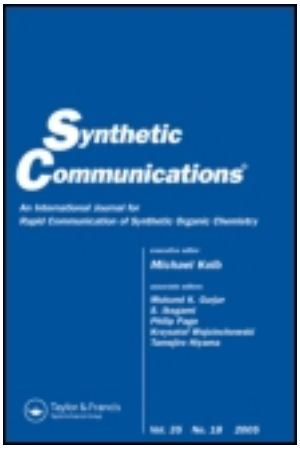

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Facile, Product-Selective Reduction of Azoxyarenes into Azoarenes or Hydrazoarenes by Aluminium/Hydrazine Hydrate

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Facile, Product-Selective Reduction of Azoxyarenes into Azoarenes or Hydrazoarenes by Aluminium/ Hydrazine Hydrate

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Abstract: Azoxyarenes, on treatment with hydrazine hydrate in presence of aluminium powder in methanol, undergo reduction. The reactions have been carried under microwave irradiation as well at reflux to get the corresponding hydrazoarenes and azoarenes as reduced products. The reaction is very fast, which gives excellent yield of the product. Substituents such as OCH_3, OC_2H_5, and Cl are unaffected.

Keywords: Aluminium powder, azoarenes, azoxyarenes, hydrazine hydrate, hydrazoarenes

The reduction of azo and azoxyarenes has received a good deal of attention in recent years because reduction of –N–N– multiple bonds is an important reaction in connection with structural determination of azodyes. Reports are available in the literature for the reduction of azoxy and azoarenes into

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hydrazoarenes by using Raney nickel/NH_2NH_2, Pd/NH_2NH_2, Mg/NH_4Cl,[1–5] Al/KOH in methanol,[6] and a complex of the coenzyme dihydrolipoamide and iron(II).[7]

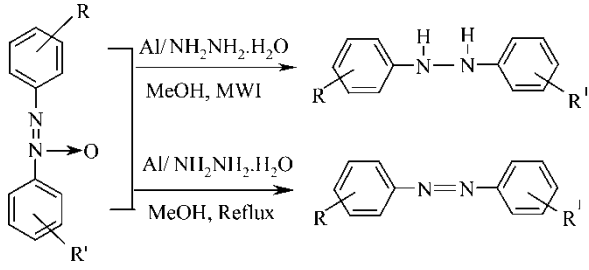
In continuation of our work on hydrazine hydrate for functional group transformations,[8–10] we report the reduction of azoxyarenes into hydrazoarenes or azoarenes in presence of aluminium metal and hydrazine hydrate. It has been found that 99% hydrazine hydrate in methanol under microwave irradiation is an exceedingly convenient system to achieve the transformation of substituted azoxyarenes to the corresponding hydrazoarenes (Scheme 1), which are summarized in Table 1.

The reaction proceeds smoothly and is completed within 1.5–2 min without affecting substituents such as OH, 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. At reflux, azoarenes are recovered within 10 min but hydrazoarenes are not. Table 2 lists the results of the conversion of various azoxyarenes are not to the corresponding azoarenes at reflux.

In conclusion, we have demonstrated the synthesis of hydrazoarenes and azoarenes from azoxyarenes with hydrazine hydrate in the presence of aluminium powder as catalyst.

EXPERIMENTAL

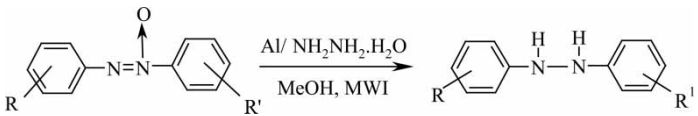
All azoxyarenes are either commercial grade or prepared according to standard procedures[11] and purified before use. Hydrazine hydrate and other solvents were purchased from Merck and BDH, purified, and dried prior to use. Yields refer to the isolated yields of the products after purification by column chromatography using 60–120 mesh silica gel with a suitable



R or R' = —H, —CH_3, —OCH_3, —OC_2H_5, —Cl.

Scheme 1.

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



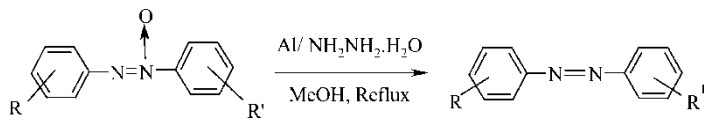
	Substrate		Product[a]				Mp (°C)	
Entry	R	R′	R	R′	Time (min)	Yield[b] (%)	Found	Lit.[11]
1	H	H	H	H	1.75	91	126	126
2	2-CH_3	2′-CH_3	2-CH_3	2′-CH_3	1.75	90	164–166	165
3	3-CH_3	3′-CH3	3-CH_3	3′-CH_3	1.75	90	37	38
4	4-CH_3	4′-CH3	4-CH_3	4′-CH_3	1.50	90	133–134	134
5	2-OCH_3	2′-OCH_3	2-OCH_3	2′-OCH_3	1.50	90	102–103	102
6	2-OC_2H_5	2′OC_2H_5	2-OC_2H_5	2′OC_2H_5	1.50	85	88	89
7	4-Cl	4′-Cl	4-Cl	4′-Cl	2.00	90	124	123–124

Caution: *Hydrazine hydrate is toxic and corrosive; handle carefully.*

[a]Products are characterized by comparison of TLC, melting point, and IR spectra of authentic samples.

[b]Isolated yields.

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



	Substrate		Product[a]				Mp (°C)	
Entry	R	R′	R	R′	Time (h)	Yield[b]	Found	Lit.[12]
1	H	H	H	H	0.167	92	67–68	68
2	2-CH_3	2′-CH_3	2-CH_3	2-CH_3	0.167	91	55	55
3	3-CH_3	3′-CH3	3-CH_3	3-CH_3	0.167	92	54–55	54–55
4	4-CH_3	4′-CH3	4-CH_3	4-CH_3	0.167	92	145–146	144–145
5	2-OCH_3	2′-OCH_3	2-OCH_3	2-OCH_3	0.167	91	142–144	143
6	4-OCH_3	4′-OCH_3	4-OCH_3	4-OCH_3	0.167	90	159–161	160
7	4-OC_2H_5	4-OC_2H_5	4-OC_2H_5	4-OC_2H_5	0.167	90	156–158	157–159
8	2-Cl	2′-Cl	2-Cl	2-Cl	0.167	90	137–138	137
9	3-Cl	3′-Cl	3-Cl	3-Cl	0.167	90	100–101	101
10	4-Cl	4′-Cl	4-Cl	4-Cl	0.167	90	185–187	185

Caution: *Hydrazine hydrate is toxic and corrosive, handle carefully.*

[a]Characterized by IR spectral analysis and on GC with authentic samples.

[b]Isolated yields.

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.

General Procedure 1

A mixture of azoxybenzene (0.2 g, 1 mmol), hydrazine hydrate (99–100%, 0.5 mL), aluminium powder (0.27 g, 10 mg atom), and methanol (5 mL) in a Pyrex cylindrical tube were irradiated in a commercial microwave oven (unmodified, LG, Little Chef, MS-194W, 230 V ~50 Hz working at 160 W) for 1.5–2 min and poured into ice. The solid was filtered, dried, and recrystallized from 95% ethanol to get hydrazobenzene (0.175 g, 95%).

General Procedure 2

These substrates and quantities were refluxed for 10 min, filtered on a bed of celite, and washed with diethyl ether. The filtrate was washed successively with saturated brine solution and water, and dried over anhydrous sodium sulfate. Solvent removal and silica-gel column chromatography gave azoarene.

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