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Tin-mediated reduction of azoarenes to hydrazoarenes using hydrazine hydrate

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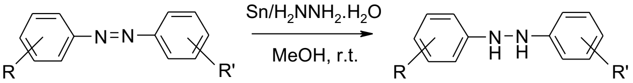
The controlled reduction of azoarenes to the corresponding hydrazoarenes using tin and hydrazine hydrate is reported. The reduction proceeds smoothly at room temperature furnishing the hydrazoarene in excellent yield without the formation of an aniline.

Keywords: reduction, tin, hydrazine hydrate, azoarenes, hydrazoarenes

Since nitro and azo compounds are reduced to their corresponding amines under mild conditions, the controlled reduction of these functionalities to hydrazo compounds is useful. Various reagents have been reported for the reduction of azoarenes to hydrazoarenes, but they are limited because of harsh conditions or cost.[1] Catalytic hydrogenation[2] has also been used, but further reductive cleavage of the –NH–NH– bond can occur. Zn and other metals have also been used for reduction but strongly acidic conditions have to be avoided in order to prevent the benzidine rearrangement of the hydrazoarenes.

Metal catalysed hydrogen transfer using hydrogen donors such as hydrazine hydrate, formic acid, formate salts, cyclohexene and cyclohexadiene is emerging as a useful tool for reductive functional group transformation in organic synthesis.[3,4] This approach involves mild reaction conditions, easy bulk management, minimal effluents, and facile product separation. The hydrogen transfer reduction of nitro and azo compounds using various metal catalysts such as Pd–C,[3a,3b,5] Raney Ni,[3a,3b,6] Zn,[7] Mg,[8] PdMCM-41 and NiMCM-41 molecular sieves[9] has been reported. However, all these metal catalysts in conjunction with hydrogen donors reduce both nitro and azo compounds to their corresponding amino derivatives. Although tin and organotin compounds are widely employed in organic synthesis,[10,11] to the best of our knowledge, tin has not been used in conjunction with hydrazine hydrate for reduction reactions. We investigated the reduction of azoarenes using tin and hydrazine hydrate. Azoarenes underwent smooth reduction to hydrazoarenes at room temperature in methanol without further reduction to aniline derivatives (Scheme 1).

A wide range of azoarenes underwent reduction by this procedure to furnish the corresponding hydrazoarenes. The results are summarised in Table 1. All the products were characterised by comparison of their TLC, melting points, IR spectra, and ^1H NMR spectra with authentic samples. The reactions are reasonably fast and high yielding. This procedure is found to be compatible with several sensitive functionalities such as halogens, NO_2, OH, OMe, COOH. However, this system was not useful for the reduction of azoarenes containing carbonyl functionality due to the formation of hydrazone derivative with hydrazine hydrate. It should be emphasised that in the absence of tin, the reaction did not proceed and mainly resulted in the recovery of the starting materials. Similarly, the reduction of azoarenes in the absence of hydrazine hydrate did not yield the product. This clearly confirms that methanol serves only as a solvent but not as a hydrogen source.



Scheme 1

Attempts were also made to reduce nitroarenes using large excess of tin and hydrazine hydrate in methanol. Even after prolonged time (24 h) the starting material was recovered quantitatively (Table 1; entries 14 and 15). This distinguishes the present system from other metal-aided hydrogen transfer reductions in which both nitroarenes and azoarenes undergoes easy reduction to yield the corresponding amines.[3a,3b,5-9] Thus, tin in conjunction with hydrazine hydrate provides a system for the controlled, rapid reduction of azoarenes to hydrazoarenes in high yield without further cleavage of N–N bond. In addition, unlike organotin compounds, tin powder is non-toxic, widely available and inexpensive. The ease of product isolation, high selectivity and low cost of the reagents make this procedure attractive.

Experimental

The azoarenes (5 mmol) in methanol (10 ml), was treated with tin powder (5 mmol) and hydrazine hydrate (10 mmol). The mixture was stirred at room temperature for the specified time under nitrogen (Table 1). After consumption of the starting material, as monitored by TLC, the reaction mixture was filtered through Celite. The filtrate was evaporated under reduced pressure. The residue was taken up into chloroform or ether washed twice with 80% saturated brine solution and finally with water. The organic layer was dried over anhyd Na_2SO_4 and evaporated under reduced pressure. The crude product was found to be analytically pure in most cases. Where necessary, the crude product was purified by SiO_2 column chromatography.

CAUTION: Precautions must be taken while handling hydrazine hydrate as it is toxic and corrosive.

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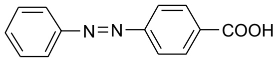
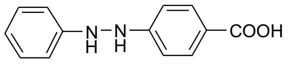
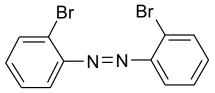
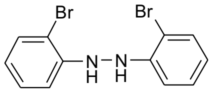
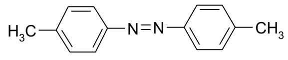
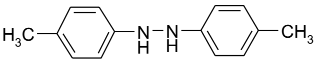
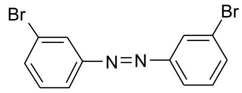
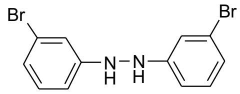
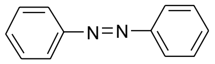
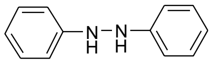
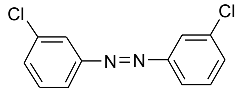
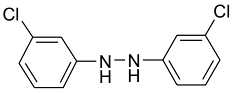
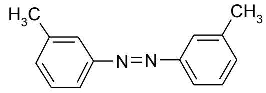
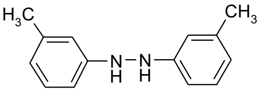
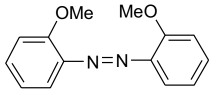
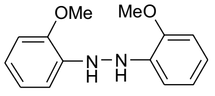
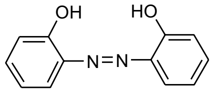
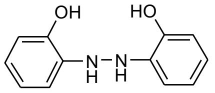
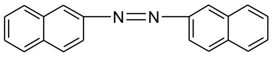
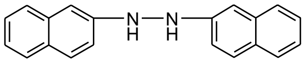
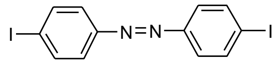
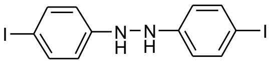
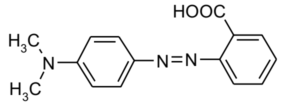
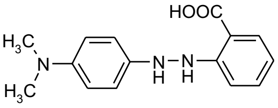
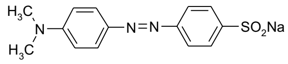
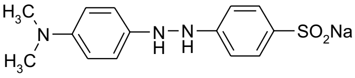
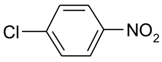
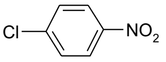
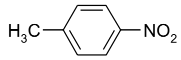
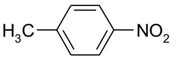
Table 1 Controlled reduction of azoarenes to hydrazoarenes using tin and hydrazine hydrate

Sl no	Azoarenes (**1**)		Hydrazoarenes (**2**)		Time/min	Yield[a]/%	Melting point/°C	
							Found	Literature
1		**1a**		**2a**	20	90	175–176	176–178[12]
2		**1b**		**2b**	15	92	96–98	97–98[13]
3		**1c**		**2c**	20	92	133–136	134[12]
4		**1d**		**2d**	22	92	106–107	107–108[14]
5		**1e**		**2e**	20	95	125–127	127[12]
6		**1f**		**2f**	20	95	89–92	90–94[13]
7		**1g**		**2g**	18	93	Oil	38[12]
8		**1h**		**2h**	20	85	98–100	102[12]
9		**1i**		**2i**	26	90	149–151	148[12]
10		**1j**		**2j**	25	89	140–143	141[12]
11		**1k**		**2k**	15	80	162–164	–
12		**1l**		**2l**	25	80	Oil	–
13		**1m**		**2m**	20	75	Oil	–
14		**1n**		**2n**	24 h	100[b]	–	–
15		**1o**		**2o**	24 h	100[b]	–	–

[a] ^{1}H NMR spectra were obtained on an AMX-400 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. IR spectra were recorded on a Shimadzu FTIR- 8300 spectrometer. The known products gave IR and ^{1}H NMR spectra in agreement with their structures.

[b] Starting material was recovered almost quantitatively.

2k: ^{1}H NMR δ 6.95 (d, 4H, Ar–H), 7.74 (d, 4H, Ar–H), 4.21 (s, 2H, NH); IR ν_{max} 3294 cm^{-1} (N–H); Anal. Calcd for $C_{12}H_{10}I_2N_2$: C, 33.05; H, 2.31; N, 6.42; Found: C, 32.88; H, 2.42; N, 6.39%.

2l: ^{1}H NMR δ 10.44 (s, 1H, OH), 6.88–6.94 (m, 4H, Ar–H), 7.32–8.26 (m, 4H, Ar–H), 3.96 (s, 2H, NH), 3.04 (s, 6H, CH_3); IR ν_{max} 3338 cm^{-1} (N–H); Anal. Calcd for $C_{15}H_{17}N_3O_2$: C, 66.40; H, 6.32; N, 15.49; Found: C, 65.64; H, 6.56; N, 15.34%.

2m: ^{1}H NMR δ 6.84–7.12 (m, 4H, Ar–H), 7.54–8.16 (m, 4H, Ar–H), 4.32 (s, 2H, NH), 3.15 (s, 6H, CH_3); IR ν_{max} 3326 cm^{-1} (N–H); Anal. Calcd for $C_{14}H_{16}N_3NaO_2S$: C, 53.66; H, 5.15; N, 13.41; Found: C, 52.55; H, 5.31; N, 13.26%.

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