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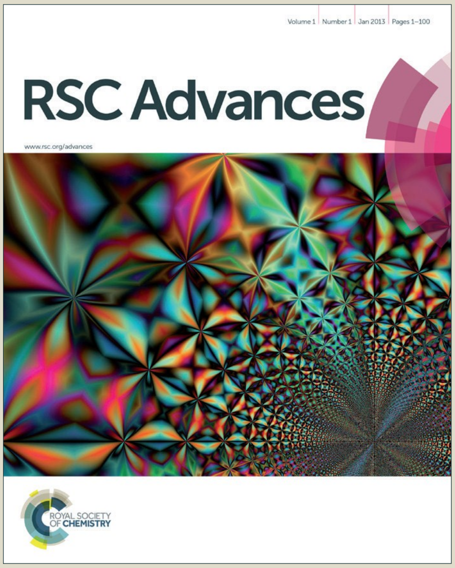

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Bismuth nanoparticles: an efficient catalyst for reductive coupling of nitroarenes to azo-compounds

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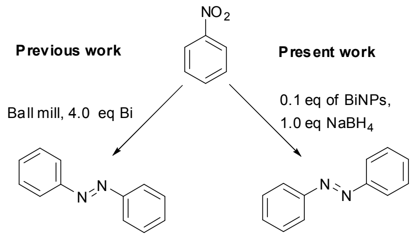
The synthesis of azoarenes from corresponding nitroarenes was developed by virtue of insitu bismuth nanoparticles. A series of aromatic azocompounds can be obtained under mild reaction conditions with excellent yields.

Rather than carbon nanostructures, in recent years researchers focused on controlled synthesis and study of nano-structures/properties of transition metals and binary alloys, such as Au, Ag, Pt, Pd, Co, and Pt/Fe, have been proven to be successful.[1] In contrast, the syntheses of main group metal nanoparticles are relatively not much studied. Bismuth is the heaviest main group element, abundant, inexpensive and non-toxic material. In addition to it, bulk bismuth exhibits semimetal behaviour with a small band overlap and an anisotropic electron effective mass. The above unique and special characteristics of bismuth impressed researchers to focus on its nano nature and followed by studying its applications. Previous studies have found that as the size decreases bismuth could transfer from a semimetal to a semiconductor.[2] over the past two decades, bismuth nanostructures such as thin films, nanowires, nanolines, nanobelts, nanopipes, nanotubes and others[3] have been extensively studied.

Though extensive research has been carried out on physical characteristics such as semiconductor and thermoelectric nature of bismuth,[4] much interest has not yet been directed on exploration of its chemical properties such as employing bismuth nanoparticles as a catalyst for the effective chemical conversions. Our research group is interested in studying "Nano-metals and exploring their applications in organic synthesis", as a course of intended above aim, we have taken up the current objective of (i) synthesis of bismuth nanoparticle (BiNPs) from reported literature[5] with some modifications and (ii) evaluation of its catalytic property in the chemoselective conversion of aryl nitro to aryl azo compounds.

"Azo" is one of the very important organic functional groups and particularly, aromatic azo-compounds have wide applications in academic and industrial research, such as radical reaction initiators, therapeutic and drug delivery agents, chelating agents, pigments, organic dyes, food additives and many others.[6] Among the various methods reported in literature, two methods are prominent for the synthesis of aromatic azo compounds, (i) coupling of diazonium salts with electron-rich aromatics[7] (ii) metal based reductive coupling of nitoraromatics by using Bi, Pt, Pd, Ru, In, Mg, Zn, Fe, Nb, Au, Sm and others.[8] Both the methods suffer from either safety related concerns or tedious work-up process, which still need to be addressed enough. Recently, oxidative coupling of arylamines into azos were also reported,[9] yet need to be explored further. Previously Azo-arenes were prepared by using stoichiometric amounts of Bi metal[8a] (Scheme 1), but the method was not suitable for wider application such as academic/industrial research.



Scheme 1 Bismuth catalyzed synthesis of Azobenzene.

As our research group has been focusing on the heterogeneous catalysis[10] for a long time, herein we report an efficient method for chemo selective preparation of aromatic azo compounds.

In a typical procedure, 0.5 mmol $BiCl_3$ was suspended in demineralized water 30 ml. After stirring for about 15 min at room temperature (RT, ~25-30 °C), the white precipitation was observed. Then 0.75 mmol of zinc dust was added in portions and the reaction mixture was further stirred for 1 hours. Black particles were observed in the reaction. pH was adjusted to 3 with aqueous hydrochloric acid. The reaction mixture was filtered and washed with water followed by ethanol then dried under vaccum for 12

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hours at 50 °C to obtain BiNPs yield 92 %. The reported procedure for BiNPs were Bamboo raft nano-tubes, here we got Nano-bismuth Particles at pH 3.

The bismuth nanoparticles were characterized by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) techniques. Figure **1a** shows the typical powder XRD pattern of the as-synthesized bismuth nanoparticle. The morphologies and structures of the as-prepared bismuth nanoparticles were investigated by TEM images Figure **1b.** Diameters of these nanoparticles varied from 3 to 8 nm.

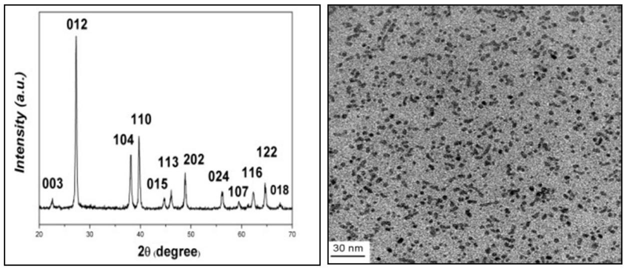
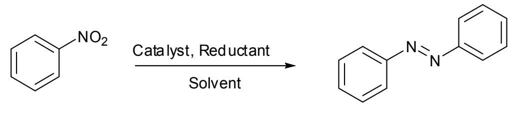


Figure 1 (a) XRD and (b) TEM images of Bismuth

The catalytic activity of bismuth nanoparticles in reductive coupling of nitroarenes in the presence of $NaBH_4$ as reducing agent and ethanol as a solvent was investigated. The reaction mixture of nitrobenzene and bismuth nanoparticles was degassed and added $NaBH_4$/ethanol solution followed by stirring the reaction mixture for 24 hours. Progress of the reaction mass was monitored by TLC (mobile phase pet ether/ethyl acetate: 9/1). The catalyst was filtered and the filtrate was evaporated under reduced pressure. The obtained product was purified by column chromatography to afford pure azo-benzene.

Table 1 Optimization of the reaction conditions[a]



1

2 a

Entry	Catalyst (equiv.)	Reductant (equiv.)	Yield (%)*b*
1	1	-	traces
2	-	1	-
3	0.5	0.5	87
4	0.2	0.5	80
5	0.2	1	92
6	0.1	1	92
7	0.05	1	65
8	0.05	1	68
9	0.05	2	68

[a] Reaction conditions: Nitro benzene (1 mmol), Catalyst BiNPs, Reductant $NaBH_4$, solvent 4 ml of ethanol, 25-30 °C, 24 h. [b] Yield with reference to nitrobenzene.

Reaction conditions were optimized by examining the influence/impact of mole ratio of catalyst and reducing agent in various experiments and the results were depicted in Table **1**. Apart from the above conditions, the reaction was also conducted in water at different temperatures (30, 50 and 80 °C), but the yield is less than 20% (see the supporting information Table **S1**). This indicates that water disfavored this reaction. During the intermediate stage of the reaction, sample was analysed on GC-Mass, finding that Nitro, Nitroso, Azoxy and Azo benzenes 10, 30, 9 and 42% respectively. To prove the conceptual bias, few control experiments (Figure **2**) were conducted by converting respective intermediates (**1a** and **1b**) into azo compound at given conditions. In terms of these experimental results, the possible mechanism is depicted in scheme **2**.

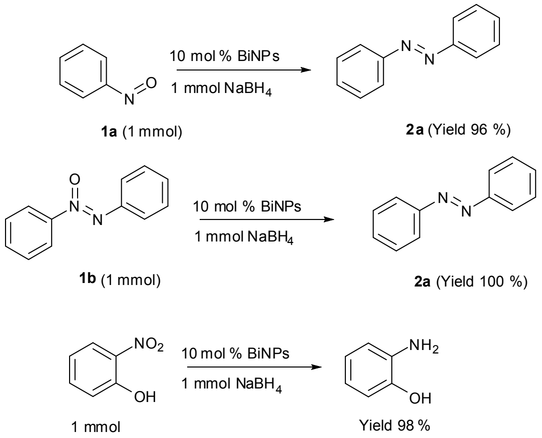
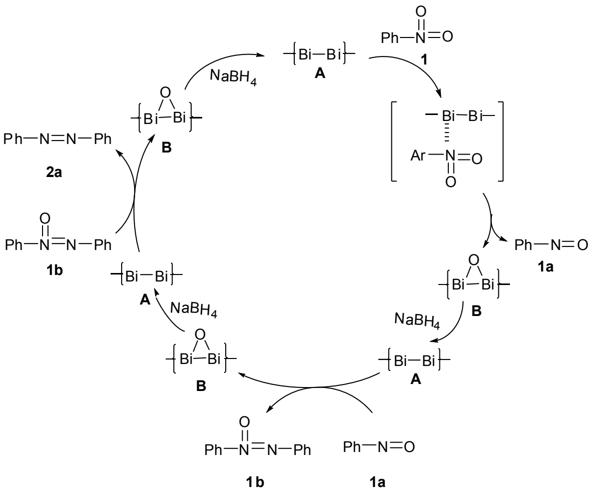


Figure 2 Control experiments for reaction mechanism.



Scheme 2 Plausible reaction mechanism

The conversion of the nitro group to the nitroso group is most likely the key step of this overall transformation. First of all, nitrobenzene **1** converted to nitrosobenzene **1a** which reacts with another molecule of nitrosobenzene and gave

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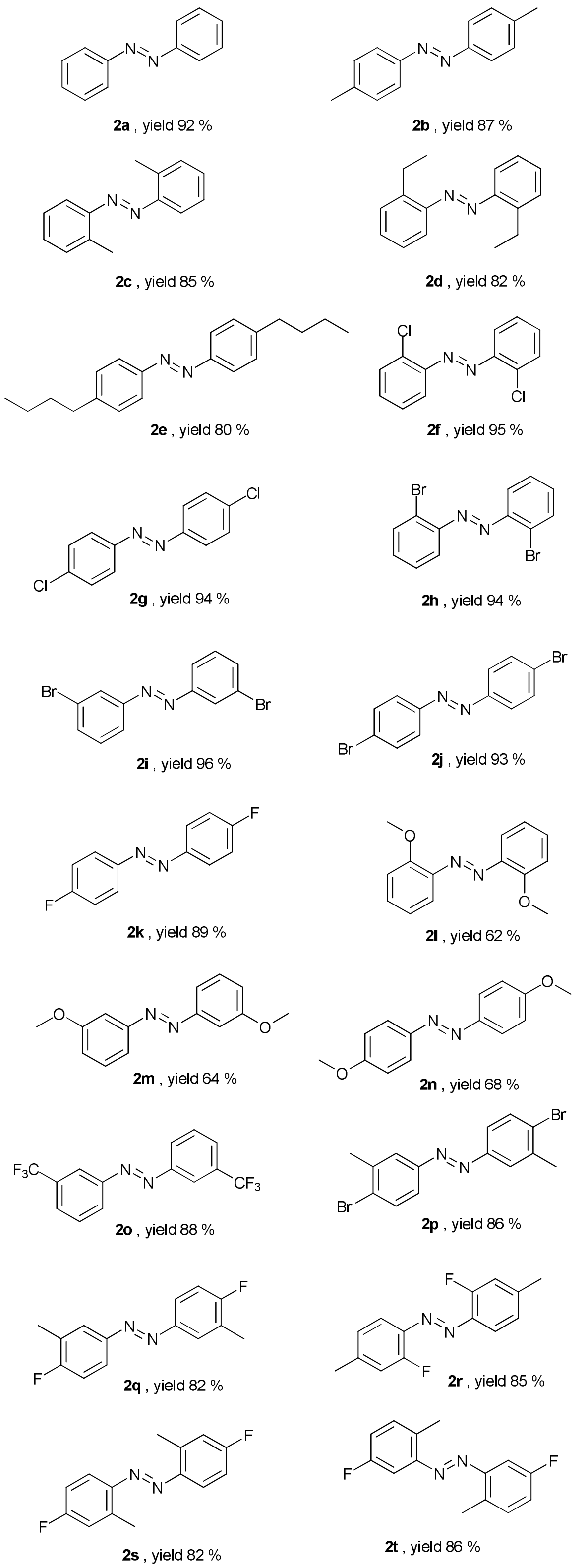
Table 2 Synthesis of Azo compounds from Nitro Arenes [a]



2a, yield 92 % **2b**, yield 87 %
2c, yield 85 % **2d**, yield 82 %
2e, yield 80 % **2f**, yield 95 %
2g, yield 94 % **2h**, yield 94 %
2i, yield 96 % **2j**, yield 93 %
2k, yield 89 % **2l**, yield 62 %
2m, yield 64 % **2n**, yield 68 %
2o, yield 88 % **2p**, yield 86 %
2q, yield 82 % **2r**, yield 85 %
2s, yield 82 % **2t**, yield 86 %

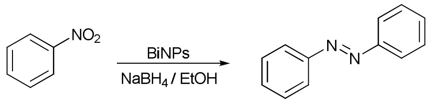
[a] Reaction conditions: Nitro benzene (1 mmol) , BiNPs 10 Mole % (0.1 mol equiv), $NaBH_4$ 1 mol equiv in 4 ml of EtOH, 25 °C, 24 h.

azoxybenzene **1b** which is further reduced to azo benzene **2a**. In each intermediate step, bismuth oxide **B** is formed and then reconverts to bismuth nanoparticle **A** by sodiumborohydrate subsequently. Moreover, the electron donating substituent would facilitate the nucleophilic attachment of the oxygen atom of the nitro function onto the surface of the bismuth nanoparticles in a push pull manner, while the electron-withdrawing group would disfavour such process. When *o*-Nitro phenol reacted under the conditions employed, it readily converted to *o*-amino phenol (Figure **2**) instead azo compound. Perhaps the eletron-donation of the hydroxyl substituent promted the reduction of the nitro to amino group while this orth-substitution blocked the cross-coupling.

The generalization of the scheme is explained by proving its efficiency on various examples (Table **2**) with diversified substitutions on aromatic ring. The reaction is general and can be employed for the synthesis of mono substituted halo (**2f – 2k**), alkoxy (**2l – 2n**), alkyl (**2b – 2e**) and di substituted (**2p – 2t**) compounds. The present methodology was successfully extended to the single step synthesis of long chain Bis-(4-butyl-phenyl)-diazene (**2e**) from 4-butyl nitrobenzene. The reaction was clean and the yield based on conversion was almost quantitative. The unsatisfactory conversion was observed with substituted alkoxy group (yield 62 – 68% for compounds **2l – 2n**), but it may also reflect some role played by alkoxy group in the reduction of nitroarenes on the structured solid surface. When two different nitroarenes (2-Methyl nitrobenzene and 2-Chloro nitrobenzene) reacted together in the given conditions, two symmetrical azo arenenes were formed in an approximate ratio of 1:1. No unsymmetrical azo arenes were observed during the reaction. All the compounds obtained were well characterized by ^1H and ^{13}C NMR spectra and melting points. Few unreported compounds (**2r – 2t**) were synthesized and charecterised by NMR spectra, HRMS, IR Spectra and melting points together.

As this is heterogeneous catalysis reaction, possibility of recycling of catalyst and reusability followed by its impact on yield was examined (Table **3**). The Yield was good(85%) even after the 5th run of bismuth nanoparticles.

Table 3 Recycling of BiNPs [a]



1 **2a**

Cycle (Run)	1	2	3	4	5
Yield (%)	95	93	90	88	85

[a] Reaction conditions: Nitro benzene (1 mmol) in 4 ml of ethanol, BiNPs (10 mol%), Sodium borohydrate (1.0 equiv.), 25-30 °C, 24 h.

In summary a remarkable heterogeneous bismuth catalyst system was developed successfully and the application of this catalyst in coupling of aromatic nitro compounds was achieved to afford the corresponding nitroarenes in excellent yields under environmentally benign conditions. The reaction has a broad scope of the reaction substrates, a variety of functional groups can tolerate the reaction conditions well. Moreover,

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the catalyst can be recovered and reused through simple phase separation. Ongoing research including further mechanistic details, expanding the substrate scope and applications in organic synthesis are currently underway.

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