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Transition-metal-free/boric acid catalysed mechanochemical synthesis of symmetrical and unsymmetrical azobenzenes: a sustainable approach

Tandra Kundu,[a] Saptadwipa Bhattacharjee,[a] Gyan Chandra Pariyar,[b] Bijeta Mitra[a] and Pranab Ghosh *[a]

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A mechanochemical protocol employing boric acid, an economical and environmentally benign inorganic acid catalyst, enables the synthesis of symmetrical and unsymmetrical azobenzenes from diverse amines. This grinding-based, solvent-free approach provides a sustainable alternative to conventional methods, avoiding harsh transition-metal catalysts. The use of oxone as a green oxidant, operation under ambient conditions, simplified work-up, and overall environmental compatibility highlight the advantages of this methodology.

Introduction

In recent years, sustainable development has become a central focus of modern organic synthesis. The urgent need to address global pollution and the ongoing environmental damage has stimulated the search for alternative strategies in organic synthesis.[1] Conventional methods often rely on petroleum-based solvents, hazardous chemicals, and harsh reaction conditions, all of which contribute significantly to environmental pollution. To overcome these challenges, alternative strategies that minimize waste, reduce energy consumption, and eliminate toxic reagents are urgently needed. Mechanochemistry has emerged as a powerful green approach, offering solvent-free and energy-efficient pathways for the synthesis of organic molecules. By replacing traditional solvent-intensive protocols with grinding-based methodologies, mechanochemical synthesis provides an environmentally sustainable alternative that is particularly attractive for both organic and pharmaceutical chemistry.

For chemists, the search for greener and eco-friendly catalysts and solvents remains both a challenge and an opportunity in the development of sustainable reaction strategies. Among various targets, aromatic azo-compounds have long attracted significant attention due to their wide range of applications in food additives, indicators, organic dyes, and therapeutic agents (Fig. 1).[2,3] Owing to their remarkable photochemical properties, these compounds have also been widely employed in liquid crystals,[4,5] smart polymers,[6] photoswitches for biological systems,[7,8] and photochromic ligands in optochemical genetics.[9] More recently, through C–H activation or functionalization, azo compounds have been exploited for the synthesis of valuable derivatives such as *o*-alkoxyazobenzenes,[10] *o*-acylazobenzenes,[11–14] and indole frameworks.[15,16] In addition, they are increasingly utilized in the fabrication of optical filters and protective glass materials.

Literature surveys indicate that several methods have been reported for the synthesis of azo compounds, including the Mills[17,18] and Wallach reactions, oxidation of amines, reduction of azobenzenes, thermolysis of azides, transformations of quinine acetals, dehydrogenation or metal-catalyzed coupling of arylhydrazines, triazene rearrangements, dimerization of diazonium salts, and opening of benzotriazoles.[19–26] Among these, the simplest and most direct strategy is the one-step oxidation of amines. This transformation has been achieved using various catalysts such as gold nanoparticles on TiO_2, silver nanoparticles, nickel peroxide, MnO_2, $NaBO_3$, $BaMnO_4$, $AgMnO_4$, $Pb(OAc)_4$, Ag_2CO_3, $Ce(OH)_3O_2H$, $RuCl_3/H_2O_2$, *t*-BuOI, *t*-BuOCl, galvinoxyl/$K_3Fe(CN)_6$, KO_2, platinum and palladium nanowires, and Cu(I)-diaziridinone.[27–46] A comparative overview of these reported processes is provided in Table 2.

Several methods have been reported for the synthesis of azobenzenes, each with certain advantages, such as high yields for specific amine derivatives. However, many of these protocols remain limited due to drawbacks including the use of expensive metal catalysts, toxic solvents, harsh conditions, long reaction times, moderate yields, and issues of functional group tolerance or metal contamination. The preparation and handling of metal catalysts, magnetic nanoparticles, or ionic liquids further increase cost and complexity. In contrast, mechanochemical

[a]Department of Chemistry, University of North Bengal, Dist. Darjeeling, West Bengal, India. E-mail: pizy12@yahoo.com

[b]Department of Food Technology, University of North Bengal, Dist. Darjeeling, West Bengal, India. Fax: +91 (0353) 2699001; Tel: +91 (0353) 2776381

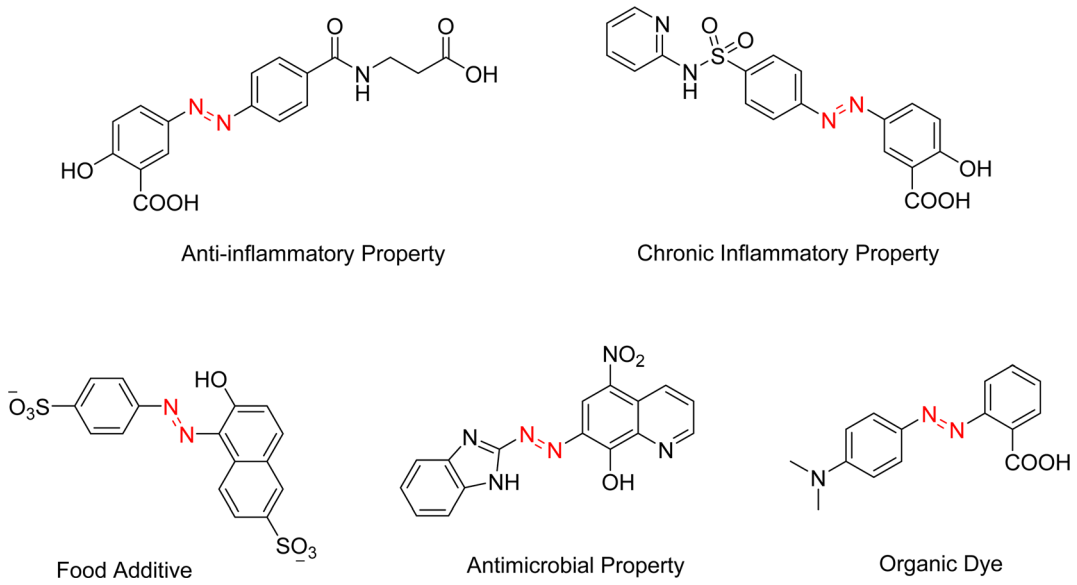
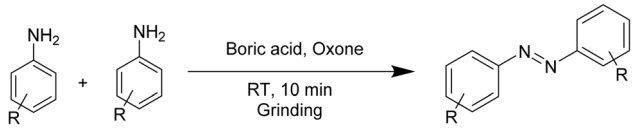


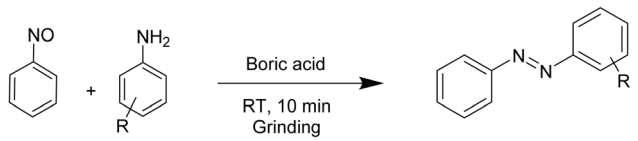
Fig. 1 Biologically active molecules having the azo-moiety.

synthesis offers a green, solvent-free, and energy-efficient alternative.[47] It enables straightforward one-pot access to symmetrical and unsymmetrical azobenzenes under ambient conditions, without the need for transition-metal or lanthanide catalysts, thereby providing a more sustainable and eco-efficient pathway highly desirable in synthetic organic chemistry.

Among inorganic acids, boric acid is a weak acid ($pK_a = 9.2$), moderately soluble in water, more soluble in warm water, and well known for its stability and environmental safety. Over the past decades, it has been widely applied in organic transformations[48–52] due to its advantages, including commercial availability, chemical stability, and ease of handling, low cost, non-toxicity, and overall green nature. In this study, we explored the catalytic potential of boric acid in a mechanochemical framework for the sustainable synthesis of azobenzenes. We report a straightforward, solvent-free grinding protocol under mild conditions for the preparation of both symmetrical (Scheme 1) and unsymmetrical azobenzenes (Scheme 2), employing oxone[53] as the oxidant in the synthesis of symmetric derivatives.



Scheme 1 Synthesis of symmetrical azobenzene from amines.



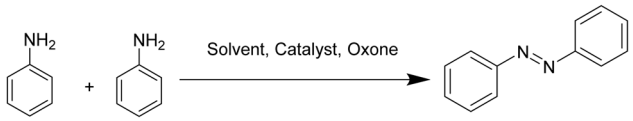
Scheme 2 Synthesis of unsymmetrical azobenzene from amines and nitrosobenzene.

Results and discussion

Synthesis of symmetrical azobenzenes

To standardize the reaction protocol, aniline (1 mmol) was taken as the starting material and the progress of the reaction was monitored by TLC. Initially, the reaction was investigated in the absence of a catalyst under solvent conditions. Even after 30 min of grinding the desired product was not obtained (Table 1, Entry 1). In the absence of boric acid, only nitrobenzene was formed in the presence of oxone and it was confirmed by matching the TLC results with those of commercially purchased nitrobenzene (Table 1, Entry 1). Then the reaction was carried out by taking 1 mmol of aniline, 25 mol% of boric acid and 0.5 mmol of oxone under aqueous conditions for 30 min when only a small amount of the product was obtained (Table 1, Entry 2). Now under the same reaction conditions, different solvents were used to monitor the reaction. However, with ethanol, methanol, acetonitrile, chloroform, and toluene we obtained moderate yields of the desired products (Table 1, Entries 3–7). When we switched from different solvents to neat conditions in the presence of varying amounts of boric acid, we were excited to find that the desired product was obtained in good yields (82–88%) (Table 1, Entries 8–12). Now with the solvent being optimized, we increased the amount of oxone to 1.0 mmol but were surprised to find that the yield decreased considerably to 66% (Table 1, Entry 13). It might be due to the oxidation of aniline to nitrobenzene before undergoing the coupling reaction. However, reducing the amount of oxone to 0.25 mmol reduced the yield to 45% (Table 1, Entry 14). To explore the effect of the oxidant, we screened our reaction with various oxidants such as CH_3COOOH, $K_2S_2O_8$ and I_2. However, either trace amounts of the product were obtained or no reaction was observed (Table 1,

Table 1 Screening of the reaction conditions for the synthesis of symmetric azobenzenes[a,b]



Entry	Oxone (mmol)	Solvent	Catalyst loading (mol%)	Time (min)	Yield (%)[c]
1	0.5	Neat	—	30	—
2	0.5	Water	25	30	35
3	0.5	Ethanol	25	30	39
4	0.5	Methanol	25	30	41
5	0.5	Acetonitrile	25	30	50
6	0.5	$CHCl_3$	25	30	56
7	0.5	Toluene	25	30	60
8	0.5	Neat	25	30	88
9	0.5	Neat	30	30	87
10	0.5	Neat	20	20	85
11	0.5	Neat	15	10	82
12	**0.5**	**Neat**	**10**	**10**	**82**
13	1.0	Neat	10	10	66
14	0.25	Neat	10	10	45
15	0.5	Neat	10	15	82
16	0.5	Neat	10	20	84
17	0.5	Neat	10	30	84
18	0.5	Neat	10	30	Trace[d]
19	0.5	Neat	10	30	—[e]
20	0.5	Neat	10	30	—[f]

[a] Bold font represents the optimized conditions. [b] Reaction of aniline (1 mmol), varying amount of oxone and boric acid with various solvents at room temperature using the grinding method. [c] Isolated yield of product by column chromatography. [d] CH_3COOOH as the oxidant. [e] $K_2S_2O_8$ as the oxidant. [f] I_2 as the oxidant.

Entries 18–20). Thus, we chose oxone as the oxidant for this reaction. We further investigated the reaction by increasing the time to 15, 20, and 30 min which did not give any significant increase in the yield of the product (Table 1, Entries 15, 16, and 17). Hence finally we chose 1 mmol of aniline, 10 mol% of boric acid and 0.5 mmol of oxone[54] as the optimal reaction conditions for the synthesis of symmetric azobenzenes under solvent-free conditions at room temperature for 10 min using the grinding method (Table 1, Entry 12). Therefore, boric acid shows great catalytic activity in the preparation of symmetric azobenzene by the mechanochemical process.

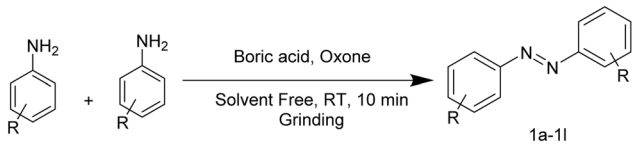
After tuning various reaction conditions, we compared our results with the previously published literature (Table 2) to demonstrate the benefits of using boric acid as a catalyst in this procedure. The results show that previously published techniques had flaws including prolonged response times, low yields, severe reaction conditions, and so on. Compared to previously reported approaches, the suggested procedures are more efficient, cost-effective, and environmentally friendly.

This protocol gave the desired products with a range of amines (Table 3). The progress of the reaction was monitored by TLC (eluent: ethyl acetate–petroleum ether). The product was collected through column chromatography. A number of amines were employed in the synthesis of symmetric azobenzenes in our methodology. As evidenced from Table 3, good yields of different products were obtained all at room temperature. The procedure was generalized for a range of amines having electron-donating and electron-withdrawing groups on the benzene ring as well as naphthyl rings. Better results were obtained for amines having the electron-donating effect

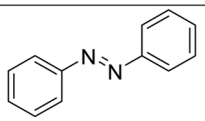
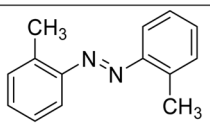
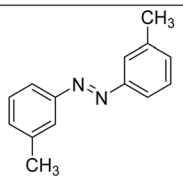
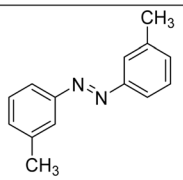
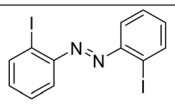
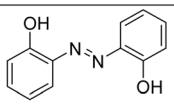
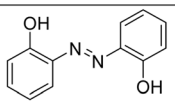
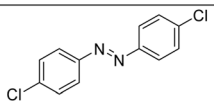
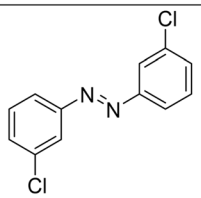
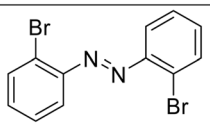
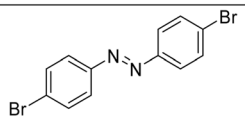
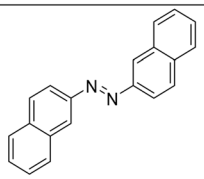
Table 2 Comparative studies for the synthesis of azobenzenes

Sl no.	Catalyst	Conditions	Time (h)	Yield (%)
1	Ag-nanoparticles (1 mmol)	KOH, DMSO, rt	24	50–97
2	Au/TiO_2-nanoparticles (1.5 wt%)	Toluene, 100 °C, O_2, 5 bar	5–31	44–99
3	*t*-BuOCl (1 mmol)	NaI (1 mmol), ether, rt	1–36	44–97%
4	CuBr (5 mol%)	Diaziridinone (1.1 equiv.), CH_3CN, rt	2	70–98%
5	$NaBO_3$ (0.01 mol)	Glacial acetic acid (20 cc), 45–50 °C	3	6.52–50.42%
Present work	**Boric acid (10 mol%)**	**Oxone (0.5 mmol), neat, rt, grinding**	**10 min**	**62–82%**

Table 3 Boric acid catalyzed and ethanol mediated synthesis of symmetric azobenzenes[a]



1a-1l

 1a Yield = 82%	 1b Yield = 84%	 1c Yield = 82%	 1d Yield = 85%
 1e Yield = 62%	 1f Yield = 74%	 1g Yield = 69%	 1h Yield = 71%
 1i Yield = 66%	 1j Yield = 63%	 1k Yield = 67%	 1l Yield = 82%

[a] Reaction conditions: aniline (1 mmol), oxone (0.5 mmol) and boric acid (10 mol%) under solvent-free conditions at room temperature using the grinding method.

compared to those having the electron-withdrawing effect. It may be due to the electron density on the nitrogen atom making them more nucleophilic. It was also observed that *ortho*-products gave fewer yields than the other products. This may be due to steric factors at the *ortho* positions.

Synthesis of unsymmetrical azobenzenes

Now to broaden the catalytic activity, boric acid was also investigated for the synthesis of unsymmetrical azobenzenes. In our attempt to synthesize unsymmetric azobenzenes directly from amines, we chose aniline (1 mmol), *p*-toluidine (1 mmol), and oxone (0.5 mmol) as model substrates which gave only trace amounts of the desired product in the presence of 25 mol% of boric acid, with nitrobenzene as the main by-product. It was also confirmed by TLC using the commercially available one. Then to synthesise unsymmetrical azobenzenes we chose nitrosobenzene rather than aniline under the same conditions. At first, in the absence of a catalyst no desired product was obtained (Table 4, Entry 1). However, under the solvent-free mechanochemical conditions, the reaction of *p*-toluidine (1 mmol) with nitrosobenzene (1 mmol) in the presence of boric acid afforded the best yield of the targeted azobenzene (Table 4, Entries 8–12). Screening of solvents such as water, ethanol, methanol, chloroform, and acetonitrile gave only moderate results, confirming the superiority of the neat grinding method (Table 4, Entries 2–7). The yield of the product was not much affected even after increasing the time of the reaction (Table 4, Entries 13–15). Thus, the optimal protocol involved 1 mmol *p*-toluidine, 1 mmol nitrosobenzene, and 10 mol% of boric acid using the grinding process for 10 min, providing excellent yield of the unsymmetric azobenzene at room temperature (Table 4, Entry 12).

Amines with diverse substituents were efficiently transformed into unsymmetric azobenzenes in good yields, as shown in Table 5. Both *ortho*- and *para*-substituted amines were compatible with the methodology, though *para*-substituted derivatives generally gave higher yields. The lower yields observed with *ortho*-substituted amines can be attributed to steric hindrance at the *ortho* position.

Table 6 shows the turnover frequency (TOF) and turnover number (TON). Boric acid can be used to attain higher turnover

Table 4 Screening of the reaction conditions for the synthesis of unsymmetric azobenzenes[a,b]

Entry	Solvent	Catalyst loading (mol%)	Time (min)	Yield (%)[c]
1	Neat	—	30	—
2	Water	25	30	33
3	Ethanol	25	30	40
4	Methanol	25	30	47
5	Acetonitrile	25	30	56
6	$CHCl_3$	25	30	63
7	Toluene	25	30	69
8	Neat	25	20	86
9	Neat	30	20	86
10	Neat	20	15	84
11	Neat	15	10	82
12	**Neat**	**10**	**10**	**80**
13	Neat	10	15	80
14	Neat	10	20	81
15	Neat	10	30	82

[a] Bold font represents the optimized conditions. [b] Reaction of amines (1 mmol), nitrosobenzene (1 mmol) and varying amount of boric acid at room temperature under different solvent conditions. [c] Isolated yield of the products using column chromatography.

frequency (TOF) and turnover number (TON) values for both the symmetrical and unsymmetrical azobenzene synthesis under optimal circumstances.[55]

Table 6 Calculations of green metrics – turnover number (TON) and turnover frequency (TOF)

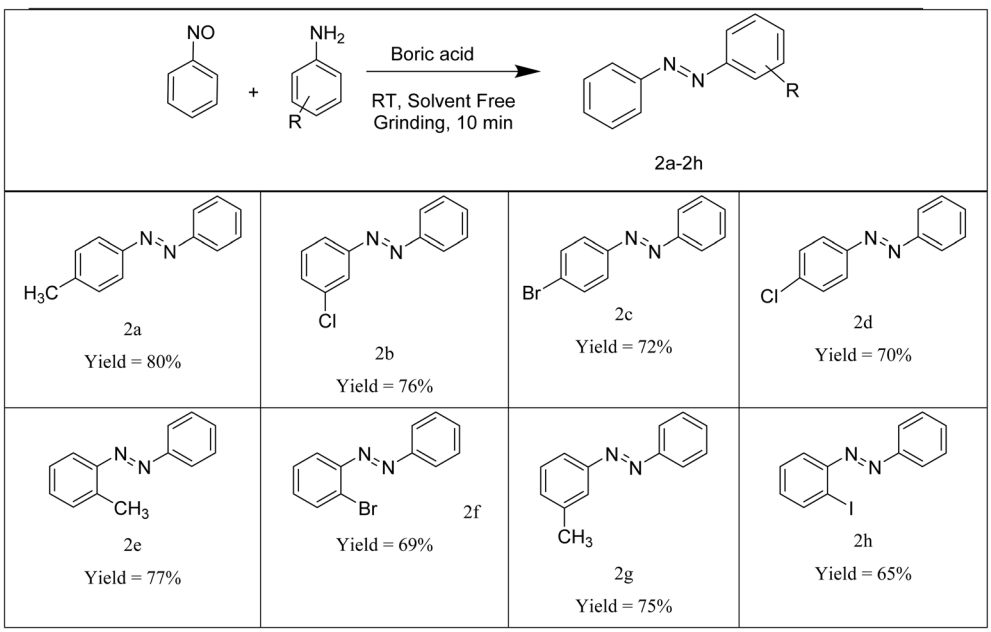
Entry	Product	TON	TOF	Entry	Product	TON	TOF
1	1a	114	11.4	11	1k	76	7.6
2	1b	119	11.9	12	1l	113	11.3
3	1c	114	11.4	13	2a	99	9.9
4	1d	144	14.4	14	2b	89	8.9
5	1e	65	6.5	15	2c	80	8.0
6	1f	92	9.2	16	2d	77	7.7
7	1g	81	8.1	17	2e	93	9.3
8	1h	85	8.5	18	2f	74	7.4
9	1i	72	7.2	19	2g	88	8.8
10	1j	67	6.7	20	2h	66	6.6

We studied the recyclability and reusability of the catalyst H_3BO_3 for the synthesis of symmetric and unsymmetric azobenzenes. It was found that after completion of the reaction, *n*-hexane was added to the residual mixture and then by simple filtration the catalyst was recovered and reused up to five times under the optimal conditions. After yielding an excellent amount of product in the 1st run, the catalyst was separated and collected to be used for the next run. In the 2nd run, the recovered catalyst provided the desired product in good yield (77%). The same process was just repeated for the 3rd, 4th and 5th run. We were glad to find that the catalytic activity of boric acid was retained up to the 5th run providing the desired product in good yields (58–82%) (Fig. 2).

Mechanism

Based on the literature survey, a plausible mechanism has been proposed in Scheme 3. In the first step, boric acid coordinates

Table 5 Boric acid catalyzed and ethanol mediated synthesis of unsymmetric azobenzenes[a]



[a] Reaction conditions: nitrosobenzene (1 mmol), amines (1 mmol) and boric acid (10 mol%) under neat conditions at room temperature using the grinding method.

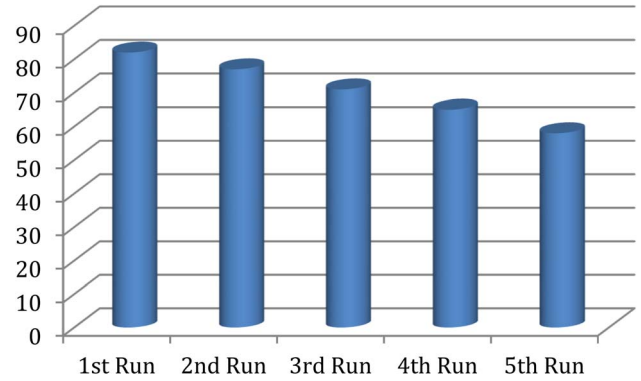
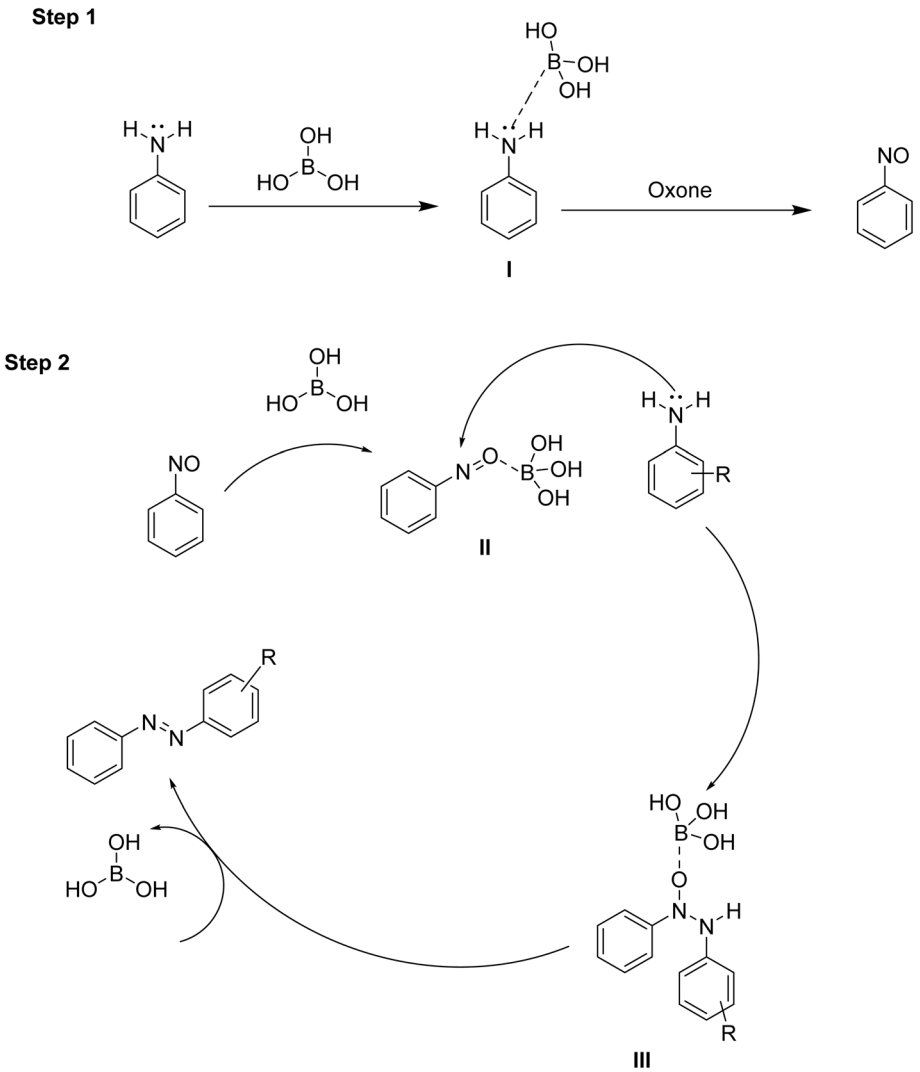


Fig. 2 Recyclability of the catalyst.

with the lone pair of the amine nitrogen (I) through its electron-deficient boron centre. This coordination reduces the reactivity of nitrogen and directs the oxidation by oxone towards the formation of nitrosobenzene (detected by FT-IR spectra) rather than nitrobenzene. In the second step, boric acid may interact with the oxygen atom of nitrosobenzene (II), thereby activating it for nucleophilic attack by aniline at the nitrogen center. This leads to the formation of intermediate (III), which subsequently transforms into the targeted product, azobenzene. The first step of the mechanism is suitable only for the synthesis of symmetrical azobenzenes, whereas the second one is applicable for the synthesis of both symmetrical and unsymmetrical azobenzenes.

Experimental details

General procedure for the synthesis of symmetrical azobenzene derivatives. Firstly, to get the desired product of the model reaction, amine (1 mmol), oxone (0.5 mmol) and boric acid (10 mol%) were mixed together and ground by using a mortar and pestle manually at room temperature for 10 min under solvent-free conditions. The progress of the reaction was observed on TLC with a mixture of ethyl acetate and petroleum ether as the eluent system. After completion of the reaction, the mixture was extracted with ethyl acetate and washed several times with water. The combined organic mixture was dried over



Scheme 3 Probable mechanism for the preparation of azobenzene.

anhydrous Na_2SO_4, concentrated and the residue was purified by column chromatography to afford a pure solid product. All the products were characterized by ^{1}H NMR and ^{13}C NMR.

The NMR data of (*E*)-azobenzene,[56] the desired product of the model reaction, are given below: ^{1}H NMR (300 M Hz, $CDCl_3$) δ(ppm): 7.54–7.49 (m, 6H), 7.93 (d, $J = 7.2$ Hz, 4H); ^{13}C NMR (75 M Hz, $CDCl_3$) δ(ppm): 122.84, 129.10, 131.00, 152.62.

General procedure for the synthesis of unsymmetrical azobenzene derivatives. Firstly, to get the desired product of the model reaction, *p*-toluidine (1 mmol), nitrosobenzene (1 mmol), and boric acid (10 mol%) were mixed and ground by using a mortar and pestle manually at room temperature for 10 min under solvent-free conditions. After completion of the reaction, checked by TLC, the mixture was separated using ethyl acetate and water. The combined organic mixture extracted in ethyl acetate was dried over anhydrous Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel 60–120 mesh using petroleum ether as the eluent to afford a pure solid product. All the products were characterized by ^{1}H NMR and ^{13}C NMR.

The NMR data of (*E*)-1-(4-methylphenyl)-2-phenyldiazene,[57] the desired product of the model reaction, are given below: ^{1}H NMR (400 M Hz, $CDCl_3$) δ(ppm): 2.44 (s, 3H), 7.3 (d, $J = 8.0$ Hz, 2H), 7.5 (d, $J = 8.0$ Hz, 3H), 7.8 (d, $J = 8.0$, 2H), 7.9 (d, $J = 7.6$, 2H); ^{13}C NMR (100 M Hz, $CDCl_3$) δ(ppm): 22.69, 122.72, 122.85, 129.05, 129.74, 130.69, 141.56, 150.77, 152.74.

Conclusion

In conclusion, we have developed a simple, eco-friendly, and efficient mechanochemical strategy for the synthesis of both symmetrical and unsymmetrical azobenzenes. The use of inexpensive and non-toxic boric acid as a recoverable catalyst makes this method sustainable and environmentally benign. The process features easy reaction conditions and a straightforward setup, and eliminates the need for hazardous solvents. Overall, this work presents a facile and green approach for azobenzene synthesis, aligning with the principles of sustainable organic chemistry.

Conflicts of interest

There are no conflicts to declare.

Data availability

All the data put/used in writing the manuscript may be made available on request following the journal's policy.

Supplementary information (SI): experimental details, ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds. See DOI: https://doi.org/10.1039/d5mr00133a.

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References

1 M. C. Bryan, B. Dillon, L. G. Hamann, G. J. Hughes, M. E. Kopach, E. A. Peterson, M. Pourashraf, I. Raheem, P. Richardson, D. Richter and H. F. Sneddon, *J. Med. Chem.*, 2013, **56**, 6007.
2 H. Böttcher, *Zeitschrift für Chemie*, 1989, **29**, 387.
3 R. G. Anderson and G. Nickless, *Anal.*, 1967, **92**, 207.
4 T. Ikeda, *J. Mater. Chem.*, 2003, **13**, 2037.
5 C. J. Barrett, J. Mamiya, K. G. Yager and T. Ikeda, *Soft Matter*, 2007, **3**, 1249.
6 G. S. Kumar and D. C. Neckers, *Chem. Rev.*, 1989, **89**, 1915.
7 A. A. Beharry and G. A. Woolley, *Chem. Soc. Rev.*, 2011, **40**, 4422.
8 W. Jones, *Solid State Ionics*, 1995, **76**, 173.
9 T. Fehrentz, M. Schönberger and D. Trauner, *Angew. Chem., Int. Ed.*, 2011, **50**, 12156.
10 Z. Yin, X. Jiang and P. Sun, *J. Org. Chem.*, 2013, **78**, 10002.
11 H. Li, P. Li, H. Tan and L. Wang, *Chem. Eur. J.*, 2013, **19**, 14432.
12 Z.-Y. Li, D.-D. Li and G.-W. Wang, *J. Org. Chem.*, 2013, **78**, 10414.
13 H. Song, D. Chen, C. Pi, X. Cui and Y. Wu, *J. Org. Chem.*, 2014, **79**, 2955.
14 F. Xiong, C. Qian, D. Lin, W. Zeng and X. Lu, *Org. Lett.*, 2013, **15**, 5444.
15 H. Li, P. Li and L. Wang, *Org. Lett.*, 2013, **15**, 620.
16 H. Wang, Y. Yu, X. Hong, Q. Tan and B. Xu, *J. Org. Chem.*, 2014, **79**, 3279.
17 C. Mills, *J. Chem. Soc., Trans.*, 1895, **67**, 925.
18 A. Baeyer, *Ber. Dtsch. Chem. Ges.*, 1874, **7**, 1638.
19 E. Merino, *Chem. Soc. Rev.*, 2011, **40**, 3835.
20 K. Haghbeen and E. W. Tan, *J. Org. Chem.*, 1998, **63**, 4503.
21 M. H. Davey, V. Y. Lee, R. D. Miller and T. J. Marks, *J. Org. Chem.*, 1999, **64**, 4976.
22 H. S. Fry and P. E. Bowman, *J. Am. Chem. Soc.*, 1930, **52**, 1531.
23 J. F. Vozza, *J. Org. Chem.*, 1969, **34**, 3219.
24 L. I. Smith and W. B. Irwin, *J. Am. Chem. Soc.*, 1941, **63**, 1036.
25 A. Thakuri, M. Banerjee and A. Chatterjee, *iScience*, 2022, **25**, 104497.
26 J. Shen, J. Xu, Q. Zhu and P. Zhang, *Org. Biomol. Chem.*, 2021, **19**, 3119.
27 S. Cai, H. Rong, X. Yu, X. Liu, D. Wang, W. He and Y. Li, *ACS Catal.*, 2013, **3**, 478.
28 A. Grirrane, A. Corma and H. García, *Science*, 2008, **322**, 1661.
29 Y. Zhu and Y. Shi, *Org. Lett.*, 2013, **15**, 1942.
30 K. Nakagawa, S. Shiba, M. Horikawa, K. Sato, H. Nakamura, N. Harada and F. Harada, *Synth. Commun.*, 1980, **10**, 305.
31 H. K. Hombrecher and K. Lüdtke, *Tetrahedron*, 1993, **49**, 9489.
32 S. M. Mehta and M. V. Vakilwala, *J. Am. Chem. Soc.*, 1952, **74**, 563.
33 E. Baer and A. L. Tosoni, *J. Am. Chem. Soc.*, 1956, **78**, 2857.

34 H. Firouzabadi and Z. Mostafavipoor, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 914.
35 H. Firouzabadi, B. Vessal and M. Naderi, *Tetrahedron Lett.*, 1982, **23**, 1847–1850.
36 M. Hedayatullah, J. Pierre Dechatre and L. Denivelle, *Tetrahedron Lett.*, 1975, **16**, 2039.
37 H. Firouzabadi and N. Iranpoor, *Synth. Commun.*, 1984, **14**, 875.
38 G. Crank and M. Makin, *Aust. J. Chem.*, 1984, **37**, 845.
39 X.-Y. Wang, Y.-L. Wang, J.-P. Li, Z.-F. Duanb and Z.-Y. Zhang, *Synth. Commun.*, 1999, **29**, 2271.
40 S. Okumura, C.-H. Lin, Y. Takeda and S. Minakata, *J. Org. Chem.*, 2013, **78**, 12090.
41 S. Minakata, Y. Takeda and S. Okumura, *Synthesis*, 2013, **45**, 1029.
42 D. Zhang, J. Mcleod, L. Hu, S. Lu, Y. Ma, J. Zhong, Z. Jiang, H. Gu and X. Sun, *J. Phys. Chem. C*, 2016, **120**, 14712.
43 B. Ortiz, P. Villanueva and F. Walls, *J. Org. Chem.*, 1972, **37**, 2748.
44 K. Seth, S. R. Roy, A. Kumar and A. K. Chakraborti, *Catal. Sci. Technol.*, 2016, **6**, 2892.
45 G. Barak and Y. Sasson, *J. Org. Chem.*, 1989, **54**, 3484.
46 K. Orito, T. Hatakeyama, M. Takeo, S. Uchiito, M. Tokuda and H. Suginome, *Tetrahedron*, 1998, **54**, 8403.
47 G. W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 7668.
48 H. Kiyani and F. Ghorbani, *Res. Chem. Intermed.*, 2013, **41**, 2653.
49 T. A. Houston, B. L. Wilkinson and J. T. Blanchfield, *Org. Lett.*, 2004, **6**, 679.
50 R. K. Mylavarapu, K. Gcm, N. Kolla, R. Veeramalla, P. Koilkonda, A. Bhattacharya and R. Bandichhor, *Org. Process Res. Dev.*, 2007, **11**, 1065.
51 Z. Hosseinzadeh, A. Ramazani, N. Razzaghi-Asl, K. Slepokura and T. Lis, *Turk. J. Chem.*, 2019, **43**, 464.
52 T. B. Nguyen, J. Sorres, M. Q. Tran, L. Ermolenko and A. Al-Mourabit, *Org. Lett.*, 2012, **14**, 3202.
53 H. Hussain, I. R. Green and I. Ahmed, *Chem. Rev.*, 2013, **113**, 3329–3371.
54 G. C. Pariyar, T. Kundu, B. Mitra, S. Mukherjee and P. Ghosh, *ChemistrySelect*, 2020, **5**, 9781–9786.
55 S. Bhattacharjee, P. Basak and P. Ghosh, *Tetrahedron Lett.*, 2025, **159**, 155518.
56 Á. Georgiádes, S. B. Ötvös and F. Fülöp, *ACS Sustain. Chem. Eng.*, 2015, **3**, 3388–3397.
57 M. Wang, J. Ma, M. Yu, Z. Zhang and F. Wang, *Catal. Sci. Technol.*, 2016, **6**, 1940–1945.