Oxidative Dehydrogenation of Hydrazobenzenes toward Azo Compounds Catalyzed by tert-Butyl Nitrite in EtOH

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ABSTRACT: We describe a tert-butyl nitrite-catalyzed oxidative dehydrogenation of hydrazobenzenes for producing azobenzenes. This method proceeds at ambient temperature and under an atmospheric environment by employing eco-friendly EtOH as the medium, representing a mild, general route to the synthesis of various symmetrical and nonsymmetrical azobenzenes in excellent yields with broad functional group tolerance.

INTRODUCTION

Azo compounds, a class of prominent compounds containing a N=N unsaturated bond, are versatile synthetic building blocks in synthesis as well as pervasive motifs in related bioactive natural products, pharmaceuticals, functional materials (e.g., dyes, pigments, indicators, photochemical switches, chemosensors, food additives, and polymers), and radical-reaction initiators. As a result, considerable efforts have been dedicated to the development of efficient, sustainable methods for azo compound synthesis.

Preparation of prominent compounds in an eco-friendly strategy is of continuous interest in organic synthesis. With this feature in mind and our interest in metal-free synthesis of organic molecules via the oxidative strategy, we sought to develop an efficient and environmentally friendly dehydrogenation reaction of hydrazobenzenes to furnish azo compounds. After a series of trials, it was found that tert-butyl nitrite (TBN) could realize the dehydrogenation of hydrazobenzenes to furnish azo compounds at room temperature. This approach offers a valuable, eco-friendly alternative to azo compounds, which is rapid, mild, general, and easy to operate, does not require additives, and is suitable for large-scale applications.

RESULTS AND DISCUSSION

We first selected 1,2-diphenylhydrazine (1a) as the model substrate to optimize the reaction conditions. First, when 1,2-

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diphenylhydrazine was treated with several common non-metallic oxidants in radical reaction (2 equiv), such as O2 (balloon), TBHP (70% in water), DTBP, H2O2, benzoic peroxyanhydride (BPO), K2S2O8, and TBN, in MeCN at room temperature, the results represent a significant difference regarding the oxidants (Table 1, entries 1–7). For examples, both BPO and TBN could effectively facilitate this transformation, affording 80% and 86% yield of the product, respectively (entries 5 and 7); however, the others exhibited no reactivity to this reaction (entries 1–4 and 6), and the starting material was recovered from the reaction system after 2 h.

Next, the effect of solvent on product yields was also examined (entries 8–14). The results showed that ethyl acetate, dioxane, DCM, DMSO, and DMF provided similar product yields (entries 9–11, 13, and 14); however, the use of toluene as a solvent reduced the yield to 26% (entry 8). Gratifyingly, an excellent yield (93%) of the product was obtained when EtOH was used as a solvent (entry 12). Finally, the amount of TBN was investigated. The results showed that decreasing the amount of TBN to 100 or 30 mol %, excellent yields of 2a could be obtained (entries 15 and 16); however, a lower yield (43%) was obtained upon decreasing the amount of TBN to 15 mol % (entry 17). Notably, air played a crucial role because <10% yield of 2a was obtained under an Ar atmosphere (entry 18). In addition, the yield of 2a reduced to 16% when 30 mol % TBN was changed to 30 mol % BPO (entry 19).

With optimized conditions in hand, the scope of diverse functionalized azobenzenes synthesis was examined (Scheme 2). As shown in Scheme 2, a wide range of substituents on the aromatic ring were tolerated to produce the corresponding azobenzenes (types I and II). For symmetrical azobenzenes (type I), both electron-donating group (−Me, −OMe) or electron-withdrawing groups (−Cl, −CF3) at the para position of the aromatic ring were compatible with this procedure (2b–e). For unsymmetrical azobenzenes (type II), one of the aromatic ring of hydrazobenzenes bearing substituents, such as methyl (2f and 2g), halide (2h–k), methoxy (2l), methylthio (2m), phenyl (2n), and trifluoromethyl (2o), underwent the transformation well to generate the azobenzenes in excellent yields. Moreover, halogen atoms (F, Cl, Br, and I) were well compatible, allowing for the construction of more complex molecules. In addition, this method exhibited good selectivity when 1-(4-(methylthio)phenyl)-2-phenylhydrazine (2m), a substrate including methylthio that could be oxidized to sulfone, was selected to produce the corresponding azobenzenes. Hydrazobenzenes containing two substituents or one cyclic structure accomplished the transformation well to achieve the azobenzenes in good yields (2p–s).

Subsequently, some continuations of our present strategy were carried out to verify the scalability and applicability (Scheme 3). When 1a was treated at a 6 mmol scale, 92% yield

| entry | [O] [mol %] | solvent | temp (°C) | yield (%) |
|-------|-------------|---------|-----------|----------|
| 1*    | air or O2   | MeCN    | rt        | trace    |
| 2     | TBHP (200)  | MeCN    | rt        | trace    |
| 3     | DTBP (200)  | MeCN    | rt        | trace    |
| 4     | H2O2 (200)  | MeCN    | rt        | trace    |
| 5     | BPO (200)   | MeCN    | rt        | 80       |
| 6     | K2S2O8 (200)| MeCN    | rt        | trace    |
| 7     | TBN (200)   | MeCN    | rt        | 86       |
| 8     | TBN (200)   | toluene | rt        | 26 (68%) |
| 9     | TBN (200)   | ethyl acetate | rt   | 83       |
| 10    | TBN (200)   | dioxane | rt        | 86       |
| 11    | TBN (200)   | DCM     | rt        | 88       |
| 12    | TBN (200)   | EtOH    | rt        | 93       |
| 13    | TBN (200)   | DMSO    | rt        | 87       |
| 14    | TBN (200)   | DMF     | rt        | 83       |
| 15    | TBN (100)   | EtOH    | rt        | 97       |
| 16    | TBN (30)    | EtOH    | rt        | 96       |
| 17    | TBN (15)    | EtOH    | rt        | 43 (54%) |
| 18†   | TBN (30)    | EtOH    | rt        | <10      |
| 19    | BPO (30)    | EtOH    | rt        | 16 (80%) |

*Reaction conditions: 1a (0.5 mmol), [O], solvent (2 mL), air (1 atm), room temperature, and 2 h. *Isolated yield. *Air or O2 (balloon; 1 atm). †In argon. ‡Recovery rate of 1a.

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Scheme 2. Formation of Various Azobenzenes

![Scheme 2](image-url)
of the target product 2a was obtained [Eq (1)]. Additionally, when \( N' \)-phenylacetohydrazide 3a was investigated under the standard conditions, a trace amount of product 4a was detected and 16% yield of the product 4a was separated from the transformation when 200 mol % TBN was utilized; however, the yield of 4a increased to 64% when changing the solvent to MeCN, together with 200 mol % TBN [Eq (2)]. To our surprise, treatment of 4-methylbenzenesulfonohydrazide (5a) with 200 mol % TBN in EtOH afforded 4-methylbenzenesulfonyl azide (6a) in 92% yield [Eq (3)].

To understand the mechanism for this reaction, we performed some control experiments. It was found that the reaction did not proceed when TBN was changed to NaNO2 (with or without HOAc) and gave a very low yield of 2a when changing TBN to AgNO2 or Fe(NO3)3 [Eq (4)]. When a stoichiometric amount of the radical inhibitor was used (3 equiv), including TEMPO and BHT [Eq (5)], the yields of product 2a represented a certain suppression. According to the results, a free radical process should be involved in this dehydrogenation strategy.

On the basis of the above results and the precedent literature, a plausible reaction mechanism was proposed (Scheme 4).\(^{12}\) Initially, \(^{1} BuONO\) would divide into a \(^{1} BuO\) radical and an NO radical, which transform into HNO2 in the presence of H2O. Then, HNO2 is rapidly decomposed into NO2, NO, and H2O. With the aid of NO2, NO, and air (O2), substrate 1a is converted into intermediate A. Finally, product 2a is generated via elimination of an equivalent HNO2 from intermediate A. HNO2 re-participate in the decomposition, thus making the reaction start a new reaction cycle.

### CONCLUSIONS

In conclusion, we herein have developed an efficient and practical dehydrogenation approach of hydrazobenzenes to furnish azobenzenes with the aid of catalytic TBN and air. The
reaction proceeds under mild conditions and using a green solvent (EtOH) without any additives. Various symmetrical and unsymmetrical azobenzenes could be successfully constructed in excellent yields (up to 98%) with broad functional group tolerance.

**EXPERIMENTAL SECTION**

**General Information.** $^1$H NMR, $^{13}$C($^1$H) NMR spectra were recorded on a Bruker 400 MHz advance spectrometer at room temperature in CDCl$_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Reactions were monitored by thin-layer chromatography. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (300−400 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

Typical Experimental Procedure for the Scale Magnification Experiments. To a 10 mL tube was added substrate (0.5 mmol) followed by EtOH (5 mL) and TBN (30 mol %). The content of the tube was stirred at room temperature under an atmospheric environment for 2 h. Then, the reaction mixture was concentrated under reduced pressure. Purification by column chromatography (Hexanes/EtOAc: 100/1) afforded corresponding azo compounds.

Typical Experimental Procedure for the Scale Magnification Experiments. To a 10 mL tube was added substrate (1a (6 mmol) followed by EtOH (5 mL) and TBN (30 mol %). The content of the tube was stirred at room temperature under an atmospheric environment for 2 h. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography (Hexanes/EtOAc: 50/1−100/1) afforded corresponding azo compounds.

(E)-1,2-Di-p-tolyldiazene (2b). 94.1 mg, 92%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 7.96−7.89 (m, 4H), 7.53−7.45 (m, 3H), 7.19 (t, J = 8.0 Hz, 2H), 1H NMR (100 MHz, CDCl$_3$ δ ppm) 164.3 (d, J = 100 Hz, 1C), 152.4, 149.1 (d, J = 1 Hz, 1C), 138.9, 131.8, 130.9, 129.0, 128.9, 122.8, 120.5, 21.4.

(E)-1-(4-Fluorophenyl)-2-phenyldiazene (2h). 91.4 mg, 93%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 7.92−7.90 (m, 2H), 7.74−7.73 (m, 2H), 7.52−7.49 (m, 2H), 7.47−7.44 (m, 1H), 7.39 (t, J = 8.0 Hz, 2H), 2.28 (s, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$ δ ppm) 152.7 (2C), 138.9, 131.8, 130.9, 129.0, 128.9, 122.8, 120.5, 21.4.

(E)-1-(4-Chlorophenyl)-2-phenyldiazene (2i). 96.3 mg, 97%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 7.86−7.92 (m, 4H), 7.47−7.52 (m, 5H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$ δ ppm) 152.3, 150.9, 136.8, 131.3, 129.1, 124.1, 122.9.

(E)-1-(4-Bromophenyl)-2-phenyldiazene (2j). 91.4 mg, 93%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 7.91 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.50−7.52 (m, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$ δ ppm) 152.3, 151.2, 132.3, 131.3, 129.1, 125.3, 124.3, 122.9.

(E)-1-(4-Iodophenyl)-2-phenyldiazene (2k). 150.0 mg, 95%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 7.91 (d, J = 4.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.53−7.47 (m, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$ δ ppm) δ152.4, 151.9, 138.3, 131.3, 129.1, 124.5, 123.0, 97.7.

(E)-1-(4-Methoxyphenyl)-2-phenyldiazene (2l). 101.6 mg, 95%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 8.03 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$ δ ppm) 154.1, 132.9 (q, J = 26.0 Hz, 1C), 126.4 (q, J = 3.0 Hz, 1C), 123.8 (q, J = 210.0 Hz, 1C), 123.3.

(E)-1-(4-Bromonitrophenyl)-2-phenyldiazene (2m). 98.4 mg, 94%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$ δ ppm) 8.03 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$ δ ppm) 152.6, 149.9, 142.9, 130.7, 129.0, 125.9, 123.3, 122.7, 15.2.
(E)-1-(1',1'-Biphenyl)-4-yl)-2-phenyldiazene (2n),15 (117.2 mg, 90%), prepared according to the typical procedure (petroleum ether/ethyl acetate = 100:1) as a brown solid. 1H NMR (400 MHz, CDCl₃, δ ppm) 7.99 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 4.0 Hz, 2H), 7.73 (d, J = 4.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.52−7.43 (m, 5H), 7.38−7.35 (m, 1H). 13C{¹H} NMR (100 MHz, CDCl₃, δ ppm) 152.6, 147.4, 146.4, 143.8, 130.4, 129.0, 122.6, 118.2, 146.2, 135.3, 130.1, 127.3, 21.5. 

1H NMR and 13C{¹H} NMR spectra of all products (PDF)

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### Notes

The authors declare no competing financial interest.

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### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04348.
Aromatic Azo Compounds using Dioxygen as an Oxidant. 

Aerobic Oxidative Reaction of Primary Aromatic Amines.

Cyanation of Disulfides by Azobisisobutyronitrile Leading to 238. (d) Ashutosh, P. N. D.; Mehrotra, J. K. Azo Dyes as and Biochemical Actions of Sulphasalazine.

Azo Dyestuffs in Analytical Chemistry. Chemistry, Properties, Applications; García, H. Gold-Catalyzed Synthesis of Aromatic Azo Compounds

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