

# A simple and efficient method for the dehydrogenation of symmetric hydrazo compounds with $\text{NaNO}_2/\text{NaHSO}_4\cdot\text{H}_2\text{O}/\text{SiO}_2^\dagger$

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In this paper, 18 symmetric hydrazo compounds undergo rapid oxidation to corresponding azo compounds using  $\text{NaNO}_2/\text{NaHSO}_4\cdot\text{H}_2\text{O}/\text{SiO}_2$  as a novel oxidising agent under mild conditions for the first time.

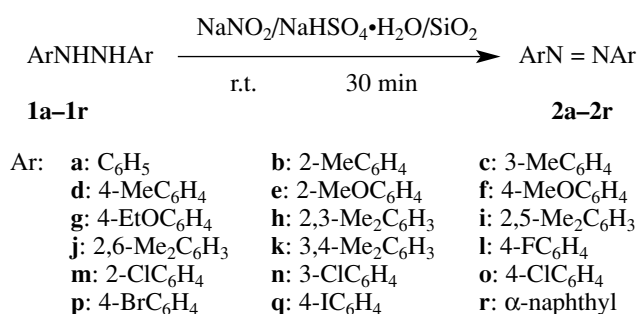
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Azo compounds have caused great interest in organic synthesis. They are widely used as dyes and analytical reagents.<sup>1</sup> Optical-switching and image storage can be made using azobenzene liquid crystal films.<sup>2,3</sup> Recently, many noteworthy studies have shown that some azo compounds possess excellent optical memory and photoelectric properties.<sup>4,5</sup>

The oxidation of  $\text{ArNHNHAr}$  to azo compounds is an important transformation in organic synthesis. We have been paying particular and continuous attention to this field. In the previous work, NBS/pyridine<sup>6</sup> and  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ <sup>7</sup> and galvinoxyl<sup>8</sup> have been used as effective reagents to synthesise azo benzene. These existing methods have their merits, but they also have drawbacks such as tedious operation and using a large amount of volatile and poisonous solvent, which affects human health and the environment.

To continue our research on the synthesis of azo compounds, we decided to develop a new reagent system for the dehydrogenation of  $\text{ArNHNHAr}$ . The combination of sodium nitrite and sodium hydrogen sulfate in the presence of wet  $\text{SiO}_2$  has been used as an effective oxidising agent for the dehydrogenation of 4-substituted-1,2,4-triazole-3,5-diones successfully.<sup>9</sup> The  $[\text{NO}^+\cdot\text{crown}\cdot\text{H}(\text{NO}_3)_2]$  complex is also reported as an effective dehydrogenation agent.<sup>10</sup> We considered that this method might be suitable for the oxidation of  $\text{ArNHNHAr}$ , which is easily subject to rearrangement or semi-rearrangement as well as being oxidised excessively to complex compounds. In our experiments, it was demonstrated that this is an effective reagent. All reactions were performed smoothly at room temperature (Scheme 1) and completed within 30min with excellent yields. The results are summarised in Table 1. Furthermore, this method only requires simple instruments, a cheap oxidant and easy work-up procedures.

In the oxidation study, we selected **1b** as a model. The optimum molar ratio was established by reaction using **1b** (1mmol) and  $\text{SiO}_2$  (0.3g, 60–100mesh) with various molar ratios of  $\text{NaNO}_2:\text{NaHSO}_4\cdot\text{H}_2\text{O}$ . The results are summarised in Table 2. If  $\text{NaNO}_2$  was used for the oxidation alone, the reaction did not occur after stirring for 24h. The oxidation of **1b** was efficiently achieved with this oxidation system. The presence of  $\text{SiO}_2$  is crucial. Although the reaction occurs without  $\text{SiO}_2$ , the reaction period was much longer and good yields



Scheme 1

**Table 1** The oxidation of  $\text{ArNHNHAr}$  using the oxidation system of  $\text{NaNO}_2/\text{NaHSO}_4\cdot\text{H}_2\text{O}/\text{SiO}_2$

Product	Ar	Yield/%	M.p./°C	Lit. M.p./°C <sup>11</sup>
<b>2a</b>	$\text{C}_6\text{H}_5$	91	66–68	68
<b>2b</b>	2- $\text{MeC}_6\text{H}_4$	95	53–55	55
<b>2c</b>	3- $\text{MeC}_6\text{H}_4$	84	52–54	54–55
<b>2d</b>	4- $\text{MeC}_6\text{H}_4$	92	143–144	144–145
<b>2e</b>	2- $\text{MeOC}_6\text{H}_4$	90	143–145	143
<b>2f</b>	4- $\text{MeOC}_6\text{H}_4$	87	160–161	160
<b>2g</b>	4-Et $\text{OC}_6\text{H}_4$	88	155–156	157–159
<b>2h</b>	2,3- $\text{Me}_2\text{C}_6\text{H}_3$	86	109–110	110–111
<b>2i</b>	2,5- $\text{Me}_2\text{C}_6\text{H}_3$	86	115–117	119
<b>2j</b>	2,6- $\text{Me}_2\text{C}_6\text{H}_3$	82	49–50	48
<b>2k</b>	3,4- $\text{Me}_2\text{C}_6\text{H}_3$	87	142–144	140–141
<b>2l</b>	4- $\text{FC}_6\text{H}_4$	93	99–100	99
<b>2m</b>	2- $\text{ClC}_6\text{H}_4$	89	135–136	137
<b>2n</b>	3- $\text{ClC}_6\text{H}_4$	86	99–100	101
<b>2o</b>	4- $\text{ClC}_6\text{H}_4$	92	185–187	185
<b>2p</b>	4- $\text{BrC}_6\text{H}_4$	90	203–205	205
<b>2q</b>	4- $\text{IC}_6\text{H}_4$	90	235–237	235
<b>2r</b>	$\alpha$ -naphthyl	83	187–189	190

were not be obtained. Therefore, we consider that the  $\text{SiO}_2$  acts as a support and provides a heterogeneous effective surface area for the generation of  $\text{HNO}_2$ . It also makes work-up easy. No additional products were identified from this reaction.

Overall, we recommend this simple, clean and economical procedure for the dehydrogenation of aryl  $\text{ArNHNHAr}$  with excellent yields under mild conditions. In all cases, clean transformation could be detected by TLC. We believe this will present a better and more practical alternative to the existing methodologies and thus find useful application in synthesis.

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**Table 2** Oxidation of **1b** (1mmol) in the presence of SiO<sub>2</sub> (0.3g, 60–100mesh) with different molar ratios of NaNO<sub>2</sub><sup>a</sup>:NaHSO<sub>4</sub>•H<sub>2</sub>O<sup>a</sup>

Entry	NaNO <sub>2</sub> :NaHSO <sub>4</sub> •H <sub>2</sub> O	Reaction time	Yield/%
1	1:1	30min	45
2	1.5:1.5	30min	55
3	2:2	30min	65
4	2.5:2.5	30min	80
5	3:3	30min	95
6	3:3	3h	93
7	3:3	2h	55 <sup>b</sup>
8	3:0	24h	little

<sup>a</sup>Crushed to a fine powder. <sup>b</sup>Without SiO<sub>2</sub>.

## Experimental

Melting points were determined on Kofler micro melting point apparatus without correction. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Infrared spectra were recorded on a SP3-300 spectro photometer using KBr pellets. <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> using TMS as internal standard with a JEOL-90Q NMR spectrometer. Mass spectra were recorded on a KRATOS-AEI- MS50 (U.K.) spediometer.

A 50ml, one-necked, round-bottomed flask equipped with magnetic stirrer was charged with 1mmol of ArNHNHAr, 0.207g of NaNO<sub>2</sub> (3mmol), 0.324 g of NaHSO<sub>4</sub>•H<sub>2</sub>O (3 mmol), 0.3 g of SiO<sub>2</sub> (60–100mesh) and 15 ml acetone. The mixture was vigorously stirred at room temperature. After completion of the reaction (TLC), the reaction mixture was filtered. Then cool water (30ml) was poured into the filtrate slowly. After 30 min, the resulting precipitate was filtered, washed with water and dried under vacuum. No further purification was needed.

**Data on products:** **Compound 2a:** Red leaflets; IR (KBr)  $\nu_{\max}$ : 3060, 1580, 1450 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.35–7.80 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>); MS (*m/z*): 182(M<sup>+</sup>); Anal. Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>: C, 79.08; H, 5.53; N, 15.38. Found: C, 79.01; H, 5.58; N, 15.42.

**Compound 2b:** Red leaflets; IR (KBr)  $\nu_{\max}$ : 3030, 2980, 2910, 1580, 1440 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.40 (s, 6H, 2CH<sub>3</sub>), 7.40–7.85 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 210(M<sup>+</sup>); Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 79.95; H, 6.72; N, 13.33. Found: C, 79.91; H, 6.76; N, 13.35.

**Compound 2c:** Orange needles; IR (KBr)  $\nu_{\max}$ : 3035, 2985, 2960, 1590, 1450 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.39 (s, 6H, 2CH<sub>3</sub>), 7.38–7.80 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 79.95; H, 6.72; N, 13.33. Found: C, 79.98; H, 6.70; N, 13.39.

**Compound 2d:** Orange leaflets; IR (KBr)  $\nu_{\max}$ : 3010, 2960, 2910, 1590, 1455 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.42 (s, 6H, 2CH<sub>3</sub>), 7.30–7.85 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 79.95; H, 6.72; N, 13.33. Found: C, 80.01.98; H, 6.69; N, 13.38.

**Compound 2e:** Yellow needles; IR (KBr)  $\nu_{\max}$ : 3040, 2980, 2840, 1590, 1430 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 3.90 (s, 6H, 2CH<sub>3</sub>), 7.00–8.00 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 242(M<sup>+</sup>); Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.39; H, 5.85; N, 11.57.

**Compound 2f:** Red needles; IR (KBr)  $\nu_{\max}$ : 3045, 2985, 2860, 1590, 1445 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 3.93 (s, 6H, 2CH<sub>3</sub>), 7.10–8.10 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.36; H, 5.85; N, 11.58.

**Compound 2g:** Yellow leaflets; IR (KBr)  $\nu_{\max}$ : 3050, 2985, 2920, 1595, 1460 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 1.40 (t, 6H, 2CH<sub>3</sub>), 4.10 (q, 4H, 2CH<sub>2</sub>), 6.90–8.20 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 270(M<sup>+</sup>); Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.09; H, 6.71; N, 10.76. Found: C, 71.03; H, 6.75; N, 10.85.

**Compound 2h:** Yellow needles; IR (KBr)  $\nu_{\max}$ : 3020, 2985, 2960, 1600, 1430 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.30 (s, 6H, 2CH<sub>3</sub>), 2.36 (s, 6H, 2CH<sub>3</sub>), 7.20–8.20 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 238(M<sup>+</sup>);

Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.58; H, 7.64; N, 11.77.

**Compound 2i:** Yellow needles; IR (KBr)  $\nu_{\max}$ : 3020, 2990, 2975, 1590, 1435 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.30 (s, 6H, 2CH<sub>3</sub>), 2.36 (s, 6H, 2CH<sub>3</sub>), 7.20–8.20 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.55; H, 7.66; N, 11.80.

**Compound 2j:** Red leaflets; IR (KBr)  $\nu_{\max}$ : 3030, 2980, 2965, 1580, 1430 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.30 (s, 12H, 4CH<sub>3</sub>), 7.20–8.30 (m, 6H, 2C<sub>6</sub>H<sub>3</sub>); Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.57; H, 7.69; N, 11.77.

**Compound 2k:** Red needles; IR (KBr)  $\nu_{\max}$ : 3020, 2980, 2970, 1560, 1420 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 2.20 (s, 6H, 2CH<sub>3</sub>), 2.30 (s, 6H, 2CH<sub>3</sub>), 7.10–8.20 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.50; H, 7.68; N, 11.81.

**Compound 2l:** Orange leaflets; IR (KBr)  $\nu_{\max}$ : 3040, 1590, 1440 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.45–8.00 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 218(M<sup>+</sup>); Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>F<sub>2</sub>: C, 66.05; H, 3.70; N, 12.84. Found: C, 65.98; H, 3.72; N, 12.90.

**Compound 2m:** Red leaflets; IR (KBr)  $\nu_{\max}$ : 3060, 1590, 1470 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.40–7.90 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 250(M<sup>+</sup>); Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 57.40; H, 3.21; N, 11.16. Found: C, 57.35; H, 3.26; N, 11.21.

**Compound 2n:** Orange needles; IR (KBr)  $\nu_{\max}$ : 3060, 1575, 1460 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.30–7.85 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 57.40; H, 3.21; N, 11.16. Found: C, 57.33; H, 3.29; N, 11.19.

**Compound 2o:** Orange needles; IR (KBr)  $\nu_{\max}$ : 3070, 1590, 1470 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.45–8.10 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 57.40; H, 3.21; N, 11.16. Found: C, 57.38; H, 3.28; N, 11.25.

**Compound 2p:** Orange needles; IR (KBr)  $\nu_{\max}$ : 3080, 1580, 1465 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.40–8.10 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 340(M<sup>+</sup>); Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>Br<sub>2</sub>: C, 42.39; H, 2.37; N, 8.24. Found: C, 42.32; H, 2.42; N, 8.29.

**Compound 2q:** Orange leaflets; IR (KBr)  $\nu_{\max}$ : 3070, 1580, 1460 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.30–7.80 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>); MS (*m/z*): 434(M<sup>+</sup>); Anal. Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>I<sub>2</sub>: C, 33.21; H, 1.86; N, 6.45. Found: C, 33.13; H, 1.90; N, 6.51.

**Compound 2r:** Purple needles; IR (KBr)  $\nu_{\max}$ : 3040, 1600, 1450 (cm<sup>-1</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 7.20–8.10 (m, 12H, 2C<sub>10</sub>H<sub>6</sub>); MS (*m/z*): 280(M<sup>+</sup>); Anal. Calcd. for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.01; H, 5.05; N, 9.97.

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