Reduction of nitrosobenzenes to azoarenes with SmI_2

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A novel method was developed to synthesise azoarenes from nitrosobenzenes under mild conditions. Samarium (II) iodine was used to achieve the N–N coupling. The method also provides evidence for the proposed mechanism involved in the reduction of nitro compounds to the amines with SmI_2.

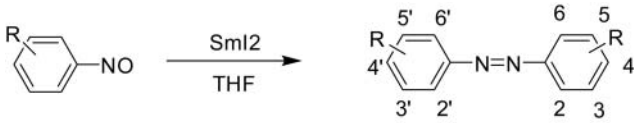
Keywords: nitrosobenzene, azoarenes, SmI_2

The versatile electron donor, samarium (II) iodide (SmI_2), which is easily prepared by a radical reaction,[1] has been extensively used in organic synthesis over the last decade especially as a coupling agent.[2–4] SmI_2 can also be employed as a reducing agent in the conversion of nitro compounds to the corresponding amines. It was previously found that the reduction of nitro groups with SmI_2 may yield intermediates between nitro groups and amines such as hydroxylamines,[5] hydrazines,[6] azoarenes,[7] or azoxyarenes.[8] The stepwise organic transformation of a nitro group to an amine was postulated to proceed by the mechanism shown in Scheme 1 with the formation of a samarium-containing product, typically written as "$I_2SmOSmI_2$".[9,10] To date there is no direct evidence for the proposed mechanism nor intermediates.

Nitrosobenzene, the intermediate shown in Scheme 1, has a highly reactive nitroso group and can be found as a reactive intermediate in biological systems and organic syntheses. To further illustrate the proposed reduction process and mechanism we describe here a novel reduction of nitrosobenzenes to azoarenes by SmI_2. These are proposed to be the reactive precursor of the amines in the conversion of nitro group to amine with SmI_2 (Scheme 2). The nitrosobenzenes were easily prepared from corresponding amines by using molybdenum oxide (MoO_3)[11] The different substituted nitroso compounds were reduced with SmI_2 in THF to afford azoarenes (Table 1).

The amount of SmI_2 used in the reaction should be exact, since a larger excess of SmI_2, for example 4 equiv, will automatically transform the nitrosobenzenes to amines while insufficient SmI_2 will leave the nitrosobenzenes unaltered. The results presented in Table 1, although in moderate yield, indicate that the reduction of nitrosobenzenes with the correct equivalent of SmI_2 could be used as a route to synthesise azoarenes. The nitrosobenzenes with strong electron-donating substituents on the aromatic ring gave relatively higher yields than the electron-withdrawing substituted ones. Specifically a nitrosobenzene with a strong electron-withdrawing trifluoromethyl group was not converted to the corresponding azoarene with SmI_2.

In conclusion, we have utilised SmI_2 as a reducing agent for the conversion of nitrosobenzenes to azoarenes which had not been reported previously. It was found that the electron donating properties of the substituent on the aromatic ring



Scheme 2

contributed significantly to the reductive efficiency of SmI_2. The results shown here also provide support for the proposed mechanism of the reduction of aromatic nitro compounds with SmI_2 through the reductive intermediate azoarenes as previously postulated.

Experimental

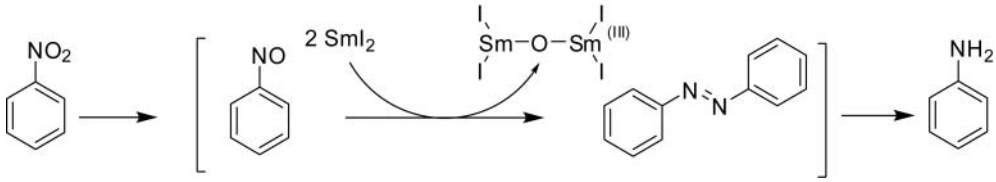
Melting points were determined with a Perkin-Taike X-4 apparatus and then corrected. ^{1}H NMR spectra were recorded using a Varian INOVA 400 spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. TLC was performed on silica gel (GF_{254}). Column chromatography was carried out on silica gel H (10–40 μm). The silica gel GF_{254} and silica gel H were purchased from Qingdao Marine Chemical Factory, China.

Preparation of **b1–9;** *general procedure*

I_2 (4.4 mmol) was added to Sm (4.4 mmol) in anhydrous THF_ (15 mL) and stirred at room temperature under inert atmosphere to prepare SmI_2. When the colour of the reaction mixture turned from yellow to dark blue, the nitrosobenzenes **a1–9** (2.2 mmol) in anhydrous THF was added to it and stirred until the colour changed from dark blue to yellow. The reaction was quenched by addition of dilute HCl (5%) until the yellow solid disappeared. It was evaporated under reduced pressure to remove THF and the remaining mixture was extracted with EtOAc. The organic extract was washed with saturated aqueous $NaHCO_3$, aqueous $Na_2S_2O_4$ (5%), and then brine and dried over anhydrous Na_2SO_4 overnight. Evaporation of the extract under reduced pressure afforded the crude product which was purified by column chromatography to afford the corresponding azobenzenes **b1–9**. The physical and spectra data of the compounds **b1–9** are as follows.

b1: M.p. 67–70°C (lit.[12] 66–68 °C). ^{1}H NMR: δ 7.38 (m, 2H, $H_{4,4'}$), 8.16 (m, 4H, $H_{3,3',5,5'}$), 8.30 (d, 4H, $H_{2,2',6,6'}$, J = 7.2 Hz); ESI: *m/z* = 183.2 ($M+H^+$).

b2: M.p. 142–145 °C (lit.[13] 145–146 °C). ^{1}H NMR: δ 2.43 (s, 6H, CH_3), 7.31 (d, 4H, $H_{3,3',5,5'}$, J = 8.0 Hz), 7.81 (d, 4H, $H_{2,2',6,6'}$, J = 8.0 Hz); ESI: *m/z*=211.3 ($M+H^+$).



Scheme 1

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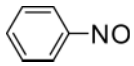
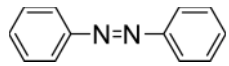
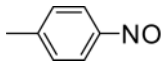
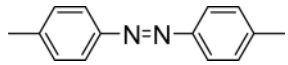
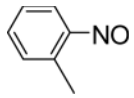
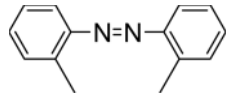
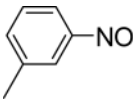
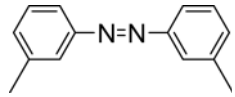
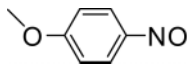
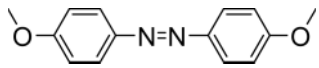
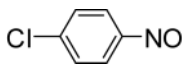
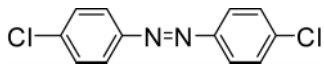
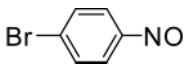
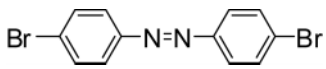
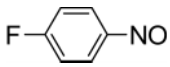
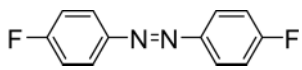
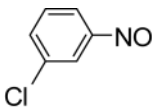
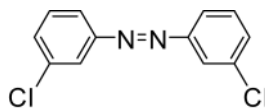
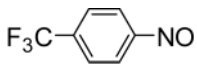
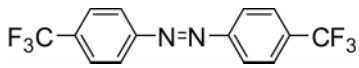
Table 1 Reduction of aromatic nitroso compounds with SmI_2

Entry	Nitrosobenzenes (**a1–10**)	Azoarenes (**b1–10**)	Yield /%[a]
1			70
2			45
3			50
4			55
5			40
6			50
7			40
8			25
9			30
10			0

[a] Isolated yield.

b3: M.p. 54–57 °C (lit.[13] 55 °C). ^{1}H NMR: δ 2.74 (s, 6H, CH_3), 7.25 (m, 2H, $H_{4,4'}$), 7.46 (m, 4H, $H_{3,3',5,5'}$), 7.62 (d, 2H, $H_{6,6'}$, J = 6.8 Hz); ESI: *m/z*=211.3(M+H$^+$).

b4: M.p. 54–57 °C (lit.[13] 54–55 °C). ^{1}H NMR: δ 2.46 (s, 6H, CH_3), 7.29 (d, 2H, $H_{4,4'}$, J = 7.2 Hz), 7.40 (m, 2H, $H_{5,5'}$), 7.72 (m, 4H, $H_{2,2',6,6'}$); ESI: *m/z*=211.3(M+H$^+$).

b5: M.p. 160–164 °C (lit.[14] 160–161 °C). ^{1}H NMR: δ 3.88 (s, 6H, OCH_3), 7.00 (d, 4H, $H_{3,3',5,5'}$, J = 7.2 Hz), 7.88 (d, 4H, $H_{2,2',6,6'}$, J = 7.2 Hz); ESI: *m/z*=243.3(M+H$^+$).

b6: M.p. 184–188 °C (lit.[13] 185–187 °C). ^{1}H NMR: δ 8.18 (d, 4H, $H_{3,3',5,5'}$, J = 7.2 Hz), 8.28 (d, 4H, $H_{2,2',6,6'}$, J = 7.2 Hz); ESI: *m/z*= 252.1(M+H$^+$).

b7: M.p. 201–204 °C (lit.[15] 203–204 °C). ^{1}H NMR: δ 7.67 (d, 4H, $H_{3,3',5,5'}$, J = 7.2 Hz), 7.81 (d, 4H, $H_{2,2',6,6'}$, J = 7.2 Hz); ESI: *m/z*= 341.0(M+H$^+$).

b8: M.p. 101–104 °C (lit.[16] 101 °C). ^{1}H NMR: δ 7.19 (m, 4H, $H_{3,3',5,5'}$), 7.92 (dd, 4H, $H_{2,2',6,6'}$, J_1 = 4.0 Hz, J_2 = 7.2 Hz); ESI: *m/z*= 219.2(M+H$^+$).

b9: M.p. 100–103 °C (lit.[13] 100–101 °C). ^{1}H NMR: δ 7.46 (m, 4H, $H_{4,4',6,6'}$), 7.83 (m, 2H, $H_{5,5'}$), 7.90 (s, 2H, $H_{2,2'}$); ESI: *m/z*= 252.1(M+H$^+$).

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