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# Bismuth(III) Chloride–Sodium Borohydride: a New and Efficient System for the Selective Reduction of Nitroarenes and Azomethines

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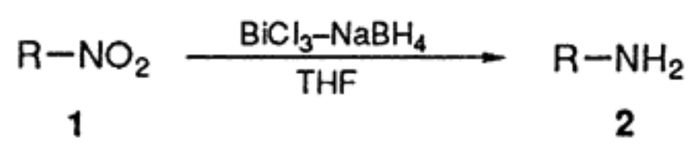
A novel reduction system prepared from bismuth trichloride and sodium borohydride reduces aromatic nitro compounds and azomethines to the corresponding amines in 65–90% yields.

The reduction of nitroarenes to arenamines is an important functional-group transformation and has been effected through a variety of methods.[1] Sodium borohydride is a weak reducing agent amongst the borohydride class; however its reactivity can be increased by adding additional transition metal halides such as $CoCl_2$, $NiCl_2$, $TiCl_4$ and $FeCl_3$ for the reduction of various functional groups including nitro groups.[2] The complex behaviour of sodium borohydride in the absence of metal for the reduction of nitro groups has also been reported, wherein either there is reduction of the aromatic ring[3] or denitration occurs.[4] Recently Han and Jang reported a montmorillonite-catalysed reduction procedure for nitroarenes,[5] but high cost of reagent, poor yield and long reaction times are the main drawbacks of this method. We herein report bismuth(III) chloride as being a new and efficient catalyst for the selective reduction of nitro compounds and conjugated azomethines when employed with sodium borohydride in tetrahydrofuran. The reaction proceeds smoothly under very mild conditions to afford the corresponding primary and secondary amines in high yields.

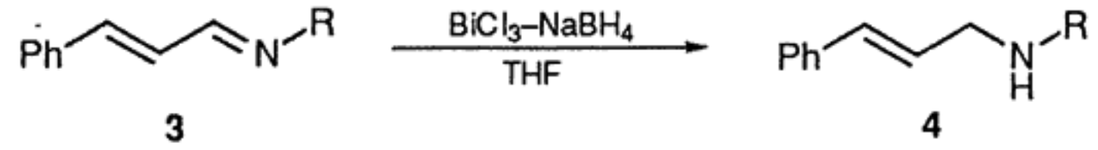



**1** **2**

**Scheme 1**

Typically, sodium borohydride was added to a mixture of bismuth trichloride and *p*-chloronitrobenzene in tetrahydrofuran. The reaction mixture was stirred for 2 h at 60 °C under an inert atmosphere and after usual work-up the product *p*-chloroaniline was obtained in 90% yield. This reduction procedure is fairly general and functional groups such as methyl, hydroxy, amino, methoxy and chloro in the benzene ring do not have any marked effect on the rate of the reaction, *i.e.* neither accelerating nor retarding the reaction. Moreover, as is seen, these functional groups survive during the reduction, making the present process fairly general and selective. In contrast the reduction of dinitroarenes proceeds slowly to give mononitro compounds selectively at 60 °C. Thus *m*-dinitrobenzene (**2j**) and 2,4-dinitrotoluene (**2k**) are selectively reduced to nitroanilines in only 40 and 35% yields respectively. Attempted reduction of benzonitrile, benzamide or nitrobenzene under the same conditions did not give the corresponding reduced products, starting material instead being recovered.

Nitro-aliphatic compounds which have been traditionally reduced by high-pressure hydrogenation,[6] lithium aluminium hydride[7] or aluminium amalgam,[8] when treated with the bismuth trichloride–sodium borohydride reagent system in tetrahydrofuran at 60 °C, give the corresponding amines **2l–n** in 60–65% yields. This reagent system is used successfully for the selective reduction of the carbon–nitrogen double bond of conjugated imines, keeping the carbon–carbon double bond intact, to the corresponding secondary amines (**4a–c**) in excellent yields (for comparison see a recent report;[9] in contrast the present method is convenient and less expensive).




**3** **4**

**Scheme 2**

In conclusion, the present new method employing bismuth trichloride as a promoter of $NaBH_4$-catalysed reduction, is more efficient, highly selective, involves simple work-up and affords products in high yields. Moreover, bismuth trichloride is inexpensive and easy to handle. As far as mechanism is concerned it is difficult to postulate any at this stage, but certainly neither acidic nor basic conditions prevailed during the reaction, as groups sensitive to these conditions remained intact.

## Experimental

Mps were determined using a Büchi apparatus and are uncorrected. IR spectra were recorded for KBr discs on a Perkin-Elmer 237B spectrophotometer. Microanalyses were performed on a Perkin-Elmer 240C analyser. $^1H$ NMR spectra were recorded on 60 MHz spectrometers and chemical shift values are recorded in $\delta$ units (ppm) relative to $Me_4Si$ as internal standard. The imines described in this report were prepared from freshly distilled primary amines and cinnamaldehyde through known methods and their mps agreed with those recorded in the literature. Solvents were dried according to literature procedures.

*Reaction of Aromatic and Aliphatic Nitro Compounds with Bismuth Trichloride and Sodium Borohydride.—Typical Procedure.* Bismuth trichloride (0.630 g, 2 mmol) was suspended in tetrahydrofuran (THF) (25 ml) and sodium borohydride (0.076 g, 2 mmol) was added with stirring at room temperature. To this solution was added *p*-chloronitrobenzene (0.314 g, 2 mmol) and the remaining sodium borohydride (0.076 g, 2 mmol) was added in portions gradually at 60 °C; the reaction mixture was then stirred for 1–2 h at 60 °C (see Table 1). After cooling, the solvent was removed under reduced pressure and water (30 ml) was added. The residue was extracted with diethyl ether (3 × 30 ml), dried over anhydrous sodium sulfate and distilled. The *p*-chloroaniline thus obtained was purified by column chromatography using ethyl acetate–light petroleum (bp 60–80 °C) (1:6) as the eluent, mp 69–70 °C, yield 90%. Other amines were prepared similarly and their characteristics are recorded in Table 1. Mixed mps with authentic samples were recorded to establish the identities of all the amines formed. The same products could also be obtained, but less effectively, under similar conditions using ethanol instead of THF as a solvent.

*Reaction of Azomethines with Bismuth Trichloride and Sodium Borohydride.—Typical Procedure.* Bismuth trichloride (0.630 g, 2 mmol) was suspended in THF (20 ml) and sodium borohydride (0.076 g, 2 mmol) was added with stirring at ambient temperature. To this solution was added *N*-cinnamylideneaniline (0.207 g, 1 mmol) in THF (5 ml) followed gradually at room temperature by sodium borohydride (0.076 g, 2 mmol) in portions. The reaction mixture was then stirred at room temperature for 2 h. After cooling, water (25 ml) was added and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (3 × 20 ml), dried over anhydrous sodium sulfate and distilled. The reduced imine **4a** was obtained in 85% yield, mp 20 °C (lit.,[10] 20 °C). Similar treatment of other conjugated imines (**3b,c**) gave the corresponding reduced imines **4b,c** in 80–85% yields (Table 1). **4b**:

**Table 1** Products from the reduction of nitro compounds **1** and azomethines **3** with bismuth trichloride–sodium borohydride

| Product | R[a] | Mp (*T*/°C) This work | Mp (*T*/°C) Lit.[b] | Isolated yield (%) | Overall conversion (%) | Reaction time (*t*/h) |
|---|---|---|---|---|---|---|
| **2a** | *p*-$ClC_6H_4$ | 68–69 | 68–71 | 90 | 96 | 2 |
| **2b** | *p*-$MeC_6H_4$ | 45–46 | 45–47 | 85 | 90 | 1 |
| **2c** | *o*-$MeC_6H_4$ | oil | oil | 80 | 85 | 1.5 |
| **2d** | *m*-$H_2NC_6H_4$ | 65–66 | 64–66 | 75 | 80 | 2 |
| **2e** | *p*-$HOC_6H_4$ | 187–188 | 188–190 | 78 | 85 | 3 |
| **2f** | *p*-$HO_2CC_6H_4$ | 188–189 | 188–189 | 85 | 90 | 1 |
| **2g** | *p*-$MeOC_6H_4$ | 57–58 | 57–60 | 85 | 92 | 1 |
| **2h** | *p*-$EtO_2CC_6H_4$ | 88–90 | 88–90 | 78 | 85 | 1.5 |
| **2i** | *p*-$NCC_6H_4$ | 82–83 | 83–85 | 70 | 80 | 1.5 |
| **2j** | *m*-$O_2NC_6H_4$ | 112–113 | 112–114 | 40 | 45 | 18 |
| **2k** | 3-$O_2N$-4-$MeC_6H_3$ | 78–79 | 77–79 | 35 | 40 | 20 |
| **2l** | $C_8H_{17}$ | oil | oil | 65 | 72 | 6 |
| **2m** | $MeCH(OH)[CH_2]_2CMe_2$ | oil | oil[2c] | 60 | 65 | 8 |
| **2n** | $HO_2C[CH_2]_2CMe_2$ | oil | oil[2c] | 65 | 70 | 8 |
| **4a** | Ph | 19–20 | 20 | 85 | 90 | 2 |
| **4b** | Me | oil | — | 80 | 85 | 2.5 |
| **4c** | Et | oil | — | 83 | 86 | 3 |

[a]Products were identified by comparison of IR and NMR spectra with those of authentic samples. [b]For literature mps see: *Catalogue Handbook of Fine Chemicals*, Aldrich Chemical Co., Gillingham, 1988–1989 edition.

oil, *m*/*z* 147 ($M^+$); $\nu_{max}$/$cm^{-1}$ (KBr) 965 (CH=CH *trans*) and 3375 (NH); $\delta$ (60 MHz, $CDCl_3$) 2.25 (3 H, s, $CH_3$), 4.25 (2 H, s, $CH_2$), 6.50 (2 H, d, olefinic), 7.25 (6 H, m). **4c**: oil, *m*/*z* 161 ($M^+$); $\nu_{max}$/$cm^{-1}$ (KBr) 960 (CH=CH, *trans*) and 3370 (NH); $\delta$ (60 MHz, $CDCl_3$) $\delta$ 1.20 (3 H, t, $CH_3$), 4.30 (4 H, m), 6.55 (2 H, d, olefinic), 7.35 (6 H, m).

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