## Unprecedented Direct Conversion of N-N and N=N bonds to *N*-(*tert*-Butyloxy)-carbamates<sup>1</sup>

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**Abstract:** For the first time a one step direct conversion of aromatic hydrazines and azo compounds to *N*-(*tert*-butoxycarbonyl) amines is achieved via reductive cleavage of N-N and N=N bonds using the inexpensive and safe hydride source polymethylhydrosiloxane (PMHS) and di-*tert*-butyl dicarbonate [(Boc)<sub>2</sub>O] in the presence of a catalytic amount of 10% Pd-C.

Key words: polymethylhydrosiloxane, hydrazines, azo compounds, *tert*-butyl carbamates, one-pot reaction

Amines, both in protected as well as unprotected forms are useful intermediates in basic as well as applied research.<sup>2</sup> This class has gained more prominence since the advent of the combinatorial chemistry, as amines undergo diverse reactions with ease.<sup>3</sup>The most common approaches to amines involve reduction of nitro compounds, imines, azides and oximes besides hydrazines and azo compounds.<sup>4</sup> There are few general methods to reduce the nitrogen-nitrogen bond in hydrazines and the conditions required to cleave this bond depend markedly on the substituents attached to it.<sup>5</sup> However, substituted hydrazines can be reduced to the corresponding amines by catalytic hydrogenation<sup>6</sup> or using metal in a protic solvent.<sup>7,8</sup> In the first case usually it is necessary to work under pressure and acidic medium and in the second case, liquid ammonia is the most common solvent. The most important methods to reduce azo compounds lead to the corresponding hydrazo derivatives.9 They include diimide, complex metal hydrides or cobalt boride in the presence of hydrazine,<sup>10</sup> as well as metal mediated procedures.<sup>11,12</sup>In addition to these NiCl<sub>2</sub>·H<sub>2</sub>O-Li-DTBB (cat.) combination has been used for the reduction of hydrazines and azo compounds to amines.<sup>13</sup> Surprisingly, no report is documented in the literature for direct conversion of hydrazines and azo compounds to Boc-protected amines, which may be desirable since, amines are often protected as Boc derivatives in the course of synthesis or in the case of isolation. Therefore one-pot conversion of hydrazines and azo compounds to N-(tert-butoxy carbonyl) amines is certainly a useful transformation in organic synthesis. Our efforts<sup>14</sup> in this direction have resulted in identifying polymethylhydrosiloxane under Pd-C catalysis as an efficient reagent (Scheme). PMHS is already gaining importance especialScheme

ly as a safe, economic reagent as exemplified in a recent review.<sup>15</sup>

In an initial study, phenylydrazine (entry 1) was treated with polymethylhydrosiloxane, Pd-C, di-*tert*-butyl dicarbonate and ethanol as a solvent, to isolate *tert*-butoxycarbonyl aniline in 85% yield. In the second instance azobenzene was treated under identical conditions to yield Boc-protected aniline in almost similar yield (entry 2). The halo aromatics (entries 5 and 6) were also stable under these conditions. Also carboxylic acid and ester substrates (entries 11 to 14) underwent smooth chemoselective reductive cleavage of N-N and N=N bonds to furnish the corresponding Boc-protected amines in good yields. Other substrates (entries 3, 4 and 7 to 10) were equally well behaved under the reaction conditions.

In conclusion, we have developed a convenient method for direct conversion of hydrazines and azo compounds to more useful Boc-protected amines. We believe that the reagent system described here may have tremendous potential use in organic synthesis due to its high chemoselectivity, efficiency, economy, simplicity and safety.

## Typical experimental procedure

To a stirred solution of substrate (1 mmol) in EtOH (10 mL) was added PMHS (0.180g, 3 mmols) and 10% Pd-C (~15 mg). Di-*tert*butyl dicarbonate (0.240g, 1.1 mmol) was added<sup>16</sup> and the mixture stirred for the given time (see Table) at room temperature. After the completion of the reaction, the reaction mixture was filtered and the filtrate was evaporated in vacuo. The residue was purified by chromatography on a silica gel to give the corresponding NH-Boc products in excellent yields (see Table).

 $<sup>\</sup>begin{array}{ccc} R-NH-NH_{2} & \underline{PMHS/Pd-C} \\ \text{or} & & & \\ R-N=N-R & (Boc)_{2}O, \text{ ethanol, r.t.} \end{array} \xrightarrow{} & R-NH-Boc \\ R=aryl & & & \\ R=aryl & & \\ H \\ & & & \\ PMHS \end{array}$ 

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 Table
 Conversion of Hydrazines and Azo Compounds to Bocaimes

| Entry | Substrate   | Time<br>(h) | Yield<br>(%) <sup>a</sup> | Product   |
|-------|---|-------------|---------------------------|-----------|
| 1     | NH-NH <sub>2</sub>  | 3           | 85                        |           |
| 2     |   | 5           | 80                        |           |
| 3     | H <sub>3</sub> C-   | 3           | 78                        |           |
| 4     | H <sub>3</sub> C-CH <sub>3</sub>  | 5           | 80                        | CH3       |
| 5     |   | 4           | 80                        | NHBoc     |
| 6     | $\begin{array}{c} X - \swarrow - N = N - \swarrow - X \\ CI \\ X = F, CI \end{array}$ | 6           | 90                        | T CI<br>X |
| 7     | HO-   | 3.5         | 81                        |           |
| 8     | но-   | 5           | 80                        | ОН        |
| 9     | EtO-  | 3           | 78                        |           |
| 10    | EtO-  | 5           | 76                        | OEt       |
| 11    | NH-NH <sub>2</sub>  | 4           | 78                        |           |
| 12    | Y=COOH  | 6           | 76                        | ·         |
| 13    | Z-  | 3           | 80                        | NHBoc     |
| 14    | $Z \rightarrow N = N \rightarrow Z$<br>Z=COOMe  | 5           | 79                        | Ý<br>z    |

<sup>a</sup> All yields refer to pure isolated products, characterised by <sup>1</sup>H NMR, mass and IR.

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