



## DEOXYGENATION OF NITRONES USING $\text{NaBH}_4$ -SILICA GEL SYSTEM

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### ABSTRACT

Reaction of nitrones with  $\text{NaBH}_4$ -silica gel system at ambient temperature yielded the corresponding imines in good yields.

**Key words:** Nitrones, Deoxygenation, Imines, Sodium borohydride, Silica gel.

### INTRODUCTION

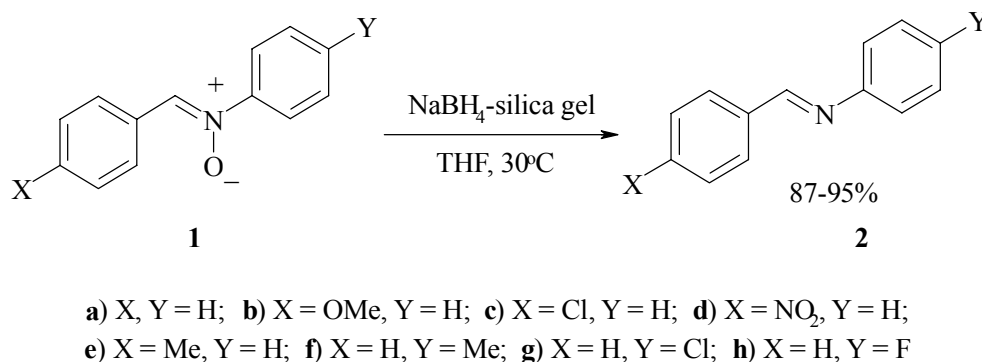
Aldimines are an important class of organic compounds<sup>1</sup>. Aldimines have been generally used as substrates in the formation of large number of industrial compounds via cycloaddition, ring closure, replacement reaction, etc<sup>2,3</sup>. In addition, the aldimines of heterocyclic carbaldehyde, which are widely used in the production of pharmaceuticals have taken an important place among the compounds of biological interest and the benzyldene derivatives display a large variety of activities<sup>4,5</sup>. Imines and their complexes have a variety of applications in biological, clinical and analytical fields<sup>6</sup>. Perusal of the literature reveals that the preferred route for the synthesis of aldimines involves the condensation of aldehydes with ammonia or amines. However, this method is sensitive to the pH of the reaction medium and substituent effects. For example, it is difficult to obtain aldimines from the condensation of 4-methoxybenzaldehyde with amines or 4-nitroanilines with aldehydes.

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Deoxygenation of nitrones is a valuable transformation in organic synthesis<sup>7-9</sup>. Several deoxygenating agents including sodium hydrogen telluride<sup>10</sup>, phosphorous<sup>11</sup>, aluminium-nickel alloy<sup>12</sup>, titanium (0) reagents<sup>13</sup>, tin derivatives<sup>14</sup>, silanes<sup>15</sup>, alkali metal hydrides<sup>7</sup>, tetrathiomolybdate<sup>16</sup>, aluminium iodide<sup>17</sup> and indium (III) chloride<sup>18</sup> may be used for this purpose. However, most of these methods are deficient in some respects, such as low yields, difficult accessibility, drastic reaction conditions which effect substituents<sup>19</sup>, uncontrolled reduction of nitrones 1<sup>11</sup> to amines rather than to the expected imines. Hence, any method that does not depend upon these factors is worthy of examination.

The sodium borohydride is one of the most widely used reducing agents in organic synthesis<sup>20,21</sup>. Titanium tetrachloride-NaBH<sub>4</sub> complex used by Kano<sup>22</sup> was found to reduce the aromatic ring in the substrate. Sodium borohydride along with other additives such as NiCl<sub>2</sub>.6H<sub>2</sub>O<sup>23</sup>, charcoal<sup>24</sup>, SbF<sub>3</sub><sup>25</sup>, ZrCl<sub>4</sub><sup>26</sup>, Pd<sup>27</sup>, thiols<sup>28</sup> and Pd-C<sup>29</sup> is used as reducing agents for various organic compounds. This reagent has also been used for the reduction of nitrones<sup>30-32</sup>. As a continuation of our work on the chemistry of nitrones<sup>33-39</sup> and uses of sodium borohydride reagent for organic reactions<sup>21</sup>, it was proposed to synthesize the aldimines through the deoxygenation of  $\alpha$ ,N-diaryl nitrones. Accordingly, we report herein, the utility of NaBH<sub>4</sub>-silica gel as an efficient deoxygenating agent for nitrones to give the corresponding aromatic derivatives (Scheme). The reaction proceeds efficiently at ambient temperature and in high yields.



### Scheme: Synthesis of aldimines

## EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer C577 spectrometer. <sup>1</sup>H NMR were recorded in CDCl<sub>3</sub> using a 90 MHz Perkin-Elmer spectrometer with TMS as the internal standard. The diaryl nitrones used for this study were prepared by condensing the

corresponding substituted benzaldehydes with various phenyl hydroxylamines.<sup>40</sup> Sodium borohydride and silica gel (TLC grade) were purchased from SD-fine and used as such without any treatment.

### Typical procedure

To a solution of benzaldehyde  $\alpha$ ,N-diphenyl nitroine **1a** (0.1 g, 0.5 mmol) in THF (15 mL) was added silica gel (0.1 g) and the mixture was stirred for five minutes and then NaBH<sub>4</sub> (0.038 g, 1 mmol) was added in small portion for about 3 minutes. The reaction mixture was stirred at ambient temperature for 1 h (monitored by TLC). After completion of the reaction, 5 mL of water was added, the reaction mixture was extracted with ether (3 x 10 mL), the extract dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed on a rotary evaporator to give the crude product, which was purified by column chromatography (petroleum ether/benzene, 4 : 1) to afford the imine **2a** in 93% yield.

**Table 1: Deoxygenation of nitrones to aldimines**

Compound	Yield (%)	m.pt (Lit/(°C))	<sup>1</sup> H NMR (CDCl <sub>3</sub> , $\delta$ )		
			CH=	aromatic	others
<b>2a</b>	93	53-54 <sup>41</sup>	8.40	7.0-8.1	--
<b>2b</b>	87	62-64 <sup>43</sup>	8.40	7.0-8.0	3.90 (OMe)
<b>2c</b>	90	65-66 <sup>42</sup>	8.35	7.0-8.0	--
<b>2d</b>	86	93-95 <sup>44</sup>	8.60	7.3-8.5	--
<b>2e</b>	87	Oil	8.30	7.0-7.9	2.20 (Me)
<b>2f</b>	95	Oil	8.40	7.1-8.1	2.30 (Me)
<b>2g</b>	87	62-64 <sup>45</sup>	8.40	7.0-8.0	--
<b>2h</b>	93	57-58 <sup>45</sup>	8.40	7.0-8.0	--

## RESULTS AND DISCUSSION

In our procedure,  $\alpha$ ,N-diaryl nitroine in THF, sodium borohydride and silica gel were mixed in a conical flask dried in a hot air oven and stirred at room temperature (Scheme). The reaction was followed by TLC. In order to generalize this method, this procedure was used with a number of differently substituted  $\alpha$ ,N-diaryl nitrones (Scheme). All nitrones were reacted and the corresponding aldimines were isolated in high yields without the formation of any other products. We carried out the deoxygenation by reducing

the amount of silica gel and found that the reaction was comparatively less effective and took more than 4 h to give 60% yields of **2a**. A further increase in the reaction time had no significant effect on the yield. All the compounds obtained were characterized and identified through their  $^1\text{H}$  NMR spectral data (Table 1). By this method higher yield was obtained when compared with the other methods such as deoxygenation using triphenyl phosphine.

## CONCLUSION

In summary, this new deoxygenative method using  $\text{NaBH}_4$ /silica gel offers a useful alternative to the other methods available for the reduction of nitrones. Its main advantages are the avoidance of strong acid media and harsh reagents and no side product formation.

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