Lithium $B$-azido-$B$-hydrido-9-BBN as an Efficient Azide Donor Rather Than a Reductant

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Numerous metal hydride reagents have been developed and successfully employed for the chemo-, regio-, and stereoselective reductions of various organic functional groups. One of them is sodium $B$-cyano-$B$-hydrido-9-BBN (1), which has the ability to displace active halides or sulfonates with hydride.1 Herein, we describe the azido group transferring ability of lithium $B$-azido-$B$-hydrido-9-BBN (2), a structurally similar reagent to 1.

Reaction of 9-BBN with two equivalents of hydrogen azide at rt and removal of excess hydrogen azide in vacuo afforded $B$-azido-9-BBN (3) in quantitative yield. The IR spectrum of the oily 3 showed the disappearance of the characteristic $B$-$\cdot$H-$\cdot$B absorption band of 9-BBN dimer at 1,560 cm$^{-1}$ and the appearance of an intense azide stretching band at 2,150 cm$^{-1}$. Treatment of 3 with tert-butyllithium at $-78^\circ$C and warming up the mixture to rt provided a clear yellowish solution of lithium $B$-azido-$B$-hydrido-9-BBN (2)$^+$ with the liberation of isobutene gas. When this solution was treated with benzoic acid, hydrogen gas evolved with the precipitation of lithium azide, and from the remaining solution $B$-benzoyloxy-9-BBN was isolated. This fact remains howevert 2 has somewhat reactive hydride.

![Structure](image)

Reaction of 2 with acyl chloride, however, did not afford any reduction products. The only product obtained in a more than 82% yield was acyl azide.4 This surprising azide transferring ability was further demonstrated when various unsymmetrical epoxides were treated with 2. As summarized in Table 1, these epoxide opening reactions provided only $B$-azidoalcohols in excellent yields. No simple alcohols were detected. These results clearly indicate that in 2 the migratory aptitude of the azide is quite superior to that of the hydride probably due to the better leaving group ability and nucleophilicity of the azide group over the hydride.

The regioselectivity of these epoxide opening reactions appeared to be governed mainly by the steric factor, and thus the azide group attacked the less hindered carbon of the unsymmetrical epoxides. In the case of styrene oxide, however, the electronic factor dominated over the steric one producing 2-azido-2-phenylethanol as a major product in a ratio of 78:22.

In conclusion, it is discovered from the above experiments that lithium $B$-azido-$B$-hydrido-9-BBN (2) has an ability to donate azide group rather than hydride even though 2 is structurally similar to sodium $B$-cyano-$B$-hydrido-9-BBN (1), and may thus be employed as one of the azide transferring reagents.5 It may also be mentioned that the epoxide-opening reaction with this reagent is somewhat different from the reported lithium azide method6 which utilizes high boiling hexamethylphosphoramide as a solvent at the elevated temperature of 60°C for 18 hrs.

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**References**

3. When 9-BBN and lithium azide were mixed in THF, a clear solution also resulted within 20 min. Treatment of this solution with styrene oxide, however, gave a mixture of azidoalcohols and reduced alcohols. In pentane, only suspension was obtained; which reduced styrene oxide to simple alcohols.
4. Typical experimental procedure: After the mixture of 0.5 M 9-BBN in THF (10 mL, 5 mmol) and 1.0 M HN$_3$ in chloroform (10 mL, 10 mmol) was stirred at rt for 6 hrs, solvents and excess HN$_3$ were evaporated in vacuo. The oily residue was dissolved in THF (5 mL) at $-78^\circ$C and 1.7 M tert-butyllithium in pentane (3.0 mL, 5.1 mmol) was added dropwise and the resulting solution was stirred for 3 hrs until no more gas was liberated. To this solution of 2 was added acyl chloride (4 mmol) in chloroform (10 mL) and the solution was stirred at rt for 2 hrs. Usual workup and silica gel column chro-

**Table 1. Ring-Opening Reactions of Epoxides with Lithium $B$-Azido-$B$-hydrido-9-BBN**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Description</th>
<th>GC ratio ( (a:b) )</th>
<th>Isolated Yield, % ( \text{(Major Isomer)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R=CH$_3$CH$_3$</td>
<td>90:10</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>R=$n$-Hexyl</td>
<td>92:08</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>R=$N$-CH$_3$-Phthalimide</td>
<td>96:04</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>R=CH$_3$OPh</td>
<td>93:07</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>R=(CH$_3$)$_2$CH=CH$_2$</td>
<td>85:15</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>R=Ph</td>
<td>22:78</td>
<td>70</td>
</tr>
</tbody>
</table>
Reduction of N-Arylmaleimides with Sodium Dithionite: Observation of Dimeric Products

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Sodium dithionite (Na₂S₂O₄) is a readily available and versatile reducing agent. However, due to the lack of solubility of the reagent in organic solvent, its use has been somewhat limited. Polar solvents such as H₂O/dioxane and H₂O/DMF mixture or phase-transfer catalysts (PTC) have been used to overcome this problem.²⁻⁵ Though there is good possibility of the involvement of one-electron transfer steps in the reduction reactions with sodium dithionite, no unequivocal evidences for the mechanism such as dimerized products from radical intermediates have been observed. We have been interested in the utilization of sodium dithionite for reduction of various organic substrates by electron transfer steps and used viologen (N,N'-dialkyl-4,4'-bipyridinium salt) as an electron-transfer catalyst for the dithionite reduction of α-halogeno ketones, α-nitrosulfones, gem-bromonitro compounds, α-nitro ketones, nitroaranes, tertiary nitroalkanes, azobenzenes, and azaoxybenzenes in CH₂Cl₂/H₂O two-phase system or CH₂CN/H₂O medium.

Several investigators have reported sodium dithionite reductions of vinyl compounds conjugated with carbonyl group.³⁻⁵ It was shown that α,β-unsaturated ketone, R(−)-carvone, is reduced to the corresponding cyclohexanol derivatives in water in the presence of β-cyclodextrin.⁶

The difference in the reaction products depending on the nature of vinyl compounds conjugated with carbonyl group and the difference in the reactivity of sodium dithionite depending on the reaction medium may make it worthwhile to investigate the reaction of other α,β-unsaturated carbonyl compounds with dithionite in different solvents. Here, we report the results on the reaction of N-arylmaleimides 1 with dithionite in CH₂CN/H₂O medium: we obtained the mixture of N-arylsuccinimides 2 and dimeric products 3 (Scheme 1), which could be taken as an evidence for the involvement of one-electron transfer step in the reduction.

N-Arylmaleimides except the commercially available N-phenylmaleimide were prepared starting from maleic anhydride and the aniline derivatives via the corresponding maleinic acid.⁷ N-Arylmaleimide (1 mmol) was reacted with sodium dithionite (0.8 g, 4.5 mmol) in 20 mL CH₂CN-12 mL H₂O containing K₂CO₃ (0.69 g, 5 mmol) at 35 °C.

![Scheme 1](image-url)

**Scheme 1.**