

ONE-POT CONVERSION OF CARBOXYLIC ACIDS TO ALDEHYDES THROUGH  
 TREATMENT OF ACYLOXY-9-BORABICYCLO[3.3.1]NONANES WITH LITHIUM  
 9-BORATABICYCLO[3.3.1]NONANE<sup>1</sup>

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*Summary:* Carboxylic acids are readily reduced to the corresponding aldehydes in high yields by treatment of acyloxy-9-borabicyclo[3.3.1]nonanes with lithium 9-boratabicyclo[3.3.1]nonane (Li 9-BBNH) at room temperature.

Thexylchloroborane-methyl sulfide<sup>2</sup> and thexylbromoborane-methyl sulfide<sup>3</sup> have appeared to be promising reducing agents, especially for the direct transformation of carboxylic acids into the corresponding aldehydes. Furthermore, the convenient and practical methods for isolation of aldehyde products have been established<sup>2c</sup>. Because the reducing characteristics of these two reagents have been fully characterized, the reagents should find useful applications in organic synthesis.

Such efforts solved an important long-standing problem in synthetic area<sup>4</sup>. In order to extend the methodology for such direct transformation, we have centered our efforts to utilize the commercially available 9-borabicyclo[3.3.1]nonane (9-BBN)<sup>5</sup>. We now describe this facile reduction of such carboxylic acids to the corresponding aldehydes by using 9-BBN.

The acyloxy-9-BBN (1), formed from the reaction of carboxylic acids and 9-BBN after immediate evolution of hydrogen (eq.1), seems to possess an adequate structural feature for its acyloxy group being converted to the aldehyde stage readily. We have discovered that the acyloxy moiety of acyloxy-9-BBN is readily reduced by lithium 9-boratabicyclo[3.3.1]nonane (Li 9-BBNH)<sup>6</sup> and the reduction stops at the aldehyde stage (eq.2). Li 9-BBNH is readily prepared by hydridating 9-BBN with lithium hydride<sup>7</sup> or tert-butyllithium<sup>8</sup> in tetrahydrofuran.

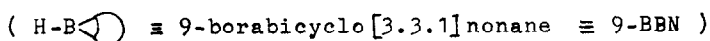
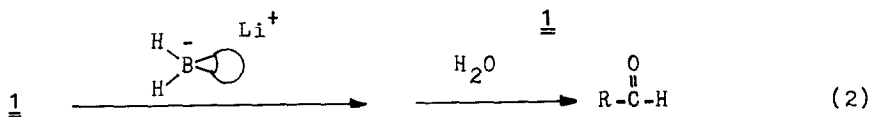
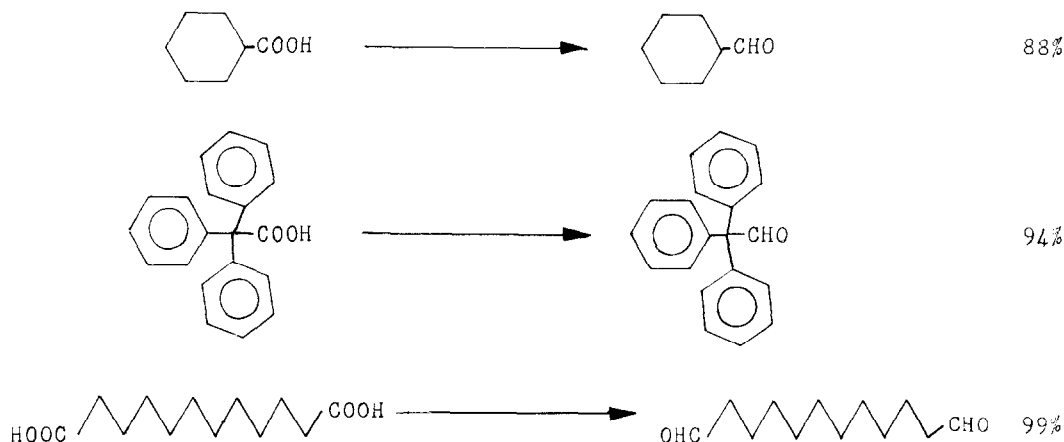


Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids through Treatment of Acyloxy-9-borabicyclo [3.3.1] nonanes with Lithium 9-Boratabicyclo [3.3.1] nonane (Li 9-BBNH) in Tetrahydrofuran at Room Temperature<sup>a</sup>

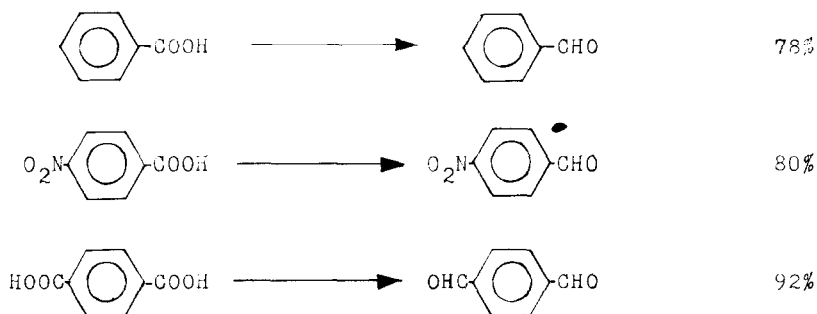
Acid	Yield of aldehyde by analysis with 2,4-dinitrophenylhydrazine (%)
Butyric	90
Hexanoic	92(80) <sup>b</sup>
Decanoic	92
Stearic	99(92) <sup>c</sup>
Isobutyric	94
Isopentanoic	89
Pivalic	85 <sup>d</sup>
Cyclopropanecarboxylic	85
Cyclohexanecarboxylic	88
Diphenylacetic	96
Triphenylacetic	94
6-Bromohexanoic	87
1,10-Decanedicarboxylic	99(92) <sup>c</sup>
Benzoic	78
$\alpha$ -Naphthoic	80
<u>p</u> -Methoxybenzoic	79
<u>p</u> -Chlorobenzoic	76
<u>p</u> -Aminobenzoic	79
<u>p</u> -Nitrobenzoic	80
Terephthalic	92

<sup>a</sup>) Reacted with 50% excess Li 9-BBNH (1.05 equiv for monocarboxylic and 2.1 equiv for dicarboxylic acid) for 1 h with aliphatic and for 6 h with aromatic carboxylic acids, both at room temperature. <sup>b</sup>) An isolated yield on distillation of the generated product after hydrolysis. <sup>c</sup>) Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde<sup>2-b,c</sup>. <sup>d</sup>) Reacted for 6 h.

Aliphatic carboxylic acids, such as butyric, hexanoic, decanoic, stearic, isobutyric, isopentanoic, and pivalic acids, are reduced to aldehydes by this system in about 1 h at room temperature in yields of 85-99%. The yields of aldehydes from alicyclic carboxylic acids, such as cyclopropanecarboxylic and cyclohexanecarboxylic acids, are 85% and 88%, respectively. Derivatives, such as diphenylacetic and triphenylacetic acids, also undergo the reaction well in yields of around 95%. 6-Bromohexanoic acid provides 6-bromohexanal in a yield of 87%. Dicarboxylic acid, such as 1,10-decanedicarboxylic acid, is converted to the corresponding dialdehyde in an essentially quantitative yield.



The reduction of aromatic carboxylic acids by this system is slow, requiring 6 h at room temperature. The yields are somewhat lower than those in the aliphatic series, but still high. Thus, the yields from the unsubstituted aromatic acids, such as benzoic and  $\alpha$ -naphthoic acids, are around 80%. The *para*-substituted aromatic acids work equally well in yields of around 80%. Finally, aromatic dicarboxylic acid, such as terephthalic acid, is readily reduced to the corresponding dialdehyde in a high yield (92%).



The aldehyde products of relatively low boiling point (less than 200°C) are readily isolable on distillation after hydrolysis (*i.e.*, 80% for hexanal), whereas in the case of products of higher boiling point the sodium bisulfite procedure<sup>2-b,c</sup> appeared to be broadly applicable (*i.e.*, 92% for stearaldehyde and 92% for 1,10-decanal).

The following procedure for the reduction of hexanoic acid is representative. An oven-dried, 200-mL flask, fitted with a side arm and a bent adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 6.47g (53 mmol) of 9-borabicyclo[3.3.1]nonane (9-BBN) and 6.16g (53 mmol) of hexanoic acid. To this mixture was added 10 mL of THF and the slurry was stirred at room temperature until hydrogen evolution ceased. After completing the hydrogen evolution, 111 mL of 0.5 M solution of Li 9-BBNH (55.6 mmol, 5% excess) in THF was injected via a double-ended needle and the reaction mixture was stirred for 1 h at room temperature. Analysis of an aliquot with 2,4-dinitrophenylhydrazine yielded

92% of the corresponding aldehyde.

The rest of the reaction mixture (50 mmol) was hydrolyzed with 20 mL of water for 1 h at room temperature. The mixture was then saturated with sodium chloride and the organic layer was separated. The separated organic layer was stirred vigorously over excess anhydrous magnesium sulfate overnight and subjected to fractional distillation: 4.0g of hexanal(80%), bp 131-132°C.

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#### References and Notes

1. A part of this work was presented at the 192nd American Chemical Society National Meeting, Anaheim, CA, U.S.A., September 7-12, 1986.
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5. 9-BBN is also easily prepared by hydroborating 1,5-cyclooctadiene with borane-methyl sulfide under reflux. See: E.F.Knights and H.C.Brown, *J. Am. Chem. Soc.*, **90**, 5280 (1968).
6. 9-BBN itself does not attack the acyloxy moiety of acyloxy-9-BBN.
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