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Preliminary communication

# THE FACILE REACTION OF *B*-ALKYL-9-BORABICYCLO[3.3.1]NONANES WITH BENZALDEHYDE

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## Summary

Certain *B*-alkyl-9-borabicyclo[3.3.1]nonanes, in contrast to the corresponding trialkylboranes, reduce benzaldehyde to benzyl alcohol under exceptionally mild conditions. Concurrently, the *B*-alkyl group is transformed into an olefin. A cyclic process is proposed for this reaction.

Trialkylboranes are well noted for their tolerance of functional groups [1]. In particular, ketones and aldehydes are known to be relatively inert to trialkylboranes [2]. For example, tri-n-butylborane reacts only at elevated temperatures with benzaldehyde (eq. 1) [3]. This reaction should be exceedingly favor-

$$(C_4H_9)_3B + C_6H_5CHO \xrightarrow[\text{neat}]{100\text{—}150^\circ C} (C_4H_9)_2BOCH_2C_6H_5 + CH_2{=}CHC_2H_5 \quad (1)$$

able due to the transformation of the boron—carbon bond to a boron—oxygen bond. A possible explanation for the low reactivity of the organoboranes towards benzaldehyde is that the boron is sterically hindered. The reagent 9-borabicyclo[3.3.1]nonane** has often been used to overcome steric problems in other transformations of organoboranes [4]. To test the generality of steric effects on the reduction of benzaldehyde we have investigated a series of *B*-alkyl-9-BBN compounds***.

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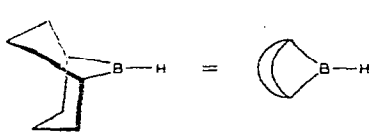
**9-Borabicyclo[3.3.1]nonane = 9-BBN 


***It has been reported that *B*-n-butyl-9-BBN reduces benzaldehyde at a rate which is only slightly faster than tri-n-butylborane [2].

A 0.5 *M* tetrahydrofuran (THF) solution of the *B*-alkyl-9-BBN compound and benzaldehyde were refluxed under nitrogen. Samples were removed periodically and analyzed by gas chromatography for remaining benzaldehyde. The rate of reaction is remarkably dependent upon the structure of the *B*-alkyl group. The results are summarized in Table 1.

TABLE 1

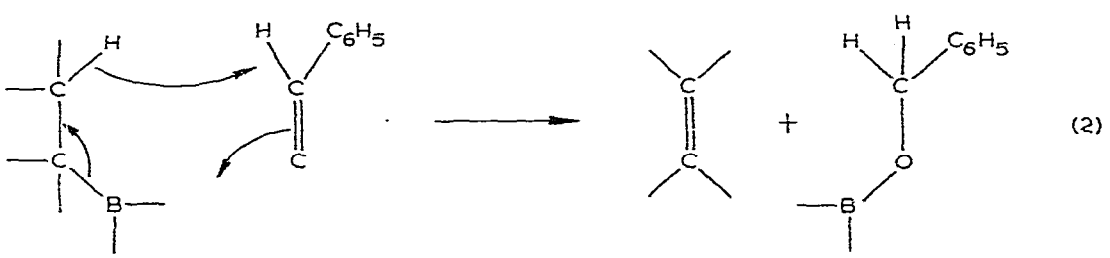
REACTION OF *B*-ALKYL-9-BBN COMPOUNDS WITH BENZALDEHYDE

| Alkyl group[a] | $t_{1/2}$ (min)[b] |
|---|---|
| Ethyl | 5500 |
| n-Butyl | 116 |
| Isobutyl | 21 |
| 3-Methyl-2-butyl | 11 |
| 2,3-Dimethyl-2-butyl | 7000 |
| Cyclohexyl | 420 |
| Cyclopentyl | 15 |
| *trans*-2-Methylcyclopentyl | 4 |

[a] 0.5 *M* *B*-alkyl-9-BBN in THF at 65° C. [b] Time for 50% completion of the reduction.

Increasing substitution at the β position greatly increases the rate of reduction (isobutyl > 1-butyl >> ethyl). Incorporation of one methyl substituent in the α position has a slight positive effect on the rate. However, incorporation of a second α methyl (2,3-dimethyl-2-butyl) causes a drastic reduction in rate. The speed of reaction also seems to be increased in systems with a more planar B—C—C—H alignment. Thus *B*-cyclopentyl-9-BBN reduces benzaldehyde much faster than does *B*-cyclohexyl-9-BBN. The fastest reductions are observed when the alkyl group possesses both a 3° β-hydrogen and the cyclopentyl ring, as in *B*-*trans*-2-methylcyclopentyl-9-BBN. This organoborane completely reduces benzaldehyde within a few minutes in refluxing THF.

Mikhailov has proposed a cyclic mechanism for the reduction of benzaldehyde by trialkylboranes (eq. 2) [3]. However, cyclooctyl—boron bonds are exceptionally prone to undergo boron migration, presumably by a dehydroboration—hydroboration process [5]. Thus the *B*-alkyl-9-BBN reductions could occur either by the cyclic process or by a dehydroboration—reduction process (eq. 3).




(2)

$$R_3B \xrightarrow[\text{slow}]{\Delta} R_2BH + \text{olefin} \xrightarrow[\text{fast}]{C_6H_5CHO} R_2BOCH_2C_6H_5 \qquad (3)$$

In the case of *B*-n-octyl-9-BBN, one mol of 1-octene is produced for each mol

of benzaldehyde consumed. No participation by the cyclooctyl ring is seen as would be required for eq. 3. The rigid cyclooctyl ring of 9-BBN presumably cannot achieve the proper geometry for a cyclic transition state. The freely-rotating n-octyl group can achieve the proper geometry. Also in accord with the cyclic mechanism rather than the dehydroboration process, the rate of reduction is affected by *para* substituents in the benzaldehyde (Table 2) and is much slower for

TABLE 2

REACTION OF *B*-n-OCTYL-9-BBN WITH SUBSTITUTED BENZALDEHYDES

| Substituent[a] | $t_{1/2}$ (hours)[b] |
|---|---|
| *p*-Chloro | 1.5 |
| *p*-Hydrogen | 3 |
| *p*-Methoxy | 12 |

[a] 0.35 *M* solutions of *B*-n-octyl-9-BBN and benzaldehyde in THF at 65°C. [b] Time for 50% completion of the reduction.

acetophenone. Finally, the reaction obeys second order kinetics as would be required for the cyclic mechanism.

The use of organoboranes containing functional groups, and the reaction of organoboranes with substrates containing functional groups are important processes for preparing complex molecules. One should be aware that certain organoboranes may react with unexpected facility with functional groups such as aldehydes. The facile reaction of *B*-alkyl-9-BBN compounds with benzaldehyde indicates that these compounds may be exceptionally selective reducing agents for carbonyls and protecting agents for olefins. We are continuing to explore these possibilities.

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