

hexane using *p*-bromo-*tert*-butoxybenzene and *n*-BuLi. It was hoped that the bulky *tert*-butyl group would hinder coordination of the *n*-BuLi hexamer to the aryl oxygen and thus show a reduced rate of exchange; however, this compound was found to undergo exclusively base-induced elimination to give isobutene and *p*-bromophenol. Further studies in progress in this laboratory are directed toward establishing the possibly concerted (or nearly synchronous) nature of the transition state for metal-halogen exchange by examining solvent effects and steric effects with respect to the alkyllithium component.

Experimental Section

General. Aryl halides, anisole, and *p*-methylanisole (Aldrich) and *n*-butyllithium (2.4 M in hexane, Alfa-Ventron) were used as received; *n*-hexane was distilled under argon from sodium/benzophenone. Unless otherwise indicated, kinetics runs were conducted at 40 °C under argon using either syringe and cannula techniques¹⁵ or a Vacuum-Atmospheres Dri-Lab glove box. GLC was performed on either a 15% SE-30/Chromosorb W, 1/8-in. by 3-m stainless steel column, or a 20% Carbowax 20M/Chromosorb W-AW, 1/8-in. by 1.3-m stainless steel column using a Hewlett-Packard Model 810 gas chromatograph fitted with flame detectors with output to a Hewlett-Packard Model 3380S electronic integrator/plotter. NMR spectra were recorded at 60 MHz on a Varian Model EM-360 nuclear magnetic resonance spectrometer. Concentrations of *n*-BuLi in hexane were determined by the Gilman double titration procedure;¹⁶ the concentration of the stock *n*-BuLi solution, stored at -30 °C, was checked periodically.

Kinetic Runs. Typical Procedure. A flame-dried 25-mL round-bottomed flask, equipped with a Teflon-covered magnetic stirring bar, was

charged with *n*-BuLi (2.4 M in hexane, 10 mL) and *n*-decane (internal standard, 0.6 mL) while under an argon atmosphere. The system was equilibrated to 40 °C in a thermostated oil bath. With rapid stirring, the run was initiated with the addition of aryl bromide (5.7 mmol). An ca. 0.5-mL aliquot was immediately removed (time = 0); additional aliquots were removed at intervals ranging from 20 min for the slower bromides to ca. 15 s for the faster compounds. The aliquots were quenched with ice or 1,2-dibromoethane, and the organic phase was analyzed by GLC. The disappearance of aryl bromide was followed relative to the internal standard. Observed rate constants were determined by plotting $\ln [\text{ArBr}]$ vs. time and obtaining the least-squares slope.

***p*-Bromo-*tert*-butoxybenzene**, prepared in 75% yield from *p*-bromophenylmagnesium bromide¹⁷ and *tert*-butyl peroxybenzoate following the procedure of Frisell and Lawesson¹⁸ had bp 53-54 °C (0.04 torr) (lit.¹⁹ bp 63-65 °C (0.4 torr)). ¹H NMR (CDCl₃, internal tetramethylsilane reference): δ 1.34 (s, 9 H), 6.97 (d of d, 4 H).

Acknowledgment. This work is supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation through Grants SCP-79-24320 and SPI-79-26855, and the Departmental Associations Council at CSUF through a grant to one of us (J.H.).

Registry No. 4-CH₃OC₆H₄Br, 104-92-7; 4-CH₃C₆H₄Br, 106-38-7; 3-CH₃C₆H₄Br, 591-17-3; C₆H₅Br, 108-86-1; 4-FC₆H₄Br, 460-00-4; 3-CH₃OC₆H₄Br, 2398-37-0; 4-ClC₆H₄Br, 106-39-8; 4-BrC₆H₄Br, 106-37-6; 3-FC₆H₄Br, 1073-06-9; 3-ClC₆H₄Br, 108-37-2; 3-BrC₆H₄Br, 108-36-1; 4-*t*-BuC₆H₄Br, 3972-65-4.

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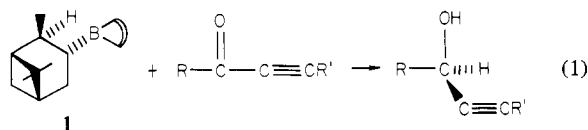
Kinetics of Reductions of Substituted Benzaldehydes with *B*-Alkyl-9-borabicyclo[3.3.1]nonane (9-BBN)

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Abstract: Second-order rate constants for the reaction of *B*-*n*-octyl-9-BBN with para-substituted benzaldehydes were obtained. Electron-withdrawing groups on the benzaldehyde increase the rate of reduction. The rate constants correlate with σ^+ ($\rho + 1.03$). Relative rates for reduction of para-substituted benzaldehydes with *B*-3-pinanyl-9-BBN gave a ρ of +0.49. The relative rates are consistent with a hydride addition to the carbonyl carbon in the rate-determining step. Activation parameters were obtained for the reaction of three benzaldehydes with *B*-*n*-octyl-9-BBN. The major barrier to the reaction is entropy. The large negative entropies of activation (-43 to -49 eu) indicate a highly ordered transition state. It is postulated that an organoborane-carbonyl oxygen complex is an intermediate in the reduction.

The trialkylborane *B*-3-pinanyl-9-BBN (1), readily prepared by hydroboration of α -pinene with 9-BBN, is a highly effective asymmetric reducing agent for aldehydes² and alkynyl ketones (eq 1).³ Enantiomeric purities of nearly 100% may be obtained.

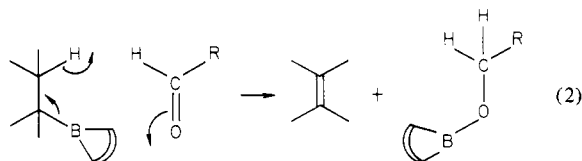


(1) Alfred P. Sloan Foundation Fellow, 1978-1982.

(2) (a) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* 1977, 99, 5211. (b) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *Ibid.* 1979, 101, 2352.

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Likewise, *B*-3-methyl-2-butyl-9-BBN is a highly chemoselective reducing agent which is able to reduce aldehydes in the presence of unhindered ketones.⁴ It has been proposed that these reactions generally proceed by a cyclic mechanism reminiscent of the Meerwein-Ponndorf-Verley (MPV) reaction (eq 2).^{5,6}



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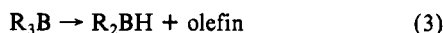
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Table I. Second-Order Rate Constants for the Reduction of Para-Substituted Benzaldehydes with *B*-*n*-Octyl-9-BBN

substituent	temp, °C	k , M ⁻¹ s ⁻¹ × 10 ⁴
NO ₂	0	66.4 ± 4.1
NO ₂	15	173 ± 18
NO ₂	25	311 ± 41
CN	25	233 ± 37
Cl	25	55.5 ± 0.7
H	25	45.8 ± 1.1
H	40	105 ± 3
H	55	227 ± 15
CH ₃	25	21.7 ± 1.1
OCH ₃	25	8.19 ± 0.64
OCH ₃	40	19.8 ± 0.6
OCH ₃	55	38.9 ± 2.3
N(CH ₃) ₂	25	0.825 ^a

^a Determined from a competition experiment with *p*-anisaldehyde (R = OCH₃).

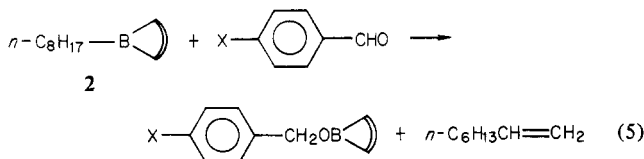
Unlike most other organometallics or metal alkoxides which undergo this type of reaction, the organoborane reduction is not complicated by oligomerization of the reagent, reversibility of the reaction, addition of the organometallic to the carbonyl, or other problems. It can thus serve as a simplified model of the MPV reaction. However, with slower reacting and sterically hindered carbonyl compounds the organoborane reaction may take an alternate pathway involving a prior dehydroboration process (eq 3, 4).⁷



In our initial explorations of asymmetric and chemoselective reductions of substituted benzaldehydes, we noted that electron-releasing substituents generally gave slower reactions. To gain a better understanding of this electronic effect on the rate of reduction, we have undertaken a kinetic study of the reduction of substituted benzaldehydes with *B*-alkyl-9-BBN compounds.

Results

The rate of reduction of aldehydes by *B*-alkyl-9-BBN compounds is greatly dependent upon the structure of the alkyl group on boron.⁵ In general, an organoborane containing a tertiary β hydride provides a very rapid rate of reduction while an organoborane with a primary β hydride provides a very slow rate. For example, **1** reacts rapidly and exothermically with benzaldehyde at room temp. Attempts to follow the reaction by conventional techniques such as VPC or NMR were futile since the reaction was so fast. We therefore chose to examine the slower reacting *B*-*n*-octyl-9-BBN (**2**). The production of 1-octene (eq 5) could be conveniently followed by VPC.



Second-order rate constants were obtained for a series of para-substituted benzaldehydes (Table I). Relative rate constants for the reductions at 25 °C are given in Table II. A Hammett plot of the log of the relative rate constants vs. σ^+ ⁸ gave a linear correlation with a ρ of +1.03 (correlation coefficient of 0.9995) (Figure 1).

Although reductions with **1** were too fast to follow by the VPC method, relative rates could be obtained by competition experiments (Table II). A Hammett plot (Figure 1) for these relative

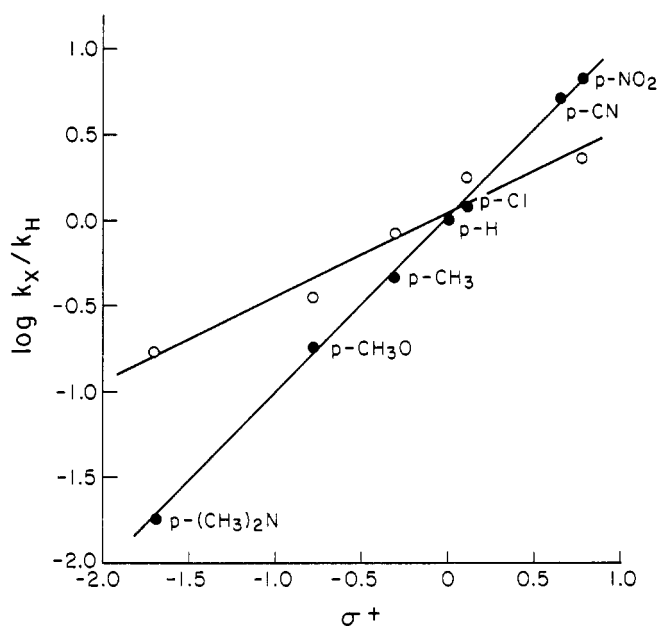
Table II. Relative Rate Constants for the Reduction of Para-Substituted Benzaldehydes with *B*-3-Pinanyl-9-BBN and *B*-*n*-Octyl-9-BBN at 25 °C

substituent	k_X/k_H	
	1 ^a	2 ^b
NO ₂	2.3	6.8
CN		5.1
Cl	1.8	1.2
H	1.0	1.0
CH ₃	0.84	0.47
OCH ₃	0.35	0.18
N(CH ₃) ₂	0.17	0.018

^a From competition experiments. ^b From data in Table I.

Table III. Activation Parameters for the Reduction of Para-Substituted Benzaldehydes with *B*-*n*-Octyl-9-BBN

substituent	E_{act} , kcal mol ⁻¹	ΔG_{298}^\ddagger , kcal mol ⁻¹	ΔH_{298}^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal deg ⁻¹ mol ⁻¹
NO ₂	10.1 ± 1.7	22.3 ± 3.5	9.5 ± 1.7	-43 ± 6
H	10.4 ± 0.8	23.2 ± 1.7	9.8 ± 0.8	-45 ± 3
OCH ₃	10.5 ± 1.0	23.7 ± 2.2	9.1 ± 1.0	-49 ± 4

**Figure 1.** Hammett Plot for reduction of substituted benzaldehydes with *B*-*n*-octyl-9-BBN (●) and *B*-3-pinanyl-9-BBN (○).

rates vs. σ^+ gave a ρ of +0.49 (correlation coefficient of 0.9759).

Rates of reduction with **2** were measured at three temperatures for three of the benzaldehydes (Table I). The activation parameters were obtained from the data (Table III).

Discussion

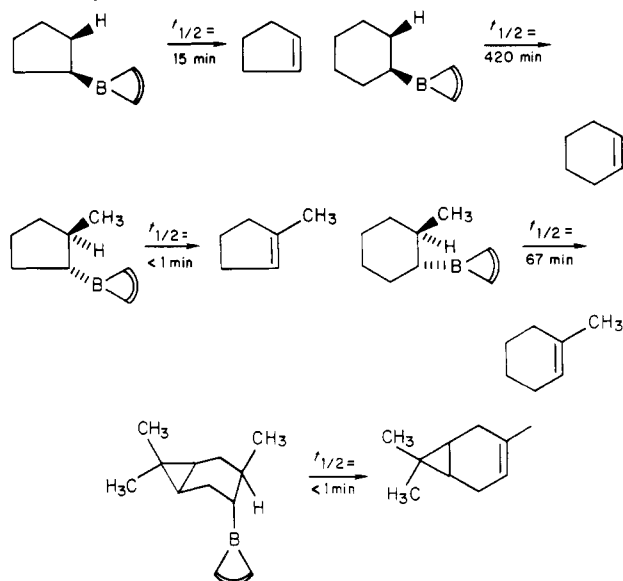
Two possible mechanisms have been considered for the reduction of aldehydes via *B*-alkyl-9-BBN compounds: a dehydroboration-reduction process (eq 3 and 4) and a cyclic process (eq 1). We have concluded that the reaction proceeds predominantly by the cyclic process.⁵ The conclusion is based on preliminary second-order kinetic data, the change in rate with structural and electronic changes in the aldehyde, and the results of asymmetric reductions. However, if steric effects in the organoborane and the substrate become great enough, the dehydroboration process can become more important.⁷

It was originally reported that the reaction of tri-*n*-butylborane with benzaldehyde required forcing conditions of 100–150 °C.⁶ Thermodynamically this reaction should be very favorable since the conversion of a boron-carbon bond to a boron-oxygen bond is energetically favorable. Our activation parameters (Table III)

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Scheme I.^a Reaction of *B*-Alkyl-9-BBN Compounds with Benzaldehyde To Form Olefins

^a Data from ref 5, $t_{1/2}$ is the time for 50% completion of the reaction at 65 °C (refluxing THF).

suggest that the major barrier to the reaction is entropy.

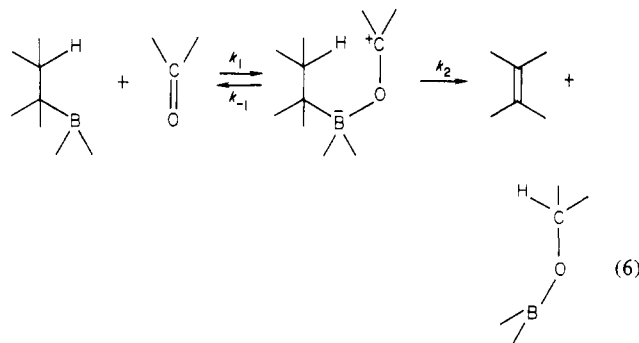
The ability of the B-C-C-H group in these boranes to form a syn coplanar arrangement (see, for example, eq 1) is very important in determining the rate of reduction.⁵ For example, *B*-cyclopentyl- and *B*-*trans*-2-methylcyclopentyl-9-BBN react very rapidly with benzaldehyde. On the other hand, *B*-cyclohexyl- and *B*-*trans*-2-methylcyclohexyl-9-BBN are unusually slow reducing agents. To achieve the syn coplanar B-C-C-H arrangement these latter boranes must assume a boat cyclohexane conformation. When the boat conformation is more favorable, as in the case of *B*-4-isocaranyl-9-BBN (from 9-BBN and 3-carene), the reduction is very rapid (Scheme I). The syn coplanar arrangement presumably allows a maximum overlap of the developing π system of the displaced olefin. This need for a coplanar B-C-C-H arrangement is also probably the cause for the large negative entropies.

The rate of reduction of para-substituted benzaldehydes correlates with σ^+ (Figure 1). This is indicative of a resonance interaction of the para substituent with the carbonyl. The positive slope is consistent with a hydride addition to the carbonyl. Resonance interactions of the para substituent with the carbonyl group are destroyed upon going to the transition state. The rate of the more reactive *B*-3-pinanyl-9-BBN is affected by the para substituent to a lesser degree. Presumably this decrease in selectivity is a consequence of the much greater reactivity of the pinanyl system.

During most of the reductions a yellow color appears as soon as the aldehyde is added to the organoborane.^{2,6} By using *B*-methyl-9-BBN and *p*-(dimethylamino)benzaldehyde, we have shown that this yellow color is due to an aldehyde-organoborane complex.^{2b} Benzaldehyde also forms a complex, but to a much lesser degree. The greater degree of complexation brought about by the electron supplying group is consistent with a stabilization of the positive charge on the carbonyl carbon in the complex.⁹

The complex is presumably a part of the overall reaction mechanism, since only a rotation is required to bring the hydride into proper orientation for transfer. For the reaction to occur through a purely concerted six-centered process, one would have to argue that this bimolecular process occurs at a rate faster than internal rotation in the complex. The overall reaction can thus be represented as shown in eq 6.

(9) Boron trifluoride forms complexes with aromatic aldehydes which are stabilized by electron-donating groups. See: Grinvald, A.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* 1974, 94, and references therein.



The hydride transfer, k_2 , is presumably the rate-determining step, since if complex formation were rate determining, then electron-donating groups should increase the rate of reaction by stabilizing the intermediate. The reaction also shows a deuterium isotope effect of 2-3 which is indicative of the rate-determining step being hydride transfer.⁵ However, since the deuterium isotope effect was determined by an intramolecular competition for deuterium vs. hydrogen, the isotope effect could reflect a rate-determining complex-forming step followed by a fast, product-determining hydride-transfer step.

On the basis of the mechanism described in eq 6, the apparent second-order rate constant is equal to $(k_1/k_{-1})k_2$. Thus, the observed Hammett ρ for the reaction would be a linear combination of the ρ for the equilibrium constant (k_1/k_{-1}) and that for hydride transfer. The former should be negative (e.g., the ρ for protonation of substituted benzaldehydes is -1.85^{10}) while the latter should be positive (e.g., the ρ for sodium borohydride reductions of substituted acetophenones is $+3.06^{11}$). The resultant positive value for ρ_{obsd} indicates that the hydride transfer ρ is dominant. For comparison, the ρ for MPV reductions of substituted acetophenones is $+1.45$ to $+1.75^{12}$. The ρ for the organoborane reduction is, thus, slightly lower than that for the MPV reduction and may reflect less hydride character in the transferring hydrogen.

The more highly substituted and, therefore, more sterically hindered *B*-3-pinanyl-9-BBN (**1**) reacts more rapidly than **2**. This fact again indicates that hydride transfer is rate determining. Complex formation should be much less favorable for **1** than for the less hindered *B*-*n*-octyl-9-BBN (**2**). The increased reactivity of **1** after complex formation could be due to a relief of steric strain, to a more favorable cis coplanar arrangement of the β hydrogen and boron, or to an electronic effect associated with hydride transfer from the tertiary carbon. The effect of changing electronic characteristics in the organoborane remains to be explored.

Conclusions

The reduction of aldehydes by *B*-*n*-octyl-9-BBN compound proceeds through a highly organized transition state. This fact is probably also true for other *B*-alkyl-9-BBN compounds. Electron-withdrawing groups increase the rate of reduction of substituted benzaldehydes. This effect is presumably also important for alkynyl ketones³ where the small steric size of the acetylene and its negative inductive effect can combine to make reduction possible. These observations suggest that it may be possible to reduce other carbonyl compounds if the proper electronic effects are present.

Experimental Section

All operations involving air-sensitive reagents were performed under a dry nitrogen atmosphere with syringe techniques.¹³ Proton NMR spectra were recorded on a Varian EM-390 (90 MHz) instrument. The PVC analysis was performed on a Hewlett-Packard 5732TCD chromatograph using 6 ft \times $1/8$ in. SE-30, DC-710, or XE-60 columns as needed.

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Integrations were performed on a Linear Instruments integrating recorder. Least-squares analysis of the kinetic data was performed on a Hewlett-Packard 3000 computer using a statistics package. Kinetic runs were performed in a circulating water bath (Sargent-Welch heater and circulator). Temperatures were controlled with a Sargent-Welch Model ST temperature controller (± 0.01 °C).

Solvents were distilled under nitrogen from potassium benzophenone ketyl. Olefins were distilled from a small quantity of lithium aluminum hydride and stored under nitrogen. Liquid aldehydes were distilled under vacuum just prior to use. Solid aldehydes were used as received after checking their purity by NMR. Solid 9-BBN was prepared by the method of Brown¹⁴ and was dissolved in THF to make a 0.5 M solution.

General Kinetic Procedure. A 500-mL flask equipped with a side arm covered with a rubber stopple, a reflux condenser, and a magnetic stirring bar was flushed with nitrogen. The flask was charged with 200 mL (100 mmol) of a 0.5 M 9-BBN solution followed by 110 mmol of 1-octene. The solution was stirred overnight and then the solvent and excess olefin was removed under vacuum. The product was transferred to a dry, nitrogen-flushed 100-mL volumetric flask equipped with a stopcock. The product was weighed and diluted to 100 mL with THF. The concentration of the stock solution of *B*-*n*-octyl-9-BBN was verified by oxidizing an aliquot and analyzing for 1-octanol and 1,5-cyclooctanediol.

Prior to each kinetic run a stock solution of the aldehyde was prepared in a nitrogen-flushed volumetric flask. A 10-mL volumetric flask equipped with a stopcock and septum was flushed with nitrogen and flame-dried. The flask was charged with 5.0 mmol of *B*-*n*-octyl-9-BBN solution and 2.5 mmol of dodecane which was used as an internal standard. Both the aldehyde and organoborane flasks were then equilibrated in the constant temperature bath. After equilibration a 5.0-mmol aliquot of the aldehyde was transferred to the organoborane solution and

the volume adjusted to 10.0 mL by the addition of a small amount of THF. The reaction progress was measured at regular time intervals by following the appearance of 1-octene by VPC. A least-squares plot of $1/([1\text{-octene}]_0 - [1\text{-octene}]_t)$ vs. time gave a straight line with a slope of the rate constant. Kinetic runs were done in triplicate, and each run used 8-15 data points. Errors quoted are standard deviations. Activation parameters were calculated by least-squares analysis of the Arrhenius plots.

General Competition Studies. A reaction flask was charged with 5.0 mmol of 9-BBN in THF followed by 5.5 mmol of α -pinene. The solution was refluxed for 3 h and then cooled to 25 °. A mixture of 10.0 mmol of two aldehydes (5.0 mmol of each) in THF was then injected into the organoborane. A sample of the reaction was removed and placed in a nitrogen-flushed NMR tube for analysis. The amount of each aldehyde was determined by integration of the two aldehydic protons and comparison of the area to that of the total aromatic protons. The relative rates were determined from the Ingold-Shaw equation:¹⁵

$$\frac{k_x}{k_y} = \frac{\log x_0 - \log x_t}{\log y_0 - \log y_t}$$

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Registry No. *p*-Nitrobenzaldehyde, 555-16-8; *p*-cyanobenzaldehyde, 105-07-7; *p*-chlorobenzaldehyde, 104-88-1; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; *p*-methoxybenzaldehyde, 123-11-5; *p*-(dimethylamino)benzaldehyde, 100-10-7; *B*-*n*-octyl-9-BBN, 30089-00-0; *B*-3-pinanyl-9-BBN, 64106-79-2.

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Thermal Reactions of *B*-Alkyl-9-borabicyclo[3.3.1]nonane (9-BBN). Evidence for Unusually Facile Dehydroboration with *B*-Pinanyl-9-BBN

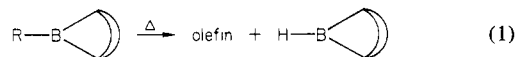
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Abstract: *B*-Alkyl-9-BBN compounds undergo a slow olefin-alkyl group exchange when refluxed with an olefin in tetrahydrofuran. The half-life of the process for *B*-*trans*-2-methylcyclopentyl- and *B*-3-methyl-2-butyl-9-BBN is approximately 4 days. However, *B*-3-pinanyl-9-BBN undergoes an exceptionally rapid olefin-alkyl group exchange with a half-life of less than 10 h. Kinetic and competition experiments support a dehydroboration-hydroboration process. The isomerization of the *B*-3-pinanyl-9-BBN to *B*-myrtanyl-9-BBN, which one would expect to accompany such a facile dehydroboration, is not seen until 145 °C. After 24 h at 165 °C, the reaction reaches equilibrium with *B*-*trans*-myrtanyl-9-BBN as the major product. Treatment of this organoborane with benzaldehyde liberates the rare (+)- β -pinene. The facility with which *B*-3-pinanyl-9-BBN undergoes dehydroboration has important consequences for asymmetric reductions with this reagent.

Certain *B*-alkyl-9-BBN compounds are extremely chemo-² and enantioselective³ reducing agents. For example, *B*-3-pinanyl-9-BBN (prepared from 9-BBN and α -pinene) may be used to reduce alkynyl ketones to propargyl alcohols in enantiomeric excesses which approach 100%.^{3c} However, with more hindered ketones or with forcing conditions (refluxing tetrahydrofuran, THF), enantiomeric purities can drop dramatically. For example, acetophenone may be reduced to 1-phenylethanol upon reflux for 24

h (THF) with a 2-fold excess of *B*-3-pinanyl-9-BBN. However, the 1-phenylethanol product exhibits only a 5-7% enantiomeric purity. We suspected that the drop in enantiomeric purity could be attributed to a competitive dehydroboration process which would generate achiral 9-BBN (eq 1). However, in contrast to



the corresponding trialkylboranes, *B*-alkyl-9-BBN compounds are thought to be remarkably thermally stable.⁴ For example, it has been observed that the hydroboration of 1-methylcyclooctene,

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