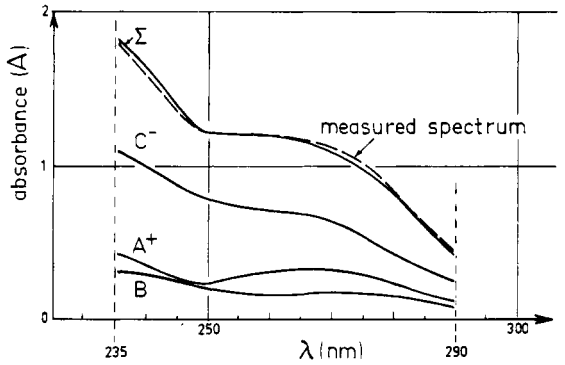

Figure 9. Thiamine spectrum reconstructed from the contributions of the calculated spectra of A^+, B and C^- (25 °C, pH 9.41, $c = 1.3 \times 10^{-4}$ M; Σ corresponds to the experimental thiamine spectrum measured under the same conditions).

constants (10^{-3}–10^8 M^{-1} s^{-1}) for heterocyclic cation formation from pseudobases.[25,26] Reaction 10 is expected to become very fast in acidic media, whereas reaction 9, pseudobase formation by addition of OH^- on position 2 of thiamine, is shown to be slow and rate limiting in basic media with a second-order rate constant $k_{12} = 19.6$ M^{-1} s^{-1}, in agreement with rate values reported for similar pseudobase formation[17] and with the estimated kinetic constants of the rate-limiting step of mechanism I.[6]

The fast relaxation (Figures 1 and 2) can only be due to the ring opening of the pseudobase B because it is too slow to be a proton transfer, even if the transfer is not diffusion controlled.[27] This suggests that equilibrium 3 is relatively acidic, as supposed by Yount and Metzler.[5] If it were not acidic, reaction 3, which is faster than reaction 4, would occur before reaction 4 and its amplitude would be detected by pH jump. The second-order rate constant of reaction 1, $k_{12} = 6.75 \times 10^4$ M^{-1} s^{-1} indicates a fast reaction in basic media. Reaction 4 is not a standard tautomeric ring opening, because it probably involves a proton transfer. The high values of the second-order rate constant is not surprising, because some ring-opening reactions are diffusion controlled.[28]

Conclusion

Pseudobase B exists to the extent of 16% of the analytical thiamine concentration between pH 9.2 and 9.5 (Figure 8). This is explained by the fact that the difference between $pK_1 = 8.9$ and $pK_2 = 9.70$ is not high enough to impose a lower concentration of the B form in the basic media *where the observed spectrum of thiamine consists of the contributions of the three different thiamine species, A^+, B, and C^-* (Figure 9). The pseudobase exists under certain conditions of pH *in detectable amounts*, and it may have some effect on the reactivity of the vitamin, especially via its deprotonated form, B^-.

Thiamine is considered as the most important sulfur-containing coenzyme of nonredox enzymatic reactions involving a general acid- or general base-catalyzed proton transfer.[8] In the structural transformations of thiamine itself, a proton transfer is always involved: (i) in the base-promoted ring opening of the pseudobase intermediate, (ii) in the acid–base-promoted hydrolysis and formation of a rather stable pseudobase intermediate from the thiazolium ring. The latter reaction is intimately related to the covalent hydration of electron-deficient heteroaromatic cycles[17] and to Meisenheimer type complex formation. All these reactions involve the formation of a σ complex on electron-deficient molecules.[29]

Acknowledgment. We are grateful to Dr. J. Lomas and J. Guillerez for helpful discussions.

Registry No. A^+, 70-16-6; B, 82326-17-8; C^-, 23148-74-5.

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Hydroboration Kinetics. 7.[1] Kinetics and Mechanism of the Reduction of Aldehydes and Ketones with 9-Borabicyclo[3.3.1]nonane Dimer

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Abstract: The kinetics of the reduction of a number of aldehydes and ketones with 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$, was studied at 25.0 °C. The reduction of aldehydes and reactive ketones followed first-order kinetic behavior; with less reactive ketones, intermediate or three-halves-order kinetics was observed. Thus the mechanism is very similar to that of the hydroboration of alkenes and alkynes by $(9\text{-BBN})_2$, involving 9-BBN monomer as the intermediate. The relative rates of reduction of representative aldehydes and ketones were determined by the competitive method since the kinetic study could not reveal the effect of the structure upon the reactivity. A comparison with $NaBH_4$ shows that $(9\text{-BBN})_2$ is less susceptible to steric effects, though the same trend is observed with both reagents. Increasing the steric hindrance on one side of the carbonyl function in ketones leads to a modest rate decrease while that on both sides leads to a considerable rate decrease. Electron-withdrawing substituents decrease and electron-releasing ones increase the rate of reduction of aldehydes and ketones. These facts strongly suggest that the boron atom of the reducing species, 9-BBN monomer, is coordinated with the carbonyl oxygen during the reduction process.

The rapid reduction of aldehydes and ketones with diborane at 0 °C was discovered more than 40 years ago.[3] Since then, a wide variety of hydride reducing agents have been developed[4] for the selective reduction of many functional groups. As a result,

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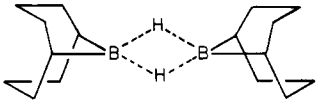
the selective reduction of a functional group A in the presence of a functional group B and vice versa could be realized.[5] However, despite this rapid development and wide application,[6] the intimate details of the mechanism of the reduction of carbonyl compounds with diborane are still not clearly understood. This is definitely, in part, due to the complexity of the reaction, as in the case of hydroboration of alkenes with diborane.[7]

We recently investigated the kinetics and mechanism of the hydroboration of alkenes and alkynes with 9-borabicyclo-[3.3.1]nonane dimer, $(9\text{-BBN})_2$.[1] Since 9-BBN has only one

$(9\text{-BBN})_2 =$ 

reactive center per boron, the kinetics proved to be much simpler. These studies unequivocally established that the hydroboration of alkenes and alkynes with $(9\text{-BBN})_2$ proceeds through the prior dissociation of the dimer to the monomer (eq 1), followed by the reaction of the monomer with the unsaturated substrate (eq 2).

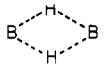
$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ 9\text{-BBN} \qquad (1)$$

$$9\text{-BBN} + \text{alkene or alkyne} \xrightarrow{k_2} \text{product} \qquad (2)$$

Earlier studies on the hydroboration of alkenes with disiamylborane dimer had provided kinetic evidence for the reaction of the alkene with the borane dimer rather than with the dissociated monomer.[8] We were intrigued by the differences between these two results and decided to explore the mechanisms of the reactions of $(9\text{-BBN})_2$ with other types of substrates such as aldehydes and ketones, alcohols, and amines. In this paper, we report our results on the reduction of aldehydes and ketones with $(9\text{-BBN})_2$.

Results and Discussion

The reduction of aldehydes and ketones with $(9\text{-BBN})_2$ was followed at 25.0 °C in THF by monitoring the rate of disappearance of the absorbance at 1570 cm^{-1} using a quantitative IR



spectrometer, as described previously.[1c] The kinetic data are given in Table I. In two cases, hexanal and cyclohexanone, the reaction was followed in cyclohexane and carbon tetrachloride also.

Reductions with First-Order Kinetics. The reduction of hexanal with $(9\text{-BBN})_2$ in CCl_4 at 25 °C exhibits first-order kinetics, first-order in $(9\text{-BBN})_2$:

$$-d[(9\text{-BBN})_2]/dt = k_1[(9\text{-BBN})_2] \qquad (3)$$

Doubling the initial concentration of hexanal has no effect on the reaction rate. The first-order rate constant, 1.42×10^{-4} s^{-1}, is in good agreement with those observed for the hydroboration of reactive alkenes and alkynes. For example, the first-order rate constant for the hydroboration of 1-hexene with $(9\text{-BBN})_2$ in CCl_4 at 25 °C is 1.54×10^{-4} s^{-1}.[1a] Obviously, the rate-limiting step is the dissociation of $(9\text{-BBN})_2$ (eq 4), which is followed by further reaction of the aldehyde with 9-BBN monomer (eq 5).[9]

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ 9\text{-BBN} \qquad (4)$$

$$9\text{-BBN} + \text{aldehyde} \xrightarrow{k_2} \text{product} \qquad (5)$$

Since the dissociation of $(9\text{-BBN})_2$ is rate limiting, essentially the same rate constants are observed for the hydroboration of reactive alkenes or the reduction of aldehydes. Similar first-order kinetics were observed in THF and cyclohexane solvents.

Several other aldehydes were also studied in THF solvent. All of the aldehydes studied exhibit first-order kinetics. Good agreement among the first-order rate constants for these aldehydes is realized (Table I). These results support the dissociation mechanism. As in the case of hydroboration,[1b] a much larger first-order rate constant was observed in THF than in noncomplexing solvents. This solvent effect has been attributed to the direct attack of a THF molecule on $(9\text{-BBN})_2$ to help in breaking up the boron–hydrogen bridge bonds.[1g]

In addition to aldehydes, the reduction of several ketones also exhibits first-order kinetics, first-order in $(9\text{-BBN})_2$ (Table I).

Reduction with Three-Halves-Order Kinetics. As in the case of hydroboration, the rate of reduction of a highly sterically hindered ketone, such as 2,4-dimethyl-3-pentanone, is considerably slower and exhibits three-halves-order kinetics, first-order in ketone and one-half-order in $(9\text{-BBN})_2$:

$$-d[(9\text{-BBN})_2]/dt = k_{3/2}[(9\text{-BBN})_2]^{1/2}[\text{ketone}] \qquad (6)$$

Clearly, the dissociation of $(9\text{-BBN})_2$ is much faster than the

Table I. Rate Constants for the Reduction of Representative Aldehydes and Ketones with $(9\text{-BBN})_2$ at 25 °C[a]

compound[b]	10^4k_1, s^{-1}			$10^4k_{3/2}$, $M^{-1/2}$ s^{-1}
	THF	CCl_4	cyclohexane	THF
hexanal	14.2	1.42	1.41	
propanal	12.8			
2-methylpropanal	13.2			
2,2-dimethylpropanal	11.7			
2-phenylpropanal	12.4			
benzaldehyde	13.7			
p-methoxybenzaldehyde	13.1			
p-chlorobenzaldehyde	15.2			
cyclohexanone	14.4	1.41	1.49	
2-methylcyclohexanone	12.8			
cyclopentanone[c]	11.7			
cycloheptanone[c]	12.7			
acetone[c]	13.7			
norbornanone[c]	12.7			
acetophenone[c]	12.8			
p-methylacetophenone[c]	11.9			
p-methoxyacetophenone[c]	11.9			
2,4-dimethyl-3-pentanone				0.98

[a] The standard deviations of the rate plots, as obtained by least-squares method,[1c] are less than 1.5% of the rate constants. [b] The following compounds failed to obey the integrated rate expressions of both first order and three-halves order: 2-methylcyclopentanone, 2-heptanone, 3-methyl-2-butanone, camphor, cyclooctanone, benzophenone, *p*-chloroacetophenone, 3,3-dimethyl-2-butanone, and 2-methyl-3-pentanone. [c] The reaction exhibits slight intermediate behavior in THF solvent.

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Table II. Relative Reactivities for the Reduction of Representative Aldehydes and Ketones with $(9\text{-BBN})_2$ in THF at 25 °C

compound	relative rate: 1-hexene = 100	relative rate: hexanal = 100
p-methoxybenzaldehyde	1154	142
p-tolualdehyde	911	112
hexanal	813	100
benzaldehyde	672	87.0
p-chlorobenzaldehyde	494	64.0
2,2-dimethylpropanal	479	62.0
cyclohexanone	197	25.5
cyclopentanone	51	6.61
p-methoxyacetophenone	32.1	4.15
cycloheptanone	22.0	2.85
norbornanone	19.6	2.54
p-methylacetophenone	16.8	2.18
acetone	13.8	1.78
2-butanone	11.3	1.46
acetophenone	9.8	1.27
2-heptanone	9.0	1.17
3-methyl-2-butanone	8.9	1.15
benzophenone	7.2	0.93
p-chloroacetophenone	7.0	0.90
3,3-dimethyl-2-butanone	6.9	0.89
cyclooctanone	3.9	0.50
camphor	3.6	0.46
3-pentanone	3.0	0.39
2,4-dimethyl-3-pentanone	0.94	0.122

subsequent reaction of 9-BBN monomer with the ketone in this case.[9] Presumably, more hindered ketones, such as 2,2,4-trimethyl-3-pentanone and 2,2,4,4-tetramethyl-3-pentanone would exhibit similar behavior.

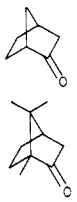
Reductions with Intermediate Kinetics. The reduction of several ketones, such as 2-methylcyclopentanone, 2-heptanone, 3-methyl-2-butanone, camphor, cyclooctanone, benzophenone, *p*-chloroacetophenone, 3,3-dimethyl-2-butanone, and 2-methyl-3-pentanone, does not show either first-order or three-halves-order kinetics cleanly. Apparently in these cases, the rates of the dissociation of $(9\text{-BBN})_2$ and of reduction by 9-BBN monomer are comparable, leading to complex kinetic behavior.

Competition Experiments. Although many aldehydes and ketones have essentially the same first-order rate constant, they by no means have the same reactivity toward $(9\text{-BBN})_2$. Since the kinetic data did not reveal the effects of structure on the rate of reduction of carbonyl compounds with $(9\text{-BBN})_2$, we determined their relative rates by the competition method (Table II). The very fact that many aldehydes and ketones having widely different reactivity toward $(9\text{-BBN})_2$ show the same first-order constant provides strong support for the dissociation mechanism.

Structural Effects. The relative rates of the reduction of aldehydes and ketones with $(9\text{-BBN})_2$ permit us to understand the steric and electronic effects in this reaction. We were interested in comparing the behavior of the acidic reducing agent, 9-BBN, with that of nonacidic BH_4^-, which has been extensively studied.[10]

A. Steric. The relative rate data show that the reduction of carbonyl compounds with 9-BBN is less susceptible to steric effects than $NaBH_4$, in spite of the bulky nature of the former reagent. For example, we can consider the effect of ring size on the reduction of cycloalkanones by 9-BBN and $NaBH_4$. Cyclooctanone is reduced by 9-BBN by a factor of 50 slower than cyclohexanone while the factor is as much as 2050 for reduction by BH_4^-[10c]. This huge difference in reactivity is certainly not attributable to electronic factors alone, since the change in electronic effect on going from cyclohexanone to cyclooctanone cannot be large. Again, camphor is reduced by only a factor of 6 slower than norbornanone by 9-BBN, while in the case of $NaBH_4$ reduction,[10d] the factor is more than 900. The lower susceptibility of 9-BBN to steric effects indicates that the boron atom of 9-BBN monomer

	$(9\text{-BBN})_2$	$NaBH_4$[11]
cyclopentanone	26.0	4.35
cyclohexanone	100	100
cycloheptanone	11.0	0.64
cyclooctanone	2.0	0.049



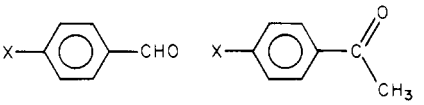
$(9\text{-BBN})_2$	$NaBH_4$
1.00	1.00
0.18	0.011

is coordinated with the carbonyl oxygen of the substrate during reduction; such a coordination will keep the bulky bicyclooctyl moiety of 9-BBN away from the alkyl groups of the substrate. The same conclusion is arrived from the rates of reduction of acyclic ketones as well. Introduction of two methyl groups at the α position in acetone (3-methyl-2-butanone) leads only to a modest decrease in the rate of reduction. On the other hand, introducing methyl groups on both the α positions (3-pentanone) leads to a considerable rate decrease. Since the change in electronic effect is comparable in both cases, this observation shows that the reagent, 9-BBN monomer, can approach the carbonyl group easier in the case of 3-methyl-2-butanone than 3-pentanone. Increasing

	rel rate
acetone	1.00
3-methyl-2-butanone	0.67
3-pentanone	0.20
2,4-dimethyl-3-pentanone	0.069

the steric hindrane on one side of the carbonyl function may not affect the complexation of the ketone with the reagent, since it can approach the carbonyl from the less hindered side. In fact, even methyl *tert*-butyl ketone is reduced by only a factor of 2 slower than acetone while 2,4-dimethyl-3-pentanone is reduced much slower (factor of 15).

B. Electronic. Since the relative rates of reduction of cyclic and acyclic ketones suggested a coordination of the 9-BBN monomer with the carbonyl oxygen of the substrate, we undertook to study the electronic effect in this reaction. Consequently, we measured the rates of reduction of some para-substituted benzaldehydes and acetophenones. Electron-releasing substituents increase and electron-withdrawing ones decrease the rate, providing



X		
OMe	1.63	3.27
Me	1.29	1.72
H	1.00	1.00
Cl	0.74	0.71

evidence for the fact that the carbonyl oxygen is complexed with the boron atom of the reagent. Opposite electronic effects are observed in BH_4^- reduction.[12]

Mechanism of Reduction. The steric and electronic effects on this reaction suggest that the borane reagent is complexed with the carbonyl oxygen of the substrate during reduction. We consider that acidic borane reductants will be coordinated with the carbonyl oxygen before or during the actual reduction process, since such an interaction will make the boron atom electron rich, thereby facilitating the transfer of hydrogen with the bonded electron pair. Though our present results do not show whether the complex is formed as an intermediate (**1**) or there is a co-

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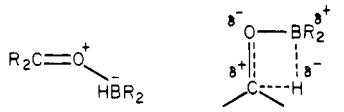

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ordination between the borane and the carbonyl oxygen in the transition state (**2**), they do indicate a strong interaction between the borane and the carbonyl oxygen. It may be mentioned that BF_3 forms complexes with aldehydes.[3,13] Trialkylboranes are also reported to form complexes with aldehydes.[14]

In conclusion, while the kinetics of the reduction of aldehydes and ketones with $(9\text{-BBN})_2$ identifies the actual reducing agent as the 9-BBN monomer formed by the dissociation of the dimer, the relative rates obtained by the competitive method show that the 9-BBN monomer is coordinated with the carbonyl oxygen during reaction. Together, these two studies define the mechanistic details of this reaction.

Experimental Section

General Methods. Detailed procedures for the manipulation of boron reagents have been outlined in Chapter 9 of ref 15. Glassware, syringes, and needles were dried for several hours in an oven at 140 °C and cooled in a stream of dry nitrogen before use. Syringes were assembled while hot and cooled as assembled units in a nitrogen atmosphere. GC analyses were carried out using an HP 5750 research chromatograph. For relative reactivity measurements, 12 ft × 0.125 in. column of 10% SE-30 on 100/120 mesh Chromosorb W, protected by a short column of Theed, was used. For kinetic studies, a Miran-1A variable-filter infrared spectrometer from Wilks Scientific Corp. was used. The calculations of the kinetic data were carried out on a Hewlett-Packard 9820 calculator.

Materials. The purification of solvents was carried out as described elsewhere.[15] The aldehydes and ketones were obtained commercially and were distilled before use, after drying over Drierite. Commercial 9-BBN (aldrich) was used as received.

Kinetics Studies. The kinetics of the reduction of aldehydes and ketones were followed by monitoring the absorbance of the boron–hydrogen bridge vibration of $(9\text{-BBN})_2$ at 1570 cm^{-1} using a quantitative IR spectrometer.[1c] A typical example is given as follows. A solution of $(9\text{-BBN})_2$ in CCl_4 (0.27 M, 9.25 mL) was taken in a 50-mL reaction flask equipped with septum inlet and a connecting tube. CCl_4 (15.13 mL) was added to it and the mixture was equilibrated at 25.00 ± 0.05 °C. It was then pumped through a 0.10-mm NaCl IR cell at a rate of 4 mL/min to determine the absorbance of boron–hydrogen bridge bonds at 1570 cm^{-1}. The reaction was initiated by adding hexanal (0.62 mL) using a syringe. The initial concentrations of hexanal and $(9\text{-BBN})_2$ were 0.200 and 0.100 M, respectively. The absorbance was recorded on a chart paper. When the absorbance ceased to decrease, pure CCl_4 was pumped through the cell to determine the background absorbance. The concentrations of $(9\text{-BBN})_2$ at desired time intervals were calculated. The first-order rate constant was obtained graphically.[1c]

Relative Reactivity. The procedure to determine the relative reactivities of aldehydes and ketones toward $(9\text{-BBN})_2$ in THF at 25 °C has been described previously.[16] The substrate pairs were so chosen that their relative rates did not differ by a factor of more than 10. The relative rates obtained are listed in Table II.

Acknowledgment. We thank the National Science Foundation for Grants 76-20846 and 79-18881.

Registry No. $(9\text{-BBN})_2$, 70658-61-6; hexanal, 66-25-1; propanal, 123-38-6; 2-methylpropanal, 78-84-2; 2,2-dimethylpropanal, 630-19-3; 2-phenylpropanal, 93-53-8; benzaldehyde, 100-52-7; *p*-methoxybenzaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; acetone, 67-64-1; norbornanone, 497-38-1; acetophenone, 98-86-2; *p*-methylacetophenone, 122-00-9; *p*-methoxyacetophenone, 100-06-1; 2,4-dimethyl-3-pentanone, 565-80-0; *p*-tolualdehyde, 104-87-0; 2-butanone, 78-93-3; 2-heptanone, 110-43-0; 3-methyl-2-butanone, 563-80-4; benzophenone, 119-61-9; *p*-chloroacetophenone, 99-91-2; 3,3-dimethyl-2-butanone, 75-97-8; cyclooctanone, 502-49-8; camphor, 76-22-2; 3-pentanone, 96-22-0.

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Solvolysis of 1-Aryl-2,2,2-trifluoroethyl Sulfonates. Kinetic and Stereochemical Effects in the Generation of Highly Electron-Deficient Carbocations

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Abstract: Solvolysis rates of sulfonates $XC_6H_4CH(O_3SR)CF_3$ (R = *p*-Tol or CF_3) correlate with $\sigma^+(X)$ with values of ρ^+ between −6.7 and −11.9 depending upon solvent. For the tosylates the rates depend on the solvent parameter Y_{OTs} with values of m_{OTs} of 0.76 (X = *p*-MeO), 0.94 (X = *p*-Me), and 0.69 (X = H). These results are interpreted in terms of rate-limiting carbocation formation (the k_C process). Rates for $PhCH(OTf)CF_3$ (**12e**) in ten solvents gave a scattered correlation with Y_{OTs}, and optically active **12e** reacted with racemization in TFA and HFIP and significant inversion in EtOH and AcOH. These results indicate that nucleophilic solvent participation becomes important with this derivative in the more nucleophilic solvents. Deuterium isotope effects for $PhCD(OTf)CF_3$ are not a definitive criterion of mechanism but are consistent with this interpretation.

The reactivity of 1-aryl-1-methyl-2,2,2-trifluoroethyl tosylates (**1**) has been investigated by ourselves[1] and by Liu and co-workers.[2] These substrates have been found to react by rate-limiting ionization to form intermediate cations **2** and then to form mixtures of elimination products **3** and substitution products **4** (eq 1).

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