518 *J. Org. Chem.* 1985, *50*, 518-520

Hydroboration Kinetics. 11. A Reinvestigation of the Kinetics of Hydroboration of Representative Alkenes with Disiamylborane Dimer. Conclusive Evidence for the Dissociation Mechanism in the Hydroboration of Alkenes with Dialkylborane Dimers

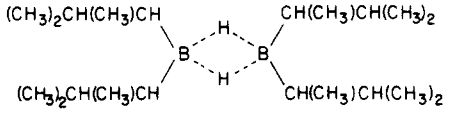
J. Chandrasekharan[1] and Herbert C. Brown*

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received October 11, 1984

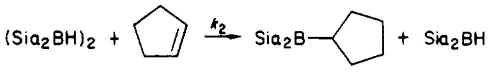
The kinetics of hydroboration of representative alkenes with disiamylborane dimer was studied in THF at 0 °C by using the quantitative IR procedure. With many alkenes the reaction exhibits three-halves-order kinetics, indicating that the reaction involves a prior dissociation of the dimer, followed by the hydroboration step. The reaction of highly reactive alkenes, such as 1-octene, proceeds extremely rapidly, precluding a reliable kinetic analysis of the data. The earlier results supporting a bimolecular reaction of alkene with disiamylborane dimer must now be revised. The present results clearly support those obtained earlier with 9-borabicyclo[3.3.1]nonane and borinane dimers. It can now be generalized that the hydroboration of alkenes with dialkylborane dimers proceeds via the dissociation mechanism.

More than 20 years ago we initiated a program on the kinetics and mechanism of hydroboration.[2] Hydroboration of alkenes with diborane in ether solvents is extremely fast.[3] It is a complex reaction involving several consecutive steps, redistribution processes, and monomer–dimer equilibria.[4] As a result, kinetics studies became impractical. However, we studied the kinetics of hydroboration of alkenes with disiamylborane dimer, $(Sia_2BH)_2$, 1, in THF at 0 °C in an attempt to simplify the complexities associated with B_2H_6 reactions.[2] The reaction of a typical alkene, such as cyclopentene, with $(Sia_2BH)_2$ exhibited second-order kinetics, first-order in cyclopentene and first-order in $(Sia_2BH)_2$ (eq 1), suggesting that the reaction proceeds by a direct attack of the alkene on the dimer (eq 2 and 3). In the absence of any other kinetic data, this mechanism was considered to be general, applicable to all dialkylborane dimers.[5]

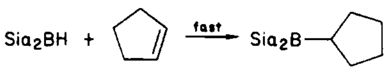


1

$$-\frac{d[\text{cyclopentene}]}{dt} = k_2[(\text{Sia}_2\text{BH})_2][\text{cyclopentene}] \tag{1}$$



(2)



(3)

We later came across a highly stable dialkylborane dimer, 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$. We could conveniently measure the kinetics of hydroboration of representative alkenes with $(9\text{-BBN})_2$ at 25 °C in a variety of solvents using a quantitative IR procedure.[6] The results were totally different from those realized with disiamylborane. Faster reacting alkenes exhibited first-order kinetics, first-order in $(9\text{-BBN})_2$. Less reactive ones exhibited three-halves-order kinetics. In no case were second-order kinetics observed. The results are explicable only in terms of the dissociation mechanism (eq 4 and 5).

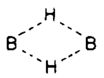
$$(\text{9-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ \text{9-BBN} \tag{4}$$

$$\text{9-BBN} + \text{alkene} \xrightarrow{k_2} B\text{-alkyl-9-BBN} \tag{5}$$

We were very much intrigued by the difference in the behavior of $(9\text{-BBN})_2$ and $(Sia_2BH)_2$ and decided to explore it in detail. Consequently, we studied the kinetics of hydroboration of alkenes with borinane dimer in *n*-heptane at 0 °C.[7] With borinane dimer, many alkenes, except highly reactive ones, exhibited three-halves-order kinetics. The reaction was very fast in the case of highly reactive alkenes such as 1-hexene, precluding reliable kinetic analysis of the rate data. The results with the borinane dimer clearly supported those with $(9\text{-BBN})_2$. However, our early results with $(Sia_2BH)_2$ concerned us. Conventional wisdom indicates that disiamylborane dimer should also react with alkenes by the dissociation mechanism since, on steric grounds, it would be expected to dissociate even more readily than borinane dimer. Consequently, we reinvestigated the kinetics of hydroboration of representative alkenes with $(Sia_2BH)_2$ by using the quantitative IR procedure. We report our results in this paper.

Results and Discussion

The kinetics of hydroboration of alkenes with disiamylborane dimer was earlier monitored by a quenching procedure.[2] Aliquots of the reaction mixture were removed and quenched with excess methanol at desired time intervals in the presence of a suitable internal standard. The unreacted alkene was estimated by GLC. This method is painfully tedious. Hence, we used the more reliable, highly elegant IR determination of $(Sia_2BH)_2$ by monitoring the absorbance of



stretching mode at 6.51 μm in THF at 0 °C.[6c,8] We also

---

[1] Postdoctoral research associate on Grant CHE 79-18881 of the National Science Foundation.

[2] Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1961**, *83*, 3417.

[3] Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 2582; **1959**, *81*, 6423.

[4] Pasto, D. J.; Balasubramanian, V.; Wojtkowski, P. W. *Inorg. Chem.* **1969**, *8*, 594.

[5] Brown, D. R.; Kettle, S. F. A.; McKenna, J.; McKenna, J. M. *Chem. Commun.* **1967**, 667.

[6] (a) Brown, H. C.; Scouten, C. G.; Wang. K. K. *J. Org. Chem.* **1979**, *44*, 2589. (b) Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698. (c) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303.

[7] Brown, H. C.; Chandrasekharan, J.; Nelson, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 3768.

0022-3263/85/1950-0518$01.50/0

Table I. Effect of Concentration of the Reactants on the Rate Constants for the Hydroboration of Representative Alkenes with Disiamylborane Dimer in THF at 0 °C

	initl concn, M		rate constants		
alkene	alkene	$(Sia_2BH)_2$	10^4k_1, s^{-1}	$10^4k_{3/2}$, $M^{-1/2}\,s^{-1}$	10^4k_2, $M^{-1}\,s^{-1}$
cyclopentene	0.400	0.200	4.10	6.84	23.6
	0.400	0.100	9.63	6.97	32.6
	0.200	0.100	3.11	7.25	35.0
cis-3-hexene	0.400	0.200	3.85	6.90	25.8
	0.400	0.100	8.78	6.45	28.2
	0.200	0.100	3.14	6.42	26.6
trans-3-hexene	0.400	0.200	0.844	1.28	3.98
	0.400	0.100	2.03	1.47	6.67
	0.200	0.100	0.663	1.36	5.70

Table II. Three-Halves-Order Rate Constants for the Hydroboration of Representative Alkenes with Disiamylborane Dimer in THF at 0 °C

alkene	$10^4k_{3/2}$, $M^{-1/2}\,s^{-1}$	rel rate[a]
2-methyl-1-pentene	50.5	100
cyclopentene	7.02	29
cis-3-hexene	6.59	41
cis-4-methyl-2-pentene	2.55	10
trans-3-hexene	1.36	4.1
trans-4-methyl-2-pentene	0.782	2.0
cyclohexene[b]	0.065	0.2
1-methylcyclopentene[b]	0.035	

[a] From ref 9. [b] The reaction was followed only up to 50% due to its extreme slowness.

overcame other technical difficulties in our earlier investigation.[2] For example, under our earlier experimental conditions, there was a 5° temperature rise when the alkene was added to the disiamylborane solution. At that time, we attempted to solve this problem by precooling the reaction flask to −2.5 °C and adding the alkene. Considering that this might have distorted the kinetics, we carried out our experiments so that the amounts of the reactants were much smaller and used highly efficient constant temperature baths.

Kinetics Results. The reaction of cyclopentene with $(Sia_2BH)_2$ in THF at 0 °C exhibits three-halves-order kinetics. The rate data fit the three-halves-order rate equation nicely, but not first- or second-order equations (Figure 1). Changing the initial concentration of each of the reactants does not alter the three-halves-order rate constant appreciably (Table I). The hydroboration of several other alkenes (Table II) exhibits three-halves-order kinetic behavior as well. The hydroboration of reactive alkenes, such as 1-octene, was exceptionally fast, precluding reliable kinetic analysis. For example, the reaction of 1-octene (0.200 M) with $(Sia_2BH)_2$ (0.100 M) was 90% complete in 36 s.

Reaction Mechanism. The three-halves-order kinetics observed with many alkenes clearly supports the conclusion that the reaction must involve an equilibrium dissociation of the disiamylborane dimer, followed by a slow reaction of the alkene with the monomer (eq 6 and 7). The

$$(Sia_2BH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Sia_2BH \qquad (6)$$

$$Sia_2BH + \text{alkene} \xrightarrow[\text{slow}]{k_2} Sia_2BR \qquad (7)$$

governing rate equation, derived by using the steady-state hypothesis[6b] (eq 8), indicates that the three-halves-order

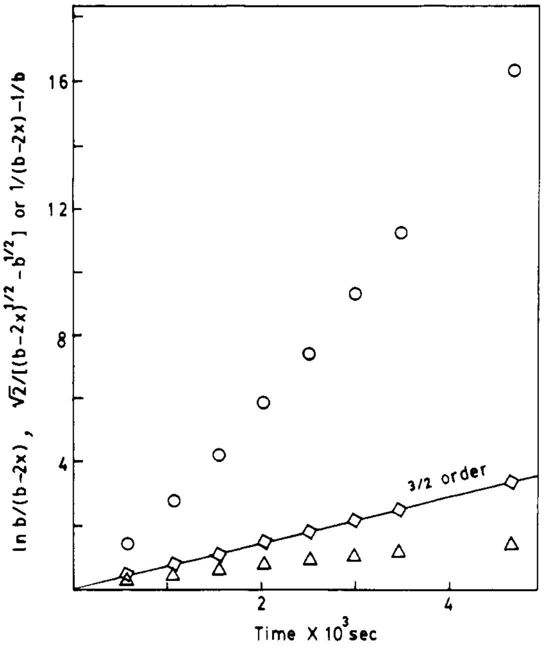


Figure 1. Rate plot for the reaction of cyclopentene (0.200 M) with $(Sia_2BH)_2$ (0.100 M) in THF at 0 °C: first order, △; three-halves order, ◇; second order, ○.

rate constants must be parallel to the relative reactivities established by the competitive method.[9] In fact, the

$$-\frac{d[(Sia_2BH)_2]}{dt} = \tfrac{1}{2}(k_1/k_{-1})^{1/2}k_2[(Sia_2BH)_2]^{1/2}[\text{alkene}] \qquad (8)$$

three-halves-order rate constants are reasonably parallel to the relative reactivities established by competition experiments[9] (Table II). For example, the ratio of the three-halves-order rate constants of cyclopentene and *cis*-4-methyl-2-pentene is 2.75. The ratio of the relative reactivities obtained from competition experiments is 2.80.[10]

With faster reacting alkenes such as 1-octene, the reaction is too fast to measure the rate constants. 2-Methyl-1-pentene is the fastest reacting alkene for which we could determine the kinetics accurately. It also exhibits three-halves-order kinetics. It is possible that with very reactive alkenes, such as 1-octene, the reaction might become first order, as observed for 9-BBN.

Conclusion

The three-halves-order kinetic behavior observed in the hydroboration of many alkenes with disiamylborane dimer agrees very well with our results on $(9\text{-BBN})_2$ and borinane dimer, clearly demonstrating that the dissociation mechanism generally applies to hydroborations involving dialkylborane dimers. Thus the dissociation mechanism can now be safely extended to other dialkylborane dimers such as diisopinocampheylborane dimer, $(Ipc_2BH)_2$, which are not amenable to kinetic studies due to practical difficulties such as poor solubility. The conclusion that the dialkylborane dimer dissociates prior to the hydroboration step is of immense value in proposing a suitable model for asymmetric hydroboration involving such reagents. In fact,

---

(8) Disiamylborane exists predominantly as the dimer in THF solution (Brown, H. C.; Klender, G. J. *Inorg. Chem.* **1962**, *1*, 204).

(9) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063.

(10) It appears that a strict agreement between the ratios of the three-halves-order rate constants and the relative rates obtained by competition experiments is not realized in some cases. In such cases we believe the kinetic data represent the true situation since the kinetic method is far more accurate.

consequent to our earlier report on the kinetics of hydroboration of alkenes with $(Sia_2BH)_2$, McKenna et al. proposed a model based on the dimer for asymmetric hydroborations involving $(Ipc_2BH)_2$.[5] Our present results on $(Sia_2BH)_2$, $(9\text{-}BBN)_2$, and borinane dimer settle this ambiguity. Any good model for asymmetric hydroboration by $(Ipc_2BH)_2$ must utilize the monomer rather than the dimer.[11]

Experimental Section

General Methods. Detailed procedures for the manipulation of boron reagents have been outlined in Chapter 9 of ref 12. 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. For kinetic studies, a Miran-1A variable-filter infrared spectrometer from Wilks Scientific Corporation was used. The calculations of the kinetic data were carried out on a Hewlett-Packard 9820 calculator.

Materials. Tetrahydrofuran was purified as described elsewhere.[12] All of the alkenes used were obtained commercially and were distilled over LAH in a nitrogen atmosphere before use. $BH_3\cdot THF$, obtained from Aldrich, was used as such for the preparation of disiamylborane.[13] Disiamylborane was prepared freshly before each kinetic run.[14]

Kinetic Studies. The following procedure is typical. To $BH_3\cdot THF$ (4.90 mL of 1.02 M solution in THF), well-cooled with ice–salt bath, was added 2-methyl-2-butene in THF (5 mL of a 2.0 M solution) dropwise over a period of 15 min. The mixture was kept at 0 °C for 8 h for the complete formation of disiamylborane. Precooled THF (14.66 mL) was then added and the solution was allowed to equilibrate at 0.0 ± 0.1 °C for 0.5 h. It was then pumped[15] through a 0.20-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 started by adding cyclopentene (0.44 mL) by using a syringe. The initial concentrations of cyclopentene and $(Sia_2BH)_2$ are 0.200 and 0.100 M, respectively. The reaction mixture was pumped through the IR cell continuously and the absorbance was recorded on chart paper. After the reaction was over, pure THF was pumped through the cell to determine the background absorbance. The three-halves-order rate constant was obtained graphically[6c] (Figure 1).

Acknowledgment. We thank the National Science Foundation for financial support (Grant CHE 79-18881).

---

[11] Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964**, *86*, 1071.

[12] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

[13] Commercial $BH_3\cdot THF$ contains a small amount of $NaBH_4$ (< 5 mol %) as a stabilizer. It does not affect the hydroboration kinetics; $BH_3\cdot THF$ free from BH_4^- behaved exactly like the commercial sample in trial experiments. Hence, the commercial sample was used for all kinetic runs.

[14] Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 3222.

[15] The IR cell holder was surrounded by a metal jacket through which a coolant at −2 °C was circulated in order to maintain the temperature of the reaction mixture at the reaction temperature.

Hydroboration. 70. The Polycyclic Hydroboration of Acyclic and Cyclic Trienes with Borane in Tetrahydrofuran and Triethylamine–Borane. Reexamination of the Stereochemistry of Isomeric Perhydro-9b-boraphenalenes[1,2]

Herbert C. Brown,* Ei-ichi Negishi,[3a] and William C. Dickason[3b]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received May 22, 1984

The hydroboration of 1,4,8-nonatriene (**1**), 5-methyl-1,4,8-nonatriene (**2**), 1,3,7-octatriene (**3**), and *trans,-trans,trans*-1,5,9-cyclododecatriene (**4**) with borane in tetrahydrofuran (THF) and triethylamine–borane was studied. The hydroboration of the acyclic trienes with borane in THF at 0 °C produced monomeric bicyclic boranes in low yields. Moreover, thermodynamically stable organoboranes with fused six-membered rings, such as 9-boradecalin (**15**) and 10-methyl-9-boradecalin (**20**), were not formed as the major monomeric cyclic products. However, thermal treatment of the hydroboration product from **1** produced **15** as the only monomeric bicyclic organoborane in high yield. The thermodynamically favored major product from **2** was **20** which amounted to 62% of the monomeric boranes formed in 74% yield. With **1** and **2**, both borane in THF and triethylamine–borane gave comparable results after thermal treatment. However, in the hydroboration of **3**, use of triethylamine–borane resulted in a considerably higher yield of perhydro-8-boraindan. The carbonylation–oxidation of **15** provided an 80:20 mixture of *cis*- and *trans*-9-decalols. The ratio of *cis*-10-methyl-9-decalol to its trans isomer obtained by the carbonylation–oxidation of **20** was at least 62:1. The carbonylation–oxidation of **3** produced only *cis*-8-hydrindanol. The hydroboration of the cyclic triene **4** followed by thermal treatment at 160 °C for 6 h produced a mixture consisting largely of *cis,trans*-perhydro-9b-boraphenalene (**6**) and a constitutional isomer in 83% yield. However, thermal treatment at 200 °C for 6 h provided a 92:8 mixture of **6** and its all-cis isomer **5**, uncontaminated with the constitutional isomer. The hydroisomerization of **5** or **6** at 220 °C in the presence of triethylamine under 140 atm of hydrogen gave an equilibrium mixture of 88 ± 1% **5** and 12 ± 1% **6**. The difference between the free energies of **5** and **6** was estimated to be 1.9 ± 0.1 kcal/mol. The stereochemistry of **5** and **6** was established by ^{1}H NMR examination of the pyridine adducts of **5** and **6** as well as of free **5** and **6**. The original structural assignments by Rotermund and Köster must therefore be reversed.

We have previously established that the hydroboration of dienes that are capable of forming common rings (five- to seven-membered) with borane in tetrahydrofuran (THF)[4] or thexylborane[5] is generally highly cyclic.[6] On the