Distribution of Alkylboranes in the Reaction of Norbornene and Cyclopentene with Borane-THF

Hiroaki TANIGUCHI*

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47902, USA

(Received February 28, 1979)

Systematic studies of the partial alkylation of diborane with norbornene and cyclopentene were carried out in THF and the equilibrium distribution of the borane derivatives was determined. Di-*exo*-norbornylborane was obtained in 71% yield with no mono-*exo*-norbornylborane as a by-product, under the conditions: initial ratio of norbornene to borane 2: 1, temperature 0 °C and reaction time 1 h. Mono-*exo*-norbornylborane was obtained in 72—75% yield under the conditions: initial ratio of norbornene to borane 1: 1, temperature 25 °C, and reaction time 48 h. In the dialkylborane $[R_2BH]_2$, norbornene and cyclopentene exhibit very different behavior during the course of equilibration reaction.

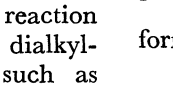
Di-*exo*-norbornylborane is promising as a new agent for the contrathermodynamic isomerization of olefins.[1] It is desirable to find a simple synthetic route for this dialkylborane.

The easiest route to obtain the disubstituted boranes would be the partial alkylation of BH_3, but direct partial alkylation of BH_3 by norbornene does not seem to have been studied. It is possible to obtain a mixture of BH_3, RBH_2, R_2BH, and R_3B from the direct reaction of 2 mol olefin and 1 mol BH_3, but not pure dialkylboranes.[2] However, pure dialkylboranes such as bis(1,2-dimethylpropyl)borane and dicyclohexylborane can be obtained from some special types of hindered olefins.[3] A complete study of the composition or the equilibrium distribution realized in the partial alkylation of diborane with different types of olefins does not seem to have been carried out. I herewith report a systematic study on the partial alkylation of diborane with norbornene, cyclopentene being considered as a comparable raw material.

Results and Discussion

Kinetic Study of Partial Alkylation. (1) Partial Alkylation of Diborane with Norbornene and Cyclopentene in THF at 0 °C: Partial alkylation of BH_3 with norbornene in the ratios 1: 1, 1: 2, and 1: 3 was carried out at 0 °C.

A solution of norbornene in THF was slowly added to a solution of diborane in THF at 0 °C. After 1 h, excess methanol was added and the amounts of methyl borate $[B(OCH_3)_3]$, dimethoxy-*exo*-norbornylborane methoxy-di-*exo*-norbornylborane obtained were determined by titration and NMR analysis. The amounts of tri-*exo*-norbornylborane were calculated from the difference between the theoretical amounts of the borane compounds found and the sum of the amounts of the rest three boron derivatives found. Partial alkylation of BH_3 with cyclopentene under the same conditions was also undertaken to clearify the influence of the particular olefin and to compare results with the data obtained by Brown *et al.*[2] The results are summarized in Table 1.

We see that the derivative of the alkylboranes formed is dialkylborane $[R_2BH]$. Under mild conditions it is possible to obtain R_2BH as the main product of both the 1: 1 and 1: 2 ratio reaction mixtures. This could be accounted for as follows: RBH_2 exists neither as a complex with other alkylboranes nor THF, but exists either free or as a very weak complex reacting much faster than BH_3 which undergoes fairly strong complexation with THF. On the other hand, R_2BH sould form a relatively stable dimer  . The rate of reaction of this dimer with olefin should be smaller than that of the corresponding dimer of monoalkylborane.

The difference between norbornene and cyclopentene is not remarkable but appreciable. In the case of norbornene, it is possible to obtain alkylborane products containing no RBH_2. If the reaction is to be used for synthesis, this undesirable by-product should be avoided.

The data differ considerably from those obtained in the earlier study.[2] Cause of this difference might be due to the difference in analytical procedure. The amounts of the alkylborane derivatives were determined by distillation of the methoxyalkylboranes formed after methanolysis of reaction products. It was found that methoxyalkylboranes can easily undergo redistribution at higher temperature.[4] In the present procedure, NMR analysis was carried out for the methanolyzed product, no high temperature treatment being involved.

The conditions for these experiments were too mild to complete the hydroboration of norbornene. Thus in Expt. H-60 (Table 1) large amounts of R_2BH and unreacted norbornene remained in the reaction mixture.

(2) Partial Alkylation of Diborane with Norbornene and Cyclopentene in THF at Room Temperature: Interesting results were obtained in the kinetic study of partial alkylation. Partial alkylation reactions were carried out at 25—28 °C for 24 h. Olefins were added to the BH_3–THF solution at 0 °C, and the reaction mixture was left to stand at room temperature for 24 h with stirring. Excess methanol was added, the same analytical procedure as that given in (1) being applied. The results are summarized in Table 2.

RBH_2 is obtained as the main product in the reaction at the ratio 1: 1, indicating the complex $[(R_2BH)_2]$, which is evidently formed initially, undergoes rearrangement during the course of longer reaction time at higher temperature to produce RBH_2.

* On leave of absence from the Research Center, Maruzen Oil Co., Ltd. Present address: Research Center, Maruzen Oil Co., Ltd., Satte-cho, Kitakatsushika-gun, Saitama, 340-01.

Table 1. Partial alkylation[a] of diborane with cyclopentene and norbornene at 0 °C for 1 h

Expt.	Olefin	$\left(\frac{\text{Olefin}}{BH_3}\right)$ Ratio $\frac{\text{mol}}{\text{mol}}$	H_2 Gas generated by methanolysis $\left(\frac{H_2\ \text{mmol}}{BH_3\ \text{mmol}}\right)$	Yield (per 100 mmol BH_3) BH_3 %	RBH_2 %	R_2BH %	R_3B %
H-56	Norbornene	1.02	1.74	43(52)[b]	2	37	9
H-59	Norbornene	2.04	1.15	16	0	71	13
H-60	Norbornene	3.08	0.42	1	0	46	53
H-57	Cyclopentene	1.04	1.92	39(49)[b]	2	45	4
H-62	Cyclopentene	2.04	1.01	13	2	56	29
c)	Cyclopentene	1		46	6	32	8 (loss 8)
	Cyclopentene	2		17	8	30	31 (loss 14)

a) Olefin was added dropwise into BH_3–THF solution at 0 °C over a period of 13 min. b) Correct value calculated from theoretical amounts of olefin. c) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Am. Chem. Soc.*, **82**, 4703 (1960).

Table 2. Partial alkylation[a] of diborane with cyclopentene and norbornene at room temperature for 24 h

Expt.	Olefin	$\left(\frac{\text{Olefin}}{BH_3}\right)$ Ratio $\frac{\text{mol}}{\text{mol}}$	H_2 Gas $\left(\frac{H_2\ \text{mmol}}{BH_3\ \text{mmol}}\right)$	Yield (per 100 mmol BH_3) BH_3 %	RBH_2 %	R_2BH %	R_3B %
H-65-1	Norbornene	1.02	2.02	11(16)[b]	65	19	0
H-64-6	Norbornene	2.04	1.13	3	30	57	15
H-66-4	Norbornene	3.10	0.00	1	0	4	95
H-58	Cyclopentene	1.04[e]	1.93	22	43	33	2
H-70-1	Cyclopentene	1.02[e]	1.79	19	45	31	5
H-67-6	Cyclopentene	2.01	1.04	6	25	48	21
	Cyclopentene	1[e]		30	45	2	19 (loss 4)
d)	Cyclopentene	2[e]		11	19	22	37—39
	Cyclopentene	2		15	44	10	42—44

a) Olefin was added dropwise into BH_3–THF at 0 °C over a period of 13 min. b) Correct value calculated from theoretical amounts of olefin. c) The same experiments were repeated in order to check the accuracy. d) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Am. Chem. Soc.*, **82**, 4703 (1960). e) BH_3 gas was passed into olefin–THF solution.

$$R_2BH + BH_3 \rightleftarrows 2RBH_2$$

The most evident difference between norbornene and cyclopentene is the disparity in the (RBH_2/R_2BH) ratio in the 1:1 reaction. The (RBH_2/R_2BH) ratio in norbornene is 3:4 (Expt. H-65). In contrast, the (RBH_2/R_2BH) ratio in cyclopentene is only 1:4—1:5 (Expt. H-58, H-70). This indicates that the stability of the (dicyclopentylborane)$_2$ complex is much higher than that of (di-*exo*-norbornylborane)$_2$ complex. A possible reason could be the difference in the steric hindrance of the two alkyl groups with large steric requirement of norbornyl group in the dimer decreasing the stability of $(R_2BH)_2$. In the 1:3 mixture of BH_3 and norbornene, the reaction proceeds almost completely to form the trialkylborane.

Thermodynamic Study of Partial Alkylation. Equilibration of BH_3–Norbornene and BH_3–Cyclopentene System in THF at Room Temperature: The reaction of BH_3 and norbornene or cyclopentene in THF was studied at room temperature in order to estimate the approximate rate of equilibration and the composition at equilibrium. The equilibration reaction was carried out using two kinds of starting materials in order to confirm that the attained composition was that of true equilibrium mixture: distribution of the kinetic mixture from BH_3 and olefin, redistribution of trialkylborane with borane. It was confirmed that the same equilibrium distribution is attained from both combinations of starting materials.

In the experiments using (BH_3+olefin) as the starting materials, the addition of olefin to BH_3–THF solution was carried out at 0 °C by the usual method, the reaction mixtures being stirred at room temperature. 1/10 aliquots were taken out at appropriate intervals and analyzed.

In the experiments using (R_3B+BH_3) as the starting material, R_3B was synthesized first by the reaction of BH_3 with olefin in 1:3 ratio at room temperature for 1 h and BH_3 was added to the solution of R_3B in THF at 0 °C. The reaction mixtures were allowed to stand at room temperature and the same sampling procedure was carried out. Representative results are shown graphically in Figs. 1—5. Data of the equilibrium

TABLE 3. EQUILIBRIUM DISTRIBUTION OF THE PARTIAL ALKYLATION OF DIBORANE WITH CYCLOPENTENE AND NORBORNENE AT ROOM TEMPERATURE IN THF

Olefin	Olefin: BH_3 Ratio	Starting material	Time to attain equilibrium distribution h	Equilibrium distribution BH_3 %	RBH_2 %	R_2BH %	R_3B %
Norbornene	1.02	Olefin+BH_3 ⟶	48	12—14	72—74	13—16	0—2
		⟵ R_3B+BH_3[a)]	48—72	14—17	72—75	13—12	0—2
	2.04	Olefin+BH_3 ⟶	24	1—3	26—27	56—57	15—18
		⟵ R_3B+BH_3[a)]	24	4—2	26—27	54—60	11—17
Cyclopentene	1.02	Olefin+BH_3 ⟶	48	24—27	46—51	24	0—6
		⟵ R_3B+BH_3[b)]	48	20—24	48—52	27—30	0—2
	2.02	Olefin+BH_3 ⟶	48	3	28—29	52—56	11—17
		⟵ R_3B+BH_3[b)]	48	3—4	25—30	52—55	12—15

a) R=tri-*exo*-norbornyl-. b) R=cyclopentyl-.

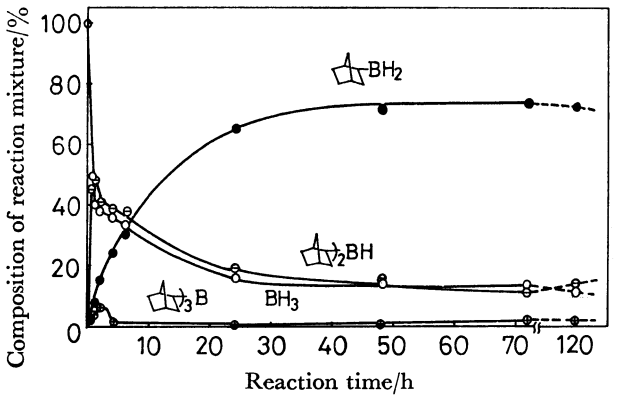


Fig. 1. The equilibration of BH_3+norbornene (1: 1)⟶ in THF solution at R.T.

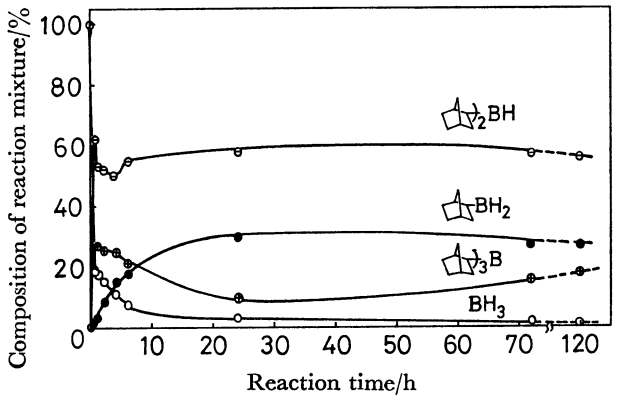


Fig. 2. The equilibration of BH_3+norbornene (1: 2)⟶ in THF solution at R.T.

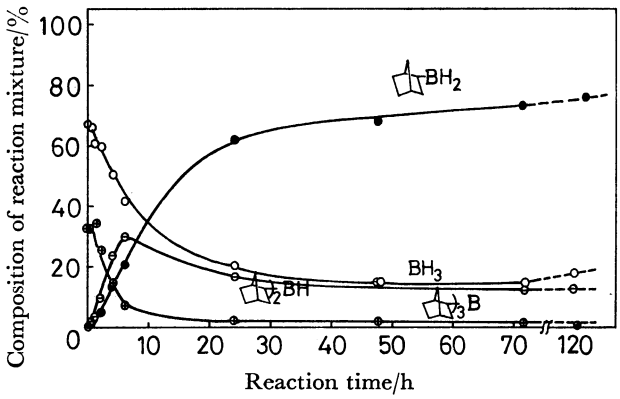


Fig. 3. The equilibration of tri-*exo*-norbornylborane +BH_3 (1: 2)⟶ in THF solution at R. T.

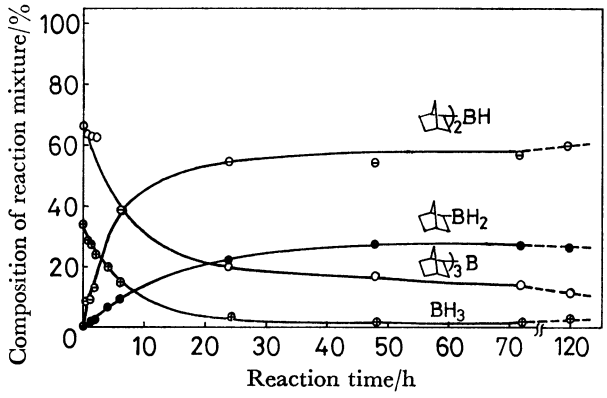


Fig. 4. The equilibration of tri-*exo*-norbornylborane +BH_3 (2: 1)⟶ in THF solution at R. T.

distributions are summerized in Table 3.

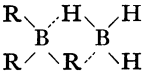
We see that the distribution of the borane products from borane and olefin and that from borane and trialkylborane of the same (olefin: BH_3) ratio are almost the same, indicating they are true equilibrium distributions. In the (olefin: BH_3) ratio=2, the composition of the equilibrium is almost the same in both norbornene and cyclopentene. On the other hand, in the (olefin: BH_3) ratio=1, it is quite different, indicating that the stabilities of the $(R_2BH)_2$ complexes of these two olefins differ considerably. The main route to give RBH_2 is postulated to be as follows.

(i) Starting material: Olefin+BH_3

$$BH_3 + 2\text{Olefin} \xrightarrow{\text{fast}} R_2BH$$

$$R_2BH + BH_3 \xrightarrow{\text{slow}} 2RBH_2$$

(ii) Starting material: R_3B+BH_3

(ii-a) $R_3B + BH_3 \rightleftharpoons$  ⟶ $R_2BH + RBH_2$

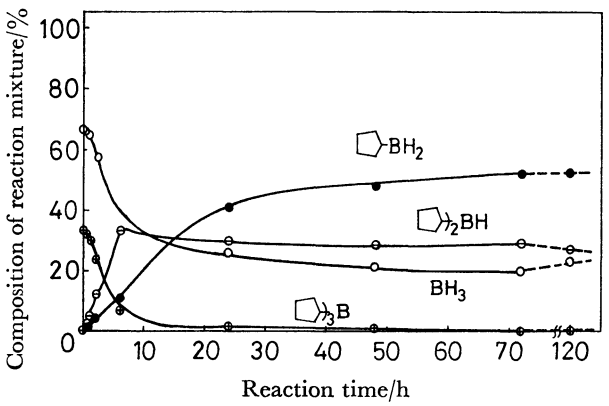
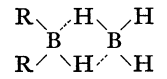
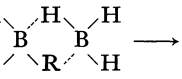


Fig. 5. The equilibration of tricyclopentylborane+BH_3 (1:2)→ in THF solution at R. T.

(ii-b) $R_2BH + BH_3 \rightleftharpoons$  $\rightleftharpoons$  $\longrightarrow 2RBH_2$

In the case of norbornene (Fig. 3), the rate of (ii-b) reaction should be much smaller than that of cyclopentene (Fig. 5).

Mono-*exo*-norbornylborane can be synthesized in 72—75% yield by the reaction of norbornene and BH_3 in 1:1 ratio at room temperature for 40 h.

Experimental

Materials. Norbornene (reagent grade, Aldrich Chemical Co.), mesitylene (Coleman and Bell Co.) for the internal standard of NMR analysis and methanol (Mallinckrodt Chemical Works) for the methanolysis of products were used without further purification. Cyclopentene (Phillips Petroleum Co.) was distilled from lithium aluminum hydride and stored under nitrogen. The other reagents were the same as those used by Brown *et al.*[2]

Partial Alkylation of BH_3 with Olefin at 0 °C. Experiments were carried out with use of a 100-ml 2-necked round-bottom flask fitted with a reflux condenser which was connected with glass stopcock and a bubbling gas outlet at the top and a side arm fitted with a rubber cap to permit the flushing of all systems with nitrogen before the reaction.

A solution of 10 mmol, 20 mmol, or 30 mmol norbornene in THF (2.20 M) was added to a solution of 10 mmol of BH_3 in THF (2.69 M) at 0 °C over a period of 13 min.

The reaction was carried out at 0 °C for 1 h. The ice bath was then removed and methanol (50—100% excess) was added dropwise at room temperature. Stirring was continued for 10 min, and all the hydrogen gas generated during the course of methanolysis was collected into the gas burrette and measured. The solvent (THF), excess MeOH, and methylborate [$B(OCH_3)_3$] were removed by vacuum distillation (30—35 °C, 15—13 mmHg, 20 min) and trapped with a Dry Ice bath. The trapped mixture was analyzed for boric acid by titration with standard sodium hydroxide in the presence of 10 mmol of mannitol.

The residue containing dimethoxy-*exo*-norbornylborane, methoxy-di-*exo*-norbornylborane, and tri-*exo*-norbornylborane was analyzed by NMR. The amounts of mono- and di-*exo*-norbornylborane could be estimated. The amount of tri-*exo*-norbornylborane was calculated as the difference of the sum of the initial borane and the amounts of $B(OCH_3)_3$, $RB(OCH_3)_2$, $R_2B(OCH_3)$ found.

Equilibration of BH_3 and Olefin (1: 1 or 1: 2). 80 mmol of norbornene in 26 ml of THF was added slowly to a stirred solution of 80 mmol (2.69 M) BH_3–THF solution at 0 °C over a period of 13 min. The ice bath was then removed and the reaction mixture was stirred at room temperature.

At certain intervals, 1/10 aliquots were withdrawn with a hypodermic syringe, weighed and put into a 50-ml two-necked flask fitted with a reflux condenser and a side arm for a rubber cap purged with nitrogen, subsequent treatment being the same as described above.

Equilibration of BH_3 and R_3B. 90 mmol of norbornene in 20 ml of THF was added slowly to a stirred solution of 30 mmol BH_3–THF at 0 °C over a period of 13 min. The reaction mixture was kept at room temperature for 1 h to complete the formation of tri-*exo*-norbornylborane. The mixture was then cooled in an ice bath to 0 °C and 15 mmol of BH_3–THF solution was added dropwise to the mixture. The ice bath was removed and the reaction mixture was stirred at room temperature. At certain time intervals, 1/10 aliquots were withdrawn with a syringe, subsequent treatment being the same as described above.

NMR Analysis. The methoxyl protons of $RB(OCH_3)_2$ and $R_2B(OCH_3)$ have a sharp singlet peak. The contents of these compounds in the residue were measured by use of mesitylene as an internal standard. It has a sharp singlet peak of benzene proton at $\delta=6.67$, no absorption at $\delta=3$—4. The experiments were carried out in nitrogen. NMR spectral data are given in Table 4.

Table 4. NMR spectral data

Methoxy borane	δ/ppm
Methoxydi-*exo*-norbornylborane	3.61
Dimethoxy-*exo*-norbornylborane	3.50
Methoxydicyclopentylborane	3.65
Dimethoxycyclopentylborane	3.52

The author wishes to express his sincere thanks to Prof. Herbert C. Brown for his guidance throughout the course of this study.

References

1) H. Taniguchi, *Bull. Chem. Soc. Jpn.*, **52**, 2942 (1979).
2) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Am. Chem. Soc.*, **82**, 4703 (1960).
3) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press (1972), p. 269.
4) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 6983 (1970).