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An Examination of the Displacement Reactions in Alkyldicyclohexylborane and Alkyldi-exo-norbornylborane

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Displacements involving the reaction of olefins with alkyldicyclohexylborane and alkyldi-*exo*-norbornylborane were studied. In the case of alkyldicyclohexylborane, the 1-ethylbutyl group could be displaced selectively by 1-decene to produce hexenes. However, the hexyl group could not be displaced selectively, the reaction proceeding to produce both 1-hexene and cyclohexene. In contrast, in the case of alkyldi-*exo*-norbornylborane, the norbornyl group bonded so tightly to the boron atom that it was possible to displace both the 1-ethylbutyl and the hexyl groups selectively and completely by 1-decene with no loss of 2-norbornyl–boron bonds. The results suggest the possibility of contrathermodynamic isomerization of olefins by the combination of "isomerization-displacement" with di-*exo*-norbornylborane.

Organoboranes undergo displacement of contained olefins when they are heated in the presence of another olefin.[1-4]

$$(RCH_2CH_2)_3B + 3R'CH{=}CH_2 \rightleftharpoons 3RCH{=}CH_2\uparrow + (R'CH_2CH_2)_3B$$

Detailed studies of this reaction have been published by Brown and his coworkers using homogeneous trialkyl- or dialkylboranes (R_3B or R_2BH).[5,6]

The displacement reaction is a reversible reaction and can be brought to completion by using an excess of olefin or by removing the displaced olefin from the reaction media by distillation.

The rate of the displacement reaction is essentially independent of the concentration of the displacing olefin.

The rate of displacement varies with the type and structure of the olefin bonded to boron atom.

Results and Discussion

In this study, the displacement reaction involving the organoboranes derived from the hydroboration of several types of olefins with dicyclohexylborane and di-*exo*-norbornylborane has been examined. It was thought to be interest to clarify the displacement reaction with organoboranes which have more than one alkyl group in a molecule in order to confirm which alkyl group is more easily displaced. Such a study would establish the conditions under which only one attached alkyl group could be selectively displaced, making it possible to use repeatedly a particular dialkylboryl unit, such as dicyclohexylboryl- or di-*exo*-norbornyl-boryl-group.

In studying the displacement reaction, it was very difficult to follow on a small scale the reaction process quantitatively by determining the amounts of olefin displaced.

An alternative procedure was adopted. Aliquots of the reaction mixture were removed and oxidized and the decreasing or increasing amounts of alcohols determined by glpc analysis were taken as a measure of the displacement reaction. The following standard procedure was utilized.

A three-necked flask fitted with a thermometer and a side arm closed by rubber septum was attached to a microdistillation system. The olefins were hydroborated using dicyclohexylborane or di-*exo*-norbornylborane, which had been prepared from cyclohexene or norbornene in THF solvent and used *in situ*. Hydroboration was carried out in diglyme or triglyme solution. After the completion of the hydroboration, all THF was removed by vacuum evaporation. Then a 100% excess of 1-decene and calculated amount of the internal standard were added to the reaction mixture. The mixture was rapidly heated to the desired temperature. At appropriate intervals of time, aliquots were withdrawn from the reaction flask and oxidized with alkaline hydrogen peroxide. Alcohols thus produced were taken up in ether and the dried ether extract was analyzed by NMR. The ratio of the original alkyl groups displaced from the organoborane was calculated from the decreasing amount of alcohols found in each aliquot.

During the course of reaction, the displaced olefins were removed from the distillation system into a cooled receiver and the distillate was analyzed by GLPC. A static nitrogen atmosphere was maintained throughout the reaction.

Displacements Involving Hexyldicyclohexylboranes. The displacement reaction with hexyldicyclohexylborane was carried out at different temperatures in the hope that only the hexyl group would be displaced by 1-decene so that the dicyclohexylborane moiety could be used repeatedly. However, it was found that the cyclohexyl group was readily eliminated to generate cyclohexene so that it was not practical to remove the hexyl group selectively. The results are given in Table 1. We see that the hexyl moiety of hexyldicyclohexylborane is displaced a little more easily than cyclohexyl moiety. However, the difference in the rate of displacement is too small to displace only the hexyl group. Both the hexyl and the cyclohexyl groups are displaced almost completely under these conditions and analysis of the decanols by GLPC established that there is no significant loss of boron–hydrogen bond in the process.

The purity of displaced hexene is much more selective at higher temperature than at lower temperature. This indicates that at lower temperature the displacement rate of the hexyl group is low. Consequently, some of

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Table 1. Displacement reaction with hexyldicyclohexylborane[a)]

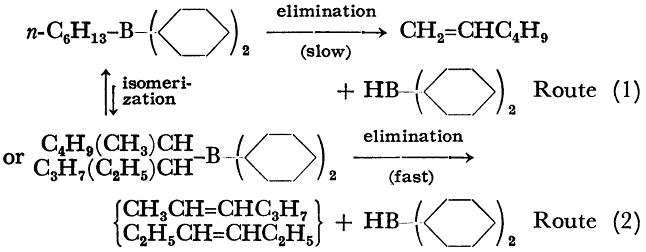
Reaction temp	Displaced ratio of original alkyl group 160 °C		130 °C	
Reaction time/h	Hexyl %	Cyclohexyl %	Hexyl %	Cyclohexyl %
0	0	0		
0.5	37	14	0	0
1	60	38	0	0
2	76	44	17	0
4	89	62	54	24
6	93	78	63	33
8	97	85	65	33
24	100	99	83	68
48			93	86
72			100	94

Distilled olefins

Hexene	%	Cyclohexene %	Hexene	%	Cyclohexene %
1-Hexene	94.3	100	1-Hexene	73.5	100
trans-2-Hexene	0.7		*trans*-2-Hexene	1.3	
cis-2-Hexene	3.9		*cis*-2-Hexene	22.6	
3-Hexene	1.1		3-Hexene	2.6	

a) Initial charge: hexyldicyclohexylborane 10 mmol, 1-decene 60 mmol, solvent (diglyme or triglyme) 10 ml, internal standard (tridecane) 5 mmol.

the hexyldicyclohexylborane is isomerized to the isomeric *sec*-hexyldicyclohexylborane and the *sec*-hexyl groups thus formed are much more easily eliminated from the boron atom than the hexyl group. The relationship is illustrated as follows:



At lower temperature, Route 1 is so slow that Route 2 would play an important role.

$C_3H_7(C_2H_5)CH$-B-(cyclo-C_6H_{11})$_2$: It has been established that the secondary alkyl group is displaced much more easily than the normal alkyl group.[6)] The displacement reaction with 1-ethylbutyldicyclohexylborane was undertaken in order to compare the displacement rate of the secondary alkyl group with that of the cyclohexyl group. The results are given in Table 2. We see that it is possible to displace the 1-ethylbutyl group selectively. The best results were obtained under the conditions 130 °C for 1—1.5 h in triglyme solvent, more than 94% of the 1-ethylbutyl group being displaced by 1-decene with negligible loss of the cyclohexyl group.

Table 2. Displacement reaction with 1-ethylbutyldicyclohexylborane[a)]

Reaction temp	Displaced ratio of original alkyl group 160 °C		130 °C	
Reaction time/h	1-Ethylbutyl %	Cyclohexyl %	1-Ethyl butyl %	Cyclohexyl %
0	0	0		
0.5	98	24	81	0
1	98	52	94	0
2	98	65	98	11
4	98	85	98	31
6	99	92	98	45
8	99	96	97	49
24	100	99	99	79
48			99	92
72			100	98

Distilled olefins

Hexene	%	Cyclohexene %	Hexene	%	Cyclohexene %
1-Hexene	0.1	100	1-Hexene	0.1	100
cis-2-Hexene	42.8		*cis*-2-Hexene	57.3	
trans-2-Hexene	57.1		*trans*-2-Hexene	42.6	
3-Hexene			3-Hexene		

a) Initial charge: 1-ethylbutyldicyclohexylborane 10 mmol, 1-decene 60 mmol, solvent (triglyme) 10 ml, internal standard (tridecane) 4.83, 5.33 mmol

The concentration of 1-hexene in the displaced olefins was very low although under these conditions some isomerization of 1-ethylbutyldicyclohexylborane to hexyldicyclohexylborane would have been expected. The reason must be that the elimination of 1-ethylbutyl group is relatively fast and the dissociated internal hexenes fail to associate again with the dicyclohexylborane because of the faster reason with 1-decene. This behavior is different from that observed in the case of hexyldicyclohexylborane in which only a little of 2- and 3-hexenes were present in the distilled hexenes.

There is a considerable difference in the distribution of the displaced hexenes at different temperatures.

n-*C_6H_{13}-B-(cyclo-C_6H_{11})$_2$*. *Under Neat Conditions*: The displacement reaction with hexyldicyclohexylborane under neat conditions was carried out in the hope that the rate of elimination of the cyclohexyl group would be much smaller in the absence of etheric solvent so that the selective displacement of the hexyl group would be possible. The results are summarized in Table 3 and compared with those of the displacement reaction in diglyme.

It was unexpected that the absence of the etheric solvent failed to decelerate the rate of the displacement reaction (Table 3). It was impossible to displace only the hexyl group under the conditions of a neat reaction.

Cyclopentyldicyclohexylborane. In order to examine which group, cyclopentyl- or cyclohexyl-, is more easily eliminated from the mixed organoborane, the displacement reaction with cyclopentyldicyclohexylborane was

Table 3. Effect of solvent in the displacement reaction with hexyldicyclohexylborane[a] at 160 °C

Solvent	Displaced ratio of original alkyl group: Neat		Diglyme 10 ml	
Reaction time/h	Hexyl %	Cyclohexyl %	Hexyl %	Cyclohexyl %
0	0	0		
0.5	40	26	37	14
1	55	41	60	38
2	62	43	76	44
4	88	61	89	62
6	95	84	93	78
8	97	91	97	85
24	100	99	100	99

Distilled olefin: Hexene	%	Cyclohexene %	Hexene	%	Cyclohexene %
1-Hexene	86.9	100	1-Hexene	94.3	100
trans-2-Hexene	1.1		*trans*-2-Hexene	0.7	
cis-2-Hexene	9.9		*cis*-2-Hexene	3.9	
3-Hexene	2.1		3-Hexene	1.1	

a) Initial charge: hexyldicyclohexylborane 10 mmol, 1-decene 60 mmol, solvent neat or diglyme, internal standard (tridecane) 5.0 mmol.

Table 4. Displacement reaction with cyclopentyldicyclohexylborane at 160 °C

Reaction time/h	Displaced ratio of original alkyl group: Cyclopentyl	Cyclohexyl
0	0	0
0.5	62	23
1	87	46
2	97	65
4	99	84
6	99	91
8	100	96
24	100	100

a) Initial charge: cyclopentyldicyclohexylborane 10 mmol, 1-decene 60 mmol, solvent (triglyme) 10 ml, internal standard (dodecane) 5.5 mmol.

undertaken. The cyclopentyl group is displaced at approximately twice the rate of the cyclohexyl group (Table 4).

*Displacement Reaction with Alkyldi-*exo*-norbornylborane.* The norbornyl group is so tightly bound to a boron atom that is not displaced by 1-decene under the same conditions as at which displacement of other olefins could proceed.[6)] Thus, it was anticipated that treatment of hexyldi-*exo*-norbornylborane with 1-decene might result in selective elimination of the hexyl group. Difficulty in testing this procedure is caused by the relative unavailability of pure dinorbornylborane which cannot be synthesized directly from norbornene and BH_3.[7)] Thus crude (71%) di-*exo*-norbornylborane, which can be prepared directly from BH_3 and norbornene, was used.

The best conditions for preparing di-*exo*-norbornylborane directly are as follows. A norbornene solution in THF is added to a BH_3–THF solution in the ratio (norbornene/BH_3)=2.0 at 0 °C and the mixture is stirred at 0 °C for 1 h. On completion of the process, the mixture contained 71% di-*exo*-norbornylborane, 13% tri-*exo*-norbornylborane, 16% BH_3, but no mono-*exo*-norbornylborane.

It might be possible to determine the relative elimination rate of the norbornyl group and other alkyl groups from the data obtained by using the crude di-*exo*-norbornylborane.

Table 5. Displacement reaction with hexyldi-*exo*-norbornylborane and 1-ethylbutyldi-*exo*-norbornylborane[a] at 160 °C

Raw material	Displaced ratio of original alkyl group: Hexyldi-*exo*-norbornylborane		1-Ethylbutyldi-*exo*-norbornylborane	
Reaction time/h	Hexyl %	Norbornyl %	1-Ethylbutyl %	Norbonyl %
0	0	0	0	0
0.5	13	0	96	0
1	28	0	96	0
2	47	0	97	0
4	77	0	96	0
6	86	0	97	9
8	90	2.3	98	11
24	98	21	100	21

Distilled olefins: Hexene	%	Norbornene %	Hexene	%	Norbornene %
1-Hexene	95.7	100	1-Hexene	0.1	100
2-Hexenes 3-Hexene	4.3		*cis*-2-Hexene	41.3	
			trans-2-Hexene 3-Hexene	58.6	

a) Initial charge: raw material 10 mmol, 1-decene 60 mmol, solvent (triglyme) 10 ml, internal standard (tridecane) 5.1 mmol.

*Hexyldi-*exo*-norbornylborane and 1-Ethylbutyldi-*exo*-norbornylborane.* Displacement reaction with hexyldi-*exo*-norbornylborane and 1-ethylbutyldi-*exo*-norbornylborane were carried out to see whether selective displacement of hexyl group is possible in these derivatives (Table 5). It was confirmed that selective displacement of the hexyl group is possible. For example, 90% of the hexyl group was removed with only 2% loss of the norbornyl group by the displacement reaction with hexyldi-*exo*-norbornylborane at 160 °C for 8 h. Even more favorable conditions would be found for complete selective displacement in hexyldi-*exo*-norbornylborane by working at lower temperatures. The results indicate

Table 6. Displacement reaction with cyclohexyldi-*exo*-norbornylborane[a] at 160 °C

Reaction time/h	Displaced ratio of original alkyl group Cyclohexyl %	Norbornyl %
0	0	0
0.5	28	0
1	47	0
2	63	0
4	85	1.7
6	94	14
8	97	11.5

a) Initial charge: cyclohexyldi-*exo*-norbornylborane 10 mmol, 1-decene 60 mmol, solvent (triglyme) 10 ml, internal standard (tridecane) 5.29 mmol.

that the norbornyl group can be eliminated by 1-decene under severe conditions. It was found by means of GLPC analysis of the distilled olefins after 24 h reaction that norbornene is present in a large amount.

*Cyclohexyldi-*exo*-norbornylborane.* The displacement reaction with cyclohexyldi-*exo*-norbornylborane was carried out to make clear the relative rate of displacement by 1-decene of the cyclohexyl group and the norbornyl group (Table 6). It is evident that the cyclohexyl group can be displaced selectively by 1-decene from cyclohexyldi-*exo*-norbornylborane.

Di-*exo*-norbornylborane is an excellent agent for the contrathermodynamic isomerization of olefin.[8] The isomerization rate was almost the same as that of dicyclohexylborane, the selectivity of the primary position being a little better. It was found that di-*exo*-norbornylborane is an excellent agent for a selective displacement reaction, much better results being expected by using pure di-*exo*-norbornylborane which could be synthesized by indirect methods.

Di-*exo*-norbornylborane is an excellent agent for achieving the movement of a double bond from the interior of a carbon chain to the terminal position of olefins *via* hydroboration-isomerization displacement.

Experimental

Materials. The solvents, olefins and preparation of the BH_3–THF solution have been described.[6] Norbornene (reagent grade, Aldrich Chemical Co.) was used without further purification and stored under nitrogen as a THF solution in a volumetric flask. 1-Decene (Chem Samples Co.) was distilled from lithium aluminum hydride and stored under nitrogen.

Hydroboration-Displacement Experiments. *Alkyldicyclohexylborane*: After all systems were dried and flushed with nitrogen, 4 ml (10.8 mmol) of BH_3–THF solution (2.70 M) and 10 ml of solvent (diglyme or triglyme) were placed in a 50 ml three-necked flask fitted with a thermometer, a side arm containing a rubber septum and a distillation system, consisting of a Vigreaux column ($2\phi \times 13$ 1 cm), a distillation head, a Liebig condenser, and a receiver which can be cooled in an ice bath, the top of which is connected to a Hg bubbler to maintain a static pressure of nitrogen gas. 2.10 ml (21 mmol) of cyclohexane was added slowly at 0 °C by means of a hypodermic syringe. After addition, the ice bath was removed and the mixture was stirred at room temperature for 2 h. The dicyclohexylborane thus prepared was used *in situ* in subsequent processes.

The reaction mixture, containing precipitated dicyclohexylborane dimer was cooled in an ice bath and 10 mmol of each olefin (directly or as a THF solution) was added dropwise at 0 °C. Stirring was continued at 0 °C for 3 h. The ice bath was then removed and the reaction mixture was stirred overnight (13—15 h) at room temperature in order to complete the reaction.

The flask was connected to a vacuum system at the top of the receiver and almost all of the THF and unreacted olefins were removed from the mixture by vacuum evaporation (35 °C, 10—13 mmHg, 20 min). 11.4 ml (60 mmol) of 1-decene and a measured amount of internal standard (*n*-dodecane or *n*-tridecane) were then added by means of a hypodermic syringe. The flask was dipped into an oil bath, the temperature of which was controlled with an electric temperature controller. At certain time intervals, 1 ml aliquots were withdrawn with a hypodermic syringe, the samples being oxidized by alkaline hydrogen peroxide in the usual manner. The alcohols formed were extracted with 10 ml of ether and dried on K_2CO_3.

The samples were analyzed by gas chromatography (Carbowax 20 M, 10% on Varaport 100/120, 1/8″×12 ft, FID). During the course of displacement reaction, the displaced olefin was collected into an ice-cooled receiver, and the distribution of isomers of displaced olefins was analyzed by gas chromatography. During the entire operation, the system was maintained under a static pressure of nitrogen gas.

*Alkyldi-*exo*-norbornylborane*: A 4 ml sample of BH_3–THF solution (10.7 mmol) was placed in a 50 ml three-necked flask and cooled in an ice bath. A 6.69 ml (21.4 mmol) of norbornene–THF solution (3.20 M) was added slowly at 0 °C by means of a hypodermic syringe and the mixture was maintained at 0 °C for 1 h. Crude di-*exo*-norbornylborane solution was used *in situ* in subsequent processes. 10 ml of each of the olefins and 10 ml of solvent (diglyme or triglyme) were added slowly at 0 °C to the mixture. The same procedure as that for monoalkyldicyclohexylborane then followed.

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