and 4.72 mL of the cold ThxBHCl·SMe_2 (10.0 mmol) solution in CH_2Cl_2 was added quickly via syringe. A 0.5-mL sample was analyzed with time, as described above. As shown in Figure 2, the reaction was analyzed at 15 (65%), 30 (74%), 45 (79%), 60 (82%), 90 (86%), 120 (87%), 180 (90%), 240 (91%), and 630 min (95%).

This procedure was then repeated with 2 equiv of methyl sulfide as follows. A 50-mL flask was charged at 25 °C with 1.80 mL of CH_2Cl_2, 1.00 mL of *n*-octane (0.663 g, 5.80 mmol, internal standard), 1.01 mL of cyclohexene (0.820 g, 10.0 mmol), and 1.48 mL of methyl sulfide (1.265 g, 20.7 mmol). The resulting clear solution was then equilibrated at 25.0 ± 0.05 °C and 4.72 mL of the cold ThxBHCl·SMe_2 (10.0 mmol) solution in CH_2Cl_2 was added quickly via syringe. Aliquots of 0.5 mL were analyzed with time, as described above. As shown in Figure 2, the reaction was analyzed at 15 (55%), 30 (65%), 45 (70%), 60 (73%), 90 (78%), 120 (81%), 180 (85%), 240 (87%) and 600 min (93%).

Acknowledgment. We express our thanks to Dr. K. K. Wang for his assistance in the preparation of the figures for this manuscript. This study was facilitated by grants from the National Science Foundation (CHE 79-18881) and the National Institutes of Health (GM 10937-18).

Registry No. $BH_2Cl·SMe_2$, 63348-81-2; ThxBHCl·SMe_2, 75067-06-0; thexylcyclopentyl ketone, 80375-46-8; 1-decene, 872-05-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 2-methyl-1-butene, 563-46-2; 4-pentenyl acetate, 1576-85-8; 2-methyl-2-butene, 513-35-9; *cis*-2-pentene, 627-20-3; *cis*-3-hexene, 7642-09-3; *cis*-4-methyl-2-pentene, 691-38-3; cyclopentene, 142-29-0; 2-methyl-1-pentene, 763-29-1; *p*-methoxystyrene, 637-69-4; 1-methylcyclopentene, 693-89-0; styrene, 100-42-5; norbornene, 498-66-8; *cis*-4,4-dimethyl-2-pentene, 762-63-0; cyclohexene, 110-83-8; α-methylstyrene, 98-83-9; 1-methylcyclohexene, 591-49-1; α-pinene, 80-56-8.

Hydroboration. 60. Effect of Structure on the Relative Reactivity of Representative Olefins toward Hydroboration by Thexylchloroborane–Methyl Sulfide

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The relative reactivities of 24 alkenes of different structural types toward hydroboration by thexylchloroborane–methyl sulfide (ThxBHCl·SMe_2) were determined in CH_2Cl_2 at 25 °C. The data for these reactions are presented to show how structural variations in the olefins are reflected in their relative reactivities. Whenever possible, the selectivity observed with ThxBHCl·SMe_2 is compared and contrasted with that observed previously for 9-borabicyclo[3.3.1]nonane (9-BBN), disiamylborane (Sia_2BH), and dibromoborane–methyl sulfide ($HBBr_2·SMe_2$). Like Sia_2BH and 9-BBN, ThxBHCl·SMe_2 has large steric requirements, reacting preferentially with the least hindered carbon atom of the double bond. However, ThxBHCl·SMe_2 is much more sensitive to electronic factors than either Sia_2BH or 9-BBN. This is attributed to the higher Lewis acidity of the ThxBHCl·SMe_2 reagent. The reagent exhibits a far higher reactivity toward cis alkenes relative to trans than any hydroborating reagent hitherto examined, giving cis/trans reactivity ratios of the order of 100/1.

Thexylchloroborane–methyl sulfide[2,3] (ThxBHCl·SMe_2) is a new, stable reagent for the selective hydroboration of alkenes of different structural types. For most olefins, hydroboration with ThxBHCl·SMe_2 proceeds cleanly with high regio- and stereospecificity.[2] This reagent reacts with simple terminal or disubstituted alkenes to produce isomerically pure thexylalkylchloroboranes. These versatile intermediates have been used effectively to couple two different primary alkyl groups on boron, providing new syntheses of unsymmetrical ketones,[3,4] alkynes,[5] and trans olefins.[6] As a prelude to incorporating unsaturated substrates in these synthetic procedures, we undertook a relative rate study of olefin hydroboration utilizing ThxBHCl·SMe_2 in CH_2Cl_2 at room temperature to determine the potential of this new reagent for selective hydroborations.

Results and Discussion

Competitive Hydroboration of Alkenes with ThxBHCl·SMe_2. The time required to achieve essentially complete hydroboration of different types of oelfins with ThxBHCl·SMe_2 in CH_2Cl_2 was established in an earlier study.[2] In general, longer reaction times were required as the steric requirements of the double bond increased. It seemed likely that the selective hydroboration of terminal alkenes in the presence of highly hindered double bonds could be achieved. For comparison of the reactivities of more structurally similar olefins, the relative reactivities were determined under competitive conditions. A solution containing equimolar quantities of two olefins (0.50 M in CH_2Cl_2) and a suitable inert hydrocarbon as an internal standard for GLC analysis was treated with only 1 equiv of ThxBHCl·SMe_2 (0.50 M in CH_2Cl_2). The resulting solution was stirred at 25.0 °C for sufficient time to allow complete consumption of the ThxBHCl·SMe_2. After the reaction was quenched at 0 °C, the ratios of unreacted substrates to the internal standard were determined by GLC. The relative reactivity of each olefin pair was then calculated by using the Ingold and Shaw expression (see the Experimental Section).[7] Each olefin pair was carefully

(1) Graduate research assistant on temporary academic leave from Monsanto Agricultural Products Co.
(2) Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D., preceding paper in this issue.
(3) Zweifel, G.; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919–5920.
(4) (a) Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 4542–4543. (b) Kulkarni, S. U.; Lee. H. D.; Brown, H. C., *Synthesis*, in press.
(5) Wang, K. K.; Sikorski, J. A.; Brown, H. C., manuscript in preparation.
(6) Brown, H. C.; Lee, H. D.; Kulkarni, S. U., *Synthesis*, in press.
(7) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918–2926.

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Table I. Normalized Relative Reactivities of Representative Olefins toward ThxBHCl·SMe_2 in CH_2Cl_2 at 25 °C (1-Hexene = 100)

olefin	relative reactivity
1-hexene	100
1-octene	98
cyclooctene	89
3-methyl-1-hexene	48
2-methyl-1-pentene	41
cycloheptene	12
cis-3-hexene	11
cis-2-pentene	8.5
cis-4-methyl-2-pentene	7.7
4-vinylanisole	6.3
cyclopentene	2.2
styrene	1.1
3,3-dimethyl-1-hexene	0.96
norbornene	0.63
cis-4,4-dimethyl-2-pentene	0.28
2-methyl-2-pentene	0.26
1-methylcyclopentene	0.15
trans-3-hexene	0.12
trans-2-pentene	0.12
trans-2-hexene	0.12
α-methylstyrene	0.11
trans-4-methyl-2-pentene	0.070
cyclohexene	0.072
1-methylcyclohexene	0.0016

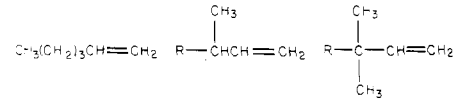
selected so that the observed relative reactivity never exceeded 10, in order to minimize the effect of the experimental error inherent in the GLC analyses. The relative reactivity data obtained for ThxBHCl·SMe_2 are arranged in decreasing order of reactivity relative to 1-hexene (100) and are summarized in Table I.

Whereas diborane is rather insensitive to the structural features of the olefin in the hydroboration reaction,[8] other borane derivatives are much more discriminating. Sia_2BH,[8] 9-BBN,[9] and $HBBr_2·SMe_2$[10] have all exhibited unusual selectivity in the monohydroboration of alkenes. The data in Table I suggest that ThxBHCl·SMe_2 also possesses unique selectivity as a hydroborating agent. The data obtained for ThxBHCl·SMe_2 is presented below to show how structural modifications of the olefins are reflected in their relative reactivities. Whenever possible, the selectivity observed with ThxBHCl·SMe_2 is compared and contrasted with that observed previously for 9-BBN, Sia_2BH, and $HBBr_2·SMe_2$.

Terminal Alkenes, RCH=CH_2. The rate of hydroboration of straight-chain terminal alkenes with ThxBHCl·SMe_2 is essentially independent of chain length. Thus, 1-hexene and 1-octene exhibit comparable reactivities with ThxBHCl·SMe_2. Similar results have been observed previously in the hydroboration of simple terminal olefins with 9-BBN and Sia_2BH.

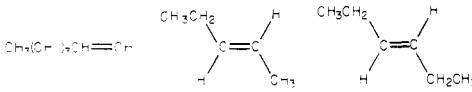
	$CH_3(CH_2)_3CH=CH_2$	$CH_3(CH_2)_5CH=CH_2$
ThxBHCl·SMe_2	1.00	0.98
Sia_2BH	1.00	1.08
9-BBN	1.00	1.10

Added branching at the allylic position causes a significant decrease in the rate of hydroboration with ThxBHCl·SMe_2. The addition of one methyl group at this position (3-methyl-1-hexene) decreases the rate by a factor of 2. This decrease in reactivity displayed by ThxBHCl·SMe_2 parallels that observed previously with Sia_2BH and 9-BBN. The addition of two methyl groups at the allylic carbon (3,3-dimethyl-1-hexene) causes a tenfold decrease in the rate of hydroboration with ThxBHCl·SMe_2. In this respect, ThxBHCl·SMe_2 resembles Sia_2BH much more closely than 9-BBN. These results suggest that ThxBHCl·SMe_2, like Sia_2BH, is quite sensitive to the steric requirements of the double bond in the hydroboration reaction.



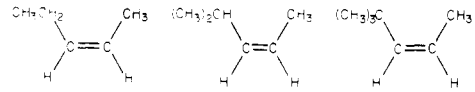
ThxBHCl·SMe_2 (R = *n*-C_3H_7)	1.00	0.48	0.010
Sia_2BH (R = CH_3)	1.00	0.57	0.047
9-BBN (R = CH_3)	1.00	0.50	0.24

Internal Alkenes. Internal alkenes are much less reactive than terminal alkenes toward hydroboration by ThxBHCl·SMe_2. The observed rate of hydroboration of *trans*-2-pentene or *trans*-3-hexene is 800 times slower than 1-hexene. In this respect, the selectivity of ThxBHCl·SMe_2 significantly exceeds that observed previously with 9-BBN. The sensitivity of ThxBHCl·SMe_2 to the steric environment of the double bond again parallels that observed with Sia_2BH.



ThxBHCl·SMe_2	830	1.0	1.0
Sia_2BH	500	1.5	1.0
9-BBN	83		1.0

As observed previously with terminal alkenes, additional branching at a site close to the double bond also decreases the rate of hydroboration of internal alkenes with ThxBHCl·SMe_2. While the introduction of one methyl group (*cis*-4-methyl-2-pentene) causes only a moderate reduction in reactivity, the addition of two methyl groups (*cis*-4,4-dimethyl-2-pentene) causes the rate of hydroboration to drop sharply. In this regard, the sensitivity of ThxBHCl·SMe_2 toward steric influences again parallels that observed previously with Sia_2BH.



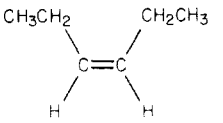
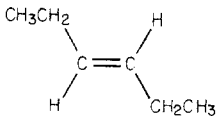
ThxBHCl·SMe_2	1.00	0.90	0.033
Sia_2BH	1.00	0.25	0.040
9-BBN	1.00	0.61	0.38

Cis and Trans Isomers. Sia_2BH hydroborates cis alkenes at a significantly faster rate than that of the corresponding trans isomers. This marked preference for the cis isomer has been attributed to the increased strain of the cis double bond.[12] In contrast, 9-BBN was reported to hydroborate trans alkenes faster than their cis isomers.[9a] A more recent investigation of the hydroboration of cis/trans pairs with 9-BBN demonstrated that there was little selectivity with this reagent.[13] A slight preference for the trans isomer was observed in some cases, while a slight preference for the cis isomer was observed in others.

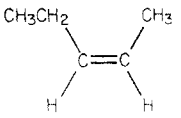
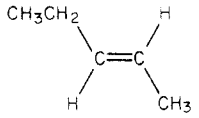
On the other hand, ThxBHCl·SMe_2 displays a much higher selectivity than Sia_2BH in the hydroboration of

(8) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063–2065.
(9) (a) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297–5301. (b) Vishwakarma, L. C.; Fry, A. *J. Org. Chem.* **1980**, *45*, 5306–5308.
(10) Brown, H. C.; Campbell, J. B., Jr. *J. Org. Chem.* **1980**, *45*, 389–395.
(11) Values observed for 1-octene vs. *cis*-4-octene.
(12) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1961**, *83*, 3417–3422.
(13) Brown, H. C.; Nelson, D. J., unpublished results.

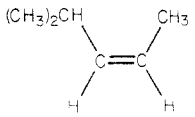
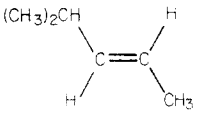
cis/trans pairs. In every pair studied, ThxBHCl·SMe_2 exhibited a much higher preference for the cis isomer than was previously observed with Sia_2BH.

ThxBHCl·SMe_2	92	1.0
Sia_2BH	10	1.0
9-BBN[13]	2.0	1.0

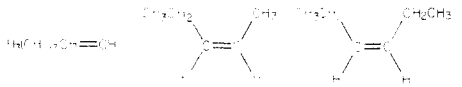



ThxBHCl·SMe_2	71	1.0
Sia_2BH	6.7	1.0
9-BBN[9a]	0.35	1.0

ThxBHCl·SMe_2	110	1.0
Sia_2BH	5.0	1.0
9-BBN[13]	3.3	1.0

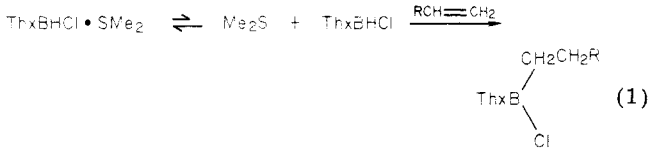
The higher reactivity of cis alkenes reduces the ability of ThxBHCl·SMe_2 to distinguish cis alkenes from terminal alkenes. Thus, the reactivity of cis alkenes relative to simple terminal alkenes is much smaller than that previously discussed for the trans isomers. In this respect, the selectivity of ThxBHCl·SMe_2 resembles that observed with $HBBr_2$·SMe_2. However, these reagents are much less selective than either Sia_2BH or 9-BBN in their ability to distinguish cis alkenes from terminal alkenes.



ThxBHCl·SMe_2	9.1	0.77	1.0
$HBBr_2$·SMe_2[11]	5.0		1.0
Sia_2BH	50	1.0	1.0
9-BBN	180	1.8	1.0

This higher preference for cis olefins displayed by ThxBHCl·SMe_2 can be attributed to a combination of steric and electronic factors. As discussed earlier, the sensitivity of ThxBHCl·SMe_2 to the steric requirements of terminal and internal double bonds closely parallels that of Sia_2BH. Since most of the selectivity exhibited by Sia_2BH can be attributed to steric effects, one would expect ThxBHCl·SMe_2 to hydroborate cis alkenes at a rate 5–10 times faster than their trans isomers.

In our previous study,[2] we observed that excess methyl sulfide significantly lowered the rate of hydroboration of 1-decene or cyclohexene with ThxBHCl·SMe_2. These results indicate that predissociation of the ThxBHCl·SMe_2 complex (eq 1) is a necessary condition for the hydroboration reaction. This suggests that monomeric ThxBHCl is the reactive species in this system.



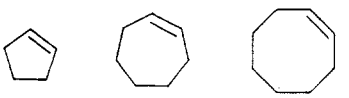
(1)

On the basis of symmetry, one would expect cis alkenes to possess a more highly basic π system than their trans isomers. The higher Lewis acidity of ThxBHCl relative to Sia_2BH should cause it to interact more quickly with the cis π system. Thus, ThxBHCl would be more effectively trapped by the cis isomer. The combination of both steric and electronic effects leads to a higher selectivity with ThxBHCl·SMe_2 in the hydroboration of cis/trans pairs. However, this increased reactivity of cis alkenes toward the more acidic ThxBHCl species significantly reduces the ability of this reagent to distinguish terminal olefins from cis internal alkenes.

Cyclic Alkenes. Cyclohexene has traditionally been a rather unreactive substrate for the hydroboration reaction. Cyclopentene, on the other hand, is much more reactive. This difference in reactivity has been attributed to the greater strain associated with the double bond in cyclopentene.[12] ThxBHCl·SMe_2 hydroborates cyclopentene at a rate 31 times faster than that of cyclohexene. However, this selectivity observed with ThxBHCl·SMe_2 is lower than that obtained with either Sia_2BH or 9-BBN.

ThxBHCl·SMe_2	1.0	31
Sia_2BH	1.0	140
9-BBN	1.0	107

Cycloheptene and cyclooctene also contain highly strained double bonds.[14] Like cyclopentene, both of these olefins exhibit reactivities considerably higher than cyclohexene. Like Sia_2BH, ThxBHCl·SMe_2 can distinguish somewhat between these three strained systems, while 9-BBN cannot. However, the precise reason for this difference in selectivity is not known.



ThxBHCl·SMe_2	1.0	5.5	40
Sia_2BH	1.0	18.6	41
9-BBN	1.0	1.10	0.96

If strain were to be an important criteria for reactivity, one would expect norbornene, which contains a highly strained double bond, to be very reactive in the hydroboration reaction. With 9-BBN, norbornene undergoes reaction at a rate 20 times faster than cyclopentene. On the other hand, with ThxBHCl·SMe_2, norbornene is much *slower* than cyclopentene.

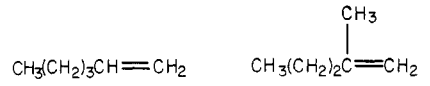
ThxBHCl·SMe_2	1.0	0.29
9-BBN	1.0	20

In this case, the rigid, bridged methylene group limits access to the double bond. The greater sensitivity of ThxBHCl·SMe_2 toward the steric environment of the alkene lowers the reactivity of norbornene relative to cyclopentene.

Effect of α-Methyl Substituents. Addition of an α-methyl substituent to a terminal alkene increases its rate of hydroboration with 9-BBN. On the other hand, with Sia_2BH, a significant decrease in the rate of hydroboration relative to terminal olefins is observed. With ThxBHCl·SMe_2, the rate of hydroboration again decreases,

(14) Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133–4136.

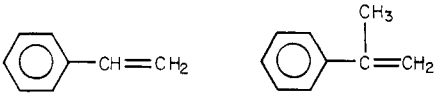
but the effect is not as dramatic as that observed with Sia_2BH.



ThxBHCl·SMe$_2$	1.0	0.41
Sia_2BH	1.0	0.049
9-BBN	1.0	1.94

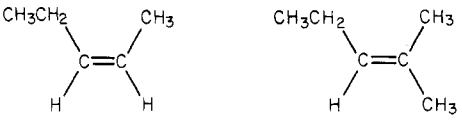
In the hydroboration of disubstituted terminal olefins with ThxBHCl·SMe$_2$, the increased steric requirements of the double bond are evidently tempered somewhat by the additional electron density provided by the alkyl substituent.

A similar decrease in reactivity is observed with ThxBHCl·SMe$_2$ when an α-methyl substituent is introduced into styrene. In this case, ThxBHCl·SMe$_2$ displays a higher selectivity than Sia_2BH.



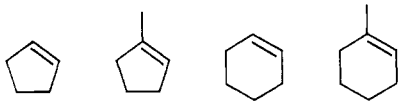
ThxBHCl·SMe$_2$	1.0	0.10
Sia_2BH	1.0	1.21
9-BBN	1.0	5.6

Addition of an α-methyl substituent to an internal alkene has little effect on the rate of hydroboration with 9-BBN. In contrast, there is a significant decrease in the rate of reaction when ThxBHCl·SMe$_2$ is the hydroborating agent. This effect again demonstrates the sensitivity of ThxBHCl·SMe$_2$ to the steric requirements of the double bond.



ThxBHCl·SMe$_2$	33	1.0
9-BBN[15]	1.2	1.0

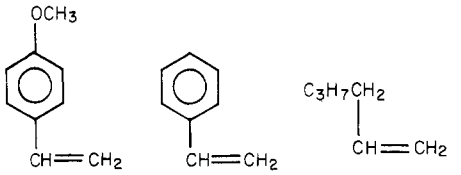
This increased steric effect is also dramatically evident when an α-methyl substituent is added to a cyclic olefin. Thus, ThxBHCl·SMe$_2$ can readily distinguish cyclopentene from 1-methylcyclopentene or cyclohexene from 1-methylcyclohexene. With 9-BBN, however, the difference in relative reactivity is significantly lower.



ThxBHCl·SMe$_2$	15	1.0	45	1.0
9-BBN	4.8	1.0	6.1	1.0

Effect of Phenyl Substituents. The addition of a phenyl substituent to a simple terminal alkene dramatically decreases the rate of hydroboration with either Sia_2BH or 9-BBN. Most of this effect can be attributed to the powerful electronic effect of the phenyl substituent, which lowers the overall π basicity of the olefin, with a weak steric effect due to the bulky but more remote phenyl substituent. Since ThxBHCl·SMe$_2$ exhibits an enhanced reactivity to cis olefins, attributed to the higher π density of the strained double bonds, it might be expected that the decrease in π basicity of styrene would cause a reduction in the rate of hydroboration. Indeed, a significant decrease in the rate of hydroboration is observed with ThxBHCl·SMe$_2$.

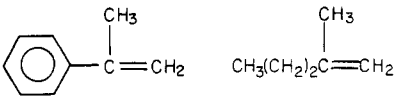
(15) Value observed for 2-methyl-2-butene vs. *cis*-2-pentene.



ThxBHCl·SMe$_2$	5.7	1.0	91
Sia_2BH	1.4	1.0	36
9-BBN[9b]	3.0	1.0	40
$HBBr_2$·SMe$_2$		1.0	16

When electron-releasing substituents are added, a slight increase in the rate of hydroboration with Sia_2BH and 9-BBN occurs. When ThxBHCl·SMe$_2$ is used as the hydroborating agent, the increase in reactivity is even larger.

The lower reactivity resulting from the introduction of a phenyl substituent is also apparent in the decreased rate of hydroboration of α-methylstyrene relative to 2-methyl-1-pentene with ThxBHCl·SMe$_2$. Again, the observed effect with ThxBHCl·SMe$_2$ is much more dramatic than that of Sia_2BH or 9-BBN.



ThxBHCl·SMe$_2$	1.0	370
Sia_2BH	1.0	2.1
9-BBN	1.0	13.8

Conclusions

It is evident from this study that ThxBHCl·SMe$_2$ is a highly selective hydroborating agent. The sensitivity of this reagent to the steric requirements of the double bond often parallels that observed with Sia_2BH. The added sensitivity of ThxBHCl·SMe$_2$ to electronic effects produces a unique selectivity that often complements that displayed by 9-BBN or Sia_2BH.

The unusual selectivity exhibited by ThxBHCl·SMe$_2$ in the hydroboration reaction significantly expands the versatility of this reagent in organic synthesis. ThxBHCl·SMe$_2$ is the first example of a haloborane derivative to selectively monohydroborate alkenes. The rich chemistry associated with the dialkylhaloboranes may be expanded to include unsaturated substrates with this new reagent. In particular, selective hydroboration of terminal alkenes in the presence of other unsaturated sites should be possible with ThxBHCl·SMe$_2$. Thus, the coupling of two different unsaturated primary alkyl groups on boron may be possible with this reagent. A detailed study of the selective hydroboration properties of ThxBHCl·SMe$_2$ is in progress. Finally, the exceptionally large differences in the reactivities of cis/trans olefin pairs should find useful application in the preferential hydroboration of cis alkenes in the presence of their trans isomers.

Experimental Section

The reaction flasks and other glassware required for these experiments were predried at 140 °C for several hours, assembled hot, and cooled under a stream of prepurified nitrogen (Airco). Syringes were assembled and fitted with needles while hot and then cooled. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered sidearms, using standard techniques for handling air-sensitive materials.[16]

Materials. Solutions (2.1 M) of ThxBHCl·SMe$_2$ in CH_2Cl_2 were prepared and standardized as described previously.[2] Spectroquality methylene chloride (Aldrich) was degassed and

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

stored under nitrogen over anhydrous potassium carbonate. The hydrocarbons employed as internal standards for GLC analysis were obtained from Phillips Petroleum Co. and were labeled >99% pure. Cycloheptene, cyclooctene, norbornene, styrene, α-methylstyrene, and p-methoxystyrene were obtained from the Aldrich Chemical Co. The styrene derivatives were stored at 0 °C and distilled from $LiAlH_4$ immediately before use. The remaining alkenes, except norbornene, were distilled from $LiAlH_4$ and stored under nitrogen at ambient temperatures. The other alkenes employed in this study were used as received from the Chemical Samples Division of Albany International after their refractive indices and ^1H NMR spectral characteristics were checked.

GLC Analyses. GLC analyses were carried out with a Varian Model 1200 FID chromatograph equipped with an injection port lined with a 6 in. × 0.25 in. column of 10% THEED on 80/100 mesh Supelcoport to protect the GLC columns from contamination by organoborane species. Olefins with boiling points below 50 °C were analyzed on a 12 ft × 0.125 in. column of 30% adiponitrile on 60/80 mesh Firebrick. All other alkenes were analyzed on a 12 ft × 0.125 in. column of 10% SE-30 on 100/120 mesh Supelcoport.

Competitive Hydroboration of Olefin Pairs with ThxBHCl·SMe_2. A typical experimental procedure for determining the relative reactivities of cyclooctene vs. cycloheptene follows. A clean, dry, 100-mL round-bottom flask equipped with magnetic stirring bar, septum-covered sidearm, and connector tube leading to a mercury bubbler was charged at 0 °C with 5.90 mL of CH_2Cl_2, 0.50 mL of n-decane (0.395 g, 2.78 mmol, internal standard), 0.58 mL of cycloheptene (0.499 g, 5.2 mmol), and 0.65 mL of cyclooctene (0.552 g, 5.0 mmol). The resulting solution was stirred at 0 °C for 15 min. A 0.10-mL aliquot was withdrawn to obtain the initial olefin/(n-decane) ratios by GLC (12 ft × 0.125 in. 10% SE-30 on 100/120 mesh Supelcoport maintained at 75 °C). The following ratios were obtained: cycloheptene/n-decane = 1.26 (theoretical = 0.499/0.395 = 1.26) and cyclooctene/n-decane = 1.37 (theoretical = 0.552/0.395 = 1.40). Meanwhile, the flask was immersed in a constant temperature bath, and the contents were quilibrated with stirring at 25.0 ± 0.05 °C for 20 min. Then 2.35 mL of cold 2.1 M ThxBHCl·SMe_2 (5.0 mmol) in CH_2Cl_2 were quickly added via syringe. The overall concentration of each olefin and ThxBHCl·SMe_2 was 0.50 M. The resulting solution was then stirred at 25.0 °C for sufficient time to allow complete reaction (3 h), cooled to 0 °C, and quenched with excess NaOH (5.0 mL of 3 N). After 1 h at 0 °C, the aqueous layer was saturated with solid NaCl. A 0.5-mL aliquot of the CH_2Cl_2 layer was withdrawn, dried over anhydrous K_2CO_3, and analyzed immediately by GLC to obtain the final olefin/n-decane ratios. Found: cycloheptene/n-decane = 1.01 (20% consumed), cyclooctene/n-decane = 0.274 (80% consumed). The relative reactivity of this substrate pair, as well as other substrate pairs, was then calculated by using the Ingold–Shaw equation (eq 2),[7] where X_0 and Y_0 are the initial concentrations of x and y and X and Y are the residual concentrations of the two olefins being compared. For this example, $k_{cyclooctene}/k_{cycloheptene} = 7.4$.

$$\text{relative rate} = \frac{k_x}{k_y} = \frac{\ln X_0 - \ln X}{\ln Y_0 - \ln Y} \quad (2)$$

Acknowledgment. This study was facilitated by grants from the National Science Foundation (CHE 79-18881) and the National Institutes of Health (GM 10937-18).

Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; cyclooctene, 931-88-4; 3-methyl-1-hexene, 3404-61-3; 2-methyl-1-pentene, 763-29-1; cycloheptene, 628-92-2; *cis*-3-hexene, 7642-09-3; *cis*-2-pentene, 627-20-3; *cis*-4-methyl-2-pentene, 691-38-3; 4-vinylanisole, 637-69-4; cyclopentene, 142-29-0; styrene, 100-42-5; 3,3-dimethyl-1-hexene, 3404-77-1; norbornene, 498-66-8; *cis*-4,4-dimethyl-2-pentene, 762-63-0; 2-methyl-2-pentene, 625-27-4; 1-methylcyclopentene, 693-89-0; *trans*-3-hexene, 13269-52-8; *trans*-2-pentene, 646-04-8; *trans*-2-hexene, 4050-45-7; α-methylstyrene, 98-83-9; *trans*-4-methyl-2-pentene, 674-76-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; ThxBHCl·SMe_2, 75067-06-0.

Active Metals from Potassium–Graphite. Iron–Graphite as a New Debrominating Agent of *vic*-Dibromoalkanes and of α-Bromo Ketones

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Iron–graphite (Fe-Gr), easily prepared by reduction of $FeCl_3$ with potassium–graphite (C_8K) in tetrahydrofuran, is conveniently used for the stereospecific debromination of *vic*-dibromoalkanes to alkenes and for the reductive debromination of α-bromo ketones to ketones in high yields. The latter reaction proceeds via Fe(II) enolates, which undergo deuteration, condensation, or O-silylation by reaction respectively with D_2O, heptanal, or chlorotrimethylsilane. Moreover, the reaction of α,α′-dibromo ketones with Fe-Gr leads to 2-oxyallyl cations which can be trapped by suitable electron-rich olefins (enamines) or dienes (furan).

We have been recently engaged with the preparation of active forms of transition metals by reduction of transition metal salts with potassium–graphite (C_8K).[1] Highly dispersed nickel[2] and palladium[3] on the graphite surface obtained by this method were found to act as effective catalysts in hydrogenation and vinylic substitution reactions.

We now report the preparation of iron–graphite (Fe-Gr) according to stoichiometric eq 1 and its use as a new debrominating agent of *vic*-dibromoalkanes and of α-bromo ketones.

$$3C_8K + FeCl_3 \rightarrow C_{24}Fe + 3KCl \quad (1)$$

When a solution of anhydrous $FeCl_3$ in tetrahydrofuran (THF) is added dropwise to a stirred suspension of C_8K in THF, a fast and exothermic reaction takes place, affording a black powder, the metal content (15.4%)[4] of

(1) Braga, D.; Ripamonti, A.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1978**, 927.
(2) Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A., *J. Org. Chem.* **1982**, *47*, 564.
(3) Savoia, D.; Trombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 540, 541.

(4) A higher iron loading (22%) can be obtained by starting from $FeCl_2$; however, owing to the poor solubility of this salt in ethereal solvents, it is necessary to reflux the heterogeneous mixture of C_8K and $FeCl_2$ in 1,2-dimethoxyethane at least for 3 h to achieve an almost complete reduction. Furthermore, the obtained material is less active in comparison to that obtained from $FeCl_3$ (see Table II), probably owing to a worse surface area/mass ratio of iron particles.

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