Hydroboration. 64. Effect of Structure on the Relative Reactivity of Representative Alkenes and Alkynes toward Hydroboration by Dibromoborane-Methyl Sulfide

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

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

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The relative reactivities of 22 alkenes and 5 alkynes toward hydroboration by dibromoborane-methyl sulfide ($Br_2BH{\cdot}SMe_2$) have been determined in CH_2Cl_2 at 25 °C by the competitive method. The data are compared and contrasted with those available on 9-borabicyclo[3.3.1]nonane (9-BBN), disiamylborane (Sia_2BH), and thexylchloroborane-methyl sulfide ($ThxBHCl{\cdot}SMe_2$). $Br_2BH{\cdot}SMe_2$ exhibits a uniquely high selectivity toward an internal triple bond compared to a terminal triple or double bond, while the reverse is true with 9-BBN. Consequently, 1-octen-4-yne has been selectively converted to (4*Z*)-1,4-octadiene by hydroboration with $Br_2BH{\cdot}SMe_2$, followed by protonolysis. The terminal double bond, on the other hand, is selectively hydroborated by 9-BBN. The far higher reactivity of $Br_2BH{\cdot}SMe_2$ toward the $C(CH_3)=CH_2$ structure, as compared with the $CH=CH_2$ structure makes possible the selective hydroboration of the 1,2-positions of 2-methyl-1,5-hexadiene; Sia_2BH, on the other hand, is known to hydroborate the 5,6-positions selectively. Thus we have at hand several monofunctional hydroborating agents with widely different selectivities, making them highly useful for selective hydroborations for synthesis.

Dibromoborane-methyl sulfide is a synthetically important hydroborating agent. It has been effectively used for stepwise hydroboration via hydridation.[2] It has also been successfully employed for the stereodefined syntheses of *Z,E*, and trisubstituted alkenes.[3-5] Its reactions with terminal or internal alkynes proceed cleanly to vinyldibromoboranes without the accompanying formation of 1,1-dibora compounds.[6] Its elegance in carrying out conversions useful for organic synthesis warranted a study of the selectivity of this reagent among the types of unsaturated centers commonly encountered in synthetic work. Consequently, we undertook a systematic investigation of the relative rates of the reaction of $Br_2BH{\cdot}SMe_2$ with representative alkenes and alkynes in CH_2Cl_2 at 25 °C. The relative rates for a few alkenes and alkynes had been reported earlier,[6] but the compounds included are not sufficient to permit reliable conclusions as to the full selectivity of this reagent. Hence we extended the study to alkenes and alkynes of widely different structural types and compared and contrasted the results with the corresponding data available on other available monofunctional hydroborating agents such as 9-borabicyclo[3.3.1]nonane[7] (9-BBN), disiamylborane[8] (Sia_2BH), and thexylchloroborane-methyl sulfide[9] ($ThxBHCl{\cdot}SMe_2$).

Results and Discussion

Competitive Hydroboration of Alkenes and Alkynes by Dibromoborane-Methyl Sulfide. The relative reactivities of alkenes and alkynes toward hydroboration by $Br_2BH{\cdot}SMe_2$ were determined in CH_2Cl_2 at 25 °C by the competitive method. A solution containing 1 equiv each of two alkenes and a suitable internal standard was treated with 1 equiv of $Br_2BH{\cdot}SMe_2$. After the hydroboration was over, as detected by the disappearance of the ^{11}B peak of the reagent, the reaction mixture was quenched with excess aqueous sodium hydroxide and analyzed for the residual alkenes by GLC. The initial and the final quantities of the alkenes were fitted into the Ingold-Shaw expression (see Experimental Section)[10] to arrive at the relative rate.

Table I. Relative Rates of and Regioselectivity in the Hydroboration of Representative Alkenes and Alkynes with Dibromoborane-Methyl Sulfide in CH_2Cl_2 at 25 °C

compd	rel rate[a]	regioselectivity[b] A	B
3-hexyne	4880 (5620)		
4-octyne	3560		
2-methyl-1-pentene[c]	2050	98	2
cyclooctene	312		
1-hexyne[d]	234 (276)		
2-methyl-2-butene[c]	214	93	7
1-methylcyclopentene	126	98	2
1-hexene[c]	100	99.6	0.4
1-octene	95.2		
cycloheptene	66		
1-phenyl-1-propyne[d]	53 (59)	64	36
cis-3-hexene	42.1		
cis-4-methyl-2-pentene	40.2	79	21
cis-4-octene	26.2		
trans-3-hexene	22.6		
3,3-dimethyl-1-butene	20.1	>99.9	<0.1
cyclopentene	16.5		
trans-4-methyl-2-pentene	12.0	82	18
phenylacetylene[d]	10.9 (37.1)	91	9
trans-2,5-dimethyl-3-hexene	9.2		
2,3-dimethyl-2-butene	6.33		
cis-2,5-dimethyl-3-hexene	5.60		
1-methylcyclohexene	4.03	98	2
styrene[d]	2.67 (6.00)	96	4
cyclohexene	1.00		
trans-β-methylstyrene	0.066	64	36
cis-β-methylstyrene	0.029 (2.38)	75	25

[a] Values in parentheses are from ref 6. [b] A indicates the less hindered and B the more hindered olefinic position. [c] Regioselectivity data taken from ref 17. [d] Regioselectivity data taken from ref 20.

(1) Postdoctoral research associate on Grant CHE 79-18881 of the National Science Foundation.
(2) Kulkarni, S. U.; Basavaiah, D.; Zaidlewicz, M.; Brown, H. C. *Organometallics* **1982**, *1*, 212-214.
(3) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 3806-3808.
(4) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U. *J. Org. Chem.* **1982**, *47*, 3808-3810.
(5) (a) Brown, H. C.; Kulkarni, S. U.; Basavaiah, D., unpublished results. (b) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 5407-5409.
(6) Brown, H. C.; Campbell, J. B., Jr. *J. Org. Chem.* **1980**, *45*, 389-395.
(7) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297-5301.
(8) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063-2065.
(9) Sikorski, J. A.; Brown, H. C. *J. Org. Chem.* **1982**, *47*, 872-876.
(10) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918-2926.

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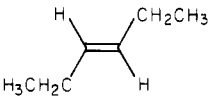
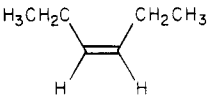
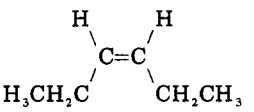


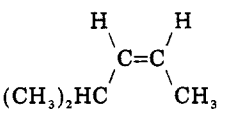
$Br_2BH·SMe_2$	1.0	0.52	0.40
9-BBN	1.0	0.51	0.069



$Br_2BH·SMe_2$	1.0	0.96	0.13
9-BBN	1.0	0.78	0.0025



$Br_2BH·SMe_2$	1.9	1.0
9-BBN	2.0	1.0
Sia_2BH	10	1.0
ThxBHCl·SMe_2	92	1.0



$Br_2BH·SMe_2$	3.4	1.0
9-BBN	3.3	1.0
Sia_2BH	5.0	1.0
ThxBHCl·SMe_2	110	1.0

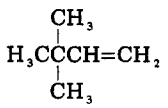
As far as possible, the alkene pairs were so chosen that their relative rates did not differ by a factor of more than 10. The relative rates of the alkenes and the alkynes chosen for this study are given in Table I. The regioselectivities in the hydroboration of the unsymmetrical alkenes and alkynes were also determined by the hydroboration–oxidation procedure in order to know the position of attachment of boron in these cases. These results are also given in Table I.

In contrast to the poor selectivity of diborane in hydroboration, monofunctional hydroborating agents such as 9-BBN, Sia_2BH, ThxBHCl·SMe_2, and $Br_2BH·SMe_2$ exhibit unusual selectivities. The data in the present study are compared below with the data on the other monofunctional hydroborating agents. Such a comparison will be highly helpful in choosing the proper reagent for selective hydroborations.

Terminal Alkenes. The terminal alkenes are rapidly hydroborated by $Br_2BH·SMe_2$. Changing the chain length has only an insignificant effect on the relative rate.

	$CH_3(CH_2)_3CH=CH_2$	$CH_3(CH_2)_5CH=CH_2$
$Br_2BH·SMe_2$	1.0	0.95
9-BBN	1.0	1.1
Sia_2BH	1.0	1.1
ThxBHCl·SMe_2	1.0	0.98

Branching of the alkyl group of a terminal alkene causes a considerable retardation in the rate, probably the result of steric effects. A comparison with other reagents shows that $Br_2BH·SMe_2$ is less sensitive to such steric effects than ThxBHCl·SMe_2 or Sia_2BH.



	$CH_3(CH_2)_3CH=CH_2$	
$Br_2BH·SMe_2$	1.0	0.20
9-BBN	1.0	0.24
Sia_2BH	1.0	0.047
ThxBHCl·SMe_2	1.0	0.010

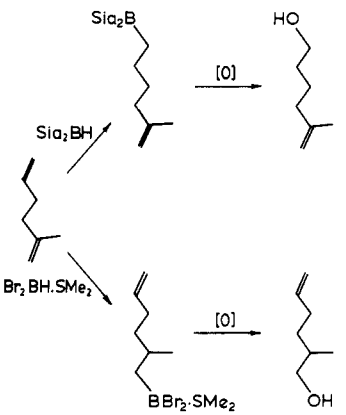


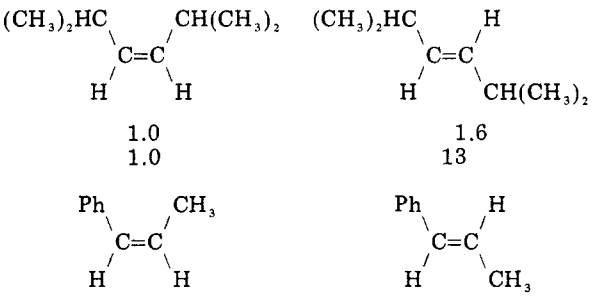
Figure 1. Selective hydroboration of 2-methyl-1,5-hexadiene.

$Br_2BH·SMe_2$ is highly regioselective in the hydroboration of terminal alkenes.

Internal Alkenes. Disubstituted internal alkenes are hydroborated considerably slower than terminal alkenes by $Br_2BH·SMe_2$. For example, *cis*- and *trans*-3-hexene react slower than 1-hexene. Branching of the alkyl groups of internal alkenes causes a further decrease in the rate. With branched internal alkenes such as 4-methyl-2-pentene the boron becomes attached to the less hindered position to the extent of about 80%.

Cis and Trans Isomers. In general, the hydroboration of a *cis*-alkene proceeds faster than that of its trans isomer. The *cis*-alkenes are more strained than their trans isomers. The relief of this extra strain may be responsible for the rate acceleration observed for the cis isomers. We find similar behavior in the reactions of less hindered alkenes such as 3-hexene and 4-methyl-2-pentene with $Br_2BH·SMe_2$. However, the rate ratio is very modest. ThxBHCl·SMe_2 and Sia_2BH show much greater selectivity toward *cis*-alkenes than does $Br_2BH·SMe_2$.

In the case of hindered alkenes, the trans isomer reacts faster than the cis. For example, *trans*-2,5-dimethyl-3-hexene is hydroborated by $Br_2BH·SMe_2$ 1.6 times faster



$Br_2BH{\cdot}SMe_2$	1.0	1.6
9-BBN	1.0	13

$Br_2BH{\cdot}SMe_2$	1.0	2.3
9-BBN	1.0	2.6

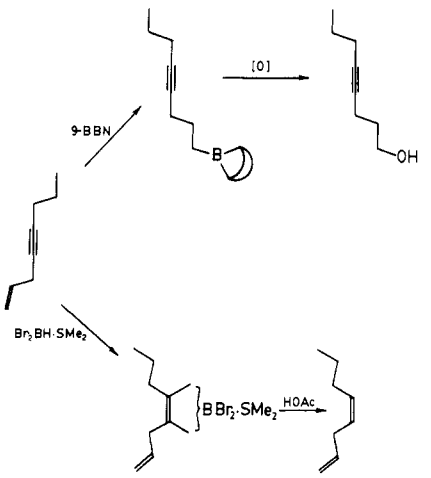
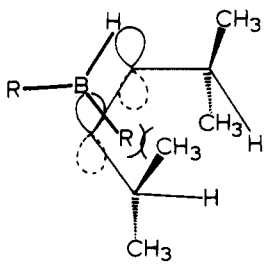


Figure 2. Selective hydroboration of 1-octen-4-yne.

than the cis isomer. A similar pattern of behavior is observed for *cis*- and *trans*-β-methylstyrene. It may be noted that this reversed trend in reactivity on increasing steric hindrance about the olefinic bond is also observed in hydroboration by 9-BBN.[11]

The slower rate of hydroboration of *cis*-2,5-dimethyl-3-hexene than that of its trans analogue is probably due to steric hindrance involving the approach of the hydroborating agent to the olefinic center. *cis*-2,5-Dimethyl-3-hexene has two isopropyl groups in close proximity. An examination of the molecular model reveals that there is a serious restriction for rotation of the two isopropyl groups about the C2–C3 and C4–C5 bonds. This may cause the methyl moieties of the isopropyl groups to be directed above and below the mean molecular plane (1). The



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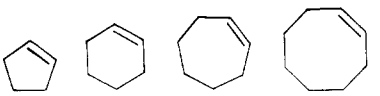
methyl groups will then offer significant steric hindrance to the approach of the hydroborating agent, which, on stereoelectronic grounds, should be in a direction perpendicular to the mean molecular plane of the olefin (1). In *trans*-2,5-dimethyl-3-hexene, the isopropyl groups can easily rotate to direct the methyl groups away from the region of approach of the hydroborating agent. In *cis*-β-methylstyrene, the steric effect may be caused by the tilted phenyl group.

Cycloalkenes. $Br_2BH{\cdot}SMe_2$ hydroborates cyclohexene much slower than cyclopentene, cycloheptene, or cyclooctene. This trend is also observed for all other hydroborating agents examined. The greater reactivities of the lower and higher ring homologues of cyclohexene are attributable to the larger ring strain associated with the latter systems.[12] The effect of ring size on reactivity appears to be less pronounced for $Br_2BH{\cdot}SMe_2$ than for Sia_2BH or $ThxBHCl{\cdot}SMe_2$. Cyclooctene, the fastest reacting compound in the series, is only 310 times more reactive than cyclohexene toward hydroboration by $Br_2BH{\cdot}SMe_2$, while this factor is about 5700 in the case of Sia_2BH.



$Br_2BH{\cdot}SMe_2$	16	1.0	64	312
9-BBN	1070	1.0	118	103
Sia_2BH	140	1.0	2600	5740
$ThxBHCl{\cdot}SMe_2$	31	1.0	171	1240

Effect of Methyl Substitution. As a result of introducing a methyl group at the α-position to the carbon to which boron is attached, the rate of hydroboration increases remarkably. This behavior is uniquely different from those of the other reagents. 9-BBN shows a modest rate enhancement while Sia_2BH and $ThxBHCl{\cdot}SMe_2$ show significant rate decreases. $Br_2BH{\cdot}SMe_2$ thus shows a unique selectivity to the $C(CH_3)=CH_2$ structure, as compared to $CH=CH_2$. In order to demonstrate the utility of this characteristic, 2-methyl-1,5-hexadiene was hydroborated with 1 equiv of $Br_2BH{\cdot}SMe_2$ and the intermediate was oxidized by alkaline H_2O_2. The product was found to be 2-methyl-5-hexen-1-ol by ^1H and ^{13}C NMR studies. On the other hand, hydroboration–oxidation of 2-methyl-1,5-hexadiene with disiamylborane yields 5-methyl-5-hexen-1-ol[13] (Figure 1). Thus, it is now possible to selectively hydroborate $C(CH_3)=CH_2$ in the presence of $CH=CH_2$ and vice versa.

	1-hexene	2-methyl-1-pentene
$Br_2BH{\cdot}SMe_2$	1.0	21
9-BBN	1.0	1.9
Sia_2BH	1.0	0.049
$ThxBHCl{\cdot}SMe_2$	1.0	0.41

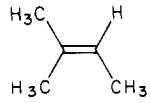
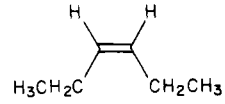
Introduction of a methyl group at the olefinic position of an internal alkene also leads to a considerable increase in the rate of hydroboration by $Br_2BH{\cdot}SMe_2$. With other

(11) Brown, H. C.; Nelson, D. J.; Scouten, C. G. *J. Org. Chem.*, previous paper in this issue.

(12) Dauben, W. G.; Pitzer, K. S. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed., Wiley: New York, 1956; Chapter 1.

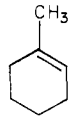
(13) Zweifel, G.; Nagase, K.; Brown, H. C. *J. Am. Chem. Soc.* **1962**, *84*, 190–195.

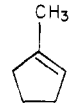
reagents, only a rate decrease, or a small increase, is observed.

$Br_2BH\cdot SMe_2$	5.1	1.0
9-BBN	1.66	1.0
ThxBHCl·SMe_2	0.03	1.0

Introducing a methyl group at the olefinic carbon of a cycloalkene causes a rate enhancement in the case of $Br_2BH\cdot SMe_2$, contrary to the behavior of the other hydroborating agents.






$Br_2BH\cdot SMe_2$	4.0	1.0	7.6	1.0
9-BBN	0.16	1.0	0.21	1.0
ThxBHCl·SMe_2	0.022	1.0	0.067	1.0

These results indicate that $Br_2BH\cdot SMe_2$ may be more sensitive to electronic and less to steric effects, compared to the other monofunctional hydroborating agents. This may stem from the presence of bromine atoms in Br_2BH, which will make it a stronger Lewis acid and thereby increase its susceptibility to electronic effects.

The regioselectivity experiments indicate that introduction of a methyl group on the olefinic carbon causes the boron to attack preferentially on the less hindered adjacent position.

Introducing a methyl group at the site of hydroboration leads to a considerable rate decrease. For example, 2,3-dimethyl-2-butene reacts with $Br_2BH\cdot SMe_2$ 34 times slower than 2-methyl-2-butene. With 9-BBN, the factor is 140.

Phenyl Substitution. Introduction of a phenyl group at the olefinic carbon decreases the rate of hydroboration significantly, as has already been found with other reagents. The slower reactivity of styrene is due to the electronic effect of the phenyl group, which lowers the overall π basicity of the olefinic bond, and possibly to the introduction of a modest steric effect.

	1-hexene	styrene
$Br_2BH\cdot SMe_2$	37	1.0
9-BBN	40	1.0
Sia_2BH	36	1.0
ThxBHCl·SMe_2	91	1.0

Alkynes. Terminal alkynes are hydroborated by $Br_2BH\cdot SMe_2$ faster than terminal alkenes. Internal alkynes are much more reactive than terminal alkynes or alkenes toward hydroboration by $Br_2BH\cdot SMe_2$. The vast difference in the reactivities of an internal alkyne and a terminal alkene is highly important in organic synthesis. For example, 1-octen-4-yne on hydroboration by 1 equiv of $Br_2BH\cdot SMe_2$, followed by protonolysis with acetic acid, affords (4Z)-1,4-octadiene (Figure 2). Brown and Coleman[14] have demonstrated that 9-BBN selectively hydroborates the terminal double bond in 1-octen-4-yne. Thus, we now have reagents to hydroborate either the internal triple bond or the terminal double bond in the presence of the other.

	1-hexene	1-hexyne
$Br_2BH\cdot SMe_2$	1.0	2.3
9-BBN	1.0	0.15
Sia_2BH	1.0	3.7
ThxBHCl·SMe_2	1.0	5.0

	1-hexyne	3-hexyne	4-octyne
$Br_2BH\cdot SMe_2$	1.0	21.2	15.2
9-BBN	1.0	0.042	
Sia_2BH	1.0	2.25	
ThxBHCl·SMe_2	1.0	1.24	

Experimental Section

General procedures for the manipulation of boron reagents have been outlined elsewhere.[16] All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware were assembled hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and cooled as assembled units.

Materials. Dibromoborane–methyl sulfide was prepared from BBr_3, Me_2S, and $BH_3\cdot SMe_2$ by a reported procedure.[17] The crude $Br_2BH\cdot SMe_2$ was purified by successive recrystallizations from CH_2Cl_2 at −78 °C until all of the $BBr_3\cdot SMe_2$ was removed. The overall recovery was ~60%. All of the alkenes used in this study were distilled over $LiAlH_4$ in a nitrogen atmosphere. The alkynes were distilled in a nitrogen atmosphere.

GLC Analyses. GLC analyses were carried out with a HP 5750 chromatograph. When residual alkenes were analyzed, the injection port was lined with a 6 in. × 0.25 in. column of 10% THEED on firebrick. Residual alkenes were analyzed by using a 6 ft × 0.25 in. column of 10% SE-30 on 60/80-mesh Chromosorb W or a 6 ft × 0.25 in. column of 20% adiponitrile on 60/80-mesh firebrick. Alcohols were analyzed on a 12 ft × 0.125 in. column of 10% Carbowax 20M on 100/120-mesh Chromosorb W or on a 12 ft × 0.125 in. column of 10% glycerol on 100/120-mesh firebrick.

Spectra. ^{11}B and ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer equipped with a broad-band probe and a Hewlett-Packard 3335A frequency synthesizer. ^1H NMR spectra were obtained with a Varian T-60 (60 MHz) spectrometer.

Relative Reactivities. The competition method was used for the determination of relative reactivities. Two alkenes (A and B, 5 mmol each) and a suitable internal standard were dissolved in CH_2Cl_2 (15 mL), and the solution was kept at 25 °C. Several minute aliquots were removed and analyzed by GLC for the response factors. Dibromoborane–methyl sulfide (5 mmol; 3.0 mL of a 1.67 M solution in CH_2Cl_2) was added dropwise. After allowing sufficient time for the completion of the reaction, the reaction mixture was quenched into excess aqueous NaOH (7 mL; 3 N) at 0 °C. The aqueous layer was saturated with NaCl.

The organic layer was dried over K_2CO_3 and analyzed by GLC for the residual olefins. The initial and final quantities were fitted into the Ingold–Shaw expression[10] (eq 1), where $[A]_0$ and $[A]_f$ are

$$\frac{k_A}{k_B} = \frac{\ln [A]_0 - \ln [A]_f}{\ln [B]_0 - \ln [B]_f} \quad (1)$$

the initial and final quantities of the olefin A and $[B]_0$ and $[B]_f$ are the corresponding quantities of the olefin B. The olefin pairs were so chosen that their relative rates, as far as possible, did not differ by a factor of more than 10. The relative rate of 1-hexene was arbitrarily assigned a value of 100, and the values for other compounds were calculated accordingly. The relative rates are given in Table I.

Regioselectivity in the Hydroboration of Alkenes by $Br_2BH\cdot SMe_2$. The regioselectivity in the hydroboration of unsymmetrical alkenes with $Br_2BH\cdot SMe_2$ was determined by oxidizing the boron intermediates with H_2O_2 and analyzing the alcohols by GLC.[18] The following procedure is typical. *trans*-4-Methyl-2-pentene (5 mmol) in CH_2Cl_2 (10 mL) was refluxed

(14) Brown, C. A.; Coleman, R. A. *J. Org. Chem.* **1979**, *44*, 2329–2330.
(15) Brown, H. C.; Sikorski, J. A., unpublished results.
(16) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapter 9.
(17) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1977**, *99*, 7097.
(18) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384–389.

with $Br_2BH{\cdot}SMe_2$ (5 mmol) for 8 h in the presence of *n*-decane (internal standard, 0.50 mL). The reaction mixture was quenched with NaOH (3 N, 12 mL) and oxidized with H_2O_2 (2 mL, 30%) in the presence of ethanol and THF (5 mL each) as cosolvents. The aqueous layer was saturated with K_2CO_3, and the organic layer was analyzed by GLC. There were formed 0.40 g (3.96 mmol) of 4-methyl-2-pentanol and 0.086 g (0.85 mmol) of 2-methyl-3-pentanol. Hence the regioselectivity is 82% in the 2-position and 18% in the 3-position of *trans*-4-methyl-2-pentene. Similarly, *cis*-4-methyl-2-pentene, 1-methylcyclohexene, *trans*-β-methylstyrene, and 3,3-dimethyl-1-butene were also studied. The data are given in Table I.

2-Methyl-5-hexen-1-ol. To 2-methyl-1,5-hexadiene (30 mmol) in CH_2Cl_2 (10 mL) was added $Br_2BH{\cdot}SMe_2$ in CH_2Cl_2 (30 mmol) dropwise, and the resulting solution was stirred for 1 h at room temperature. The reaction mixture was carefully quenched by addition to ice-cold NaOH (3 N, 30 mL). THF and ethanol (10 mL each) were added as cosolvents, and the boron intermediate was oxidized by H_2O_2 (15 mL, 30%). The organic materials were extracted with ether. The ether layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was stripped off and the crude 2-methyl-5-hexen-1-ol was purified by distillation under reduced pressure. There was obtained 2.2 g of the unsaturated alcohol (2.1 mmol, 70%) whose ^1H and ^{13}C NMR spectra were in agreement with the expected structure: bp 88 °C (25 mmHg); n^{20}_D 1.4415 [lit.[19] bp 68 °C (12 mmHg); n^{20}_D 1.4380].

(19) Colonge, J.; Lasfargues, P. *Bull. Soc. Chim. Fr.* **1962**, 177-182.
(20) Campbell, J. B., Jr. Ph.D. Thesis, Purdue University, 1978.

(4*Z*)-1,4-Octadiene. $Br_2BH{\cdot}SMe_2$ (30 mmol) was added dropwise to a cooled (water bath) solution of 1-octen-4-yne (Farchan, 30 mmol) in CH_2Cl_2. The resulting solution was stirred at room temperature for 1 h and then added carefully into an ice-cold solution of sodium methoxide in methanol (60 mmol). The volatiles were pumped off with the help of aspirator vacuum. The residue was refluxed with HOAc (30 mL) for 3 h. After a conventional workup and distillation, 2.40 g of (4*Z*)-1,4-octadiene (73% yield: bp 116 °C; n^{20}_D 1.4288) was obtained. Its structure and purity were checked by ^{13}C and ^1H NMR analyses.

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Registry No. 3-Hexyne, 928-49-4; 4-octyne, 1942-45-6; 2-methyl-1-pentene, 763-29-1; cyclooctene, 931-88-4; 1-hexyne, 693-02-7; 2-methyl-2-butene, 513-35-9; 1-methylcyclopentene, 693-89-0; 1-hexene, 592-41-6; 1-octene, 111-66-0; cycloheptene, 628-92-2; 1-phenyl-1-propyne, 673-32-5; *cis*-3-hexene, 7642-09-3; *cis*-4-methyl-2-pentene, 691-38-3; *cis*-4-octene, 7642-15-1; *trans*-3-hexene, 13269-52-8; 3,3-dimethyl-1-butene, 558-37-2; cyclopentene, 142-29-0; *trans*-4-methyl-2-pentene, 674-76-0; phenylacetylene, 536-74-3; *trans*-2,5-dimethyl-3-hexene, 692-70-6; 2,3-dimethyl-2-butene, 563-79-1; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; 1-methylcyclohexene, 591-49-1; styrene, 100-42-5; cyclohexene, 110-83-8; *trans*-β-methylstyrene, 873-66-5; *cis*-β-methylstyrene, 766-90-5; 1-octen-4-yne, 24612-83-7; 2-methyl-1,5-hexadiene, 4049-81-4; 2-methyl-5-hexen-1-ol, 55671-55-1; (*Z*)-1,4-octadiene, 25913-88-6; $Br_2BH{\cdot}SMe_2$, 53793-30-9.

Empirical Force Field Calculations. 20. Routes in the Inversion of *cis-transoid-cis*- and of *cis-cisoid-cis*-Perhydroanthracene[1,2]

Paul Vanhee,[3a] Bastiaan van de Graaf,*[3b] Dirk Tavernier,[3a] and Jan M. A. Baas[3b]

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands, and the Department of Organic Chemistry, State University of Gent, Krijgslaan 281 (S4bis), B-9000 Gent, Belgium

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The inversion of the all-chair (CCC) conformation of *cis-transoid-cis*- (**1**) and of *cis-cisoid-cis*-perhydroanthracene (**2**) has been explored by molecular mechanics. The inversion proceeds by the stepwise conversion of chair (C) to twist (T) and twist to inverted chair (C̄) forms of the constituent rings. The three basic step sequences leading from CCC to the "half inverted" intermediates TTT and CTC̄ have been studied: (1) CCC ⇄ CCT ⇄ CTT ⇄CTC̄; (2) CCC ⇄ CCT ⇄ CTT ⇄ TTT; (3) CCC ⇄ CCT ⇄ TCT ⇄ TTT. In both **1** and **2** sequence 1 provides the calculated path of inversion with the lowest barrier. The CTT to CTC̄ conversion is rate determining in both compounds. The calculated enthalpies of activation for **1** and **2** amount to 13.8 and 10.0 kcal mol^{-1}, respectively. The experimental barriers are $\Delta G^{\ddagger}_{319}$ = 14.1 kcal mol^{-1} for **1** and $\Delta G^{\ddagger}_{241}$ = 11.3 kcal mol^{-1} for **2**. The geometries of the ground states and the transition states are discussed in relation to the earlier computational work on the *cis*-decalin inversion. Of the two isomers **1** has the more stable ground state, but it also features the more strained transition state. The calculated energy differences between the ground states (2.0 kcal mol^{-1}) and between the transition states (−1.8 kcal mol^{-1}) explain the relatively high barrier of **1** and the relatively low barrier of **2**. The pseudorotating manifolds of **1** and **2** and the interconversions between the various conformations are discussed.

The perhydroanthracenes have played an important role in the development of conformational analysis. The relative stabilities of the five isomers have been predicted successfully quite early.[4] The heat of combustion of the trans-transoid-trans isomer has provided one of the first estimates of the chair–twist energy difference in cyclohexane.[5] More recently, Allinger and Wuesthoff[6] have studied the equilibrium of the five isomers both experimentally and by force field methods. We[7] have now obtained the Gibbs energy of activation for the inversion of the all-chair conformation of *cis-transoid-cis*-perhydroanthracene (**1**) and of *cis-cisoid-cis*-perhydroanthracene (**2**, Figure 1). The present $\Delta G^{\ddagger}$ values, 14.1 and 11.3 kcal mol^{-1} for **1** and **2**, respectively, are recalculated by using a value of $^1/_2$ for the transmission coefficient κ in the

(1) Part 19: Peters, J. A.; van Ballegoyen-Eekhout, G. W. M.; van de Graaf, B.; Bovée, W. M. M. J.; Baas, J. M. A.; van Bekkum, H. *Tetrahedron*, in press. Part 18: Vanhee, P.; van de Graaf, B.; Baas, J. M. A.; Tavernier, D. *Tetrahedron Lett.* **1982**, *23*, 3837-8.
(2) Baas, J. M. A.; van de Graaf, B.; Tavernier, D.; Vanhee, P., presented in part at the International Conference on Conformational Analysis, Durham NH, June 1981.
(3) (a) Gent University. (b) Delft University.
(4) Johnson, W. S. *J. Am. Chem. Soc.* **1953**, *75*, 1498-500.
(5) Margrave, J. L.; Frisch, M. A.; Bautista, R. G.; Clarke, R. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1963**, *85*, 546-8.
(6) Allinger, N. L.; Wuesthoff, M. T. *J. Org. Chem.* **1971**, *36*, 2051-3.
(7) Vanhee, P.; De Pessemier, F.; Anteunis, M.; Tavernier, D. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 294-7.

0022-3263/83/1948-0648$01.50/0