(14) Å, β = 99.25 (3)°, V = 4781 (9) Å^3, d_0 = 1.20 g/cm^3, d_c = 1.163 g/cm^3 for Z = 8 molecules/unit cell, space group $P2_1/c$ (the 2 unique molecules denoted A and B). Anisotropic refinement of non-hydrogen atoms (H's put in calculated positions as above) over 3878 statistically significant [$I > 2\sigma(I)$] reflections converged at R = 0.118 and R_w = 0.160 where R is as above, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/[\sigma(F_o)^2]$, and $\sigma(F_o)^2 = [\sigma(I)^2 + (0.07F^2)^2]^{1/2}/(\mathrm{Lp})$ where $F_o^2 = F^2/(\mathrm{Lp})$. The final difference map was featureless with maxima and minima ranging down from ±0.80 e/Å^3. The poor quality of the best available crystal and the large number of independent atoms in the unit cell vs. the number of significant reflections limited the structure solution to a demonstration of stereochemistry and gross conformation (shown for molecules A and B in Figure 3).[9]

Acknowledgment. We express our appreciation to Martin Mutter, Joan Rodgers, Dr. Sai Chang, James Kalbron, and Dr. Ruth Inners for spectroscopic analysis. We also thank William Sisco and Thomas DiFeo for TLC densitometry.

Registry No. **4a**, 75715-72-9; **4a**·hexamate, 75688-93-6; **4b**, 75715-73-0; **4c**, 75715-68-3; **5a**, 87680-29-3; **5a**·HCl, 87640-70-8; **5b**, 87680-30-6; **5c**, 87680-31-7; **6a**, 87680-23-7; **6b**, 87680-24-8; **6c**, 87680-25-9; **7a**, 87680-26-0; **7b**, 87680-27-1; **7c**, 87680-28-2; **8**, 21409-26-7; **9**, 87640-68-4; **10a**, 87680-32-8; **10b**, 87680-33-9; **11**, 87640-69-5; **13**, 87640-72-0; **14**, 87640-71-9; $CF_3CH_2NH_2$, 753-90-2; phosgene, 75-44-5; dimethylamine, 124-40-3; vinyl chloroformate, 5130-24-5; 1,8-bis(dimethylamino)naphthalene, 20734-58-1.

Supplementary Material Available: Tables of positional and thermal parameters, bond distances and angles, selected least-squares planes, Figures 2 and 3, Tables III–V containing high-field ^{1}H NMR data for **7a–7c**, and experimental procedures for the preparation of **10a**, (**10b**), and **13** (12 pages). Ordering information is given on any current masthead page.

Hydroboration. 65. Relative Reactivities of Representative Alkenes and Alkynes toward Hydroboration by Catecholborane

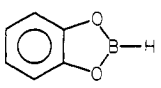
Herbert C. Brown* and J. Chandrasekharan[1]

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

Received June 21, 1983

The relative reactivities of a number of alkenes and alkynes toward hydroboration by catecholborane were determined in refluxing THF and were compared with data available for other monofunctional hydroborating agents such as 9-borabicyclo[3.3.1]nonane, disiamylborane, thexylchloroborane–methyl sulfide, and dibromoborane–methyl sulfide. Catecholborane is less selective than the other reagents, even though the trend is the same as that for the dialkylboranes. This may be attributed, in part, to the inherent low steric and electrophilic properties of this reagent and, in part, to the relatively high temperture (65 °C) required to achieve a reasonable rate of hydroboration.

Catecholborane ((1,2-phenylenedioxy)borane, 1) is a mild hydroborating agent.[2,3] It hydroborates alkynes cleanly



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to the monohydroborated products.[2b] It has been effectively used in the preparation of alkyl- and alkenylboronic acids. It has been employed in the synthesis of vinylmercurials[4] and haloalkenes of controlled stereochemistry.[5] In spite of its synthetic importance,[6] its selectivity in the hydroboration of alkenes and alkynes is not yet known.

Moreover, catecholborane has unique structural features. Due to electron donation from the adjacent oxygen, it is a much weaker Lewis acid than dialkylboranes and dihaloboranes. The boron atom is part of a planar five-membered ring and hence its steric requirements are much less than those of bulky reagents such as disiamylborane. We have long been interested in establishing the effects of variation of the structural features of hydroborating agents on their selectivities for hydroboration.[7–10] Consequently, we determined the relative rates of hydroboration of representative alkenes and alkynes by catecholborane in refluxing THF by the competition method in order to compare the data with the analogous data available for other monofunctional hydroborating agents such as 9-borabicyclo[3.3.1]nonane[8] (9-BBN), disiamylborane[7] (Sia_2BH), thexylchloroborane–methyl sulfide[9] ($ThxBHCl{\cdot}SMe_2$) and dibromoborane–methyl sulfide[10] ($Br_2BH{\cdot}SMe_2$). We report out results in this paper.

Results and Discussion

Competitive Hydroboration of Alkenes and Alkynes by Catecholborane. Catecholborane does not hydroborate alkenes and alkynes at 25 °C. Consequently, we determined the relative reactivities of alkenes and alkynes toward hydroboration by catecholborane in refluxing THF by the competition method. Two alkenes (1 equiv each) were treated with catecholborane (1 equiv) in THF so that the concentrations were ~1.0 M. The reaction mixture was refluxed until at least 50% of the reaction was over.[11] An aliquot was then quenched with excess aqueous NaOH,

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(11) With some alkene pairs, the reaction was very slow; since the Ingold–Shaw expression is to be obeyed at any point in a reaction, we analyzed the reaction mixtures after 50% of the catecholborane was consumed.

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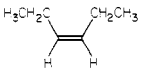
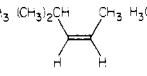
Table I. Relative Rates of Hydroboration of Representative Alkenes and Alkynes by Catecholborane in Refluxing THF

compound	relative rate
tert-butylacetylene	171
cyclohexylacetylene	146
4,4-dimethyl-2-pentyne	106
1-hexene	100
1-octene	96.0
1-decene	91.4
norbornene	81.4
1-octyne	62.6
2-methyl-1-pentene	53.0
4-octyne	49.1
cis-3-hexene	33.8
3,3-dimethyl-1-butene	28.8
styrene	26.7
phenylacetylene	23.4
cycloheptene	20.9
cyclooctene	12.2
α-methylstyrene	10.3
trans-3-hexene	9.3
cyclopentene	6.3
cis-4-methyl-2-pentene	6.1
1-methylcyclopentene	4.8
cis-β-methylstyrene	4.3
cyclohexene	4.1
trans-4-methyl-2-pentene	3.4
2-methyl-2-butene	3.2
trans-β-methylstyrene	1.7
1-methylcyclohexene	0.62
2,3-dimethyl-2-butene	0.36

Table II

	1-hexene	1-octene	$(CH_3)_3CCH=CH_2$
catecholborane	1.0	0.96	0.29
9-BBN	1.0	1.1	0.24
Sia_2BH	1.0	1.1	0.047
$ThxBHCl\cdot SMe_2$	1.0	0.98	0.01
$Br_2BH\cdot SMe_2$	1.0	0.95	0.20

Table III

				
catecholborane	1.0	0.18	1.0	0.37
9-BBN	1.0	0.78	1.0	0.51
$Br_2BH\cdot SMe_2$	1.0	0.96	1.0	0.52

and the alkenes were analyzed by GLC. From the initial and final amounts of the two alkenes, the relative rates were calculated by using the Ingold–Shaw expression (see Experimental Section). The rate of 1-hexene was arbitrarily assigned a value of 100 and the relative rates of other substrates were calculated accordingly. The data are reported in Table I.

Terminal Alkenes. In straight-chain terminal alkenes, the rate of hydroboration is nearly independent of chain length (Table II). This is true for other hydroborating agents as well.[12] Branching of the alkyl group at the α-position to the double bond causes a rate decrease. (Table II).

Internal Alkenes. Internal alkenes are hydroborated slower than terminal alkenes. For example, *cis*-3-hexene is hydroborated 2.8 times slower than 1-hexene. Branching of the alkyl groups causes a further decrease in the rate (Table III).

(12) In all of the following tables, only the relative rates are being used for comparison; the absolute rates of the reaction of a given alkene, example, 1-hexene, with these reagents are not identical.

Table IV

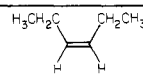
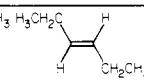
				
catecholborane	3.6	1.0	1.8	1.0
9-BBN	2.0	1.0	3.3	1.0
Sia_2BH	10	1.0	5.0	1.0
$ThxBHCl\cdot SMe_2$	92	1.0	110	1.0
$Br_2BH\cdot SMe_2$	1.9	1.0	3.4	1.0

Table V

		
catecholborane	1.0	0.38
$Br_2BH\cdot SMe_2$	1.0	2.3
9-BBN	1.0	2.6

Table VI

				
catecholborane	1.5	1.0	5.1	3.0
9-BBN	107	1.0	118	103
Sia_2BH	140	1.0	2600	5740
$ThxBHCl\cdot SMe_2$	31	1.0	171	1340
$Br_2BH\cdot SMe_2$	16	1.0	14	312

Table VII

	1-hexene	2-methyl-1-pentene
catecholborane	1.0	0.53
9-BBN	1.0	1.9
Sia_2BH	1.0	0.049
$ThxBHCl\cdot SMe_2$	1.0	0.41
$Br_2BH\cdot SMe_2$	1.0	21

Table VIII

					
catecholborane	0.15	1.0	0.76	1.0
9-BBN	0.16	1.0	0.21	1.0
$ThxBHCl\cdot SMe_2$	0.022	1.0	0.067	1.0
$Br_2BH\cdot SMe_2$	4.0	1.0	7.6	1.0

Cis–Trans Isomers. Like other reagents, catecholborane hydroborates a *cis*-alkene faster than its trans isomer. However, the cis–trans rate ratio is modest. Only with hindered hydroborating agents such as $ThxBHCl\cdot SMe_2$ or Sia_2BH are reasonably high cis–trans rate ratios observed (Table IV). With hindered alkene pairs such as β-methylstyrene we earlier observed that the cis isomer reacts with 9-BBN or $BHBr_2\cdot SMe_2$ slower than the trans isomer, which we attributed to steric interactions in the transition state, arising from rotation of the phenyl group caused by the neighboring cis methyl.[8b,10] With catecholborane, however, *cis*-β-methylstyrene reacts 2.6 times faster than its trans isomer (Table V). This may reflect the lower sensitivity of the reagent to steric factors arising from its planar geometry.

Cycloalkenes. Generally, cyclohexene is less reactive toward hydroboration when compared with its lower and higher ring homologues. The same trend is observed with catecholborane as well (Table VI). However, we do not observe the large differences in reactivity among these cycloalkenes that we encountered with the other reagents. This again may be attributed both to the unusually low steric requirements of catecholborane and its low elec-

Table IX

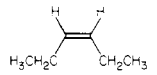
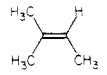
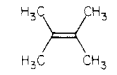
			
catecholborane	1.0	0.09	0.011
9-BBN	1.0	1.66	0.011
ThxBHCl·SMe_2	1.0	0.03	
$Br_2BH·SMe_2$	1.0	5.1	0.15

Table X

	1-hexene	styrene
catecholborane	1.0	0.27
9-BBN	1.0	0.025
Sia_2BH	1.0	0.028
ThxBHCl·SMe_2	1.0	0.011
$Br_2BH·SMe_2$	1.0	0.027
	2-methyl-1-pentene	α-methylstyrene
catecholborane	5.1	1.0
9-BBN	13.9	1.0
ThxBHCl·SMe_2	372	1.0

Table XI

	1-hexene	1-hexyne	3-hexyne
catecholborane	1.0	0.63[13]	0.49[14]
9-BBN	1.0	0.15	0.006
Sia_2BH	1.0	3.7	8.33
ThxBHCl·SMe_2	1.0	5.0	6.20
$Br_2BH·SMe_2$	1.0	2.3	48.8

trophilicity when compared with other monofunctional hydroborating agents.

Norbornene reacts considerably faster than these cycloalkenes. This is attributed to the strain associated with the double bond in the bicyclo[2.2.1]heptyl system.

Effect of Methyl Substitution. Introducing a methyl group at the 2-position in a terminal alkene leads to a modest rate decrease (Table VII). Similarly, a methyl group on the olefinic carbon of a cycloalkene also causes a rate decrease (Table VIII).

Progressive introduction of methyl groups on the double bond of an internal alkene causes a considerable decrease in rate (Table IX).

Phenyl Substitution. Introduction of a phenyl group at the olefinic carbon causes a modest rate decrease. It is much less when compared to the rate decrease observed with other reagents. (Table X).

Alkynes. 1-Hexyne reacts slightly slower than 1-hexene (Table XI). Internal alkynes react slightly slower than terminal alkynes. The results show that catecholborane does not seem to exhibit the unique selectivities of either 9-BBN or $Br_2BH·SMe_2$.

Branching of the alkyl group at the α-position to the unsaturation center causes a rate increase in alkynes. For example, cyclohexylethyne reacts 2.3 times faster than 1-octyne; 3,3-dimethyl-1-butyne reacts 2.7 times faster than the latter. A similar trend has been observed with 9-BBN as well.[8] This is contrary to the trend observed in the case of alkenes. The cause for this behavior may be as follows. Branching at the α-position of an alkene simultaneously increases both the electron density on the double bond (by the +I effect) and the steric crowding. The steric effect apparently outweighs the electronic effect. The more open nature of an alkyne may minimize the effects of steric crowding in the alkyne substituent. Consequently, in these systems, the inductive effect could outweigh the steric factor, resulting in a net rate increase.

In conclusion, the reactivity trend of catecholborane toward the hydroboration of alkenes and alkynes is more or less similar to other dialkylboranes such as 9-BBN, but the selectivity is much less. This may be attributed, in part, to the inherent lower steric and electronic requirements of this reagent and, in part, to the higher temperature (65 °C) required to achieve a reasonable rate of hydroboration.

(13) Result for 1-octyne vs. 1-hexene.
(14) Results for 1-octyne vs. 4-octyne.

Experimental Section

General procedures for the manipulation of boron reagents have been outlined elsewhere.[15] All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware was assembled hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and then cooled as assembled units.

Materials. All alkenes use in this study were distilled over $LiAlH_4$ in a nitrogen atmosphere. The alkynes were distilled in a nitrogen atmosphere. Catecholborane from Aldrich was used as such. It was dissolved in THF and standardized by hydride analysis using a 1:1 glycerol–water mixture.[15]

GLC Analyses. All GLC analyses were carried out with a HP 5750 Research Chromatograph. The analysis of the residual alkenes, or alkynes, were made by using a 12 ft × 0.125 in. column of 10% SE-30 on 80/100 mesh Chromosorb W or a 6 ft × 0.25 in. column of 20% adiponitrile on 60/80 mesh Firebrick.

Relative Reactivities. The competition method was employed for the determination of relative reactivities. Five millimoles each of two alkenes A and B and a suitable internal standard were treated with 5 mmol of catecholborane in THF (3.85 mL of a 1.30 M solution). The resulting solution (~1 M in each reactant) was refluxed. An aliquot was removed after at least 50% of the catecholborane was consumed and quenched into excess aqueous NaOH (ice cold). After stirring for 15 min, the alkenes were extracted into ether or pentane. The organic layer was dried over K_2CO_3 and analyzed by GC for the residual alkenes. From the initial and final amounts of alkenes, the relative reactivity was calculated by using the Ingold–Shaw expression.[16] The alkene

$$\frac{k_A}{k_B} = \frac{\ln [A]_{init} - \ln [A]_{final}}{\ln [B]_{init} - \ln [B]_{final}}$$

pairs were so chosen that their relative rates did not differ by a factor of more than 10. With volatile alkenes and alkynes, the loss while refluxing was prevented by using a dry ice–acetone condenser on top of a regular water reflux condenser.

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

Registry No. 1, 274-07-7; 9-BBN, 280-64-8; Sia_2BH, 1069-54-1; ThxBHCl·SMe_2, 75067-06-0; $Br_2BH·SMe_2$, 55671-55-1; *tert*-butylacetylene, 917-92-0; cyclohexylacetylene, 931-48-6; 4,4-dimethyl-2-pentyne, 999-78-0; 1-hexene, 592-41-6; 1-octene, 111-66-0; 1-decene, 872-05-9; norbornene, 498-66-8; 1-octyne, 629-05-0; 2-methyl-1-pentene, 763-29-1; 4-octyne, 1942-45-6; *cis*-3-hexene, 7642-09-3; 3,3-dimethyl-1-butene, 558-37-2; styrene, 100-42-5; phenylacetylene, 536-74-3; cycloheptene, 628-92-2; cyclooctene, 931-88-4; α-methylstyrene, 98-83-9; *trans*-3-hexene, 13269-52-8; cyclopentene, 142-29-0; *cis*-4-methyl-2-pentene, 691-38-3; 1-methylcyclopentene, 693-89-0; *cis*-β-methylstyrene, 766-90-5; cyclohexene, 110-83-8; *trans*-4-methyl-2-pentene, 674-76-0; 2-methyl-2-butene, 513-35-9; *trans*-β-methylstyrene, 873-66-5; 1-methylcyclohexene, 591-49-1; 2,3-dimethyl-2-butene, 563-79-1; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4.

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